

Carbon Dioxide Insertion into Light Metal Pyrazolates

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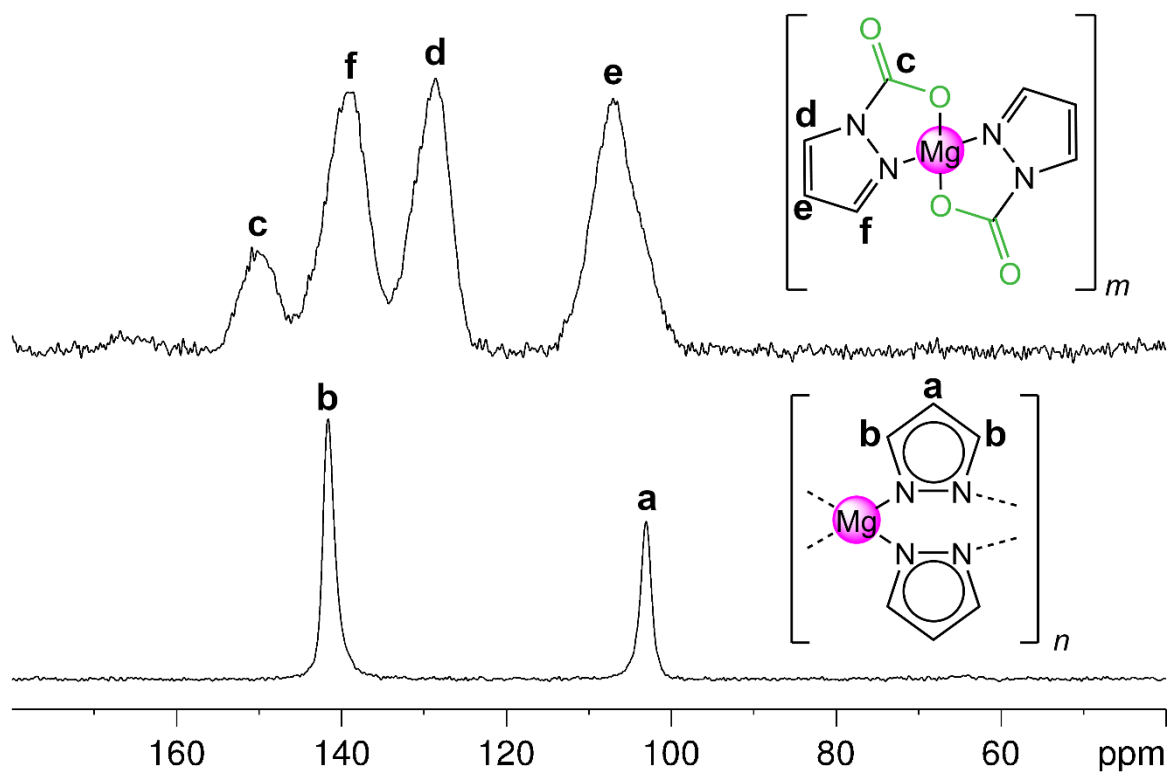
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Carbon Dioxide Insertion into Light Metal Pyrazolates

Felix Kracht



Preface

This PhD thesis is submitted for the acquisition of the degree doctor rerum naturalium (Dr. rer. nat.) in chemistry. This work has been carried out during the period of September 2019 to December 2024 under the supervision of Professor Dr. Reiner Anwender at the Department of Chemistry, Institute of Inorganic Chemistry at the Eberhard Karls University Tübingen. Funding has been gratefully received from the Vector foundation and the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG).

The following thesis contains a short review on carbon capture and further utilization, a summary of the main results including the synthesis of new light metal pyrazolates, reversible CO₂ insertion into light metal pyrazolates, CO₂ activation of light metal pyrazolates grafted onto a mesoporous silica surface and light metal pyrazolates as catalyst in the cycloaddition of CO₂ and cyclic carbonates as well as a compilation of scientific papers.

Parts of this thesis have been presented at several national and international conferences and meetings as poster or oral presentation.

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Abbreviations

AE	Alkaline-earth metal	Hex	Hexyl
Ar	Aryl	HMBC	Heteronuclear Multiple Bond Correlation
BBL	β -Butyrolacton	HMPA	Hexamethylphosphoramide
BET	Brunauer Emmett Teller	HMTETA	1,1,4,7,10,10- Hexamethyltriethylene- tetramine
CHO	Cyclohexene Oxide	HSQC	Heteronuclear Single Quantum Coherence
CP	Cross-Polarization		
Cp	Cyclopentadienyl		
CCS	Carbon Capture and Storage		
Do	Donor Ligand	<i>i</i> Bu	<i>iso</i> -Butyl
DAC	Direct Air Capture	ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
DOSY	Diffusion-ordered Spectroscopy	IL	Ionic Liquid
DRIFT	Diffuse Reflectance Infrared Fourier Transform	<i>i</i> Pr	<i>iso</i> -Propyl
EA	Elemental Analysis	IPr	1,3-bis(2,6-di <i>iso</i> propyl- phenyl)imidazolium
EC	Ethylene Carbonate	L	Ligand
ECH	Epichlorohydrin	Ln	Sc, Y, La–Lu
EH	1,2-Epoxyhexane	MAS	Magic-Angle Spinning
Equiv.	Equivalent	Me	Methyl
EO	Ethylene Oxide	MOF	Metalorganic Framework
Et	Ethyl	<i>n</i> Bu	<i>n</i> -Butyl
EVP	3-Ethyl-6-vinyltetrahydro- 2 <i>H</i> -pyran-2-one	M_n	Number Average Molar Mass
HC	1,2-Hexylene Carbonate	M_w	Mass Average Molar Mass

NMR	Nuclear Magnetic Resonance	SO	Styrene Oxide
OAc	Acetate	SOMC	Surface Organometallic Chemistry
PC	Polycarbonates	TBAAc	Tetra- <i>n</i> -butyl Ammonium Acetate
Pc	Phthalocyanine	TBAB	Tetra- <i>n</i> -butyl Ammonium Bromide
PCHC	Poly(cyclohexene carbonate)	TBAI	Tetra- <i>n</i> -butyl Ammonium Iodide
PDI	Polydispersity Index (M_w/M_n)	TBD	1,5,7-Triazabicyclo(4.4.0)dec-5-en
PEA	Poly(ethylene glycol bismethacrylate)	<i>t</i> BO	2- <i>tert</i> -butyloxirane
Ph	Phenyl	<i>t</i> Bu	<i>tert</i> -Butyl
PMDTA	Bis(2-dimethylaminoethyl) methylamine	tet ^R	R-tetrazolate
PO	Propylene Oxide	TGA	Thermogravimetric Analysis
PPC	Poly(propylene carbonate)	THF	Tetrahydrofuran
ppm	parts per million	TMEDA	Tetramethylethylenediamine
[PPN]Cl	Bis(triphenylphosphine)-iminium Chloride	TOF	Turnover Frequency
PrC	Propylene Carbonate	Tol	Toluene
PS	Polystyrene	TON	Turnover Number
Py	Pyridine	Tp	Tris(pyrazolyl)borate
pz ^{R,R'}	3-R-5-R'-Pyrazolate	TPP	Tetraphenylporphyrin
ROP	Ring-opening Polymerization	tz ^{R,R'}	3-R-5-R'-Triazolate
sccm	Standard Cubic Centimeters per Minute	VT	Variable Temperature

Summary

Previous work has shown that cerium pyrazolates can reversibly insert CO₂ under formation of the corresponding carbamate complexes. Earth-abundant light metals are even more environmentally friendly and the reactivity of their pyrazolate complexes toward CO₂ has not been examined.

A series of new light metal pyrazolate complexes were synthesized and characterized with a focus on pyrazolates with lighter substitutes to minimize the “mass penalty” of the ligand scaffold. Magnesium-based examples are the donor stabilized [Mg₃(pz^{*i*Pr₂})₆(thf)₂] and the fluorinated [Mg₂(pz^{CF₃,CF₃})₄(thf)₃]. Although [Mg(pz^{R₂})₂]_{*n*} (R = Me, H) is insoluble in common solvents and thus could not be structurally characterized, their formation via protonolysis of Mg(*n*Bu)₂ and Hpz^{R₂} (R = Me, H) could be unambiguously proofed by solid-state NMR. With a salt-metathesis protocol dimeric [Al(pz^{*i*Pr₂})₃]₂ could be isolated. For the synthesis of rare-earth metal pyrazolates Ln(pz^{*t*Bu₂})₃(thf)_{*x*} (Ln: Sc, *x* = 1; Y, *x* = 2) a mercury-free salt-metathesis protocol could be applied. Additionally, literature-known light metal pyrazolates were successfully immobilized at the surface of mesoporous silica and the hybrid materials [Mg(pz^{*t*Bu₂})₂]₂@SBA-15₅₀₀, Al(pz^{*t*Bu₂})₃@SBA-15₅₀₀ and Ti^{+IV}(pz^{Me₂})₄@SBA-15₅₀₀ were synthesized.

This study was started with literature-known [Mg(pz^{*t*Bu₂})₂]₂ which showed not only exhaustive CO₂ insertion to monomeric Mg(CO₂·pz^{*t*Bu₂})₂(thf)₂, but also a complete reversible behavior in solution and solid-state when exposed to elevated temperature or reduced pressure. Reversible and exhaustive CO₂ insertion also occurs in the solid state without a solvent. Over this pathway insoluble, unsubstituted [Mg(CO₂·pz)₂]_{*n*} showed an exceptional high capacity of 35.7 wt% CO₂. For Al(pz^{*t*Bu₂})₃ only a twofold CO₂ insertion was observed Al(CO₂·pz^{*t*Bu₂})₂(pz^{*t*Bu₂}) due to the steric bulk of the *t*Bu moieties. The insertion step is reversible at elevated temperature but not under reduced pressure. The scandium pyrazolate Sc(pz^{*t*Bu₂})₃(thf) yielded the mono-insertion dimeric complex [Sc(CO₂·pz^{*t*Bu₂})(pz^{*t*Bu₂})₂]₂, which only could be isolated under permanent cooling. This was necessary due to immediate CO₂ release already at ambient pressure and temperature. Tetravalent Ti^{+IV}(pz^{Me₂})₄ inserts two CO₂ molecules under formation of Ti^{+IV}(CO₂·pz^{Me₂})₂(pz^{Me₂})₂ which showed a deoxygenation behavior to oxo-bridged titanium complexes only in solution. Trivalent Ti^{+III}(pz^{*t*Bu₂})₃ yielded Ti^{+III}(CO₂·pz^{*t*Bu₂})₂(pz^{*t*Bu₂}) which is isostructural to the aluminum congener.

Lastly, all light metal pyrazolates as well as their corresponding grafted materials were active catalysts in the cycloaddition of CO₂ and epoxides to cyclic carbonates. The highest catalytic activity was achieved with Sc(pz^{*t*Bu₂})₃(thf) with a maximal TOF of 120 h⁻¹. An inverse correlation of carboxophilicity (CO₂ affinity) and catalytic activity was observed. The best catalysts showed either no visible CO₂ insertion or immediate CO₂ release. For example [Mg₂(pz^{CF₃,CF₃})₄(thf)₃] showed no visible CO₂ insertion at ambient temperature but revealed the highest catalytic activity for magnesium-based catalyst in this study. An increase of catalytic activity for light metal pyrazolates grafted onto a mesoporous silica surface was observed for the hybrid material [Mg(pz^{*t*Bu₂})₂]₂@SBA-15₅₀₀. The heterogenous catalyst showed a higher catalytic conversion compared to its homogenous congener at already ambient temperature. At elevated temperatures a quantitative conversion was achieved even for bulky epoxides.

Zusammenfassung

Frühere Arbeiten haben gezeigt, dass Cer-Pyrazolate reversibel Kohlenstoffdioxid einfangen können unter Bildung der entsprechenden Carbamat-Komplexen. Die in der Erdkruste häufiger vorkommenden Leichtmetalle könnten die CO₂ Speicherung noch nachhaltiger gestalten. Bisher wurde die Reaktivität von Leichtmetall-Pyrazolaten gegenüber CO₂ noch nicht untersucht.

Eine Reihe von neuen Leichtmetall Pyrazolaten wurde synthetisiert und charakterisiert mit einem Schwerpunkt auf Pyrazolaten mit leichteren Substituenten um eine möglichst hohe Massenbilanz zu erreichen. Beispiele für neue Magnesiumpyrazolate sind das donor-stabilisierte [Mg₃(pz^{*i*Pr₂})₆(thf)₂] und das fluorinierte [Mg₂(pz^{CF₃,CF₃})₄(thf)₃]. Aufgrund schlechter Löslichkeit in gebräuchlichen Lösungsmitteln konnte amorphes [Mg(pz^{R₂})₂]_n (R = Me, H) nicht strukturell untersucht werden. Deren Bildung aus der Protonolysereaktion von Mg(*n*Bu)₂ und dem entsprechenden Pyrazol konnte jedoch zweifelsfrei durch Festkörper-NMR Experimente bestätigt werden. Über eine Salzmetathesevorschrift konnte das Dimer [Al(pz^{*i*Pr₂})₃]₂ erhalten werden. Die Seltenerd-Pyrazolate Ln(pz^{*t*Bu₂})₃(thf)_x (Ln: Sc, *x* = 1; Y, *x* = 2) waren zugänglich über eine quecksilber-freie Salzmetathese. Zusätzlich konnten bereits literaturbekannte Leichtmetall-Pyrazolate auf eine mesoporöse Silica Oberfläche immobilisiert werden. So konnten die Hybridmaterialien [Mg(pz^{*t*Bu₂})₂]₂@SBA-15₅₀₀, Al(pz^{*t*Bu₂})₃@SBA-15₅₀₀ und Ti^{+IV}(pz^{Me₂})₄@SBA-15₅₀₀ synthetisiert werden.

Diese Arbeit wurde mit literaturbekannte [Mg(pz^{*t*Bu₂})₂]₂ gestartet, welches in Lösung nicht nur eine vollständige CO₂-Insertion unter Bildung von Mg(CO₂·pz^{*t*Bu₂})₂(thf)₂ zeigte, sondern auch ein vollständig reversibles Verhalten in Lösung und als Feststoff bei Temperaturerhöhung oder Druckminderung. Die unlöslichen Magnesium-Pyrazolate zeigten auch eine reversible und vollständige CO₂-Insertion in den Feststoff ohne die Notwendigkeit eines Lösungsmittels. Über diesen Reaktionsweg zeigte insbesondere das unsubstituierte [Mg(CO₂·pz)₂]_n eine außergewöhnlich hohe Kapazität von 35.7 wt% CO₂. Für Al(pz^{*t*Bu₂})₃ wurde aufgrund der sterisch anspruchsvollen *t*Bu-Gruppen nur eine zweifache CO₂-Insertion beobachtet unter Bildung von Al(CO₂·pz^{*t*Bu₂})₂(pz^{*t*Bu₂}). Diese Insertion ist ebenfalls reversibel, jedoch nur bei Temperaturerhöhung und nicht bei Druckminderung. Das Scandium-Pyrazolat Sc(pz^{*t*Bu₂})₃(thf) unterliegt einer einfachen CO₂-Insertion und es bildet sich das Dimer [Sc(CO₂·pz^{*t*Bu₂})(pz^{*t*Bu₂})₂]₂. Dieses konnte nur unter ständiger Kühlung isoliert werden, da eine CO₂-Freisetzung schon bei Raumtemperatur und Umgebungsdruck erfolgt. Tetravalentes Ti^{+IV}(pz^{Me₂})₄ zeigte eine zweifache CO₂-Insertion zu Ti^{+IV}(CO₂·pz^{Me₂})₂(pz^{Me₂})₂ und kann in Lösung CO₂ desoxygenieren

unter Bildung von oxo-verbrückten Titankomplexen. Trivalentes $\text{Ti}^{+\text{III}}(\text{pz}^{\text{tBu}_2})_3$ zeigte eine zweifache CO_2 -Insertion zu $\text{Ti}^{+\text{III}}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$, welches isostrukturell zum Aluminium Kongener ist.

Alle untersuchten Leichtmetall-Pyrazolate sowie die Hybridmaterialien sind aktive Katalysatoren in der Cycloadditionsreaktion von CO_2 und Epoxiden zu zyklischen Carbonaten. Die höchste katalytische Aktivität wurde für $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ gefunden mit einer Wechselzahl von 120 h^{-1} . Eine umgekehrt proportionale Beziehung zwischen Carboxyphilie (CO_2 -Affinität) und der katalytischen Aktivität wurde beobachtet. Die besten Katalysatoren zeigten entweder keine CO_2 -Insertion bei Raumtemperatur oder sofortige CO_2 Freisetzung. Ein Beispiel ist $[\text{Mg}_2(\text{pz}^{\text{CF}_3, \text{CF}_3})_4(\text{thf})_3]$, welches keine sichtbare CO_2 -Insertion bei Raumtemperatur eingeht, jedoch die höchste katalytische Aktivität der Magnesium-Katalysatoren dieser Studie aufweist. Eine Steigerung der katalytischen Aktivität für immobilisierte Leichtmetall-Pyrazolate auf einer mesoporösen Silica-Oberfläche für das Hybridmaterial $[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ wurde beobachtet. Der heterogene Katalysator zeigte schon bei Raumtemperatur eine höhere katalytische Umsetzung als sein homogener Kongener. Bei höheren Temperaturen wurde selbst für sterisch anspruchsvolle Epoxide eine quantitative Umsetzung beobachtet.

Publication Overview

Publications incorporated into this thesis

- Paper I** Organomagnesia: Reversibly High Carbon Dioxide Uptake by Magnesium Pyrazolates
F. Kracht, P. Rolser, P. Preisenberger, C. Maichle-Mössmer, R. Anwander
Adv. Sci. **2024**, *11*, 2403295
<https://doi.org/10.1002/advs.202403295>
- Paper II** Carbon dioxide affinity (“carboxophilicity”) of trivalent light metal pyrazolates
F. Kracht, P. Rolser, K. Eichele, C. Maichle-Mössmer, R. Anwander
Inorg. Chem. Front. **2024**, *11*, 6948–6959
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- Paper III** Reactivity of $\text{Mg}(\text{AlMe}_4)_2$ towards neutral tris(pyrazolyl)alkanes
F. Kracht, C. Stuhl, C. Maichle-Mössmer, R. Anwander
Dalton Trans. **2024**, *53*, 19280–19291
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- Paper IV** Reactivity of titanium pyrazolates towards CO_2 , CS_2 and N_2O
F. Kracht, S. Mayer, C. Maichle-Mössmer, R. Anwander
Dalton Trans., **2025**, *54*, 10890–10897
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Publications with minor contributions

- Paper V** A Rare-Earth-Metal Ensemble of the Tebbe Reagent: Scope of Coligands and Carbonyl Olefination
V. M. Birkelbach, F. Kracht, H. M. Dietrich, C. Stuhl, C. Maichle-Mössmer, R. Anwander
Organometallics **2020**, *39*, 3490–3504
<https://doi.org/10.1021/acs.organomet.0c00447>

- Paper VI** [(CH₃)Al(CH₂)]₁₂: Methylaluminomethylene (MAM-12)
G. Spiridopoulos, M. Kramer, F. Kracht, C. Maichle-Mössmer, R. Anwander
Chem. Eur.J. **2022**, 28, e202200823
<https://doi.org/10.1002/chem.202200823>
- Paper VII** Rare-earth-metal trimethylsilylmethyl ate complexes
A. Mortis, F. Kracht, T. Berger, J. Lebon, C. Maichle-Mössmer, R. Anwander
Dalton Trans. **2023**, 52, 44–51
<https://doi.org/10.1039/D2DT03491C>
- Paper VIII** Potential precursors for terminal ytterbium(II) imide complexes bearing the hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borato ligand
M. Katzenmayer, F. Kracht, C. Maichle-Mössmer, R. Anwander
Dalton Trans. **2023**, 52, 6273–6283
<https://doi.org/10.1039/D3DT00861D>
- Paper IX** Samarium- and Ytterbium-Grafted Periodic Mesoporous Silica for Carbon Dioxide Capture and Conversion
J. Poolwong, F. Kracht, E. Moinet, Y. Liang, V. D’Elia, R. Anwander
Inorg. Chem. **2023**, 62, 17972–17984
<https://doi.org/10.1021/acs.inorgchem.3c02995>
- Paper X** Gram-Scale Selective Telomerization of Isoprene and CO₂ by Palladium Catalysis: Toward 100% Renewable Materials
M. D. R. Lutz, F. Kracht, K. Marumoto, K. Nozaki
Nat. Commun. **2025**, 16, 7326
[10.1038/s41467-025-62409-2](https://doi.org/10.1038/s41467-025-62409-2)

Poster Presentations

Poster I Reversible CO₂ Insertion into Scandium and Yttrium Pyrazolates

F. Kracht, C. Maichle-Mössmer, R. Anwander

XXXI. Tage der Seltenen Erden; Terrae Rarae, Leipzig, Germany, *September 27.–29., 2022.*

Oral Presentations

Presentation I Reversible CO₂ Insertion into Scandium and Aluminum Pyrazolates

F. Kracht, C. Maichle-Mössmer, R. Anwander

XXX. Tage der Seltenen Erden; Terrae Rarae, Montpellier, France, *September 22.–24., 2021.*

Personal Contribution

Paper I:

All reactions and analyses described were planned by myself and conducted by my lab course students Philipp Rolser, Paul Preisenberger and myself. Analyses include one-dimensional (^1H , $^{13}\text{C}\{^1\text{H}\}$, variable temperature ^1H) and two-dimensional (^1H - ^{13}C HSQC, ^1H - ^{13}C HMBC) NMR spectroscopy methods as well as DRIFT and *in-situ* IR measurements. Sample preparation for elemental analysis were conducted by my lab course students Philipp Rolser, Paul Preisenberger and myself. Sample preparation for single-crystal X-ray diffraction, the solid-state NMR experiments and SEM measurements were done by myself. The manuscript was written by me.

Elemental analyses were performed by Wolfgang Bock and Mohammed Ghani. Solid-state (^{13}C CP/MAS) NMR experiments were performed by Dr. Klaus Eichele. DOSY NMR measurements were performed by Dr. Wolfgang Leis. Thermogravimetric analyses were performed by Dr. Markus Ströbele. SEM measurements were performed by Elke Nadler. The structural analyses by single-crystal X-ray diffraction were performed by Dr. Cäcilia Maichle-Mössmer.

Paper II:

All reactions and analyses described were planned by myself and conducted by my lab course student Philipp Rolser and myself. Analyses include one-dimensional (^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{27}Al , ^{45}Sc , variable temperature ^1H) and two-dimensional (^1H - ^{13}C HSQC, ^1H - ^{13}C HMBC) NMR spectroscopy methods as well as DRIFT and *in-situ* IR measurements. Sample preparation for elemental analysis were conducted by my lab course student Philipp Rolser and myself. Sample preparation for single-crystal X-ray diffraction and the solid-state NMR experiments were done by myself. The manuscript was written by me.

Elemental analyses were performed by Mohammed Ghani. Solid-state (^1H , ^{13}C , ^{27}Al and ^{45}Sc CP/MAS) NMR experiments were performed by Dr. Klaus Eichele. Thermogravimetric analyses were performed by Dr. Markus Ströbele. The structural analyses by single-crystal X-ray diffraction were performed by Dr. Cäcilia Maichle-Mössmer.

Paper III:

All reactions and analyses described were planned and conducted by Christoph Stuhl and myself. Analyses include one-dimensional (^1H , $^{13}\text{C}\{^1\text{H}\}$, variable temperature ^1H) and two-dimensional (^1H - ^{13}C HSQC, ^1H - ^{13}C HMBC) NMR spectroscopy methods as well as DRIFT and *in-situ* IR measurements. Sample preparation for elemental analysis and single-crystal X-ray diffraction were done by Christoph Stuhl and myself. The manuscript was written by me.

Elemental analyses were performed by Wolfgang Bock. The variable temperature ^1H NMR experiment of $[(\text{MeCTp}^{3-p-t\text{BuPh}})\text{Mg}(\text{AlMe}_4)][\text{AlMe}_4]$ was performed by Kristina Strohmaier. The structural analyses by single-crystal X-ray diffraction were performed by Dr. Cäcilia Maichle-Mössmer and Christoph Stuhl.

Some reactions and analyses were conducted during my master thesis. The project was finished during the beginning of this thesis.

Paper IV:

All reactions and analyses described were planned by myself and conducted by my lab course student Sophie Mayer and myself. Analyses include one-dimensional (^1H , $^{13}\text{C}\{^1\text{H}\}$, variable temperature ^1H) and two-dimensional (^1H - ^{13}C HSQC, ^1H - ^{13}C HMBC) NMR spectroscopy methods as well as DRIFT and *in-situ* IR measurements. Sample preparation for elemental analysis were conducted by my lab course student Sophie Mayer and myself. Sample preparation for single-crystal X-ray diffraction and the solid-state NMR experiments were done by myself. The manuscript was written by me.

Elemental analyses were performed by Mohammed Ghani. Solid-state (^1H and ^{13}C CP/MAS) NMR experiments were performed by Dr. Klaus Eichele. Thermogravimetric analyses were performed by Dr. Markus Ströbele. The structural analyses by single-crystal X-ray diffraction were performed by Dr. Cäcilia Maichle-Mössmer.

Publications with minor contributions

Paper V:

The synthesis and analyses of complex $\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Br})\text{AlMe}_2$ and the corresponding methylenide transfer reaction with ketones were conducted by myself. Analyses include ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy methods.

Paper VI:

The synthesis and analyses of complex $[\text{Li}(\text{thf})_4][\text{LiSc}_2(\text{CH}_2\text{SiMe}_3)_8]$ was conducted by myself. The analyses include (^1H , ^7Li , $^{13}\text{C}\{^1\text{H}\}$, ^{29}Si and ^{45}Sc) and two-dimensional (^1H - ^{29}Si HSQC) NMR spectroscopy methods as well as DRIFT measurements.

Paper VII:

Analyses of complex $[(\text{CH}_3)_{12}\text{Al}_{12}(\text{CH}_2)_{12}]$, AlMe_3 and $\text{AlMe}_3\cdot\text{THF}$ and evaluation were done by myself. Analyses include all ^{27}Al NMR experiments as well as variable temperature ^1H NMR experiments for $[(\text{CH}_3)_{12}\text{Al}_{12}(\text{CH}_2)_{12}]$.

Paper VIII:

All ^1H - ^{171}Yb HSQC NMR experiments as well as some ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B , ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC were conducted by myself. Data of all ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^1H - ^{171}Yb HSQC, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC NMR data were evaluated by Markus Katzenmayer and myself.

Paper IX:

Parts of the planning and evaluation of analytical data were done by me. Some DRIFT measurements and catalytic reactions were conducted by me.

Paper X:

The initial reaction condition screening and the corresponding analyses with isoprene, $\text{Pd}(\text{acac})_2$, TMEDA, tetraethylethyldiamine, N,N -diisopropylethylamine, N,N,N',N' -tetramethyl-1,4-butandiamine, 1,4-dimethylpiperazine and tetra-*n*-butylammonium acetate as well as the isolation and characterization of both isoprene-based EVP isomers and early polymerization attempts were planned and conducted by myself. Analyses and characterization include ^1H NMR, FTIR and GC-MS experiments.

Objective of this Thesis

The main emphasis of this thesis is the synthesis of new light metal pyrazolates and to investigate the reactivity of new and reported light metal pyrazolates toward carbon dioxide and the capability to act as catalyst in the cycloaddition of CO₂ and epoxides into cyclic carbonates.

Chapter A of this thesis gives a brief review on carbon capture and further utilization. This includes chapter to carbon capture and carbon dioxide transformation, CO₂ insertion into metalorganic light metal compounds, light metal pyrazolates, cycloaddition of CO₂ and epoxides to cyclic carbonates as well as copolymerization of CO₂.

Chapter B gives a summary of the published and unpublished results of this thesis, with the focus on the following topic:

- Synthesis of new light metal pyrazolates
- Reversible CO₂ insertion into light metal pyrazolates
- CO₂ activation with light metal pyrazolates grafted onto a mesoporous silica surface
- Catalytic conversion of CO₂ and epoxides into cyclic carbonates

Chapter C includes unpublished results that are not part of publications and manuscripts. This contains CO₂ insertion with alkaline metal and zinc pyrazolates, light metal pyrazolates grafted onto a mesoporous silica surface as well as synthesis of bulky tris(pyrazolyl)borates ligands.

Chapter E contains a cumulative collection of publication with major contributions.

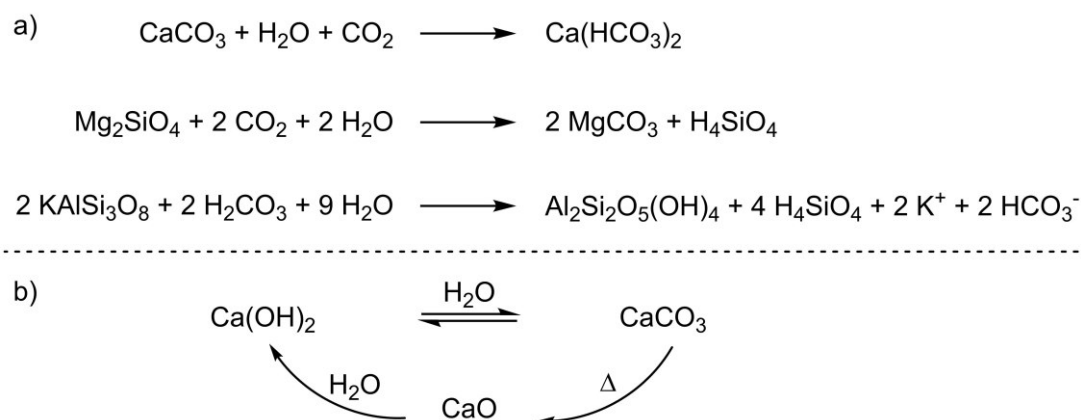


Carbon Dioxide Capture and further Utilization

1. Carbon Capture and Carbon Dioxide Transformation

This thesis will give an overview of carbon dioxide capture with light metal metalorganic compounds as well as carbon dioxide conversion into organic compounds with a focus on the cycloaddition and copolymerization of CO₂ and epoxides by using catalysts based on light metals. In addition, an overview of light metal pyrazolates as promising carbon capture material is included. The group of light metals is defined with a density below 5 g/cm³. This includes the alkali metals and alkaline-earth metals as well as aluminum, scandium, yttrium and titanium. A distinct color code was used for the variety of metals and metal groups and their corresponding oxidation state (alkaline metals: light blue, alkaline-earth metals (Ae): magenta, group III metals: orange, Ti^{+III}: dark blue, Ti^{+IV}: yellow, rare-earth metals (Ln): Ln^{+III}: magenta, Ln^{+II}: cyan, Ce^{+IV}: red, transition metals: grey) to differentiate between the metals included in thesis. In addition, when CO₂ is inserted into an organometallic compound it is marked in green.

The main reason for the anthropogenic climate change is the rising carbon dioxide level in earth's atmosphere caused by the burning of fossil fuel and the formation as side product in industrial processes.^[1-4] For this reason, the development of new technologies for CO₂ management is one of the main focuses of today's research. Two approaches are carbon capture and storage (CCS) and direct air capture (DAC).^[5-8] Aqueous amine scrubbers have been used as sorbent for CCS in the industry for almost a century, however, they have low capacities (<15 wt% CO₂) and high regeneration energies.^[9-11] Earth's natural carbon cycle through geochemical weathering revolves around minerals containing carbonate or silicate such as calcite (CaCO₃), forsterite (MgSiO₄) or feldspar (KAlSi₃O₈) (see Scheme A1a).^[12] Carbonic acid that originates from CO₂ dissolved in water transforms the minerals into soluble bicarbonates. Sea organisms transform the bicarbonates back into CaCO₃ in the process of shell



Scheme A1. a) Carbon capture in earth's natural carbon cycle *via* the formation of bicarbonates from carbonates and silicates. b) Carbon capture with aqueous Ca(OH)₂ solution and regeneration *via* calcination.

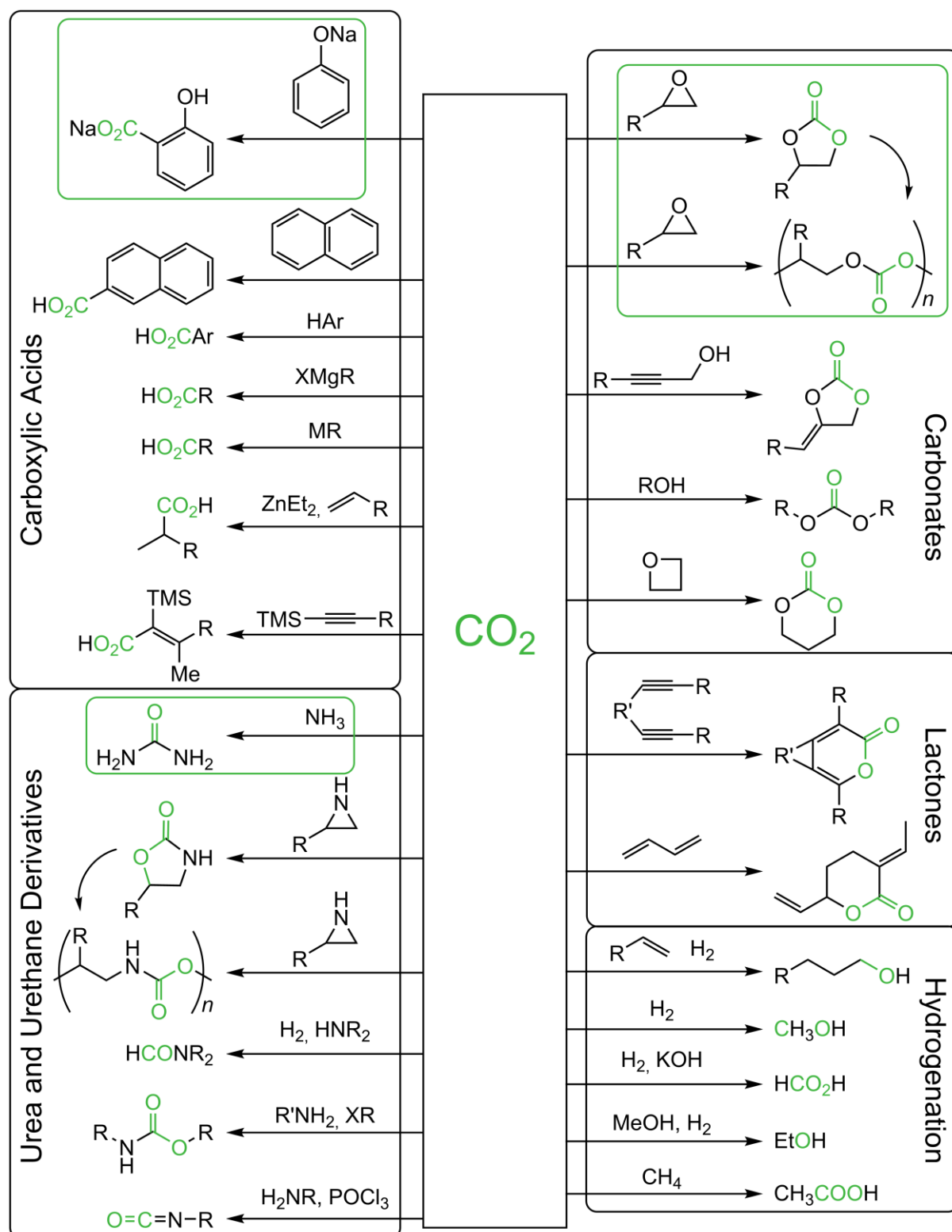
formation. The dead organism's deposit at the ocean floor and over time CO₂ is culminated in form of calcite.

Another approach in the industry is the precipitation of CaCO₃ from aqueous Ca(OH)₂ solutions. The carbonate can be regenerated to CaO *via* calcination at above 900 °C (see Scheme 1b).^[7] The energy barrier of the regeneration can be lowered when CO₂ is captured with NaOH and then transferred to Ca(OH)₂. This process is called causticization. However, this method still suffers from high regeneration energies and limited solubility of Ca(OH)₂ in water (1 mol/L).^[13]

Besides alkali/alkaline-earth metal hydroxides, amine-containing ionic liquids^[14,15] or high surface materials with amine-functional groups such as mesoporous silica, zeolites^[16,17] or metal-organic frameworks (MOF) are currently under research,^[18–21] with the latter reaching a record capacity of up to 35 wt% CO₂ for Mg₂(dobdc) (dobdc = 2,5-dioxido-1,4-benzendicarboxylate).^[18] Further, the MOF Mg₂(dobpdc) (dobpdc = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate) currently shows the most promising result for carbon capture from simulated flue gas.

CCS alone suffers from an appropriate storage place and transportation of stored CO₂, so further utilization is highly desirable.^[22] As inexpensive, abundant (biprodukt in a lot of industrial processes), non-toxic, non-flammable gas, CO₂ is an attractive C1 synthon for organic synthesis. However, because CO₂ has the lowest energy level of organic compounds, a high activation energy is necessary. To overcome this energetic barrier and convert CO₂ into useful chemicals is a top-prioritized research field.^[23–27] An overview of reported CO₂ conversion into higher-value organic compounds can be seen in Scheme A2. Few of them are already industrialized processes such as the cycloaddition or copolymerization of epoxides and CO₂ to cyclic carbonates or polycarbonates, respectively. Both reactions together with the coupling of olefins and CO₂ will be discussed in detail in a later chapter. Similar conversions are also possible with aziridine and oxetane derivatives.^[28–30] Further, CO₂ is already used as feedstock in the industrial synthesis of both salicylic acid from sodium phenolate and urea from ammonia.^[31–33]

CO₂ can also be used as a replacement for toxic gases such as phosgene, as reported for the synthesis of dialkyl carbonates, isocyanates, urethanes as well as polyurethanes.^[34] Urethane can be obtained by reacting ammonia or amines with CO₂. In the presence of a dehydration agent like POCl₃ tertiary amines can be transformed into terminal isocyanates. Carbamate esters are formed when a mixture of an amine and a halocarbon are reacted with CO₂.



Scheme A2. Overview of possible CO_2 transformation into organic compounds. Already industrialized processes are marked with a green box. Adapted from ref. [25,27].

Carboxylic acids can be obtained by reactions with organometallic compounds such as metal alkyls or Grignard reagents and a subsequent hydrolysis. Aryl compounds can be carboxylated *via* C–H bond activation with metal carbonates/halides and CO_2 . Addition of CO_2 to olefins and the formation of acrylic acids is also possible. Further, addition of CO_2 and ZnR_2 ($\text{R} =$

alkyls) to olefins and alkynes lead to carboxylic acids and acrylic acids, respectively. The reaction of both greenhouse gases CO_2 and CH_4 would be an ideal synthesis route for acetic acid with a 100% atomic-efficiency, however, because of their high activation energies it currently remains unattractive.

Adducts of dienes and dialkynes with CO_2 form cyclic lactones. One example is 3-ethyl-6-vinyltetrahydro-2*H*-pyran-2-one (EVP) from the telomerization of two 1,3-butadiene units and CO_2 . This lactone can be further polymerized with either a radical or a ring-opening polymerization.^[35,36]

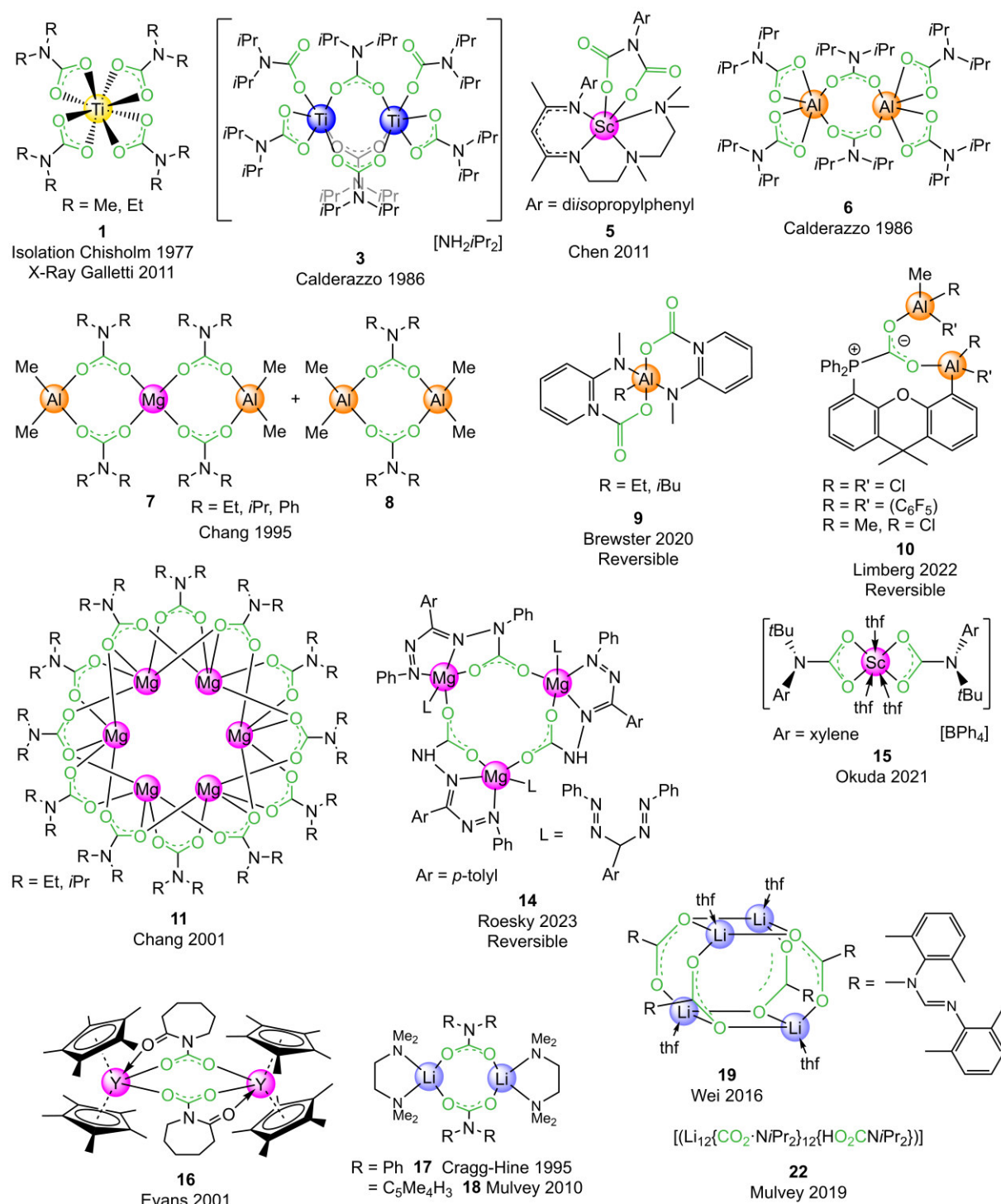
Another example is the replacement of toxic carbon monoxide in the synthesis of fuels such as hydrocarbons (Fischer Tropsch synthesis) or highly desirable methanol, the latter also being one of the most important starting materials for industrial processes.^[37–40] For methanol the technology is already in a stage for an industrial application, it is only held back by a lack of a sustainable H_2 source. Multicomponent catalysts such as $\text{CuO}/\text{ZnO}/\text{ZrO}_2/\text{Al}_2\text{O}_3/\text{SiO}_2$ are used in these hydrogenation reactions. Generating hydrocarbons from CO_2 is even less attractive, because of a much higher H_2 consumption. A direct hydrogenation of CO_2 to form formic acid is possible with iridium pincer hydride complexes as catalyst with an already promising conversion of a turnover frequency (TOF) up to $150,000 \text{ h}^{-1}$ and a turnover number (TON) of 3,500,000.^[41]

2. CO₂ Insertion into Metalorganic Compounds

Since GRIGNARD reported the conversion of CO₂ with alkyl magnesium halides (RMgX) to carboxylic acids in 1901, metalorganic compounds and their reactivity toward CO₂ have been well studied.^[42] Another example is the reaction of AlMe₃ and CO₂ reported by ZIEGLER and WEIDLEIN in the 60/70ies.^[43,44] When CO₂ is added to a trialkyl aluminum solution the main products are the corresponding tertiary alkoxides, AlR₂(OR) (R = alkyls). These are formed via a rearrangement alongside R₂AlOAlR₂, because the reactivity of the Al–C bond is drastically reduced after the first insertion. However, when AlR₃ is added slowly to a saturated CO₂ solution the main products are the corresponding carboxylates. Besides the reaction of metal alkyls to carboxylates, other transformations of organometallic compounds are possible, such as hydrides to formates, alk/aryloxides to carbonates, silylamides to siloxides or amides to carbamates. In most cases these transformations are irreversible.^[45–48] Since amine functional groups play a significant role for the most efficient CO₂ absorbent materials and the focus of this work is on light metals, only light metal carbamate complexes will be discussed in this chapter.

CHISHOLM described already in 1977 the formation of carbamates Ti^{+IV}(CO₂·NR₂)₄ (**1**, R = Me, Et) from the reaction of CO₂ with the corresponding amides Ti^{+IV}(NR₂)₄, however, the products were characterized *via* X-ray crystallography only more than four decades later.^[49–52] Since then, a number of light metal carbamate complexes obtained via CO₂ insertion into a M–N bond could be crystallographically authenticated. An overview can be found in Scheme A3. Other examples for titanium carbamates are [Ti^{+III}(CO₂·N*t*BuPh)₂(N*t*BuPh)]₂ (**2**) and the separated ion pair [Ti^{+III}₂(CO₂·N*i*Pr₂)₇][NH₂*i*Pr₂] (**3**) which were obtained from a one pot reaction of TiCl₃, HN*i*Pr₂ and CO₂.^[53–55] Metal imide complexes are able to insert two CO₂ molecules per M=N bond, as evidential revealed for example for the half-sandwich complex [Cp*Ti^{+IV}({CO₂}₂·NR₂)(L)] (**4**, R = Me, Ph; L = N,N'-*diisopropyl*-2-methylamidinate) or [Sc({CO₂}₂·N{o-*i*Pr₂Ph}₂)(L)] (**5**).^[56,57]

The first homoleptic aluminum carbamate complex, [Al(CO₂·N*i*Pr₂)₃]₂ (**6**), was reported by CALDERAZZO in 1993 again by an one-pot reaction of AlCl₃, CO₂ and HN*i*Pr₂.^[58] Later, CHANG reported the heterometallic [(Me₂Al)₂({μ-CO₂·NR₂}₂)₂Mg] (**7**, R = Et, *i*Pr) and the alkyl complex [AlMe₂(μ-CO₂·N*i*Pr₂)]₂ (**8**) both originating from the same starting complex [Me₂Al(μ-NR₂)₂Mg(μ-Me)]_n (*n* = 2, R = Et; *n* = 4, R = *i*Pr).^[59] A recent examples is [Al(κ²-N,*O*-2-{methylamino}CO₂·Py)₂R] (**9**, R = Et, *i*Bu) in which one CO₂ inserts into each M–N_{Py}-



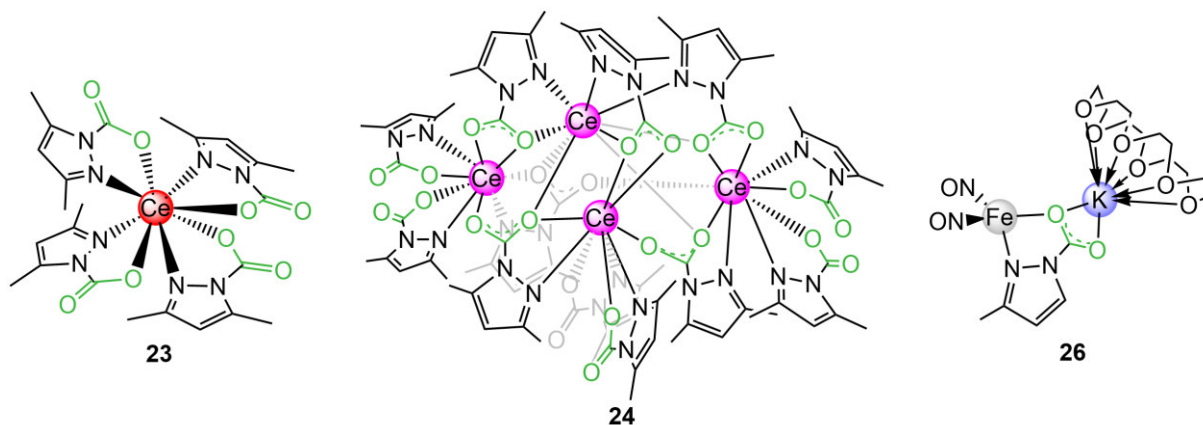
Scheme A3. Overview of light metal carbamate complexes originated from CO₂ insertion. Complexes which were proven to insert CO₂ reversibly are marked as such.

bond of Al(κ^2 -N,N-2-{methylamino}Py)₂R reversibly.^[60] A prolonged reaction time favored an additional CO₂ insertion into the Al–C bond. Another reversible CO₂ insertion is possible with the frustrated Lewis pair [9,9-Me₂Xant(4-PPh₂–AlMe₂Cl–5-AlMeCl)].^[61] The nucleophilic phosphorus interacts with the carbon atom and both electrophilic aluminum atoms interact with one oxygen atom each to form [9,9-Me₂Xant(4-PPh₂·{ μ_3 -CO₂}·AlMe₂Cl–5-AlMeCl)] (**10**).

For magnesium the first homoleptic carbamate complex, the hexameric $[\text{Mg}_6(\text{CO}_2\cdot\text{NR}_2)_{12}]$ (**11**, $\text{R} = \text{Et}, \text{Ph}$) was isolated in 2001 by CHANG.^[62] Other examples for magnesium carbamates formed by CO_2 insertion are the donor stabilized complexes $[(\text{thf})_3\text{Mg}(\text{Mg}\{\mu\text{-CO}_2\cdot\text{N}-\text{C}(=\text{NAr})-\text{C}(=\text{NAr})-\text{N}\cdot\mu\text{-CO}_2\}_3)\text{Mg}(\text{thf})_3]$ (**12**, $\text{Ar} = \text{Ph}, p\text{-Tol}$) and $[\text{Mg}_2(\text{CO}_2\cdot\text{NCy}_2)_4(\text{hmpa})]$ (**13**).^[63,64] Recently, ROESKY described the first reversible CO_2 insertion into a $\text{Mg}-\text{N}$ bond by using the bis(formazanate) complex $[\text{Mg}(\text{L})_2]$ ($\text{L} = \text{N}(\text{Ph})\text{NC}(p\text{-}t\text{BuPh})\text{NN}(\text{Ph})$).^[65] Under a CO_2 atmosphere the trimeric complex $[\text{Mg}(\mu\text{-CO}_2\cdot\text{L})(\text{L})]_3$ (**14**) is formed, which releases CO_2 at 110°C (monitored by ^1H NMR spectra) or when dissolved in donor solvents such as THF. Besides the earlier mentioned **5**, there is only one scandium complex for which CO_2 insertion was reported, the separated ion pair $[\text{Sc}(\text{CO}_2\cdot\text{N}t\text{BuAr})_2(\text{thf})_3][\text{BPh}_4]$ (**15**).^[66] For yttrium only one CO_2 insertion carbamate complex is characterized by X-ray analysis, the dimer $[\text{Cp}^*_2\text{Y}(\mu\text{-CO}_2\cdot\epsilon\text{-caprolactam})]_2$ (**16**).^[67] The CO_2 inserts into the $\text{Y}-\text{N}$ bond and the carbonyl oxygen coordinates to one yttrium center each as donor. Alkali metals appear often in ate-complexes of other metal carbamates, however, a number of monometallic alkali metal carbamates are known. All are donor stabilized and form dimers, $[\text{Li}(\text{CO}_2\cdot\text{NPh}_2)(\text{tmeda})]_2$ (**17**) and $[\text{Li}(\text{CO}_2\cdot\text{pipMe}_4)(\text{tmeda})]_2$ (**18**), tetra-/hexamers, $[\text{Li}(\text{CO}_2\cdot\{\text{N},\text{N}'\text{-bis}[\text{Ar}]\text{aminidate}\})(\text{thf})]_n$ (**19**, $n = 4$ ($\text{Ar} = o\text{-Me}_2\text{Ph}$), $n = 6$ ($\text{Ar} = p\text{-MePh}$)) and $[\text{Li}(\text{CO}_2\cdot 2,3\text{-bis}\{\text{Me}\}\text{indol})(\text{thf})]_4$ (**20**) or polymeric $[\text{Li}(\text{CO}_2\cdot\text{pyrrolyl})(\text{thf})]_\infty$ (**21**).^[68–72] Interestingly, MULVEY succeeded in isolating the dodecametallic complex $[\text{Li}_{12}(\text{CO}_2\cdot\text{N}i\text{Pr}_2)_{12}(\text{HO}_2\text{CN}i\text{Pr}_2)_2]$ (**22**), containing two carbamic acids, which is the only example of a crystallized carbamic acid metal complex.^[72]

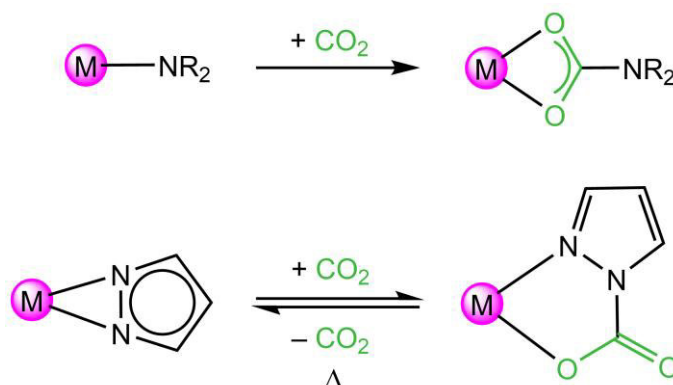
3. Light Metal Pyrazolates

Recently, we found that both tri- and tetravalent cerium pyrazolates, $[\text{Ce}(\text{pz}^{\text{Me}_2})_3]_4$ and $[\text{Ce}(\text{pz}^{\text{Me}_2})_4]_2$, respectively, are capable of inserting one CO_2 reversibly into one Ce–N_{pz}-bond of each pyrazolato ligand under formation of the carbamate complexes $[\text{Ce}^{\text{IV}}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_4]$ (**23**) and $[\text{Ce}^{\text{III}}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_3]_4$ (**24**) with a capacity of up to 25 wt% CO_2 (see Scheme A4). These reactions were conducted with excess of CO_2 , but even equimolar reactions with the ceric



Scheme A4. Reported carbamate complexes emerging from CO_2 insertion into the metal-pyrazolato bonds.

pyrazolates, afforded isolable insertion products as revealed for $[\text{Ce}^{\text{IV}}_3(\text{pz}^{\text{Me}_2})_9-(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_3(\text{thf})]$ (**25**).^[73] After a CO_2 insertion into a classic metal-amide complex the carbamate ligand coordinates in a carboxylate-like $\kappa^2(\text{O},\text{O}')$ mode. In contrast, metal pyrazolates insert CO_2 only in one of the two $\kappa^2(\text{N},\text{N}')$ nitrogen-atoms with one nitrogen of the pyrazolato ligand still attached to the metal center (see Scheme A5). The inserted CO_2 only coordinates with one oxygen atom to the metal center, which hinders electron delocalization as revealed by distinct C–O single and double bonds. This allows an easy CO_2 releasing step and therefore metal pyrazolates can insert CO_2 reversibly. Shortly thereafter, the group of LU reported about CO_2 insertion into the iron pyrazolate $[\text{K}(18\text{-crown-6})]_2[\text{Fe}(\text{pz}^{\text{Me}})(\text{NO})_2]_2$ under formation of the contact ion pair $[\text{K}(18\text{-crown-6})][\text{Fe}(\text{CO}_2\cdot\text{pz}^{\text{Me}})(\text{NO})_2]$ (**26**, see Scheme

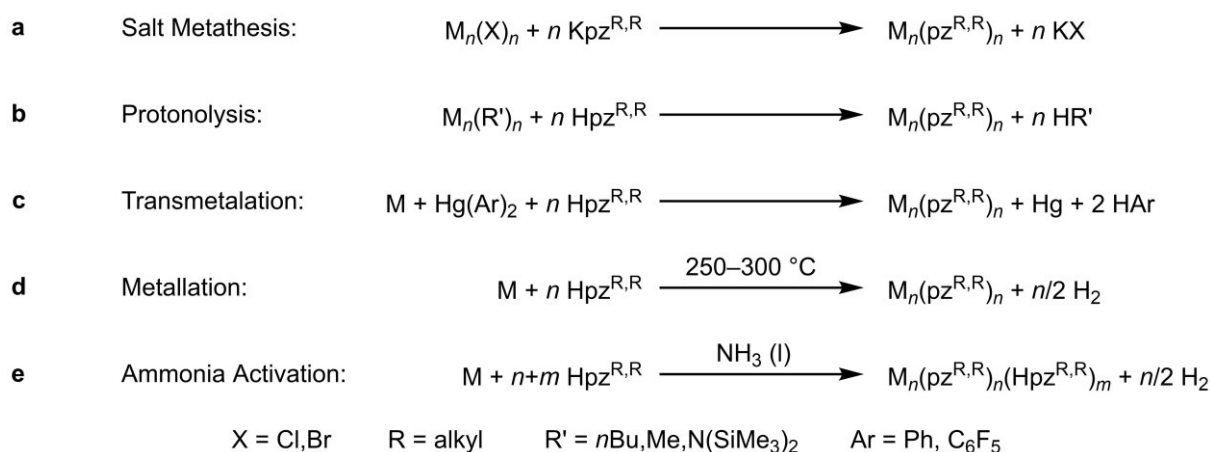


Scheme A5. Non-reversible CO_2 insertion into metal amides and reversible CO_2 insertion into metal pyrazolates.

A4).^[74] With a reductive coupling *via* the pair ferrocenium/ferrocene they were able to convert CO₂ to CaC₂O₄, which makes the overall insertion process reversible. Later, we could adapt this protocol to even bulkier cerium pyrazolates with *t*Bu or Ph moieties and also the mixed pz^{*t*Bu,Me}, although the efficiency decreased with steric bulk.^[75] Even after being immobilized onto mesoporous silica SBA-15₅₀₀, the cerium pyrazolates kept their CO₂ insertion properties and we were able to get capacities up to 20 wt% CO₂, which features the highest uptake for silica materials to the best of our knowledge.^[76] To reach high capacities light metal pyrazolates are highly desirable. Not only are most light metals abundant, inexpensive, nontoxic and thus favorably environmentally friendly, but the sorption capacity could also be improved by counteracting any “mass penalty”. This chapter gives a survey on the well-established compound class of light metal pyrazolato complexes. The aromatic pyrazolato ligand has a wide range of coordination modes and thus often a rather complex coordination chemistry can be found. Not only can the free electron pair of the nitrogen coordinate in a terminal [$\kappa^1(N)$]/[$\kappa^2(N,N')$], side-on [$\mu^2: \mu^2(N,N')$] or end-on bridging [$\mu^1: \mu^1(N,N')$] fashion, but also η^1 to η^5 π -interactions are feasible.

3.1 Synthesis routes for light metal pyrazolates

Literature reported synthesis approaches for light metal pyrazolates comprise salt metathesis reactions (route **a**, Scheme A6) of light metal halides (X = Cl, Br) and the corresponding potassium pyrazolates, protonolysis reactions (route **b**) between light metal alkyls, hydrides or amides and pyrazoles, transmetalation (route **c**) with the light metal, pyrazole and Hg(Ar)₂ (Ar = Ph, C₆F₅) under formation of the corresponding light metal pyrazolates and elemental mercury, direct metalation (route **d**) of solvent-free light metal and pyrazole by heating to 250–300 °C in a glass ampoule or ammonia activation (route **e**) of the light metal. Most light metal pyrazolates are straightforwardly accessible over route **a** or **b**. The salt metathesis route is more

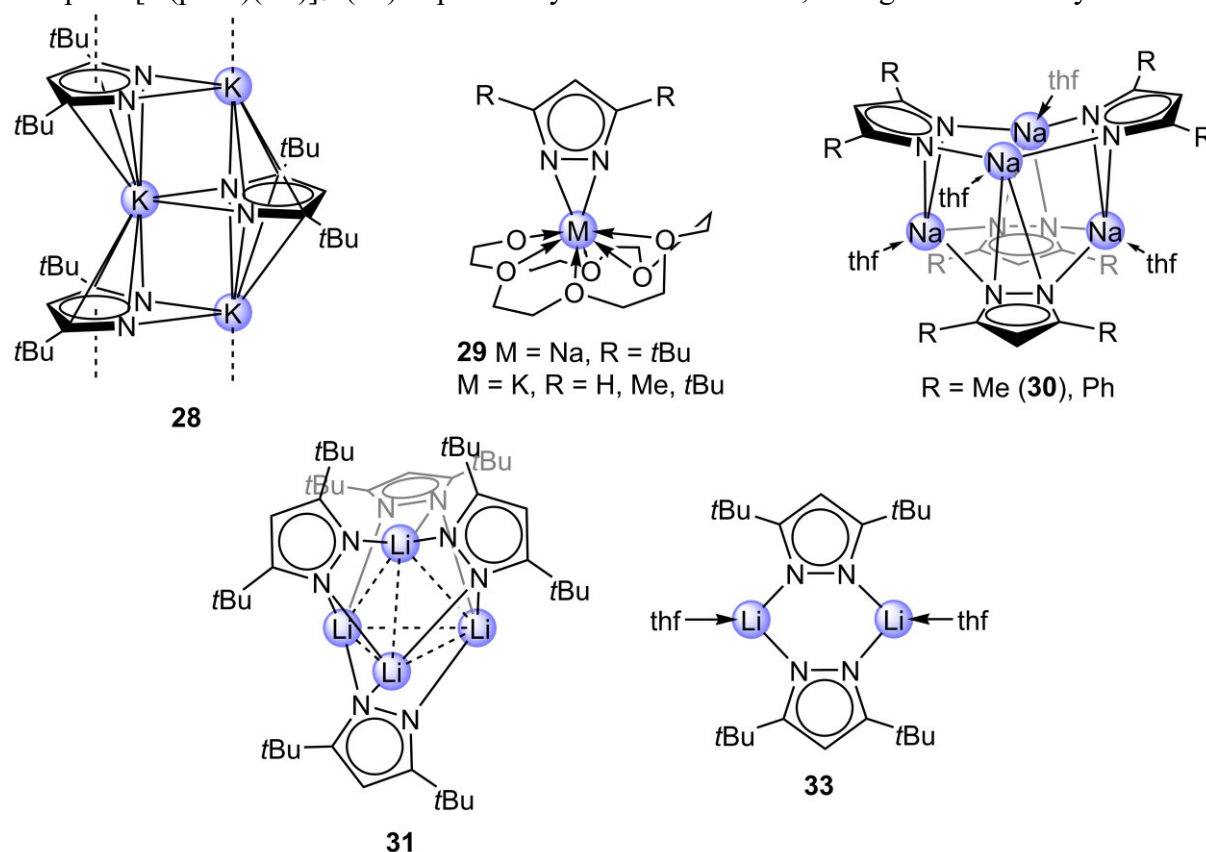


Scheme A6. Synthesis routes toward metal-pyrazolates complexes.

suitable for pyrazolates with large alkyl substituents such as *t*Bu or Ph, because of the decreased solubility for smaller moieties such as Me or the unsubstituted pyrazole. Whereas pyrazolate complexes with smaller alkyl substituents are readily accessible *via* the protonolysis route. However, the light metal alkyl precursor has to be carefully selected, because decomposition of the pyrazole and incomplete protonolysis are likely to occur, if the alkyl is too reactive or not reactive enough, respectively. Early reports for the synthesis of rare-earth-metal pyrazolates almost exclusively were accessible over route **c** despite the need to use mercury aryls for the metal activation.

3.2 Alkali-metal pyrazolates

Alkali metal pyrazolates are important pyrazolate precursors for the salt-metathesis route targeting almost all other light metal pyrazolates. The structural motifs of alkali-metal pyrazolates are dominated by either tetrameric complexes $[\text{Mpz}^{\text{R}_2}]_4$, ladder structures $[\text{Mpz}^{\text{R}_2}]_n$ or monomeric/dimeric compositions stabilized by donors $[\text{M}(\text{pz}^{\text{R}_2})(\text{do})]_n$ ($n = 1$ or 2 ; $\text{do} = \text{thf}$, Et_2O or 18-crown-6) (see Scheme A7). However, the first alkali-metal-pyrazolate complexes mentioned in the literature were either generated *in situ* or isolated as amorphous powders.^[77–79] The first structurally characterized alkali-metal pyrazolate was the hexameric potassium complex $[\text{K}(\text{pz}^{\text{Ph}_2})(\text{thf})]_6$ (**27**) reported by WINTER in 1998, alongside with a synthesis of

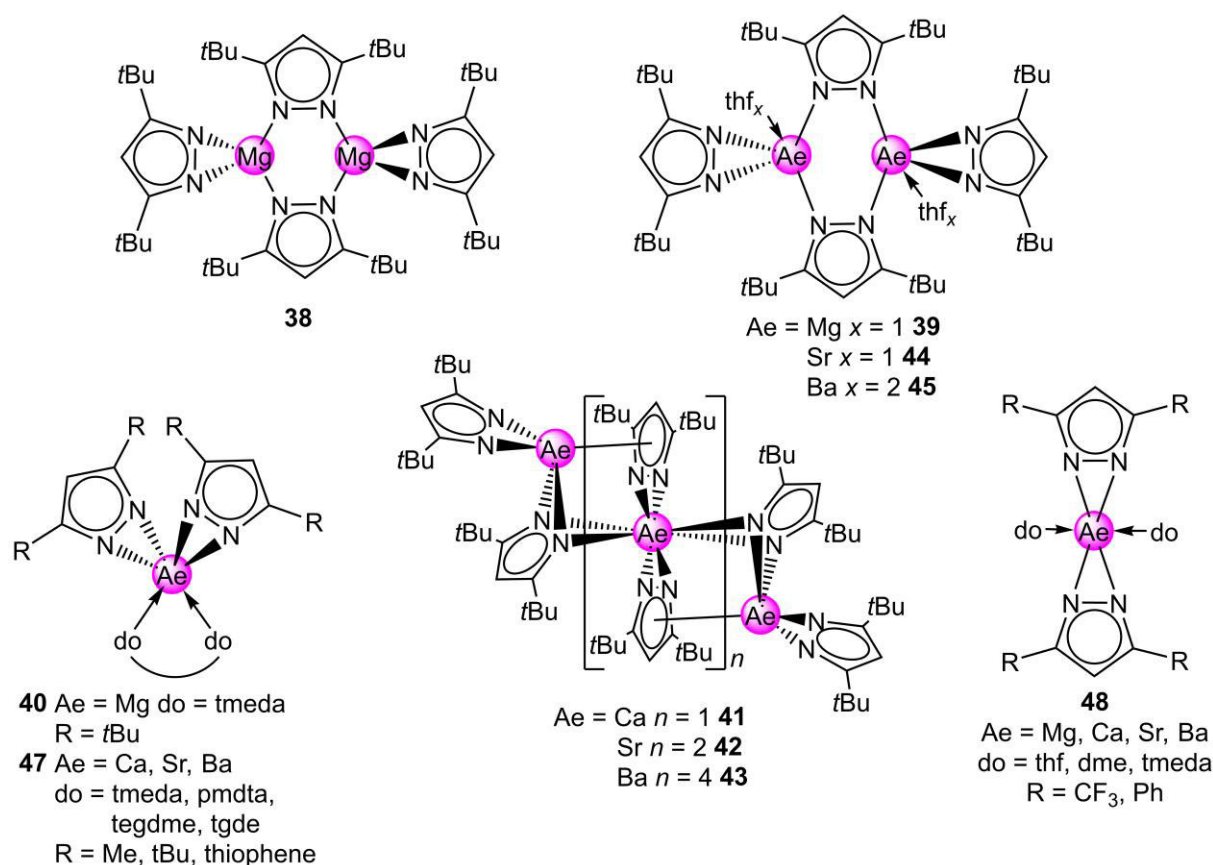


Scheme A7. Overview of alkali-metal-pyrazolate complexes.

amorphous $[\text{K}(\text{pz}^{t\text{Bu}_2})]_n$ (**28**).^[78] Six years later, WINTER reported also the first monomeric sodium pyrazolate $\text{Na}(\text{pz}^{\text{R}_2})(18\text{-crown-6})$ (**29**, $\text{R} = t\text{Bu}$, Ph) stabilized by a crown ether.^[80] Since then, several isostructural examples with sodium and potassium were reported.^[81–83] Soon after, the group of MUÑOZ-HERNÁNDEZ reported the tetrameric complex $[\text{Na}(\text{pz}^{\text{Me}_2})(\text{thf})]_4$ (**30**)^[84] and later the donor free $[\text{Li}(\text{pz}^{t\text{Bu}_2})]_4$ (**31**).^[81] For both metals other donor stabilized examples followed later.^[85,86] In the same work, MUÑOZ-HERNÁNDEZ also described the crystal structure of the above mentioned complex **28**, which revealed a highly symmetric ladder arrangement $[\text{K}(\text{pz}^{t\text{Bu}_2})]_\infty$, in which the potassium center is coordinated $\kappa_2(N, N')$ to one pyrazolate and simultaneously forms a sandwich complex with the neighboring units. The sodium derivative $[\text{Na}(\text{pz}^{t\text{Bu}_2})]_\infty$ (**32**) also forms a ladder structure, however, of reduced symmetry. Two independent ladder arrays can be found in one crystal structure, $\{[\text{Na}(\text{pz}^{t\text{Bu}_2})]_3\}_\infty$ and $\{[\text{Na}(\text{pz}^{t\text{Bu}_2})]_6\}_\infty$ respectively.^[85] Two examples of dimeric lithium pyrazolate complexes $[\text{Li}(\text{pz}^{\text{R}_2})(\text{do})]_2$ (**33**, $\text{R} = t\text{Bu}$, $\text{do} = \text{thf}$; **34**, $\text{R} = \text{Ph}$, $\text{do} = \text{Et}_2\text{O}$) were reported by DEACON and MUÑOZ-HERNÁNDEZ, respectively.^[85,87] As an overall trend, it is noteworthy that the only alkali-metal pyrazolates that have been crystallized donor-free contain the pz^{tBu_2} ligand. For smaller moieties like methyl or the unsubstituted pyrazolates donors are necessary to prevent the formation of amorphous polymeric structures. Two additional examples are the complexes $[\text{Li}_3(\text{pz}^{\text{Me}_2})_3(\text{tmeda})]_2$ (**35**), $[\text{Li}(\text{pz}^{t\text{Bu}_2})(\text{Hpz}^{t\text{Bu}_2})]_2$ (**36**) and $[\text{K}_2(\text{pz}^{\text{Me}_2})_2(\text{Hpz}^{\text{Me}_2})(18\text{-crown-6})]_2$ (**37**), with the latter being an example for mixed pyrazolato/pyrazole complexes featuring a hydrogen bond between both ligands.^[81,86,87]

3.3 Alkaline-earth metal pyrazolates

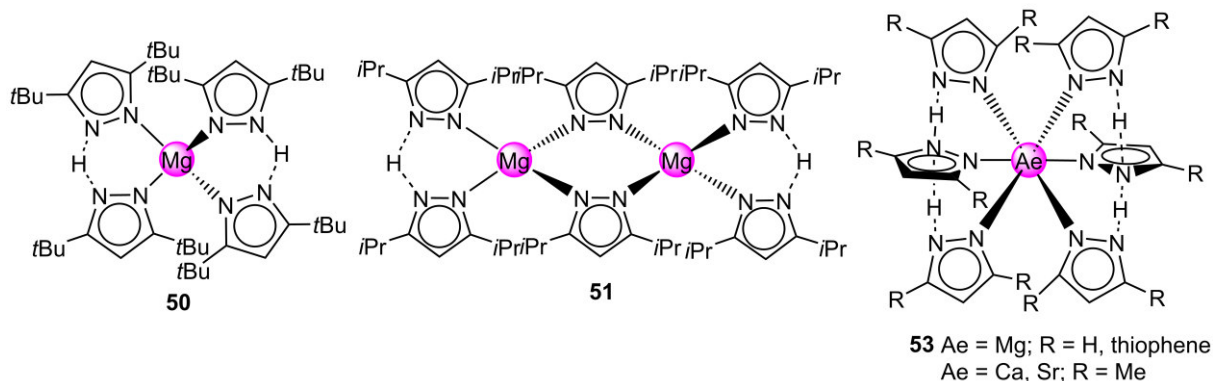
The first alkaline-earth metal ($\text{Ae} = \text{Mg}$, Ca , Sr , Ba) pyrazolate complex, the homoleptic $[\text{Mg}(\text{pz}^{t\text{Bu}_2})_2]_2$ (**38**), was reported by WINTER in 1998 *via* a salt-metathesis utilizing MgBr_2 and $\text{Kpz}^{t\text{Bu}_2}$ (see Scheme A8).^[88] The dimeric complex **38** contains two bridging pyrazolato in the $\mu\text{-}\eta^1:\eta^1(N, N')$ -mode and two terminal pyrazolato in the $\eta^2(N, N')$ -mode. This study also described the donor-stabilized dimer $[\text{Mg}(\text{pz}^{t\text{Bu}_2})_2(\text{thf})]_2$ (**39**) and monomer $[\text{Mg}(\text{pz}^{t\text{Bu}_2})_2(\text{tmeda})]_2$ (**40**). Complex **39** could be transformed back to **38** under reduced pressure. The chain-like structural motif of **38** is recurring for the three heavier alkaline-earth metals and consequently the chain length increases with increasing ionic radio of Ae in $[\text{Ae}(\text{pz}^{t\text{Bu}_2})_2]_n$ (**41** Ca : $n = 3$; **42** Sr : $n = 4$; **43** Ba : $n = 6$) up until six units for barium.^[89] There are several examples for the heavier alkaline-earth metals of the donor stabilized dimer $[\text{Ae}(\text{pz}^{t\text{Bu}_2})_2(\text{thf})_x]_2$ (**44** Sr $x = 1$, **45** Ba $x = 2$)^[90] and $[\text{Ae}(\text{pz}^{\text{R}_2})_2(\text{do})_x]_2$ (**46**).^[91–93] Further, the donor-stabilized monomeric $\text{Ae}(\text{pz}^{\text{R}_2})(\text{do})$ displays two coordination modes, one with a *cis*



Scheme A8. Overview of homoleptic alkaline-earth-metal pyrazolate complexes.

arrangement (47) of the pyrazolato like complex 40^[92–94] and the other with a *trans* configuration (48).^[92,95–97] *Cis* configured complex 40 is the only example of a monomeric magnesium pyrazolate, while the *trans* configuration is exclusively found for the heavier alkaline earth metals. For barium an example of a polymeric chain is reported, [Ba(pz^{Me2})₂(thf)]_∞ (49).^[98]

Given the divalent nature of the alkaline-earth metals and hence the resulting tendency of donor coordination to saturate the coordination sphere, there are several examples of mixed pyrazole/pyrazolato complexes (see Scheme A9). Monomeric Mg(pz^{tBu2})₂(Hpz^{tBu2})₂ (50) by MÖSCH-ZANETTI et al. was the first example.^[99] It was achieved by adding two equivalents of



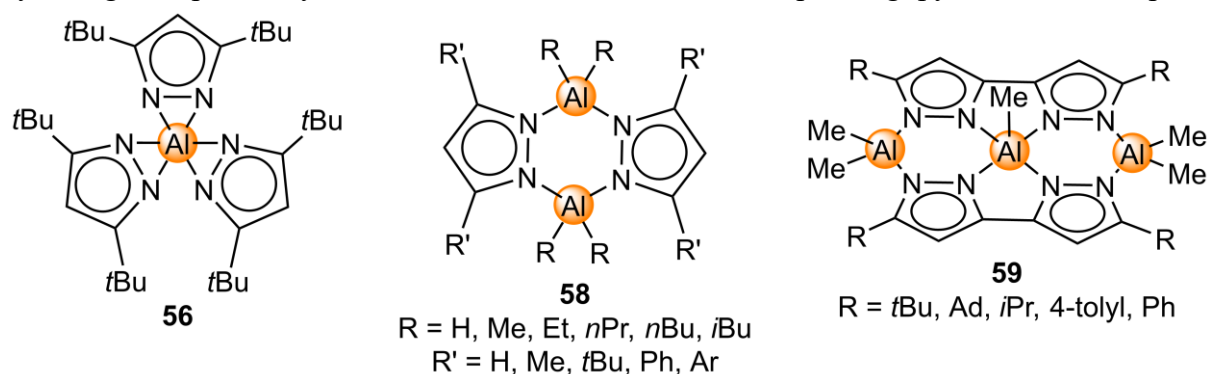
Scheme A9. Overview of alkaline-earth metal mixed pyrazolato/pyrazole complexes.

Hpz^{*t*Bu}₂ to the salt metathesis approach for complex **38**. The pyrazole coordinates as a donor and forms a hydrogen bond with one of the pyrazolates. Because of this, complex **50** is tetrahedrally coordinated with only one nitrogen of each ligand bond to the magnesium center. RUHLANDT-SENGE reported on the mixed dimer [Mg(pz^{*i*Pr})₂(Hpz^{*i*Pr})₂]₂ (**51**) bearing the slightly smaller *i*Pr moiety.^[91] Pyrazole donors engage in hydrogen bonding with the terminal pyrazolato ligand and two pyrazolato are in bridging position. Remarkably, only one pyrazole donor per magnesium center was found in **51**, although in the protonolysis reaction with Mg(*n*Bu)₂ and Hpz^{*i*Pr} a ratio of 1:4 was used. In the same work, the dimeric complex [Ca(pz^{*i*Pr})₂(Hpz^{*i*Pr})₂]₂ (**52**) was reported, in which two pyrazole donors coordinate to each calcium atom. Additionally, also monomeric complexes of the form Ae(pz^R)₂(Hpz^R)₄ (**53**, Ae = Mg, Ca, Sr) with four donor pyrazole bond to one metal center are feasible.^[93,95] In this octahedral structural motive, two hydrogen bonds are formed to each of the two pyrazolato ligands.

Although not being an alkaline-earth metal it is noteworthy that two pyrazolate complexes of zinc are reported in the literature. Because of the almost identical ionic radii of magnesium and zinc, complexes of these two often share similarities in reactivity and structure. Striking is the homoleptic chain [Zn(pz)₂]_{*n*} (**54**), which was determined via *ab-initio* X-ray powder diffraction.^[100] This indicates that the elusive [Mg(pz)₂]_{*n*} might be feasible as well. The second reported zinc pyrazolate is Zn(pz^{*t*Bu})₂(Hpz^{*t*Bu})₂ (**55**), which is isostructural to complex **50**.^[86]

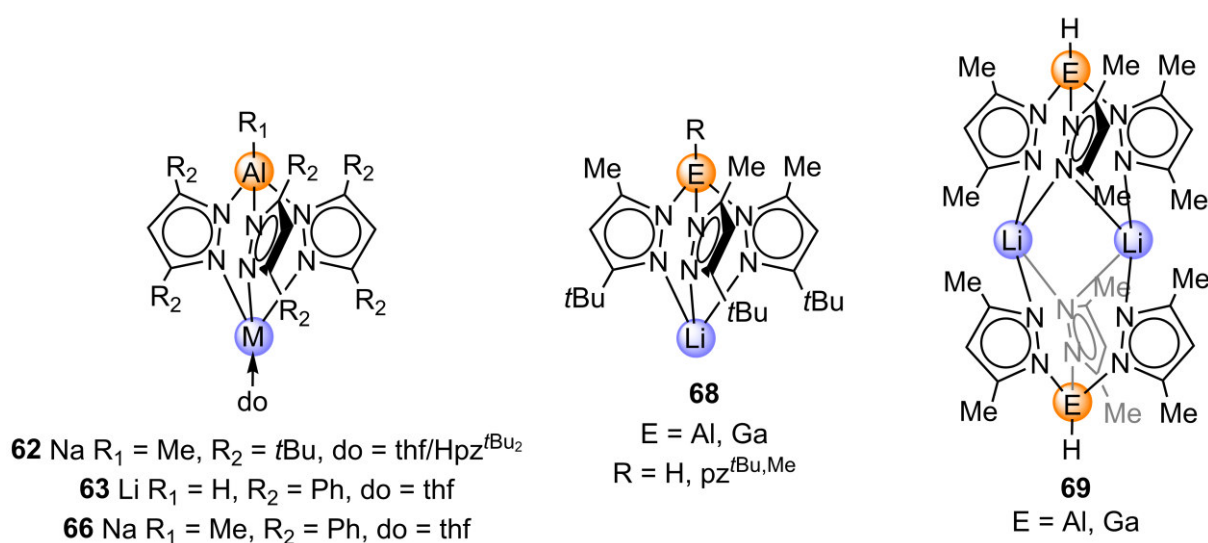
3.4 Aluminum pyrazolates

There is only one known homoleptic aluminum pyrazolate Al(η²-pz^{*t*Bu})₃ (**56**) and its donor stabilized derivative Al(η²-pz^{*t*Bu})₃(thf) (**57**) (see Scheme A10).^[101,102] Unlike to the alkali and alkaline-earth metals a monomeric complex is possible without donor stabilization. It is easily accessible *via* the salt-metathesis route starting with AlCl₃ and Kpz^{*t*Bu}. Compound **56** contrast, by using the protonolysis route with AlMe₃ and a corresponding pyrazole no complete



Scheme A10. Overview of aluminum-pyrazolate complexes.

conversion can be achieved. At ambient temperature only a single ligand exchange to the dimer $[\text{AlMe}_2(\mu\text{-pz}^{\text{Me}_2})]_2$ (**58**) is feasible, with both pyrazolato ligands bridging between the two aluminum centers and two terminal alkyl groups.^[103] Since then, many examples of this structural motif have been reported with a wide variety of organoaluminum compounds and differently substituted pyrazolato ligands.^[104–114] Recently, a higher conversion could be accomplished in $\text{Me}_2\text{Al}([\mu^2\text{-}\eta^2\text{-bp}]_2\text{AlMe})\text{AlMe}_2$ (**59**) using a 2H,2'H-3,3'-bipyrazole (bp) as a precursor.^[115] The trinuclear **59** contains two terminal AlMe_2 groups connected with two bp ligands. In the center of the two bp ligands is one AlMe group coordinated to the four inner nitrogen atoms.



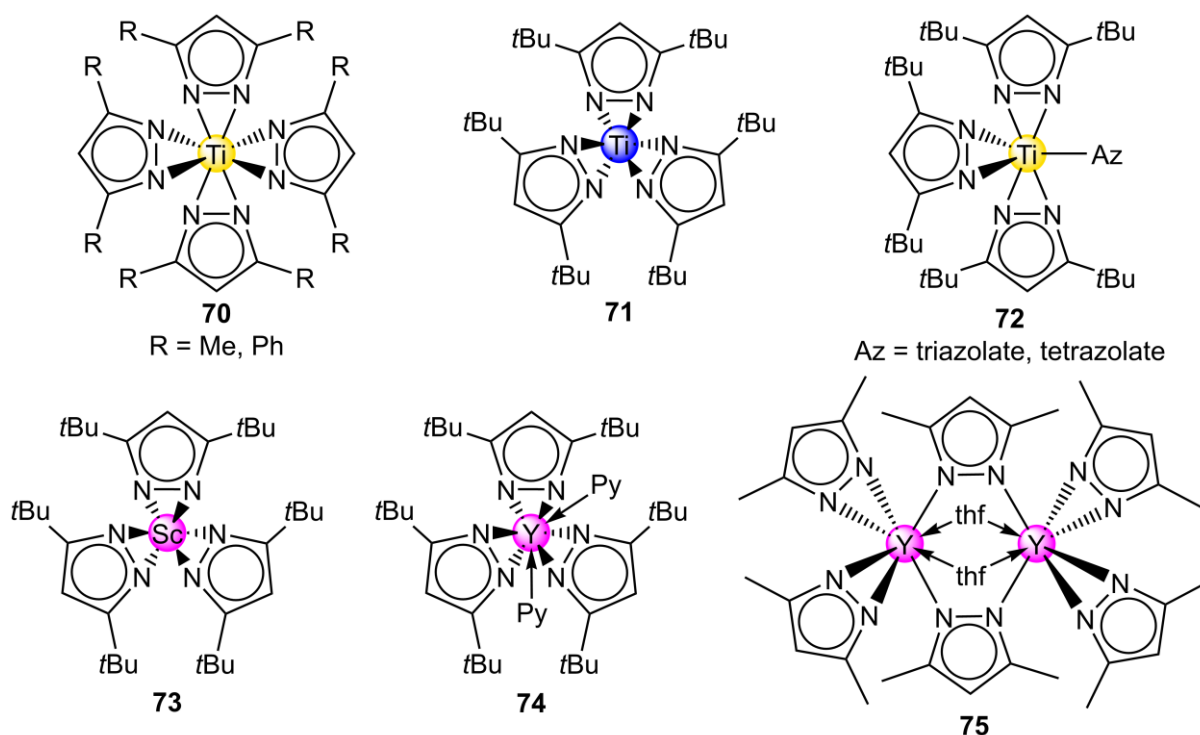
Scheme A11. Examples of Al/Ga Tp-analogous complexes.

Using AlMe_3 as a precursor in a salt metathesis with $[\text{Na}(\text{pz}^{t\text{Bu}_2})]_n$ provided the poly(pyrazolyl)aluminate $[(\text{Na}\{\text{Al}(\text{pz}^{t\text{Bu}_2})\text{Me}_3\})_3(\text{thf})_2]_\infty$ (**60**).^[116] Subsequent protonolysis of **60** with one equivalent $\text{Hpz}^{t\text{Bu}_2}$ per aluminum center gave dimeric $[\text{Na}\{\text{Al}(\text{pz}^{t\text{Bu}_2})_2\text{Me}_2\}]_2$ (**61**). However, adding two equivalents of $\text{Hpz}^{t\text{Bu}_2}$ to **60** lead to the scorpionate complex $\text{MeAl}(\text{pz}^{t\text{Bu}_2})_3\text{Na}(\text{do})$ (**62**, do = thf, $\text{Hpz}^{t\text{Bu}_2}$) in which the aluminum center adopts the position of the boron atom in a classic Tp ligand (see Scheme A11). This aluminum Tp-analogue is also directly isolable by employing $\text{Li}[\text{AlH}_4]$ in a protonolysis with Hpz^{R_2} , forming the corresponding lithium salt with one hydrido still attached to the aluminum center.^[117] Since then, several similar examples have been reported.^[117–119] These complexes include $\text{HAl}(\text{pz}^{\text{Ph}_2})_3\text{Li}(\text{thf})$ (**63**), $\text{HAl}(\text{pz}^{\text{Ph}_2})_3\text{ZnH}$ (**64**), $\text{Al}(\text{pz}^{t\text{Bu},\text{Me}})(\text{pz}^{t\text{Bu},\text{Me}})_3\text{Li}$ (**65**), $\text{MeAl}(\text{pz}^{\text{Ph}_2})_3\text{Na}(\text{thf})$ (**66**), $\text{MeAl}(\text{pz}^{\text{Ph}_2})(\mu\text{-pz}^{\text{Ph}_2})_2\text{Rh}(\text{cod})$ (**67**) and even some gallium Tp-analogue such as $\text{RE}(\text{pz}^{t\text{Bu},\text{Me}})_3\text{Li}$ (**68**, E = Al R = H, $\text{pz}^{t\text{Bu},\text{Me}}$; Ga R = H) and the dimer $[\text{HE}(\text{pz}^{t\text{Bu},\text{Me}})_3\text{Li}]_2$ (**69**, E = Al, Ga).

3.5 Early transition metal pyrazolates

Due to the higher valance of early transition metals, their pyrazolate complexes form mostly monomeric or dimeric structures in dependence of the ionic radii and the alkyl substituents of the pyrazolato ligand (see Scheme A12). In 1997, WINTER reported the first homoleptic titanium pyrazolate complex $\text{Ti}^{+IV}(\eta^2\text{-pz}^{\text{R}_2})_4$ ($\text{R} = \text{Me}, \text{Ph}$) (**70**).^[120] It was accessible *via* the protonolysis route utilizing $\text{Ti}^{+IV}(\text{NMe}_2)_4$ and the corresponding pyrazole. Besides tetravalent **70**, the homoleptic trivalent $\text{Ti}^{+III}(\eta^2\text{-pz}^{\text{tBu}_2})_3$ (**71**) has been reported by MÖSCH-ZANETTI.^[121] Later, WINTER also reported the mixed tetravalent complexes of the form $\text{Ti}^{+IV}(\eta^2\text{-pz}^{\text{tBu}_2})_3(\text{L})$ (**72**, $\text{L} = \text{triazolato}, \text{tetrazolato}$) in which one pyrazolato ligand is replaced by a triazolato or a tetrazolato ligand.^[122]

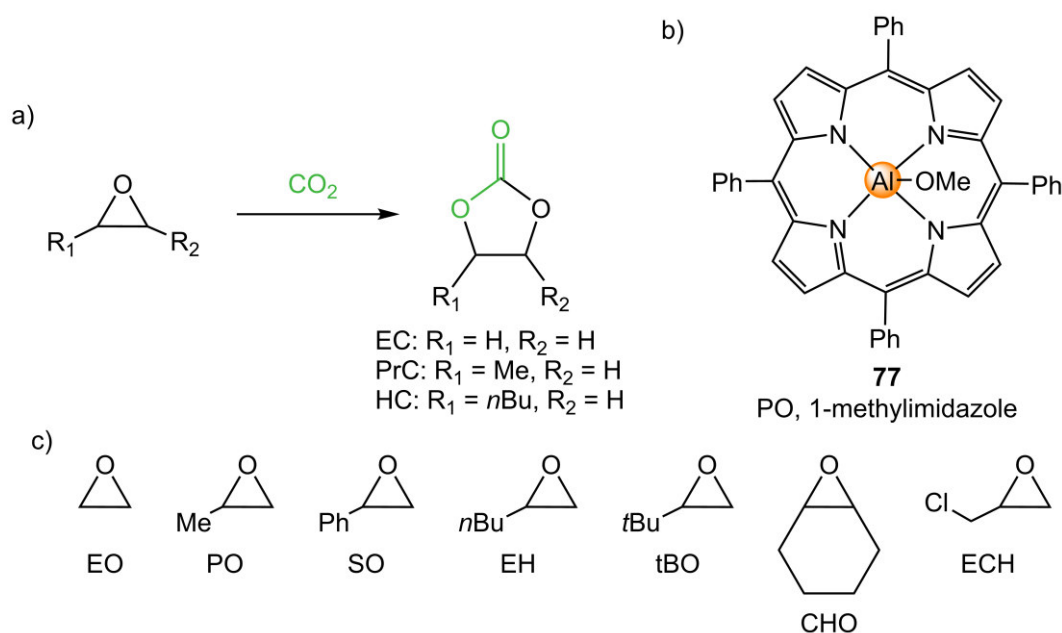
Both scandium and yttrium form a monomeric complex with di-*tert*-butylpyrazolate, $\text{Sc}(\eta^2\text{-pz}^{\text{tBu}_2})_3$ (**73**) and the donor stabilized $\text{Y}(\eta^2\text{-pz}^{\text{tBu}_2})_3(\text{Py})_2$ (**74**), respectively, with several other examples of scandium and yttrium with other donors for the latter.^[123–126] By decreasing the steric bulk of the pyrazolato ligand, dimeric complexes are formed. One example is the donor stabilized $[\text{Y}(\eta^2\text{-pz}^{\text{Me}_2})_2(\mu_2\text{-pz}^{\text{Me}_2})(\mu_2\text{-thf})]_2$ (**75**) with an end-on bridging of the pyrazolato ligand,^[127] whereas in the donor free $[\text{Sc}(\eta^2\text{-pz}^{\text{Ph}_2})_2(\mu_2\text{-pz}^{\text{Ph}_2})]_2$ (**76**) the pyrazolato moieties are bridging in the $\mu\text{-}\eta^2\text{:}\eta$ mode.^[128]



Scheme A12. Overview of early transition-metal pyrazolate complexes.

4. Cycloaddition of CO₂ and Epoxides to Cyclic Carbonates

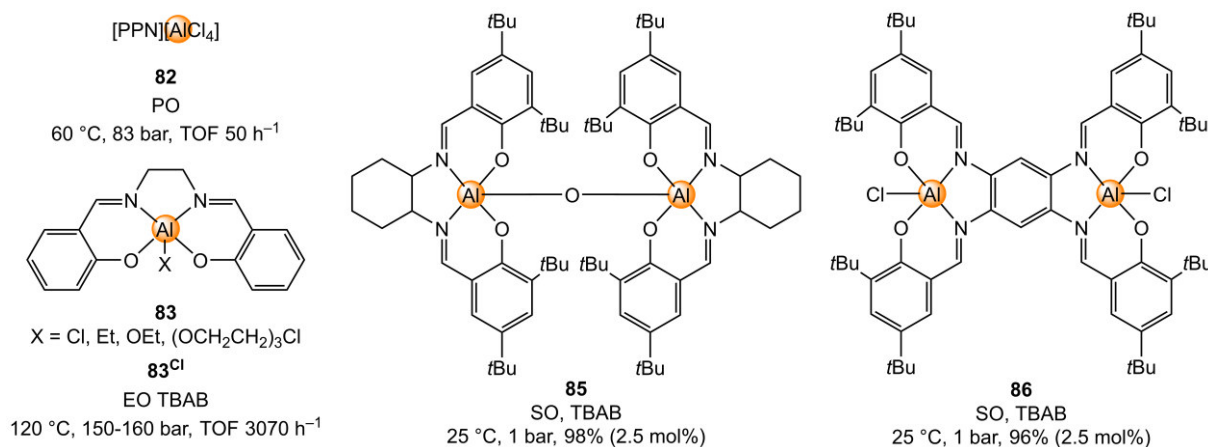
The cycloaddition of epoxides and CO₂ to cyclic carbonates is a carbon dioxide transformation, which is already well established in the industry (see Scheme A13a). This very reaction is also a side reaction of the copolymerization with the same compounds, which is discussed in detail in the next chapter. Nevertheless, the cyclic carbonates are highly sought-after and versatile products by themselves, since ethylene carbonate (EC) and propylene carbonate (PrC) are used as electrolytes in lithium ion batteries.^[129–133] PrC was used for the first commercially available lithium ion battery, but was later outperformed by its smaller derivative EC. Not only has EC a higher dielectric constant ($\epsilon = 78$), which is necessary to dissolve the corresponding salts, but also a better conductivity.^[134,135] Further applications of cyclic carbonates are the replacement of phosgene in the synthesis of polyurethanes^[136] and as fuel additives.^[137–140] When cyclic carbonates are added to diesel fuel the amount of unburnt hydrocarbons, carbon monoxide and particle pollution can be reduced remarkably.



Scheme A13. a) Cycloaddition of epoxides and CO₂ to the corresponding cyclic carbonates. b) First catalyst system of INOUE for the cycloaddition of propylene oxide and CO₂ with 1-methylimidazole as cocatalyst. c) Abbreviations for epoxides used in this thesis.

The catalytic cycloaddition of CO₂ with epoxides using organometallic compound as catalysts was first described by INOUE in 1978.^[141] He reported that the tetraphenylporphyrin (TPP) complex (TPP)Al(OMe) (**77**) can convert propylene oxide (PO) and CO₂ to PrC at ambient temperature and pressure by using a catalyst load of 5 mol% and 1-methylimidazole as cocatalyst (see Scheme A13b). The addition of a cocatalyst was crucial for this transformation, because when only the catalyst **77** is used, the corresponding polycarbonate formed exclusively.

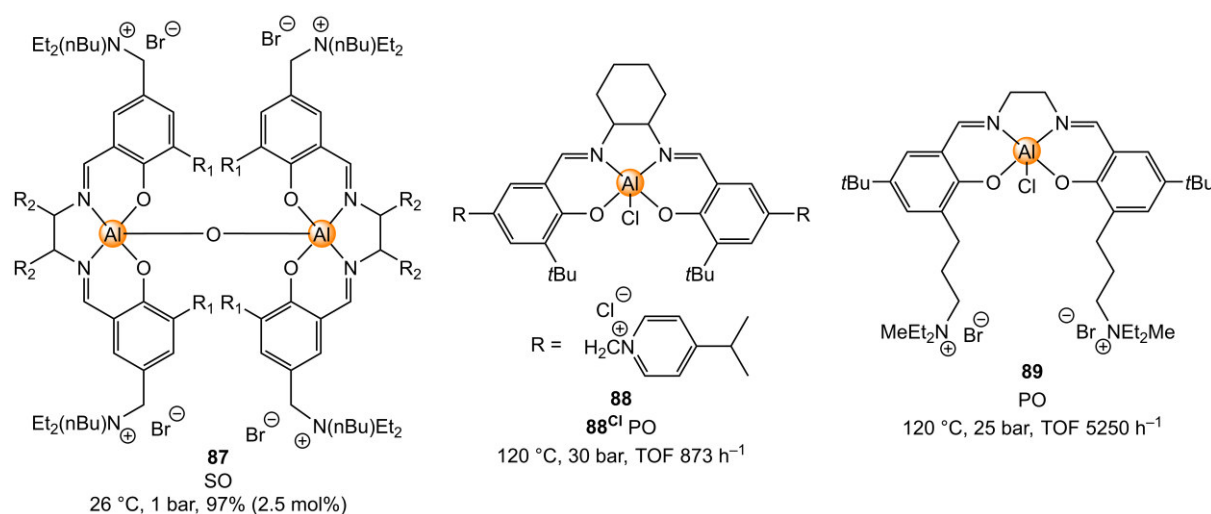
Since then, a wide variety of catalysts have been reported which also includes various light metal complexes. In later works, INOUE reported several additional porphyrin based catalysts, such as (TPP)Al(OCHMe-CH₂)_n-Cl (**78**) containing a homopolymerized poly(oxyalkyl) chain or the zinc complex (TPP(N-Me))ZnEt (**79**), which engages in a light-induced reaction with a secondary amine and carbon dioxide to the carbamate (TPP(N-Me))Zn(CO₂·NR₂) (**80**, R = Et, *n*Pr, *i*Pr, *i*Bu).^[142,143] Both showed the same reactivity towards CO₂ and epoxides as **77**.



Scheme A14. Salen-based catalysts for the cycloaddition of epoxides and CO₂ to cyclic carbonates. Conditions, cocatalysts and TOFs (conversion if no TOF was stated) for the turnover of the best substrate are stated below the complexes.

Since the groundbreaking work of INOUE, several catalyst systems have been reported and well-optimized. One early example was reported by DARENSBOURG in 1996 involving the separated ion pairs [(HB{pz^{3-Ph}}₂{pz^{5-Ph}}₂)₂Al][AlCl₄] (**81**) and [PPN][AlCl₄] (**82**). Complex **82** showed a turnover frequency (TOF) of 50 h⁻¹ at 60 °C and 83 bar.^[144] A well-studied class of catalysts are aluminum bis(salicyldiimine) (salen) complexes (see Scheme A14). The first example was (salen)AlX (**83**, X = Cl, Et, OEt, (OCH₂CH₂)₃Cl) described by HE in 2002.^[145,146] Complex **83^{Cl}** was able to catalyze the cycloaddition of EO and supercritical CO₂ at 120 °C and 150–160 bar with tetra-*n*-butylammonium bromide (TBAB) as cocatalyst with a significantly increased TOF of 3070 h⁻¹. By using only 40 bar and 110 °C the conversion still reached a TOF of 1140 h⁻¹. Tetra-*n*-butylammonium halides play a significant role as cocatalysts and are involved in most of the leading catalysts today. Other early examples of aluminum salen complexes with a wide variety of substitution patterns were reported by LU.^[147,148] Later, GARCÍA reported the complex (salen)AlCl incorporated on polystyrene (**84^{PS}**) and poly(ethylene glycol bismethacrylate) (**84^{PEA}**).^[149] These heterogeneous catalysts show a moderate catalytic activity with styrene oxide (SO) with a turnover number (TON) of 59 at 80 °C and 100 °C. However, they revealed a high stability and reusability. NORTH presented the oxo-bridged bimetallic salen complex [(salen)Al]₂O (**85**) as catalyst for the reaction of SO with CO₂ and reported a high conversion

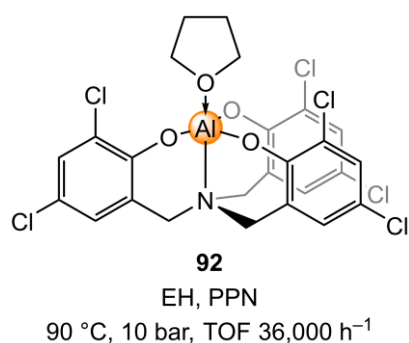
at already mild conditions (25 °C, 1 bar).^[150,151] In 2017, the same group reported the bimetallic complex $[\text{Ph}\{(\text{salen})\text{AlCl}\}_2]$ (**86**), in which two salen ligands are connected *via* a phenyl moiety.^[152] Compound **86** showed only moderate catalytic activity, however, was able to convert a wide variety of epoxide containing terminal and internal epoxides in a quantitative yield at 25–50 °C and 10 bar. The highest catalytic activity of aluminum salen complexes are reached with ligand systems already containing a quaternary ammonium salt in the backbone, which were shown to act as single component catalysts (see Scheme A15). The first example was described by NORTH in 2009.^[153,154] The bimetallic $[(\text{R}_2\text{salen})\text{Al}]_2\text{O}$ (**87**, $\text{R} = -\text{CH}_2\text{N}(\text{nBu})\text{Et}_2$) with two embodied ammonium salt moieties per salen ligand at the 3-position showed a quantitative yield even with bulkier epoxides such as SO and EH at ambient temperature and pressure. In the same work, **87** was incorporated into polystyrene (**87^{PS}**) and used in the cyclization of SO and CO₂, which yielded >99, 94 and 70% of styrene carbonate (SC) in three consecutive reactions. In 2012, DARENSBOURG reported the complex $(\{3\text{-R}\}_2\text{salen})\text{AlCl}$ (**88**, $\text{R} = [\text{N-CH}_2\text{DMAP}][\text{X}]$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) containing two dimethyl pyridinium bromide moieties at the salen 3-position.^[155] The catalytic activity of **88^{Cl}** in the reaction of PO with CO₂ reached a TOF of 873 h⁻¹ at 120 °C and 30 bar. A drastically increased catalytic activity was achieved by the complex $(\{5\text{-R}\}_2\text{salen})\text{AlCl}$ (**89**, $\text{R} = -[\text{C}_2\text{H}_4\text{NEt}_2\text{Me}][\text{Br}]$) reported by REN and LU.^[28] By positioning the quaternary ammonium moieties on the inner site of the salen ligand, TOFs of up to 5250 h⁻¹ were possible at 120 °C and 25 bar for the conversion of PO to PrC and a TON of 116,230. Even for bulkier epoxides high TOFs were obtained, comprising EH (830 h⁻¹), SO (750 h⁻¹), epoxy butane (3000 h⁻¹), 2-(chloromethyl)oxirane (1240 h⁻¹) and 2-(phenoxyethyl)oxirane (1210 h⁻¹), respectively. Catalyst **89** was also able to perform a similar transformation with aziridine. Aluminum and



Scheme A15. Salen-based catalysts containing quaternary ammonium salts in the ligand scaffold. Conditions and TOFs (conversion if no TOF was stated) for the turnover of the best substrate are stated below the complexes.

transition-metal complexes of the salen-like ligand *N,N'*-bis(salicylene)-2-aminobenzylamine (salabza) of the form (*t*Bu₄salabza)MX (**90**, M = Al, Cr, Fe, Co; X = Cl, OAc) were also tested as catalysts.^[156] The aluminum congener **90^{Al}** revealed the highest catalytic activity with TOFs of up to 901 and 3434 h⁻¹ for PO and ECH, respectively, with TBAB as a cocatalyst. In 2019, HOR and WU reported the cage-like complex Al(salen)@cage (**91**, M = Al, Co) in which three salen ligands are connected over two 1,3,5-phenylbenzene units.^[157] At ambient temperature and pressure the heterogeneous catalyst **91** showed a quantitative conversion of even bulky epoxides like SO and EH to their corresponding cyclic carbonates and only a small decrease of catalytic activity was observed after five consecutive runs. Interestingly, for the smaller PO only a conversion of 58% was found.

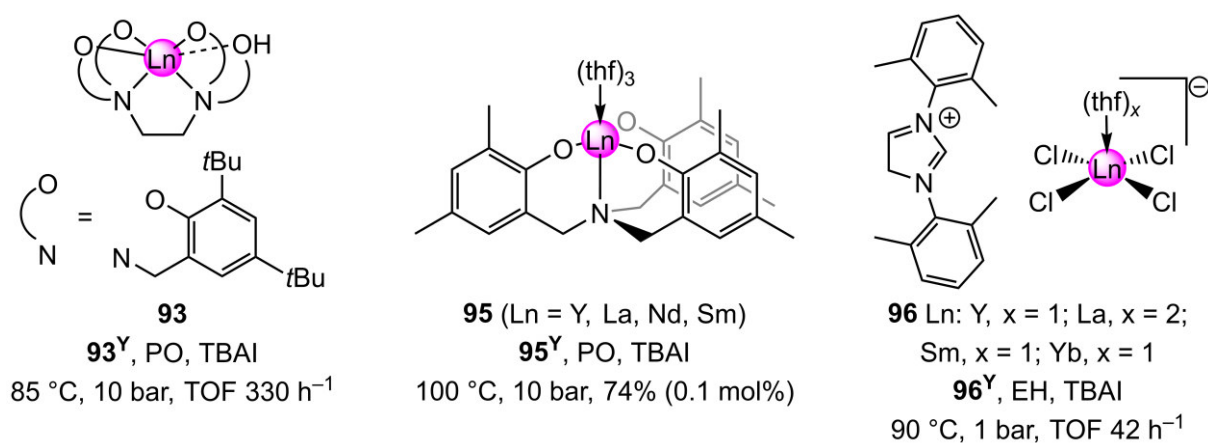
Further, aluminum trisphenolate complexes were examined as catalysts for the cycloaddition of epoxides and CO₂. In 2013, KLEIJ presented the tris(phenolate) aluminum complex (N{CH₂-6-[2,4-dichlorophenolate]})₃Al(thf) (**92**).^[158,159] Due to the strong inductive effect of the chloride moieties, the aluminum center gains a stronger oxophilicity and thus acts as a more efficient catalyst. For 1,2-epoxyhexane (EH) TONs of up to 112,000 and a maximum TOF 36,000 h⁻¹ were observed at 90 °C and 10 bar with tetra-*n*-butyl ammonium iodide (TBAI) as a cocatalyst. Not only has **92** an exceptionally high catalytic activity, but also high tolerance for functional groups and so a wide scope of epoxides could be transformed to their corresponding cyclic carbonates in good to quantitative yield. For example olefins, esters, alkynes, bisepoxides, fatty acids and even the higher homologous oxetane.^[158,160]



Scheme A16. Superior performance of tris(phenolate) aluminum complex (N{CH₂-6-[2,4-dichlorophenolate]})₃Al(thf) (**92**) in the cycloaddition of CO₂ and epoxides. Conditions, cocatalyst and TOF for the turnover of the best substrate are stated below the complexes.

Poly(phenolate) ligands were also applied for designing rare-earth metal-based catalysts (see Scheme A17). YAO reported the tetraphenolate complex (Et{N[CH₂-6-(2,4-*t*Bu-phenolato)]₂})₂Ln(thf) (**93**, Ln = Y, Nd, Sm, Yb) in 2014.^[161] The light metal complex **93^Y** reached a TOF of 330 h⁻¹ for PO at 85 °C and 10 bar when TBAI is used as cocatalyst. However, it was outperformed by its heavier congener **93Nd** with a TOF of 4000 h⁻¹ under the

same conditions. Other examples are $(N\{CH_2-6-[2,4-bis-tBu-phenolato]\}_3)M(thf)_x$ (**94**, $M = Al$, $x = 1$; $M = Y$, $x = 2$) and $(N\{CH_2-6-[2,4-bis-Me-phenolato]\}_3)Ln(thf)_3$ (**95**; $Ln = Y, La, Nd, Sm$).^[162,163] Both derivatives of **94** show moderate catalytic activity for the sterically demanding cyclohexene oxide (CHO) at 80 °C, 20.7 bar and TBAB as a cocatalyst (**94^{Al}** TON = 260, TOF = 65 h⁻¹; **94^Y** TON = 970, TOF = 80.8 h⁻¹).^[162] For **95**, it was again observed that the heavier Nd-based **95Nd** (TON = 1760) performed with a higher catalytic activity than its light metal derivative **95^Y** (TON = 740) for PO at 100 °C and 10 bar when TBAI is used as a cocatalyst.^[163] In addition, **95** is able to transform a wide variety of epoxides in good to quantitative yield including terminal, internal and bis-epoxides. Furthermore, **95Nd** is even able to convert PO and CO₂ with several aniline derivative into oxazolidinones.

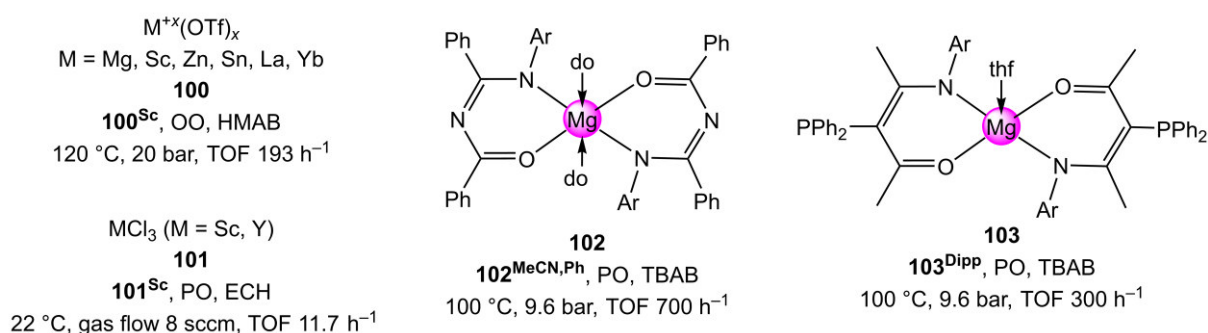


Scheme A17. Overview of rare-earth metal-based catalysts with a focus on yttrium. Conditions, cocatalysts and TOFs (conversion if no TOF was stated) for the turnover of the best substrate are stated below the complexes.

Another rare-earth metal catalyst for the coupling of epoxides and CO₂ is the separated ion pair $[IPr][LnCl_4(thf)_2]$ (**96**, $Ln = Y, La, Sm, Yb$; $IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolium$) reported by YUAN and YAO in 2017.^[164] Complex **96** acts as a single-component catalyst, while the samarium complex accomplished a TON up to 480 and a maximum TOF of 48 h⁻¹ for EH already at ambient pressure and 90 °C. Additionally, **96** is recyclable and transforms several epoxides to their corresponding cyclic carbonates covering terminal, internal and bisepoxides. The so far best rare-earth metal based catalyst is the heteroscorpionate complex $(CpCHC\{Ph\}_2\{N-pz^{Me_2}\})La[N\{SiHMe_2\}_2]_2$ (**97**) reported by OTERO, CASTRO-OSMA and LARA-SÁNCHEZ in 2017.^[165] At 110 °C and 10 bar complex **97** exhibited showed a TON of 306,667 and TOFs up to 15,000 h⁻¹ for SO. On top of that, **97** revealed quantitative yield for a wide scope of terminal epoxides with high acceptance for functional groups. The yields for internal epoxides amounted to 43–99%, applying the same conditions (70 °C and 10 bar).

Heteroscorpionate complexes of aluminum were also reported and used in the cycloaddition of epoxides and CO₂ a few years earlier by NORTH and OTERO. Utilizing a bis(pyrazolyl)methane ligand complexes of the type (HC{pz^{Me2}}₂CXR')AlEt₂ (**98**, X: =S, =NR; R': -N(Ph)-, -O-) or (HC{pz^{Me2}}₂CHRO)AlR'₂AlR'₃ (**99**, R = *t*Bu, *p*-tolyl, ; R' = Me, Et) were obtained.^[166,167] Although several epoxides could be converted to their corresponding cyclic carbonates, only minor catalytic activities of TOFs 0–1 h⁻¹ were observed.

Although the catalytic transformation can also proceed with basic compounds like the oxides or oxychlorides such as MgO, Al₂O₃ and SmOCl as reported by SAKAKURA in 2002 (see Scheme A18), only minor conversions for PO (TON 1–3) are observed even under harsh condition by using supercritical CO₂ at 140 bar and 200 °C.^[168] Other simple systems like the triflates M(OTf)_x (**100**, M = Mg, Sc, La, Yb, Zn, Sn) can also catalyze the cycloaddition of epoxides and CO₂ with hexadecyltrimethylammonium bromide (HMAB) as a cocatalyst as reported by DE VOS already in 2009.^[169] Likewise, they exhibit only a moderate catalytic activity for the transformation of octylene oxide at 120 °C and 20 bar with TONs of 770 and 534 for **100**^{Sc} and **100**^{Mg}, respectively. The simple Lewis acid MCl₃ (**101**, M = Sc, Y) showed good conversion (98/77%) of terminal epoxides like PO and epichlorohydrin (ECH), respectively, at ambient pressure and under a constant gas flow of 8 sccm of a 50% mixture of CO₂ in O₂.^[170] Despite the fact only small TOFs (up to 11.7 h⁻¹) were achieved, **101** was able to convert ECH with CO₂ from flue gas (10.2% CO₂, 7.7% O₂, 0.1% CO, NO_x, SO_x, 2% H₂O). The CO₂ content could be reduced by 97% (TOF 5.4 h⁻¹).

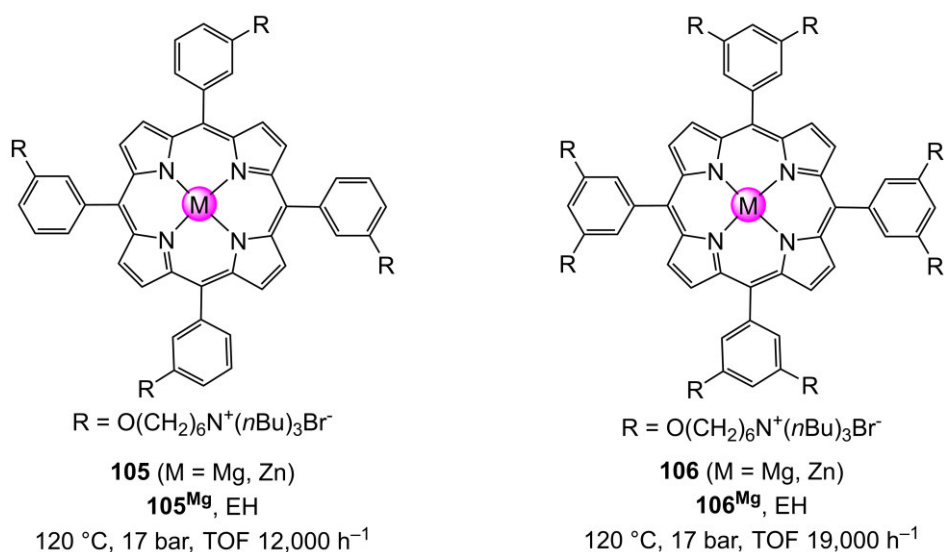


Scheme A18. Overview of simple binary catalyst systems and amidinate/ketiminato based catalysts. Conditions, cocatalysts and TOFs for the turnover of the best substrate are stated below the complexes.

Catalytic systems drawing on amidinate or ketiminato complexes were reported by REDDY (see Scheme A18).^[171,172] These contain the magnesium and aluminum complexes [(L¹)₂Mg(do)₂] (**102**, do = THF, MeCN, L¹ = *N*-benzoyl-*N'*-arylbenzamidinate; Ar = Ph, *p*-methoxyphenyl, *p*-fluorophenyl, *o*-methoxyphenyl), [(L²)₂Mg(thf)_x] (**103**, L² = Ph₂PC(COMe)(C{Me}NAr); Ar = 2,6-diisopropylphenyl (x = 1), 2,6-difluorophenyl (x = 2)) and [(L²)AlMe₂] (**104**). For **102**, the

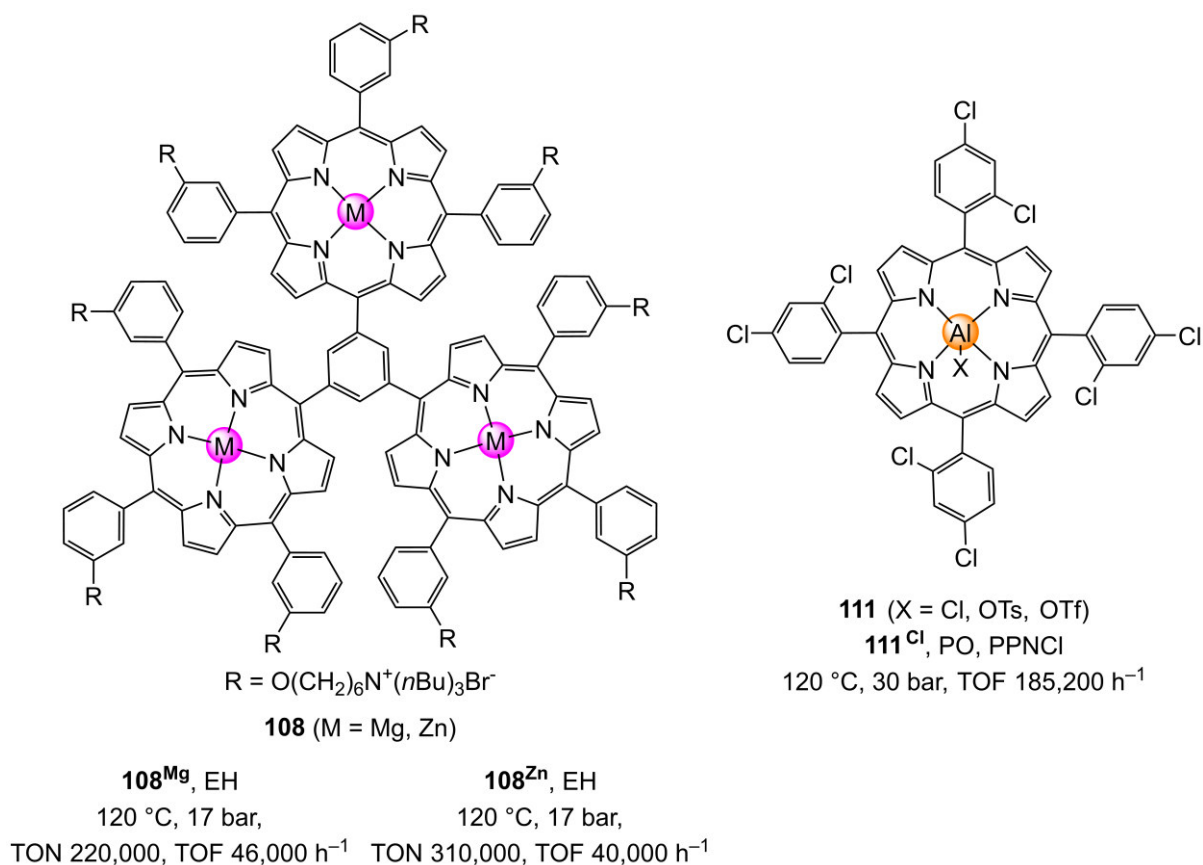
derivative **102**^{MeCN,Ph} showed the highest catalytic activity with TONs of 2800/830 and TOFs of 700/63.8 h⁻¹ for PO/CHO at 100 °C and 9.6 bar. For the ketiminate complexes, the magnesium derivatives **103** which bear a 2,6-diisopropylphenyl group revealed a slightly lower catalytic activity with TONs of 1200/750 and TOFs of 300/64.4 h⁻¹ for PO/CHO under the same conditions.

In 2012, EMA and SAKAI combined the porphyrin complexes of INOUE and the intramolecular ammonium salt units introduced by NORTH and presented the complexes ($\{[m\text{-O}(\text{CH}_2)_x\text{XR}_3]^+[\text{Br}]^-\}_4\text{TPP}\}\text{M}$ (**105**, M = Zn, Mg; $x = 4, 6, 8$; X = N, P; R = Ph, *n*Bu, $=(\text{CH})_5-$), with four quaternary ammonia units incorporated as cocatalyst into the porphyrin backbone (see Scheme A19).^[173] These single component catalysts displayed drastically increased catalytic activities at low catalyst loads, in comparison to simple porphyrin-based complexes. The magnesium complex **105**^{Mg} with four $-\text{[O}(\text{CH}_2)_6\text{N}(\text{nBu})_3]^+[\text{Br}]^-$ units showed the highest catalytic activity for the conversion of EH and CO₂ to 1,2-hexylene carbonate (HC) with a TON of 103,000 and a maximum TOF of 12,000 h⁻¹ at 120 °C and 17 bar. In comparison, the transition metal derivatives (Cr, Mn, Fe, Co) only accomplished TOFs of 225 h⁻¹ and lower.^[174] Two years later, EMA and HASEGAWA varied the counterion and the alkyl chains at the ammonium nitrogen, however, it was revealed that the catalytic activity decreased in the order $\text{Br}^- > \text{Cl}^- > \text{I}^-$ and $\text{nBu} > \text{nPr} > \text{nHex} > \text{nOct} > \text{Et}$, respectively.^[175,176] In the same work the number of $-\text{[O}(\text{CH}_2)_6\text{N}(\text{nBu})_3]^+[\text{Br}]^-$ units at one TPP ligand was increased to eight to form ($\{[m\text{-O}(\text{CH}_2)_6\text{N}(\text{nBu})_3]^+[\text{Br}]^-\}_8\text{TPP}\}\text{M}$ (**106**, M = Mg, Zn) with even better catalytic activity. Under the same conditions **106**^{Mg} achieved a TON of 138,000 and a TOF of 19,000 h⁻¹ for EH. Additionally, MAEDA and EMA conducted the catalysis toward HC with multiporphyrin



Scheme A19. Highly active porphyrin-based magnesium catalysts containing quaternary ammonium groups in the ligand scaffold. Conditions and TOFs for the turnover of the best substrate are stated below the complexes.

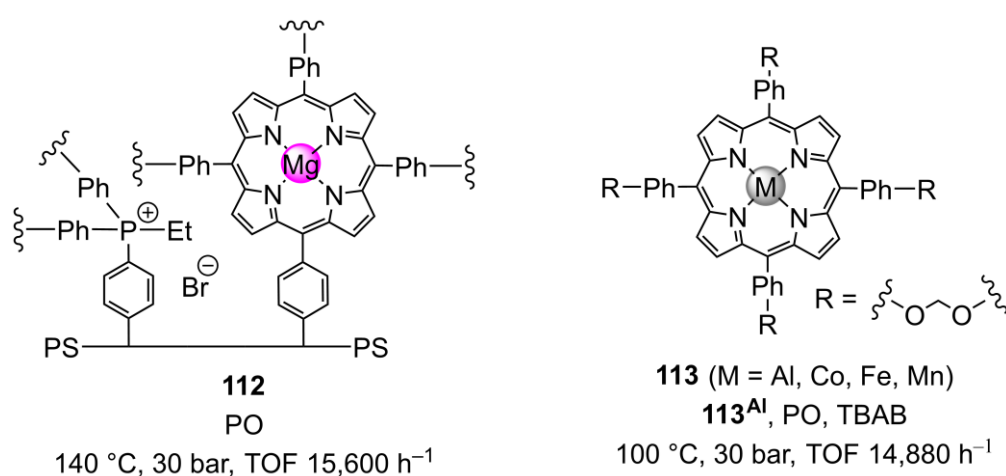
complexes of the type $\text{Ph}[(\text{Ar}_3\text{porphyrin})\text{M}]_x$ ($\text{M} = \text{Mg}, \text{Zn}$; $\text{Ar} = \text{Ph}[m\text{-O}(\text{CH}_2)_6\text{NR}_3]^+[\text{Br}]^-$; **107**: $x = 2$; **108**: $x = 3$) (see Scheme A20).^[177] The tris(porphyrin) complexes achieved exceptionally high TONs/TOFs with **108**^{Mg} (220,000/46,000 h⁻¹) exhibiting the highest activity and **108**^{Zn} (310,000/40,000 h⁻¹) being more stable over time. In 2016, EMA, MAEDA and HASEGAWA introduced the monometallic ($\{[m/p\text{-O}(\text{CH}_2)_6\text{N}(n\text{Bu})_3]^+[\text{Br}]^-\}_{12}\text{TPP}\text{Mg}$ (**109**, $\text{M} = \text{Mg}, \text{Zn}$) bearing twelve $-\text{[O}(\text{CH}_2)_6\text{N}(n\text{Bu})_3]^+[\text{Br}]^-$ units in total and compared it with **106**.^[178] At 120 °C and 17 bar the yield after 24 h obtained by **106** and **109**^{Mg} was slightly higher than with **106**^{Zn}. However, after 48 h the yield for both magnesium complexes **106**^{Mg} and **109**^{Mg} did not increase anymore, whereas the yield of **106**^{Zn} was still rising even after 120 h, proving again the zinc complex to be more stable. In the same study, **106**^{Zn} was able to catalyze the formation of cyclic carbonates from a wide scope of terminal and internal epoxides with quantitative or moderate yields, respectively.



Scheme A20. Catalysts with the highest catalytic activity for the cycloaddition of CO_2 and epoxides. Conditions, cocatalyst and TOFs for the turnover of the best substrate are stated below the complexes.

JING revisited aluminum, magnesium and tin porphyrin complexes of the type ($\{o\text{-R-phenyl}\}_4\text{porphyrin}\text{M}$ (**110**, $\text{M} = \text{Mg}, \text{AlX}$ ($\text{X} = \text{halides}, \text{OAc}$), SnX_2 ($\text{halides}, \text{OTf}$); $\text{R} = \text{H}, \text{NO}_2, \text{NH}_2$).^[179] The catalytic activity increased in the order of $\text{Sn}^{\text{II}} < \text{Sn}^{\text{IV}} < \text{Mg}^{\text{II}} < \text{Al}^{\text{III}}$ corresponding the order of Lewis acidity. By changing the counter anion the catalytic activity increased in the

order of $F^- < I^- < OAc^- < Br^- < Cl^-$ making **110**^{Al,Cl} the most active catalyst with a TOF of 200 h^{-1} at ambient temperature and 10 bar, with two equivalents phenyltrimethylammonium tribromide as a cocatalyst. It was stated that the catalytic activity increases with increasing electronegativity of the halide and hence higher Lewis acidity of the aluminum center. This observation lead QIN and WANG to design the chlorinated porphyrin complex (tetra(2,4-chloro)phenylporphyrin)AlX (**111**, X = Cl, OTs, OTf) (see Scheme 20).^[180] The highly electron withdrawing groups in the ligand scaffold activate the aluminum center drastically, boosting the TOF up to $185,200\text{ h}^{-1}$ (**111**^{Cl}) for PO, the highest TOF reported in literature so far. Here, bis(triphenylphosphine)iminium chloride ([PPN]Cl) was used as a cocatalyst at $120\text{ }^\circ\text{C}$ and 30 bar. Even at ambient pressure and $30\text{ }^\circ\text{C}$ TOFs of 3700 h^{-1} were observed.

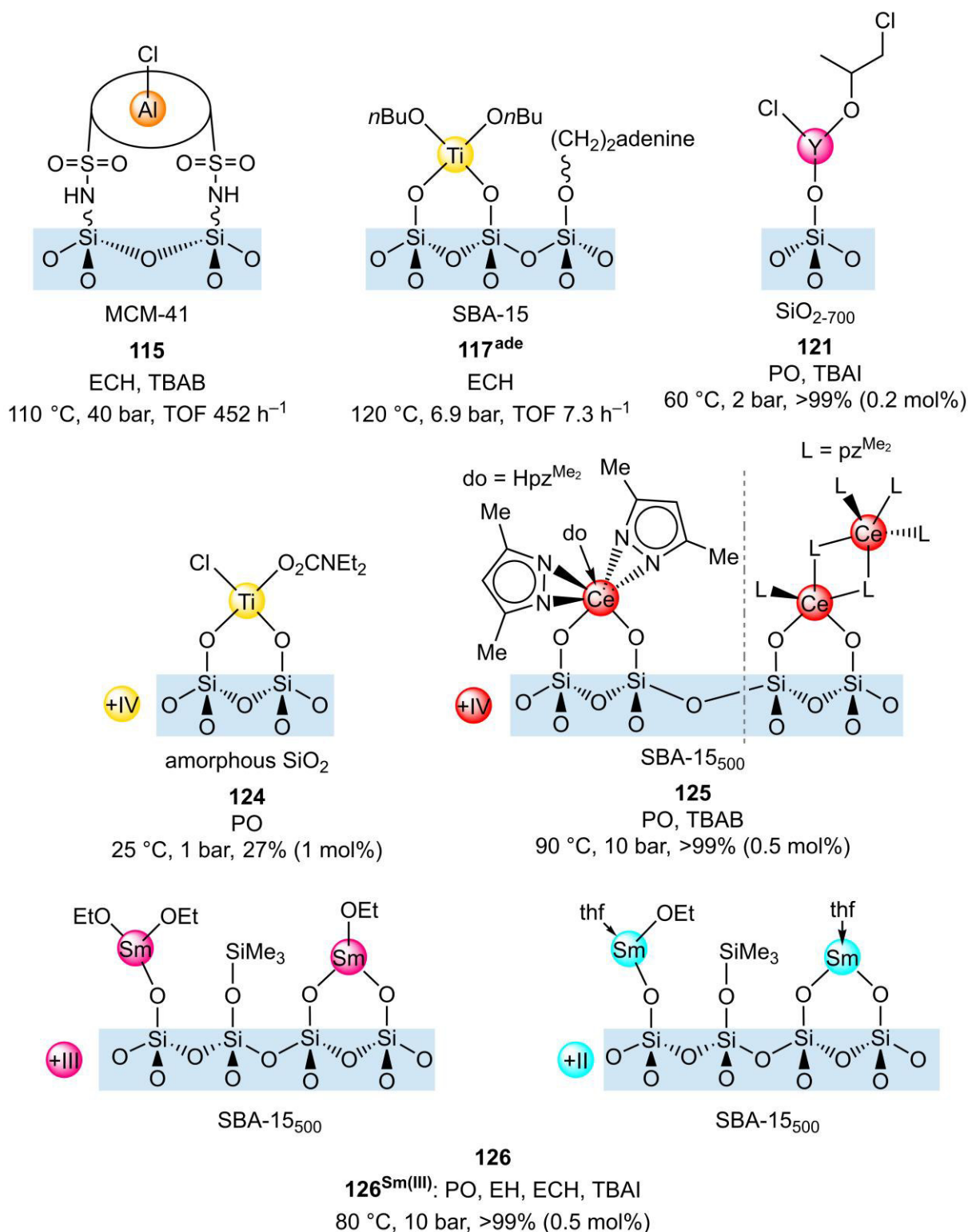


Scheme A21. Examples of catalysts incorporated into polymers. Conditions, cocatalyst and TOFs for the turnover of the best substrate are stated below the complexes (PS = polystyrene).

In 2017, YAN and DING reported a polystyrene system in which a magnesium porphyrin and a phosphonium salt are incorporated by polymerizing (tetra{4-vinylphenyl}₄porphyrin)Mg together with [PEt(4-vinylphenyl)₃]⁺[Br]⁻ to yield (TPP)Mg/pho@POP (**112**, POP = porous organic polymer) (see Scheme A21).^[181] This heterogeneous single-component catalyst showed a high catalytic activity for the conversion of PO with a maximum TOF of $15,600\text{ h}^{-1}$ at $140\text{ }^\circ\text{C}$ and 30 bar and even under milder condition a good TOF of 300 h^{-1} and 87.5 h^{-1} at 10 bar and at $40\text{ }^\circ\text{C}$ and $25\text{ }^\circ\text{C}$, respectively. Aluminum porphyrin complexes were also incorporated onto hyper-crosslinked polymers (HCPs) by LUO via a Friedel-Crafts alkylation of (TPP)MCl (M = Al, Co, Fe, Mn) and formaldehyde dimethyl acetal yielding M(HCP) (**113**, M = Al, Co, Fe, Mn).^[182] The catalytic activity of **113**^{Al} outperformed the other metal congeners by far, with a TOF of 860 h^{-1} and $14,880\text{ h}^{-1}$ for PO (TBAB) at 30 bar and at $40\text{ }^\circ\text{C}$ and $100\text{ }^\circ\text{C}$, respectively. The heterogeneous catalyst displayed a high reusability with no significant decrease of conversion even after ten consecutive runs. Recently, the same authors reported on the synthesis

of a hyper-crosslinked ionic polymer (HIP) Al(HIP) (**114**) *via* addition of the ionic liquid (3-{3-methylimidazolomethyl}phenyl) triphenylmethane bromide to a mixture of (TPP)Al and organic linker.^[183] A TOF of 4000 h⁻¹ and 3700 h⁻¹ for PO and ECH, respectively, was achieved at 120 °C and 10 bar. In addition, system **114** was probed as a catalyst with simulated flue gas (15% CO₂ in N₂) at 20 bar and 100 °C, which resulted in a yield of 91% already after 6 h, with a catalyst loading of 0.1 mol% corresponding to a TOF of 152 h⁻¹.

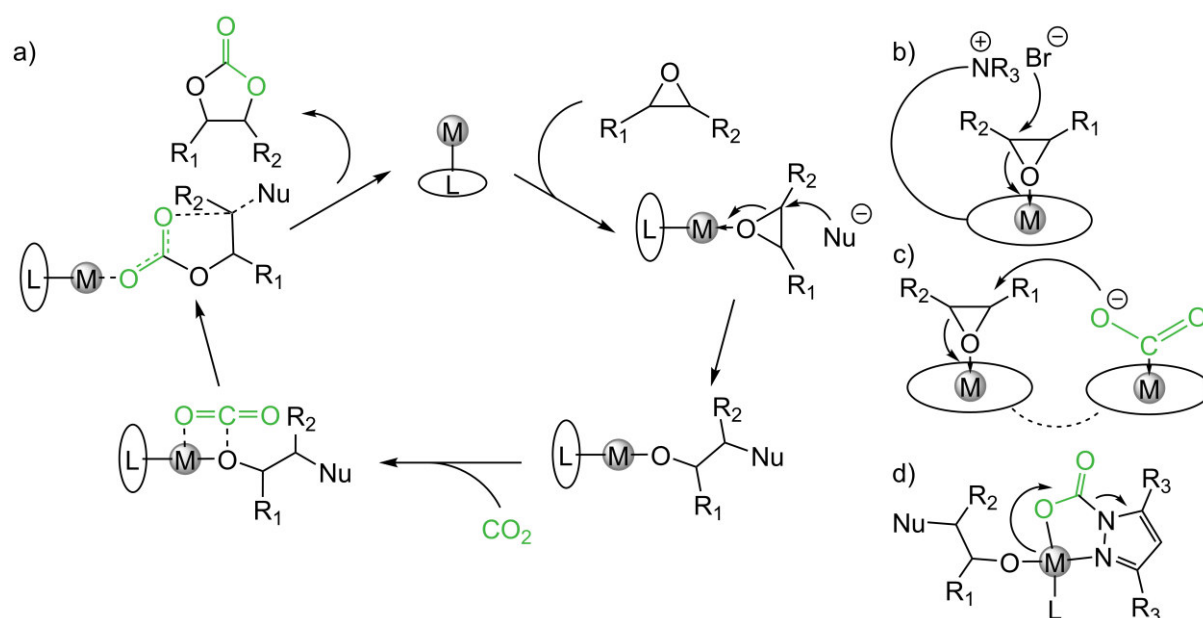
Another material approach for the catalytic cycloaddition of epoxides and CO₂ is surface organometallic chemistry (SOMC).^[184] According to this methodology metal complexes are grafted onto a support material i.e. mesoporous silica, with a large surface area, emerging in highly active surface species. Different to other materials such as MOFs^[18-21] or polymers,^[149,181-183] which require advanced syntheses, often with an additional metal catalyst or a high energy penalty, grafting onto a silica surface is feasible at ambient conditions. The lower catalytic activity due to the heterogeneous nature is compensated by enhanced stability and recyclability. An overview of catalysts based on SOMC on mesoporous silica can be found in Scheme A22. In 2002, HE reported the phthalocyanine (Pc) aluminum complex (Pc)AlCl@MCM-41 (**115**), which was immobilized on mesoporous MCM-41 silica.^[185] With TBAB as cocatalyst **115** showed TOFs of 415, 280 and 452 h⁻¹ for EO, PO and ECH, respectively, at 110 °C and 40 bar. The catalytic activity remained almost constant even after ten consecutive runs. RATNASAMY and SRINIVAS presented the SBA-15-based Ti(OnBu)₄@SBA-15 (**116**) and its organo-functionalized derivatives R@Ti(OnBu)₄@SBA-15 (**117**, R = 3-amino, 3-adenino or (3-chloropropyl)triethoxysilane).^[186] All materials showed not only quantitative conversion (**117^{adenine}**) of epoxides (ECH TOF 7.3 h⁻¹) with CO₂ to cyclic carbonates at 120 °C and 6.9 bar, but they were also able to transform alkyl and aryl amines to carbamates using CO₂. NORTH described the immobilization of the single component catalyst **87** onto support material, which gave [(R₂salen)Al]₂O@M (**118**, R = -CH₂N(*n*Bn)Et₂; M = amorphous silica, MCM-41, Al pillared clay, silica sol gel).^[187] These materials showed moderate conversions (52–97%) with a maximum TOF of 26 h⁻¹ (**118^{MCM-41}**). However, due to loss of the quaternary ammonium moieties it was necessary to add TBAB after several runs. Further, BASSET and D'ELIA reported several early transition metal chlorides grafted onto a silica surface which include NbCl₅@SiO₂₋₇₀₀ (**119**), ZrCl₄(OEt)₂@SiO₂₋₇₀₀ (**120**) and YCl₃@SiO₂₋₇₀₀ (**121**).^[188-190] All three materials showed a quantitative conversion of PO to PrC with CO₂ at 60 °C and 10 bar when TBAI is used as a cocatalyst. Remarkably, yttrium-based **121** was able to quantitatively convert several epoxides (PO, ECH, 1,2-epoxybutane) even at ambient pressure and 60 °C. In 2018, PAMPALONI reported several transition metal and main



Scheme A22. Overview of catalysts crafted onto mesoporous silica. Conditions, cocatalysts and TOFs (conversion over 24 h if no TOF was stated) for the turnover of the best substrate are stated below the complexes.

group carbamate complexes and their corresponding immobilized derivatives $M(\text{CO}_2\cdot\text{NR}_2)_x$ (**122**, $M = \text{Ti, Zr, Hf, Nb, Ta, Cu, Ag, Al, Si, Sn}$; $R = \text{Me, Et}$), $M\text{Cl}_2(\text{CO}_2\cdot\text{NEt}_2)_x$ (**123**, $M = \text{Ti, Zr}$) and $M\text{Cl}_2(\text{CO}_2\cdot\text{NEt}_2)_x@\text{SiO}_2$ (**124**, $M = \text{Ti, Zr}$) on silica, respectively.^[191] In this study, the highest conversion was achieved with the mixed chloride carbamate complex **123^{Ti}** (69%) at

ambient temperature and pressure with TBAB as a cocatalyst. As mentioned earlier, we reported the hybrid material $[\text{Ce}(\text{pz}^{\text{Me}_2})_4]_2@\text{SBA-15}_{500}$ (**125**) and tested its catalytic activity in the transformation of epoxides and CO_2 to cyclic carbonates.^[76] At 90 °C and 10 bar, **125** achieved good to quantitative yields (>99% PrC, 94% EH, 91% SO, 66% 2-*tert*-butyloxirane (*t*BO)) with a maximum TON of 355. Lately, our group investigated the immobilization of samarium and ytterbium silylamide complexes on periodic mesoporous silica and subsequent ligand exchange with alcohols to form $\text{HOEt}@\text{Ln}(\text{N}(\text{SiMe}_3)_2)_x@\text{M}$ (**126**, Ln = Sm(II), Sm(III), Yb(II); M = SBA-15₅₀₀, MCM-41, MCM-48).^[192] These materials were all active catalysts in the cycloaddition of epoxides and CO_2 with **126**Sm, showing quantitative conversions at 80 °C and 10 bar for several epoxides (PO, EH, ECH, SO) with a high tolerance for functional groups (ether, ester and olefin).



Scheme A23: a) Most commonly proposed mechanism of the cycloaddition of CO_2 and epoxides to cyclic carbonates in literature.^[28,177,190] b) Activation of the epoxide by a single component catalyst. c) Proposed bimetallic mechanism in which the CO_2 activation occurs at a different metal center.^[151,193] d) CO_2 activation via insertion into a metal-pyrazolato bond.^[73,76]

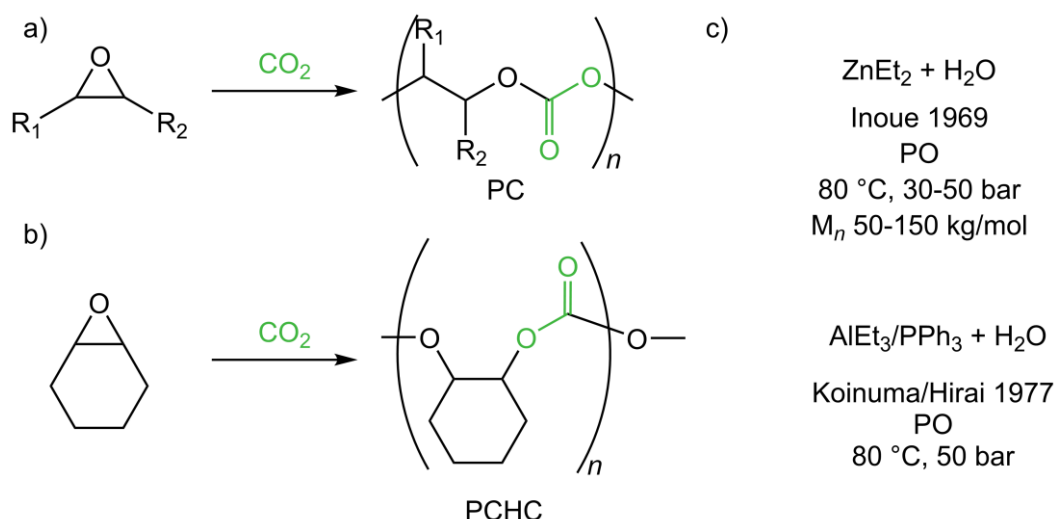
In most cases an initial ring-opening of the coordinated epoxide by nucleophilic attack of a nucleophile (for example a halide of a quaternary ammonium salt) is discussed (see Scheme 23a).^[28,177,190] This explains the drastically increased catalytic activity of catalysts, that contain quaternary ammonium chains in the ligand scaffold, because the nucleophile is already close to the metal center (see Scheme A23b). The CO_2 molecule is activated by the metal center and subsequent inserts into the metal alkoxide bond under formation of a carboxylate complex. The coordinated oxygen can then eliminate the nucleophile under ring formation and the cyclic carbonate dissociates. In some cases, a bimetallic mechanism is also discussed especially for

bimetallic systems.^[151,193] A second metal center (intra- or intermolecularly) activates the carbon dioxide and the ring-opened epoxide is transferred to the activated CO₂ (see Scheme A23c). For our pyrazolate complexes we proposed a CO₂ activation by an insertion into the metal-pyrazolato bond with a subsequent transfer of the alkoxide to the inserted CO₂ (see Scheme A23d). However, due to a lack of crystallographically analyzed epoxide complexes, a full confirmation of this mechanism has remained elusive. One example of the few characterized epoxide complexes is the calcium complex $\text{Tp}^{t\text{Bu}}\text{Ca}(\text{O-2,6-}i\text{Pr}_2\text{Ph})(\text{PO})$ by CHISHOLM.^[194]

5. Copolymerization of CO₂

5.1 Copolymerization of CO₂ and Epoxides

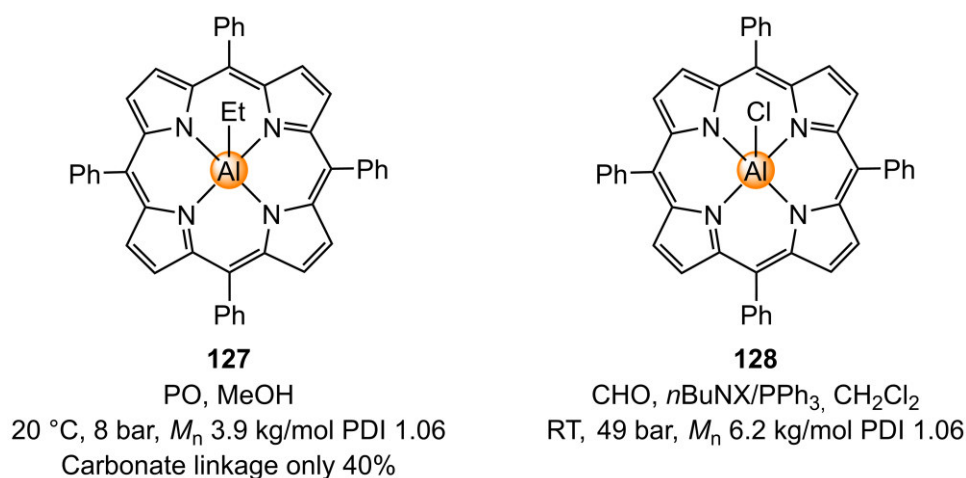
The best studied copolymerization of CO₂ is with epoxides to biodegradable polycarbonates (PC, see Scheme A24a). Consequently, it is already well established in industrial synthesis. Most studies involved poly(cyclohexene carbonate) (PCHC), especially for comparison of catalysts, mainly because of its excellent properties (see Scheme A24b). PCHC stands out with a high tensile strength as well as a high glass transition temperature.^[195,196] In addition, its ductility and toughness can be easily adjusted with block polymerization and therefore PCHC has a wide variety of application areas.^[197] Besides their physical properties, PC also have a high CO₂ capacity with mass fractions of 42.7 and 31.0 wt% for poly(propylene carbonate) (PPC) and PCHC, respectively, when the polymer has an ideal carbonate linkage. The cyclization reaction competes with the copolymerization and cyclic carbonates occur often as side products. Less sterically demanding epoxides have a high affinity toward the formation of cyclic carbonates. This is caused by a backbiting reaction in which the nucleophilic alkoxy chain end attacks a neighboring carbonate.^[198] This reaction pathway is blocked by steric epoxides especially CHO. To prevent cyclic carbonate formation well-adjusted catalyst systems and reaction conditions are necessary.



Scheme A24. a) Copolymerization of epoxides and CO₂ to the corresponding polycarbonates. b) Copolymerization of cyclohexene oxide and CO₂ to poly(cyclohexene carbonate) c) First binary catalyst systems by INOUE and KOINUMA/HIRAI for the copolymerization of propylene oxide and CO₂.

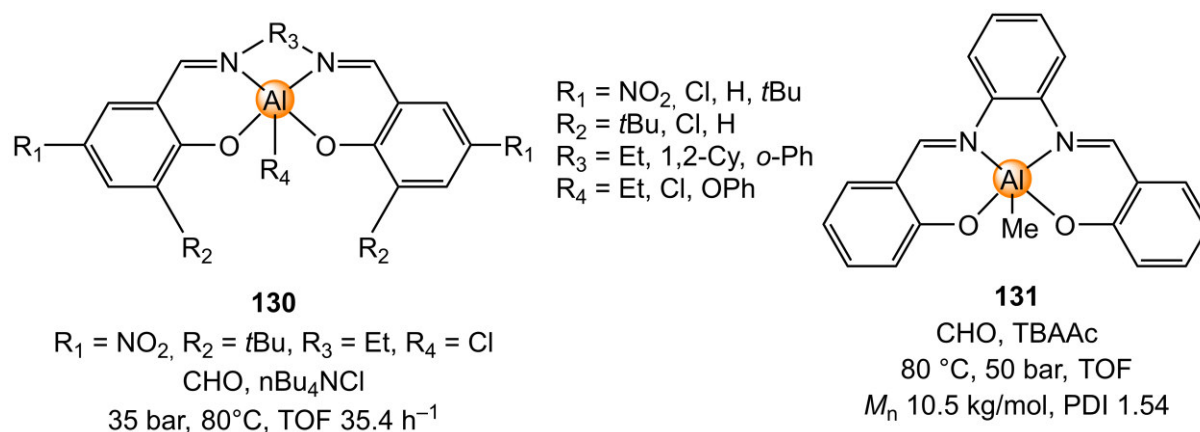
First discovered was the ring-opening copolymerization of epoxides and CO₂ by INOUE in 1969 with the binary system comprised of either ZnEt₂ or AlMe₃ with H₂O (see Scheme A24c).^[199,200] Accordingly, the ZnEt₂-derived catalyst yielded PPC from PO and CO₂ at 80 °C and 20–50 bar

with M_n of 50–150 kg/mol. A decade later, HIRAI reported an improved catalytic activity of AlEt_3 when the Lewis base PPh_3 is added to the mixture.^[201] By adding acetylacetone to the $\text{AlEt}_3/\text{H}_2\text{O}$ mixture, oxetane could be copolymerize with CO_2 for the first time yielding poly(trimethylene carbonate).^[202] In 1978, INOUE used a catalyst mixture of the porphyrin based complex (TPP) AlEt and different additives (**127**, additives: MeOH , H_2O , Et_2AlCl) for the copolymerization of PO and CO_2 at 20 °C and either 1 or 8 bar (see Scheme A25).^[203] At ambient pressure only a carbonate linkage of 15% was observed for **127** ^{MeOH} , which could be increased to 40% (M_n 3.9 kg/mol PDI 1.15) at 8 bar. Interestingly, **127** ^{Et_2AlCl} gave exclusively the homopolymer and the zinc complex ((*N*-methyl)TPP) ZnEt gave the cyclic carbonate PrC exclusively under the same conditions. By using the quaternary onium salts Et_4NBr or EtPh_3PBr as cocatalysts together with (TPP) AlCl (**128**), INOUE found an active catalyst system yielding a narrow molecular weight distribution (PDI = PPC 1.09; PCHC 1.06).^[204] At ambient temperature and 49 bar **128** achieved M_n of 4.5 kg/mol for PPC and 6.2 kg/mol for PCHC in CH_2Cl_2 . This catalyst system revealed a living polymerization behavior and thus allowed the generation of block polymers with polyesters. Mechanistic studies revealed that the polymer chain is formed on both sides of the porphyrin plane.^[205] In 1999, REE reported a catalysis study of **128** and (TPP) $\text{Al}(\text{R})_2\text{Cl}$ (**129**, $\text{R} = \text{OCHMeCH}_2$) containing a PO dimer adduct.^[206] Complex **129** produced without cocatalyst oligomers of PO with a high ether linkage (PC/PE: 23/77%), however, with TBAB a selectivity switch to carbonate linkage (75/25%) occurred (ambient temperature and 52 bar). Similarly, **129** showed selectivities of 20/80% without cocatalyst and 72/28% with TBAB. Overall, the content of PrC as side product is lower when no cocatalyst (TBAB) is used (4.2–7.7%) versus (17–22.4%), with $M_n = 3.3$ kg/mol and PDI = 1.24.



Scheme A25. Porphyrin-based aluminum complexes as catalysts. Conditions, cocatalyst, M_n and PDIs for the turnover of the best substrate are stated below the complexes.

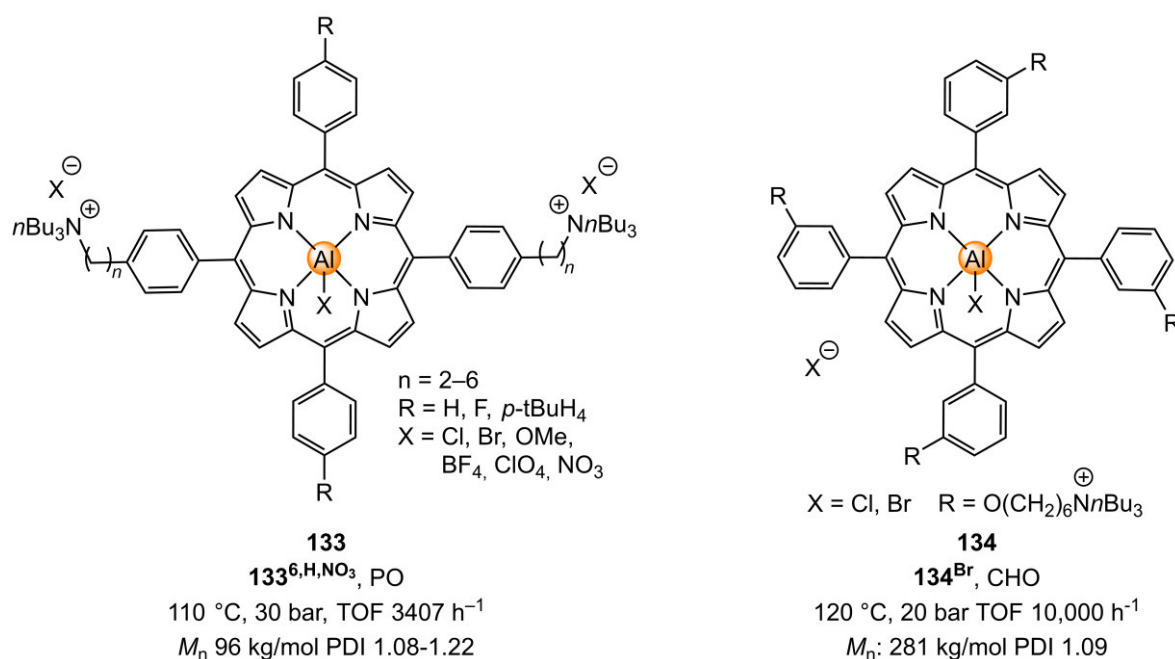
Besides the already mentioned examples, aluminum-based catalyst first showed a rather high affinity toward homopolymerization of epoxides.^[207–210] For the copolymerization the catalytic activity often was lower compared to other metals and for this reason early studies were dominated by transition-metal based catalysts, in particular chromium,^[211] cobalt,^[212] and zinc.^[213–216] Considering the non-toxicity and abundance of aluminum, catalysts derived from it received an increasing research interest in the past two decades.^[217] One type of catalyst system which was reported by DARENSBOURG in 2005 are salen-based aluminum complexes of the type (salen)AlR (**130**, R = Et, Cl, OPh) with a wide variety of substitution patterns at the ligand backbone (see Scheme A26).^[218] TOFs of 5.2 to 35.4 h⁻¹ were obtained for the formation of PCHC at 35 bar and 80 °C using a series of ammonium salts (TBAX, X = Cl, N₃, Ac) as cocatalysts. Although PCHC was obtained with a high carbonate linkage (93–99%), the catalytic activity was significantly lower in comparison to the corresponding chromium derivatives (salen)CrR (TOF: 1966 h⁻¹), under the same conditions. A further activation of the



Scheme A26. Salen-based aluminum complexes as catalysts. Conditions, cocatalyst, TOFs, M_n and PDIs (if given in the publication) for the turnover of the best substrate are stated below the complexes. When different catalysts are included only the conditions for the best system are mentioned.

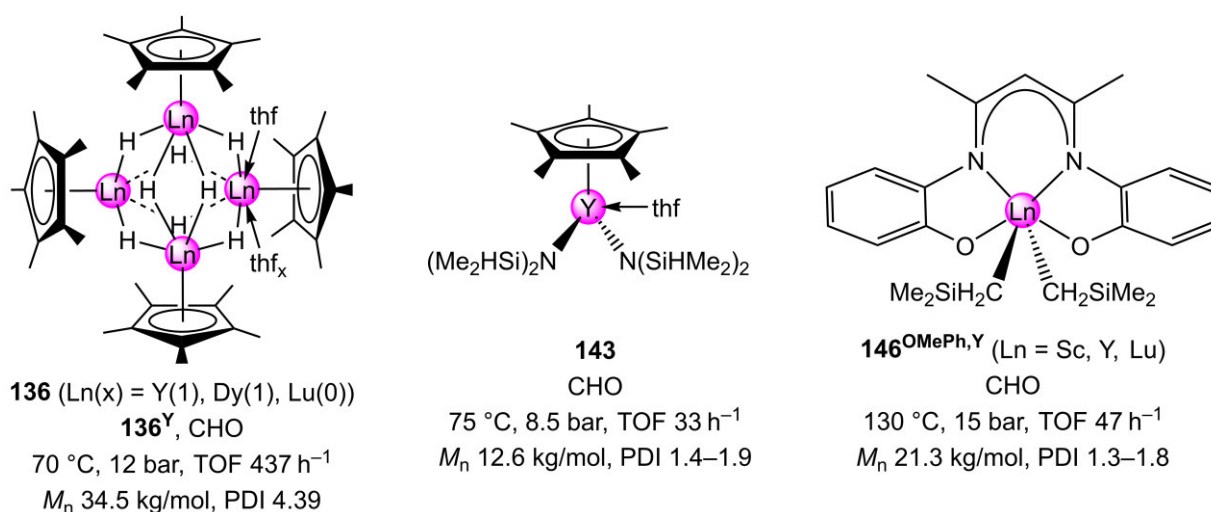
aluminum center was observed when *N*-donor ligands were added, with DMAP affording the highest increase of catalytic activity. In the same year, SUGIMOTO reported the salen complex (salen)AlMe (**131**), which yielded PCHC with an M_n of 10.5 kg/mol and a PDI of 1.54 in CH₂Cl₂ at 80 °C and 50 bar when TBAAc is used as cocatalyst.^[219] It is noteworthy, that the selectivity of copolymerization versus cycloaddition could be manipulated by changes in temperature and amount of cocatalyst. For example, using 1 equiv. TBAAc at 80 °C gave a ratio of >95:<5% PCHC:CHC. By raising the temperature to 140 °C a shift to a ratio of 60:40% was achieved. When 3 or 5 equiv. of TBAAc were used, the ratio shifted to 60:40 and 45:55%, respectively. QIN and WANG incorporated alkyl chains containing quaternary ammonium salts at two of the four phenyl moieties of the TPP ligand and consequently increased the catalytic activity significantly.^[220,221] In their detailed studies they varied the counter ion, the electronic

properties of the phenyl groups and the chain length of the ammonium units; this includes the complexes $((RC_6H_4)_2(C_6R'_5)_2\text{porphyrin})AlX$ (**132**, $R = p\text{-(CH}_2)_3NnBu_3X$; $R' = H, F, p\text{-}tBuH_4$; $X = Cl, CO_3, BF_4, ClO_4$) and $((C_6H_5R)_2(C_6H_4\text{-}p\text{-}R')_2\text{porphyrin})AlX$ (**133**, $R = p\text{-(CH}_2)_xNnBu_3X$; $x = 2\text{--}6$; $R' = H, Br, OMe$; $X = Br, NO_3$) (see Scheme 27). The single-component catalysts **132**^{H,NO₃} and **133**^{6,Br,NO₃} showed the highest catalytic activity for the copolymerization of PO and CO₂ at 30 bar with TOFs of 3407 h⁻¹ (110 °C) and 449 h⁻¹ (70 °C) for the former and 560 h⁻¹ (80 °C) for the latter. For complexes **132**^{H,NO₃} and **133**^{6,Br,NO₃} polymers with high molar masses of 36 kg/mol and 96 kg/mol, respectively, are obtained, the latter with a narrow PDI of 1.08–1.22. Both systems showed a change of selectivity when the temperature is increased, ranging from 95% PPC content at 25 °C to 71% at 110 °C. Recently, HESEGAWA, NOZAKI and EMA presented the aluminum complex (R₄TPP)AlX (**134**, $R = O(CH_2)_6NnBu_3X$; $X = Cl, Br$) with four ammonium units incorporated into the ligand, which resulted in a drastically increased catalytic activity for the formation of PCHC.^[222] It is striking that the copolymer can be obtained exclusively in case of an aluminum center, in contrast to the Mg/Zn **105** congener which exclusively formed the cyclic carbonate. TONs of 55,000 and TOFs of up to 10,000 h⁻¹ were achieved, ranking among the highest values published for the solvent-free copolymerization. Furthermore, high molecular weights of up to 281 kg/mol were obtained with a small polydispersity of 1.09, a carbonate linkage between 96–>99% and no visible traces of cyclic CHC in IR measurements. Strikingly, the magnesium and zinc derivatives (**105**) only showed low catalytic activities (TOF 27–48 h⁻¹) and a poor selectivity between 52–63%.



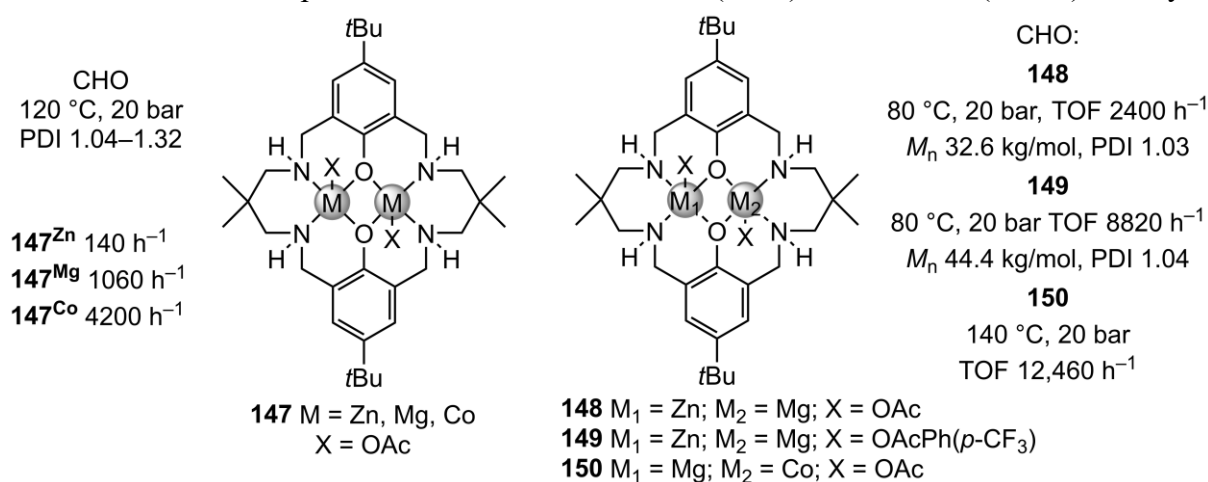
Scheme A27. Porphyrin-based aluminum complexes containing quaternary ammonium on the ligand scaffold as catalysts. Conditions, cocatalyst, TOFs, M_n and PDIs for the turnover of the best substrate are stated below the complexes. When different catalysts are included only the conditions for the best system are mentioned.

Some catalysts containing rare-earth metals were also studied for the copolymerization of CHO and CO₂ (see Scheme A28). However, in most cases the light metals scandium and yttrium are outperformed by their heavier congeners.^[223–225] In the 2000s, HOU used half-sandwich alkyl, hydride and aryloxy complexes as catalysts, comprising Cp'Ln(CH₂SiMe₃)₂(thf) (**135**, Ln = Sc, Y, Dy, Lu), [Cp'Ln(μ-H)₂]₄(thf)_x (**136**, Ln: Y, *x* = 1; Dy, *x* = 2; Lu, *x* = 1), [Cp'LnH(OAr)]₂ (**137**, Ln = Y, Dy, Lu; Ar = 2,6-*i*Bu-4-Me-Ph) and the CO₂ insertion compounds [Cp'Ln(CO₂·CH₂SiMe₃)₂]₂ (**138**, Ln = Sc, Y, Lu) and [Cp'Ln(CO₂·H)(CO₂·OAr)]₂ (**139**, Ln = Y, Dy, Lu).^[223,226] Although high catalytic activities and *M_n* were achieved (**136**^{Lu}: 3693 h⁻¹; 39.8 kg/mol) only poor PDIs were observed (1.79–10.68). **135**^{Sc} showed a high content of ether linkages (77%), whereas all other catalysts reached carbonate linkages between 90–97%. The group of HULTZSCH reported various rare-earth-metal complexes coordinated by nacnac and silylamido ligands, comprising (nacnac^{Mes})Ln(SiXMe₂)₂ (**140**, Ln, Y, La, X = H, Me), (Et{nacnac^{Ar}}₂)Ln(SiXMe₂) (**141**, Ar = mesityl, *o*-*i*PrPh; Ln = Y, La; X = H, Me), (1,2-*N,N'*-Cy{nacnac^{Ar}}₂)La(SiXMe₂) (**142**, Ar = mesityl, *o*-EtPh, *o*-*i*PrPh; X = H, Me), (nacnac^{Ph})₂Y(N(SiHMe₂)₂) (**143**), Cp*Y(SiHMe₂)₂(thf) (**144**), Cp*Y(nacnac^{Ph})(SiHMe₂) (**145**).^[227,228] Yttrium complex **143** featured the catalyst with the highest activity (33 h⁻¹) at 75 °C and 8.5 bar, yielding PCHC with a maximum *M_n* of 12.6 kg/mol and a PDI of 1.6. However, the carbonate linkages ranged only between 85–91%. In 2008, CUI used rare-earth metal nacnac complexes bearing neosilyl ligands of the type (nacnac^{Ar})Ln(CH₂SiMe₃)₂(thf)_x (**146**, Ar = *m*-OMePh, *m,p*-MePh, Ph; Ln = Sc, Y, Lu) as catalysts in the copolymerization of CHO and CO₂.^[229] Complex **146**^{OMePh,Y} turned out to be the most active catalyst (47.4 h⁻¹, 15 bar, 130 °C). In 1,2-dioxane polymers with *M_n* of up to 21.3 kg/mol and a PDI between 1.3 and 1.8 were obtained.



Scheme A28. Selection of scandium- and yttrium-based catalysts. Conditions, TOFs, *M_n* and PDIs for the turnover of the best substrate are stated below the complexes. When different catalysts are included only the conditions for the best Sc/Y species are mentioned.

In the 2010s, the group of WILLIAMS developed a homodinuclear catalyst $[\text{LM}_2(\text{OAc})_2]$ (**147**, $\text{M} = \text{Mg}$, Co^{II} , Zn) with the macrocyclic ligand di-*tert*-butyl-tetramethyl-tetraaza-dibenzenacyclohexadecaphanebis(olate) (**L**) (see Scheme A29).^[230–233] Perfectly alternating PCHC (>99%) could be obtained with an almost ideal selectivity for polymerization ($\text{CHC} < 1\%$) already at ambient pressure and 120 °C with a narrow PDI between 1.04 and 1.32 and without a cocatalyst. The catalytic activity (1/20 bar) increased in the order of **147**^{Zn} (25/140 h⁻¹) < **147**^{Mg} (368/1060 h⁻¹) < **147**^{Co} (712/4200 h⁻¹). Complex **147**^{Mg} even reached high TOFs in the range of 2300–5400 h⁻¹ with CO₂ from post-combustion CCS (10 bar, mechanically stirred reactor) containing excess of water (48–400 equiv.) and other post-combustions gases such as H₂S, NO_x, SO_x and amines.^[234] The M_n decreased with rising water content from 54.9 kg/mol (48 equiv.) to 2.3 kg/mol (400 equiv.) due to the chain transfer effect of H₂O, however, the catalytic activity peaked at 192 equivalents with a TOF of 5400 h⁻¹. By using the heterodinuclear catalyst $[\text{LZn,Mg}(\text{OAc})_2]$ (**148**), the catalytic activity could be further increased even more.^[235,236] Complex **148** achieved TOFs of 438 (1 bar) and 2400 h⁻¹ (20 bar) already at

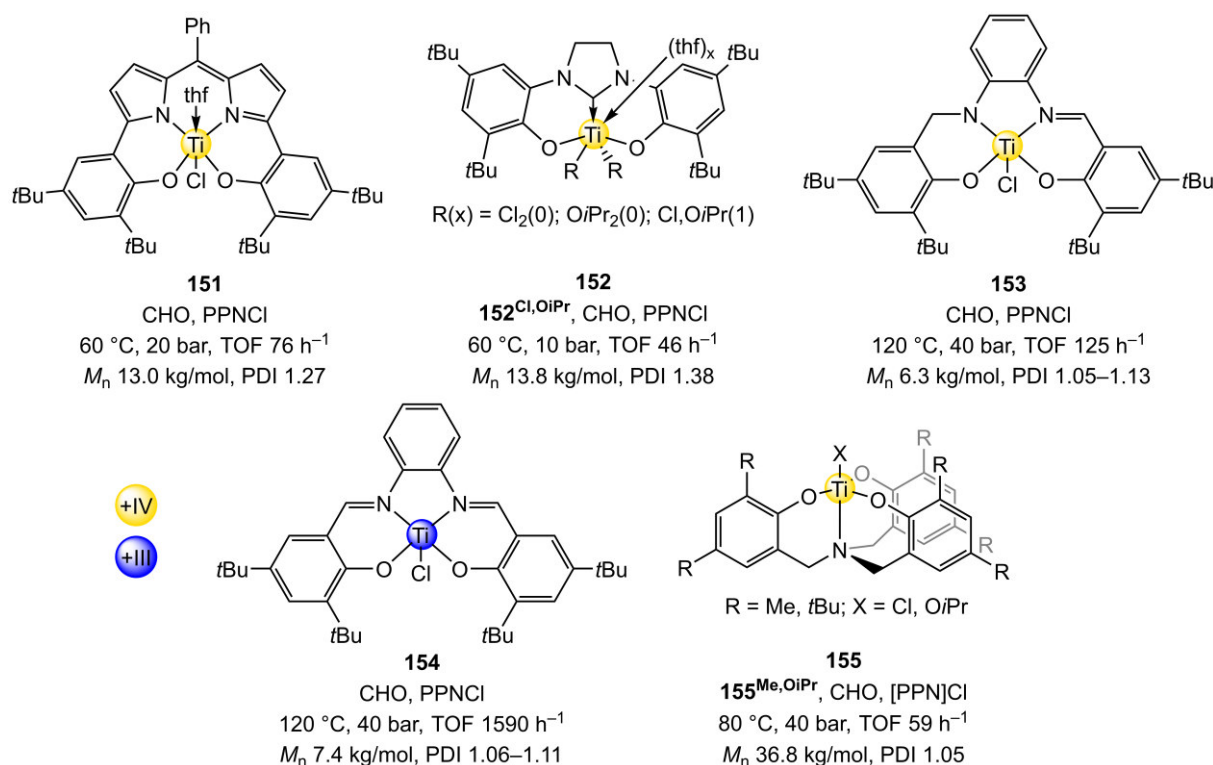


Scheme A29. Homo/heterodinuclear catalyst systems Conditions, cocatalyst, TOF, M_n and PDI (if stated in the publication) for the turnover of the best substrate are stated below the complexes.

80 °C, which is significantly higher than the homometallic **147**^{Mg} and **147**^{Zn} complexes. Using a more electron withdrawing co-ligand $[\text{LZn,Mg}(\text{OAc}\{p\text{-CF}_3\}\text{Ph})_2]$ (**149**), the catalytic activity could be increased to 8830 h⁻¹.^[236] The combination of divalent magnesium and cobalt, $[\text{LMg,Co}(\text{OAc})_2]$ (**150**), turned out to be the most active catalyst system.^[233] At 120 °C and 1 bar a TOF of 1205 h⁻¹ was obtained and at 20 bar 7200 h⁻¹. When the temperature is raised to 140 °C the catalytic activity even reached 12,460 h⁻¹. Interestingly, at 1 bar when the temperature is increased gradually the catalytic activity reached its maximum at 100 °C and drastically decreased over 100 °C. Due to poor CO₂ solubility, the formation of the cyclic carbonate is favored. Consequently, at 20 bar the polymerization rate increased exponentially with the temperature and no CHC formation was observed. Recently, the WILLIAMS group

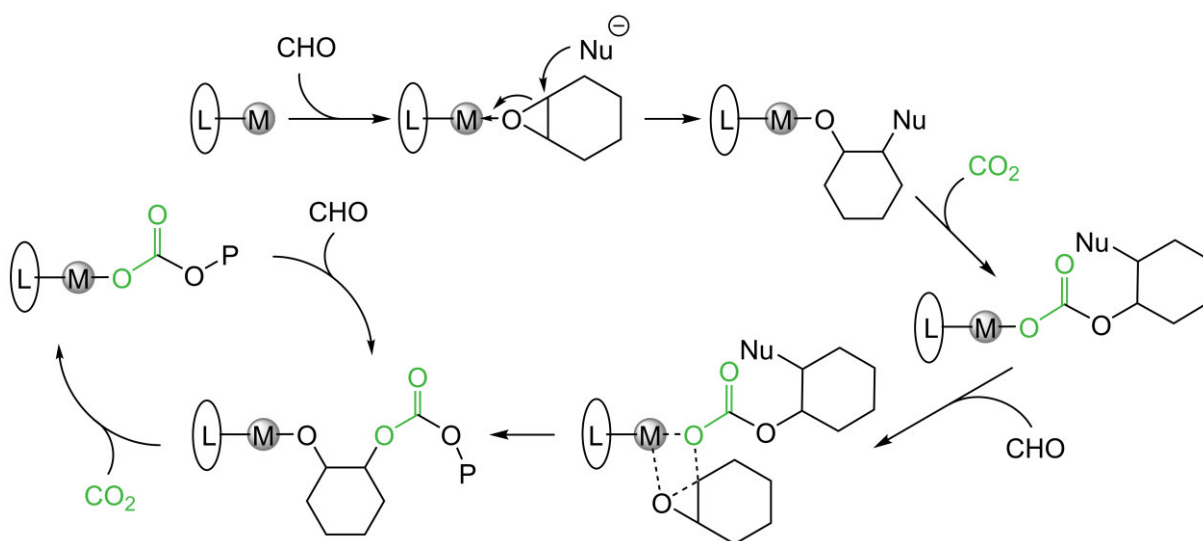
reported that **148**^{Mg} is even able to depolymerize PCHC which is the first example for any catalyzed recycling of PCHC.^[237] The monomer epoxide CHO was almost exclusively formed (>98%) at 120 °C with a rate of 150 h⁻¹.

A number of titanium-based complexes were also studied as catalysts in the copolymerization of epoxides and CO₂ (see Scheme A30). Although low catalytic activities were observed with TOFs in the range of 40 to 84 h⁻¹, titanium catalysts stayed in the focus of research as more environmentally friendly alternatives. The first Ti-based catalyst, (L)TiCl(thf) (**151**, L = 1,9-bis(2-oxidophenyl)dipyrrinate), was reported by NOZAKI in 2011.^[238] Because of the tetravalent titanium center, a trianionic ligand was used to mimic the common salen ligand for trivalent metals. With one equiv. [PPN]Cl as a cocatalyst, highly alternating copolymers (98–99%) were obtained for both PO (14 kg/mol, PDI 1.19–1.36) and CHO (13 kg/mol, PDI 1.27) at 60 °C and 20 bar. The overall copolymerization/cyclization selectivity ranged from 67 to 85% polymer (PPC). When the temperature was raised to 100 °C or 1.5 equiv. of cocatalyst are used, PC is formed almost exclusively. The group of LE ROUX presented the complexes LTiX₂(thf)_x (**152**, L = bis-*m*-(*o,m*-{di-*tert*-butyl}phenolate)-NHC; X: Cl, *x* = 0; OiPr, *x* = 0; Cl + OiPr, *x* = 1) with a dianionic NHC ligand.^[239] The mixed **152**^{Cl,OiPr} gave PCHC as almost perfectly alternating copolymer (>99%) with molar masses up to 13.8 kg/mol and a narrow PDI of 1.38 at 60 °C and 10 bar with [PPN]Cl as cocatalyst. Without cocatalyst polyether was obtained exclusively in



Scheme A30. Titanium based catalysts. Conditions, cocatalyst, TOFs, *M_n* and PDIs for the turnover of the best substrate are stated below the complexes. When different catalysts are included only the condition for the best system is mentioned.

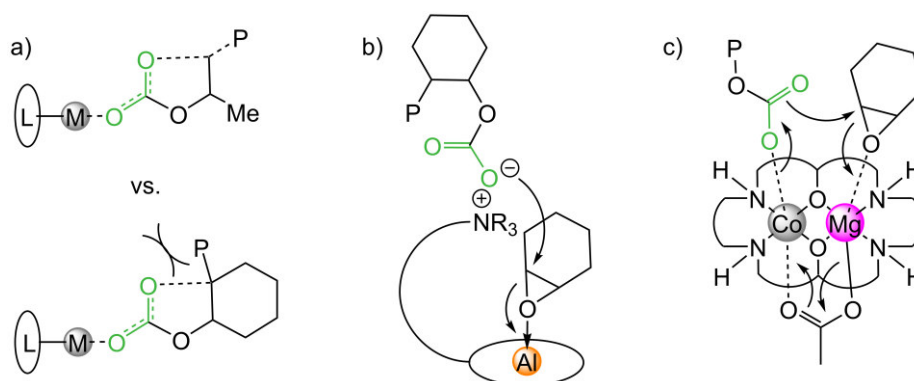
minor yields. The salen-based tri- and tetravalent complexes (salalen) Ti^{+VI}Cl (**153**, salalen = reduced salen) and (salen) $\text{Ti}^{+III}\text{Cl}$ (**154**) showed a slightly higher catalytic activity at harsher conditions for the copolymerization of CHO and CO_2 with TOFs up to 125 h^{-1} and 1590 h^{-1} ($120\text{ }^\circ\text{C}$, 40 bar, [PPN]Cl), respectively.^[240,241] Both tri- and tetravalent catalysts gave a narrow molar mass distribution between 1.05–1.13 with M_n in the range of 4–7.4 kg/mol with a general high selectivity for copolymer over polyether and cyclic carbonate. The trivalent titanium complex **154** showed a significantly higher catalytic activity than the tetravalent **153** and can almost compete with the chromium derivative (salen)CrCl.^[211] Lately, WILLIAMS examined the tris(phenolate) complexes LTiX (**155**, L = amino-tris-*m*-(*o,m*-R-phenolato); X = Cl, OiPr; R = Me, *t*Bu) and the oxo-bridged $[\text{L}^{\text{Me}}\text{Ti}]_2\text{O}$ (**156**) as catalyst in the copolymerization of CHO and CO_2 .^[242] Complex **155**^{Me, OiPr} yielded highly alternating PCHC (>99%) with M_n of up to 36.8 kg/mol and a narrow PDI of 1.05 at $80\text{ }^\circ\text{C}$ and 40 bar when [PPN]Cl is used as a cocatalyst. The catalytic behavior of oxo-bridged **156** is almost identical to **155**. By raising the temperature above $80\text{ }^\circ\text{C}$ the formation of cyclic CHC is favored, while at $120\text{ }^\circ\text{C}$ the selectivity for copolymer is only 34%.



Scheme A31. Proposed mechanism for the copolymerization of CO_2 and epoxides to poly(carbonates) with CHO as example.

Similar to the cycloaddition, an initial coordination of CHO to the metal center and a subsequent ring-opening induced by an nucleophilic attack is discussed for the mechanism of the copolymerization of CO_2 with epoxides (see Scheme A31).^[243,244] Nucleophiles like DMAP or halides with or without quaternary ammonium salts have shown to significantly increase the catalytic conversion. Carbon dioxide inserts into the metal alkoxide bond under formation of a carbonate. The chain growth starts with an additional insertion of a CHO unit and continues with alternating insertions of CO_2 and CHO. As mentioned earlier, a side reaction is the

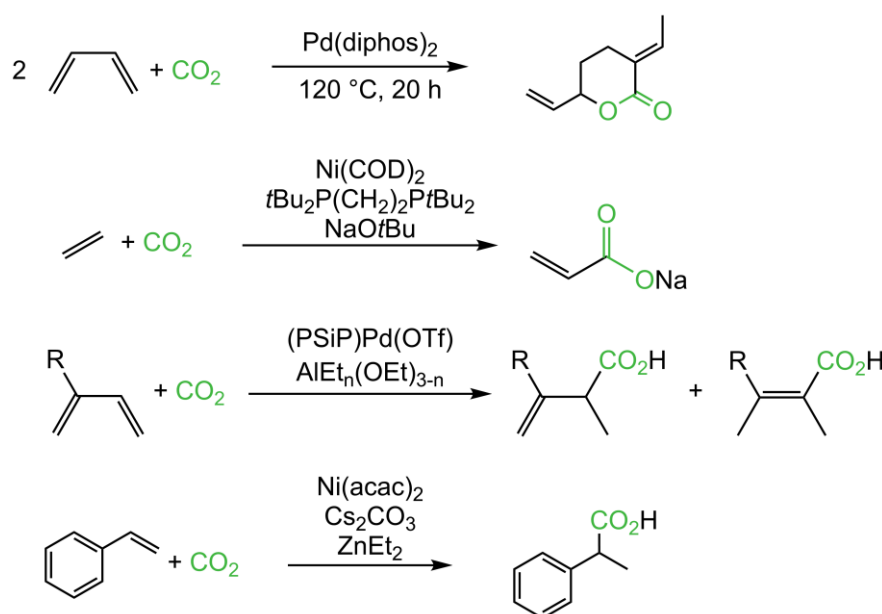
backbiting which resulted in the formation and dissociation of a cyclic carbonate. The backbiting is favored for epoxides with smaller substituents such as PO and is hindered for bulkier epoxides like CHO (see Scheme A32a). Most salen-based aluminum complexes showed cyclization for PO and polymerization for CHO. For the complexes containing intramolecular quaternary ammonium chains at the ligand scaffold (**133/134**) a transfer of the polymer chain with the carbonate anion to the quaternary ammonium unit under formation of an ion pair is discussed (see Scheme A32b).^[222] The metal center is thereby open for a coordination of another CHO unit, which further accelerates the catalytic reaction. Because the polymer chain is already close to the metal center it can easily ring open the CHO with a nucleophilic attack. In binary catalyst systems, when the carbonate polymer chain disassociates, it can diffuse into the solution. This is prevented by the integrated quaternary ammonium unit. For the heterobimetallic systems of WILLIAMS, especially complex **150**, a synergetic effect of both metals was observed (see Scheme A32c).^[233] The magnesium center enhances the entropy of the transition state by activating the epoxide by coordination and the cobalt center reduces the enthalpy by increasing the nucleophilicity of the carbonate anion.



Scheme A32. a) Hindering of the backbiting side reaction in case of sterically demanding epoxides. b) Enhanced catalytic activity by polymer chain transfer to the integrated quaternary ammonium chain. c) Synergetic effect of heterobimetallic catalyst systems.

5.1 Copolymerization of CO₂ and Olefins

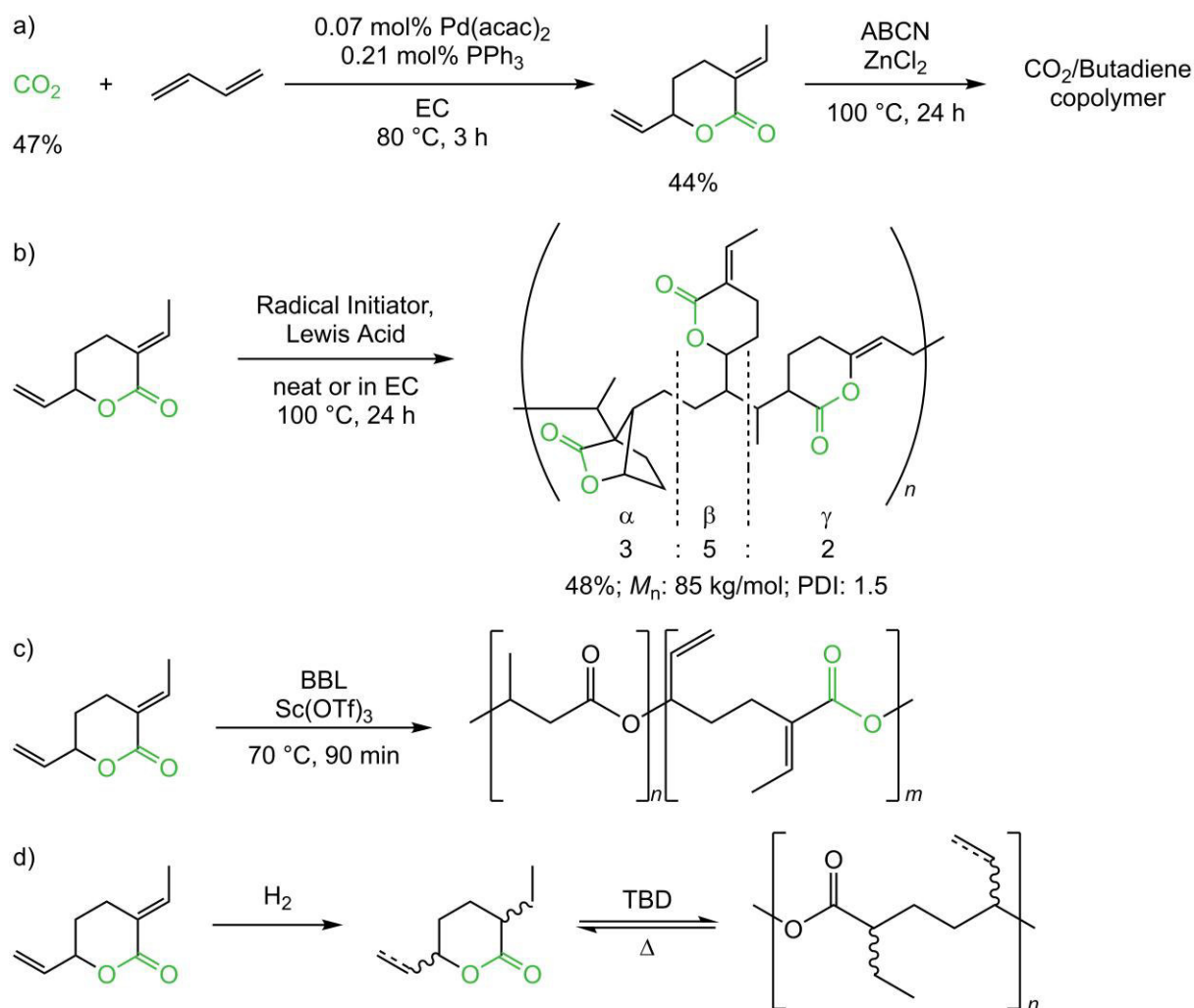
Although the telomerization of two units 1,3-butadiene and one CO₂ molecule to the lactone 3-ethyl-6-vinyltetrahydro-2*H*-pyran-2-one (EVP) catalyzed by Pd(Ph₂PEtPPh₂)₂ was already discovered by INOUE and MUSCO in the late 70s, examples for the coupling of CO₂ with olefin are rather scarce (Scheme A33).^[245–247] There are reports for one to one coupling of CO₂ with ethylene^[248], butadiene^[249] and styrene.^[250] Copolymerization of CO₂ with olefins was not feasible for a long time and early attempts with dienes and vinyl ethers yielded only oligomeric products.^[251,252] Over the years, the catalytic synthesis of EVP was further optimized and the yield could be increased.^[253–255] DINJUS even reported the telomer of two units of isoprene and CO₂, but only in poor yield.^[254] Pd nanoparticles generated *in situ* from Pd(acac)₂ and TBAAc were able to yield EVP with 51% and a high selectivity.^[255]



Scheme A33. Examples of the coupling of CO₂ with olefins.

In 1998, DINJUS reported the first copolymerization of EVP with dithiols.^[256] The first homopolymerization of EVP was described by NOZAKI in 2014.^[35] In a one-pot reaction, butadiene and CO₂ could be polymerized in two-steps (see Scheme A34a). In the first step, EVP is formed with the catalyst system Pd(acac)₂ and PPh₃ at 80 °C in EC. In this step, EVP could also be isolated. In the second step the Lewis acid ZnCl₂ and the radical starter ABCN (1,1'-azobis(cyclohexanecarbonitrile)) is added and poly(EVP) was obtained at 100 °C after 24 h with *M_n* of 19 kg/mol and a PDI of 1.6. EVP can also be polymerized in a solution of EC with addition of ZnCl₂ and a radical starter ABCN or V-40 (1,1'-azobis(cyclohexane-1-carbonitrile)) (see Scheme A34b). With this procedure a *M_n* of 85 kg/mol and a PDI of 1.5 were obtained. The polymer contains the bicyclic camphor-like structure α and the monocyclic structures β and

γ . Mixtures of butadiene and isoprene or 1,3-pentadiene yielded polymeric material too, however, a lactone species could not be isolated. In later works, the NOZAKI group was able to modify the polymer with a ring-opening reaction at the α -unit and conduct a copolymerization of EVP and ethylene.^[257,258]



Scheme A34. a) One-pot reaction the coupling of butadiene and CO_2 with a subsequent radical polymerization to poly(EVP). b) Radical polymerization of EVP and the three possible isomers.

A different polymerization approach is the ROP of EVP which was successfully conducted only recently.^[259,260] NI used Sc(OTf)_3 as catalyst and could copolymerize EVP with β -butyrolactone (BBL) to yield the poly(ester) poly(EVP/BBL) with M_n of up to 4.1 kg/mol and PDI between 1.86–3.66.^[259] TONKS used the organocatalyst of 1,5,7-triazabicyclo(4.4.0)dec-5en (TBD). In a first step EVP was hydrogenated with H_2 with a subsequent polymerization step. Poly(EVP) with M_n of 13.6 kg/mol could be obtained which is recyclable by heating to 138 $^\circ\text{C}$.^[260]

B

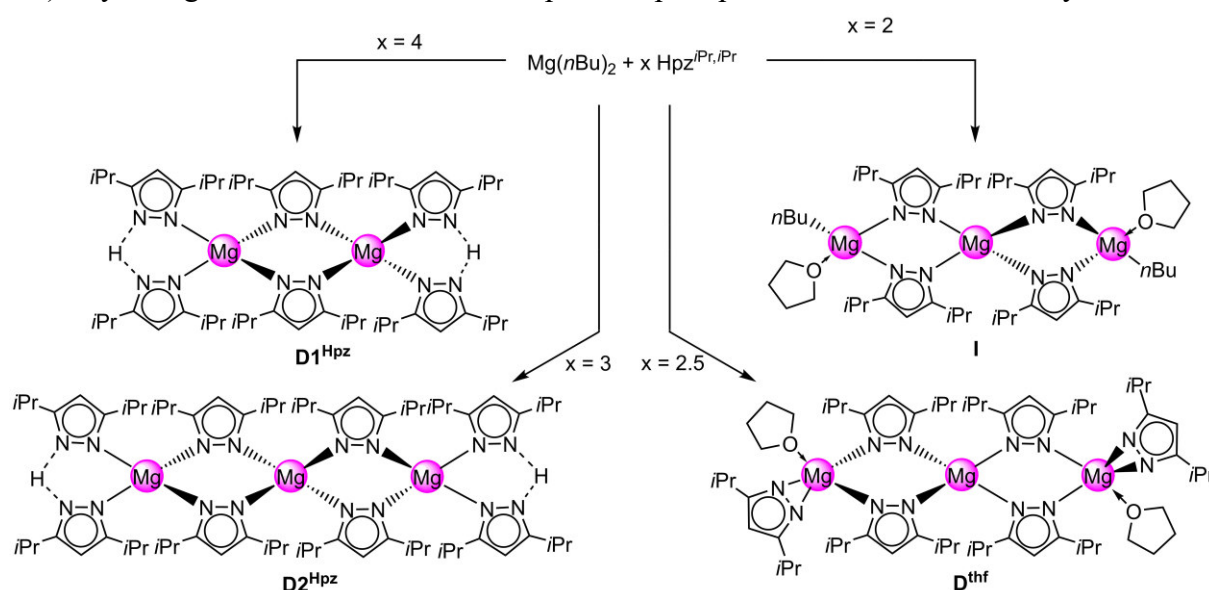
Summary of the Main Results

1. Synthesis of New Light Metal Pyrazolates

For the start of this study a number of literature-known light metal pyrazolates were synthesized to test their reactivity toward CO₂. These include the following in previous chapter A.2 introduced complexes [K(pz^{*t*Bu})₂]_{*n*} (**A**),^[78,81] [Li(pz^{*t*Bu})₂]₄ (**B**),^[81] [Mg(pz^{*t*Bu})₂]₂ (**C**),^[88] [Mg(pz^{*t*Bu})₂(Hpz^{*t*Bu})₂] (**C^{Hpz}**),^[99] [Mg(pz^{*i*Pr})₂(Hpz^{*i*Pr})₂] (**D1^{Hpz}**),^[91] Al(η²-pz^{*t*Bu})₃ (**E**),^[101] Ti^{IV}(η²-pz^{Me})₄ (**F**),^[120] Ti^{III}(η²-pz^{*t*Bu})₃ (**G**),^[121] and [Y(η²-pz^{Me})₂(μ₂-pz^{Me})(μ₂-thf)]₂ (**H**).^[127] Complex **C** could be isolated by a protonolysis reaction of Mg(*n*Bu)₂ and Hpz^{*t*Bu}, alongside the salt-metathesis protocol reported in the literature. For complex **H** the same salt-metathesis synthesis route as for **E** was used.

Besides the literature-known complexes a number of new pyrazolates was synthesized. The focus was on derivatives bearing smaller alkyl substituents on the pyrazolato ring such as *i*Pr, Me and H. Especially the unsubstituted pyrazolates are highly desirable, because they are easily accessible and the highest CO₂ capacity (wt%) can be expected.

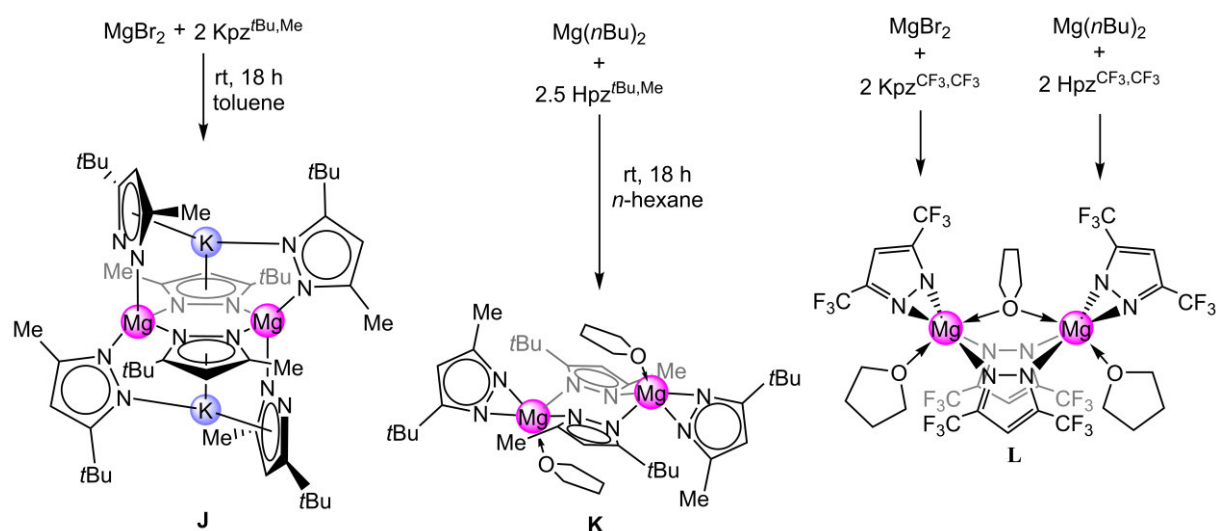
The mixed pyrazolato/pyrazole complex **D1^{Hpz}** reported by RUHLANDT-SENGE was obtained in a protonolysis reaction of Mg(*n*Bu)₂ with Hpz^{*i*Pr} in a ratio of 1:4 in THF. We were interested if homoleptic [Mg(pz^{*i*Pr})₂] is feasible by adjusting this ratio. A ratio of 1:2 resulted in an incomplete protonolysis to the trinuclear complex [Mg₃(pz^{*i*Pr})₄(*n*Bu)₂(thf)₂] (**I**) with two terminal butyl groups. Applying a ratio of 1:3 led to the formation of heteroleptic trimetallic [Mg₃(pz^{*i*Pr})₆(Hpz^{*i*Pr})₂] (**D2^{Hpz}**) with one extra Mg(pz^{*i*Pr})₂-unit compared to **D1^{Hpz}** (see Scheme B1). By using a ratio of 1:2.5 a white powder precipitated. After several recrystallization



Scheme B1. Different products in the reaction of Mg(*n*Bu)₂ and Hpz^{*i*Pr} with distinct ratios in THF. Complex **D1^{Hpz}** has been reported in the literature.^[91]

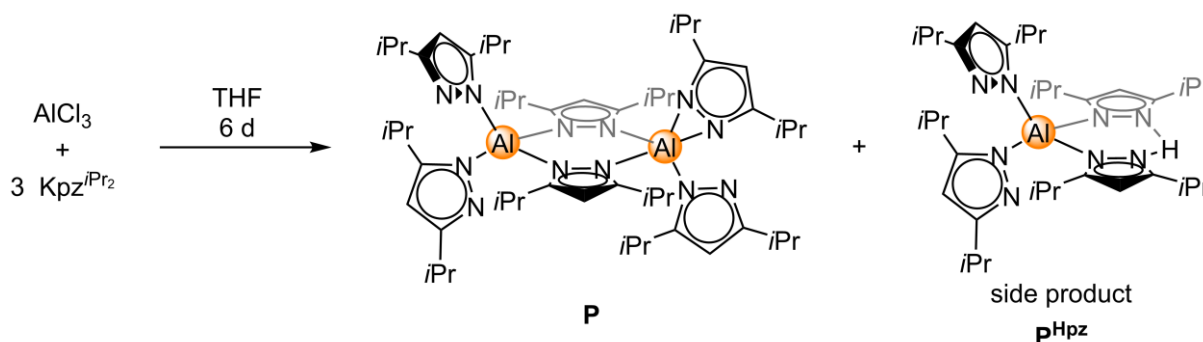
attempts in *n*-pentane donor-stabilized $[\text{Mg}_3(\text{pz}^{i\text{Pr}_2})_6(\text{thf})_2]$ (**D**^{thf}) could be obtained as a crystalline material. The amorphous white powder is most likely putative $[\text{Mg}(\text{pz}^{i\text{Pr}_2})_2]_n$ (**D**) and the recrystallization mixture contained just enough residual THF that complex **D**^{thf} is formed.

A salt-metathesis attempt with MgBr_2 and $\text{Kpz}^{t\text{Bu},\text{Me}}$ in THF gave the ate-complex $[\text{KMg}(\text{pz}^{t\text{Bu},\text{Me}})_3]_2$ (**J**) (see Scheme B2). Donor-stabilized $[\text{Mg}(\text{pz}^{t\text{Bu},\text{Me}})_2(\text{thf})_2]$ (**K**) was obtained, when a ratio of 1:2.5 is used in a protonolysis reaction of $\text{Mg}(n\text{Bu})_2$ with $\text{Hpz}^{t\text{Bu},\text{Me}}$. This distinct ratio seems to be necessary for protonolysis reactions with pyrazoles containing alkyl substituents with medium steric bulk. Fluorinated $[\text{Mg}_2(\text{pz}^{\text{CF}_3,\text{CF}_3})_4(\text{thf})_3]$ (**L**) was feasible via both the salt-metathesis and protonolysis protocol. Protonolysis reactions of $\text{Mg}(n\text{Bu})_2$ with the smaller pyrazoles Hpz^{Me_2} and unsubstituted Hpz yielded amorphous $[\text{Mg}(\text{pz}^{\text{Me}_2})_2]_n$ (**M**) and $[\text{Mg}(\text{pz})_2]_n$ (**N**). The formation of both **M** and **N** was validated by ^{13}C CP/MAS spectroscopy. Further, the IR spectrum of **N** is almost identical to the one reported for $\text{Zn}(\text{pz})_2$.^[100] Bulky $[\text{Mg}(\text{pz}^{\text{Ph}_2})_2]_n$ (**O**) was obtained via salt metathesis. This indicates that magnesium pyrazolates with a steric bulk equal of *t*Bu/Ph or above are readily feasible via salt metathesis.



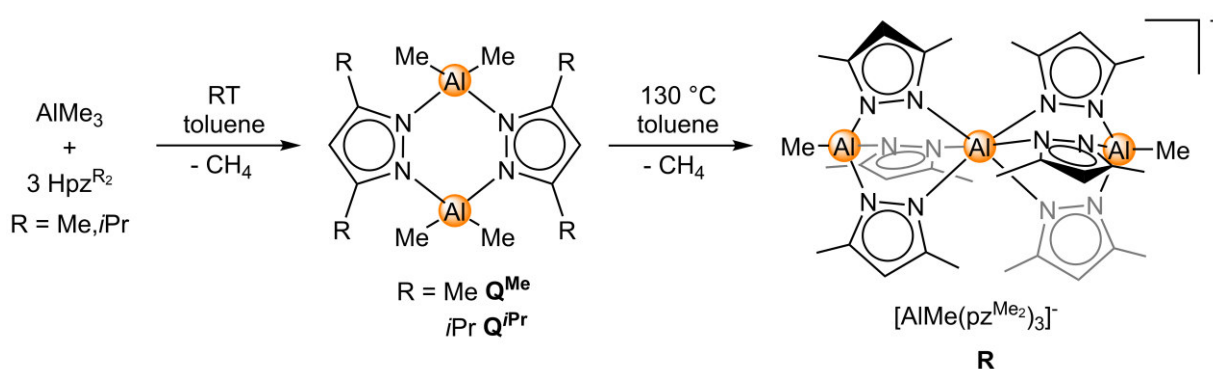
Scheme B1. Synthesis of a variety of new magnesium pyrazolate complexes including the ate-complex $[\text{KMg}(\text{pz}^{t\text{Bu},\text{Me}})_3]_2$ (**J**) and the donor stabilized $[\text{Mg}(\text{pz}^{t\text{Bu},\text{Me}})_2(\text{thf})_2]$ (**K**) and $[\text{Mg}_2(\text{pz}^{\text{CF}_3,\text{CF}_3})_4(\text{thf})_3]$ (**L**).

By applying AlCl_3 and $\text{Kpz}^{i\text{Pr}_2}$ according to a salt-metathesis protocol in THF homoleptic $[\text{Al}(\text{pz}^{i\text{Pr}_2})_3]_2$ (**P**) could be isolated as crystalline material (see Scheme B3). In several attempts few crystals of $[\text{Al}(\text{pz}^{i\text{Pr}_2})_3(\text{Hpz}^{i\text{Pr}_2})]$ (**P^{Hpz}**) were obtained most likely due to residual water in the solvent THF.



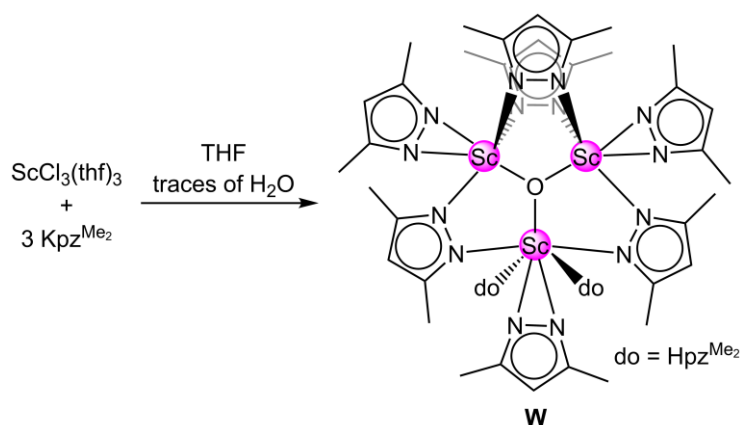
Scheme B2. Synthesis of the aluminum complex $[\text{Al}(\text{pz}^{i\text{Pr}_2})_3]_2$ (**P**). On several occasions side product $[\text{Al}(\text{pz}^{i\text{Pr}_2})_3(\text{Hpz}^{i\text{Pr}_2})]$ (**P^{Hpz}**) was visible in NMR experiments.

Attempts using AlMe_3 as starting material in the protonolysis with Hpz^{R_2} ($\text{R} = \text{Me}, i\text{Pr}$) did not lead to the desired $[\text{Al}(\text{pz}^{\text{R}_2})_3]_n$. At ambient temperature only a 1:1 conversion into $[\text{Me}_2\text{Alpz}^{\text{R}_2}]_2$ (**Q**, $\text{R} = \text{Me}, i\text{Pr}$) is achievable (see Scheme B4). By heating to 130°C in toluene further conversion into the separated ion pair $[\text{Al}(\text{N},\text{N}',\text{N}''-\text{Al}\{\text{pz}^{\text{Me}_2}\}_3\text{Me})_2][\text{Al}(\text{pz}^{\text{Me}_2})_3\text{Me}]$ (**R**) is possible which contains three tris(pyrazolyl)borate-like $[\text{Al}(\text{pz}^{\text{Me}_2})_3\text{Me}]$ -units. Heating to 180°C in xylene led to no isolatable product. However, when instead $\text{Al}(\eta^2\text{-pz}^{t\text{Bu}_2})_3$ (**E**) and unsubstituted pyrazole is reacted in toluene an immediate formation of a white amorphous powder was observed. ^{13}C CP/MAS spectroscopy revealed a complete conversion into homoleptic $[\text{Al}(\text{pz})_3]_n$ (**S**).



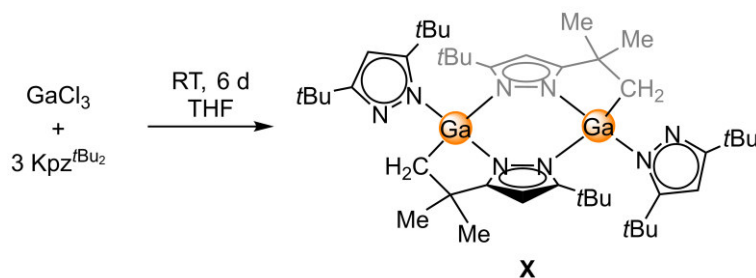
Scheme B3. Stepwise protonolysis in the reaction of AlMe_3 and three equivalents Hpz^{R_2} to 1:1 conversion product $[\text{Me}_2\text{Alpz}^{\text{R}_2}]_2$ (**Q**, $\text{R} = \text{Me}, i\text{Pr}$) at ambient temperature and to the separated ion pair $[\text{Al}(\text{N},\text{N}',\text{N}''-\text{Al}\{\text{pz}^{\text{Me}_2}\}_3\text{Me})_2][\text{Al}(\text{pz}^{\text{Me}_2})_3\text{Me}]$ (**R**) at 130°C .

To avoid the use of mercury, which is required for the synthesis of $\text{Sc}(\eta^2\text{-pz}^{t\text{Bu}_2})_3$ reported by DEACON, the same salt-metathesis protocol in THF as for $\text{Al}(\eta^2\text{-pz}^{t\text{Bu}_2})_3$ (**E**) was used.^[101,124] Activated $\text{ScCl}_3(\text{thf})_3$ and $\text{Kpz}^{t\text{Bu}_2}$ yielded $\text{Sc}(\eta^2\text{-pz}^{t\text{Bu}_2})_3(\text{thf})$ (**T**) with one donor molecule THF at the metal center. Applying the same protocol $[\text{Y}(\text{pz}^{t\text{Bu}_2})_3(\text{thf})_2]$ (**U**) was obtained from activated $\text{YCl}_3(\text{thf})_{2.5}$ and $\text{Kpz}^{t\text{Bu}_2}$. Complex **T** is isostructural to literature known $[\text{Y}(\text{pz}^{t\text{Bu}_2})_3(\text{py})_2]$ described by WINTER.^[123] Amorphous $[\text{Sc}(\text{pz})_3]_n$ (**V**) could be accessed from **T** comparable to the synthesis of **S**. The reaction of $\text{ScCl}_3(\text{thf})_3$ and Kpz^{Me_2} did not yield any clean product. However, on one occasion the trinuclear oxo-cluster $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2]$ (**W**) was isolated in a good yield (see Scheme B5). In total there is one water molecule in the complex, which most likely originated from residual water in the solvent THF.



Scheme B4. Synthesis of oxo cluster $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2]$ (**W**).

The synthesis of putative homoleptic gallium pyrazolates was not successful. However, a salt-metathesis approach using GaCl_3 and $\text{Kpz}^{t\text{Bu}_2}$ in THF produced a few crystals of the dimer $[\text{Ga}(\text{pz}^{t\text{Bu}_2})(\mu\text{-N,N,C-pz}^{t\text{Bu,C}(\text{CH}_3)_2\text{CH}_2})]_2$ (**X**, see Scheme B6). The solid-state structure revealed that one *t*Bu-group of a pyrazolato ligand underwent CH-bond activation under elimination of one pyrazole. Similar to aluminum, a protonolysis reaction of GaMe_3 with three equivalents $\text{Hpz}^{t\text{Bu}_2}$ at ambient temperature only led to a single ligand exchange, affording literature-known $[\text{Me}_2\text{Ga}(\text{pz}^{t\text{Bu}_2})]_2$.^[261]

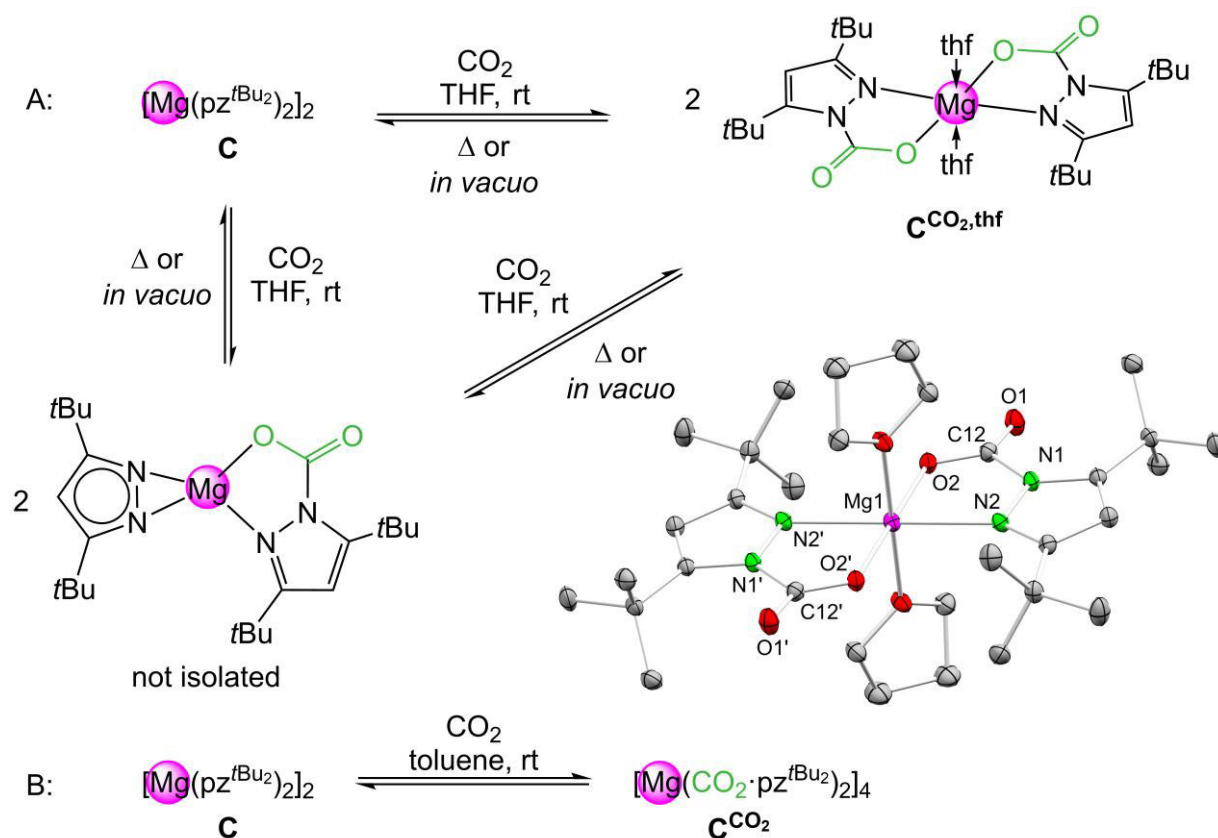


Scheme B5. C–H-bond activation to $[\text{Ga}(\text{pz}^{t\text{Bu}_2})(\mu\text{-N,N,C-pz}^{t\text{Bu,C}(\text{CH}_3)_2\text{CH}_2})]_2$ (**X**) in the salt-metathesis reaction of GaCl_3 and $\text{Kpz}^{t\text{Bu}_2}$.

To compare the behavior of magnesium and zinc pyrazolates toward CO₂ the literature-known [Zn(pz^{*t*Bu₂})₂(Hpz^{*t*Bu₂})₂] (**Y^{Hpz}**) was synthesized via a salt-metathesis protocol applying ZnCl₂ and Kpz^{*t*Bu₂}, which is different to the reported protonolysis procedure.^[86]

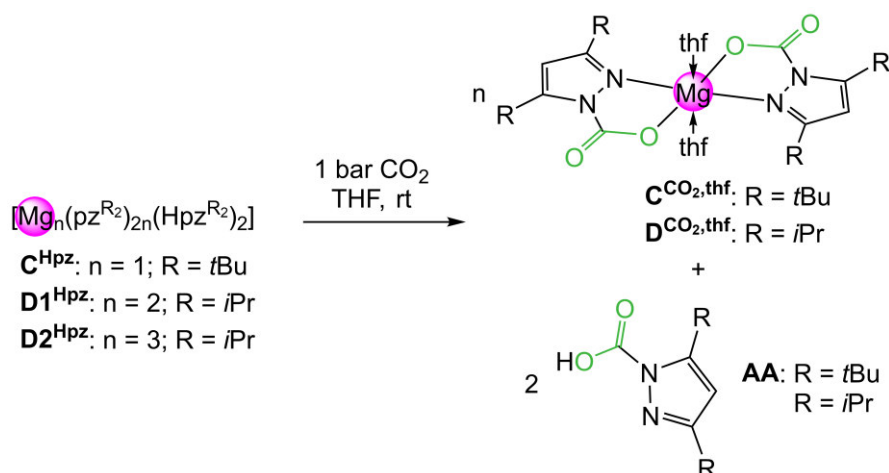
2. Reversible Carbon Dioxide Insertion into Light Metal Pyrazolates

Reacting complex **C** with 1 bar CO₂ in THF led to insertion of CO₂ into both Mg–(pyrazolato) moieties and the formation of carbamate complex [Mg(CO₂·pz^{*t*Bu₂})₂(thf)₂] (**C**^{CO₂,thf}) (see Scheme B7). This equals an uptake of 14.3 wt% or 3.3 mmol CO₂/g. This process is completely reversible in solution (VT NMR: 70–105 °C) and in the solid state (TGA: 134–233 °C). Solid **C**^{CO₂,thf} slowly releases CO₂ over time, which can be speed up under reduced pressure or elevated temperature. NMR studies revealed a stepwise de-insertion, which could be also observed in two distinct CO₂-releasing steps in the TGA. However, putative [Mg(CO₂·pz^{*t*Bu₂})(pz^{*t*Bu₂})(thf)₂] could not be isolated. In toluene **C** showed also an immediate and complete reaction with CO₂, however, no crystalline material could be isolated. An ¹H DOSY NMR study revealed that one distinct product is formed. A subsequent molar mass calculation resulted in *M* = 1875 g mol^{−1} which is close to the tetrameric [Mg(CO₂·pz^{*t*Bu₂})₂]₄ (**C**^{CO₂}) with a molar mass of 1883.59 g mol^{−1}. This would equal an uptake of 18.7 wt% CO₂.



Scheme B6. Reversible CO₂ insertion with [Mg(pz^{*t*Bu₂})₂]₂ (**C**) to A) monomeric [Mg(CO₂·pz^{*t*Bu₂})₂(thf)₂] (**C**^{CO₂,thf}) and B) donor-free tetrameric [Mg(CO₂·pz^{*t*Bu₂})₂]₄ (**C**^{CO₂}).

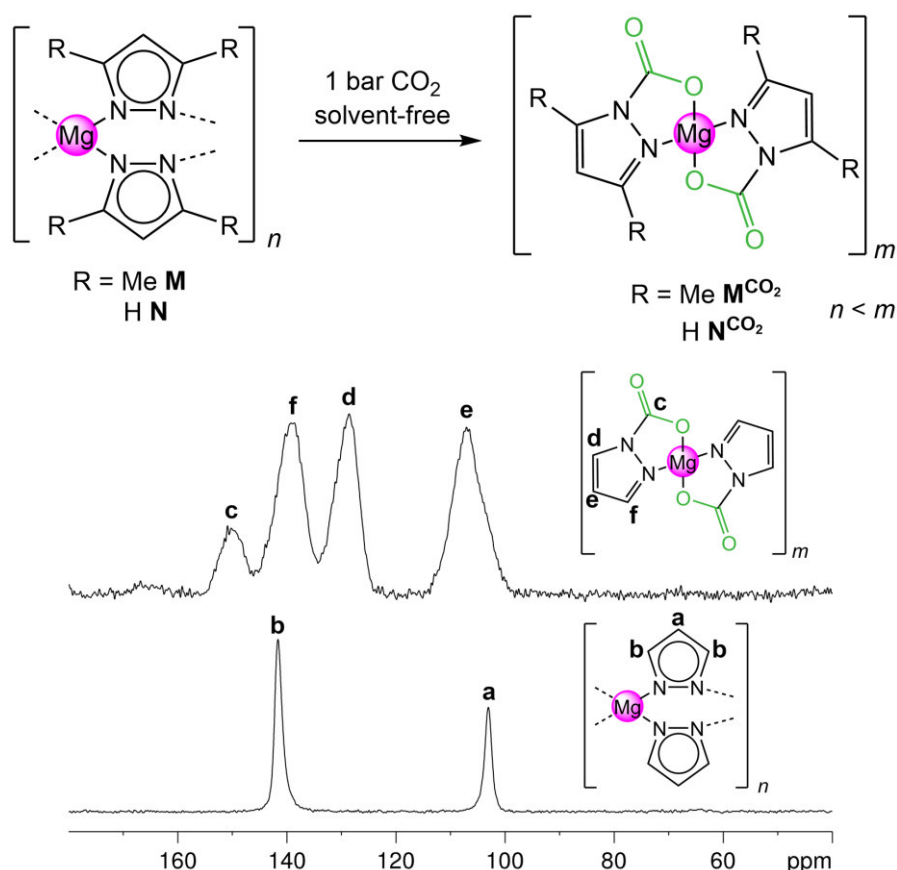
Complex **D^{thf}** is also capable of inserting CO₂ in THF to yield [Mg(CO₂·pz^{*i*Pr})₂(thf)₂] (**D^{CO₂,thf}**). Although no crystal structure could be obtained, both ¹H and ¹³C NMR confirmed the formation. In toluene, the reaction of **D^{thf}** with CO₂ showed a rather complicated ¹H NMR spectrum, however, a SC-XRD analysis of the few obtained crystals revealed the ate-complex [LiMg₄(CO₂·pz^{*i*Pr})₉] (**Z**). The lithium atom most likely originated from residual lithium contained in Mg(*n*Bu)₂ as verified by a ⁷Li NMR experiment. The formation of **Z** most likely



Scheme B7. Reactivity of the mixed pyrazolato/pyrazole magnesium complexes toward CO₂ under the formation of the corresponding CO₂ insertion complexes and disassociation of the carbamic acid HO₂Cpz^{R₂} (**AA**, $R = iPr, tBu$).

was induced by the lithium contaminated [Mg₃(pz^{*i*Pr})₆(thf)₂] (**D^{thf}**). Reacting the mixed pyrazolato/pyrazole magnesium complexes **C^{Hpz}**, **D1^{Hpz}** and **D2^{Hpz}** with 1 bar CO₂ led to the formation of **C^{CO₂,thf}** and **D^{CO₂,thf}**, respectively (see Scheme B8). In addition, signal sets were observed in the NMR spectra, that can be assigned to the carbamic acids HO₂Cpz^{R₂} (**AA**, $R = tBu, iPr$). The donor pyrazole dissociates after CO₂ insertion. In contrast to the metal carbamates no CO₂ release is observed for **AA**.

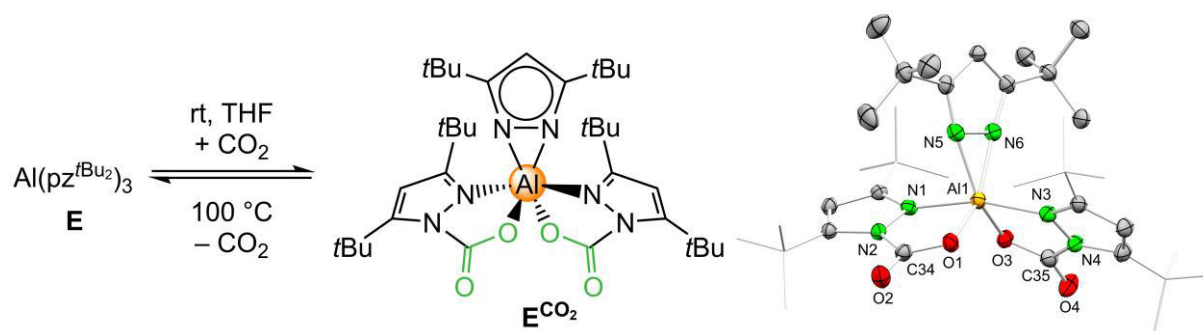
Because both **M** and **N** are not soluble in common solvents, we exposed the solid compounds to a 1 bar CO₂ atmosphere without any solvent. Surprisingly, an immediate heat evolution and a mass gain in accordance to full CO₂ insertion was observed. This was proven by IR and ¹³C CP/MAS experiments that showed the quantitative formation of [Mg(CO₂·pz^{Me})₂]_{*n*} (**M^{CO₂}**) and [Mg(CO₂·pz)₂]_{*n*} (**N^{CO₂}**), respectively (see Scheme B9). Both compounds reach exceptionally high uptake of 29.4 wt% and 35.7 wt% CO₂, respectively. Complex **M^{CO₂}** even became soluble in THF and solution NMR experiments confirmed its formation as well. However, no crystalline material was obtained. Both compounds display a reversible CO₂ insertion, which was confirmed by TGA, IR and solid-state NMR studies.



Scheme B8. Solvent-free CO₂ insertion into magnesium pyrazolates with small substituents (R = H, Me) at the pyrazolato ligand (top). Comparison of ¹³C CP/MAS spectra of **N** and **N**^{CO₂} (bottom).

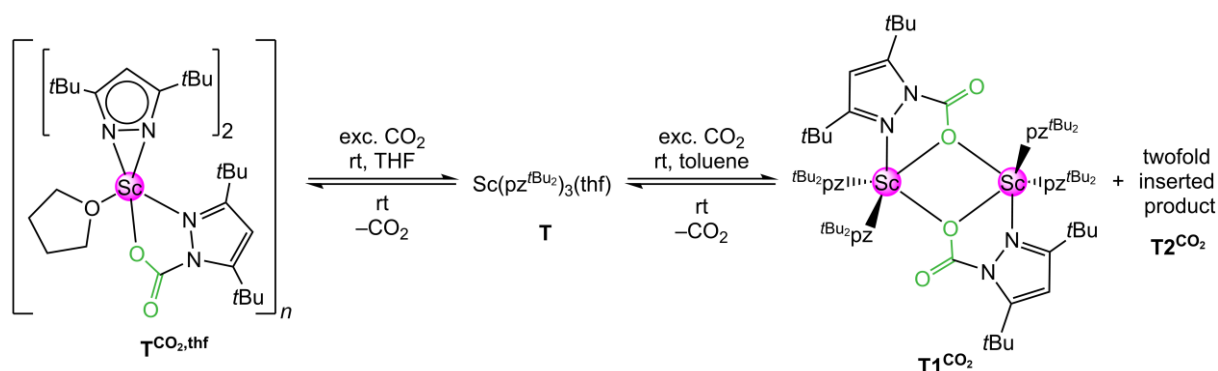
The magnesium complexes **J**, **K** and **O** showed also an immediate CO₂ insertion, however, the ¹H NMR spectra were rather complicated and no clean product could be assigned. Crystallization attempts were not successful. Fluorinated **L** showed no visible CO₂ insertion in NMR experiments. Most likely, the reduced nucleophilicity of the pyrazolato ligand disfavors interaction with CO₂.

Exhaustive CO₂ insertion was not detected for the aluminum complex **E** (15.8 wt% CO₂), but the doubly inserted [Al(CO₂·pz^{*t*Bu₂})₂(pz^{*t*Bu₂})] (**E**^{CO₂}) formed in THF (see Scheme B10). The crystal structure revealed that the third CO₂ insertion is hindered by the steric bulk of the *t*Bu groups. The necessary tilt for the insertion of the third pyrazolato ligand is hindered by the two carbamate ligands. The insertion process of complex **E**^{CO₂} is reversible which was proved by a ¹H VT NMR study and TGA. Striking is that the required energy for the release of CO₂ is significantly higher than for the magnesium congener **C**^{CO₂}, but also that solid **E**^{CO₂} did not show any de-insertion over time, even under reduced pressure. The less steric demanding **P** showed complete CO₂ insertion to [Al(CO₂·pz^{*i*Pr₂})₃]_{*n*} (**P**^{CO₂}) in THF (21.5 wt% CO₂). Although no crystalline material was obtained, NMR studies unambiguously revealed full CO₂ insertion by showing three different signal sets for only the carbamate ligands.



Scheme B9. Twofold CO₂ insertion of complex Al(η^2 -pz^{tBu₂})₃ (**E**) to [Al(CO₂·pz^{tBu₂})₂(pz^{tBu₂})] (**E**^{CO₂}) and crystal structure of **E**^{CO₂}.

The scandium complex **T** inserted CO₂ only into one Sc–pyrazolato moiety in THF to yield donor-stabilized [Sc(CO₂·pz^{tBu₂})₃(thf)]_n (**T**^{CO₂,thf}), observable in the NMR spectra (see Scheme B11). However, no crystalline material was obtained, due to immediate de-insertion at ambient temperature upon solvent removal. This is in stark contrast to the aluminum congener **T**^{CO₂}, which did not release CO₂ even under reduced pressure. A ¹H VT NMR study uncovered a fully reversible equilibrium between **T** and **T**^{CO₂,thf}. In toluene, two different insertion species were initially observed in the ¹H NMR spectrum, but also crystalline material was formed and a SC-XRD measurement applying permanent cooling revealed the dimer [Sc(CO₂·pz^{tBu₂})(pz^{tBu₂})₂]₂ (**T1**^{CO₂}) (7.0 wt% CO₂). Complex **T**^{CO₂} could be assigned to one of the two species found in the ¹H NMR spectrum. The second species is most likely the twofold inserted [Sc(CO₂·pz^{tBu₂})₂(pz^{tBu₂})] (**T2**^{CO₂}), which immediately releases one CO₂ to convert into **T1**^{CO₂} upon opening of the NMR tube. The overall CO₂ affinity (carboxophilicity) of scandium proved to be rather weak.



Scheme B10. Reactivity of complex Sc(η^2 -pz^{tBu₂})₃(thf) (**T**) toward CO₂ in dependence of the solvent.

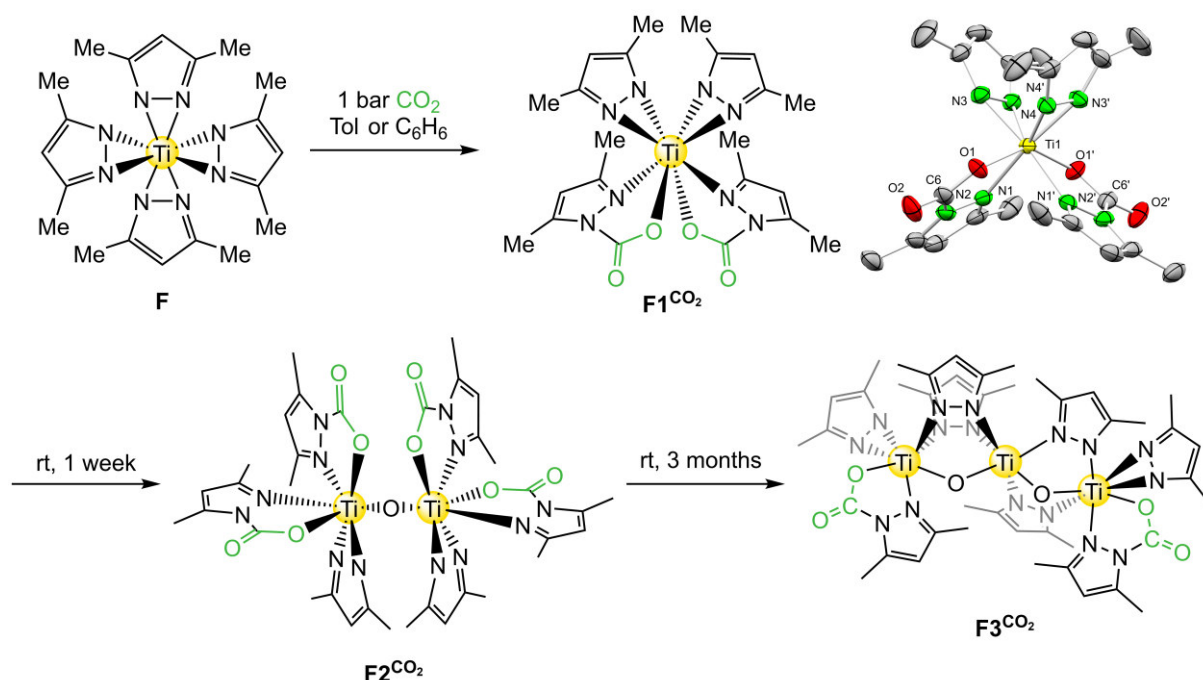
Even less carboxophilicity was observed for yttrium complex **U** showing no visible CO₂ insertion like complex **L**. In contrast, with yttrium complex **H** bearing less bulky pyrazolato ligands a CO₂ insertion was observed in NMR spectra. One signal set could be assigned to fully inserted [Y(CO₂·pz^{Me₂})₃(thf)]_n (**H**^{CO₂}) while the other signals appeared too complicated to be

assigned to one distinct product. A VT ^1H NMR study showed the reversibility of H^{CO_2} whereas the other species remained unchanged.

Surprisingly, the scandium oxo cluster **W** revealed exhaustive CO_2 insertion according to NMR spectrum with one clean product W^{CO_2} and the formation of the carbamic acid **AA** ($\text{R} = \text{Me}$). However, no crystalline material could be obtained.

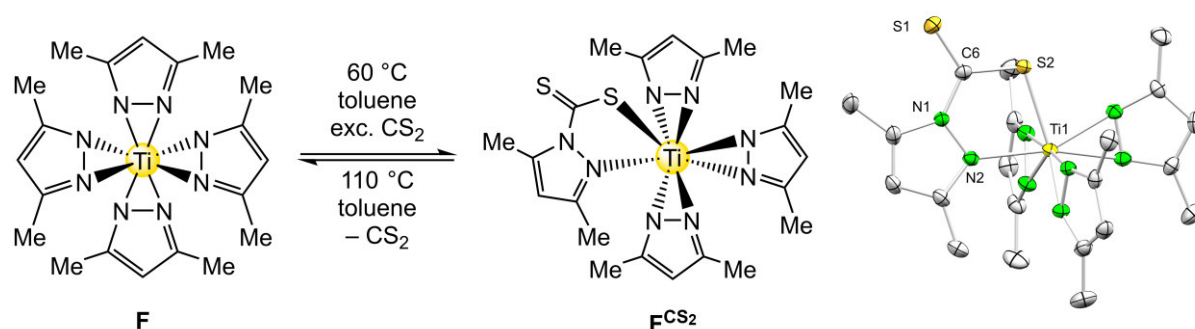
Both alkali-metal pyrazolates **A** and **B** showed clean CO_2 insertion products $[\text{Li}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})]_n$ (A^{CO_2}) and $[\text{K}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})]_n$ (B^{CO_2}) in THF, as monitored by NMR spectroscopy. However, only microcrystalline material unsuitable for a SC-XRD study was obtained.

At first, tetravalent titanium complex **F** showed a twofold CO_2 insertion to yield $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ (F1^{CO_2}) in toluene, which was verified via NMR studies and experiments with labeled $^{13}\text{CO}_2$ (see Scheme B12). However, after one day a second signal set appeared and overtime F1^{CO_2} was converted completely into this new compound in addition to several other new species. This “decomposition” process is reproducible and occurs always at ambient temperature. When a solution of F1^{CO_2} was cooled to 0°C , any decomposition was not observed. When cooled to -40°C a yellow amorphous powder precipitated but at first no crystalline material formed. After one week at ambient temperature yellow crystals could be obtained from the original solution of F1^{CO_2} which revealed the oxo-bridged dimer $\text{O}[\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})]_2$ (F2^{CO_2}). Two carbamato and one pyrazolato ligand are coordinated to each titanium center. Two possible reaction pathways come into question a hydrolysis and a



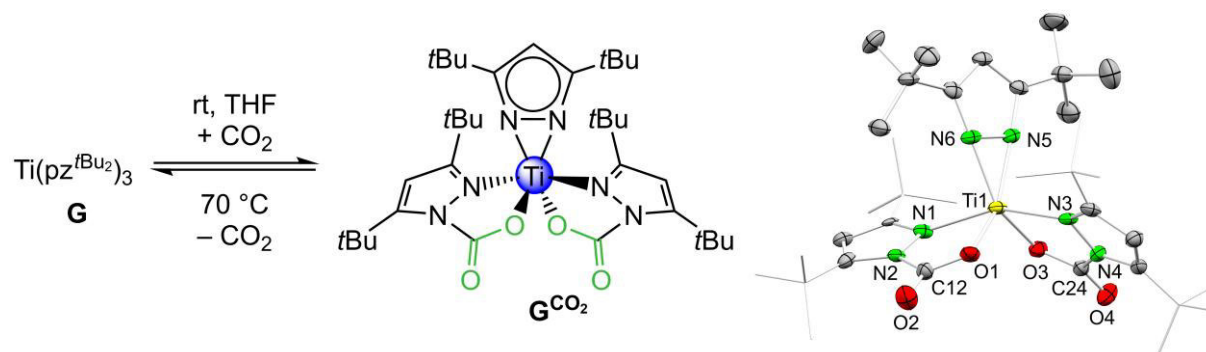
Scheme B11. CO_2 insertion into complex $\text{Ti}(\eta^2\text{-pz}^{\text{Me}_2})_4$ (**F**) to yield $[\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2]$ (F1^{CO_2}) and a subsequent deoxygenation decomposition reaction.

subsequent dissociation of pyrazole/carbamic acid or a deoxygenation of inserted CO₂. For the latter reaction some examples exist in the literature.^[262,263] A light induced reaction could be excluded by experiments with amber glass. After two months orange crystals were obtained from the original **F1**^{CO₂} solution and a further prolongation of the oxo chain to the trinuclear [Ti(μ-O)₂(μ-pz^{Me₂})₄(Ti{CO₂·pz^{Me₂}} {pz^{Me₂}})₂] (**F3**^{CO₂}) was revealed. It seems that the reaction over time leads to TiO₂. After three years at -40 °C red crystallin needles grew from the solution with the yellow precipitate. A SC-XRD measurement confirmed the proposed structure of [Ti(CO₂·pz^{Me₂})₂(pz^{Me₂})₂] (**F1**^{CO₂}), which equals an uptake of 17.0 wt% CO₂.



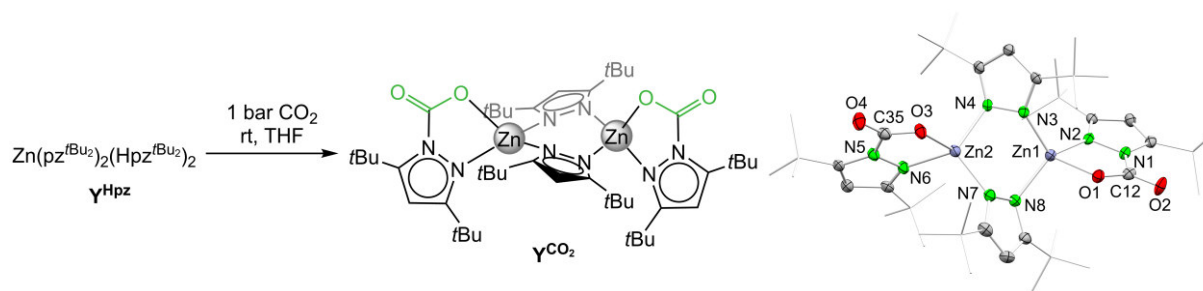
Scheme B12. Reactivity of complex Ti(η²-pz^{Me₂})₄ (**F**) towards an excess of CS₂ and the formation of [Ti(CS₂·pz^{Me₂})₂(pz^{Me₂})₂] (**F**^{CS₂}).

To examine if the feasibility of a sulfide-bridging, **F** was reacted with an excess of CS₂. At 60 °C, a full conversion to mono-inserted [Ti(CS₂·pz^{Me₂})₂(pz^{Me₂})₂] (**F**^{CS₂}) occurred. (see Scheme B13). The ¹H NMR spectrum shows different signal sets of the pyrazolato ligands positioned *trans* and *cis* to the thiocarbamate ligand. Heating up to 130 °C did not led to a formation of a sulfur bridge but instead to de-insertion of CS₂. This is caused by the softer Lewis base character of sulfur compared to oxygen.



Scheme 13. Twofold CO₂ insertion of complex Ti(η²-pz^{tBu₂})₃ (**G**) to yield [Ti(CO₂·pz^{tBu₂})₂(pz^{tBu₂})] (**G**^{CO₂}) and crystal structure of **G**^{CO₂}.

The reaction of the trivalent titanium complex $\text{Ti}^{\text{III}}(\eta^2\text{-pz}^{\text{tBu}_2})_3$ (**G**) with an excess of CO_2 led to immediate color change from blue over green and yellow to finally red. Surprisingly, the crystal structure revealed that the titanium stayed in the oxidation state of +III and that the complex $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (**G**^{CO₂}) formed (see Scheme B14). Monomeric **G**^{CO₂} is isostructural to aluminum complex **E**^{CO₂} and thus only two of the possible three pyrazolato ligands inserted a CO_2 molecule (13.1 wt% CO_2). Compared to **E**^{CO₂}, complex **G**^{CO₂} a full release of CO_2 can be observed at already 70 °C in ¹H VT NMR experiments.

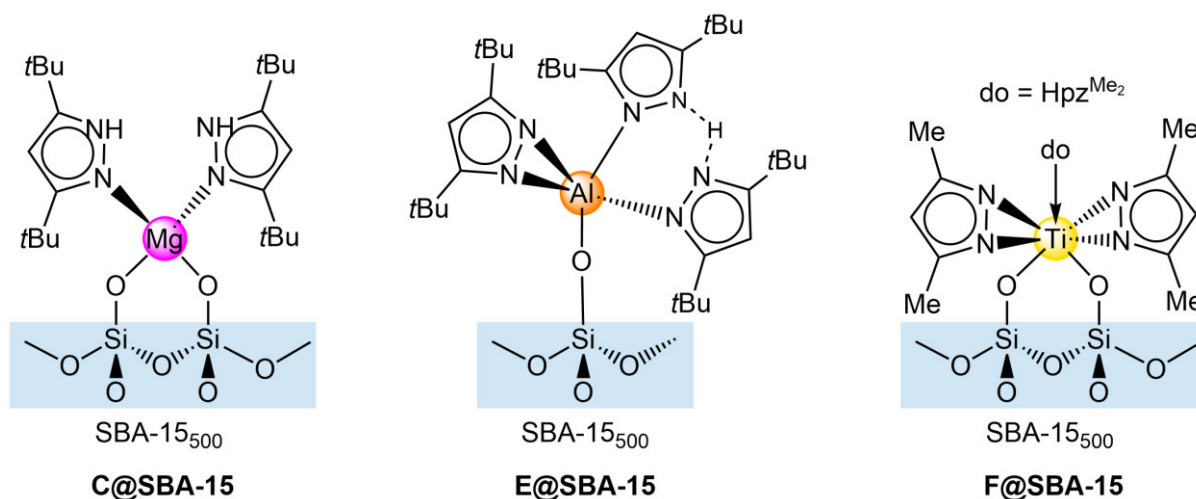


Scheme B14. Reactivity of complex $[\text{Zn}(\text{pz}^{\text{tBu}_2})_2(\text{Hpz}^{\text{tBu}_2})_2]$ (**Y**^{Hpz}) toward an excess of CO_2 .

When exposed to 1 bar CO_2 , the mixed pyrazolato/pyrazole zinc complex **Y**^{Hpz} yielded the dimeric complex $[\text{Zn}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\mu\text{-pz}^{\text{tBu}_2})_2]$ (**Y**^{CO₂}), with one inserted CO_2 per zinc center (see Scheme B15) (9.4 wt% CO_2). Although magnesium and zinc have almost identical ionic radii and the same charge, zinc only inserts CO_2 in one of two possible pyrazolato ligands, which can be explained by decreased oxophilicity of zinc. This is further reflected that no THF donor is coordinated in **Y**^{CO₂} compared to **C**^{CO₂,thf}, although both reactions take place in THF.

3. CO₂ Insertion into Light Metal Pyrazolates Immobilized onto a Mesoporous Silica Surface

Given the previous successful grafting of La/Ce pyrazolates grafted onto the mesoporous silica SBA-15₅₀₀, we were interested in the behavior of the light metal pyrazolates **C**, **E** and **F** once immobilized on a surface.^[76] The grafting reaction was conducted with an excess of light metal pyrazolates and the parent material SBA-15₅₀₀ (fully characterized in a previous work^[192]) in *n*-hexane, which yielded [Mg(pz^{*t*Bu})₂]₂@SBA-15₅₀₀ (**C@SBA-15**), Al(η²-pz^{*t*Bu})₃@SBA-15₅₀₀ (**E@SBA-15**) and Ti^{+IV}(η²-pz^{Me})₄@SBA-15₅₀₀ (**F@SBA-15**). In all three cases, a complete consumption of the surface silanol sites was confirmed by the disappearance of the Si–O–H stretching vibration signal in the DRIFT spectra together with the appearance of C–H vibration bands. Similar to the La/Ce compounds any released pyrazole was not found in the supernatant solution, which indicates the formation of mixed pyrazolate/pyrazole species at the surface. This is further emphasized by signals for NH protons in the ¹H CP/MAS spectra. ICP-OES and EA results led to the conclusion that the surface species of **C@SBA-15** mainly consists of bipodal species coordinated with two pyrazole donor molecules of the type [Mg(Hpz^{*t*Bu})₂] (see Scheme B16). For **E@SBA-15** the monopodal species [Al(pz^{*t*Bu})₂(Hpz^{*t*Bu})] and for **F@SBA-15** the bipodal [Ti(pz^{Me})₂(Hpz^{Me})₂] are plausible. For all three materials the surface area and the pore volume was decreased by 50% (see Table B1). The pore diameter was reduced from 8.2 nm to 6.2–6.6 nm.



Scheme B15. Possible surface species for the light metal pyrazolate hybrid materials based on EA, ICP-OES, DRIFTS as well as CP/MAS data.

Table B1. Analytical data of parent and hybrid materials.

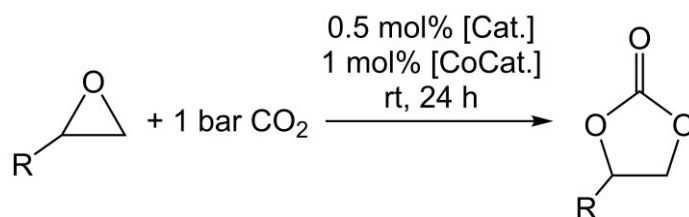
Material	CSiOH surface^[a]	$a_{\text{BET}}^{[b]}$ [m²/g]	$V_{\text{pore}}^{[c]}$ [cm³/g]	$d_{\text{pore}}^{[d]}$ [nm]	M^[e] [wt%]	CO₂ uptake^[f] [wt%]
SBA-15 ₅₀₀	2.80	848	1.11	8.2	-	-
C@SBA-15	-	410	0.57	6.2	1.85	7
E@SBA-15	-	418	0.55	6.4	1.21	6
F@SBA-15	-	405	0.53	6.6	4.39	11

^[a] Calcd. according to published procedures; ^[b] BET surface area calcd. between p/p_0 0.07 and 0.15; ^[c] BJH desorption cumulative pore volume between 2.0 and 10 nm; ^[d] Maximum pore size distribution calcd. by the BJH method from the isotherm adsorption branch; ^[e] Metal content determined by ICP-OES; ^[f] Uptake determined by weight increase of the sample after exposure to an excess of CO₂.

When the materials were exposed to a 1 bar CO₂ atmosphere a mass gain in all three cases was observed, accounting for 7% (**C@SBA-15**), 6% (**E@SBA-15**), 11% (**F@SBA-15**), respectively, which resulted in the formation of the materials CO₂@[Mg(pz^{*t*}Bu₂)₂]₂@SBA-15₅₀₀ (**CO₂@C@SBA-15**), CO₂@Al(η²-pz^{*t*}Bu₂)₃@SBA-15₅₀₀ (**CO₂@E@SBA-15**) and CO₂@Ti^{+IV}(η²-pz^{Me₂})₄@SBA-15₅₀₀ (**CO₂@F@SBA-15**). For material **CO₂@E@SBA-15** and **CO₂@F@SBA-15**, the CO₂ uptake can also be monitored by ¹³C CP/MAS experiments, in which the quaternary carbon signals at the pyrazole split into two distinct signals, due to the introduced asymmetry. In both cases the characteristic CO double bond stretching vibration band is detected in the DRIFT spectra, with a more prominent band for **CO₂@F@SBA-15** which fits well to the higher CO₂ uptake. Material **CO₂@C@SBA-15** showed no change in the ¹³C CP/MAS spectrum. Although a change of the CH vibration bands can be observed in the DRIFT spectrum, no band for a CO double bond stretching vibration appeared. However, a broad band at 1653 cm⁻¹ was resolved, which fits to a carboxylate group. This fits well with the surface character of **C@SBA-15** being mostly donor pyrazoles, which form carbamic acids upon CO₂ insertion.

4. Catalytic Conversion of Epoxides and Carbon Dioxide to Cyclic Carbonates

Given our previous work with cerium pyrazolates as catalysts for the conversion of epoxides and CO₂ to cyclic carbonates, we were interested in the behavior of above introduced light metal pyrazolates as catalysts. The scope of the catalytic study was limited to the four epoxides propylene oxide (PO), styrene oxide (SO), 2-tert-butyloxirane (*t*BO), and 1,2-epoxyhexane (EH). If not stated otherwise the standard protocol for the catalytic conversion was used, with 0.5 mol% metal center of the catalyst, 1 mol% cocatalyst TBAB or TBAI at 1 bar CO₂ atmosphere for 24 h at ambient temperature and neat in the corresponding epoxide as solvent (see Scheme B17). The conversion was determined by comparing the the integrals in α -position of the epoxide and the corresponding cyclic carbonate except for 3,3-dimethyl-1,2-butene carbonate where the integral of the *t*Bu moieties was used.



Scheme B16. Catalytic conversion of epoxides and CO₂ to cyclic carbonates by using 0.5 mol% catalyst based on the metal center.

The results of all conducted catalytic reaction can be found in Table 2. For PO the magnesium complexes showed only a moderate catalytic activity with conversions between 45% and 59%. (entries 1–6). The highest conversion was achieved with the fluorinated **L** (entry 6), however, with a polymeric side product. An almost equally high conversion was achieved with the *t*Bu congener **C** (56%, entry 2). With donor molecules such as THF or Hpz^{R₂} the conversion was found slightly reduced (entries 3–5). Apparently, the donor molecules compete with the epoxide for coordination sites at the metal center, in addition to the formation of a carbamic acid from the corresponding donor pyrazoles under a CO₂ atmosphere. A slightly higher conversion was achieved with the group 13 and transition metal pyrazolates **E** (65%), **F** (59%) and **Y^{Hpz}** (85%) (entries 7, 8 and 10). In general, the rare-earth metal based catalysts show the highest catalytic activity, which is in line with their fast ligand exchange character (entries 11–15).^[264] The scandium pyrazolates **T** achieved the highest catalytic activity of soluble pyrazolates with an almost quantitative conversion of >99% (entry 11), which equals a TON of 199. TOF studies

revealed a starting TOF of 120 h⁻¹ and an almost complete conversion after already 6 h. The TON can be further increased to 4600 when 0.01 mol% of **T** is used at 90 °C and 10 bar CO₂.

Dimeric compounds of the same metal perform slightly worse than their monomeric compounds despite having a less bulky alkyl moiety at the pyrazolato ligand (entries 8 vs. 9 and 12 vs. 13). As expected for the more sterically demanding epoxides SO, *t*BO and EH, an overall lower catalytic conversion was observed compared to PO with *t*BO giving the lowest conversion. Here, only the rare-earth-metal catalysts achieved higher conversion between 5–29% with again **T** as the most active catalyst. Not surprisingly, in the case of magnesium and aluminum, the complexes with less sterically demanding ligands perform slightly better than those with *t*Bu substitutes for all three bulky epoxides (entries 2 vs. 3, 8 vs. 9). For yttrium this is only the case for EH (entries 12 vs. 13).

Table B2. Catalytic activities of light metal pyrazolates (including Zn and Ce) in the cycloaddition of epoxides to cyclic carbonates.^{[a][b]}

Entry	Cat.	Metal	mol%/T/p	PO	SO	<i>t</i> BO	EH	CoCat.
1	TBAB ^[c]	-	0.5/RT/1	3%	-	-	-	-
2	C	Mg	0.5/RT/1	56%	4%	4%	7%	TBAB
3	D2^{Hpz}	Mg	0.17/RT/1	45%	4%	3%	11%	TBAB
4	D^{thf}	Mg	0.5/RT/1	42%	-	-	-	TBAB
5	K	Mg	0.5/RT/1	43%	-	-	-	TBAB
6	L	Mg	0.25/RT/1	59%	8%	4%	18%	TBAB
7	Y^{Hpz}	Zn	0.5/RT/1	85%	-	-	-	TBAB
8	E	Al	0.5/RT/1	65%	5%	2%	7%	TBAB
9	P	Al	0.5/RT/1	43%	8%	3%	11%	TBAB
10	F	Ti	0.5/RT/1	59%	8%	2%	7%	TBAB
11	T	Sc	0.5/RT/1	>99%	27%	24%	29%	TBAB
12	U	Y	0.5/RT/1	97%	22%	9%	18%	TBAB
13	H	Y	0.5/RT/1	84%	20%	5%	23%	TBAB
14	Ce(IV)	Ce	0.5/RT/1	88%	24%	13%	25%	TBAB
15	Ce(III)	Ce	0.5/RT/1	96%	13%	5%	9%	TBAB
16	C@SBA-15	Mg	0.5/RT/1	45% ^[d]	-	-	-	TBAB
17	C@SBA-15	Mg	0.5/RT/1	86%	-	-	-	TBAI
18	C@SBA-15	Mg	0.5/RT/1	<1% ^[e]	-	-	-	-
19	C@SBA-15	Mg	0.5/90 °C/10	>99%	99%	60%	99%	TBAI
20	C@SBA-15	Mg	0.01/90 °C/10	21%	-	-	-	TBAI
21	E@SBA-15	Al	0.5/RT/1	63% ^[f]	-	-	-	TBAB
22	F@SBA-15	Ti	0.5/RT/1	15%	-	-	-	TBAB
23	F@SBA-15	Ti	0.5/90 °C/10	97%	91%	41%	74%	TBAB

^[a] Reaction conditions not stated in the table: [Cocat] = 2x[Cat. (referred to metal center)], 24 h, neat in epoxide;

^[b] Conversion determined by comparison of the proton integrals in α -position of the epoxide and the corresponding cyclic carbonate (except for *t*BO where the integral of the *t*Bu moieties was used); ^[c] Only TBAB is used as catalyst; ^[d] Not representative due to polymer formation as side reaction; ^[e] mostly polymer as product; ^[f] Not representative because of the formation of an unidentified side product.

To probe whether if the catalytic conversion can be increased when the light metal pyrazolates are immobilized on a silica surface the materials **C@SBA-15**, **E@SBA-15** and **F@SBA-15** were tested as heterogeneous catalysts. For the aluminum-based material **E@SBA-15** a conversion of 63% for PO was observed (entry 21), however, the conversion was not representative due to a significant formation of an unidentified brown side product. The titanium material **F@SBA-15** achieved a conversion of 15% with no side product (entry 22). The conversion could be increased to 97% at 90 °C and 10 bar CO₂ (entry 23). Under these conditions a moderate to good conversion even for the bulky epoxides could be achieved (SO: 91%; *t*BO: 41%; EH: 74%). For the magnesium material **C@SBA-15**, a mixture of the desired PrC and polymer (not further analyzed) was obtained at standard conditions for PO (entry 16). Strikingly, when TBAI was used as cocatalyst **C@SBA-15** surpassed its homogeneous derivative **C** significantly already at standard condition with a conversion of 86% (entry 19). At 90 °C and 10 bar CO₂ a quantitative conversion (>99%) of PO was achievable. Even for the bulky epoxides SO and EH a conversion of 99% was obtained. This remarkable increase of catalytic activity occurs due to the surface species [Mg(Hpz^{*t*Bu})₂], which is only coordinated by donor molecules and thus the magnesium center is highly activated for catalytic reactions. When no cocatalyst is used, **C@SBA-15** yielded almost exclusively the uncharacterized polymer (entry 18). This indicates that the selectivity of **C@SBA-15** is tunable by the cocatalyst.

Table B. Inverse proportional correlation of CO₂ release temperature and catalytic conversion.

Catalyst	CO ₂ release temperature [°C]		Catalytic Conversion [%]	Oxophilicity M [θ] ^[265]
	¹ H NMR start→end	TGA start→end		
C Mg <i>t</i> Bu	70–105	134–233	56	0.6
E Al <i>t</i> Bu	100–120	114–196	65	0.8
H Y Me	rt–70	60–154	84	0.8
Ce(IV) Me	10–60 ^[a]	55–95 ^[a]	88	0.9
Ce(III) Me	-	52–90 ^[a]	96	0.9
U Y <i>t</i> Bu	-	-	97	0.8
T Sc <i>t</i> Bu	rt	rt	>99	0.8

^[a] previous work.^[76]

Interestingly, an inverse correlation between the catalytic conversion and the CO₂-affinity (“carboxophilicity”) can be stated (see Table 3). The carboxophilicity can be derived from the CO₂ release temperature of the corresponding CO₂ insertion complexes determined via VT NMR and TGA experiments. The magnesium and aluminum compounds **C** and **E** require the highest temperature to release CO₂ but exhibit the lowest catalytic conversion in this study. In contrast, the highly active **U** and **T** do not insert CO₂ at all at ambient temperature or release

CO₂ immediately. The trend of the carboxophilicity cannot be assigned only to the effects of oxophilicity, electronegativity or the Lewis acidity. Most likely it is a combination of these three effects and the nucleophilicity and the steric bulk of the corresponding pyrazolato ligand. For example, the best magnesium catalyst in this study, **L**, shows no visible CO₂ insertion at ambient condition. This originates from the fluorinated pyrazolato ligand, which has the lowest nucleophilicity of all used pyrazoles. Another example is the comparison of the magnesium and zinc carbamates **C**^{CO₂} and **Y**^{CO₂} which was discussed earlier. The zinc containing **Y**^{CO₂} show a significantly higher catalytic activity but only inserted one CO₂ molecule per zinc center.

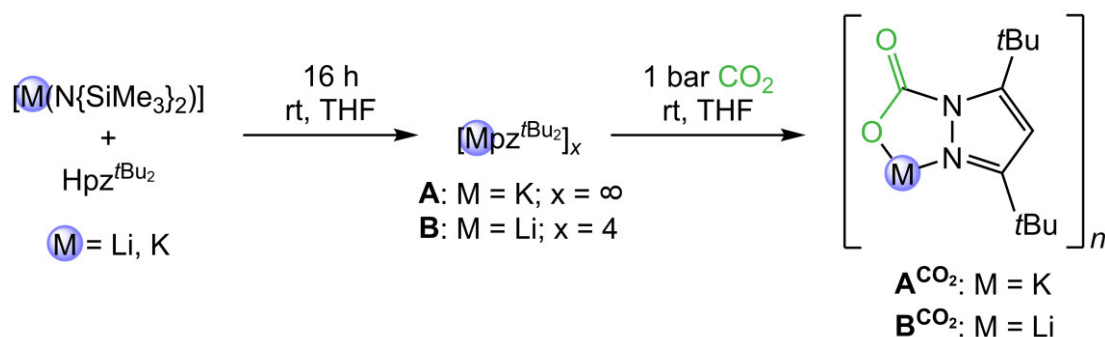
C

Unpublished Results

1. Carbon Dioxide Insertion with Alkaline Metal and Zinc Pyrazolates as well as Bulky Magnesium Pyrazolates/Triazolates

Alkaline-Metal Pyrazolates

To cover all light metal pyrazolate classes, we were interested in the reaction behavior of alkaline-metal pyrazolates toward CO₂. Both in the literature reported alkaline pyrazolates [Kpz^{tBu₂}]_∞ (**A**) and [Lipz^{tBu₂}]₄ (**B**) were synthesized by deprotonation of Hpz^{tBu₂} with the corresponding silylamide salt M[N(SiMe₃)₂] (M = K, Li) (see Scheme C1). A subsequent exposure to 1 bar of CO₂ led in both cases to an exhaustive CO₂ insertion into one of the two nitrogen metal bonds and the formation of the carbamate complexes [M(CO₂·pz^{tBu₂})]_n (**A**^{CO₂}: M = K; **B**^{CO₂}: M = Li). The formation was monitored by ¹H NMR spectroscopy, showing that the signal of the *t*Bu moieties split into two separated signals, due to the introduced asymmetry. For **A**^{CO₂} the signals appeared at δ = 1.39 ppm and δ = 1.18 ppm and for **B**^{CO₂} at δ = 1.43 ppm and δ = 1.21 ppm (see Figure CX and CX). However, only microcrystalline material was obtained not suitable for a SC-XRD analysis.

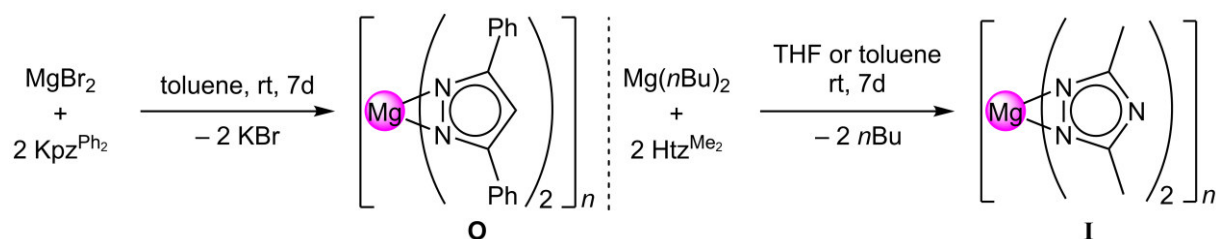


Scheme C1. Synthesis of alkaline-metal pyrazolates and their reactivity toward an excess of CO₂.

Bulky Magnesium Pyrazolate and Magnesium Triazolate.

The salt-metathesis reaction of MgBr₂ and [Kpz^{Ph₂}]_n gave the magnesium pyrazolate [Mg(pz^{Ph₂})₂]_n (**O**) with a yield of 56% (see Scheme C2). Although no crystalline material could be obtained the ¹H NMR spectrum confirmed the formation of **O**. In the aromatic region four signals appeared. The three signals at δ = 7.87, 7.19 and 7.00 ppm can be assigned to the ortho, meta and para protons of the phenyl moieties with an integral ratio of 8:8:4. The signal at δ = 6.80 ppm with an integral of two protons can be assigned to the backbone proton of the pyrazolato ligand. When **O** was reacted with an excess of CO₂ the four signals split up into several broad signals in the aromatic region, which indicates an asymmetry of the ligands,

which is expected for a CO₂ insertion. However, since a crystallin material could not be obtained, a final confirmation of the structure of **O**^{CO₂} remains elusive.

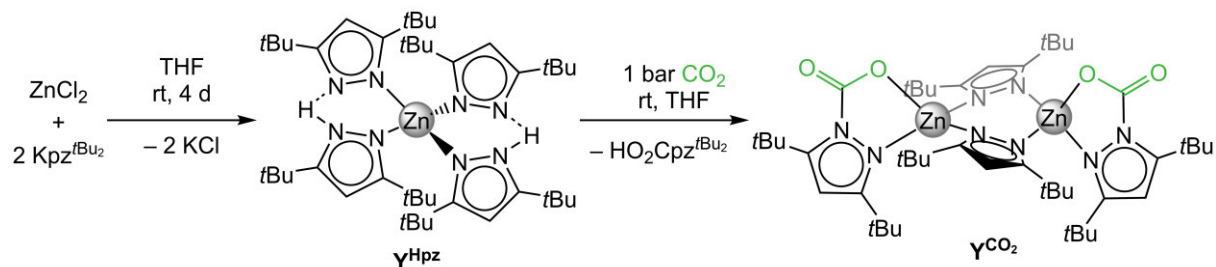


Scheme C2. Synthesis of [Mg(pz^{Ph₂})₂]_n (**O**, left) and [Mg(tz^{Me₂})₂]_n (**I**, right).

When Mg(*n*Bu)₂ was reacted with two equivalents of the triazole Htz^{Me₂} in THF or toluene an immediate white precipitate was formed. The white powder is insoluble in all common solvents, which indicates that the material most likely is amorphous [Mg(tz^{Me₂})₂]_n (**I**) (see Scheme C2). The structure could be chain-like polymer, however, an extension of the coordination *via* the nitrogen atom in 4 position seems also possible. When **I** was exposed to 1 bar CO₂ a mass gain of 11 wt% was observed, which deviates significantly from the value expected for a complete CO₂ insertion (29 wt%). However, the DRIFT spectrum shows clearly two characteristic stretching vibrations for a CO double bond at $\tilde{\nu} = 1764$ and 1732 cm^{-1} .

CO₂ insertion into Zinc Pyrazolates.

Given the similar ionic radii of magnesium and zinc (CN = 6; Mg = 0.72 Å; Zn = 0.74 Å) and divalent state, we were interested, if zinc pyrazolates behave similar to their magnesium derivatives.^[266] Attempts to synthesize homoleptic [Zn(pz^{*t*Bu₂})₂]_n via a salt-metathesis reaction of ZnCl₂ and the potassium salt **A** in THF only led to the mixed pyrazolate pyrazole complex [Zn(pz^{*t*Bu₂})₂(Hpz^{*t*Bu₂})₂] (**Y^{Hpz}**) in a yield of 41% (see Scheme C3). This complex was already reported by DEACON/JUNK, however, a protonolysis protocol with ZnEt₂ and Hpz^{*t*Bu₂} was applied.^[86] The donor pyrazoles in **Y^{Hpz}** in the salt-metathesis reaction most likely originated from residual water in the solvent THF. In addition to **Y^{Hpz}** the unsubstituted [Zn(pz)₂]_∞ (**II**) was synthesized according to the literature procedure by reacting ZnCl₂ and Hpz in water.^[100]



Scheme C3. Synthesis of complex Zn(pz^{*t*Bu₂})₂(Hpz^{*t*Bu₂})₂ and subsequent reaction with CO₂ to [Zn(CO₂·pz^{*t*Bu₂})(μ-pz^{*t*Bu₂})]₂ (**Y^{CO₂}**).

When $\mathbf{Y}^{\text{Hpz}}$ was exposed to an atmosphere of 1 bar CO_2 an insertion into only one of the two pyrazolato ligands was observed and dimeric complex $[\text{Zn}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\mu\text{-pz}^{\text{tBu}_2})_2]_2$ ($\mathbf{Y}^{\text{CO}_2}$) could be isolated. This equals a capacity of 9.4 wt% CO_2 or 2.1 mmol CO_2 per gram. Crystals could be obtained overnight at ambient temperature (see Figure C1). The zinc centers in $\mathbf{Y}^{\text{CO}_2}$ are coordinated in a distorted tetrahedral geometry, in which the two carbamato ligands coordinate terminal in a $\kappa^2(\text{N},\text{O})$ mode. The two pyrazolato ligands are bridging the two zinc centers in a $\mu\text{-}1\kappa(\text{N}):2\kappa(\text{N}')$ mode forming a six-membered metallacycle in a twist conformation. The C–O–C angle of inserted CO_2 ranges between $128.5(3)$ – $128.6(3)^\circ$ and distinct C–O double ($1.207(4)$ – $1.210(4)$ Å) and single ($1.264(4)$ – $1.265(4)$ Å) bonds can be observed.

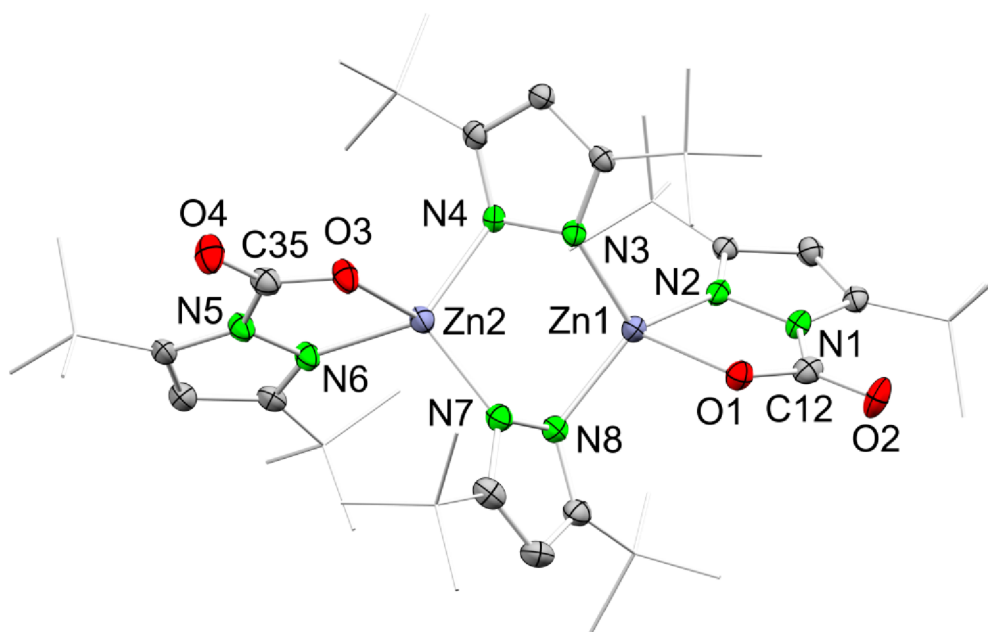


Figure C1. Crystal structure of $[\text{Zn}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\mu\text{-pz}^{\text{tBu}_2})_2]_2$ ($\mathbf{Y}^{\text{CO}_2}$). Ellipsoids are set at the 50% probability level. Hydrogen atoms as well as two lattice solvent THF are omitted and *t*Bu moieties are set as wireframe for clarity. Selected interatomic distances [Å]: Zn1–O1 1.976(2), Zn1–N2 2.042(3), Zn1–N3 1.976(3), Zn1–N8 2.004(3), Zn2–O3 1.971(2), Zn2–N6 2.053(3), Zn2–N4 2.006(3), Zn2–N7 1.986(3), C12–O1 1.264(4), C12–O2 1.207(4), C35–O3 1.265(4), C35–O4 1.210(4). Selected angles [$^\circ$]: O1–C12–O2 128.6(3), O3–C35–O4 128.5(3), O1–Zn1–N2 80.84(9), O3–Zn2–O4 80.51(10).

The ^1H NMR spectrum shows three signals for the *t*Bu moieties. One signal at $\delta = 0.95$ ppm with an integral of 36 protons can be assigned to the bridging pyrazolato ligands and the two signals at $\delta = 1.17$ ppm and $\delta = 1.27$ ppm with each an integral of 18 protons show the characteristic splitting of substituents at the carbamato ligand caused by the asymmetry introduced by the CO_2 insertion. Additionally, two signals in the aromatic region appeared for the backbone proton of the two different ligands. The same behavior can be observed in the ^{13}C NMR spectrum. Despite the similarities of magnesium(II) and zinc(II), $\mathbf{Y}$ only inserts CO_2 in one of the two possible pyrazolato ligands. This is most likely caused by the softer Lewis acid

character of zinc. Also the oxophilicity of magnesium (0.8) is significantly higher than that of zinc (0.2).^[265] Moreover, the structure of complex $\mathbf{Y}^{\text{CO}_2}$ does not exhibit any coordinating donor THF, although the reaction was conducted in THF. This is in stark contrast to the magnesium complex $\mathbf{C}^{\text{CO}_2, \text{thf}}$, in which two THF donor molecules coordinate to the metal center. Further, zinc complex $\mathbf{Y}^{\text{Hpz}}$ displayed the highest catalytic activity of all non-rare-earth metal derivatives as catalyst for the cycloaddition of epoxides and CO_2 to cyclic carbonates. Under standard conditions (0.5 mol% metal center of the catalyst, 1 mol% TBAB, 1 bar CO_2 , ambient temperature, 24 h) $\mathbf{Y}^{\text{Hpz}}$ reached a conversion of 85% for PO. This is another example for the inverse correlation of carbophilicity and catalytic activity. Bearing the less nucleophilic unsubstituted pyrazolato ligand, complex $[\text{Zn}(\text{pz})_2]_n$ showed no CO_2 insertion at all at ambient temperature, again in stark contrast to the corresponding magnesium compound $[\text{Mg}(\text{pz})_2]_n$ (**N**), for which a quantitative insertion was observed.

2. Light Metal Pyrazolates grafted onto a mesoporous Silica Surface

Introduction

The rising carbon dioxide levels since the industrial revolution are the main reason for the human made climate change.^[267] Two prominent approaches to combat the CO₂ emission are carbon capture and storage as well as using CO₂ as C1 feedstock and convert it into more valuable organic compounds.^[2–7,25,27,38,268] In the industry aqueous amine scrubbers or alkali/alkaline-earth metal hydroxides are used as capture materials, however, they have low capacities and require high regeneration energies.^[9–11] Current systems under research include amino-functionalized materials such as silica, ionic liquids, zeolites and metal-organic frameworks (MOF).^[5–8,268–270]

Surface organometallic chemistry (SOMC) is another material approach for targeting the catalytic conversions of CO₂.^[184,271] Metal complexes are grafted onto a support material with a high surface area like mesoporous silica. With this methodology well-defined and higher active metalorganic surface species can be generated, that are not only protected from deactivation due to their covalent bonding to the surface, but also are stable at ambient conditions. A number of SOMC materials which act as heterogenous catalysts in the cycloaddition of epoxides and CO₂ are already reported.^[76,190,192,272] Although heterogeneous catalysts often show lower catalytic activity compared to their homogeneous derivatives, this apparent drawback is often compensated by their high stability and reusability.

Recently, we found that cerium pyrazolates, i.e. $[\text{Ce}(\text{pz}^{\text{Me}_2})_4]_2$, are able to insert CO₂ exhaustively and reversibly under formation of the carbamate complex $\text{Ce}(\text{CO}_2 \cdot \text{pz}^{\text{Me}_2})_4$. Further, this conceptional approach could be transferred to light metal pyrazolates based on magnesium, aluminum and titanium and, *inter alia*, $\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{tBu}_2})_2(\text{thf})_2$, $\text{Al}(\text{CO}_2 \cdot \text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ and $\text{Ti}(\text{CO}_2 \cdot \text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ could be isolated (see this thesis). Reversible and extensive CO₂ uptake was also found when cerium and lanthanum pyrazolates, $[\text{Ce}(\text{pz}^{\text{Me}_2})_4]_2$, $[\text{Ce}(\text{pz}^{\text{Me}_2})_4]$ and $[\text{Ln}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (Ln = La, Ce), are grafted onto a mesoporous surface of SBA-15₅₀₀.^[76] High capacities of up to 20 wt% CO₂ were found for $[\text{Ln}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2@\text{SBA-15}_{500}$. In addition, tetravalent $[\text{Ce}(\text{pz}^{\text{Me}_2})_4]_2@\text{SBA-15}_{500}$ acts as an effective and easily recyclable heterogeneous catalyst. Therefore, we were interested whether the activity toward CO₂ observed for of light metal pyrazolates can be increased when grafted onto a mesoporous silica surface.

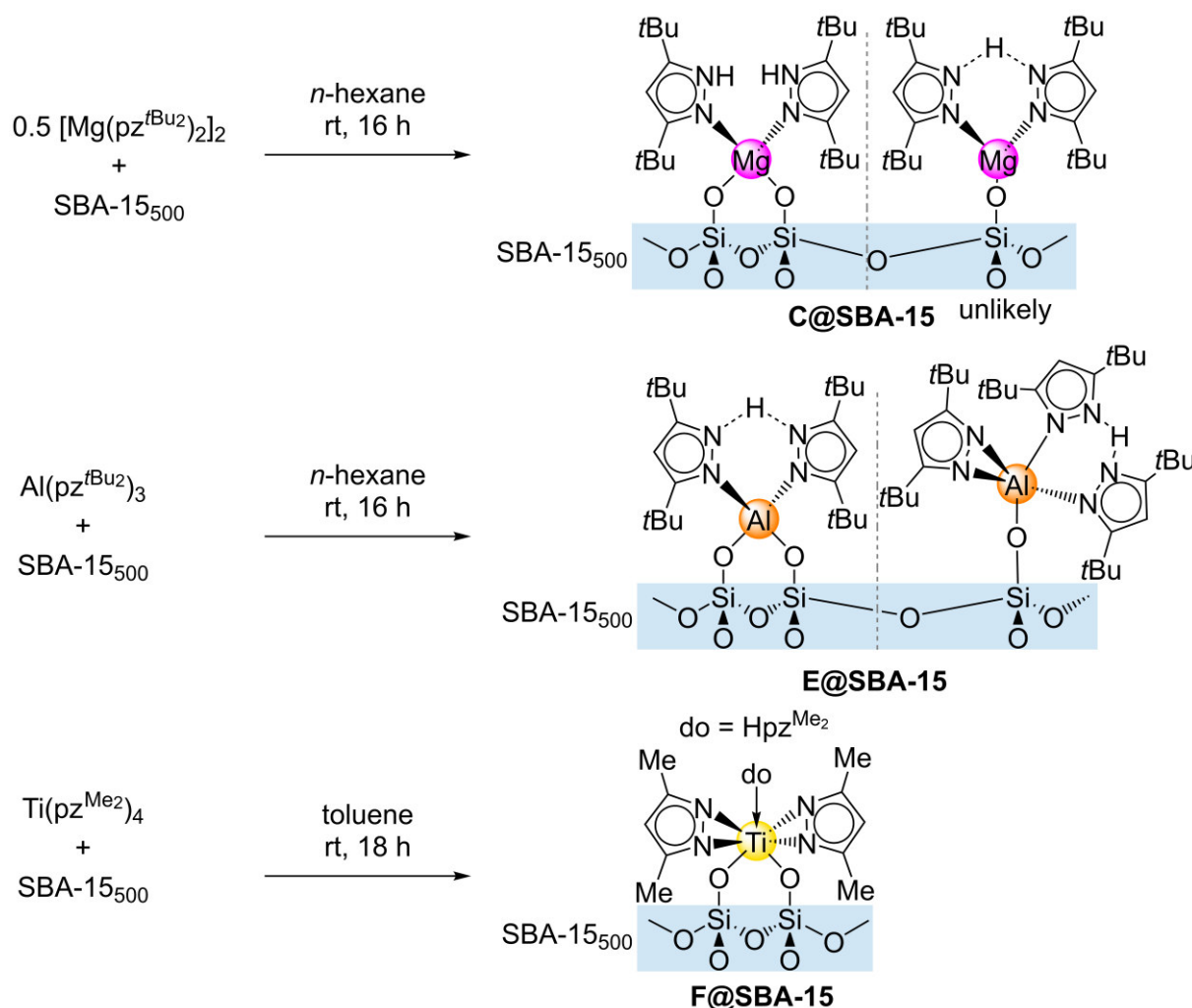
Parent material

The most fitting parent material for this study was SBA-15, because it is a large-pore mesoporous silica. Periodic, long-range ordered silicas with a smaller pore size like MCM-48 or MCM-41 are more likely to get blocked when the relatively large pyrazolate complexes are immobilized on the surface. The synthesis of SBA-15 was conducted as described in the literature.^[273] The parent material was activated at 500 °C (denoted as SBA-15₅₀₀) and 10⁻³ mbar. The synthesis, silylation experiments, N₂ physisorption experiments and full characterization of the parent material SBA-15₅₀₀ was reported in a previous work.^[192] The surface Si–OH population was determined to be 2.80 Si–OH groups per nm². The silanol groups are clearly visible in the DRIFT spectrum by a sharp signal at $\tilde{\nu} = 3746 \text{ cm}^{-1}$. N₂ physisorption experiments revealed a surface area of 848 m²g⁻¹, a pore volume of 1.11 cm³g⁻¹ and a pore diameter of 8.2 nm.

Synthesis and Characterization of Light Metal Pyrazolate Hybrid Materials

To cover a variety of metals the three pyrazolate complexes [Mg(pz^{*t*Bu})₂]₂ (C), Al(η²-pz^{*t*Bu})₃ (E) and Ti^{IV}(η²-pz^{Me})₄ (F) were chosen as metalorganic precursor. The grafting reaction was conducted by suspending the parent material in *n*-hexane (toluene for Ti) and addition of equimolar amounts of the metalorganic precursor solvated in *n*-hexane (toluene for Ti), yielding the three hybrid materials [Mg(pz^{*t*Bu})₂]₂@SBA-15₅₀₀ (C@SBA-15), Al(η²-pz^{*t*Bu})₃@SBA-15₅₀₀ (E@SBA-15) and Ti^{IV}(η²-pz^{Me})₄@SBA-15₅₀₀ (F@SBA-15). The consumption of Si–OH was confirmed by DRIFT spectroscopy. For both E@SBA-15 and F@SBA-15 a complete conversion was observed, however, in the case of C@SBA-15 a small signal at 3712 cm⁻¹ remained. For all three hybrid materials C–H vibration bands were observed. The fine white powders (pale yellow for Ti) were washed with an excess of toluene and *n*-hexane. The supernatant solutions were dried under reduced pressure and the remaining solid was analyzed via ¹H NMR experiments. In all hybrid materials only the corresponding starting metalorganic complex was found. This indicates, that the released pyrazoles Hpz^{R2} are remaining at the surface species which originated from the protonolysis reaction with the Si–OH groups during the grafting process. The presence of Hpz^{R2} was further proved by ¹H CP/MAS experiments in which a signal appeared at δ = 12.66 ppm for C@SBA-15 and δ = 11.03 ppm for E@SBA-15. For F@SBA-15 no clear signal was perceived, however, in the DRIFT spectrum a characteristic stretching vibration for N–H bonds at $\tilde{\nu} = 3396 \text{ cm}^{-1}$ was observed. Interestingly, for the magnesium and aluminum hybrid materials this signal was not visible in the DRIFT spectra. The ¹³C CP/MAS spectra also confirmed the presence of a pyrazolate species with typical signal

sets. For **C@SBA-15** two signals for the quaternary protons in the 3/5-position of the pyrazolato ligand were observed and for **F@SBA-15** two signals for the proton in the 4-position. Both can originate from the pyrazolato ligand and the donor pyrazole. For all other pyrazolate/pyrazole signals only one signal was detected.



Scheme C4. Grafting reaction of light metal pyrazolates onto mesoporous SBA-15₅₀₀. Proposed surface species based on EA, ICP-OES, DRIFT and solid-state NMR data.

ICP-OES experiments revealed metal contents of 1.85 wt% (Mg), 1.21 wt% (Al) and 4.39 wt% (Ti) (see Table C1). Compared to the rare-earth metal based materials [Ce^{IV}(pz^{Me2})₄]₂@SBA-15₅₀₀ (10.80 wt%) and [Ce^{III}(pz^{Me2})₃]₄@SBA-15₅₀₀ (22.19 wt%) the metal content is significantly lower, due to light metal character of the metals used in this study.^[76] In combination with the results of the elemental analysis it can be deduced that the surface species of **C@SBA-15** consist of either a bipodal species with a “naked” magnesium center stabilized by two donor pyrazole of the type [(-SiO)₂Mg(Hpz^{tBu2})₂] or a monopodal species of the type [(-SiO)Mg(pz^{tBu2})(Hpz^{tBu2})] (see Scheme C4). For the aluminum hybrid material **E@SBA-15** either the monopodal [(-SiO)Al(pz^{tBu2})₂(Hpz^{tBu2})] or the bipodal surface species [(-

$\text{SiO})_2\text{Al}(\text{pz}^{\text{tBu}_2})(\text{Hpz}^{\text{tBu}_2})]$ are possible. The results for the titanium-based hybrid material **F@SBA-15** indicate a bipodal species $[(-\text{SiO})_2\text{Ti}^{+\text{IV}}(\text{pz}^{\text{Me}_2})_2(\text{Hpz}^{\text{Me}_2})]$. Due to the small ionic radii of all three used metals (CN6; Mg: 0.72 Å, Al: 0.54 Å, Ti: 0.61 Å) a bimetallic surface species like it was observed for $[\text{Ln}^{+\text{III}}(\text{pz}^{\text{Me}_2})_3]_4\text{@SBA-15}_{500}$ (Ln: La, Ce; CN6 La: 1.03 Å, Ce^{+III}: 1.01 Å) seems unlikely.^[76,266] Further, the tetravalent cerium material $[\text{Ce}^{+\text{IV}}(\text{pz}^{\text{Me}_2})_4]_2\text{@SBA-15}_{500}$ (CN4 Ce^{+IV}: 0.87 Å) also exclusively consists of a monometallic surface species. In addition, the metal content of Ti^{+IV}-based material **F@SBA-15** is almost three times lower than the three times heavier Ce^{+IV} congener. A similar correlation is also found for the magnesium-based **C@SBA-15**. These similarities further indicate, that in both cases a monometallic surface species is present. However, a final statement on composition of the surface species cannot be made.

Table C1. Analytical data of parent and hybrid material

Material	CSiOH surface ^[a]	<i>a</i> _{BET} ^[b] [m ² /g]	<i>V</i> _{pore} ^[c] [cm ³ /g]	<i>d</i> _{pore} ^[d] [nm]	M ^[e] [wt%]	CO ₂ uptake ^[f] [wt%]
SBA-15 ₅₀₀ ^[g]	2.80	848	1.11	8.2	-	-
C@SBA-15	-	410	0.57	6.2	1.85	7
E@SBA-15	-	418	0.55	6.4	1.21	6
F@SBA-15	-	405	0.53	6.6	4.39	11

^[a] Calculated according to published procedures. ^[b] BET surface area calcd. between p/p_0 0.07 and 0.15. ^[c] BJH desorption cumulative pore volume between 2.0 and 10 nm; ^[d] Maximum pore size distribution calcd. by the BJH method from the isotherm adsorption branch; ^[e] Metal content determined by ICP-OES; ^[f] Uptake determined by weight increase of the sample after exposure to an excess of CO₂; ^[g] Characterized in a previous work.^[192]

The N₂ physisorption experiments revealed a drastic reduction of the surface area for all three hybrid materials (see Table C1). Compared to the parent material the surface area is reduced to 50% to 405–418 m²g⁻¹. As expected, a similar decrease can be observed for the pore volume (0.53–0.57 cm³g⁻¹) and the pore diameter (6.2–6.6 nm). The titanium material **F@SBA-15** showed the highest pore diameter, which is in line with the small Me moieties at the pyrazolato ligand, when compared to the other two materials. This reduction is comparable to again $[\text{Ce}^{+\text{IV}}(\text{pz}^{\text{Me}_2})_4]_2\text{@SBA-15}_{500}$ which further suggest a monometallic surface species. For trivalent rare-earth-metal pyrazolates materials containing bimetallic surface species a significantly higher decrease of the surface area was observed.^[76] Compared to the parent material the surface got reduced to less than a quarter.

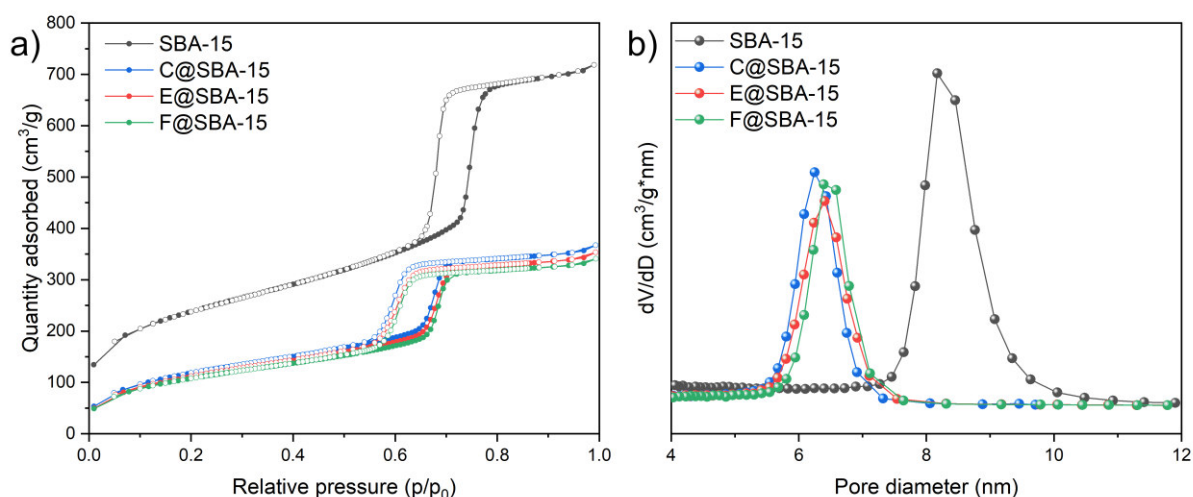


Figure C2. N₂ physisorption isotherms (a, left) and pore size distribution (b, right) of parent material SBA-15 (black), [Mg(pz^{tBu2})₂]₂@SBA-15₅₀₀ (**C@SBA-15**, blue), Al(pz^{tBu2})₃@SBA-15₅₀₀ (**E@SBA-15**, red) and Ti(pz^{Me2})₄@SBA-15₅₀₀ (**F@SBA-15**, green).

Carbon Dioxide Insertion with Mesoporous Hybrid Materials

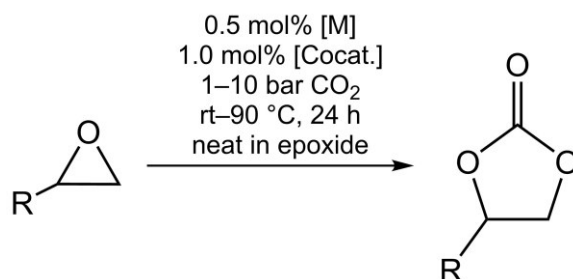
When exposed to an atmosphere of 1 bar CO₂ a mass gain for all three hybrid materials was observed, with 7% for **C@SBA-15**, 6% for **E@SBA-15** and 11% for **F@SBA-15** (see Scheme C4). Further, solid-state NMR, DRIFT and EA experiments confirmed a successful CO₂ insertion and the formation of the hybrid materials CO₂@[Mg(pz^{tBu2})₂]₂@SBA-15₅₀₀ (**CO₂@C@SBA-15**), CO₂@Al(η²-pz^{tBu2})₃@SBA-15₅₀₀ (**CO₂@E@SBA-15**) and CO₂@Ti^{IV}(η²-pz^{Me2})₄@SBA-15₅₀₀ (**CO₂@F@SBA-15**). The DRIFT spectra of **E@SBA-15** and **F@SBA-15** revealed the characteristic C–O double bond stretching vibration for pyrazolate inserted CO₂ at $\tilde{\nu} = 1786 \text{ cm}^{-1}$ and $\tilde{\nu} = 1744 \text{ cm}^{-1}$, respectively. For magnesium-based **CO₂@C@SBA-15** a broad signal at $\tilde{\nu} = 1655 \text{ cm}^{-1}$ was observed which can be assigned to a C–O stretching vibration observed for carboxylate complexes with a $\kappa^2(\text{O},\text{O})$ coordination mode.^[274] This stretching vibration would also occur, when a carbamate ligand bridges between two metal centers. However, as discussed above a bimetallic species is highly unlikely. Pyrazole donors are also able to insert CO₂ under formation of a carbamic acid when coordinated to a metal center (Paper 1). The carbamic acid is able to form a carboxylic group *via* isomerization. This indicates that the surface species of **C@SBA-15** mostly consist of the “naked” magnesium center stabilized by two pyrazole donors, [(-SiO)₂Mg(Hpz^{tBu2})₂].

The ¹³C CP/MAS spectrum of **CO₂@C@SBA-15** is almost indistinguishable to the one of **C@SBA-15**. The characteristic splitting of the quaternary carbon signals at the pyrazolato ligand after a CO₂ insertion is not visible, because for **C@SBA-15** already two signals appear in exact this region. However, for **E@SBA-15** and **F@SBA-15** this characteristic splitting into

two distinct signals can be observed, which further confirms the successful CO₂ uptake. In the case of **E@SBA-15** a signal for the quaternary carbon of inserted CO₂ was observed at $\delta = 144.9$ ppm which is reminiscent of the signal found for solvated $[\text{Al}(\text{CO}_2\cdot\text{pz}^{t\text{Bu}_2})_2(\text{pz}^{t\text{Bu}_2})]$ (**E**CO₂) at $\delta = 146.9$ ppm.

Heterogeneous Catalytic Conversion of CO₂ and Epoxides to Cyclic Carbonates

All three hybrid materials were tested as heterogeneous catalyst in the conversion of CO₂ and epoxides to cyclic carbonates. Initial reactions were conducted with a catalytic load of 0.5 mol% metal center of the hybrid material, 1.0 mol% of the cocatalyst tetra-*n*-butyl ammonium bromide/iodide (TBAB/TBAI), at room temperature, 1 bar CO₂ and neat in the epoxide for 24 h. In later conversions the temperature was increased to 90 °C and the pressure to 10 bar CO₂. The four epoxides propylene oxide (PO), styrene oxide (SO), 3,3-dimethyl-1,2-epoxybutane (*t*BO) and 1,2-epoxyhexane (EH) were tested as substrates.



Scheme C5. Catalytic conversion of epoxides and CO₂ to cyclic carbonates.

The magnesium hybrid material **C@SBA-15** converted into PO a mixture of the desired propylene carbonate and a polymeric side product when TBAB is used as cocatalyst (see Table C2, entry 1). The conversion of 63% is not representative, due to the formation of the side product. When the cocatalyst was changed to TBAI the selectivity could be drastically increased and the desired cyclic carbonate is almost exclusively formed (entry 2). The catalytic conversion is 88% which is significantly higher than the 56% achieved by the solvated $[\text{Mg}(\text{pz}^{t\text{Bu}_2})_2]$ congener (Paper 1). Strikingly, when no cocatalyst is used the selectivity is reversed and the polymeric product is formed exclusively (entry 3). Not only could the catalytic conversion be significantly increased when light metal pyrazolates are immobilized on a silica surface, but also the selectivity is tunable by the choice of cocatalyst. In contrast, the immobilized cerium pyrazolates have similar conversions when compared to their molecular congeners.^[76] At 90 °C and 10 bar CO₂ the catalytic conversion could be increased to >99% for PO as well as the bulky SO and EH (entry 4). Even for the bulkier *t*BO a conversion of 60% was achieved. These results are similar to the one achieved for the cerium hybrid material

[Ce^{+IV}(pz^{Me2})₄]₂@SBA-15₅₀₀ (entry 9). The significantly increased catalytic activity of **C@SBA-15** compared to molecular [Mg(pz^{tBu2})₂]₂ most likely occurs, due to the highly active surface species [(-SiO)₂Mg(Hpz^{tBu2})₂] which is coordinated only by donor pyrazoles. A quantitative conversion resembles a turnover number (TON) of 198 and a turnover frequency (TOF) of 8 h⁻¹. When the catalytic load was reduced to 0.01 mol% metal center the TON can be increased to 2100 affording a TOF of 88 h⁻¹ (entry 5).

Table C2. Catalytic activities of light metal pyrazolates grafted onto a mesoporous silica surface in the cycloaddition of epoxides to cyclic carbonates.^{[a][b]}

Entry	Cat.	mol%/T/p	PO	SO	<i>t</i> BO	EH	CoCat.
1	C@SBA-15 (Mg)	0.5/RT/1	63% ^[c]	-	-	-	TBAB
2	C@SBA-15 (Mg)	0.5/RT/1	88%	-	-	-	TBAI
3	C@SBA-15 (Mg)	0.5/RT/1	<1 ^[d]	-	-	-	-
4	C@SBA-15 (Mg)	0.5/90 °C/10	>99%	99%	60%	99%	TBAI
5	C@SBA-15 (Mg)	0.01/90 °C/10	21%	-	-	-	TBAI
6	E@SBA-15 (Al)	0.5/RT/1	48% ^[e]	-	-	-	TBAB
7	F@SBA-15 (Ti)	0.5/RT/1	15%	-	-	-	TBAB
8	F@SBA-15 (Ti)	0.5/90 °C/10	97%	91%	41%	74%	TBAB
9	[Ce(pz^{Me2})₄]₂@SBA^[f]	0.5/90 °C/10	>99%	91%	66%	94%	TBAB

^[a] Reaction conditions not stated in the table: [Cocat] = 2x[Cat. (referred to metal center)], 24 h, neat in epoxide.

^[b] Conversion determined by comparison of the proton integrals in α -position of the epoxide and the corresponding cyclic carbonate (except for *t*BO where the integral of the *t*Bu moieties was used). ^[c] Not representative due to polymer formation as side reaction. ^[d] Mostly polymer as product. ^[e] Not representative because of the formation of an unidentified side product. ^[f] Previous work.

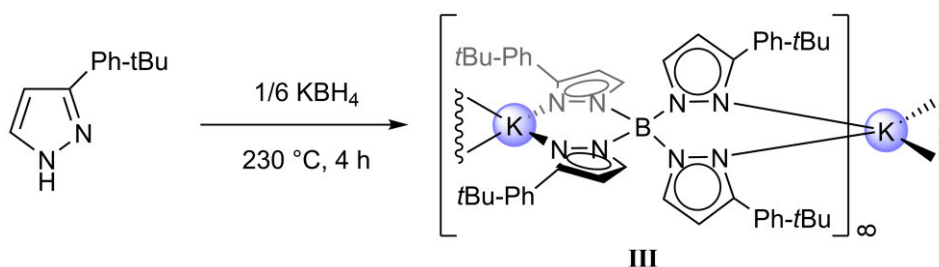
The aluminum-based hybrid material **E@SBA-15** exhibited a lower conversion of 48% for PO (entry 6). However, this conversion is not representative, due to the quantitative formation of a brown side product, which could not be further identified (see Figure CX). The titanium-based hybrid material **F@SBA-15** initially showed a low conversion of 15% for PO (entry 7). However, at 90 °C and 10 bar the conversion could be significantly increased to 97% (entry 8). Even for the bulkier epoxides high conversions could be obtained, SO (91%), *t*BO (41%) and EH (74%) respectively.

These catalytic activity results are comparable to other reported SOMC systems.^[185–192] For example the titanium-based Ti(*On*Bu)₄@SBA-15 (**116**) and its organo-functionalized derivatives R@Ti(*On*Bu)₄@SBA-15 (**117**, R = 3-amino, 3-adenino or (3-chloropropyl)triethoxysilan) achieved for epichlorohydrin at 120 °C and 6.9 bar CO₂ TOFs of 3.0 h⁻¹ and 7.3 h⁻¹, respectively.^[186] The immobilized rare-earth metal chloride YCl₃@SiO₂₋₇₀₀ (**121**) showed a quantitative conversion of PO with TBAI as cocatalyst at already mild conditions of 60 °C and 2 bar CO₂.^[190] Recently, we reported the immobilized di-/trivalent rare-

earth-metal silylamides $\text{HOEt@Ln}(\text{N}(\text{SiMe}_3)_2)_x\text{@S}$ (**126**, $\text{Ln} = \text{Sm(II)}, \text{Sm(III)}, \text{Yb(II)}$; $\text{S} = \text{SBA-15}_{500}, \text{MCM-41}, \text{MCM-48}$) which also achieved quantitative conversions for PO, EH and epichlorohydrin with TBAI as cocatalyst at 80 °C and 10 bar CO_2 .^[192]

3. Synthesis of Bulky Tris(pyrazolyl)borate Ligands

The scorpionate ligand class of the tris(3-*R*,5-*R'*-pyrazolyl)borates ($\text{Tp}^{\text{R,R'}}$) by TROFIMENKO is well known for its highly tunable steric properties.^[275–277] Representative example, is the steric stabilization of rare-earth metal imides^[278–281], phosphindenes^[282] and other reactive species. The Tp ligand can also sterically induce dissociation and formation of highly reactive alkyl species. This is the case for the reaction of rare-earth metal gallates $\text{Ln}(\text{GaMe}_4)_3$ with the bulky $\text{HTp}^{\text{tBu,Me}}$ and the formation of $[\text{Tp}^{\text{tBu,Me}}\text{LnMe}(\text{GaMe}_4)]$ ($\text{Ln} = \text{Y, Dy, Ho}$).^[281] Here, GaMe_3 is eliminated due to the steric bulk of the Tp ligand. For this reason, we were interested in the stabilization properties of Tp ligands with even bulkier substituents at the 3 position. One literature-known example is the thallium complex $\text{ThTp}^{\text{Ar,Me}}$ ($\text{Ar} = \text{para-tert-butylphenyl}$) by PARKIN.^[283]



Scheme C6. Synthesis of the inorganic polymer $[\text{K}(\text{B}\{\text{pz}^{3-p-t\text{BuPh}}\}_4)]_\infty$ (**III**).

We started this study with the synthesis of the corresponding pyrazoles. The mono-substituted 3-(para-*tert*-butylphenyl)pyrazole ($\text{Hpz}^{3-p-t\text{BuPh}}$) was synthesized via the animoprop-2-eone route^[284] and the twofold substituted 3-para-*tert*-butylphenyl-5-methylpyrazole ($\text{Hpz}^{p-t\text{BuPh,Me}}$) via the diketone route.^[285] First the Tp ligand devoid of methyl groups at the 5-position was synthesized. KBH_4 and six equivalents of $\text{Hpz}^{3-p-t\text{BuPh}}$ were heated to a melt at 230 °C (see Scheme C6). The reaction was stopped after H_2 formation ceased. Different to other Tp ligand synthesis the separation of excess pyrazole via sublimation was not possible, due to the boiling behavior of the mixture. Redissolving the mixture in *n*-pentane and slow evaporation at ambient pressure led to formation a crystallin material suitable for a SC-XRD analysis. The crystal structure revealed the inorganic polymer $[\text{K}(\text{B}\{\text{pz}^{3-p-t\text{BuPh}}\}_4)]_\infty$ (**III**) (see Figure C3). In this highly symmetric structure the tetra-substituted $[\text{B}(\text{pz}^{3-p-t\text{BuPh}})_4]^-$ ligand is bridging between two potassium centers with two pyrazole moieties each forming an endless polymeric chain. The backbone is completely linear with a K1-B1-K1' angle of 180°. The boron is surrounded by the pyrazole moieties in a slightly distorted tetrahedral fashion with angles of 108.49(4)° and 111.45(5)°. The interatomic distances between the potassium center and the nitrogen is

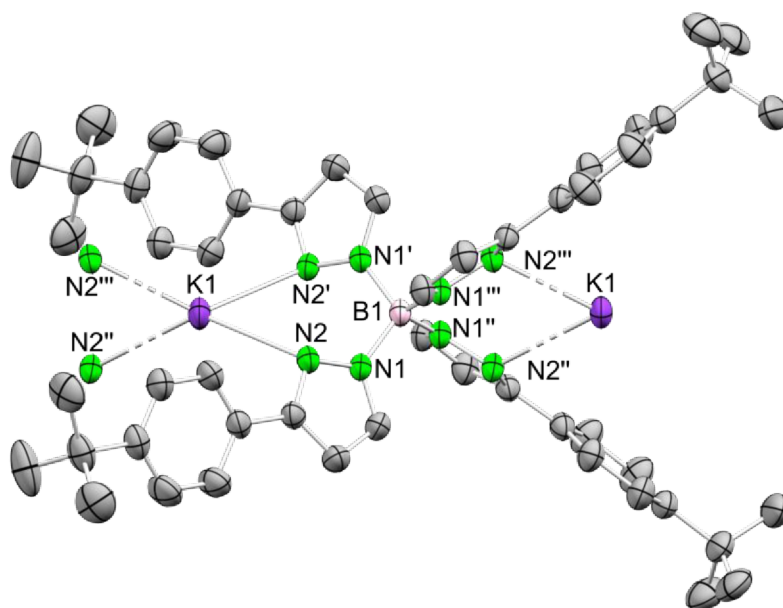
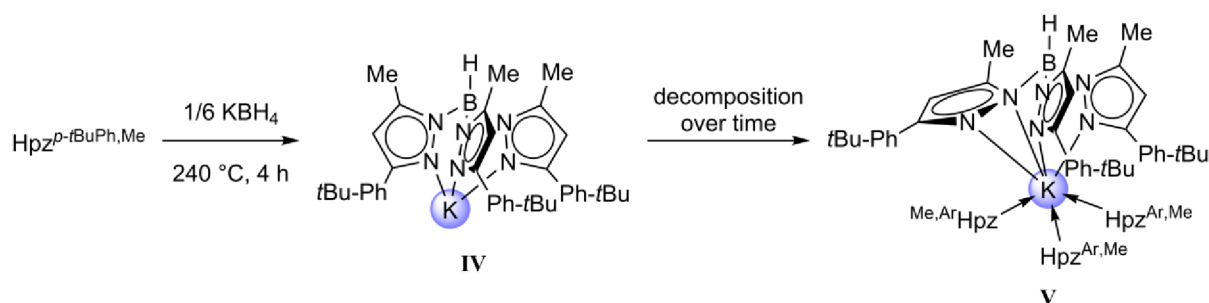


Figure C3. Crystal structure of $[K(B\{pz^{3-p-tBuPh}_4\})_\infty$ (**III**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: K1–N2 2.8504(11). Selected angles [°]: N2–K1–N2' 66.90(4), N2–K1–N2'' 134.12(3), N1–B1–N1' 111.45(8), N1–B1–N1'' 108.49(4).

2.8504(11) Å. The 1H NMR spectrum shows one signal set for the $pz^{3-p-tBuPh}$ units but no signal for a BH. The boron core is resolved in the ^{11}B NMR as one sharp signal at $\delta = 1.2$ ppm. This is different to three-fold substituted Tp ligands in which the boron signal is resolved slightly shifted to higher field and appears broader due to the 1J -coupling to the 1H core. The substitution of all four hydrogen atoms with pyrazolyl moieties can be explained by the missing methyl groups at the 5-position. In addition, the degree of substitution in the melt reaction of Tp ligands is highly dependent on the reaction temperature, with higher temperature yielding higher substituted products.^[276] In the case of **III** a combination of both led to the four-fold substitution.



Scheme C7. Synthesis of the scorpionate ligand $KTp^{p-tBuPh,Me}$ (**IV**) and subsequent decomposition to $K(Tp^{p-tBuPh,Me})(Hpz^{p-tBuPh,Me})_3$ (**V**).

To avoid the toxic thallium the synthesis using $Hpz^{p-tBuPh,Me}$ was conducted similar to the synthesis of **III** by using KBH_4 except the temperature was set at 240 °C (see Scheme C7). In this case the excess pyrazole could be separated by sublimation and the potassium salt KTp^{p-

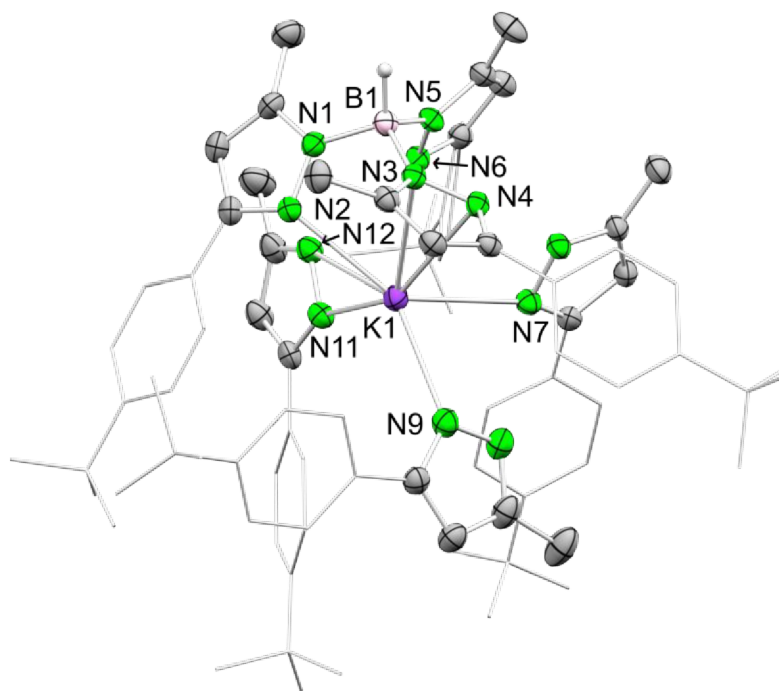


Figure C4. Crystal structure of $\text{Tp}^{p\text{-}t\text{BuPh,Me}}\text{K}(\text{Hpz}^{p\text{-}t\text{BuPh,Me}})_3$ (**V**). Ellipsoids are set at the 50% probability level. Hydrogen atoms as well as one lattice solvent *n*-hexane are omitted and *p*-*t*BuPh moieties are set as wireframe for clarity. Selected interatomic distances [Å]: K1–N2 2.759(2), K1–N3 3.040(2), K1–N4 2.958(2), K1–N6 3.151(2), K1–N7 2.84(2), K1–N9 2.765(2), K1–N11 2.775(2), K1–N12 3.367(2). Selected angles [°]: K1–N2–N1 107.98(13), K1–N6–N5 96.74(12), K1–N4–N3 80.15(12).

*t*BuPh,Me (**IV**) could be isolated in the ^1H NMR spectrum as a clean product. A signal set for the three $\text{pz}^{p\text{-}t\text{BuPh,Me}}$ units was observed in addition to a broad signal at $\delta = 4.68$ ppm. As expected, the boron signal in the ^{11}B NMR spectrum was detected at $\delta = -5.1$ ppm. However, a signal set for reprotonated $\text{Hpz}^{p\text{-}t\text{BuPh,Me}}$ appeared in the ^1H NMR spectrum and increased overtime. Recrystallization in *n*-hexane yielded colorless crystals and a SC-XRD measurement revealed the formation of $\text{Tp}^{p\text{-}t\text{BuPh,Me}}\text{K}(\text{Hpz}^{p\text{-}t\text{BuPh,Me}})_3$ (**V**) in a yield of 38% (see Figure C4). The Tp ligand is highly distorted due to the sterically demanding substituents. One pyrazolyl arm coordinates with both nitrogen atoms to the potassium center with almost equal distances (K1–N3 = 3.040(2) Å and K1–N4 = 2.958(2) Å). This is also reflected in the angle between both nitrogen atoms and the potassium K1–N4–N3 = 80.15(12)°, which is significantly smaller than the angles for a classic Tp metal coordination (110–130°). The *p*-*t*BuPh moieties of two of the three pyrazole donors intercalate with the moieties of the Tp ligand and one pyrazole is orientated in the opposite direction. All three pyrazole engage in hydrogen bonding, one between two pyrazoles (N7–N10) and the other two between one pyrazole and one pyrazolyl unit each (N4–N8 and N6–N12). Both the formation of new pyrazole in the NMR spectra and three equivalents of $\text{Hpz}^{p\text{-}t\text{BuPh,Me}}$ in the crystal structure indicate that complex **IV** decomposes over time. Especially, because already three equivalents of $\text{Hpz}^{p\text{-}t\text{BuPh,Me}}$ were separated via

sublimation. The decomposition occurs most likely, due to the high steric demand of the substituents.

Experimental Section

General Considerations. All manipulations were performed under rigorous exclusion of air and moisture under argon atmosphere (< 0.1 ppm O_2 , < 0.1 ppm of H_2O) in a MB200B glovebox (MBraun) or according to standard Schlenk techniques and in oven-dried glassware. Solvents (THF, Et_2O *n*-pentane, *n*-hexane and toluene) were purified by using SPS Grubbs-type columns (MBraun SPS-800, solvent purification system) and stored inside a glovebox. THF was dried further over molecular sieves. $[D_8]$ toluene, C_6D_6 and $[D_8]$ THF were obtained from Sigma Aldrich and dried over Na/K alloy and filtered prior to use. Di-*n*-butylmagnesium (1 M in Et_2O/n -hexane), 3,5-dimethyl pyrazole (99%), hydrazine hydrate, styrene oxide ($>97\%$, degassed prior to use) and 2,2,6,6-tetramethylheptane-3,5-dione were purchased from Sigma Aldrich and used as received. Propylene oxide and pyrazole (98%) were purchased from Acros Organics and the former was degassed prior to use. 2-*tert*-Butyloxirane was purchased from abcr and degassed prior to use. 1,2-Epoxyhexane (97%) was purchased from Thermo Fischer and degassed prior to use. 3,5-Di-*tert*-butylpyrazole,^[286] $Zn(pz)_2$ (**II**),^[86] 3-*para-tert*-butylphenylpyrazole,^[284] 3-*para-tert*-butylphenyl-5-methylpyrazole,^[286] $Ti(pz^{Me_2})_4$,^[120] $Al(pz^{tBu_2})_3$,^[101] $[Mg(pz^{tBu_2})_2]_2$,^[88] $[Mpz^{tBu_2}]_\infty$ ($M = Li, K$),^[78] $[Kpz^{Ph_2}]_n$ ^[78] and SBA-15^[273] were synthesized according to literature known synthesis route. Argon and CO_2 were supplied by Westfalen AG. Solution 1H , 7Li , ^{11}B and ^{13}C spectra were recorded in a J. Young valve NMR tube on a Bruker AVIII-300 spectrometer (1H : 300.13 MHz; ^{13}C : 75.47 MHz; 7Li : 116.64; ^{11}B : 96.29 MHz), a Bruker AVII+400 spectrometer (1H : 400.11 MHz; ^{13}C : 100.61 MHz) or a Bruker AVII+500 spectrometer (1H : 500.13 MHz; ^{13}C : 125.76 MHz) at 299 K. The chemical shifts listed in the experimental section are referenced to solvent residual resonances in parts per million in relation to tetramethylsilane. Solid-state NMR spectra were obtained at ambient temperature on a Bruker AVIIHD-300WB spectrometer (1H : 300.13 MHz, ^{13}C : 75.47 MHz, ^{29}Si : 59.62 MHz) equipped with MAS (magic angle spinning) hardware using a ZrO_2 rotor with an outside diameter of 4 mm. IR spectra were recorded on a Bruker Invenio R spectrometer (Bruker). The samples were mixed with KBr powder and measured in a DRIFT cell with KBr windows. DRIFT data were converted by using the Kubelka-Munk refinement. N_2 physisorption measurements were carried out on an ASAP2020 volumetric adsorption apparatus. The samples were degassed at ambient temperatures for 2 h. Elementary analyses were performed on an Elementar vario MICRO cube in CHNS mode. ICP-OES measurements were conducted on a Thermo Scientific iCAP 7000 series. Single crystals were grown from saturated solutions of *n*-pentane and $[D_8]$ THF by standard techniques. Crystals of Y^{CO_2} , **III** and **IV** for X-ray structure studies were selected in a glovebox and coated with Parabar 10312 (Hampton research). Crystallographic data were measured on a Bruker APEX II DUO instrument equipped with $I\mu S$ micro focus sealed tube and QUAZAR optics for MoK_α radiation ($\lambda = 0.71073$ Å). The data collection strategy was determined using COSMO^[287] employing ω - and ϕ scans. Raw data were processed using APEX^[288] and SAINT,^[289] corrections for absorption effects were applied using SADABS.^[290] The structures were solved by direct methods and refined against all data by full-matrix least-squares methods on F2 using ShelXTL and ShelXL.^[291] Disorder models are calculated using DSR, a program for refining disordered structures in SHELXL.^[292] All graphics were produced employing Mercury.^[293]

$[K(CO_2 \cdot pz^{tBu_2})]_n (A^{CO_2})$. $[Kpz^{tBu_2}]_\infty$ (**A**, 20 mg, 107 μ mol) was dissolved in 0.5 mL of $[D_8]$ THF and the atmosphere was exchanged to 1 bar CO_2 . The reaction progress was monitored by 1H NMR spectroscopy. 1H NMR (300.13 MHz, $[D_8]$ THF, 26 °C): $\delta = 5.89$ (s, 1 H, 4-*H* (pz)), 1.39 (s, 18 H, 3- $C(CH_3)_3$), 1.18 (5- $C(CH_3)_3$) ppm.

$[Li(CO_2 \cdot pz^{tBu_2})]_n (B^{CO_2})$. $[Lipz^{tBu_2}]_4$ (**B**, 20 mg, 91 μ mol) was dissolved in 0.5 mL of $[D_8]$ THF and the atmosphere was exchanged to 1 bar CO_2 . The reaction progress was monitored by 1H NMR spectroscopy. 1H NMR (400.11 MHz, $[D_8]$ THF, 26 °C): $\delta = 6.06$ (s, 1 H, 4-*H* (pz)), 1.43 (s, 18 H, 3- $C(CH_3)_3$), 1.21 (5- $C(CH_3)_3$) ppm. $^{13}C\{H\}$ NMR (75.47 MHz, $[D_8]$ THF, 26 °C): $\delta = 160.1$ (3- C (pz)),

155.7 (5-*C* (pz)), 103.5 (4-*C* (pz)), 33.3 (5-*C*(CH₃)₃), 32.1 (3-*C*(CH₃)₃), 29.8 (5-*C*(CH₃)₃), 29.5 (3-*C*(CH₃)₃) ppm. ⁷Li NMR (116.64 MHz, [D₈]THF, 26 °C): δ = 2.1 ppm.

[Mg(pz^{Ph})₂]_n (O). MgBr₂ (84.9 mg, 462 μmol) and [Kpz^{Ph}]_n (239 mg, 923 μmol) were dissolved in toluene and stirred for 16 h. After the solvent was removed under reduced pressure the residue was extracted three times with *n*-hexane. The solution was concentrated and stored at -40 °C. After removal of the solvent **O** (119 mg, 257 μmol, 56%) could be obtained as colorless powder. ¹H NMR (400.11 MHz, [D₈]THF, 26 °C): δ = 7.87 (broad s, 8 H, *o*-*H* (Ph)), 7.19 (m, 8 H, *m*-*H* (Ph)), 7.00 (m, 4 H, *p*-*H* (Ph)), 6.80 (4-*H* (pz)) ppm.

[Mg(tz^{Me})₂]_n (I). To a solution of Hpz (200 mg, 2.059 mmol) in 10 mL toluene or THF a solution of Mg(*n*Bu)₂ (1.030 mL, 1.030 mmol, 1 M in Et₂O/*n*-hexane) was added dropwise. A white precipitate is formed and the solution transforms into a gel. After the solvent is removed **I** (223 mg, 1.028 mmol, >99%) was obtained as white powder.

[Zn(pz^{tBu})₂(Hpz^{tBu})₂] (Y^{Hpz}). [Kpz^{tBu}]_∞ (**A**, 200 mg, 916 μmol) and ZnCl₂ (62 mg, 458 μmol) were dissolved in 15 mL of THF and stirred for 4 d at ambient temperature. The solvent was removed and the residue was extracted three times with *n*-hexane. After the solvent was removed under reduced pressure **Y^{Hpz}** (34%, 121 mg, 154 μmol) was obtained as colorless crystals. Analytical data is consistent with the literature.^[86]

[Zn(CO₂·pz^{tBu})(pz^{tBu})₂] (Y^{CO₂}). [Zn(pz^{tBu})₂(Hpz^{tBu})₂] (**Y^{Hpz}**, 20 mg, 25 μmol) was dissolved in 0.5 mL of [D₈]THF and the atmosphere was exchanged to 1 bar CO₂. The reaction progress was monitored by ¹H NMR spectroscopy. ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 6.33 (s, 2 H, 4-*H* (CO₂·pz)), 6.08 (s, 2 H, 4-*H* (pz)), 1.27 (s, 18 H, 3-*C*(CH₃)₃ (CO₂·pz)), 1.17 (s, 18 H, 5-*C*(CH₃)₃ (CO₂·pz)), 0.95 (s, 36 H, 3/5-*C*(CH₃)₃ (pz)) ppm. ¹³C{¹H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 168.9 (3-*C* (CO₂·pz)), 167 (3/5-*C* (pz)), 104.9 (4-*C* (CO₂·pz)), 102.4 (4-*C* (pz)), 32.7 (5-*C*(CH₃)₃ (CO₂·pz)), 32.6 (3/5-*C*(CH₃)₃ (pz)), 32.3 (3-*C*(CH₃)₃ (CO₂·pz)), 31.4 (3/5-*C*(CH₃)₃ (pz)), 30.8 (5-*C*(CH₃)₃ (pz)), 30.8 (3-*C*(CH₃)₃ (pz)) ppm.

[Mg(pz^{tBu})₂]₂@SBA-15₅₀₀ (C@SBA-15). SBA-15₅₀₀ (367 mg, 1.03 mmol of surface SiOH) was suspended in 2 mL *n*-hexane and a solution of [Mg(pz^{tBu})₂]₂ (**C**, 394 mg, 0.52 mmol ≡ 1.03 mmol Mg center) in 8 mL *n*-hexane was added dropwise. The suspension was stirred for 16 h at ambient temperature. The hybrid material was separated by centrifugation and was washed two times with toluene (5 mL) and five times with *n*-hexane (5 mL). The solvent was removed under reduced pressure and **C@SBA-15** was obtained as a colorless powder (426 mg). The supernatant solution was filtered and the solvent was removed under reduced pressure. An ¹H NMR spectrum revealed the recovery of some starting material **C**. ¹H CP/MAS spectrum (300.13 MHz, MAS at 8 kHz): δ = 12.66 (NH), 6.94 (4-*H*(pz)), 5.81 (4-*H*(pz)), 1.03 (C(CH₃)₃) ppm. ¹³C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): δ = 165.1 (3/5-*C*(pz)), 155.4 (3/5-*C*(pz)), 99.0 (4-*C*(pz)), 29.4 (C(CH₃)₃) ppm. ²⁹Si CP/MAS spectrum (59.63 MHz, MAS at 5 kHz): δ = ppm. *a*_{BET} = 410 m²/g, *V*_{pore} = 0.57 cm³/g, *d*_{pore} = 6.2 nm. DRIFTS: $\tilde{\nu}$ = 2967 (w), 2911 (vw), 2873 (vw), 1560 (vw), 1510 (vw), 1491 (vw), 1467 (vw), 1367 (vw), 1281 (vw), 1200 (m), 1079 (vs), 807 (vw), 457 (w) cm⁻¹. Elemental analysis found: Mg 1.85 (ICP-OES); C 19.25, H 2.67, N 3.71.

Al(pz^{tBu})₃@SBA-15₅₀₀ (E@SBA-15). SBA-15₅₀₀ (221 mg, 620 μmol of surface SiOH) was suspended in 2 mL *n*-hexane and a solution of Al(pz^{tBu})₃ (**E**, 350 mg, 620 μmol) in 8 mL *n*-hexane was added dropwise. The suspension was stirred for 16 h at ambient temperature. The hybrid material was separated by centrifugation and was washed two times with toluene (5 mL) and five times with *n*-hexane (5 mL). The solvent was removed under reduced pressure and **E@SBA-15** was obtained as a colorless powder (239 mg). The supernatant solution was filtered and the solvent was removed under reduced pressure. An ¹H NMR spectrum revealed the recovery of some starting material **E**. ¹H CP/MAS spectrum (300.13 MHz, MAS at 8 kHz): δ = 11.03 (NH), 6.87 (4-*H*(pz)), 5.73 (4-*H*(pz)), 0.97 (C(CH₃)₃) ppm. ¹³C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): δ = 161.7 (3/5-*C*(pz)), 99.3 (4-*C*(pz)), 30.9 (C(CH₃)₃),

29.4 (C(CH₃)₃) ppm. ²⁹Si CP/MAS spectrum (59.63 MHz, MAS at 5 kHz): δ = ppm. a_{BET} = 418 m²/g, V_{pore} = 0.55 cm³/g, d_{pore} = 6.4 nm. DRIFTS: $\tilde{\nu}$ = 2968 (vw), 2911 (vw), 2873 (vw), 1561 (vw), 1467 (vw), 1368 (vw), 1187 (m), 1075 (vs), 814 (vw), 454 (w) cm⁻¹. Elemental analysis found: Al 1.21 (ICP-OES); C 19.03, H 2.88, N 3.55.

Ti(pz^{Me2})₄@SBA-15₅₀₀ (F@SBA-15). SBA-15₅₀₀ (337 mg, 943 μ mol of surface SiOH) was suspended in 2 mL toluene and a solution of Ti(pz^{Me2})₄ (F, 404 mg, 943 μ mol) in 8 mL toluene was added dropwise. The suspension was stirred for 18 h at ambient temperature. The hybrid material was separated by centrifugation and was washed eight times with toluene (5 mL) and three times with *n*-hexane (5 mL). The solvent was removed under reduced pressure and **F@SBA-15** was obtained as a pale-yellow powder (392 mg). The supernatant solution was filtered and the solvent was removed under reduced pressure. An ¹H NMR spectrum revealed the recovery of some starting material **F**. ¹H CP/MAS spectrum (300.13 MHz, MAS at 8 kHz): δ = 6.75 (4-*H*(pz)), 5.67 (4-*H*(pz)), 1.84 (CH₃) ppm. ¹³C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): δ = 146.3 (3/5-*C*(pz)), 113.9 (4-*C*(pz)), 104.5 (4-*C*(pz)), 10.6 (CH₃) ppm. ²⁹Si CP/MAS spectrum (59.63 MHz, MAS at 5 kHz): δ = ppm. a_{BET} = 405 m²/g, V_{pore} = 0.53 cm³/g, d_{pore} = 6.6 nm. DRIFTS: $\tilde{\nu}$ = 3396 (vw), 2931 (vw), 2871 (vw), 1572 (vw), 1526 (vw), 1440 (vw), 1422 (vw), 1374 (vw), 1074 (vs), 804 (w), 460 (w) cm⁻¹. Elemental analysis found: Ti 4.39 (ICP-OES); C 17.36, H 2.35, N 7.00.

CO₂@[Mg(pz^{tBu2})₂]₂@SBA-15₅₀₀ (CO₂@C@SBA-15). A Schlenk tube was loaded with solid **C@SBA-15** (100.7 mg, = 2.0 mg (Mg metal), 83.3 μ mol (Mg metal)) and the atmosphere was changed to 1 bar CO₂. After 3 h **CO₂@C@SBA-15** could be collected as white powder (108.8 mg). ¹H CP/MAS spectrum (300.13 MHz, MAS at 8 kHz): δ = 12.12 (COOH/NH), 6.91 (4-*H*(pz)), 5.77 (4-*H*(pz)), 1.03 (C(CH₃)₃) ppm. ¹³C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): δ = 163.3 (3/5-*C*(pz)), 156.0 (3/5-*C*(pz)), 98.1 (4-*C*(pz)), 30.6 (C(CH₃)₃), 29.0 (C(CH₃)₃) ppm. DRIFTS: $\tilde{\nu}$ = 2367 (w), 2911 (vw), 2874 (vw), 1655 (vw), 1560 (vw), 1491 (vw), 1467 (vw), 1368 (vw), 1281 (vw), 1189 (s), 1080 (vs), 806 (w), 461 (w) cm⁻¹. Elemental analysis found: C 18.47, H 3.19, N 3.66.

CO₂@Al(pz^{tBu2})₃@SBA-15₅₀₀ (CO₂@E@SBA-15). A Schlenk tube was loaded with solid **E@SBA-15** (70.6 mg, = 0.9 mg (Al metal), 31.7 μ mol (Al metal)) and the atmosphere was changed to 1 bar CO₂. After 3 h **CO₂@E@SBA-15** could be collected as white powder (75.3 mg). ¹H CP/MAS spectrum (300.13 MHz, MAS at 8 kHz): δ = 11.15 (COOH/NH), 6.75 (4-*H*(pz)), 5.86 (4-*H*(pz)), 1.08 (C(CH₃)₃) ppm. ¹³C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): δ = 163.4 (3-*C*(pz)), 156.3 (5-*C*(pz)), 144.9 (CO₂), 107.2 (4-*C*(pz)), 98.5 (4-*C*(pz)), 30.6 (C(CH₃)₃), 29.1 (C(CH₃)₃) ppm. DRIFTS: $\tilde{\nu}$ = 2967 (w), 2911 (vw), 2875 (vw), 1786 (vw), 1760 (vw), 1561 (vw), 1490 (vw), 1467 (vw), 1368 (vw), 1333 (vw), 1191 (s), 1075 (vs), 812 (w), 461 (m) cm⁻¹. Elemental analysis found: C 17.81, H 2.91, N 3.56.

CO₂@Ti(pz^{Me2})₄@SBA-15₅₀₀ (CO₂@F@SBA-15). A Schlenk tube was loaded with solid **F@SBA-15** (66.4 mg = 2.9 mg (Ti metal), 60.9 μ mol (Ti metal)) and the atmosphere was changed to 1 bar CO₂. After 3 h **CO₂@F@SBA-15** could be collected as pale-yellow powder (74.7 mg). ¹H CP/MAS spectrum (300.13 MHz, MAS at 8 kHz): δ = 6.67 (4-*H*(pz)), 5.34 (4-*H*(pz)), 1.83 (CH₃), 0.84 (CH₃) ppm. ¹³C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): δ = 149.9 (3-*C*(pz)), 142.7 (5-*C*(pz)), 108.1 (4-*C*(pz)), 10.6 (CH₃) ppm. DRIFTS: $\tilde{\nu}$ = 3390 (vw), 2995 (vw), 2934 (vw), 2864 (vw), 1744 (w), 1573 (vw), 1526 (vw), 1467 (vw), 1419 (vw), 1381 (vw), 1350 (vw), 1068 (vs), 804 (w), 580 (vw), 456 (w) cm⁻¹. Elemental analysis found: C 16.39, H 1.97, N 6.77.

[K(B{pz^{3-p-tBuPh}})₄]_n (III). A 250 mL three-necked flask was charged with KBH₄ (699 mg, 12.95 mmol) and Hpz^{3-p-tBuPh} (15.5 g, 77.71 mmol). The mixture was heated to 230 °C until a melt had formed. After the H₂ formation ceased (4 h) the melt was cooled to ambient temperature. The white powder was recrystallized from *n*-pentane and via slow evaporation of the solvent **III** (1.86 g, 2.19 mmol, 17%) was obtained as colorless crystals suitable for a SC-XRD analysis. ¹H NMR (400.1 MHz, [D₈]THF, 26 °C):

$\delta = 7.71$ (d, 8 H, *o*-H (Ph)), 7.49 (s, 4 H, 5-*H* (pz)), 7.33 (d, 8 H, *m*-H (Ph)), 6.49 (s, 4 H, 4-*H* (pz)), 1.31 (s, 36 H, CH_3) ppm. ^{11}B NMR (96.29 MHz, $[\text{D}_8]\text{THF}$, 26 °C): $\delta = 1.2$ ppm.

KTp^{*p*-*t*BuPh,Me} (IV) and decomposition to Tp^{*p*-*t*BuPh,Me}K(Hpz^{*p*-*t*BuPh,Me})₃ (V). A 100 mL three-necked flask was charged with KBH_4 (166 mg, 3.072 mmol) and $\text{Hpz}^{3\text{-}p\text{-}t\text{BuPh}}$ (3.95 g, 18.43 mmol). The mixture was heated to 240 °C until a melt had formed and stirred until H_2 formation ceased (4 h). The melt was cooled to 180 °C and poured into a mortar. After the mixture cooled to ambient temperature, it was grinded down to a powder. The white powder was dissolved in *n*-pentane and filtered with subsequent removal of the solvent under reduced pressure. The excess $\text{Hpz}^{3\text{-}p\text{-}t\text{BuPh}}$ was removed via sublimation at 200 °C. The potassium salt **IV** (752 mg, 1.09 mmol, 35%) was isolated as white a powder. ^1H NMR (400.1 MHz, C_6D_6 , 26 °C): $\delta = 7.25$ (d, 6 H, *o*-H (Ph)), 7.12 (d, 6 H, *m*-H (Ph)), 6.11 (s, 3 H, 4-*H* (pz)), 4.68 (broad s, 1 H, *H*-B), 2.14 (s, 9 H, CH_3), 1.31 (s, 27 H, $\text{C}(\text{CH}_3)$) ppm. ^{11}B NMR (96.29 MHz, $[\text{D}_8]\text{THF}$, 26 °C): $\delta = -5.1$ ppm. Over a week **IV** decomposed and was completely transformed to donor-pyrazole stabilized $\text{Tp}^{p\text{-}t\text{BuPh,Me}}\text{K}(\text{Hpz}^{p\text{-}t\text{BuPh,Me}})_3$ (**V**). Crystallin material was obtained via recrystallization from *n*-pentane.

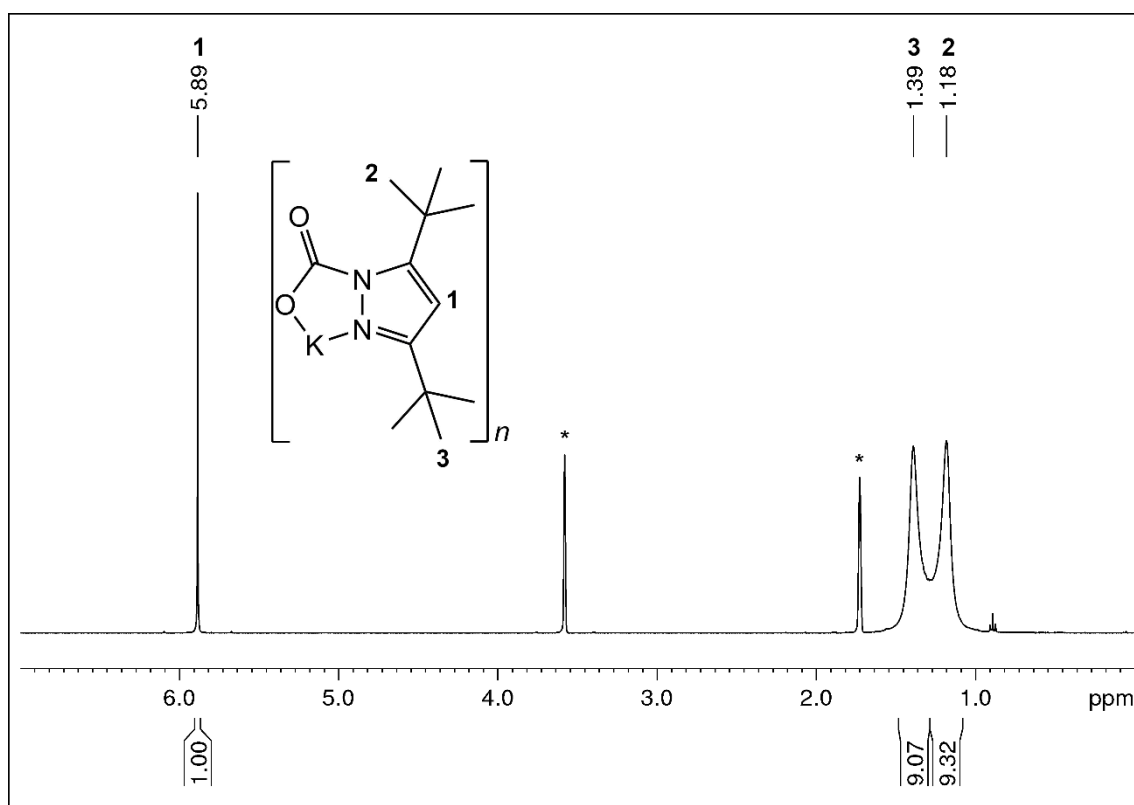


Figure C4. 1H NMR spectrum (26 °C, 400.11 MHz, $[D_8]THF$) of $[K(CO_2 \cdot pz^{tBu_2})]_n$ (A^{CO_2}).

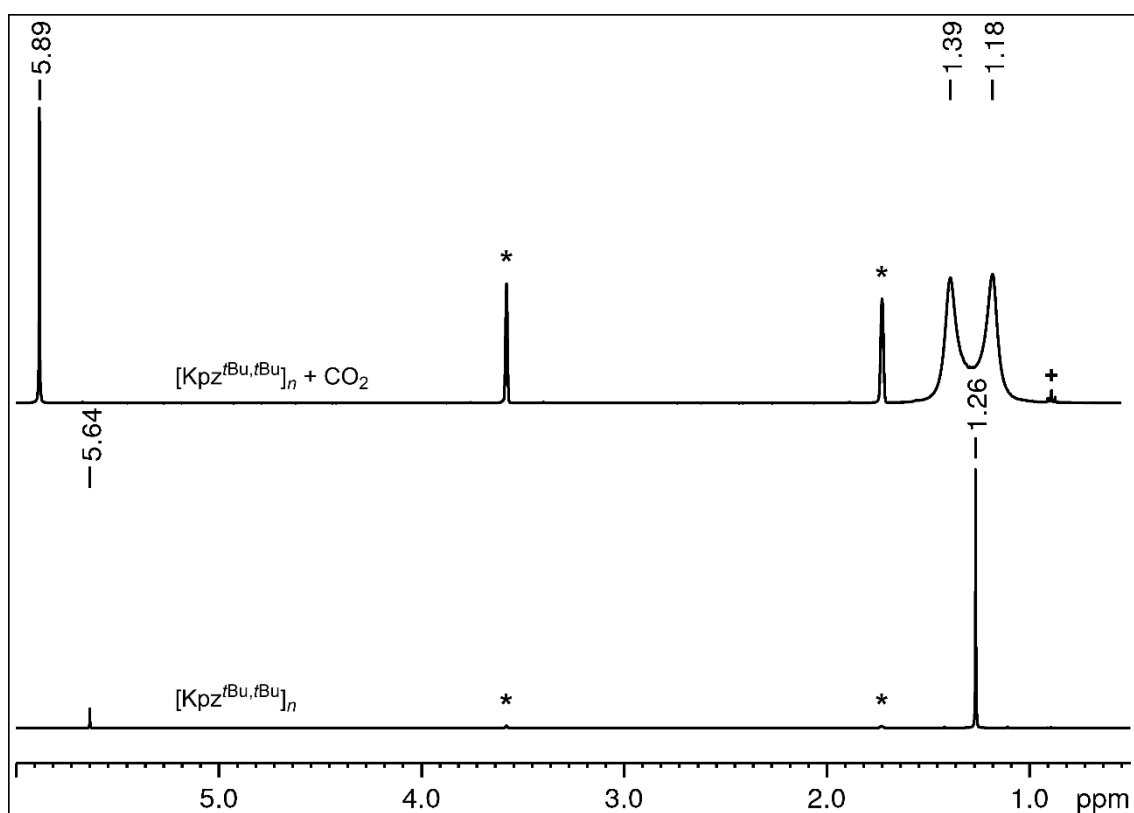


Figure C5. Comparison of 1H NMR spectra (26 °C, 400.11 MHz, $[D_8]THF$) of $[K(pz^{tBu_2})]_\infty$ (A, bottom) and $[K(CO_2 \cdot pz^{tBu_2})]_n$ (A^{CO_2} , top).

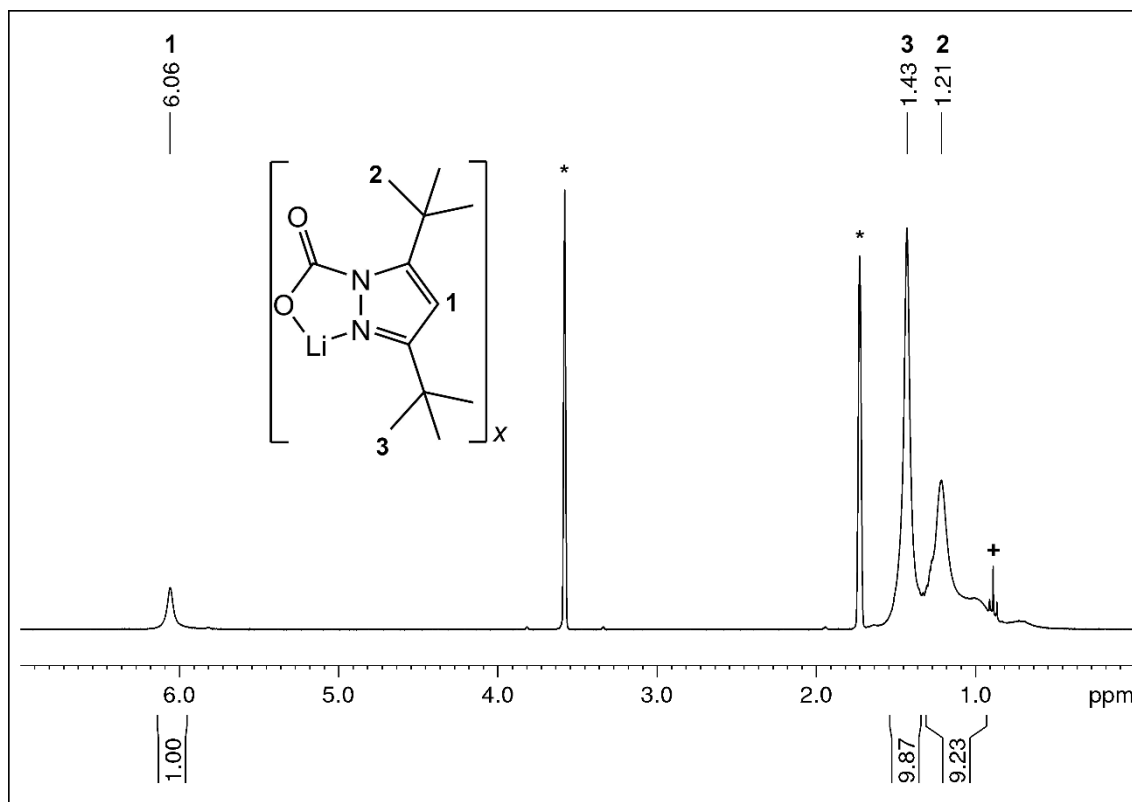


Figure C6. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Li}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})]_n$ (B^{CO_2}) (+ *n*-hexane).

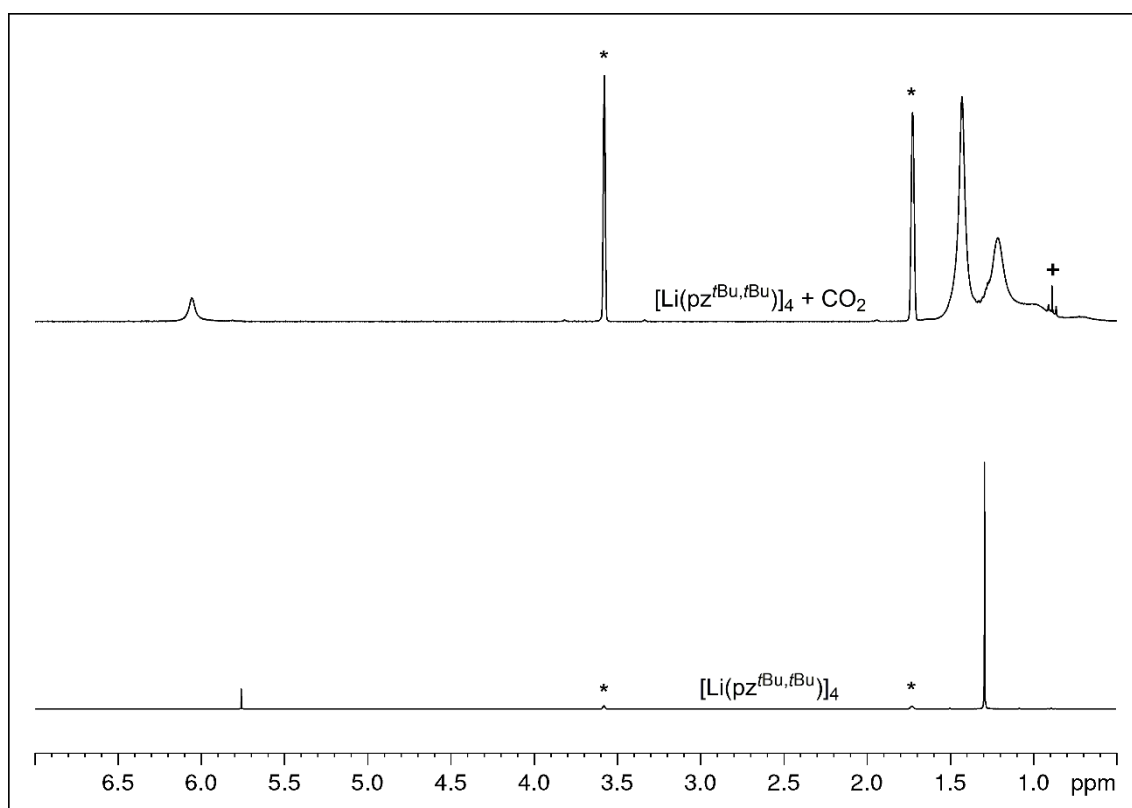


Figure C7. Comparison of ^1H NMR spectra (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Li}(\text{pz}^{\text{tBu}_2})]_4$ (B , bottom) and $[\text{Li}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})]_n$ (B^{CO_2} , top) (+ *n*-hexane).

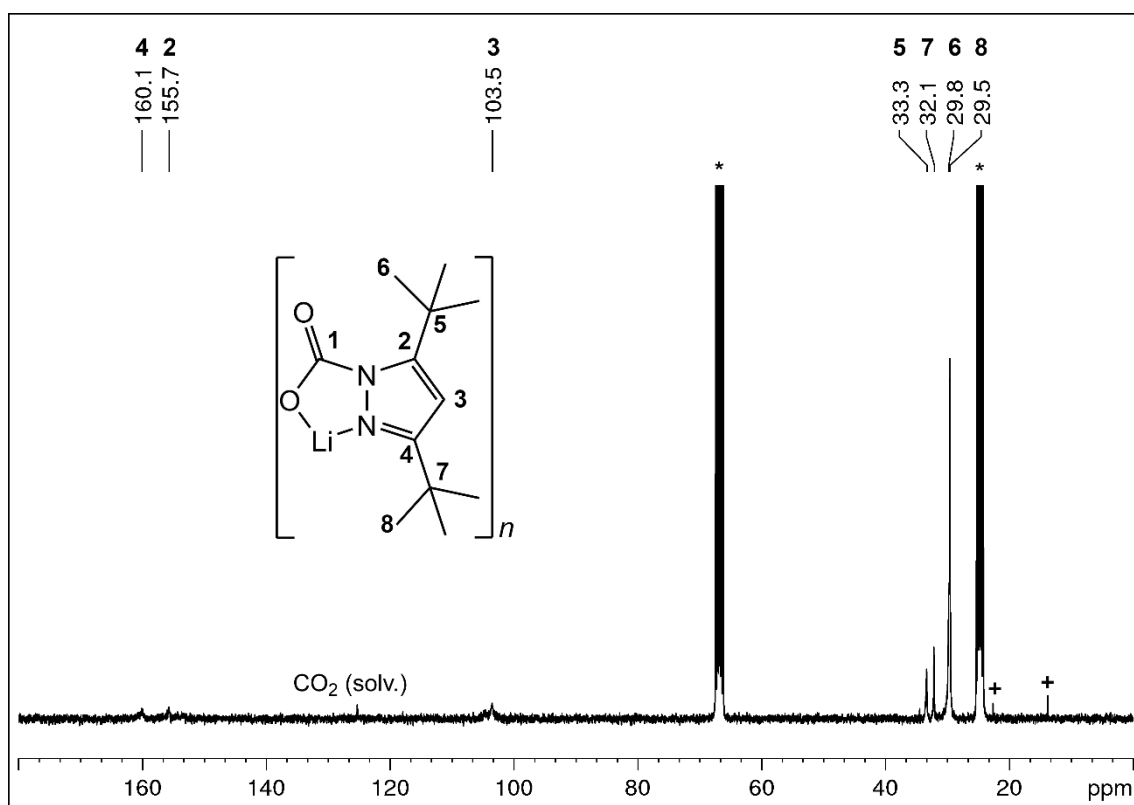


Figure C8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 75.47 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Li}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})]_n$ (**B^{CO}₂**) (+ *n*-hexane).

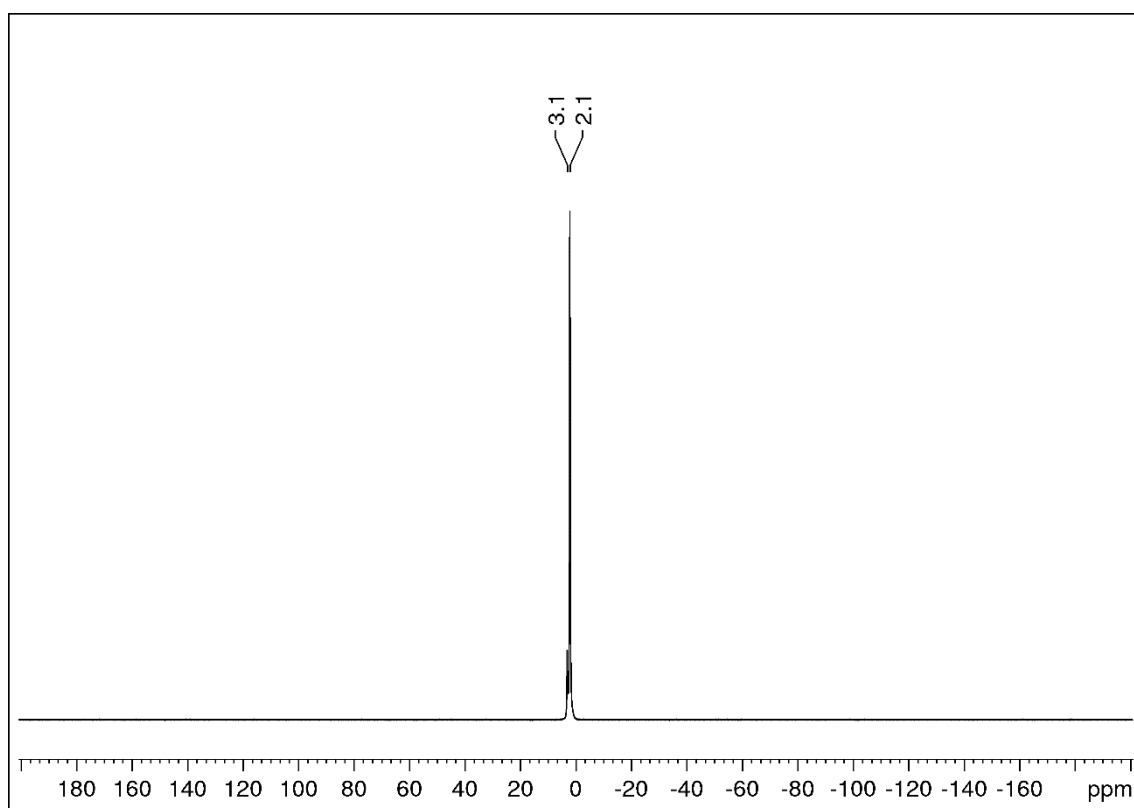


Figure C9. ^7Li NMR spectrum (26 °C, 116.64 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Li}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})]_n$ (**B^{CO}₂**) (+ *n*-hexane).

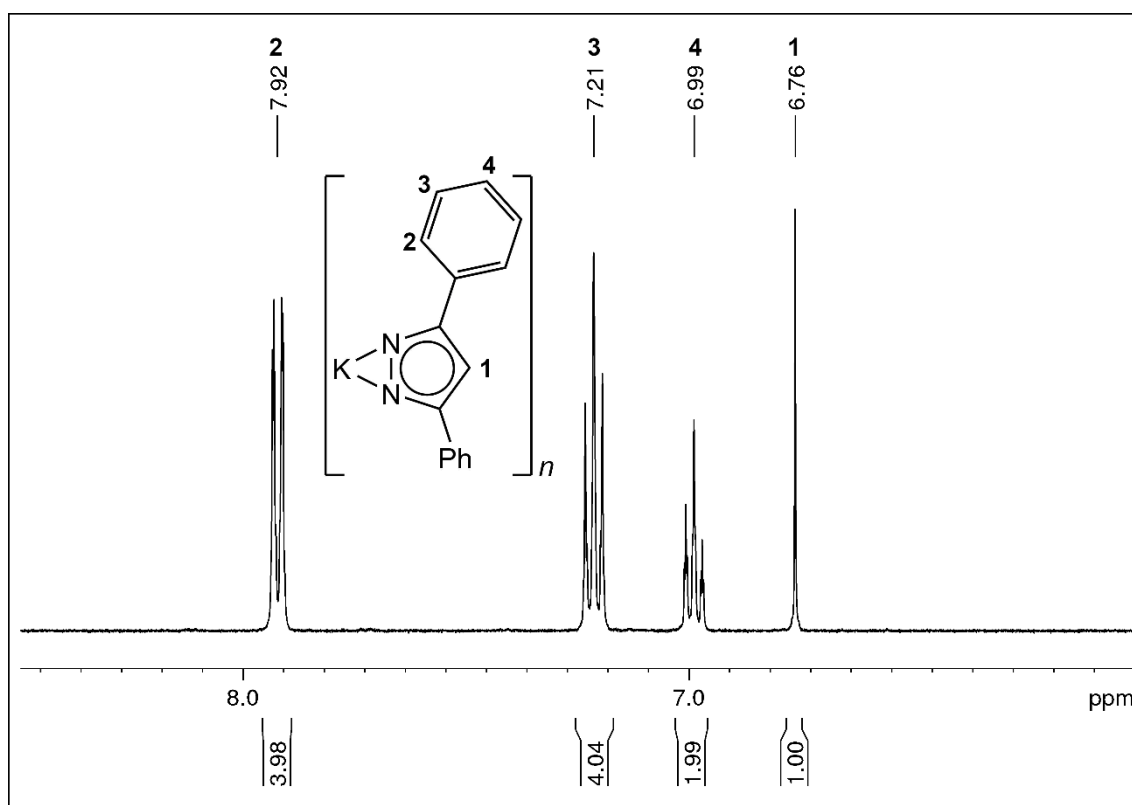


Figure C10. 1H NMR spectrum (26 °C, 400.11 MHz, $[D_8]THF$) of $[Kpz^{Ph_2}]_n$.

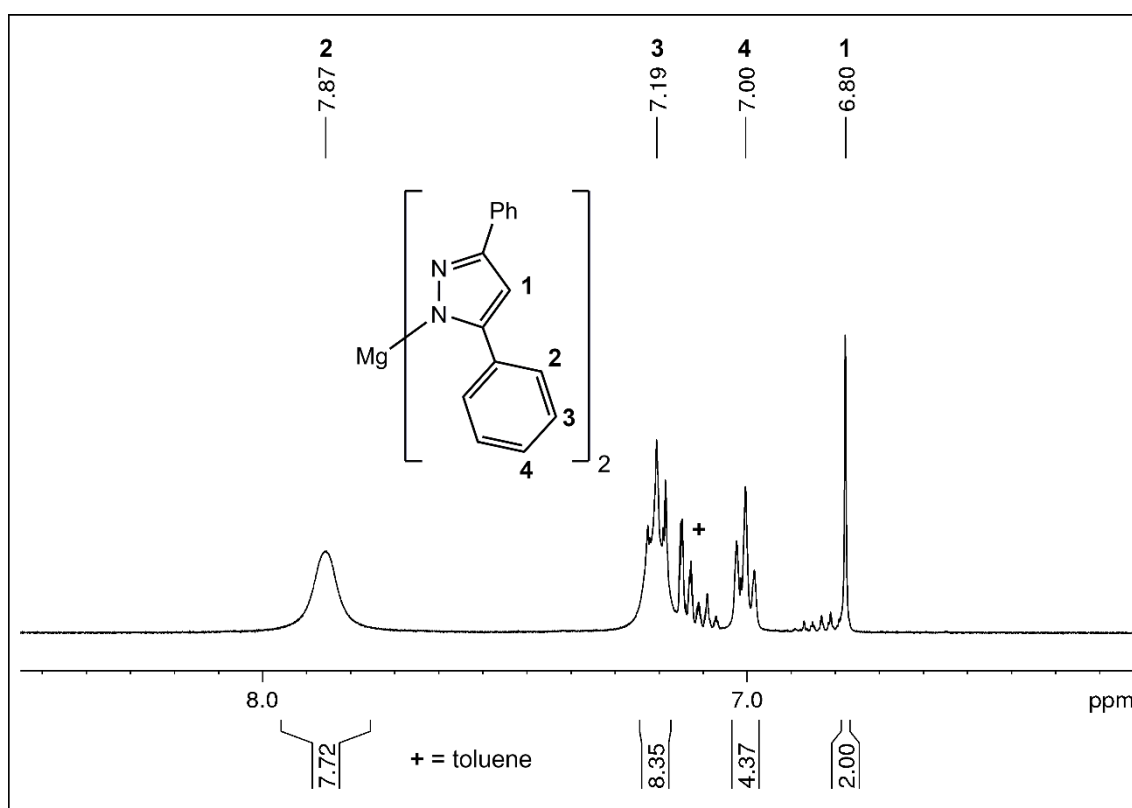


Figure C11. 1H NMR spectrum (26 °C, 400.11 MHz, $[D_8]THF$) of $[Mg(pz^{Ph_2})_2]_n$ (**O**) (+ toluene).

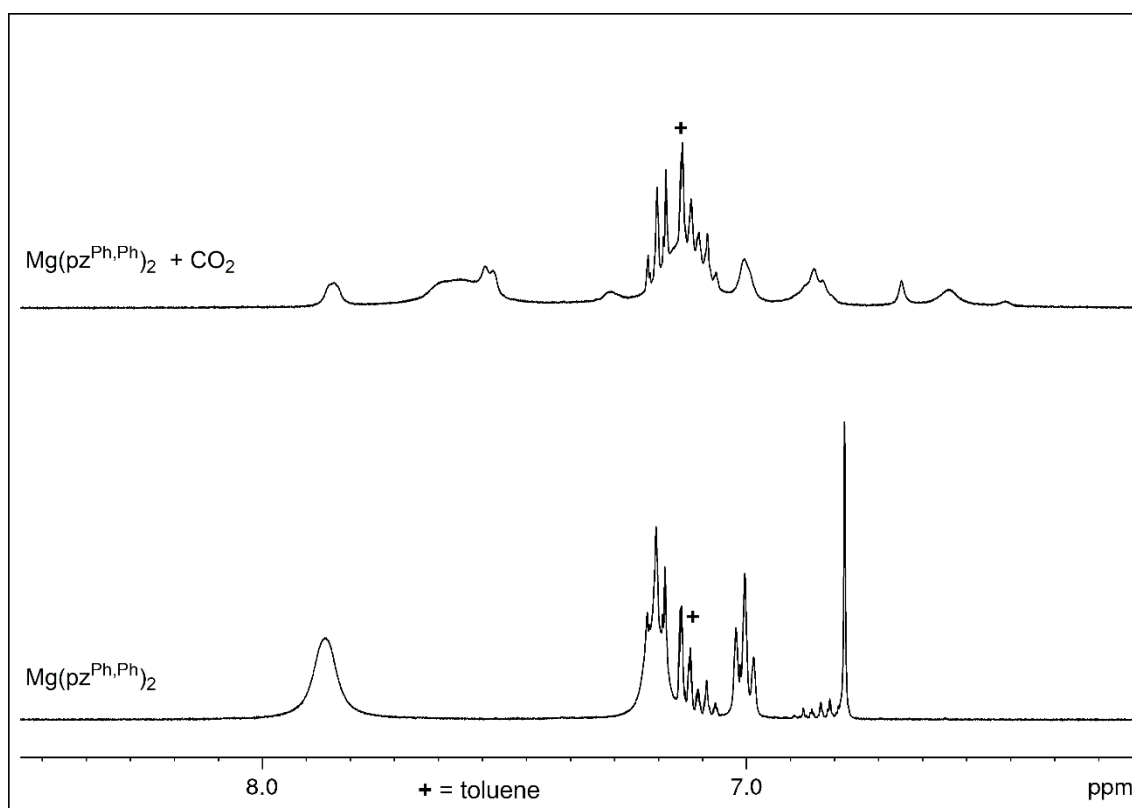


Figure C12. Comparison of the ^1H NMR spectra (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}(\text{pz}^{\text{Ph}_2})_2]_n$ (O, bottom) and the reaction of $[\text{Mg}(\text{pz}^{\text{Ph}_2})_2]_n$ and CO_2 (top) (+ toluene).

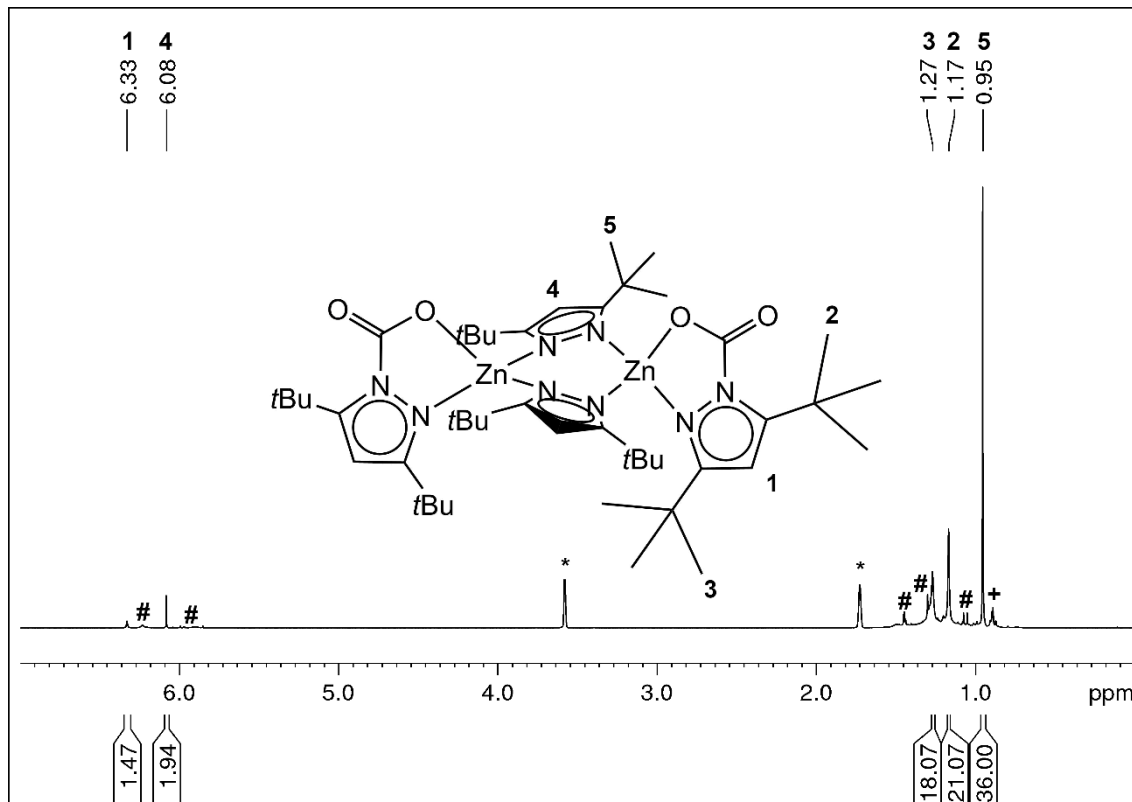


Figure C13. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Zn}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\mu\text{-pz}^{\text{tBu}_2})]_2$ (Y^{CO_2}) (#, unknown impurities; + *n*-hexane).

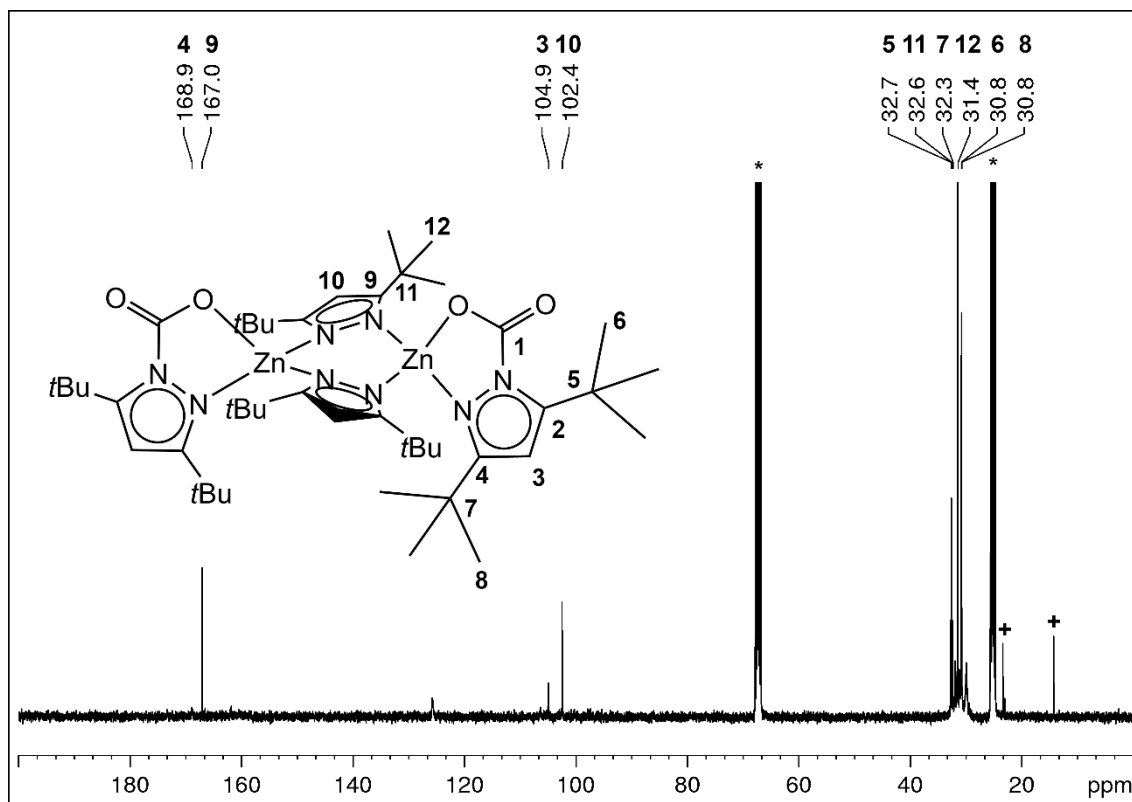


Figure C14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 100.61 MHz, $[\text{D}_8]\text{THF}$) $[\text{Zn}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\mu\text{-pz}^{\text{tBu}_2})]_2$ (Y^{CO_2}) (+ *n*-hexane).

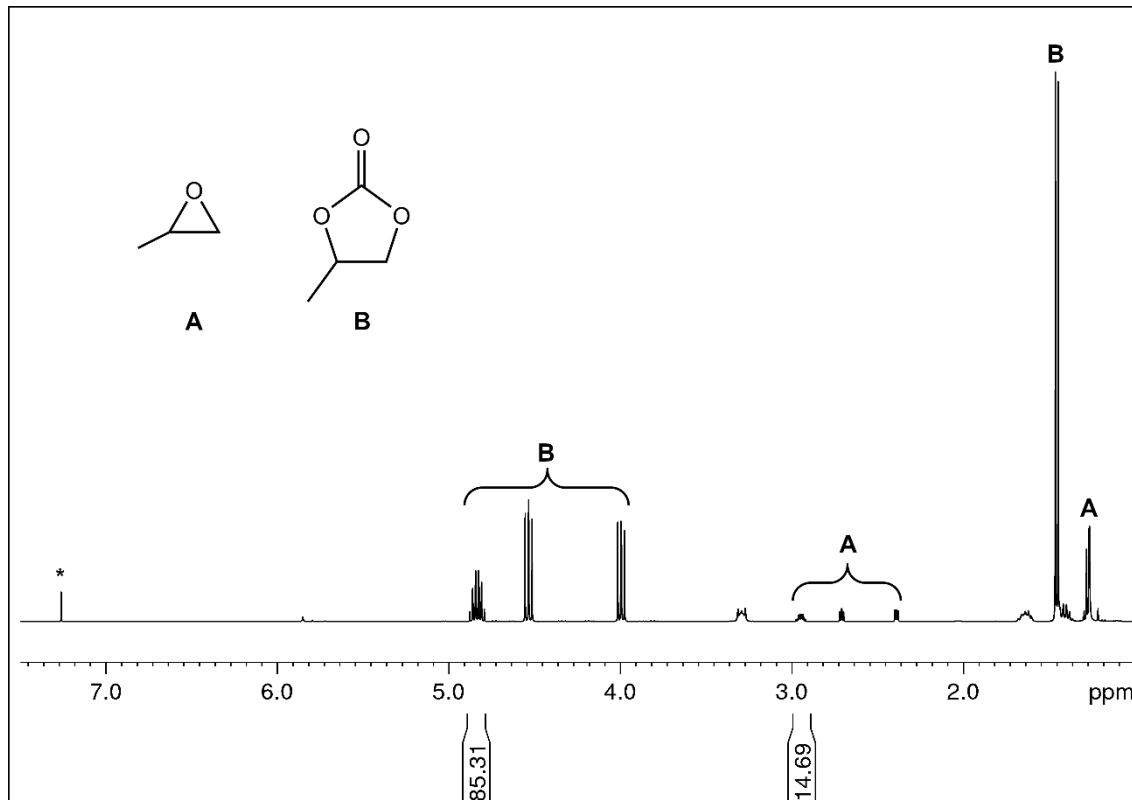


Figure C15. ^1H NMR spectrum (26 °C, 400.11 MHz, $\text{chloroform-}d$) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Zn}(\text{pz}^{\text{tBu}_2})_2(\text{Hpz}^{\text{tBu}_2})_2$ (**Y**) as catalyst.

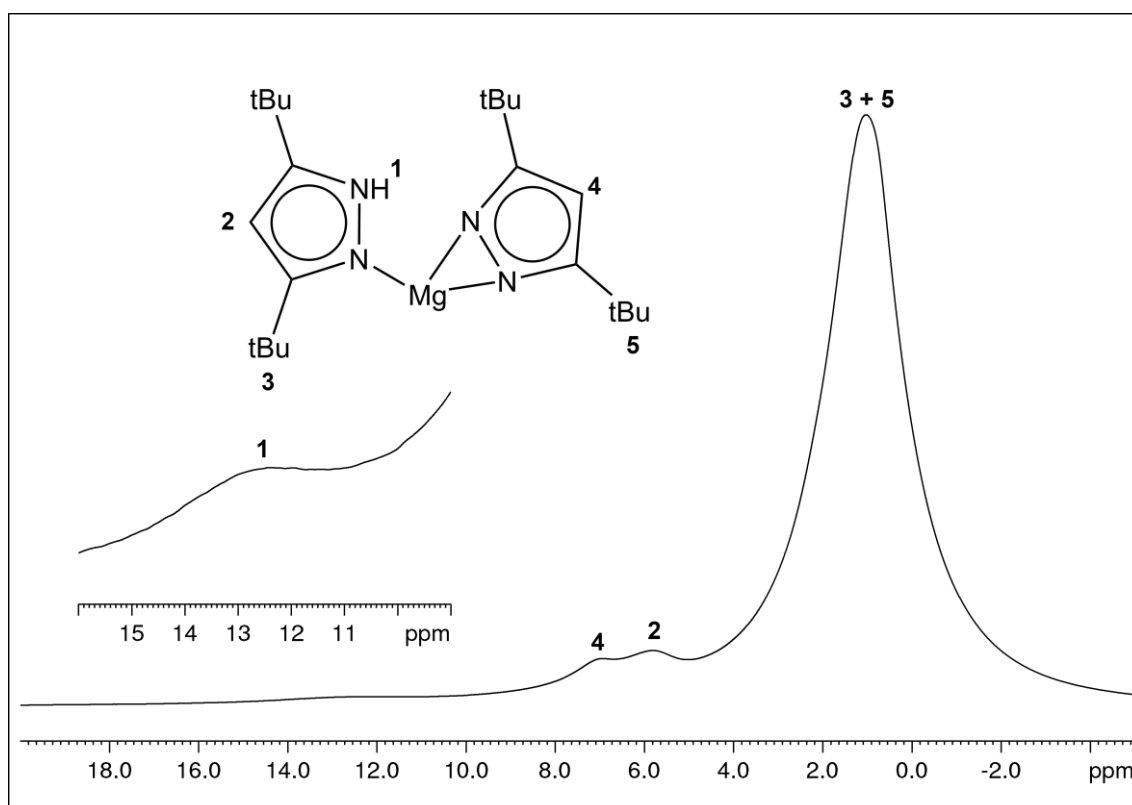


Figure C16. ^1H MAS NMR spectrum (300.13 MHz, MAS at 8 kHz) of $[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]@ \text{SBA-15}_{500}$ (**C@SBA-15**).

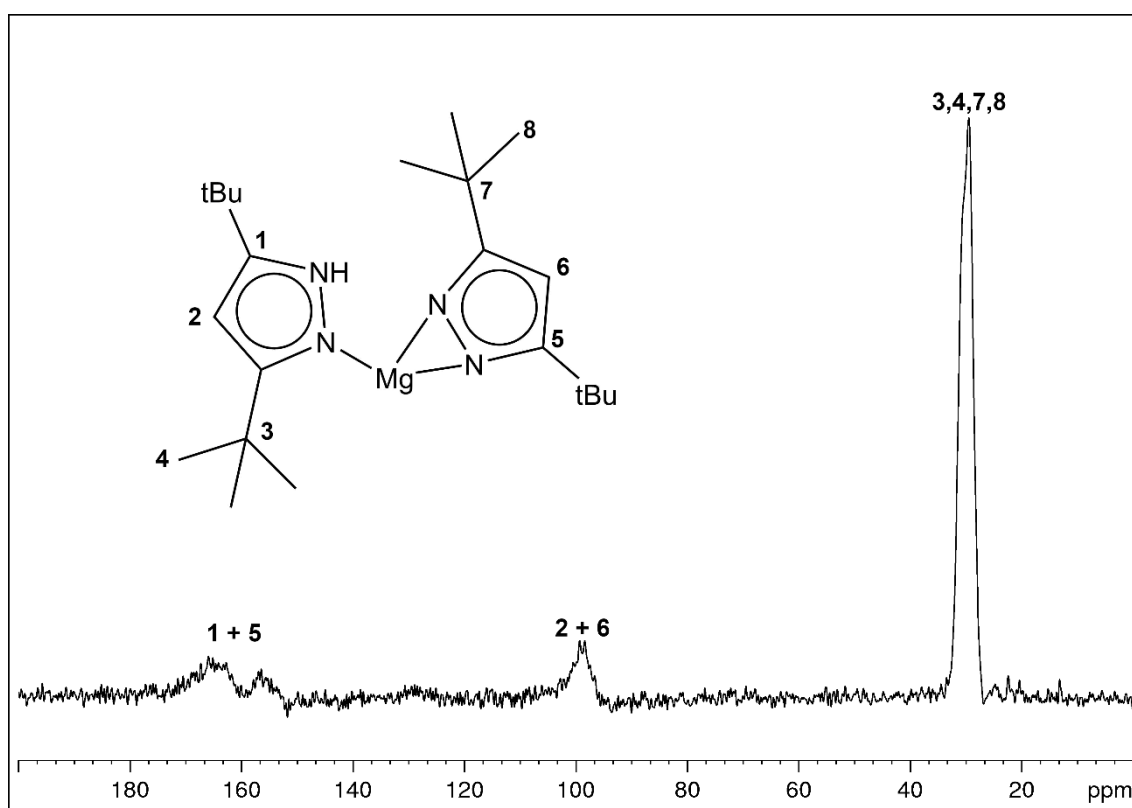


Figure C17. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]@ \text{SBA-15}_{500}$ (**C@SBA-15**).

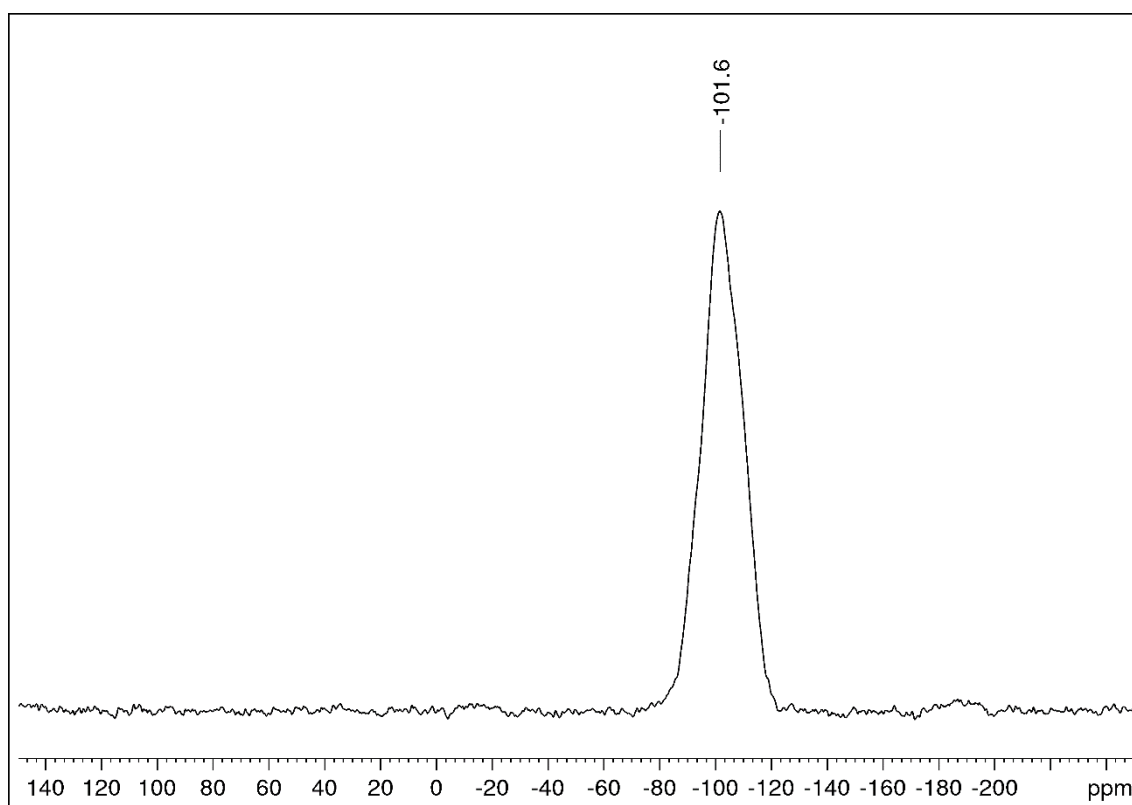


Figure C18. ^{29}Si CP/MAS NMR spectrum (59.63 MHz, MAS at 5 kHz) of $[\text{Mg}(\text{pz}^{t\text{Bu}_2})_2]_2@ \text{SBA-15}_{500}$ (**C@SBA-15**).

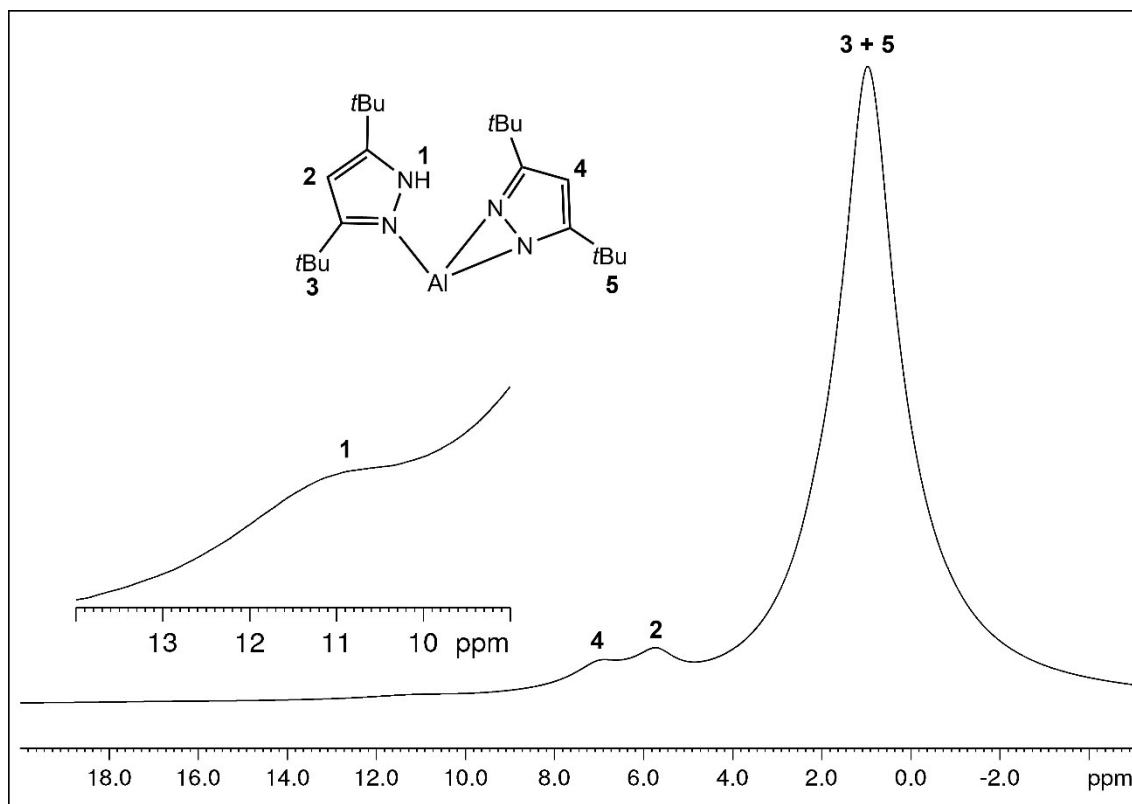


Figure C19. ^1H MAS NMR spectrum (300.13 MHz, MAS at 8 kHz) of $\text{Al}(\text{pz}^{t\text{Bu}_2})_3@ \text{SBA-15}_{500}$ (**E@SBA-15**).

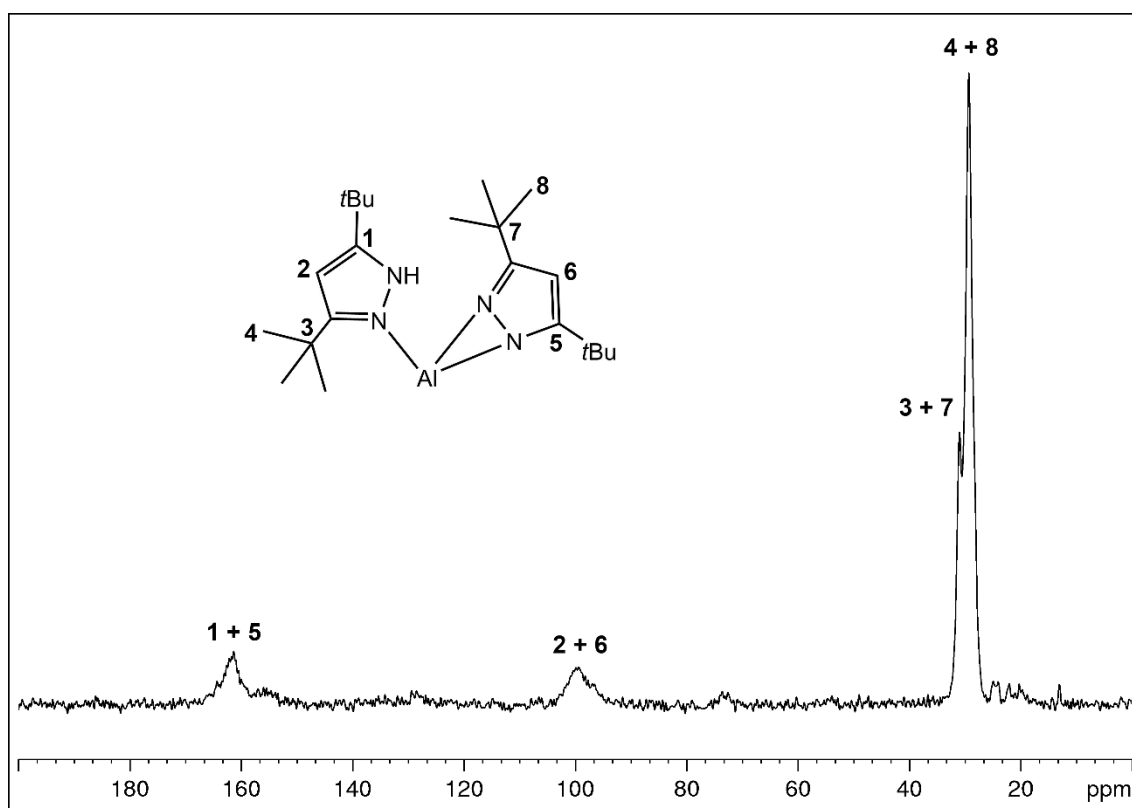


Figure C20. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $\text{Al}(\text{pz}^{\text{tBu}_2})_3@ \text{SBA-15}_{500}$ (**E@SBA-15**).

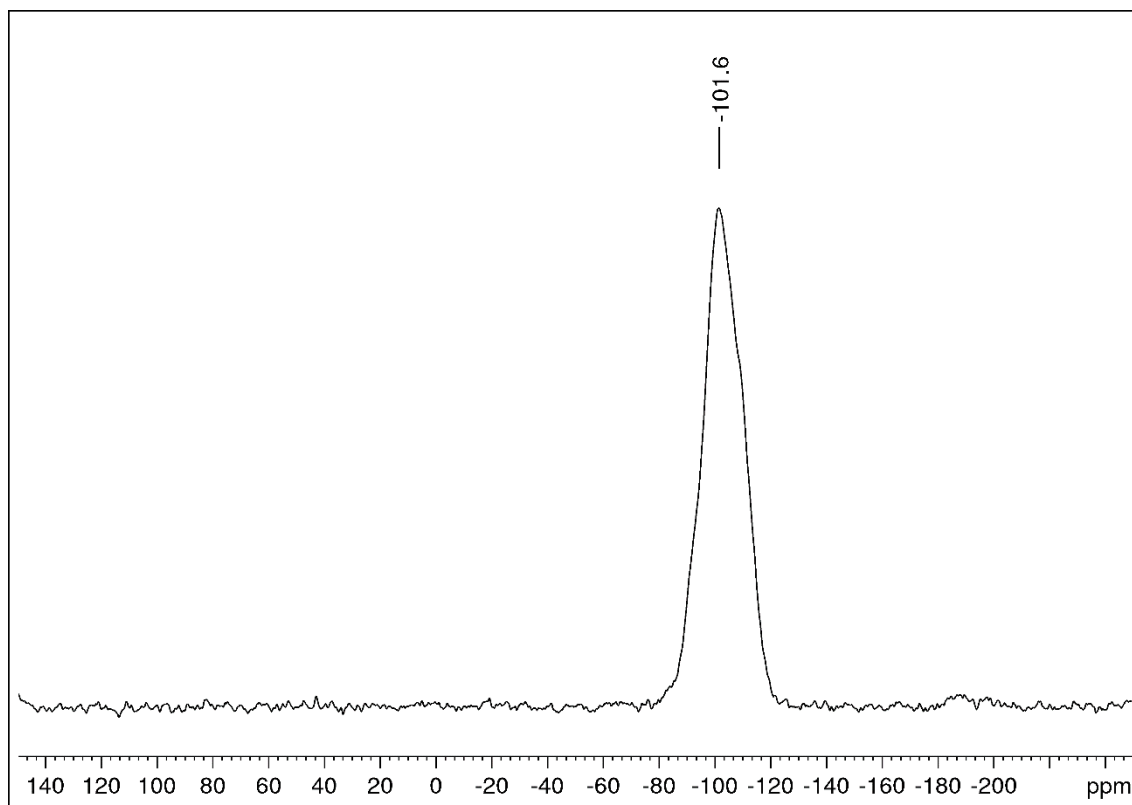


Figure C21. ^{29}Si CP/MAS NMR spectrum (59.63 MHz, MAS at 5 kHz) of $\text{Al}(\text{pz}^{\text{tBu}_2})_3@ \text{SBA-15}_{500}$ (**E@SBA-15**).

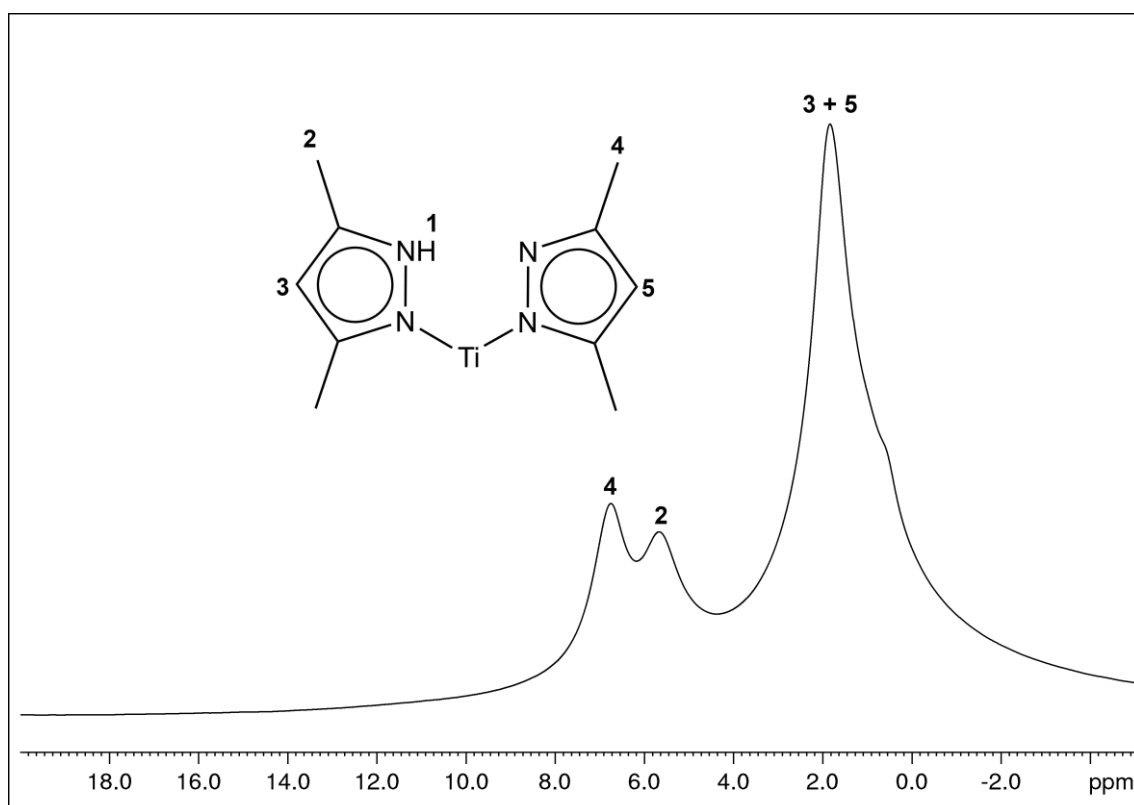


Figure C22. ^1H MAS NMR spectrum (300.13 MHz, MAS at 8 kHz) of $\text{Ti}(\text{pz}^{\text{Me}_2})_4@ \text{SBA-15}_{500}$ (F@SBA-15).

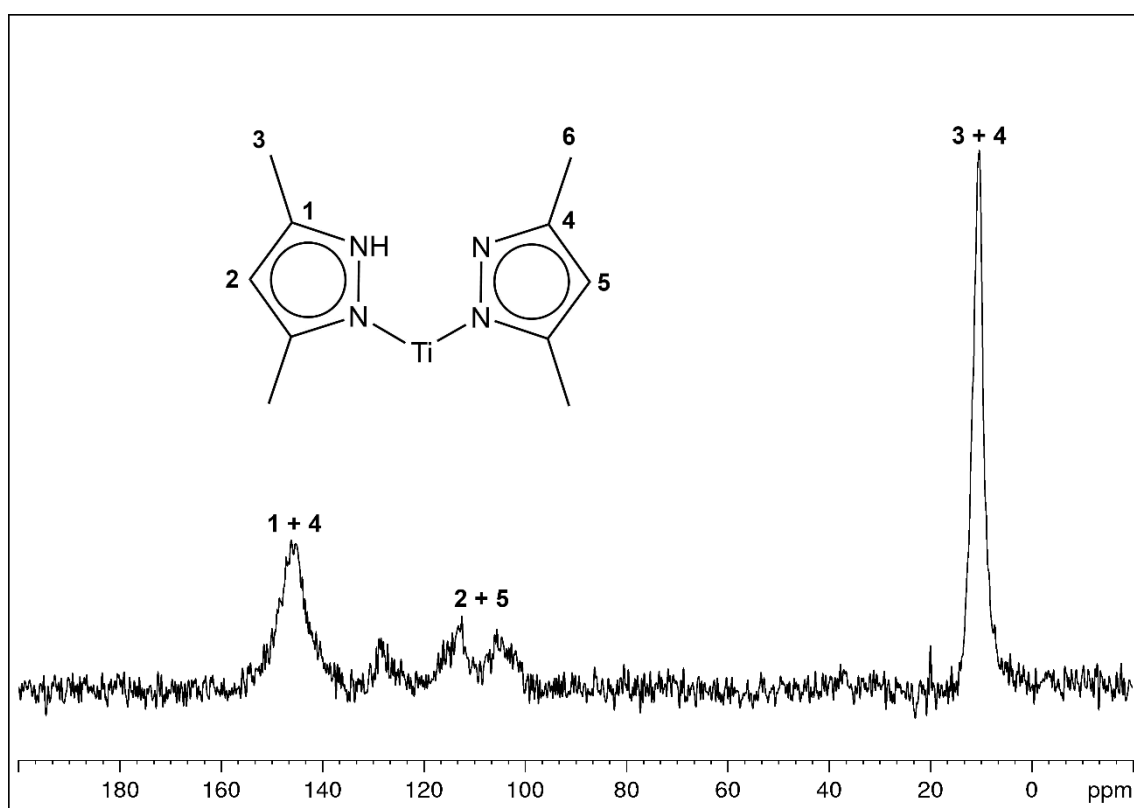


Figure C23. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $\text{Ti}(\text{pz}^{\text{Me}_2})_4@ \text{SBA-15}_{500}$ (F@SBA-15).

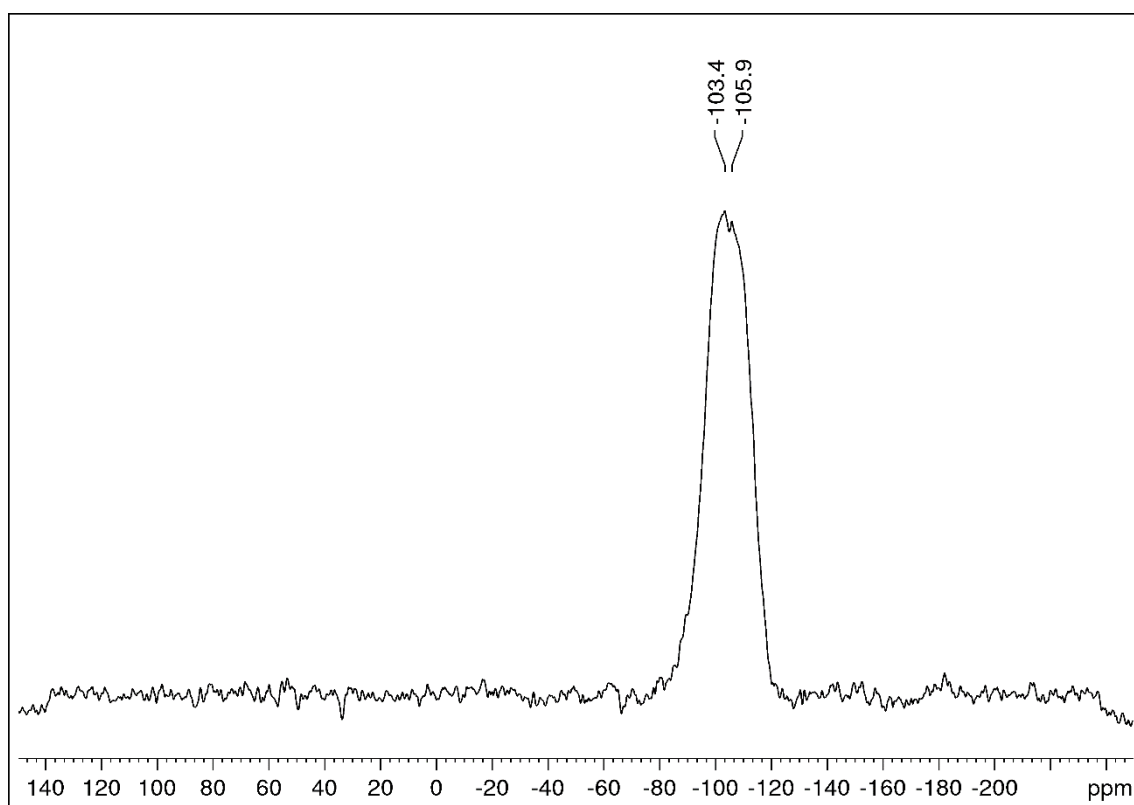


Figure C24. ^{29}Si CP/MAS NMR spectrum (59.63 MHz, MAS at 5 kHz) of $\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ (**F@SBA-15**).

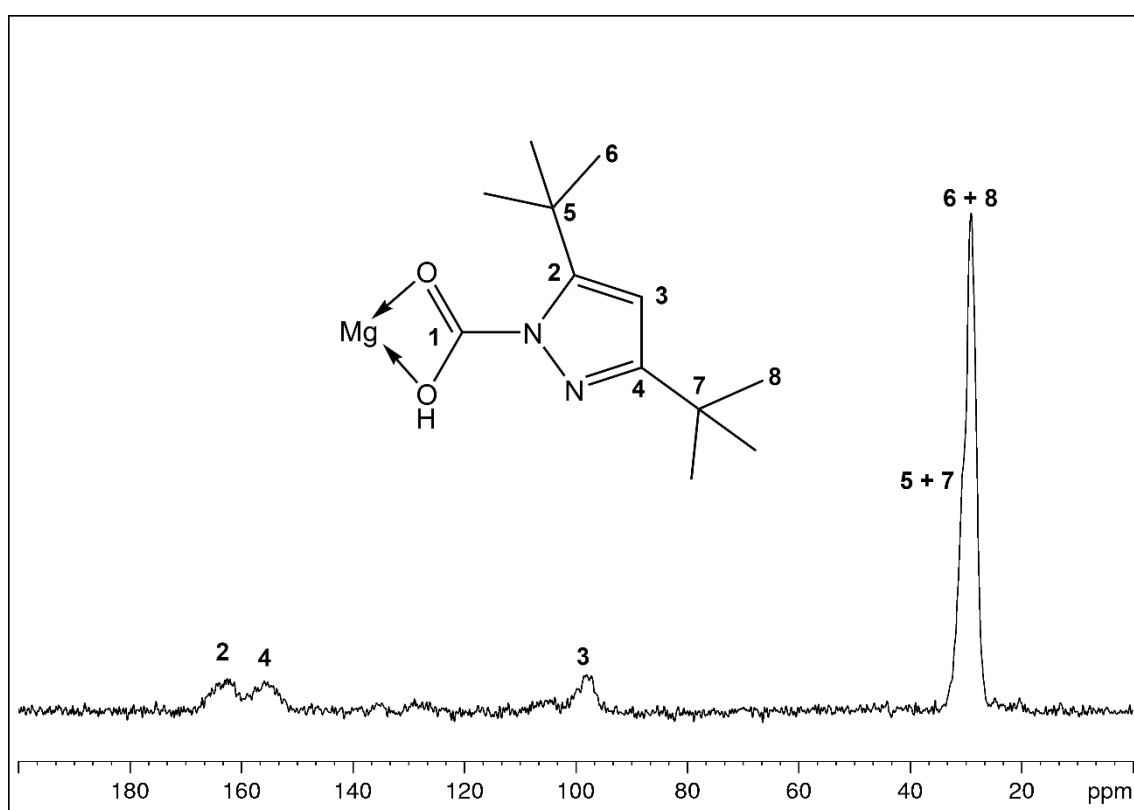


Figure C25. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $\text{CO}_2@[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ (**$\text{CO}_2@\text{C@SBA-15}$**).

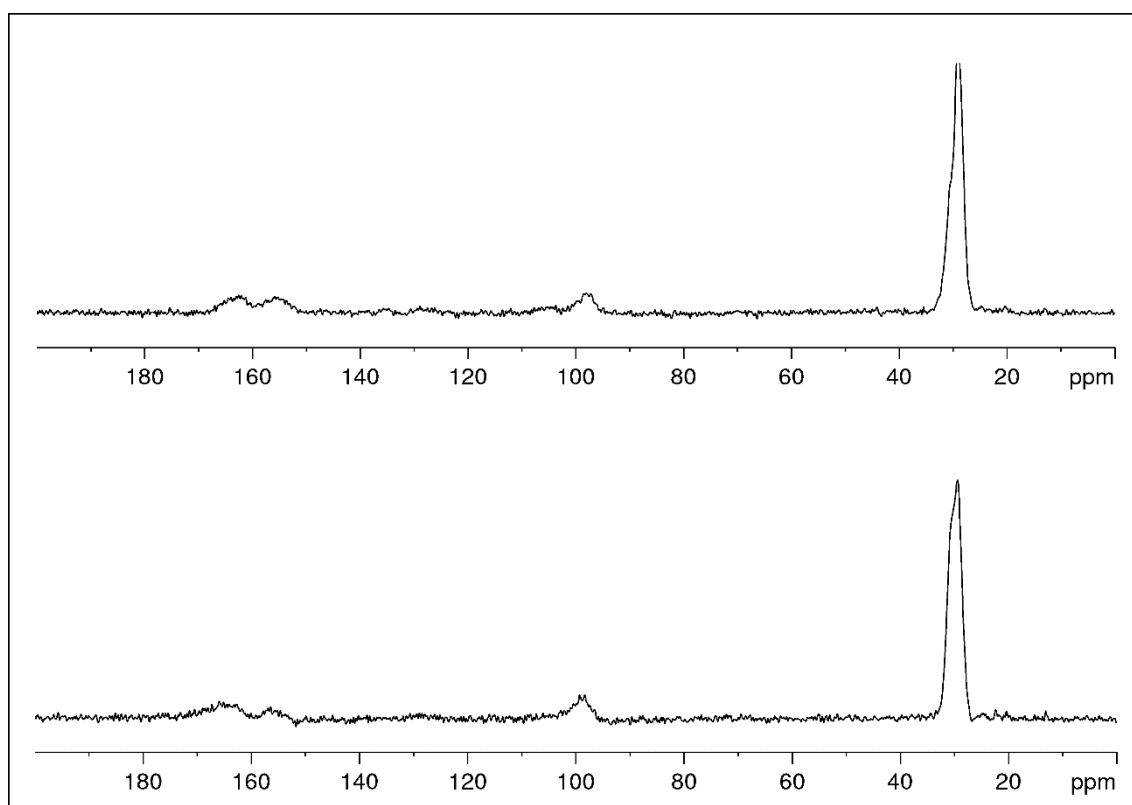


Figure C26. Comparison of ^{13}C CP/MAS NMR spectra (75.47 MHz, MAS at 8 kHz) of $[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ (**C@SBA-15**) and $\text{CO}_2@[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ (**CO₂@C@SBA-15**).

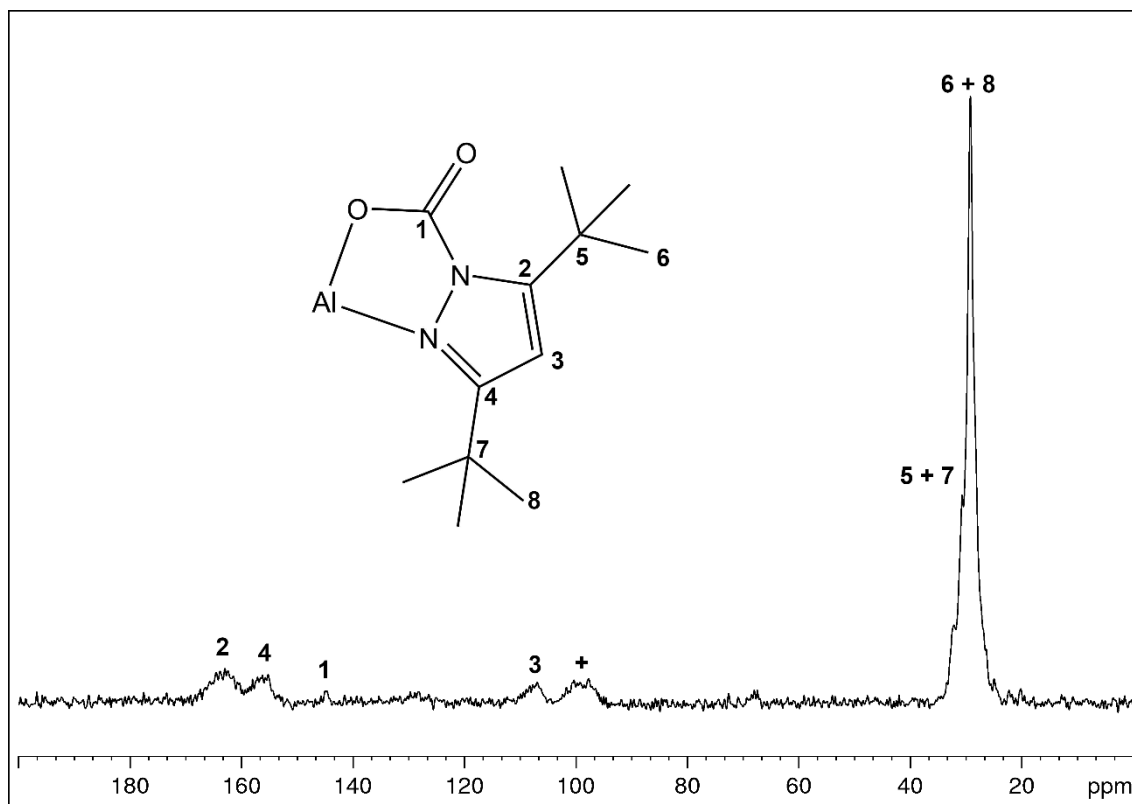


Figure C27. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $\text{CO}_2@\text{Al}(\text{pz}^{\text{tBu}_2})_3@\text{SBA-15}_{500}$ (**CO₂@E@SBA-15**).

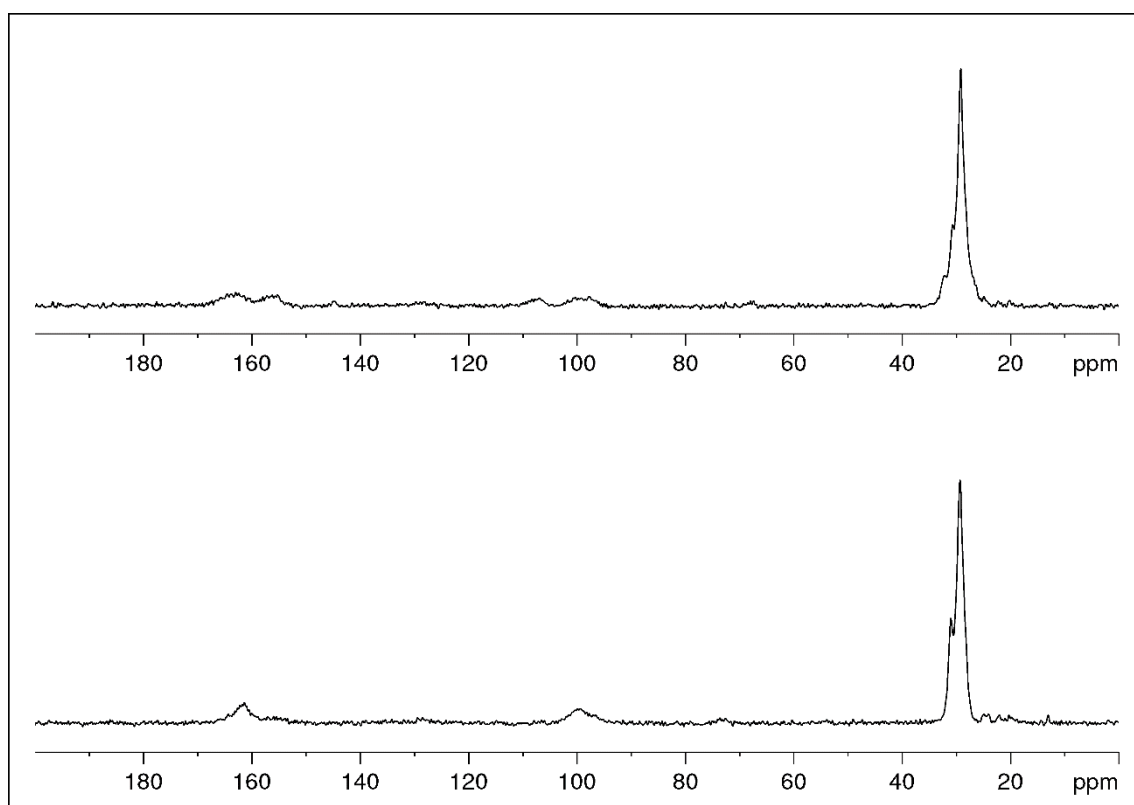


Figure C28. Comparison of ^{13}C CP/MAS NMR spectra (75.47 MHz, MAS at 8 kHz) of $\text{Al}(\text{pz}^{\text{tBu}_2})_3@ \text{SBA-15}_{500}$ (**E@SBA-15**) and $\text{CO}_2@ \text{Al}(\text{pz}^{\text{tBu}_2})_3@ \text{SBA-15}_{500}$ (**CO₂@E@SBA-15**).

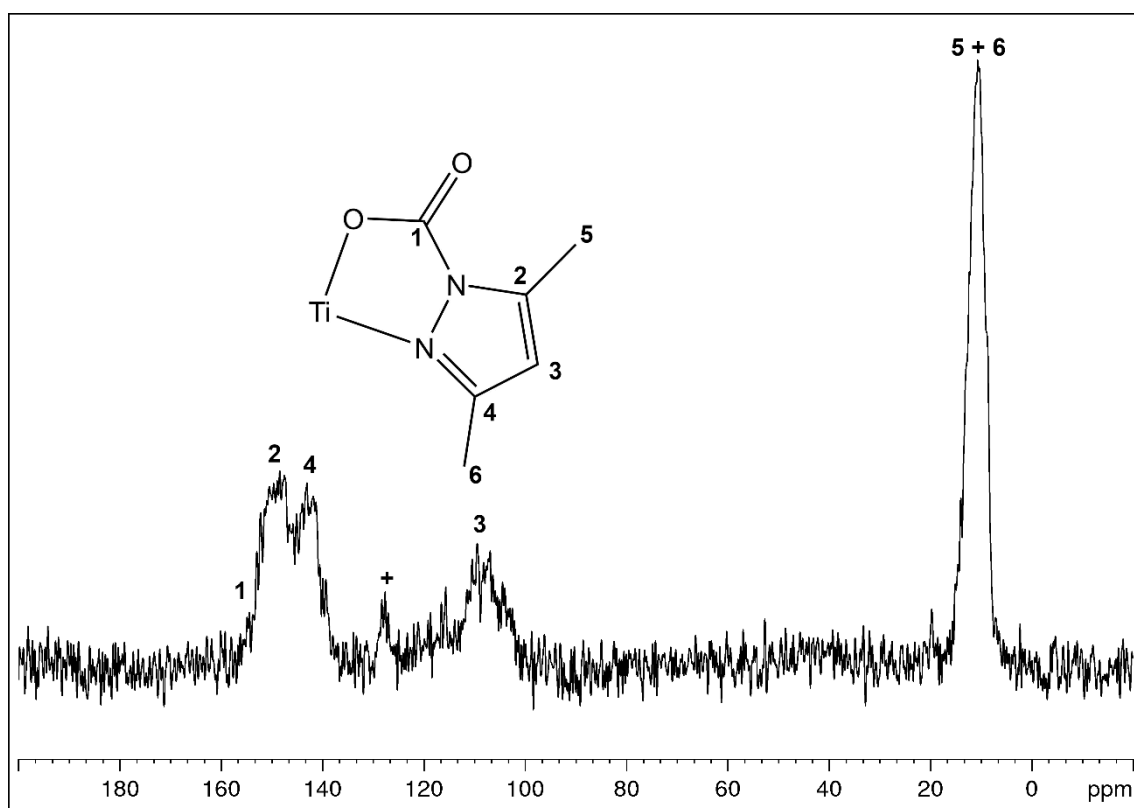


Figure C29. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $\text{CO}_2@ \text{Ti}(\text{pz}^{\text{Me}_2})_4@ \text{SBA-15}_{500}$ (**CO₂@F@SBA-15**).

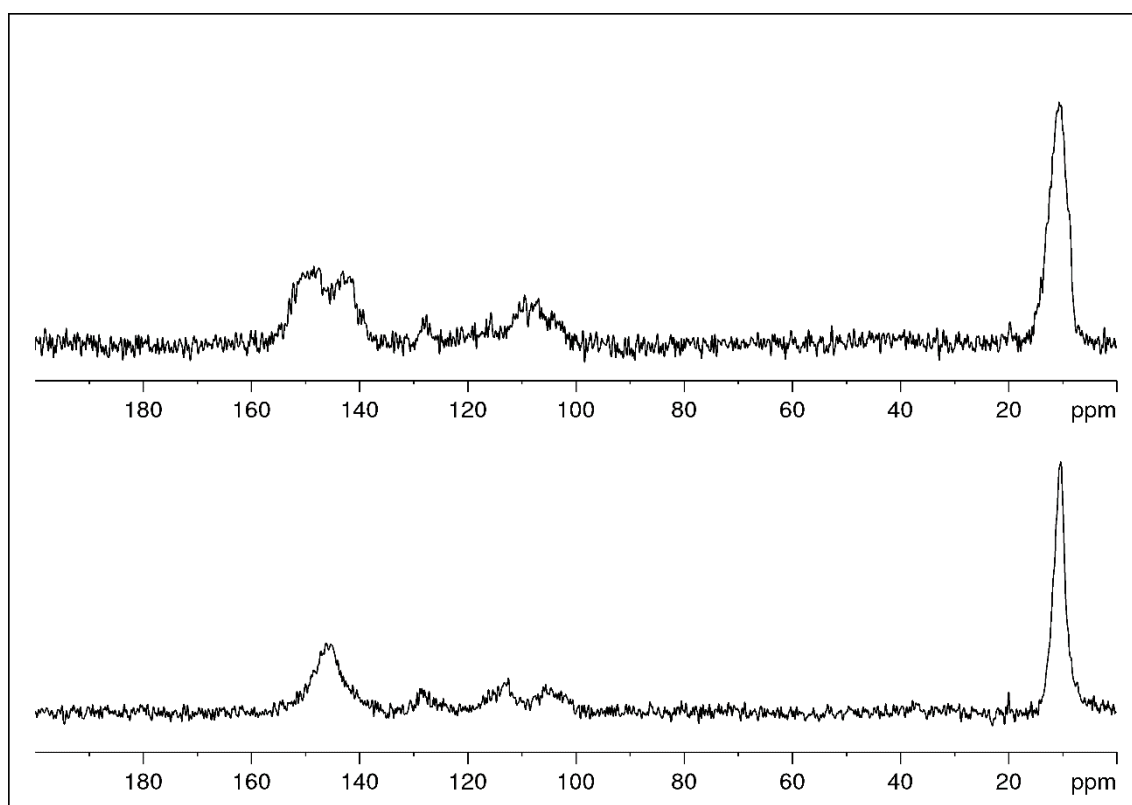


Figure C30. Comparison of ^{13}C CP/MAS NMR spectra (75.47 MHz, MAS at 8 kHz) of $\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ (**F@SBA-15**) and $\text{CO}_2@\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ (**CO₂@F@SBA-15**).

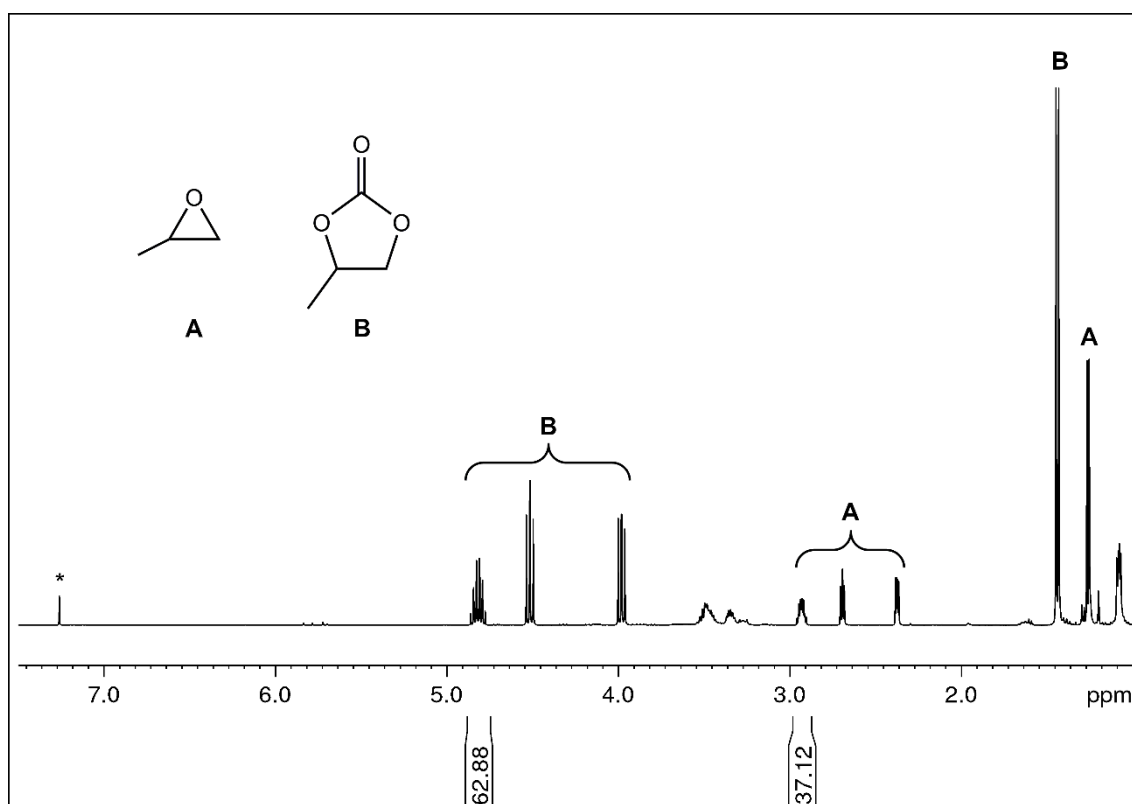


Figure C31. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ (**C@SBA-15**) as catalyst and TBAB as cocatalyst.

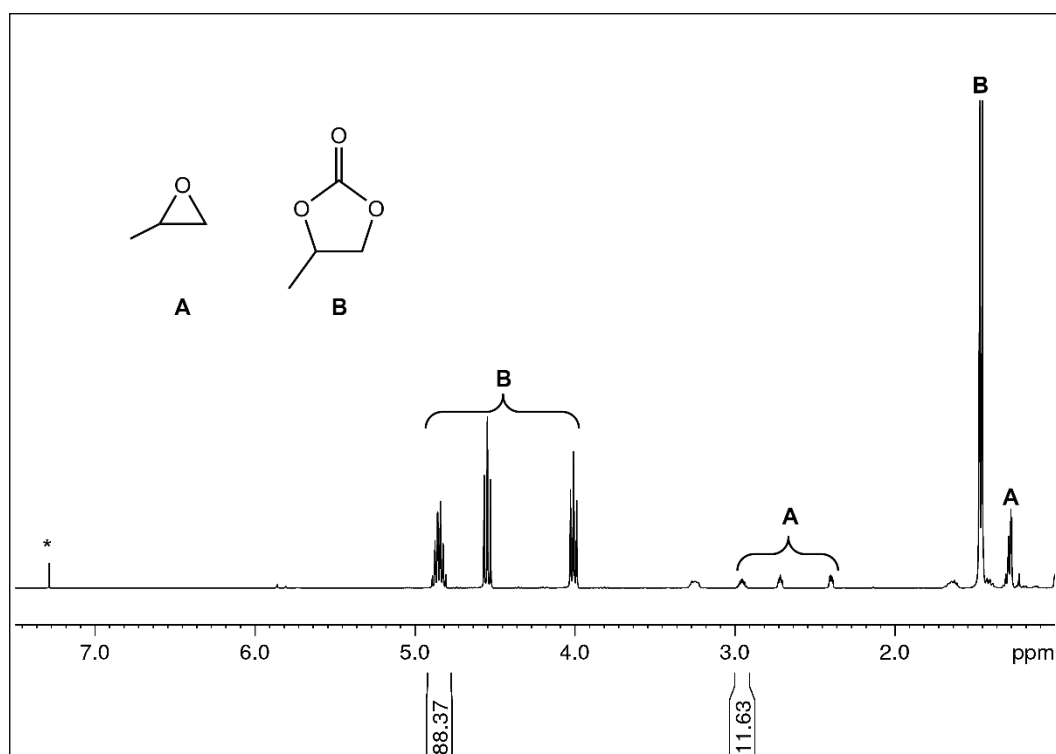


Figure C32. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.5 mol% of [Mg(pz^{*t*Bu₂})₂]₂@SBA-15₅₀₀ (C@SBA-15) as catalyst and TBAI as cocatalyst.

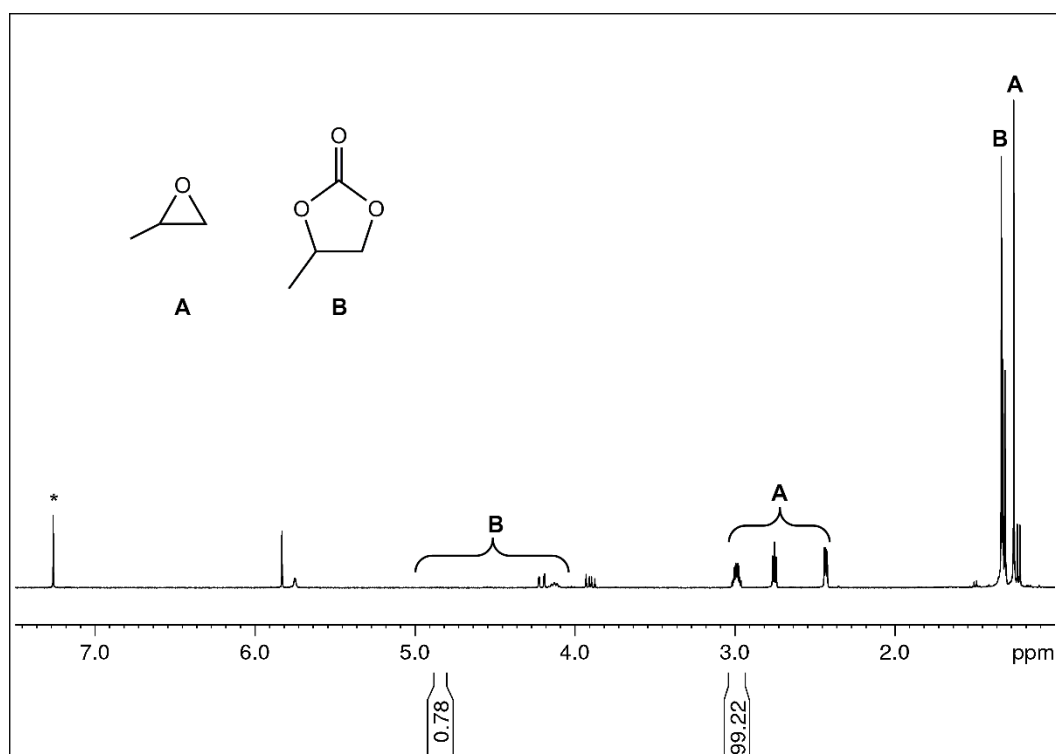


Figure C33. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.5 mol% of [Mg(pz^{*t*Bu₂})₂]₂@SBA-15₅₀₀ (C@SBA-15) as catalyst and without cocatalyst.

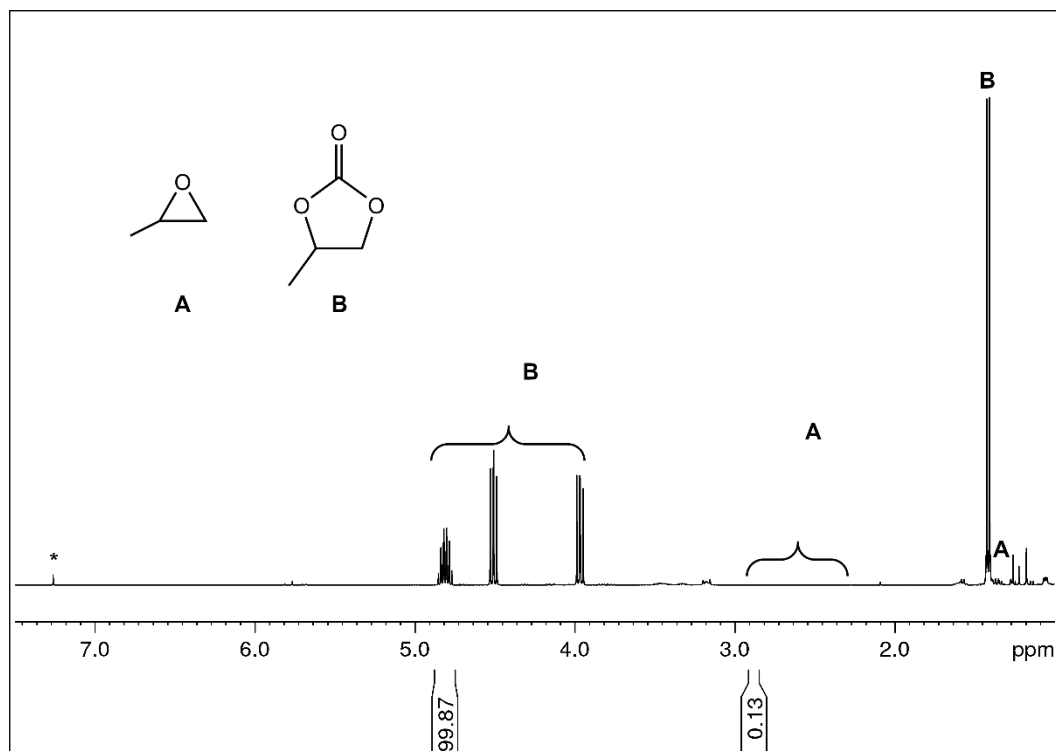


Figure C34. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ (**C@SBA-15**) as catalyst and TBAI as cocatalyst at 90 °C and 10 bar CO_2 .

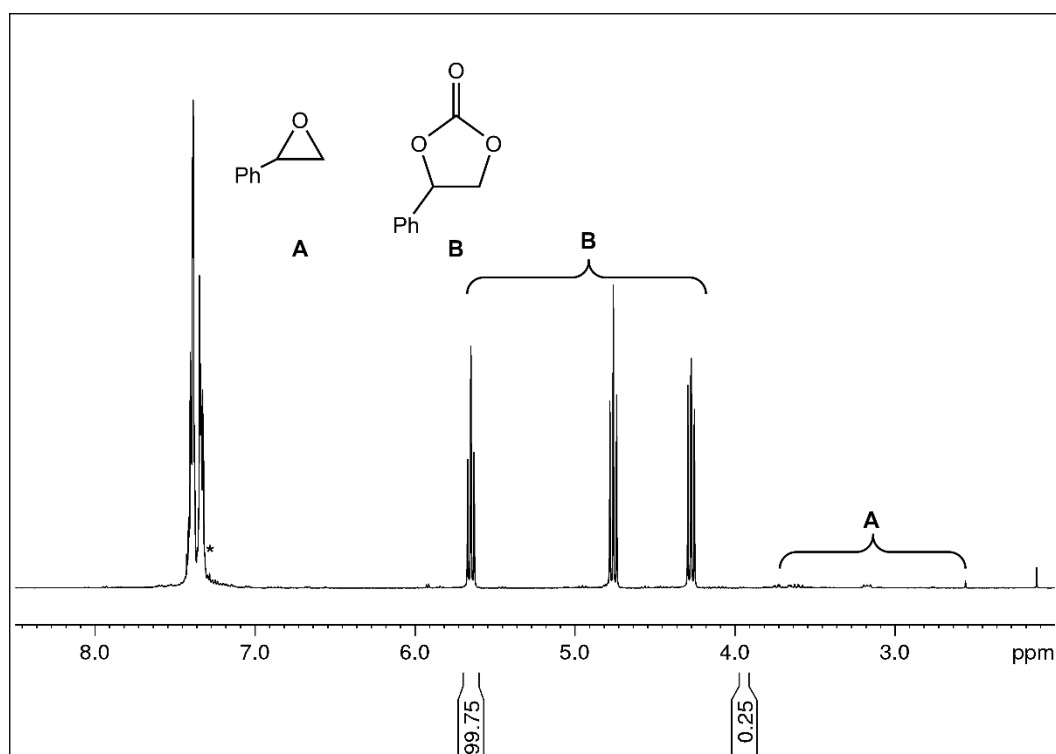


Figure C35. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of styrene oxide and CO_2 to styrene carbonate by using 0.5 mol% of $[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ (**C@SBA-15**) as catalyst and TBAI as cocatalyst at 90 °C and 10 bar CO_2 .

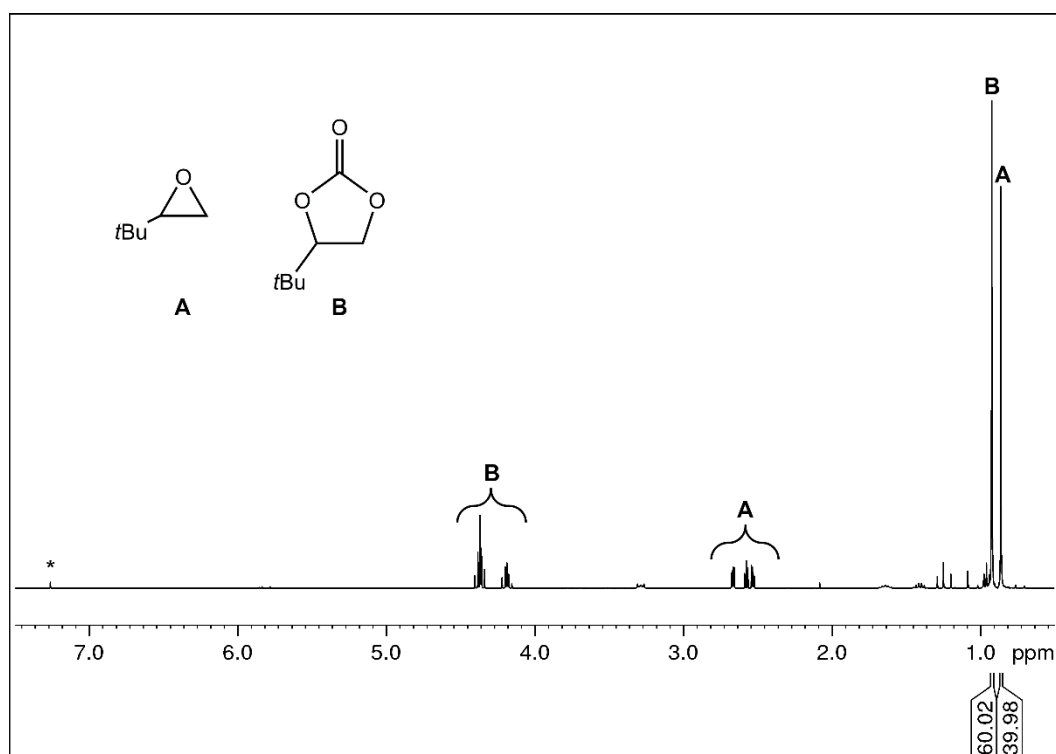


Figure C36. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% of $[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ (**C@SBA-15**) as catalyst and TBAI as cocatalyst at 90 °C and 10 bar CO_2 .

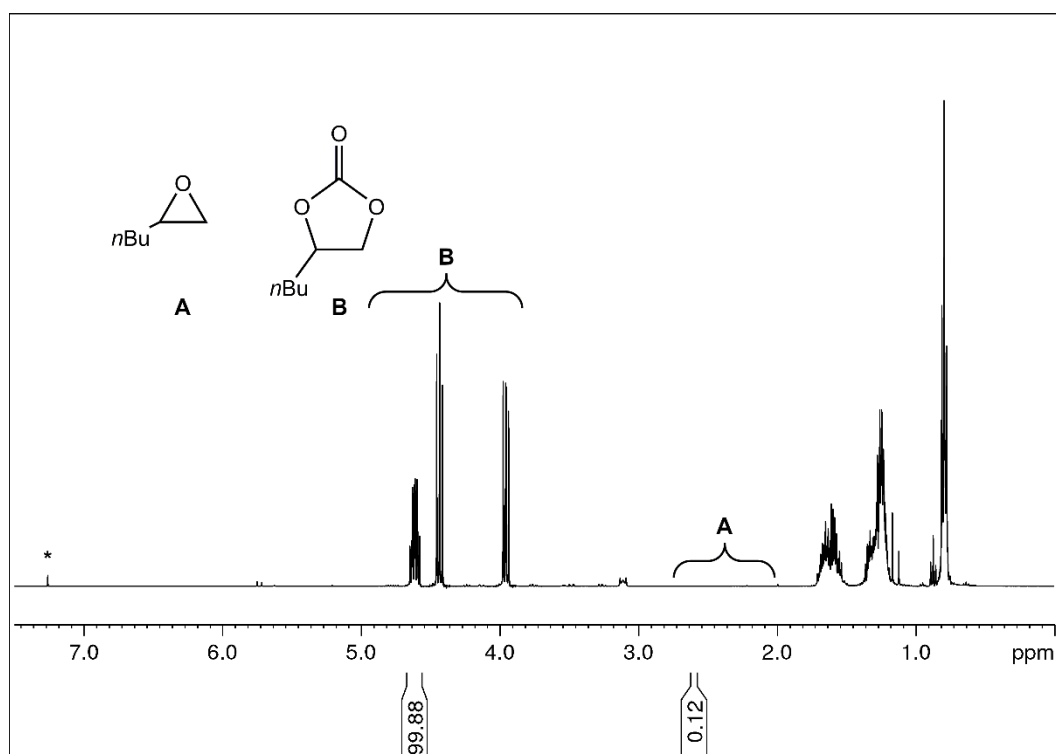


Figure C37. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO_2 to 1,2-*n*-hexylene carbonate by using 0.5 mol% of $[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ (**C@SBA-15**) as catalyst and TBAI as cocatalyst at 90 °C and 10 bar CO_2 .

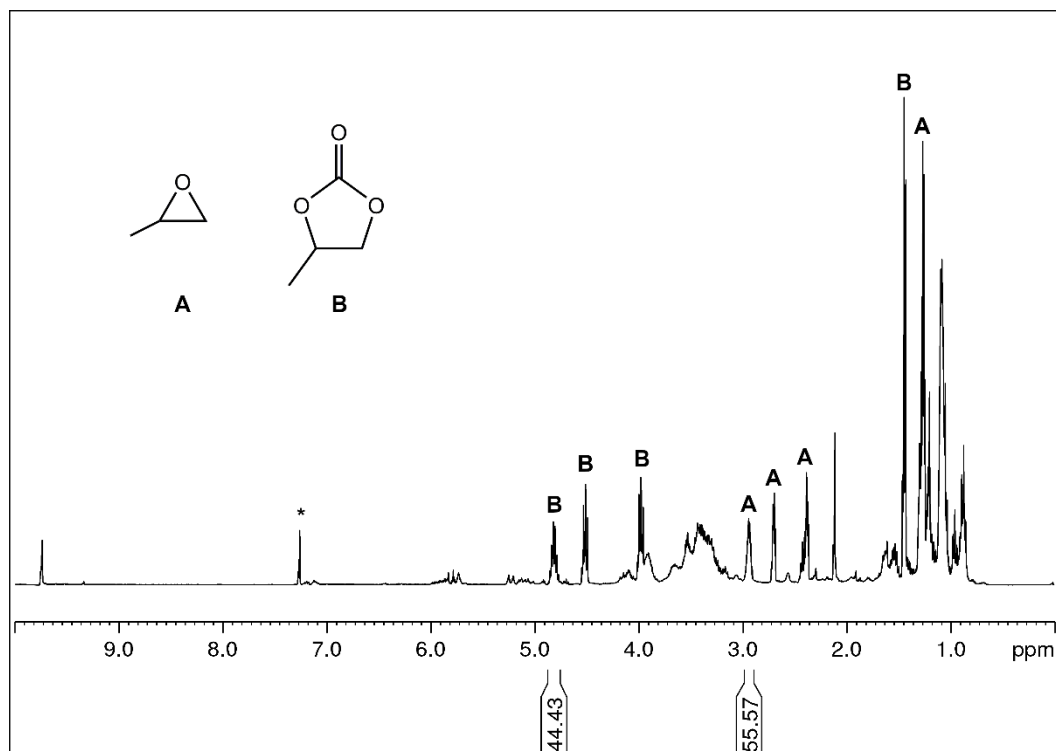


Figure C38. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Al}(\text{pz}^{\text{tBu}_2})_3@ \text{SBA-15}_{500}$ (**E@SBA-15**) as catalyst and TBAB as cocatalyst.

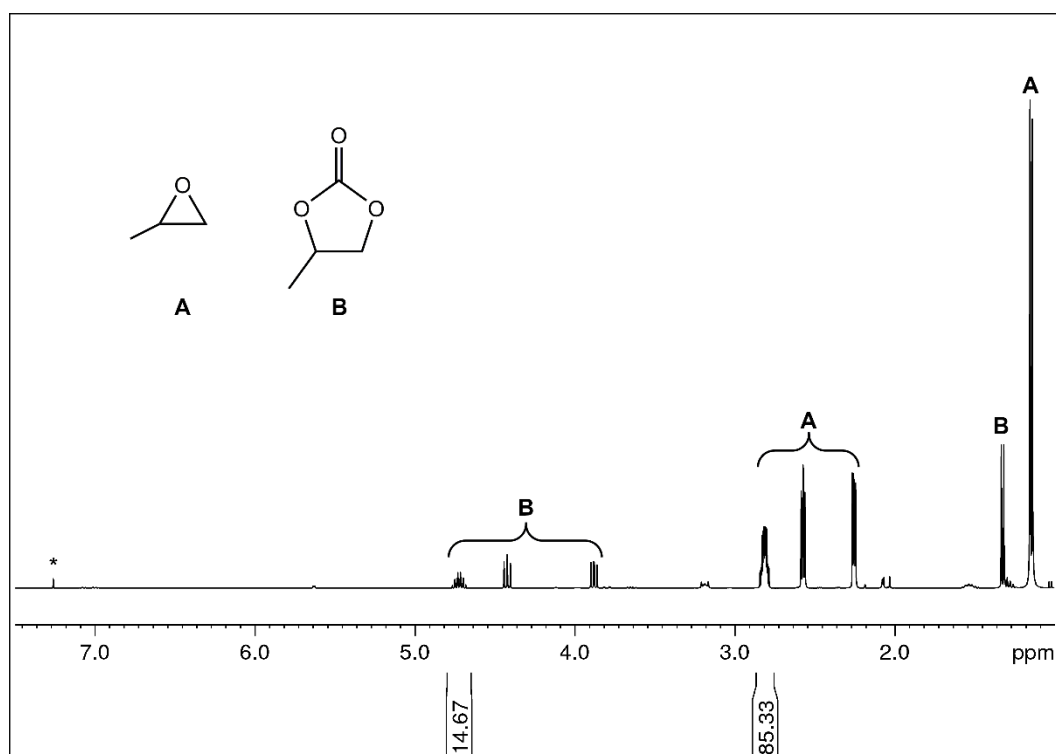


Figure C39. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Ti}(\text{pz}^{\text{Me}_2})_4@ \text{SBA-15}_{500}$ (**F@SBA-15**) as catalyst and TBAB as cocatalyst.

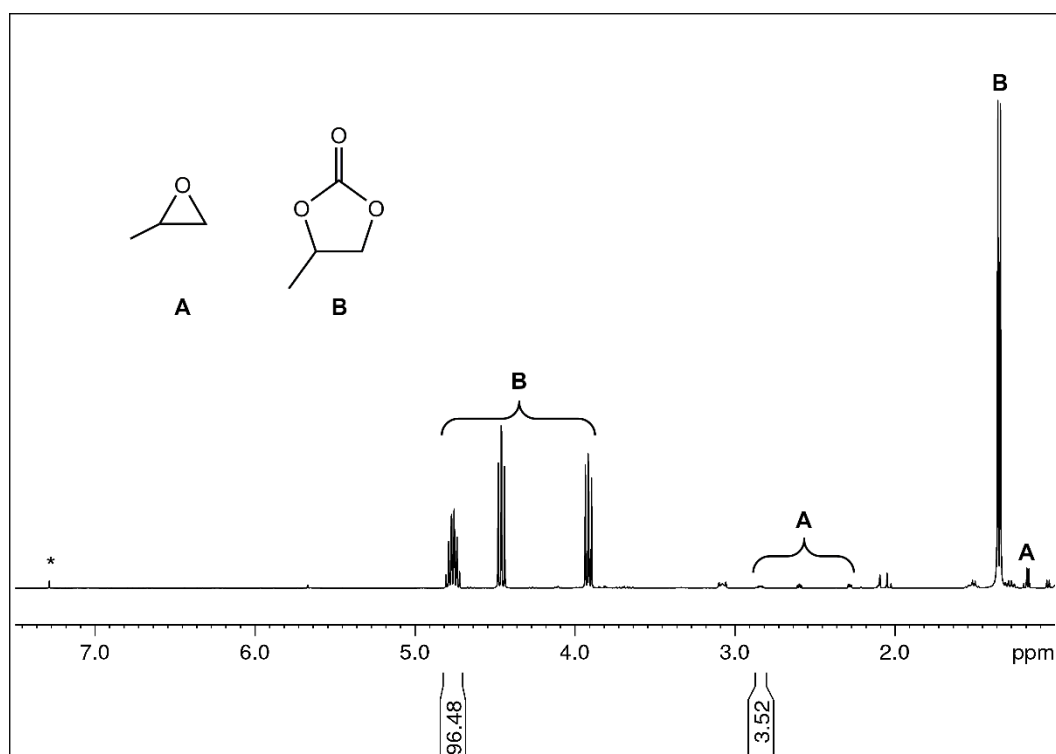


Figure C40. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.5 mol% of Ti(pz^{Me2})₄@SBA-15₅₀₀ (**F@SBA-15**) as catalyst and TBAI as cocatalyst at 90 °C and 10 bar CO₂.

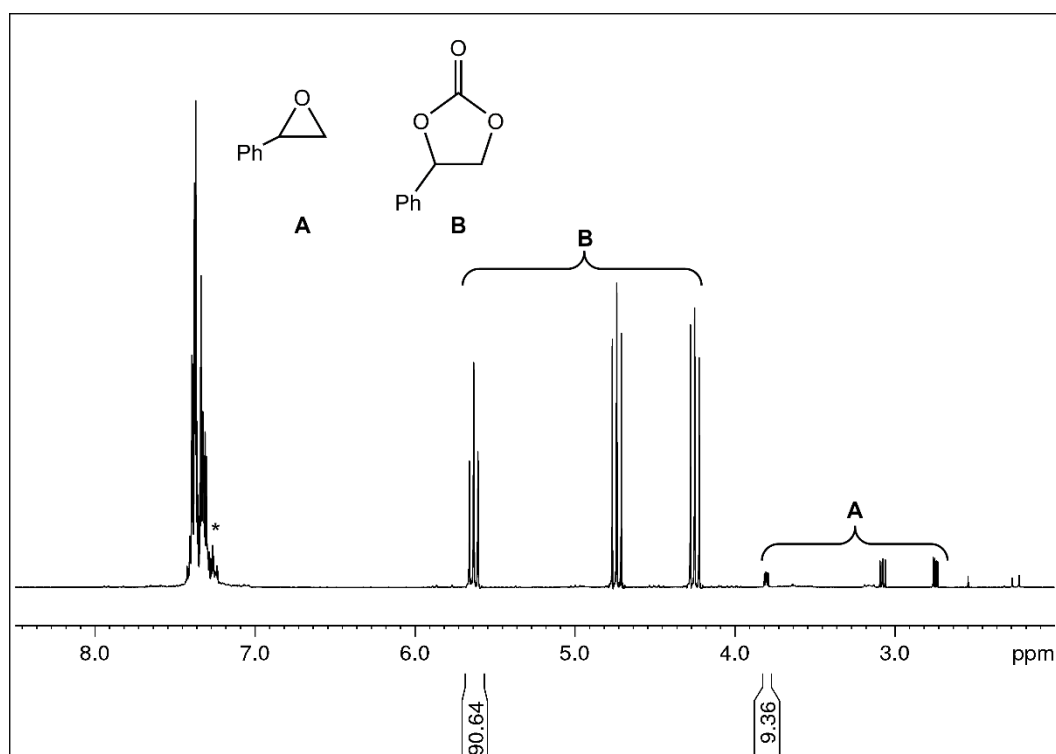


Figure C41. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of styrene oxide and CO₂ to styrene carbonate by using 0.5 mol% of Ti(pz^{Me2})₄@SBA-15₅₀₀ (**F@SBA-15**) as catalyst and TBAI as cocatalyst at 90 °C and 10 bar CO₂.

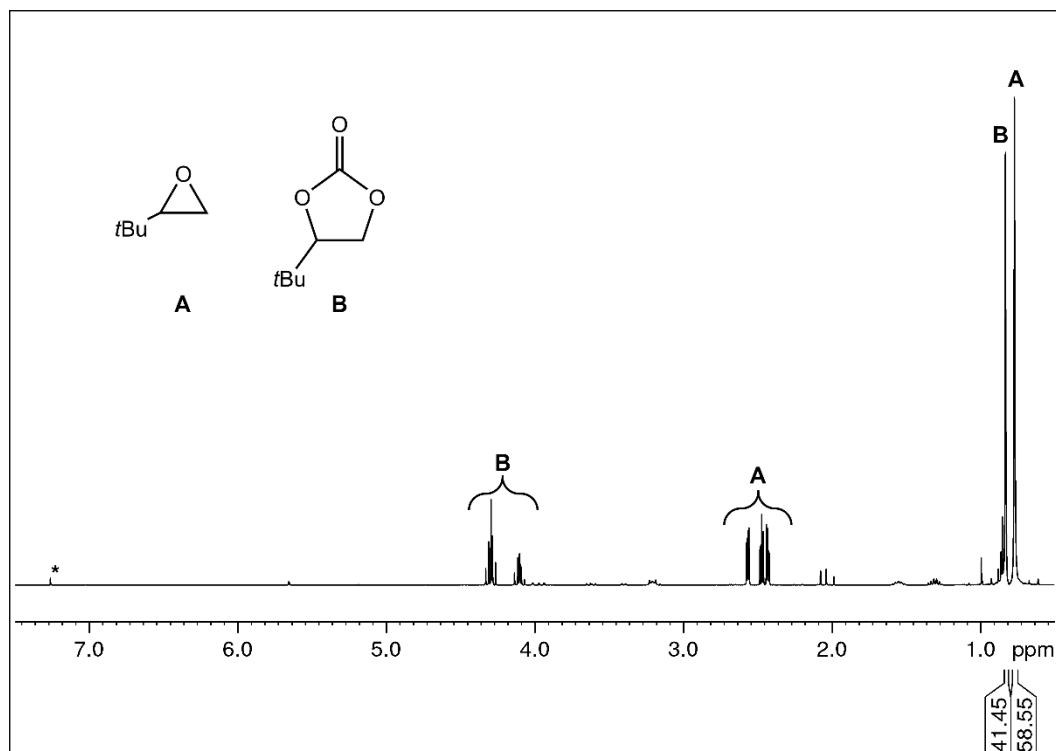


Figure C42. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% of $\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ (**F@SBA-15**) as catalyst and TBAI as cocatalyst at 90 °C and 10 bar CO_2 .

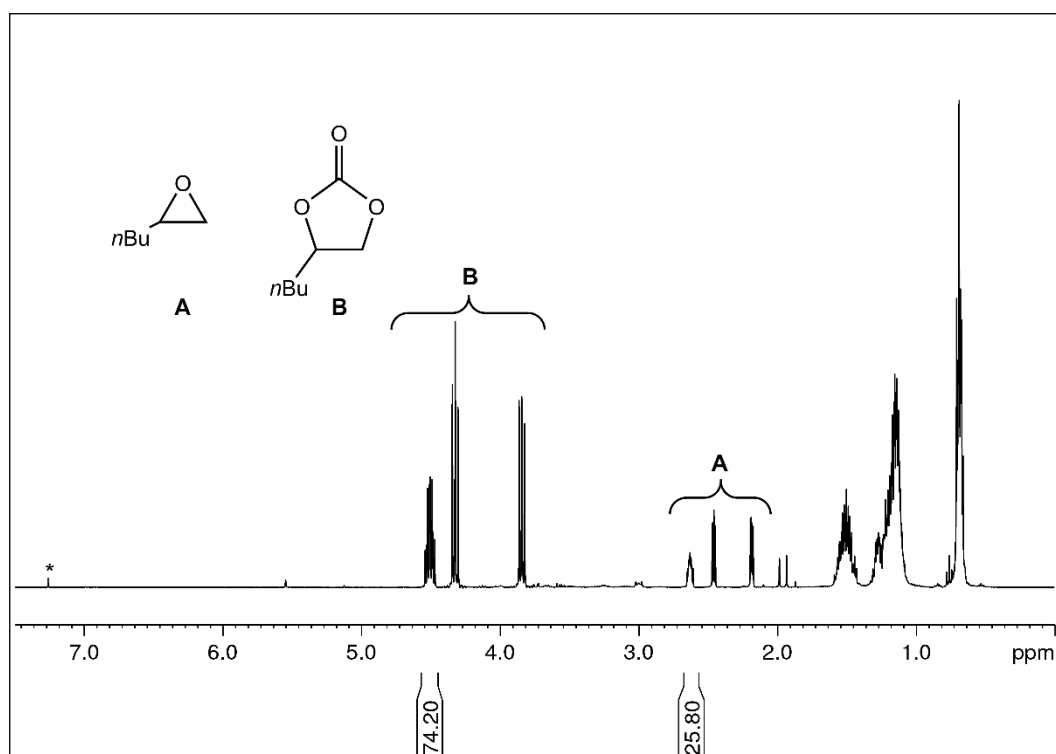


Figure C43. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO_2 to 1,2-*n*-hexylene carbonate by using 0.5 mol% of $\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ (**F@SBA-15**) as catalyst and TBAI as cocatalyst at 90 °C and 10 bar CO_2 .

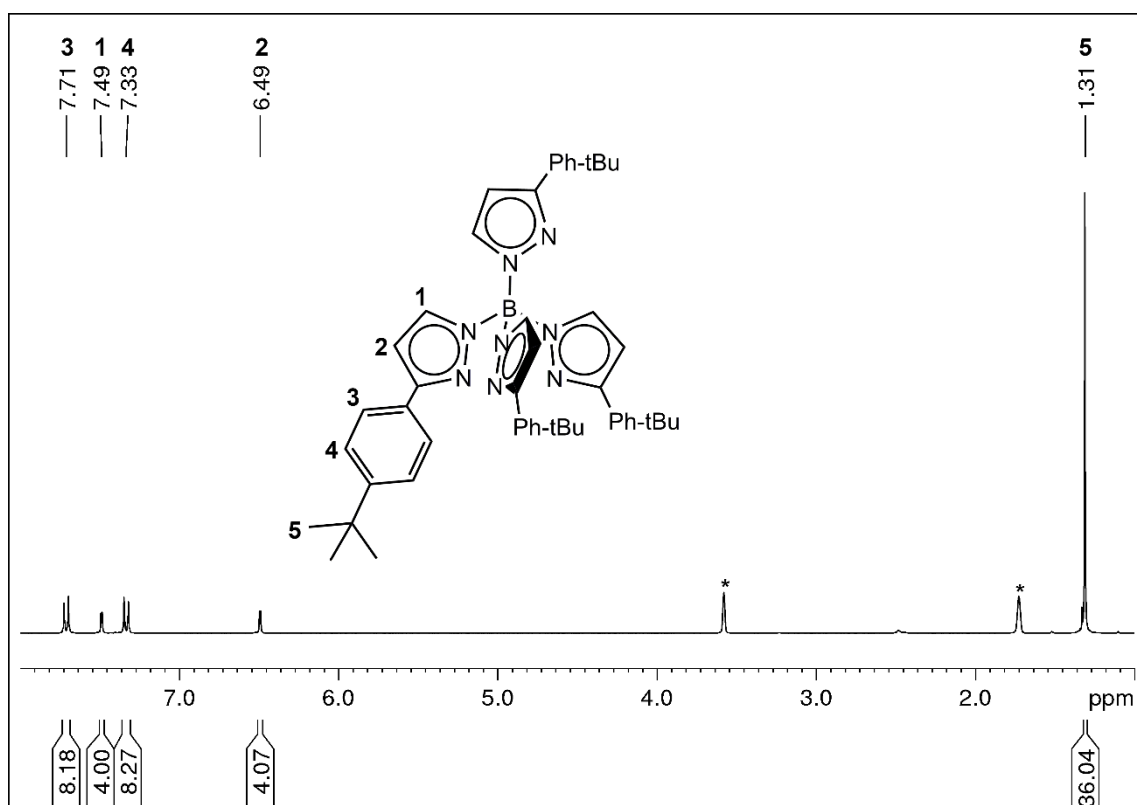


Figure C44. 1H NMR spectrum (26 °C, 400.11 MHz, $[D_8]THF$) of $[K(B\{pz^{3-p-tBuPh}\}_4)]_\infty$ (III).

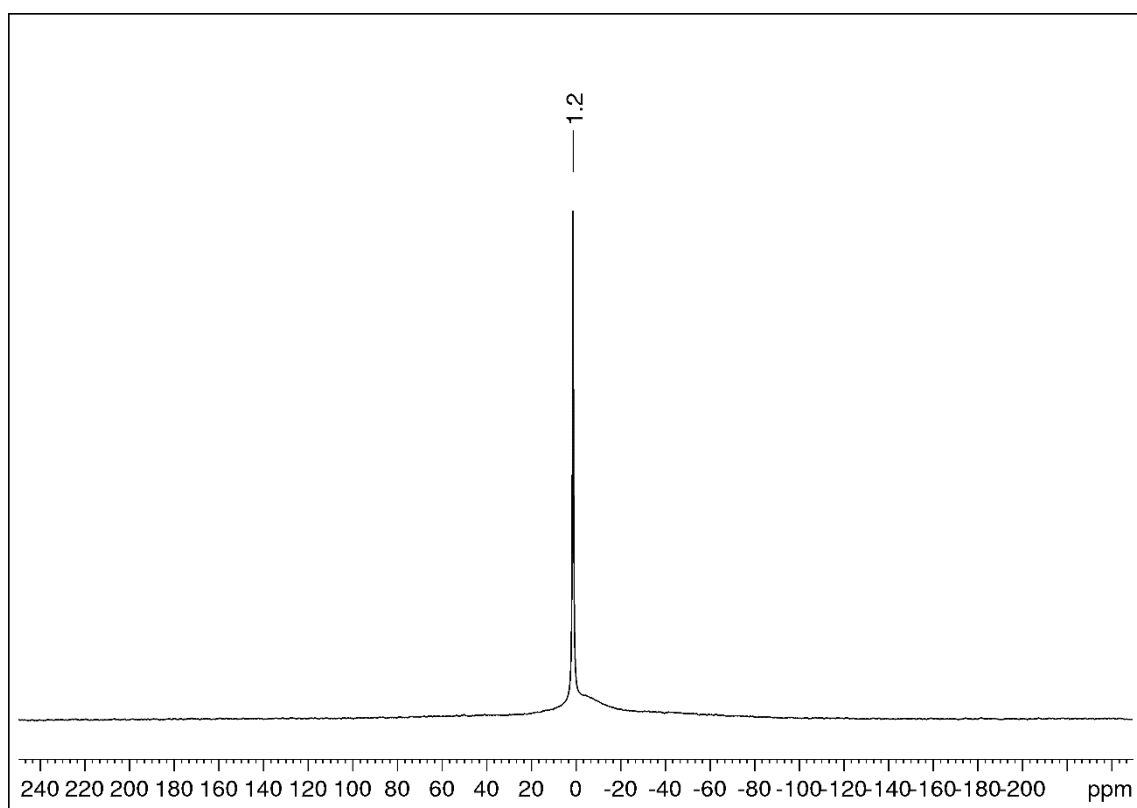


Figure C45. ^{11}B NMR spectrum (26 °C, 96.29 MHz, $[D_8]THF$) of $[K(B\{pz^{3-p-tBuPh}\}_4)]_\infty$ (III).

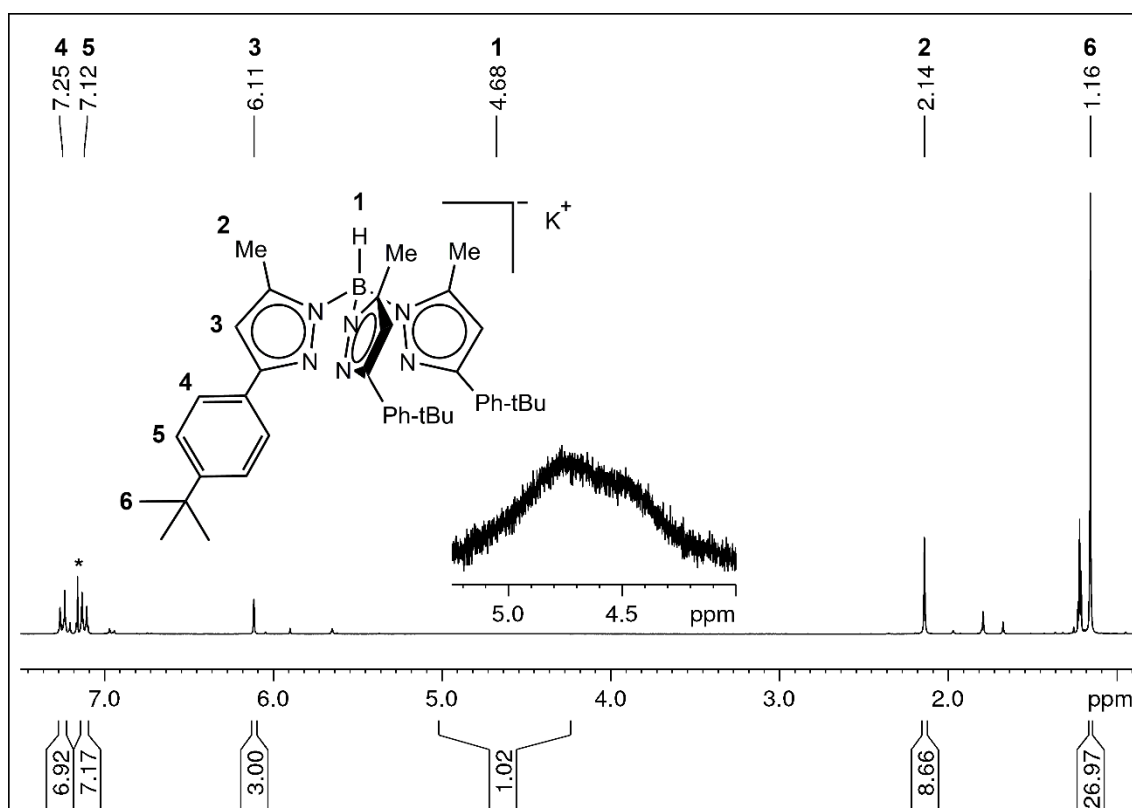


Figure C46. ^1H NMR spectrum (26 °C, 400.11 MHz, C_6D_6) of $\text{KTp}^{p\text{-}t\text{BuPh,Me}}$ (IV).

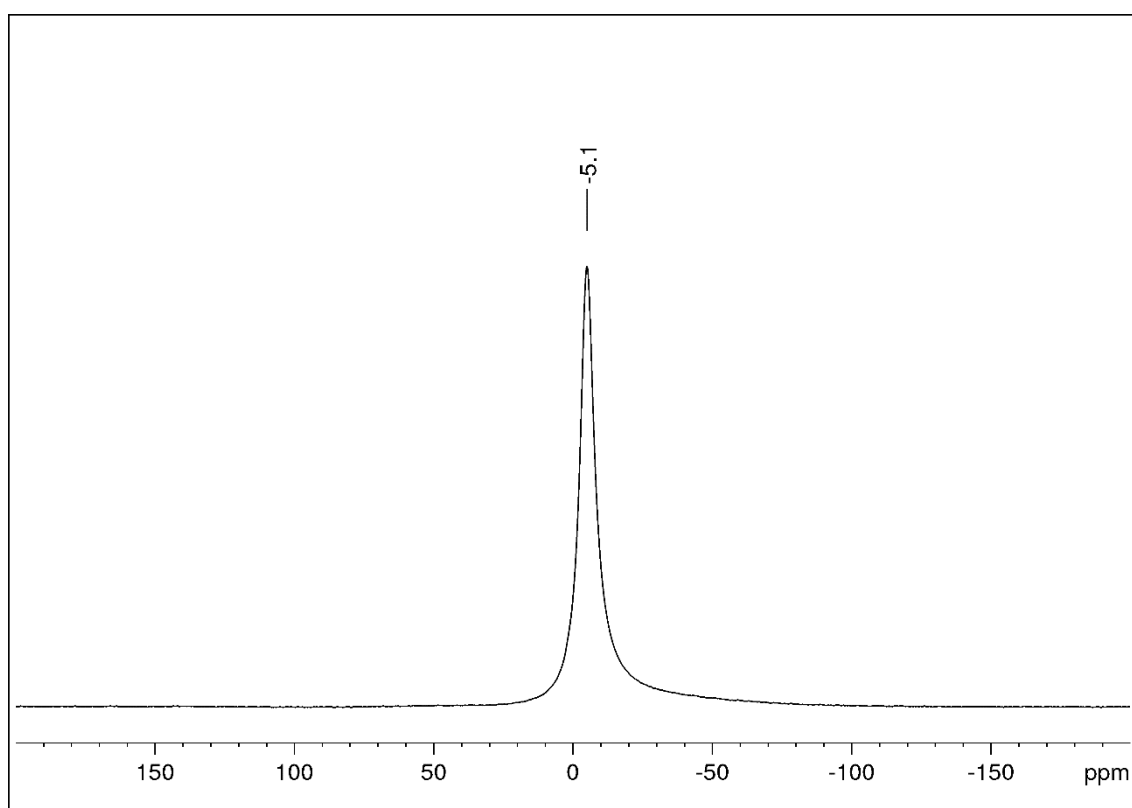


Figure C47. ^1H NMR spectrum (26 °C, 96.29 MHz, C_6D_6) of $\text{KTp}^{p\text{-}t\text{BuPh,Me}}$ (IV).

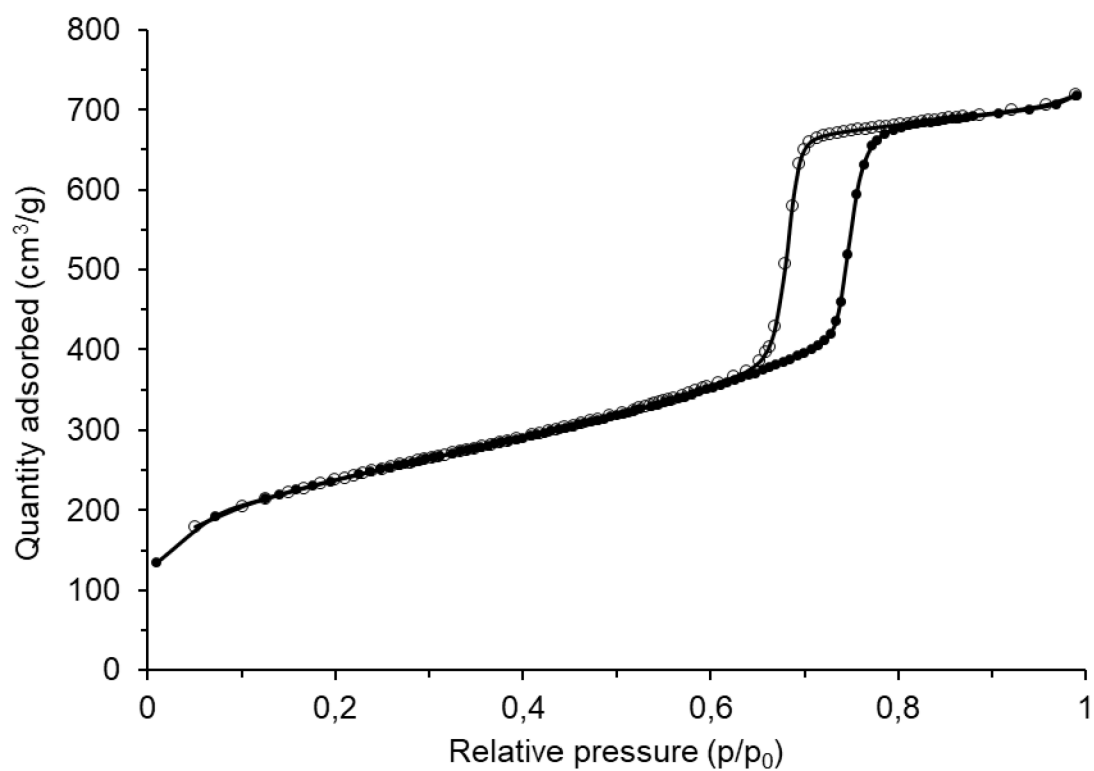


Figure C48. N₂ physisorption isotherm of parent SBA-15₅₀₀.^[192]

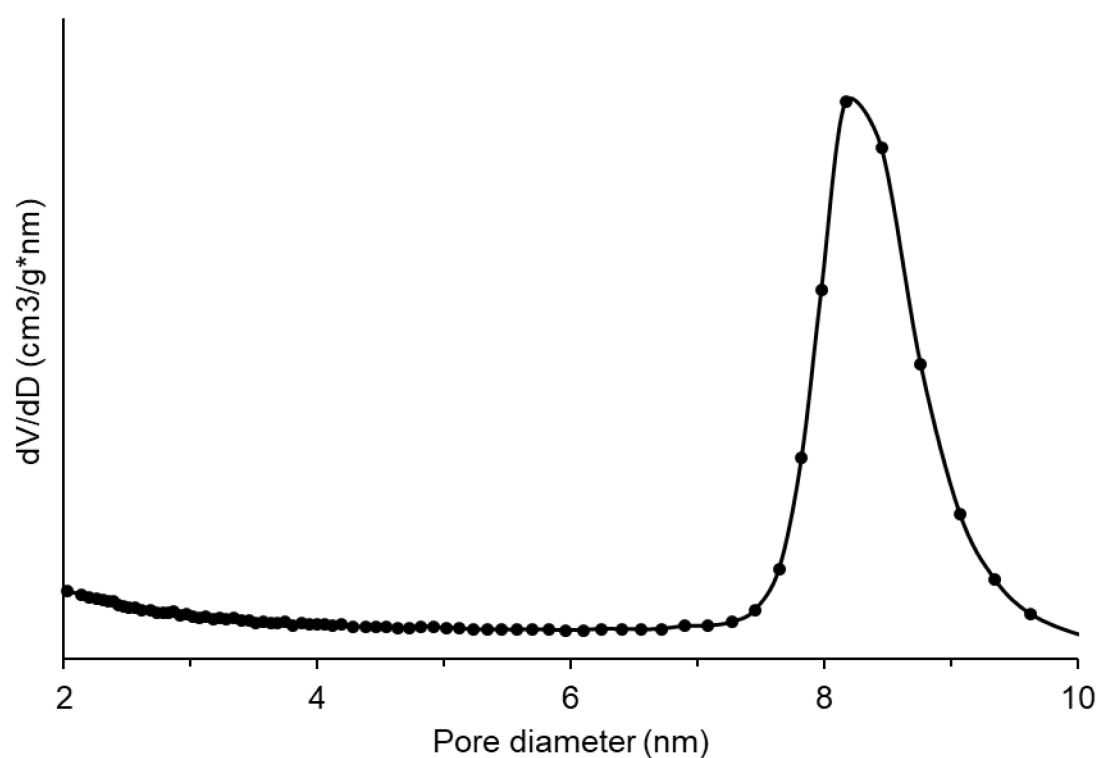


Figure C49. Maximum pore-size distribution of parent SBA-15₅₀₀ calculated by the BJH method from the isotherm adsorption branch.^[192]

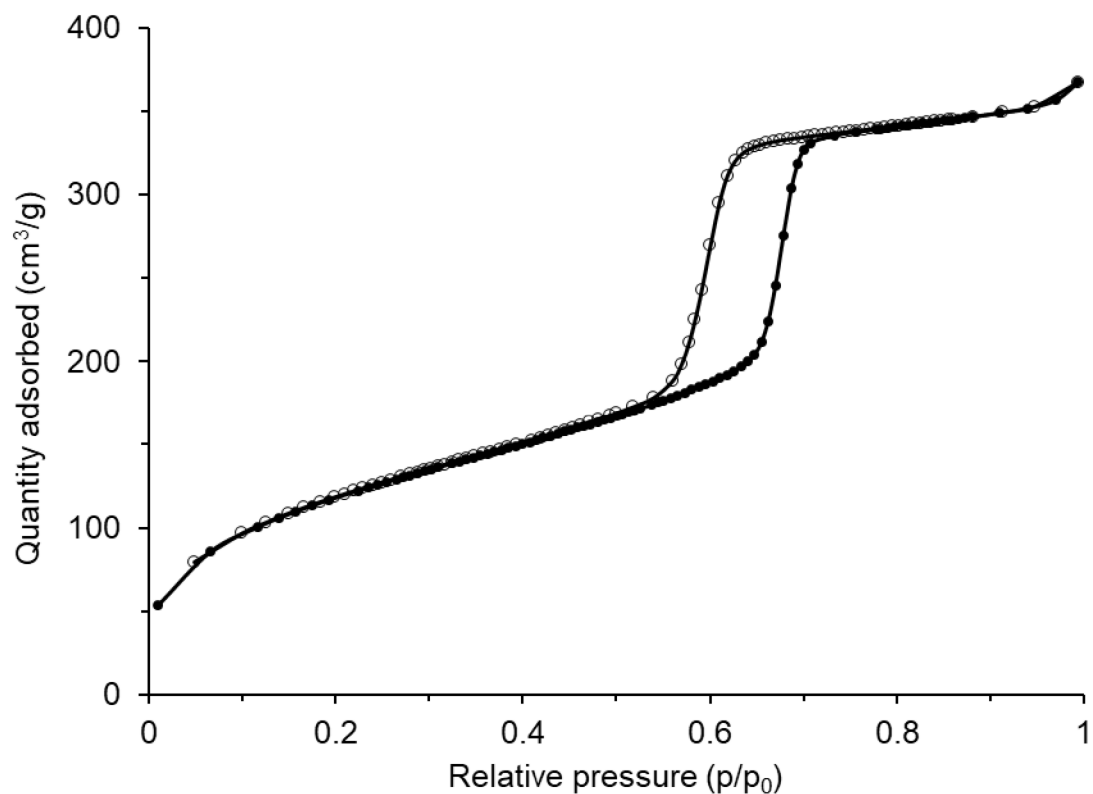


Figure C48. N₂ physisorption isotherm of [Mg(pz^{tBu2})₂]₂@SBA-15₅₀₀ (**C@SBA-15**).

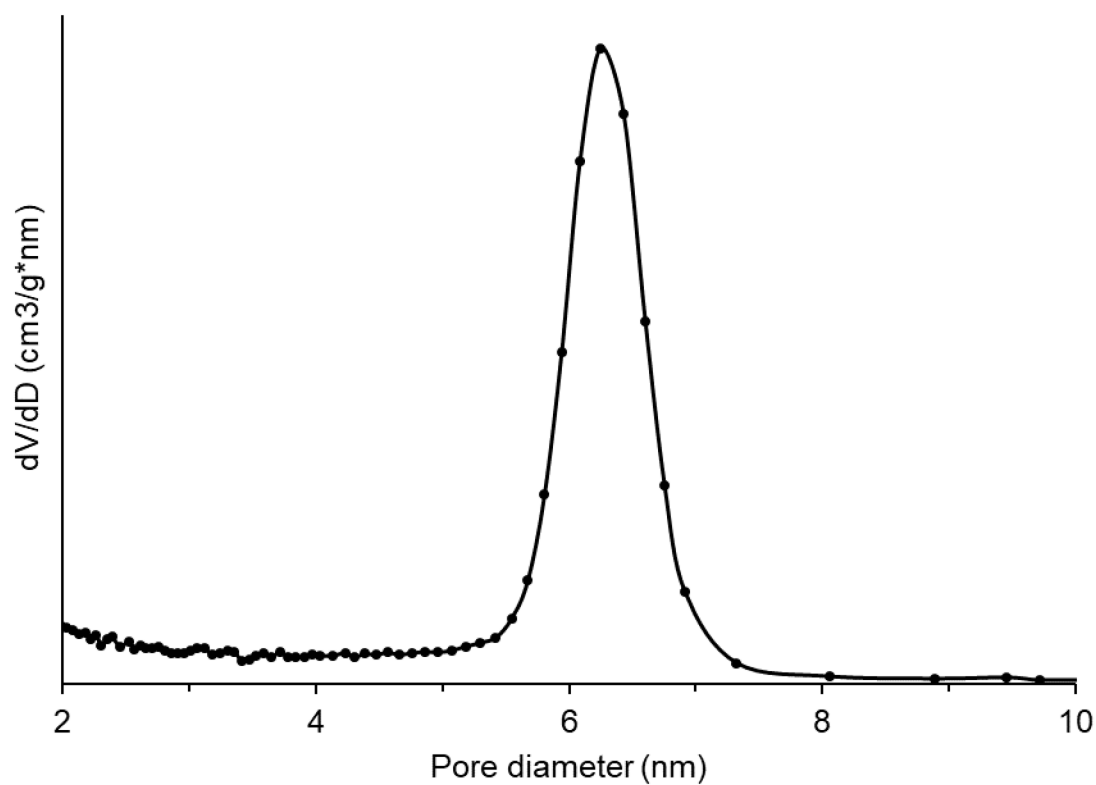


Figure C49. Maximum pore-size distribution of [Mg(pz^{tBu2})₂]₂@SBA-15₅₀₀ (**C@SBA-15**) calculated by the BJH method from the isotherm adsorption branch.

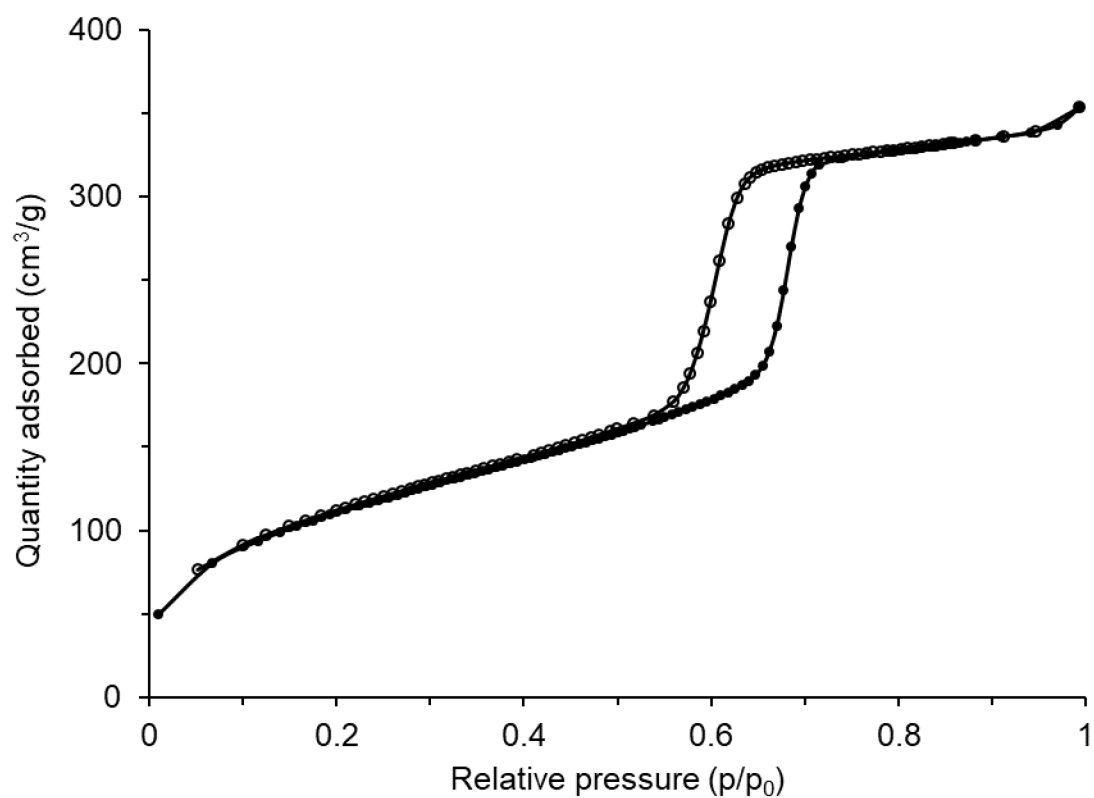


Figure C50. N₂ physisorption isotherm of Al(pz^{tBu2})₃@SBA-15₅₀₀ (**E@SBA-15**).

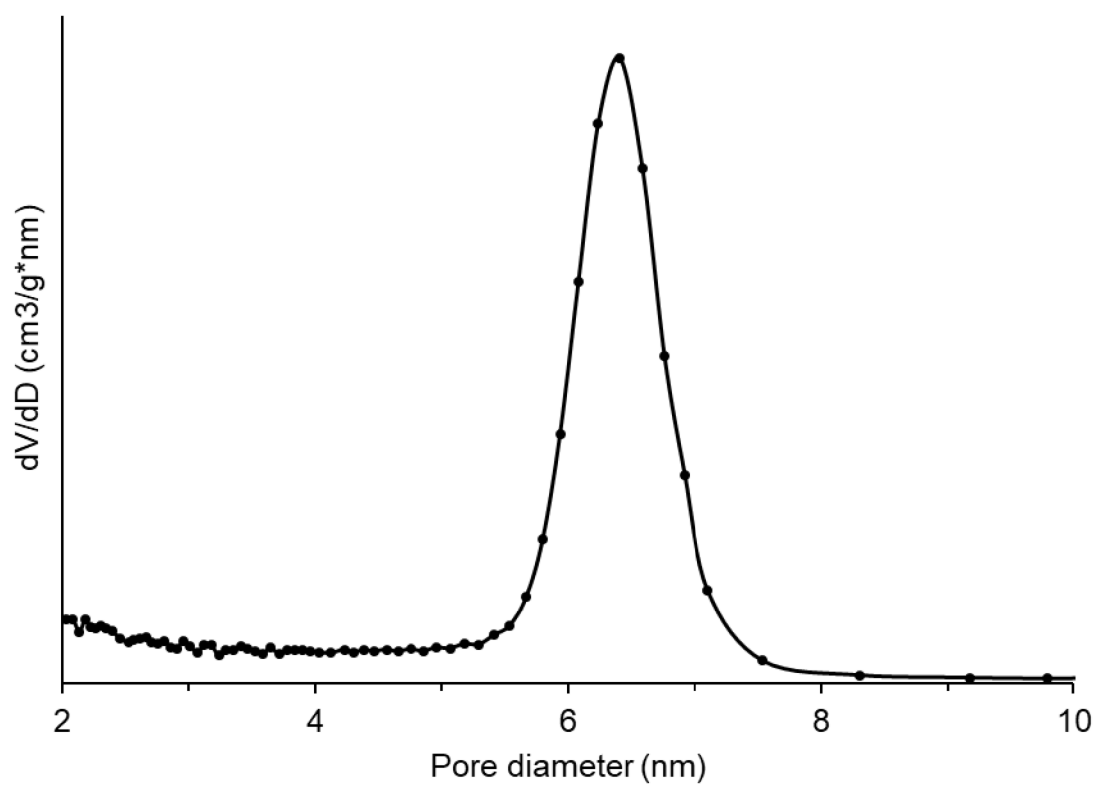


Figure C51. Maximum pore-size distribution of Al(pz^{tBu2})₃@SBA-15₅₀₀ (**E@SBA-15**) calculated by the BJH method from the isotherm adsorption branch.

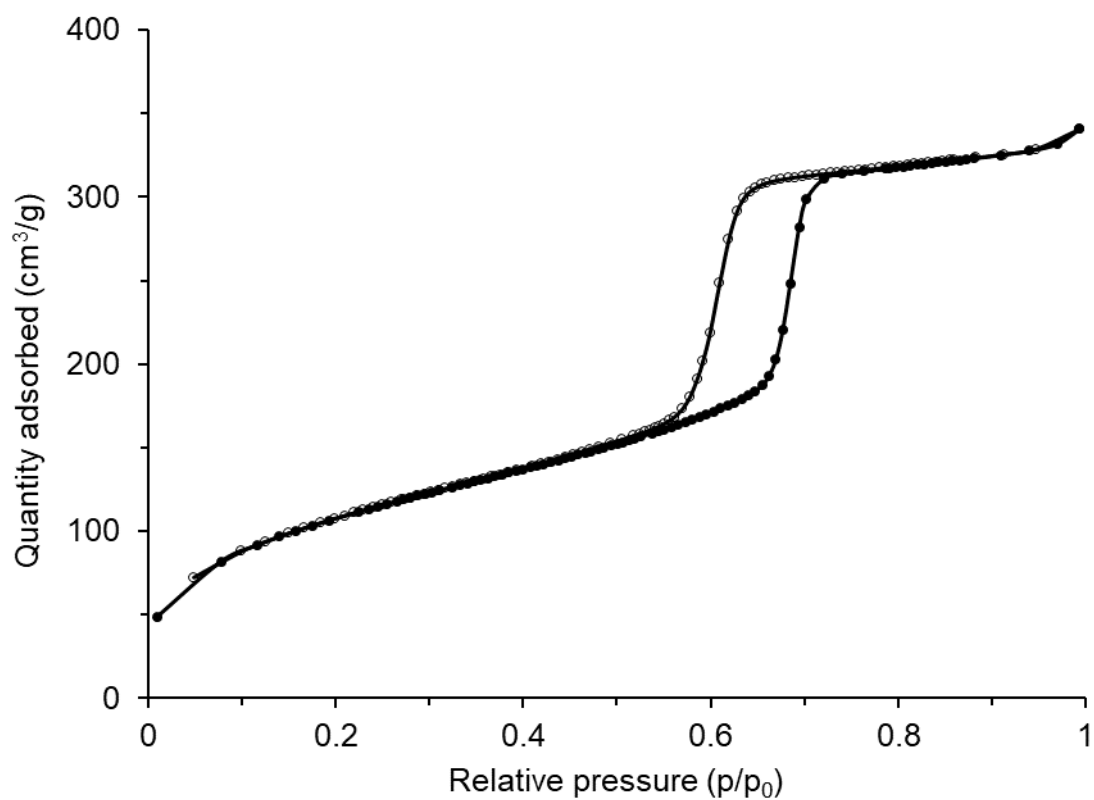


Figure C52. N₂ physisorption isotherm of Ti(pz^{Me₂})₄@SBA-15₅₀₀ (**F@SBA-15**).

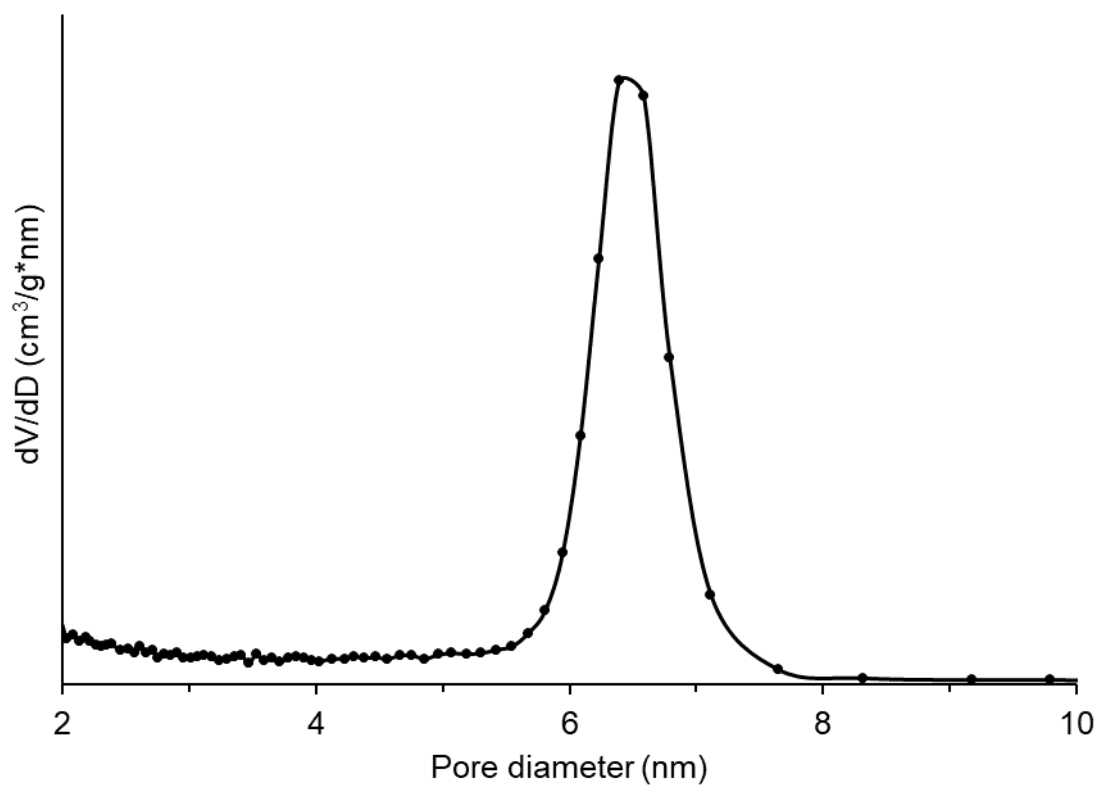


Figure C53. Maximum pore-size distribution of Ti(pz^{Me₂})₄@SBA-15₅₀₀ (**F@SBA-15**) calculated by the BJH method from the isotherm adsorption branch.

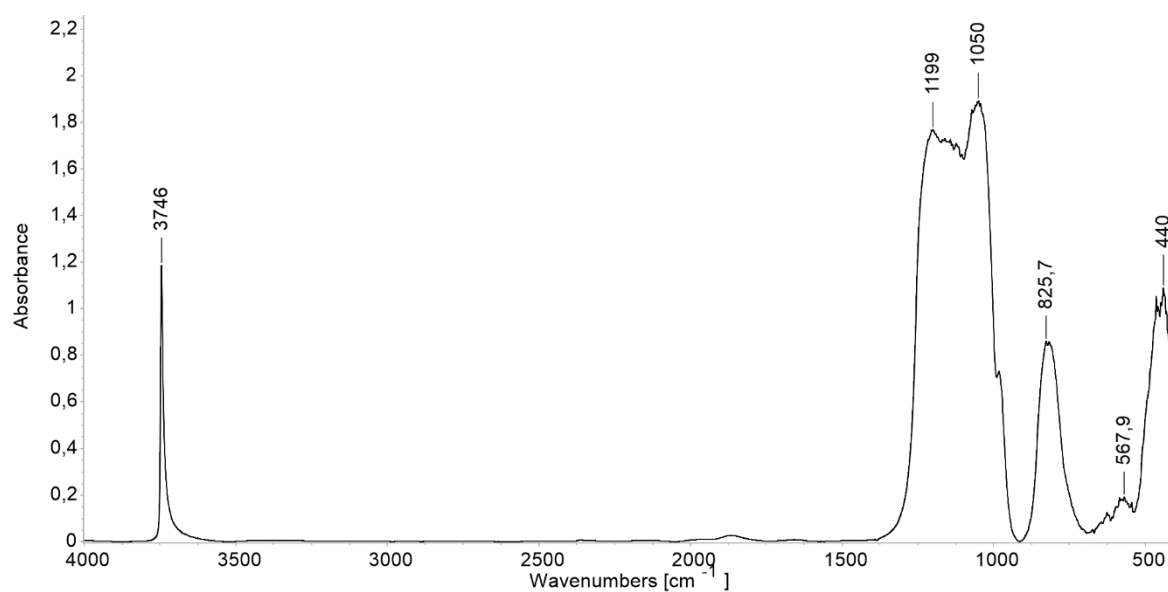


Figure S54. DRIFT spectrum of parent material SBA-15₅₀₀ at 25 °C.

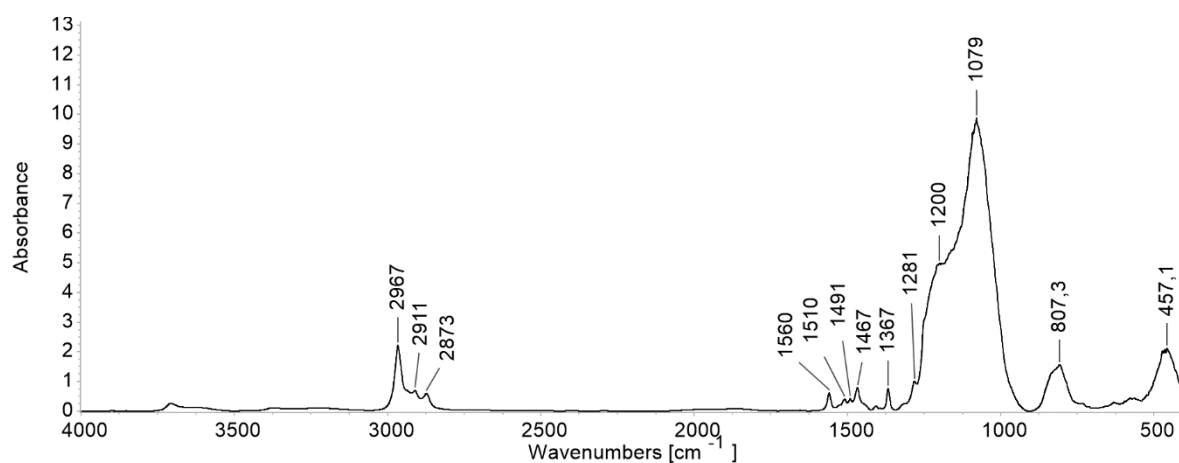


Figure S55. DRIFT spectrum of material [Mg(pz^{tBu2})₂]₂@SBA-15₅₀₀ C@SBA-15 at 25 °C.

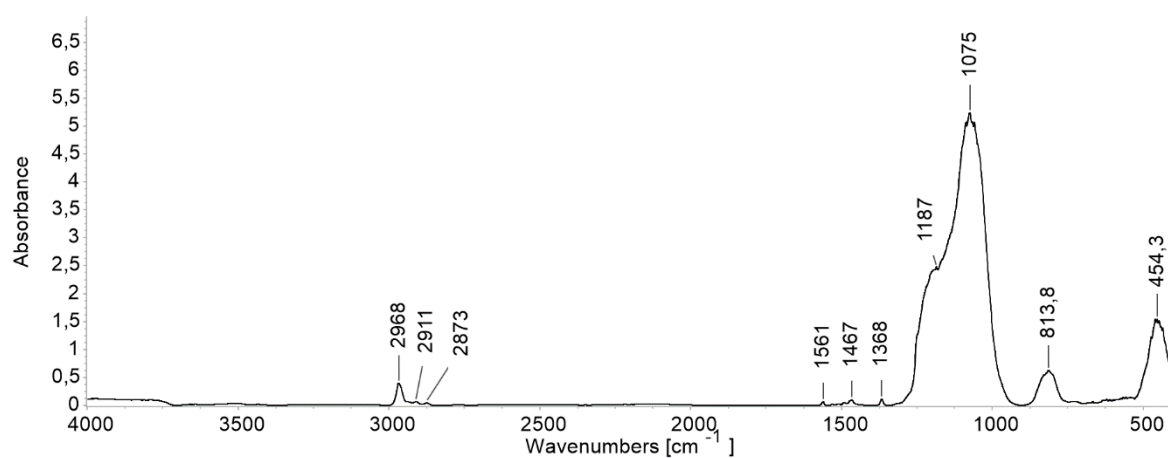


Figure S56. DRIFT spectrum of material Al(pz^{tBu2})₃@SBA-15₅₀₀ E@SBA-15 at 25 °C.

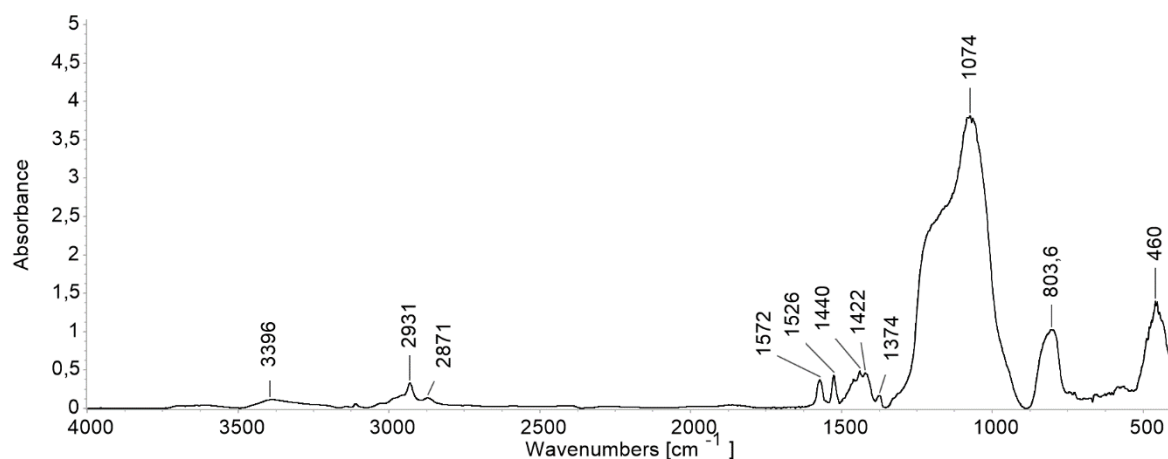


Figure S57. DRIFT spectrum of material $\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ **F@SBA-15** at 25 °C.

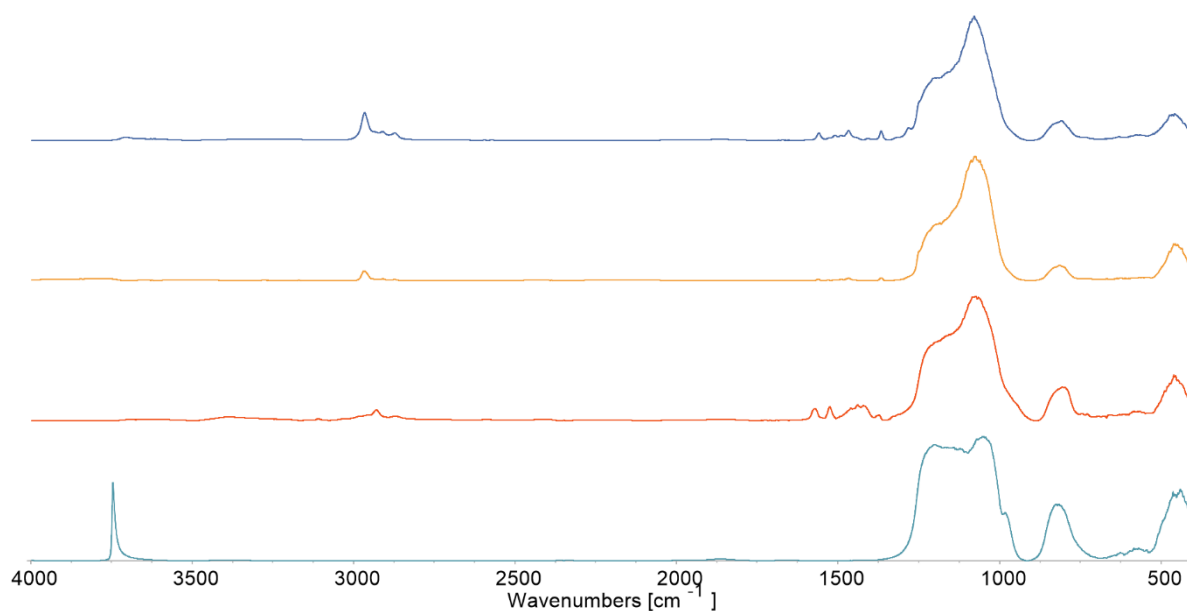


Figure C58. Comparison of DRIFT spectra of parent material SBA-15_{500} (bottom, light blue), $\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ **F@SBA-15** (red), $\text{Al}(\text{pz}^{\text{tBu}_2})_3@\text{SBA-15}_{500}$ **E@SBA-15** (yellow) and $[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ **C@SBA-15** (top, dark blue) at 25 °C.

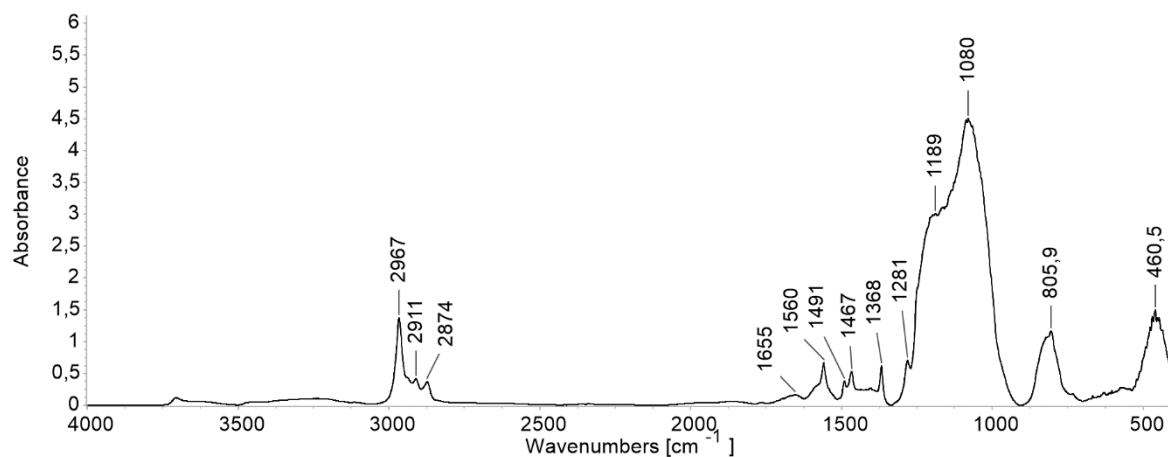


Figure S59. DRIFT spectrum of $\text{CO}_2@[\text{Mg}(\text{pz}^{\text{tBu}_2})_2]_2@\text{SBA-15}_{500}$ **CO2@C@SBA-15** at 25 °C.

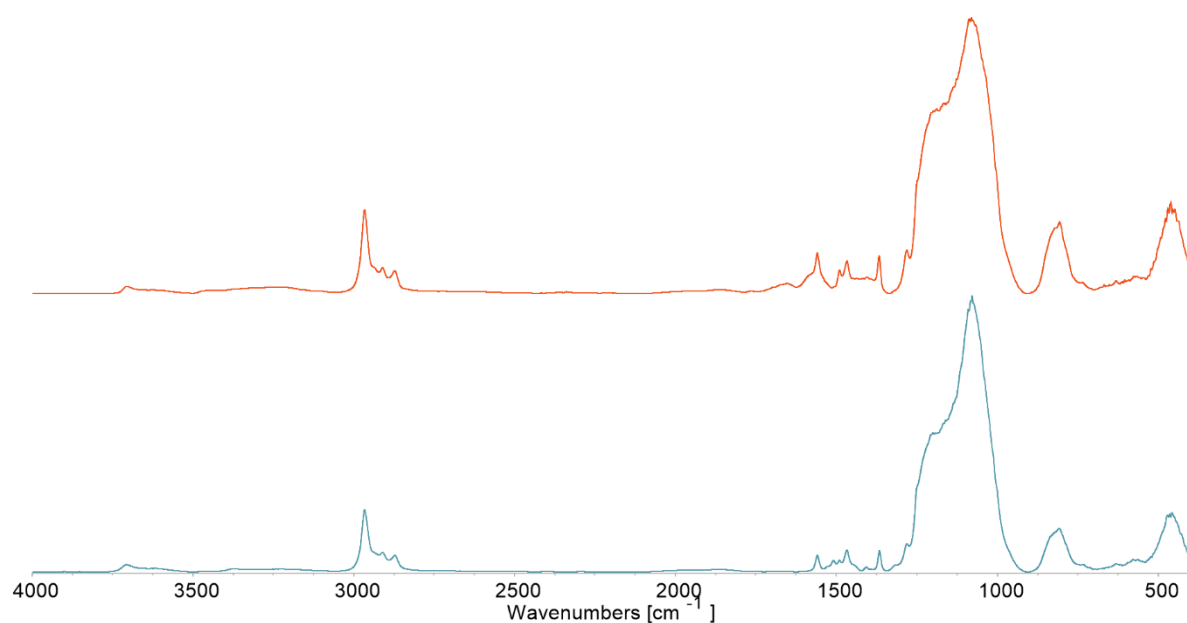


Figure S60. Comparison of DRIFT spectra of [Mg(pz^{tBu2})₂]@SBA-15₅₀₀ C@SBA-15 (bottom) and CO₂@[Mg(pz^{tBu2})₂]@SBA-15₅₀₀ CO₂@C@SBA-15 (top) at 26°C.

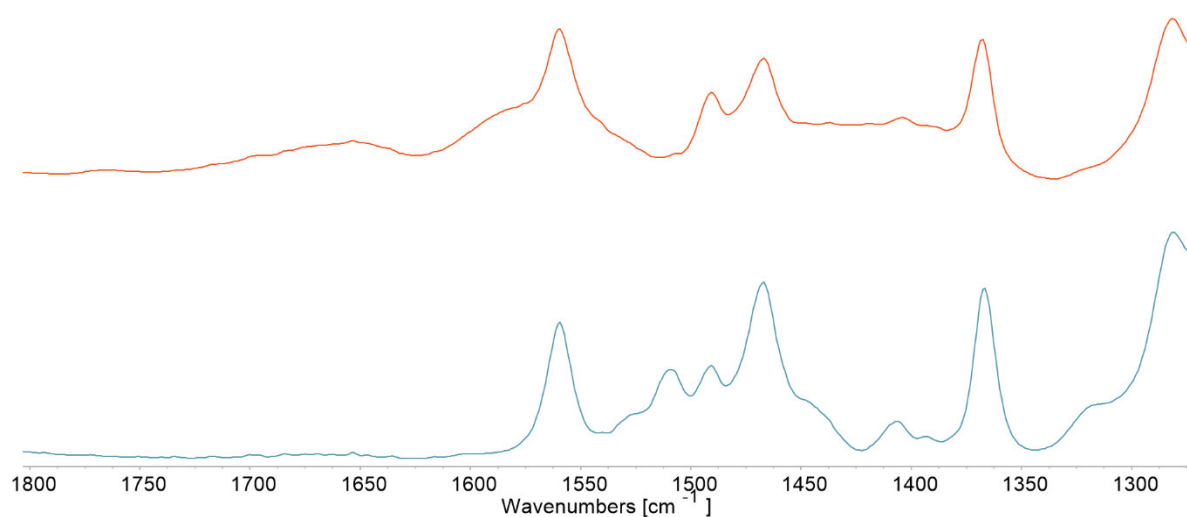


Figure S61. Comparison of zoomed in DRIFT spectra of [Mg(pz^{tBu2})₂]@SBA-15₅₀₀ C@SBA-15 (bottom) and CO₂@[Mg(pz^{tBu2})₂]@SBA-15₅₀₀ CO₂@C@SBA-15 (top) at 26°C.

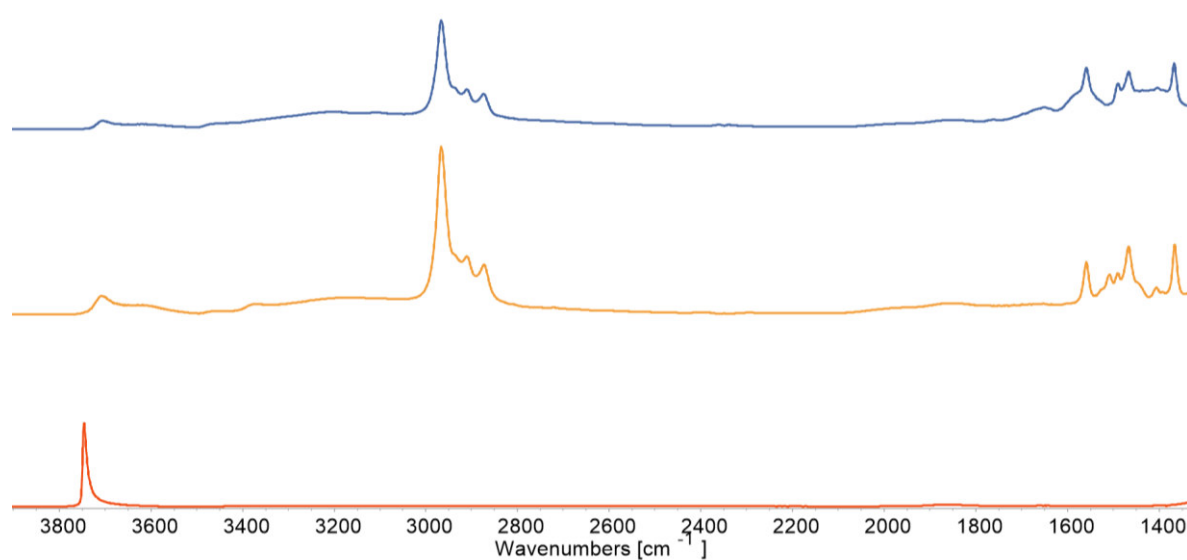


Figure S62. Comparison of DRIFT spectra of parent material SBA-15₅₀₀ (bottom, red), [Mg(pz^{tBu2})₂]₂@SBA-15₅₀₀ C@SBA-15 (middle, yellow), CO₂@[Mg(pz^{tBu2})₂]₂@SBA-15₅₀₀ CO₂@C@SBA-15 (top, blue) at 26 °C.

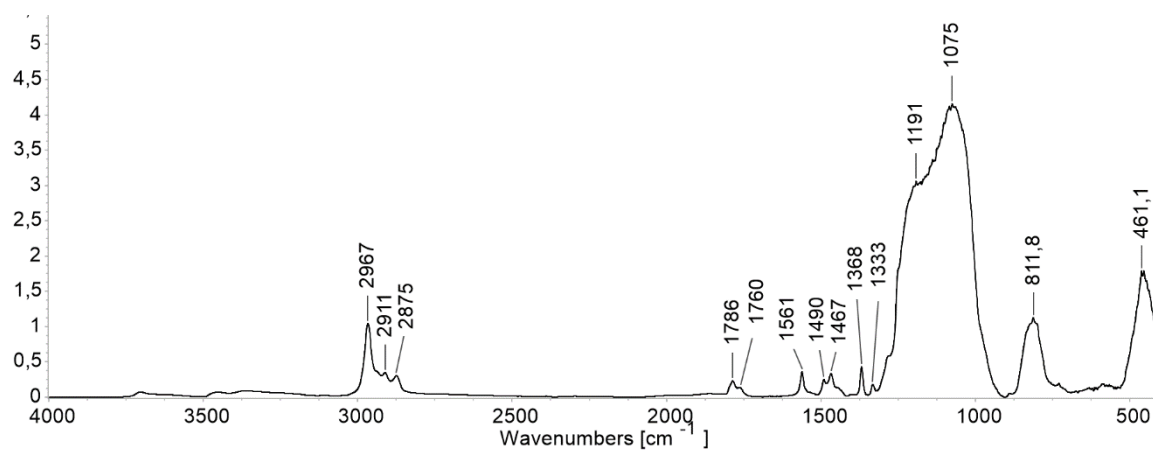


Figure S63. DRIFT spectrum of CO₂@Al(pz^{tBu2})₃@SBA-15₅₀₀ CO₂@E@SBA-15 at 25 °C.

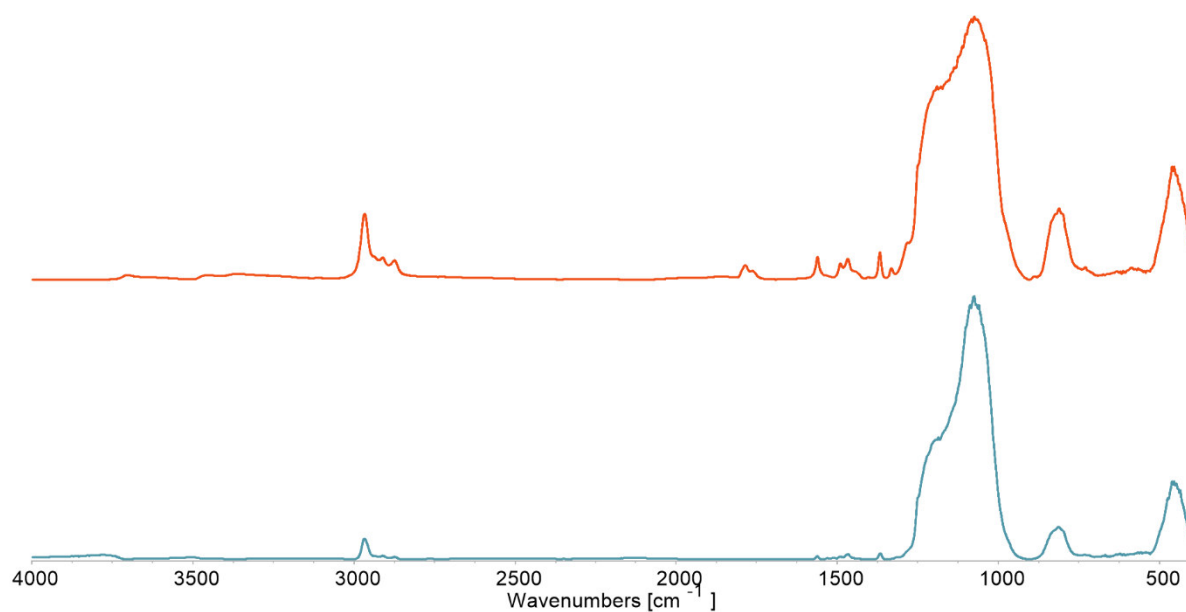


Figure S64. Comparison of DRIFT spectra of $\text{Al}(\text{pz}^{\text{tBu}_2})_3@ \text{SBA-15}_{500}$ **E@SBA-15** (bottom) and $\text{CO}_2@ \text{Al}(\text{pz}^{\text{tBu}_2})_3@ \text{SBA-15}_{500}$ **CO₂@E@SBA-15** (top) at 26°C.

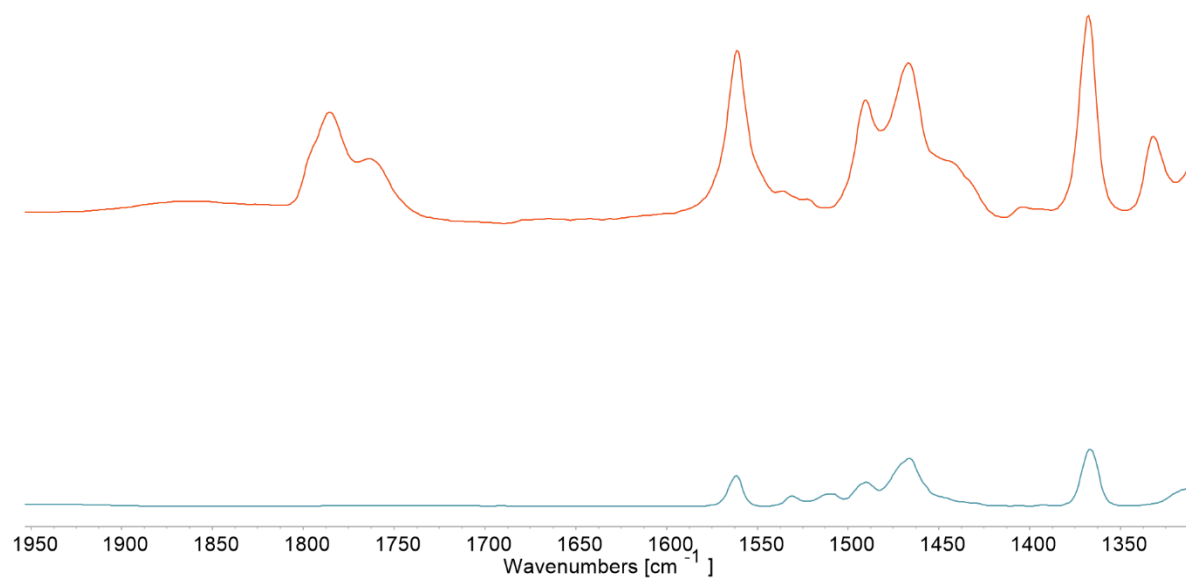


Figure S65. Comparison of zoomed in DRIFT spectra of $\text{Al}(\text{pz}^{\text{tBu}_2})_3@ \text{SBA-15}_{500}$ **E@SBA-15** (bottom) and $\text{CO}_2@ \text{Al}(\text{pz}^{\text{tBu}_2})_3@ \text{SBA-15}_{500}$ **CO₂@E@SBA-15** (top) at 26°C.

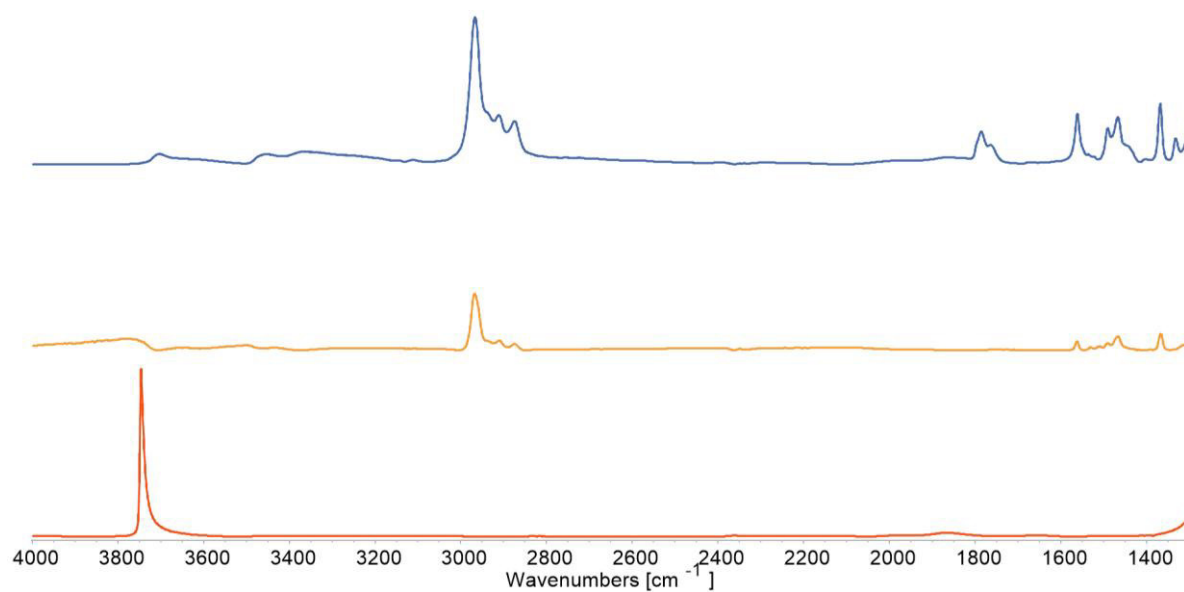


Figure S66. Comparison of DRIFT spectra of parent material SBA-15₅₀₀ (bottom, red), Al(pz^{tBu2})₃@SBA-15₅₀₀ E@SBA-15 (middle, yellow), CO₂@Al(pz^{tBu2})₃@SBA-15₅₀₀ CO₂@E@SBA-15 (top, blue) at 26 °C.

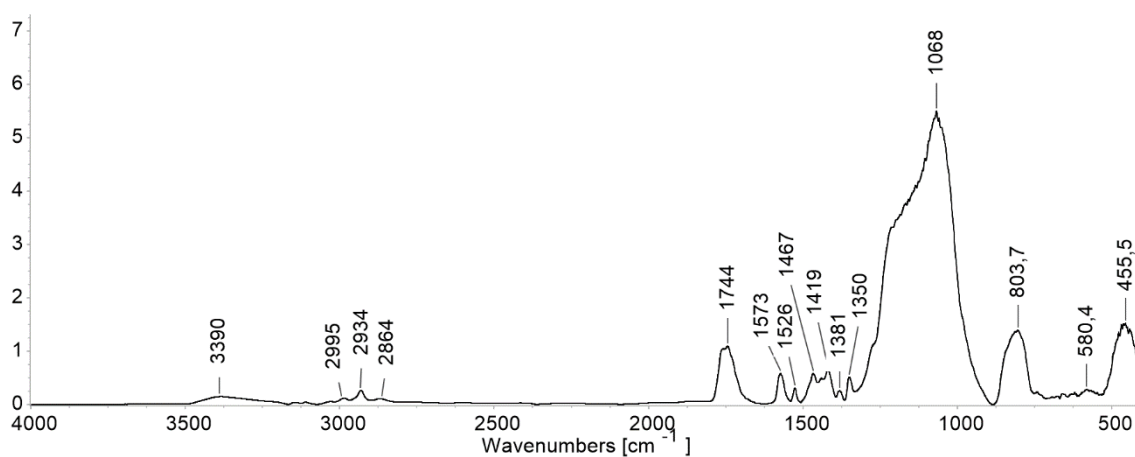


Figure S67. DRIFT spectrum of CO₂@Ti(pz^{Me2})₄@SBA-15₅₀₀ CO₂@F@SBA-15 at 25 °C.

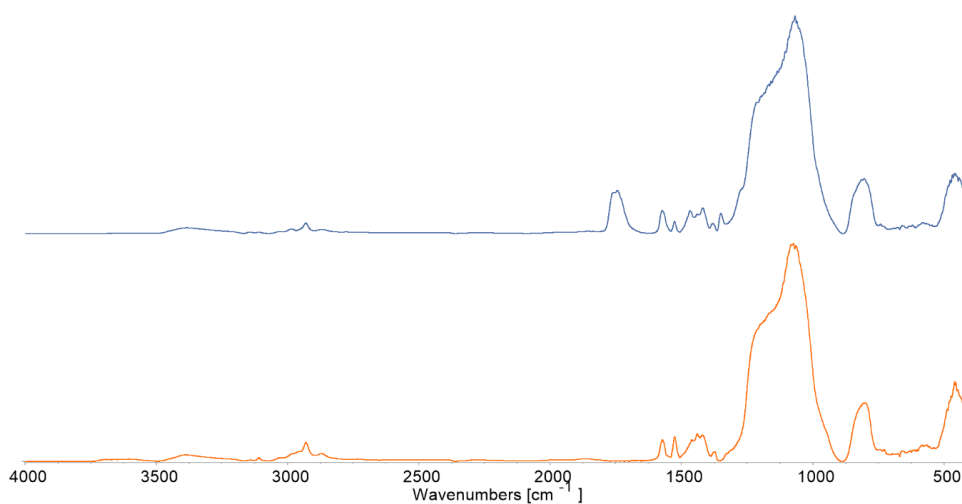


Figure S68. Comparison of DRIFT spectra of Ti(pz^{Me2})₄@SBA-15₅₀₀ F@SBA-15 (bottom) and CO₂@Ti(pz^{Me2})₄@SBA-15₅₀₀ CO₂@F@SBA-15 (top) at 26 °C.

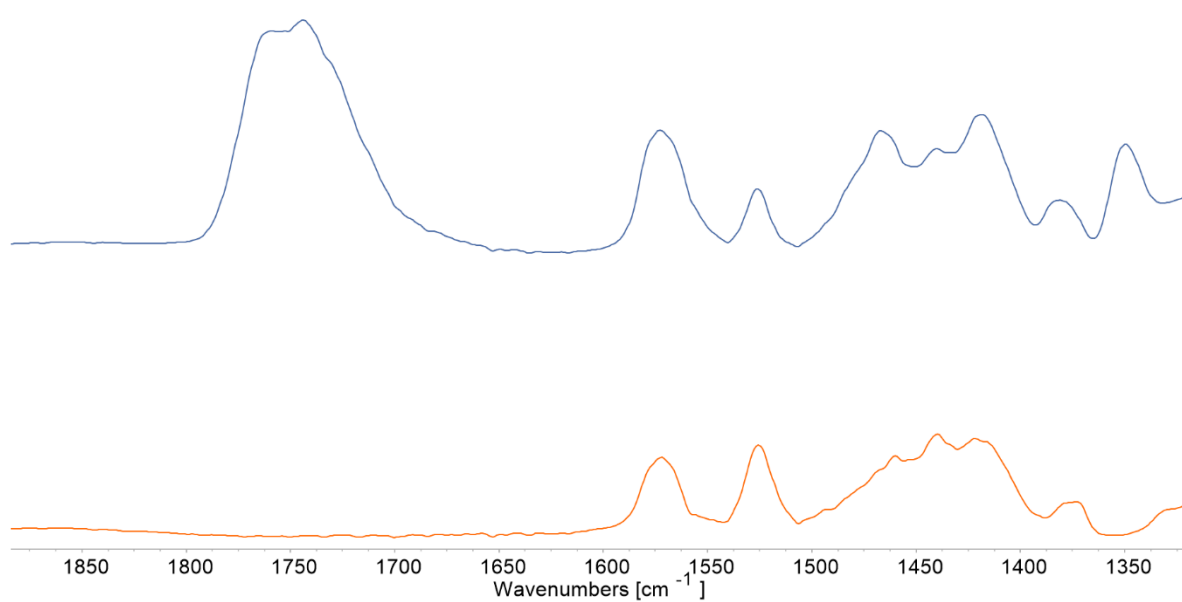


Figure S69. Comparison of zoomed in DRIFT spectra of $\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ **F@SBA-15** (bottom) and $\text{CO}_2@\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ **CO₂@F@SBA-15** (top) at 26°C.

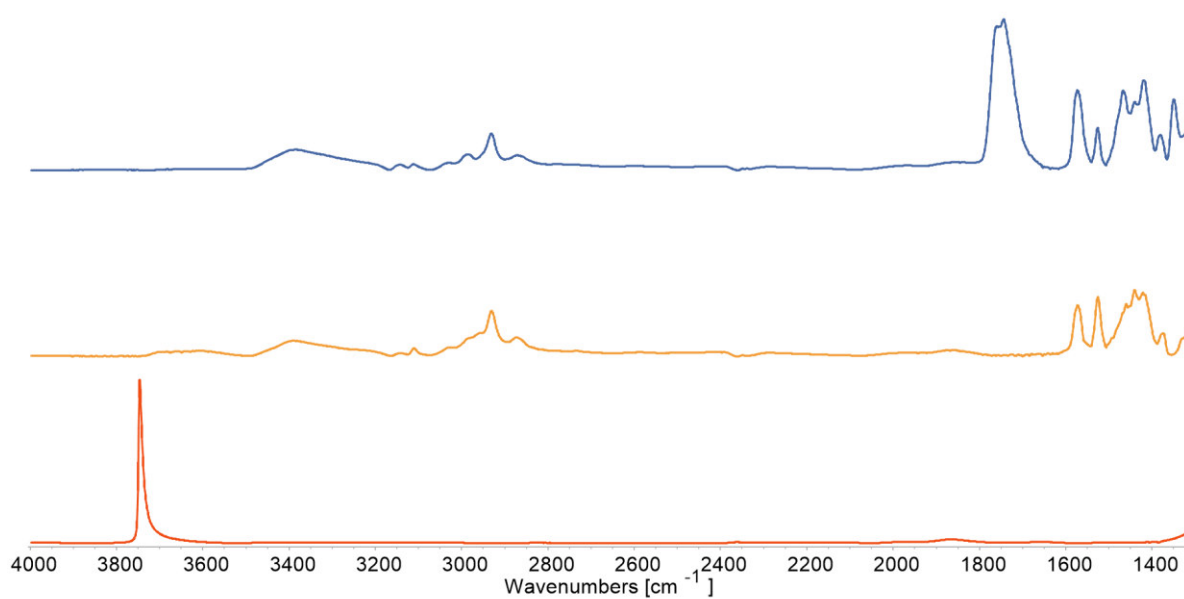


Figure S70. Comparison of DRIFT spectra of parent material SBA-15_{500} (bottom, red), $\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ **F@SBA-15** (middle, yellow), $\text{CO}_2@\text{Ti}(\text{pz}^{\text{Me}_2})_4@\text{SBA-15}_{500}$ **CO₂@F@SBA-15** (top, blue) at 26 °C.

Table C3. Crystallographic data for compounds **Y^{CO₂}**, **III**, and **V**.

	Y^{CO₂} (PP12)	III (FK28)	V (HP5)
formula	C ₅₄ H ₉₂ N ₈ O ₆ Zn ₂	C ₅₂ H ₆₀ BKN ₈	C ₈₄ H ₁₀₆ BKN ₁₂ · C ₆ H ₁₄
M [g mol ⁻¹]	1080.09	846.99	1416.86
color/shape	colorless/plate	colorless/column	colorless/block
Crystal dimensions [mm]	0.212 x 0.149 x 0.102	0.498 x 0.127 x 0.064	0.139 x 0.127 x 0.104
cryst. system	monoclinic	tetragonal	triclinic
space group	<i>P</i> 21/ <i>c</i>	<i>P</i> 4 ₂ / <i>n</i>	<i>P</i> $\bar{1}$
a [Å]	12.2745(7)	16.6466(10)	17.2424(16)
b [Å]	18.4415(10)	16.6466(10)	17.434(2)
c [Å]	25.2636(14)	8.7847(6)	18.6027(17)
α [°]	90	90	89.773(4)
β [°]	96.9830(10)	90	63.675(3)
γ [°]	90	90	60.765(3)
<i>V</i> [Å ³]	5676.3(5)	2434.3(3)	4208.9(8)
<i>Z</i>	4	2	2
<i>T</i> [K]	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073
ρ _{calcd} [g cm ⁻³]	1.264	1.156	1.118
μ [mm ⁻¹]	0.898	0.152	0.114
F(000)	2320	904	1530
θ range [°]	1.371/26.397	2.447/28.278	1.269/27.242
unique reflns	11627	3018	18689
observed reflns	11627	27178	104343
R1/wR2 (I>2σ) ^[a]	0.0525/0.1226	0.0440/0.1078	0.0654/0.1564
R1/wR2 (all data) ^[a]	0.0694/0.1295	0.0639/0.1226	0.1165/
GOF ^[a]	1.052	1.022	1.025

[a] $R1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $F_o > 4\sigma(F_o)$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

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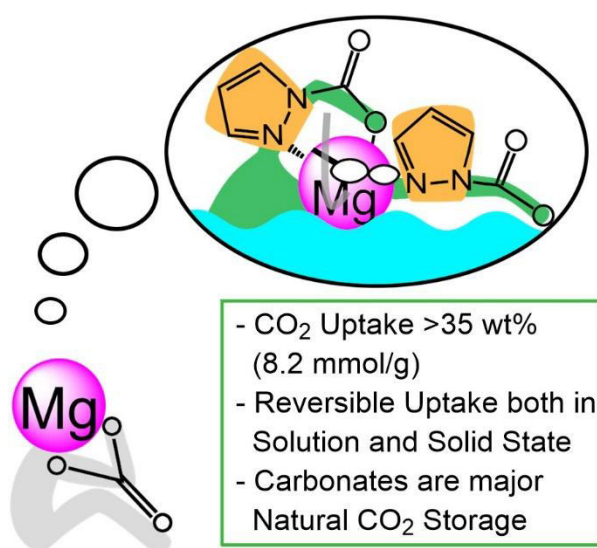
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Organomagnesia: Reversibly High Carbon Dioxide Uptake by Magnesium Pyrazolates

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A series of new pyrazolate and mixed pyrazolate/pyrazole magnesium complexes is described and their reactivity toward carbon dioxide is examined. The dimeric complex $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2]_2$ inserts CO_2 instantly and quantitatively forming the tetrameric complex $[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{tBu,tBu}})_2]_4$ and monomeric donor-stabilized $[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$. Complexes of the type $[\text{Mg}_x(\text{pz}^{\text{R,R}})_{2x}(\text{Hpz}^{\text{R,R}})_y]_n$ ($\text{R} = \text{iPr, tBu}$) engage in similar insertion reactions involving dissociation of the carbamic acid $\text{HOOCpz}^{\text{R,R}}$. Even solid polymeric derivatives $[\text{Mg}(\text{pz}^{\text{R,R}})_2]_n$ ($\text{R} = \text{Me, H}$) react instantaneously and exhaustively with CO_2 , the resulting $[\text{Mg}(\text{CO}_2 \cdot \text{pz})_2]_m$ featuring a CO_2 capacity of 35.7 wt% (8.2 mmol g^{-1}). All described magnesium pyrazolates display completely reversible CO_2 uptake in solution and in the solid state, respectively, as monitored via VT ^1H NMR and in situ FTIR spectroscopy as well as thermogravimetric analysis. Fluorinated $[\text{Mg}_2(\text{pz}^{\text{CF}_3,\text{CF}_3})_4(\text{thf})_3]$ does not yield any isolable CO_2 insertion product but exhibits the highest activity in the catalytic transformation of epoxides and CO_2 to cyclic carbonates.

1. Introduction

Carbon dioxide emissions originating from fossil fuel (including energy sector and transportation; 2023: ca. 37 billion tons = 37 Gt) and as byproduct from industrial processes have been identified as the main causes of anthropogenic climate change.^[1–5] Accordingly, CO_2 management has evolved as a top-prioritized research field. One strategy to reduce CO_2 emissions is to capture the post-combustion CO_2 before it gets released into the atmosphere, in order to either permanently sequester it or utilize it further as an effective C1 synthon in organic synthesis.^[6,7] Crucially, any sustainable valorization of CO_2 -loaded materials is dependent on energy-saving, reversible processes. Since the 1930s, aqueous amine scrubbers have been used in industry, but this

technology is affected by low capacities (max. < 15 wt% CO_2), sensitivity to oxygen and high regeneration energies (high “energy penalty”).^[8,9] Current advanced technologies for CO_2 uptake are based on alkali/alkaline-earth metal hydroxides, amine-containing ionic liquids or amine-functionalized high-surface materials such as porous silica, zeolites, or metal-organic frameworks (MOF),^[10,11] with carbamate formation as the most efficient underlying principle. Striking are the properties of magnesium carboxylate-based MOFs such as $\text{Mg}(\text{dobdc})$ (= $\text{Mg}_2[2,5\text{-dioxido-1,4-benzenedicarboxylate}]$) featuring a CO_2 capacity of up to 35 wt%,^[12] or the tetraamine-appended MOF $\text{Mg}(\text{dobpdc})$ (= $\text{Mg}_2[4,4'\text{-dioxidobiphenyl-3,3'-dicarboxylate}]$) which is currently the best system for cooperative CO_2 capture from simulated flue gas.^[13,14]

Magnesium is also a crucial component in natural CO_2 storage in the lithosphere

(insoluble sedimentary carbonates: >60 000 000 Gt) and in oceans (ca. 38 000 Gt inorganic carbon: CO_2 , bicarbonate, carbonate).^[2] Our conceptual approach of CO_2 capture is inspired by this natural role model and in a broader sense by the industrially applied (re)causticization of alkaline-earth and alkali-metal hydroxides.^[6] Accordingly, modification of the dianionic carbonate moiety in terms of charge and functional group ($\text{CO}_3^{2-} \rightarrow \text{HCO}_3^- = (\text{HO})\text{CO}_2^- \rightarrow (\text{X})\text{CO}_2^-$; $\text{X} = \text{NR}_2 \equiv \text{carbamate ligand}$) is envisaged to facilitate reversible CO_2 uptake with minimum energy penalty (Figure 1).^[15] In contrast to the aforementioned magnesium-based MOFs, carbon dioxide is supposed to interact in a cooperative manner with the monoanionic nitrogen ligand X and the metal center.

The proof of concept was recently demonstrated for homoleptic cerium pyrazolate complexes which were found to reversibly insert CO_2 to afford complexes $[\text{Ce}^{\text{IV}}(\text{CO}_2 \cdot \text{pz}^{\text{Me,Me}})_4]$ and $[\text{Ce}^{\text{III}}_4(\text{CO}_2 \cdot \text{pz}^{\text{Me,Me}})_{12}]$ (max. 25 wt% CO_2).^[16] We wondered about the applicability of this approach for magnesium as an environmentally even friendlier oxophilic earth-abundant light metal. Pertinent magnesium-carbamate complexes such as mixed metallic $[(\text{Me}_2\text{Al})_2\{\mu\text{-CO}_2 \cdot \text{NR}_2\}_2]\text{Mg}$ ($\text{R} = \text{Et, iPr}$) were already described 30 years ago, via CO_2 insertion into Mg-N amido bonds (Figure 1).^[17] The first homoleptic magnesium carbamate complex, hexameric $[\text{Mg}_6(\text{CO}_2 \cdot \text{NR}_2)_{12}]$ ($\text{R} = \text{Et, Ph}$) was reported in 2001.^[18] Since then, several more magnesium carbamate complexes appeared in the literature, however, CO_2

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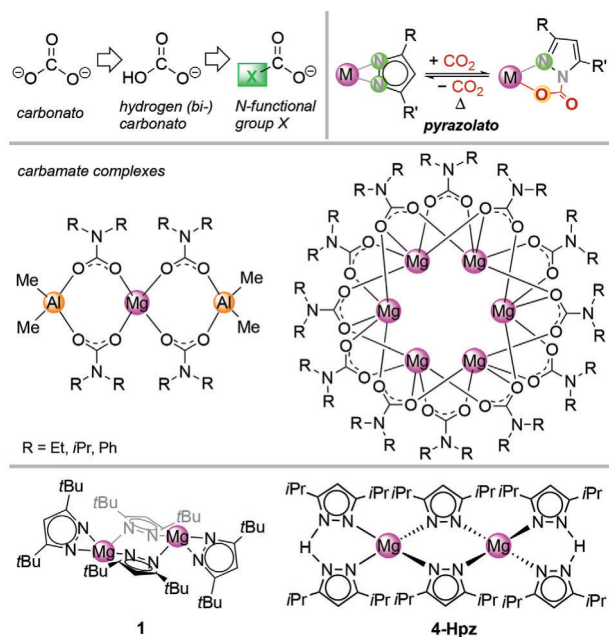


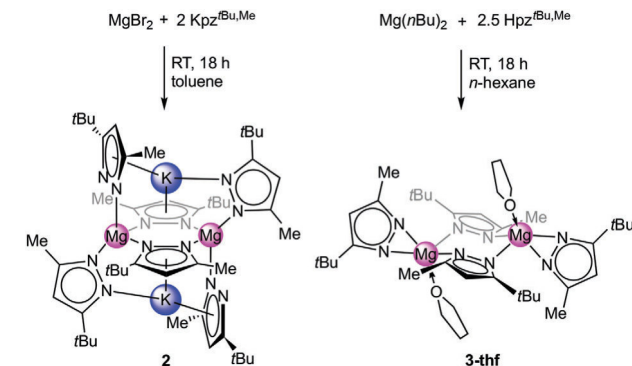
Figure 1. Top: design strategy of reversible molecular CO₂ adsorbers. Middle: examples of structurally characterized magnesium carbamate complexes via CO₂ insertion into Mg–N(amido) bonds. Bottom: examples of structurally characterized magnesium pyrazolate complexes.

insertion has proven irreversible.^[19] The first and only homoleptic magnesium pyrazolate complex [Mg(pz^{*t*Bu,*t*Bu})₂]₂ (**1**) was reported by the group of Winter as a potential CVD precursor,^[20] along with the donor adducts [Mg(pz^{*t*Bu,*t*Bu})₂(thf)₂]₂ (**1-thf**) and [Mg(pz^{*t*Bu,*t*Bu})₂(tmeda)] (**1-tmeda**). Moreover, the two mixed pyrazolato/pyrazole complexes [Mg(pz^{*t*Bu,*t*Bu})₂(Hpz^{*t*Bu,*t*Bu})]₂ (**1-Hpz**)^[21] and [Mg(pz^{*i*Pr,*i*Pr})₂(Hpz^{*i*Pr,*i*Pr})]₂ (**4-Hpz**) are known.^[22] The present study aims to adapt the class of magnesium pyrazolates for efficient CO₂ capture and contributes to a better understanding of the effectiveness of such pyrazolate complexes in the catalytic formation of cyclic carbonates.

2. Results and Discussion

2.1. Why Magnesium? Why Pyrazoles?

Magnesium features an earth-abundant, non-toxic, non-strategic light metal and hence is prone to high CO₂ uptake (resulting in low “mass penalty”). Pyrazoles feature the conceptually required adjacent nitrogen coordination sites, while displaying flexible coordination behavior as evidenced by many distinct coordination modes.^[23] As revealed by cerium pyrazolate complexes, the κ²(N,N′)-coordinating pyrazolato ligand decisively promotes reversible and cooperative CO₂ insertion by counteracting the mostly irreversible κ²(O,O′) coordination mode.^[24,25] Moreover, pyrazoles are straightforwardly synthesized with easily tunable stereoelectronic properties via the 3,5-substitution pattern. Such five-membered heterocycles occur in natural products, albeit isolated pyrazoles cause severe toxicity for the nonsubstituted parent representative.^[26]



Scheme 1. Synthesis of complexes **2** and **3-thf** bearing the mixed 3-*tert*-butyl-5-methyl pyrazolato ligand.

2.2. Choice of Magnesium Pyrazolates

This study was launched with the discrete *t*Bu-substituted complexes [Mg(pz^{*t*Bu,*t*Bu})₂]₂ (**1**) and [Mg(pz^{*t*Bu,*t*Bu})₂(thf)]₂ (**1-thf**) previously reported by Winter.^[20] However, due to the apparent high “mass penalty” caused by the *t*Bu moieties and the THF donor, further attempts were made to synthesize homoleptic magnesium pyrazolates with smaller substituents in the 3,5 positions, like *i*Pr/*i*Pr, mixed *t*Bu/Me, Me/Me, and H/H. To probe any marked electronic effects on CO₂ insertion, the CF₃/CF₃ variant was considered as well. In our hands, salt-metathesis reactions of magnesium bromide with 3,5-substituted potassium pyrazolates bearing alkyl groups smaller than *t*Bu did not lead to the isolation of homoleptic magnesium pyrazolates. The mixed *t*Bu/Me pyrazolato ligand afforded ate complex [KMg(pz^{*t*Bu,Me})₃]₂ (**2**) as the only isolable metathesis product (**Scheme 1**). For the other alkyl-substituted pyrazolato ligands either no reaction took place or a complex mixture of products was observed.

The single crystal X-ray diffraction (SCXRD) analysis of **2** revealed a dimeric structure in which the two magnesium centers are bridged by two pyrazolato ligands in the μ–1κ(N):2κ(N′) mode forming a six-membered ring, slightly distorted to a seat conformation (**Figure 2**, top).^[27] In addition, each magnesium center is κ¹(N)-coordinated by two pyrazolato ligands above and beneath the metalacyclic ring implying a strongly distorted tetrahedral coordination of the magnesium atoms. The three distinct pyrazolato ligands also encapsulate the potassium cations by bridging to the magnesium centers with the approximate coordination modes μ–1κ(N):2κ(N′), μ–1κ(N):2η⁵(pz), and μ–1κ(N):2κ(N):3η⁵(pz). The equilateral triangle N5–K1–N6 is perpendicular to the pyrazolyl plane (90.05°), while the angle between the planes of the η⁴- and η⁵-coordinating pyrazolatos is close to perpendicular (95.14°).

Despite the different coordination modes, the ¹H NMR spectrum of **2** in [D₈]toluene shows one signal set of the aromatic proton, the methyl and the *tert*-butyl groups indicating a high ligand mobility in solution.

Applying a protonolysis protocol by reacting Mg(*n*Bu)₂ with 2.5 equivalents of the corresponding pyrazole Hpz^{*t*Bu,Me} in a *n*-hexane/THF solution afforded the donor adduct [Mg(pz^{*t*Bu,Me})₂(thf)]₂ (**3-thf**) (**Scheme 1**, **Figure 2**, bottom).^[27] The crystal structure of **3-thf** revealed a dimeric complex isostructural

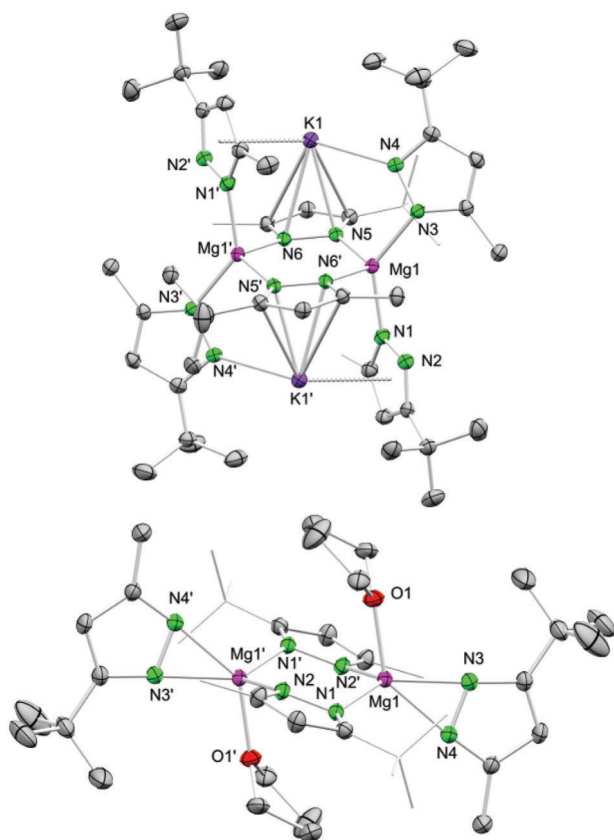
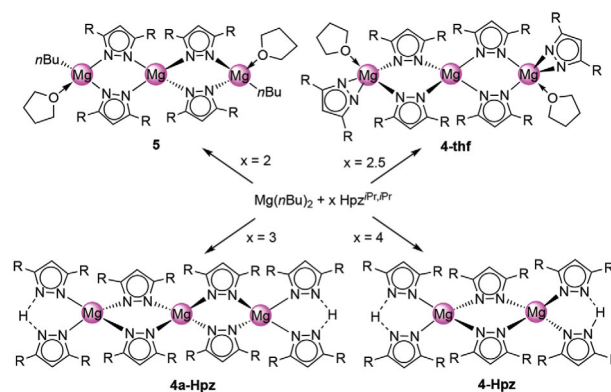


Figure 2. Crystal structures of [KMg(pz^{tBu,Me})₃]₂ (2, top) and [Mg(pz^{tBu,Me})₂(thf)]₂ (3-thf, bottom). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted and some Me/*t*Bu moieties are displayed as wireframe for clarity. See supporting information for selected interatomic distances and angles.^[27]

tural to Winter's *t*Bu/*t*Bu-congener [Mg(pz^{tBu,tBu})₂(thf)]₂ with two μ-1κ(N):2κ(N')-bridging pyrazolato ligands, two terminal κ²(N,N') pyrazolates and two THF molecules.^[20]

The mixed pyrazolato/pyrazole complex [Mg(pz^{iPr,iPr})₂(Hpz^{iPr,iPr})₂] (4-Hpz) reported by Ruhlandt-Senge and co-workers was obtained via protonolysis of Mg(*n*Bu)₂ with 4 equivalents of Hpz^{iPr,iPr} in THF.^[22] In order to avoid two potential reactive sites for CO₂ (vide infra) and since homoleptic [Mg(pz^{iPr,iPr})₂] has not yet been reported, we revisited the Mg(*n*Bu)₂/Hpz^{iPr,iPr} reaction. It was revealed that alkane elimination is very sensitive to the molar ratio employed. Applying a 1:2 ratio in THF did not give the anticipated homoleptic complex but incomplete protonolysis to trimetallic complex [Mg₃(pz^{iPr,iPr})₄(*n*Bu)₂(thf)₂] (5) with two remaining *n*-butyl moieties (Scheme 2). The crystal structure revealed a central magnesium coordinated by four pyrazolato ligands, bridging to the peripheral magnesium centers in 1κ(N):2κ(N') fashion (Figure S86, Supporting Information).^[27] The tetrahedral coordination of the outer magnesium atoms is completed by one *n*-butyl moiety and one THF molecule each. Note that Mg-alkyl moieties irreversibly insert CO₂ to afford carboxylate ligands.^[24,28]

Aiming at a suitable compromise between incomplete protonolysis and coordination of excess pyrazole, the ratio of



Scheme 2. Formation of different complexes in the reaction of Mg(*n*Bu)₂ with Hpz^{iPr,iPr} by using distinct ratios in THF. Complex 4-Hpz has been reported previously.^[22]

Mg(*n*Bu)₂ to Hpz^{iPr,iPr} was increased to 1:3. Now, crystallization accomplished the trimetallic mixed pyrazolato/pyrazole complex [Mg₃(pz^{iPr,iPr})₆(Hpz^{iPr,iPr})₂] (4a-Hpz, Figure 3, top).^[27] Like in complex 5, each magnesium center adopts a distorted tetrahedral coordination sphere. Also, the central magnesium is coordinated by four η¹(N)-pyrazolato ligands, bridging to the outer magnesium atoms in the same fashion as in 5. Overall, a spiro arrangement of two six-membered rings in half-chair conformation about the central magnesium is observed. The outer magnesium atoms are further coordinated by pyrazolato and pyrazole ligands, which are connected via a N—H—N hydrogen bond. The pyrazolato and pyrazole ligands display a staggered arrangement when viewed along the axis of the magnesium centers.

The ¹H NMR spectrum of 4a-Hpz in [D₈]toluene indicated a mixture of different species and, hence, fragmentation in solution. Remarkably, two proton signals appeared at 19.89 and 19.51 ppm, respectively, highly shifted to lower field and with a ratio of 1:0.2 (Figure S9, Supporting Information). Additionally, three signals in the region for the proton at the pyrazole ring can be observed along with several septet and doublet signals in the expected region for *i*Pr moieties. The ¹H NMR spectra of 4-Hpz and 4a-Hpz show the same signal pattern/fragments in [D₈]toluene but different signal intensities, due to distinct pyrazolato/pyrazole ratios. The two strong low-field shifted signals in 4-Hpz appear in the reversed ratio of 0.2:1. The intensity of all other signals of 4-Hpz are equally reversed, except for one signal at 5.84 ppm of the pyrazolato ring proton. The strongly low-field shifted proton signals corroborate a low-barrier hydrogen bond (LBHB) typical of symmetric hydrogen bonding.^[29]

The very same fragmentation of 4-Hpz and 4a-Hpz in solution was confirmed by ¹H DOSY (diffusion-ordered spectroscopy) NMR experiments in [D₈]toluene, revealing [Mg₂(pz^{iPr,iPr})₄(Hpz^{iPr,iPr})₂] (M = 958.02 g mol⁻¹) and [Mg₂(pz^{iPr,iPr})₄(Hpz^{iPr,iPr})] (M = 805.78 g mol⁻¹) as preferred fragments (for an in-depth discussion and other evaluation methods see the supporting information).^[30]

Using a ratio of 1:2.5 of Mg(*n*Bu)₂ and Hpz^{iPr,iPr} in the presence of THF first led to the isolation of a white amorphous powder, which after several recrystallization steps in *n*-pentane afforded single-crystalline [Mg₃(pz^{iPr,iPr})₆(thf)₂] (4-thf, Figure 3, middle).^[27] The white amorphous powder is most likely the ho-

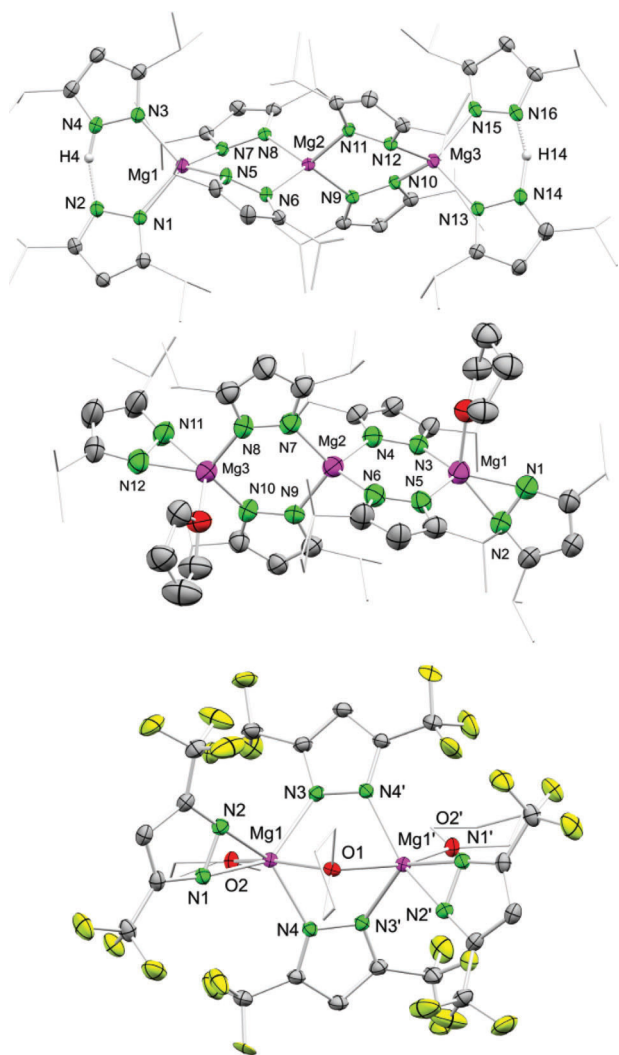
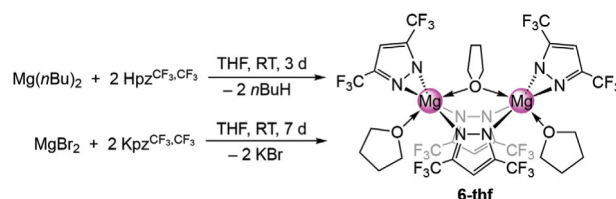


Figure 3. Crystal structures of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**, top), $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{thf})_2]$ (**4-thf**, middle) and $[\text{Mg}_2(\text{pz}^{\text{CF}_3,\text{CF}_3})_4(\text{thf})_3]$ (**6-thf**, bottom). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted as well as the *iPr* groups and THF ligands are displayed as wireframe for clarity. See supporting information for selected interatomic distances and angles.^[27]

moleptic donor-free $[\text{Mg}(\text{pz}^{i\text{Pr},i\text{Pr}})_2]_n$ (**4**) forming an insoluble infinite chain structure. The crystal structure of **4-thf** is similar to that of **4-Hpz** except for the terminating donor ligand (THF versus Hpz). The syntheses of **3-thf** and **4-thf** underline that the formation of homoleptic $[\text{Mg}(\text{pz}^{\text{R},\text{R}^*})_2]_n$ occurs preferentially when $\text{Mg}(n\text{Bu})_2$ and $\text{Hpz}^{\text{R},\text{R}^*}$ are employed in a ratio of 1:2.5.

For the 3,5-bis(trifluoromethyl)pyrazole, both the protonolysis and the salt-metathesis route in THF yielded $[\text{Mg}_2(\text{pz}^{\text{CF}_3,\text{CF}_3})_4(\text{thf})_3]$ (**6-thf**) as a crystalline material (Scheme 3). The crystal structure of **6-thf** revealed 5-coordinate magnesium centers in a strongly distorted trigonal bipyramidal geometry (Figure 3, bottom).^[27] The magnesium centers are bridged by two $\mu-1\kappa(\text{N}):2\kappa(\text{N}')$ pyrazolato and one $\mu-1\kappa(\text{O}):2\kappa(\text{O})$ THF ligand.^[31] The bridging THF distorts the six-membered metallocycle to a twisted boat conformation. The ^1H , ^{13}C and ^{19}F NMR spectra of **6-thf** revealed high mobility of the pyrazolato ligands



Scheme 3. Synthesis of complex **6-thf** according to salt-metathesis and protonolysis protocols.

in solution at ambient temperature. Both $^1J_{\text{C,F}}$ (267.77 Hz) and $^2J_{\text{C,F}}$ couplings (36.58 Hz) were observed as quartets at 123.0 ppm and 142.7 ppm, respectively.^[32]

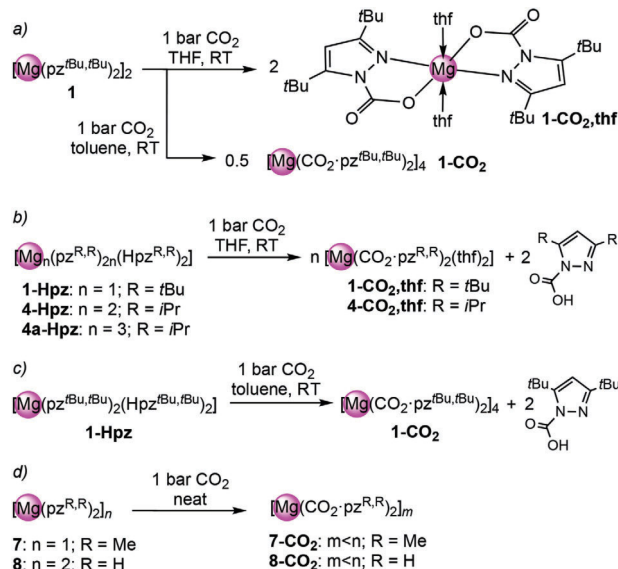
Protonolysis of $\text{Mg}(n\text{Bu})_2$ with both the 3,5-dimethylpyrazole and the unsubstituted “parent” pyrazole gave amorphous white powders, which are insoluble in common solvents. However, the ^{13}C CP/MAS (magic-angle spinning) spectra unambiguously revealed the formation of $[\text{Mg}(\text{pz}^{\text{Me,Me}})_2]_n$ (**7**) and $[\text{Mg}(\text{pz})_2]_n$ (**8**). For compound **7** the carbon resonances in the 3 and 5 position appeared as one signal at 152.1 ppm, while the carbon in the 4 position and the Me moieties were detected at 107.1 ppm and as two close signals at 12.0 and 10.9 ppm, respectively. As expected, compound **8** shows only two ^{13}C signals in the aromatic region at 141.6 and 103.1 ppm, respectively. Both compounds most likely form an infinite chain structure like $[\text{Zn}(\text{pz})_2]_n$ which was characterized by powder X-ray diffraction.^[33] This is underlined by the fact, that the DRIFT spectra of **8** and $[\text{Zn}(\text{pz})_2]_n$ are nearly identical (Figure S79, Supporting Information).

The level of magnesium pyrazolate hydrolytic stability was probed for $[\text{Mg}(\text{pz}^{t\text{Bu},t\text{Bu}})_2]_2$ (**1**) and $[\text{Mg}(\text{pz})_2]_n$ (**8**). When exposed to air (and moisture) a solution of **1** in THF shows slow decomposition as indicated by an incipient precipitation ($\text{Mg}(\text{OH})_2$) and formation of the respective pyrazole. A morphology change of mostly insoluble, flaky **8**, mainly affecting the surface of the material, was clearly visible in SEM images upon exposure to ambient atmosphere (Figures S81–S83, Supporting Information).

2.3. CO_2 Insertion into Magnesium Bis(pyrazolate)s under Anhydrous Conditions

Exposing dimeric $[\text{Mg}(\text{pz}^{t\text{Bu},t\text{Bu}})_2]_2$ (**1**) to 1 bar CO_2 in THF led to the insertion of CO_2 into the $\text{Mg}-\text{N}(\text{pyrazolato})$ bonds, forming the monomeric carbamate complex $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{t\text{Bu},t\text{Bu}})_2(\text{thf})_2]$ (**1-CO₂,thf**) (Scheme 4a).^[34] The reaction occurs instantly in a small-scale reaction and single crystals could be obtained overnight at ambient temperature. The mass fraction of **1-CO₂,thf** amounts to 14.3 wt% CO_2 or 3.3 mmol CO_2 per gram.

Complex **1-CO₂,thf** displays a distorted octahedral coordination geometry, the magnesium center being coordinated by two nearly planar $\text{CO}_2\cdot\text{pz}^{t\text{Bu},t\text{Bu}}$ carbamate moieties in the $\kappa^2(\text{N},\text{O})$ mode, and two apical THF donor molecules (Figure 4).^[35] The inserted CO_2 moiety exhibits an angle of $129.23(9)^\circ$ and distinct C–O distances of 1.2165(12) and 1.2621(11) Å, which however, are less divergent from each other than in cerium complex $[\text{Ce}(\text{CO}_2\cdot\text{pz}^{\text{Me,Me}})_4]$ (1.207 Å and 1.291 Å).^[16a] This can be attributed to the less oxophilic character of magnesium compared to cerium.^[36] The pyrazole ring of the carbamate ligand loses its aromaticity compared to the pyrazolato ligand of precursor **1**, as



Scheme 4. Reaction of magnesium pyrazolates with excess CO₂.

revealed by distinct interatomic distances of both the C—C ring bonds (C2—C1: 1.3788(13) Å; C2—C3: 1.4073(13) Å) and the C—N ring bonds (C1—N1: 1.3800(12) Å; C3—N2: 1.3310(12) Å).

Carbon dioxide insertion into homoleptic pyrazolate 1 was initially observed by DRIFTS measurements showing the characteristic stretching vibration of the C—O double bond at $\tilde{\nu} = 1745 \text{ cm}^{-1}$ and of the C—O single bond at $\tilde{\nu} = 1293 \text{ cm}^{-1}$ (Figure S75, Supporting Information). The ¹H NMR spectrum of 1-CO₂,thf in [D₈]THF revealed the characteristic splitting of the *t*Bu resonances into two signals at $\delta = 1.48 \text{ ppm}$ and $\delta = 1.24 \text{ ppm}$ (Figure S24, Supporting Information) due to the asymmetry caused by the inserted CO₂. The ¹³C NMR signal of the inserted CO₂ appeared at 149.0 ppm (Figure S25, Supporting Information) which is in the range of known complexes with CO₂·pz^{R,R} moieties.^[16a,37]

Complex 1-CO₂,thf is stable in solution at ambient temperature and as a solid at -40 °C. In neat form, CO₂ slowly volatilizes at ambient temperature, as monitored by ¹H NMR spectroscopy. Under reduced pressure (ca. 10⁻² mbar), enhanced CO₂ evapo-

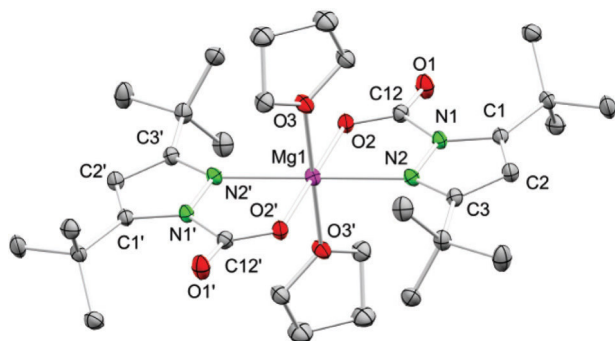
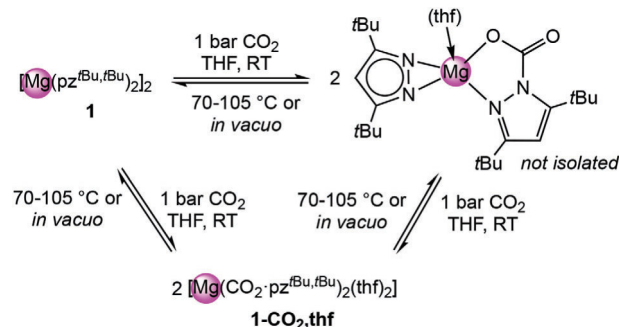


Figure 4. Crystal structure of $[\text{Mg}(\text{CO}_2\text{pz}^{\text{tBu},\text{tBu}})_2(\text{thf})_2]$ (1-CO₂,thf). Ellipsoids are set at the 50% probability level. Hydrogen atoms as well as disorder in the thf ligands are omitted for clarity. See supporting information for selected interatomic distances and angles.^[27]



Scheme 5. Reversibility of CO₂ insertion into the Mg—N bond of $[\text{Mg}(\text{pz}^{\text{tBu},\text{tBu}})_2]_2$ (1) at elaborate temperature or reduced pressure (10⁻² mbar).

ration occurred, and after 6 h a mixture of 1-CO₂,thf, 1, and a proposed mono-inserted complex was observed in the ¹H NMR spectrum, in a ratio of 1:0.8:0.8 (Figure S26, Supporting Information). Admitting in turn 1 bar of CO₂ led to the complete reformation of 1-CO₂,thf. This reversible behavior was further investigated by variable-temperature (VT) ¹H NMR spectroscopy (Figure S27, Supporting Information). The signal of 1 emerged at 70 °C, while at 105 °C 1-CO₂,thf was completely converted into 1. Cooling to ambient temperature did not afford complete reinsertion of CO₂ but again a mixture of 1-CO₂,thf, 1, and the mono inserted complex in a ratio of 1:1:1. After renewed addition of 1 bar CO₂, the mixture quantitatively reformed 1-CO₂,thf, indicating that the overall CO₂ insertion step is fully reversible (Scheme 5).^[38]

The CO₂ de-insertion process of 1-CO₂,thf was further investigated using thermogravimetric analysis (TGA) by heating the solid from 28 °C to 450 °C and applying a heating rate of 2 K min⁻¹ under constant argon flow (Figure S71, Supporting Information). The first step of 22.16 % mass loss between 78 °C and 134 °C corresponds to the release of the THF donor ligands (calcd. 23.5%). This is followed by two distinct de-insertion steps of each CO₂ (calcd. 7.2 % each) with mass-loss events of 4.70 % between 134 °C and 170 °C and 6.15 % between 170 °C and 233 °C. The deviation from the calculated value can be explained by incipient gas formation before the TGA experiment and slightly overlapping release of donor THF and the first CO₂ de-insertion step. The two distinct de-insertion steps observed by TGA support the proposed formation of the mono inserted complex, indicated by ¹H NMR spectroscopy (Scheme 5).

The reaction of unsolvated 1 with CO₂ in toluene or benzene did not afford a single-crystalline product. However, the occurrence of a CO₂ insertion was clearly indicated by the respective ¹H NMR spectrum (Figure S30, Supporting Information). Five signals for the pyrazole backbone protons between 5.89 and 6.05 ppm each with an integral of 1 and nine signals for *t*Bu moieties between 0.87 and 1.78 ppm, of which eight have an integral of 9 and one has an integral of 18, are detected. This pattern indicates that 1 reacts with CO₂ in non-donating solvents to a putatively oligomeric species 1-CO₂ (Scheme 4a). Compound 1-CO₂ was further examined by ¹H DOSY NMR spectroscopy in [D₈]toluene (Figures S31–S33, Supporting Information). Accordingly, only one large signal was revealed with a diffusion coefficient of $\log D = -8.96 \log(\text{m}^2 \text{ s}^{-1})$ for all the ¹H NMR sig-

nals mentioned above. The molar mass calculation of the measured diffusion coefficient, approximated by a highly compact sphere, accounts for a molar mass of 1875 g mol⁻¹. This suggests that 1-CO₂ is a tetrameric oligomer/cluster containing four Mg(CO₂·pz^{tBu,tBu})₂ units with *M* = 1883.59 g mol⁻¹ (see Supporting Information for a more in-depth discussion).^[30] The proposed complex [Mg(CO₂·pz^{tBu,tBu})₂]₄ (1-CO₂) achieves a capacity of 18.7 wt% CO₂ or 4.3 mmol CO₂ per gram.

Reacting 4-thf with 1 bar CO₂ led to the formation of [Mg(CO₂·pz^{iPr,iPr})₂(thf)₂] (4-CO₂,thf) (not shown in Scheme 4). Although the ¹H NMR spectrum of 4-thf is rather complicated (Figure S16, Supporting Information), due to possible fragmentation/oligomerization like in 4-Hpz and 4a-Hpz, the ¹H NMR spectrum of 4-CO₂,thf revealed complete and clean CO₂ insertion as indicated by two distinct *iPr* groups. The ¹³C NMR showed the corresponding *iPr* signal patterns and a resonance at 149.6 ppm for inserted CO₂. Unfortunately, complex 4-CO₂,thf could not be obtained in single-crystalline form. Conducting the 4-thf/CO₂ reaction in toluene (not shown in Scheme 4), gave also a complex ¹H NMR spectrum (Figures S40 and S41, Supporting Information), but resulted in a few crystals suitable for an XRD analysis. The crystal structure of LiMg₄(CO₂·pz^{iPr,iPr})₉, albeit of low quality (connectivity structure only) clearly revealed an exclusive carbamate environment of the metal centers (Figure S91, Supporting Information). The magnesium atoms are arranged tetrahedrally around a central lithium atom. Contamination of the reaction mixture with lithium originated from precursor Mg(*n*Bu)₂ as revealed by ⁷Li NMR spectroscopy. We assume that crystallization of putative donor-free [Mg₄(CO₂·pz^{iPr,iPr})₈] is strongly favored by the presence of the alkali metal.

Treatment of the mixed pyrazolato/pyrazole complexes 4-Hpz, 4a-Hpz, and known [Mg(pz^{tBu,tBu})₂(Hpz^{tBu,tBu})₂] (1-Hpz)^[22] with CO₂ was performed in the same way as for 1 (Scheme 4b). The ¹H NMR spectra of the 1-Hpz/CO₂ reactions revealed signal sets identical to those of 1-CO₂,thf ([D₈]THF) and 1-CO₂ (in [D₈]toluene); for the reaction in THF, the formation of 1-CO₂,thf could be confirmed by a unit-cell check of the obtained crystals. In both solvents, an additional set of four new broad signals is detected: two in the range of *t*Bu moieties (δ = 1.28 and 1.23 ppm), one in the aromatic range (δ = 5.82 ppm) and one in the acidic proton range at δ = 11.34 ppm, which does not align with free Hpz^{tBu,tBu} (Figure S34, Supporting Information). Furthermore, the presence of two *t*Bu signals corroborates a reaction of CO₂ with the donor pyrazole to yield the new carbamic acid HOOCpz^{tBu,tBu}. Since free pyrazoles, like aromatic amines, do not react with CO₂ under these conditions, it can be hypothesized that the hydrogen-bond pyrazolato/pyrazole arrangement is a prerequisite for forming the carbamic acid/ammonium carbamate.^[39] A similar motif was observed for compound [Cd(μ -ac)₂(Hpz)₂]_n (ac = acetate) in which the acetate has an H-bond interaction with the pyrazole.^[33] Such two-fold activation of CO₂ also applies for the isopropyl-substituted pyrazole adducts 4-Hpz and 4a-Hpz. The ¹H NMR spectra display one signal set assignable to [Mg(CO₂·pz^{iPr,iPr})₂(thf)₂] (4-CO₂,thf) with the expected splitting of the *iPr* signals. Additionally, one signal set appeared ascribed to the carbamic acid HOOCpz^{iPr,iPr}. Both starting materials lead to similar spectra, with varying signal intensities, due to the different pyrazolato/pyrazole ratios. As for [Mg(pz^{tBu,tBu})₂(Hpz^{tBu,tBu})₂] (1-Hpz), the CO₂ insertion is re-

versible for the carbamate ligand in 4-CO₂,thf, but remains irreversible for the disassociated carbamic acid, under the conditions applied (Scheme 4c).

Complex [Mg(pz^{tBu,Me})₂(thf)]₂ (3-thf) featuring the mixed *t*Bu/Me 3,5-substitution of the pyrazolato ligand clearly engaged in CO₂ insertion. The resulting ¹H NMR spectra, however, revealed very complicated signal pattern, which is why this complex was not pursued further. In contrast, CO₂ insertion was not detected for fluorinated [Mg₂(pz^{CF₃,CF₃})₄(thf)₃] (6-thf), likely due to the decreased nucleophilicity of the pyrazolato nitrogen atoms (vide infra).

Unexpectedly, the polymeric pyrazolates Mg(pz^{Me,Me})₂ (7) and [Mg(pz)₂]_n (8), which are insoluble in most common solvents, feature a rather remarkable CO₂-insertion behavior (Scheme 3d). When exposing the solids in a very simple manner to an atmosphere of 1 bar CO₂ for three hours, a mass gain of 29.4 wt% for 7 and 36.3 wt% for 8 were found, accompanied by slight morphology change and warming of the samples. This is close to the calculated exhaustive CO₂ insertion into the Mg–N(pyrazolato) bond, accounting for 29.1 and 35.7 wt% CO₂, respectively. The obtained materials [Mg(CO₂·pz^{Me,Me})₂]_n (7-CO₂) and [Mg(CO₂·pz)₂]_n (8-CO₂) were further examined by TGA (Figures S72 and S73, Supporting Information) and solid-state NMR and FTIR spectroscopy. For 7-CO₂, a CO₂ release step of 29.5 % was observed when heating a sample from ambient temperature to 210 °C, in line with the CO₂ mass fraction. Similarly, material 8-CO₂ revealed a mass-loss event of 34.3 %, in the range from 50 °C to 225 °C. Different from 1-CO₂,thf and 8-CO₂, where the CO₂ de-insertion only starts at elevated temperatures, the CO₂ release for 7-CO₂ already takes place at ambient temperature. The IR spectra of both complexes 7-CO₂ and 8-CO₂ (Figures S76 and S77, Supporting Information) show an intense and broad band between 1709 and 1744 cm⁻¹ for the C–O double bond stretching vibration of the inserted CO₂. The CO₂ insertion/de-insertion behavior of [Mg(pz)₂]_n (8) was further elucidated by conducting an in situ IR experiment. When replacing the argon atmosphere by CO₂, immediate formation to 8-CO₂ took place. When restoring the argon atmosphere and heating in 10 °C steps to 240 °C, the C–O double bond stretching vibration at 1709 cm⁻¹ slowly decreased and the overall IR spectrum converted back to that of 8 (Figure S80, Supporting Information). The ¹³C CP/MAS NMR spectrum of 7-CO₂ revealed distinct carbon atoms at the 3 and 5 positions (148.6 and 142.7 ppm) in comparison to 7 (152.1 ppm). The ¹³C signal of the inserted CO₂ appeared as a shoulder to the signal at 148.6 ppm. To further clarify the signal assignment complex 7 was treated with labeled ¹³CO₂, which resulted in two intense signals at 152.4 and 148.7 ppm. The signals of the methyl groups appeared as one signal at 12.3 ppm. Upon CO₂ insertion, 7-CO₂ is soluble in THF and the respective ¹H NMR spectrum confirmed its formation by two signals at 2.46 and 2.12 ppm of the methyl groups in 3 and 5 position. The solution ¹³C NMR signal of the inserted CO₂ could be resolved at 149.8 ppm. The ¹³C CP/MAS NMR spectrum of 8-CO₂ shows four distinct signals in the aromatic region (Figure 5). The inserted CO₂ appeared as a signal at 150.2 ppm, and the carbon atoms in 3 and 5 position at 139.1 and 128.6 ppm, and the carbon in 4 position at 107.2 ppm. Repeated CO₂ insertion/de-insertion was probed for 7/7-CO₂ and proven to be fully reversible by solid-state NMR and FTIR spectroscopy (Figures S51 and S78, Supporting Information).

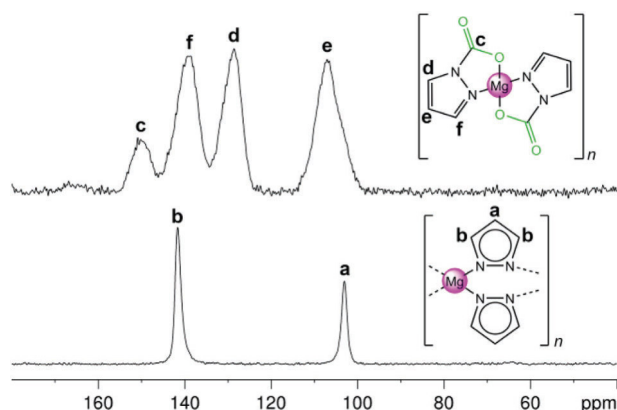


Figure 5. ^{13}C CP/MAS NMR spectra (75.47 MHz) of $[\text{Mg}(\text{pz})_2]_n$ (**8**) and $[\text{Mg}(\text{CO}_2 \cdot \text{pz})_2]_n$ (**8**· CO_2).

Comparative studies with literature known $[\text{Zn}(\text{pz})_2]_n$ and CO_2 did not indicate any appreciable CO_2 insertion.^[40] Although both metal centers have the same charge and similar ionic radii, the pronounced oxophilicity of magnesium^[36] combined with the harder $\text{Mg}(\text{II})$ ion determine the high CO_2 affinity of the pyrazolate complexes compared to the zinc congeners.

Having established these solid/gas reactions for **7** and **8**, a solid sample of **1** was exposed similarly to 1 bar CO_2 . A mass gain of 18.4 % close to the calculated mass fraction of 18.7 wt% CO_2 suggested the formation of putative **1**· CO_2 (vide supra). Dissolving the obtained solid in $[\text{D}_8]\text{THF}$ and $[\text{D}_8]\text{toluene}$ gave ^1H NMR spectra identical to those of **1**· CO_2 , thf and **1**· CO_2 , respectively. The TGA of **1**· CO_2 showed a continuous mass loss with less distinct releasing steps, which would be expected for a cluster species. For further comparison, our previously reported ceric pyrazolate $[\text{Ce}(\text{Me}_2\text{pz})_4(\text{thf})]$ did not insert the heteroallene when stored under 1 bar CO_2 pressure for three days.^[16a]

2.4. Catalytic Formation of Cyclic Carbonates from CO_2 and Epoxides

The discrete complexes $[\text{Mg}(\text{pz}^{\text{tBu}, \text{tBu}})_2]_2$ (**1**), $[\text{Mg}(\text{pz}^{\text{tBu}, \text{Me}})_2(\text{thf})]_2$ (**3**- thf), $[\text{Mg}_3(\text{pz}^{\text{iPr}, \text{iPr}})_6(\text{Hpz}^{\text{iPr}, \text{iPr}})_2]$ (**4a**- Hpz), $[\text{Mg}_3(\text{pz}^{\text{iPr}, \text{iPr}})_6(\text{thf})_2]$ (**4**- thf), and $[\text{Mg}_2(\text{pz}^{\text{CF}_3, \text{CF}_3})_4(\text{thf})_3]$ (**6**- thf) were probed as catalysts in the cycloaddition of epoxides and CO_2 to cyclic carbonates (see Scheme S2, Supporting Information for a proposed mechanism). For better comparability, the conditions stated in Table 1 have been adapted to those reported previously for the rare-earth-metal pyrazolates.^[16a]

Complex $[\text{Mg}(\text{pz}^{\text{tBu}, \text{tBu}})_2]_2$ (**1**) gave 56 % conversion of propylene oxide and CO_2 to the cyclic carbonate, with a TON of 112 (Table 1, entry 1). By using a twofold catalyst load of 1 mol% the conversion increased to 85 %, while the TON decreased to 85 (entry 2). This might result from catalyst aggregation in solution, by exceeding the solubility of **1** in epoxide or due to a solubility gradient shift between epoxide and cyclic carbonate. As expected, donor adduct **1**- thf showed a slightly lower conversion of 51 % (entry 6). Similarly, for catalysts **3**- thf , **4a**- Hpz and **4**- thf the conversion slightly decreased to 43 %, 45 % and 42 %, respectively (entries 7 to 8 and 13). As mentioned before, the pyrazole donors disassociate upon CO_2 insertion as carbamic acid which can lead

Table 1. Formation of cyclic carbonates from epoxides and CO_2 , catalyzed by magnesium pyrazolates under study.

$\text{R} \text{---} \text{epoxide} + 1 \text{ bar } \text{CO}_2 \xrightarrow[\text{rt, 24 h}]{[\text{Cat.}] \text{ 1 mol\% TBAB}} \text{R} \text{---} \text{cyclic carbonate}$				
Entry ^{a)}	Catalyst	R =	Conversion [%] ^{b)}	TON ^{c)}
1	1	Me	56	112
2 ^{d)}	1	Me	85	85
3	1	Ph	4	8
4	1	<i>t</i> Bu	4	8
5	1	<i>n</i> Bu	7	14
6	1 - thf	Me	51	102
7	3 - thf	Me	43	86
8	4a - Hpz	Me	45	90
9 ^{e)}	4a - Hpz	Me	77	51
10	4a - Hpz	Ph	4	8
11	4a - Hpz	<i>t</i> Bu	3	6
12	4a - Hpz	<i>n</i> Bu	11	22
13	4 - thf	Me	42	84
14	6 - thf	Me	59	118
15	6 - thf	Ph	8	16
16	6 - thf	<i>t</i> Bu	4	8
17	6 - thf	<i>n</i> Bu	18	36
18 ^{f)}	—	Me	3	6

^{a)} Reaction conditions if not noted otherwise: 1 bar CO_2 , 0.25 mol% catalyst or 0.167 mol% for **4a**- Hpz and **4**- Hpz ($\equiv 0.5$ mol% Mg centers), 1 mol% TBAB at ambient temperature for 24 h in neat epoxide; ^{b)} Determined by comparison of the proton integrals in α -position of the epoxide and the corresponding cyclic carbonate (expect for 3,3-dimethyl-1,2-butene carbonate where the integral of the *t*Bu moieties was used); ^{c)} ((epoxide/Mg) · conversion)/100; ^{d)} 1 bar CO_2 , 1 mol% catalyst **1**, 1 mol% TBAB, at ambient temperature for 24 h; ^{e)} 1 bar CO_2 , 0.5 mol% catalyst **4a**- Hpz , 1 mol% TBAB, at ambient temperature for 24 h; ^{f)} only TBAB without metal catalyst; TON refers to concentration TBAB.

also to solubility shifts or blocking of the metal center. Increasing the amount of **4a**- Hpz from 0.167 mol% ($\equiv 0.5$ mol% Mg centers) to 0.5 mol% complex **4a**- Hpz ($\equiv 1.5$ mol% Mg centers) led to an enhanced conversion of 77 % but also here the TON was reduced to 51 (entry 9). Accordingly, the effects of reduced catalytic activity due to high catalyst load seem to be intrinsic.

Interestingly, fluorinated complex **6**- thf shows the highest catalytic activity with a TON of 118 (entry 14), despite a side reaction, causing a highly viscous reaction mixture. Crucially, **6**- thf exhibits the highest catalytic activity although it does not insert CO_2 (vide supra). Consequently, catalytic activity and CO_2 affinity seem to be inversely proportional. As expected, switching to the more sterically demanding epoxides with *t*Bu, *n*Bu and Ph moieties, the conversion is drastically decreased ranging from 4 % to 11 % (entries 3–5, 10–12 and 15–17). Again, striking is comparatively increased catalytic activity in case of **6**- thf , giving 18 % conversion of epoxihexane in the absence of any side reaction. Complexes **7** and **8** showed also moderate conversion, however, due to high contents of insoluble oligomeric/polymeric side products, these values were not considered representative.

To determine the state of the catalyst after the catalytic reaction, each 10 mol% of **1** and TBAB were employed and the reaction mixture examined by ^1H NMR spectroscopy (Figure S70, Supporting Information). Besides the signals for TBAB and propylene carbonate, one signal set could be assigned to complex $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ ($1\text{-CO}_2\cdot\text{thf}$). Moreover, three additional signals in the region for pyrazolate backbones were detected, assignable neither to the carbamic acid, a mono-inserted species nor to a hydrolysis product.

The overall catalytic activity of the magnesium pyrazolates is only moderate in comparison to the rare-earth-metal congeners.^[16a] For example, cerium pyrazolate $[\text{Ce}(\text{Me}_2\text{pz})_4]_2$ converted up to 98 % of propylene oxide with a TON of 196, under the same conditions. By heating the cerium reaction up to 90 °C, applying a pressure of 10 bar CO_2 and using a catalytic load of 0.1 mol% the TON could even be increased to 600. This is clearly reflected in the higher CO_2 release temperatures of magnesium pyrazolates (higher CO_2 affinity), in agreement with the NMR/TGA studies (vide supra). Also, in comparison to other magnesium catalysts used in this very cycloaddition reaction, our complexes show only moderate catalytic activity.^[35,41] Although hardly comparable due to much harsher reaction conditions, a magnesium porphyrin complex with an incorporated tetra-*n*-butylammonium reported by Ema et al. reaches TONs of up to 138 000 with a catalytic load of 0.0005 mol%, at 120 °C and 17 bar CO_2 .

3. Conclusion

The conceptional approach of carbon dioxide insertion into metal pyrazolates is applicable to the light metal magnesium. Exhaustive CO_2 insertion into the $\text{Mg-N}(\text{pz}^{\text{R,R}})$ bond is proven by the crystal structure of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ as well as ^{13}C NMR spectroscopy and thermogravimetric analysis of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{R,R}})_2]_n$ ($\text{R} = \text{H, Me, iPr}$). Carbon dioxide uptake at ambient temperature is instant and reversible with de-insertion temperatures <250 °C. Remarkably, CO_2 insertion also occurs quantitatively using the magnesium pyrazolates in solid form (without solvent!). Unsubstituted $[\text{Mg}(\text{CO}_2\cdot\text{pz})_2]_n$ accomplishes a maximum capacity of 35.7 wt% CO_2 (8.2 mmol g^{-1}) leveling that of the most efficient metalorganic frameworks (MOFs). Depending on the pyrazolate substituents *R*, the homoleptic magnesium complexes are easily obtained via salt metathesis or protonolysis applying MgBr_2 and $\text{Mg}(\text{nBu})_2$, respectively. For the protonolysis protocol, stoichiometric control and hence pyrazole coordination are critical since the CO_2 uptake is affected by additional formation of the respective carbamic acids $\text{HOOCpz}^{\text{R,R}}$. The salt-metathesis protocol is prone to ate complex formation as evidenced for $[\text{KMg}(\text{pz}^{\text{tBu,Me}})_3]_2$. The magnesium pyrazolates display only moderate catalytic activity in the reaction of CO_2 and epoxides to cyclic carbonates. Crucially, catalytic activity and CO_2 affinity seem to be inversely proportional, as revealed by the fluorinated complex $[\text{Mg}_2(\text{pz}^{\text{CF}_3,\text{CF}_3})_4(\text{thf})_3]$, exhibiting the highest catalytic activity while lacking any traceable CO_2 insertion, under the applied conditions. Overall, the catalytic activity is lower than that of the cerium congeners attributable to the higher CO_2 release temperatures of the magnesium complexes. Due to significant hydrolytic instability such magnesium pyrazolate complexes are not meant for any industrial large scale carbon dioxide

removal technology but might stimulate new inorganic material design.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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carbon dioxide, catalysis, epoxides, magnesium, pyrazolates

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Supporting Information

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Organomagnesia: Reversibly High Carbon Dioxide Uptake by Magnesium Pyrazolates

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Supporting Information

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Experimental Section.

General Considerations. All manipulations were performed under rigorous exclusion of air and moisture under argon atmosphere (< 0.1 ppm O_2 , < 0.1 ppm of H_2O) in a MB200B glovebox (MBraun) or according to standard Schlenk techniques and in oven-dried glassware. Solvents (THF, *n*-pentane, *n*-hexane, Et_2O and toluene) were purified by using SPS Grubbs-type columns (MBraun SPS-800, solvent purification system) and stored inside a glovebox. THF was dried further over molecular sieves. $[D_6]$ benzene, $[D_8]$ toluene and $[D_8]$ THF were obtained from Sigma Aldrich and dried over Na/K alloy and filtered prior to use. 3,5-Bis(trifluoromethyl)pyrazole (99%), 3,5-dimethylpyrazole (99%), di-*n*-butylmagnesium (1 M in Et_2O/n -hexane), epoxystyrene ($>97\%$, degassed prior to use) and magnesium bromide (98%) were purchased from Sigma Aldrich and used as received. 3,5-Di-isopropylpyrazole (98%) was purchased from TCI and used as received. 1,2-Epoxyhexane (97%) was purchased from Thermo Fischer and degassed prior to use. Propylene oxide and pyrazole (98%) were purchased from Acros Organics and the former was degassed prior to use. 2-*tert*-Butyloxirane was purchased from abcr and degassed prior to use. 3-Methyl-5-*tert*-butylpyrazole and 3,5-di-*tert*-butylpyrazole were synthesized according to procedures known in the literature.^[1] Argon and CO_2 (99.95%) were supplied by Westfalen AG. 1H and ^{13}C NMR spectra were recorded on a Bruker AVII+400 spectrometer (1H : 400.13 MHz; ^{13}C : 100.61 MHz) at 299 K. The chemical shifts listed in the experimental section are referenced to solvent residual resonances in parts per million in relation to tetramethylsilane. The variable temperature 1H NMR spectra and some other spectra were recorded in a J. Young valve NMR tube on a Bruker AVII+500 spectrometer (1H : 500.13 MHz; ^{13}C : 125.76 MHz). The 1H DOSY NMR spectra were recorded in a J. Young valve NMR tube on a Bruker AVIII HDX 700 spectrometer (1H : 700.29 MHz). IR spectra were recorded on a NICOLET 6700 FTIR spectrometer (Thermo Fisher Scientific). The samples were mixed with KBr powder and measured in a DRIFTS cell with KBr windows. In situ IR spectra were recorded on a Bruker Invenio R spectrometer equipped with a praying mantis unit. Data were converted by using the Kubelka-Munk refinement. Elementary analyses were performed on an Elementar vario MICRO cube. SEM images were obtained on a Hitachi SU8030. Single crystals were grown from saturated solutions of *n*-hexane or THF by standard techniques. Suitable single crystals for X-ray structure analysis were selected in a glovebox and coated with Parabar 10312 (Hampton research). Crystallographic data were measured on a Bruker APEX II DUO instrument equipped with μS micro focus sealed tube and QUAZAR optics for $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and $CuK\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). Compounds **2** and **4a-Hpz** were crystallized at $-40^\circ C$ from a solution of *n*-hexane, **3-thf** at ambient temperature. Crystals of **4-thf** could be obtained from *n*-pentane at $-40^\circ C$, and for **5** a mixture of chilled Et_2O/n -hexane ($-40^\circ C$) was used. Crystals of **1-CO₂,thf** were harvested from a THF solution at ambient temperature and those of **6-thf** at $-40^\circ C$. The crystallization of $LiMg_4(CO_2Pz^{iPr,iPr})_9$ became feasible due to a slight contamination of the magnesium precursor with lithium, after many unsuccessful crystallization attempts. A few crystals were obtained in a J. Young tube at ambient temperature from a toluene solution. The crystal quality was low and only intensities up to $1 \text{ \AA}$ could be found. Although the structure could be solved, the calculated data only represent a connectivity structure, ruling out any detailed interpretation of metrical parameters. The data collection strategy was determined using COSMO^[2] employing ω - and ϕ scans. Raw data were processed using APEX^[3] and SAINT,^[4] corrections for absorption effects were applied using SADABS.^[5] The structure was solved by direct methods and refined against all data by full-matrix least-squares methods on F^2 using ShelXTL^[6] and ShelXL.^[7] Disorder models are calculated using DSR^[8], a program for refining disordered structures in SHELXL. All graphics were produced employing Mercury.^[9]

[Mg(pz^{tBu,tBu})₂(thf)]₂ (1-thf**).** $Hpz^{tBu,tBu}$ (200.0 mg, 1.109 mmol) was dissolved in 10 mL THF and a solution of $Mg(nBu)_2$ (0.56 mL, 0.56 mmol, 1 M in Et_2O/n -hexane) was added dropwise. After stirring for 2 h, the solution was concentrated under reduced pressure and stored at ambient temperature. Overnight colorless crystals were obtained suitable for an X-ray structure analysis. Drying the crystals under reduced pressure gave **1-thf** (210.0 mg, $461.6 \mu\text{mol}$, 83%). Analytical data are consistent with the literature.^[10]

[KMg(pz^{tBu,Me})₃]₂ (2**).** Magnesium bromide (121.7 mg, $661 \mu\text{mol}$) and $Kpz^{tBu,Me}$ (233.1 mg, 1.322 mmol) were dissolved in toluene and stirred for 16 h. After the solvent was removed under reduced pressure the residue was extracted three times with *n*-hexane. The solution was concentrated and stored at $-40^\circ C$. Overnight **2** (71.3 mg, $75 \mu\text{mol}$, 23%) could be obtained as colorless crystals. 1H NMR (400.1 MHz, $[D_8]$ THF, $26^\circ C$): $\delta = 5.87$ (s 6H, 4-H(pz)), 2.14 (s, 18H, CH_3), 1.17 (s, 54H, $C(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $[D_8]$ THF, $26^\circ C$): $\delta = 163.3$ (3-C(pz)), 148.1 (5-C(pz)), 100.5 (4-C(pz)), 32.3 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 13.2 (CH_3) ppm. IR (Nujol/CsI): $\tilde{\nu}_{max} = 2953$ (Nujol;

CH), 2923 (Nujol; CH), 2854 (Nujol; CH), 1515 (vs), 1497 (s), 1462 (Nujol), 1410 (vs), 1377 (Nujol), 1363 (vs), 1312 (vs), 1232 (s), 1206 (s), 1092 (m), 1072 (s), 1060 (s), 1043 (w), 1020 (s), 996 (m), 987 (m), 972 (w), 933 (vw), 923 (vw), 893 (vw), 816 (m), 772 (vs), 728 (m), 694 (m), 570 (w), 503 (w), 492 (w), 467 (w), 436 (s) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{48}\text{H}_{78}\text{K}_2\text{Mg}_2\text{N}_{12}$ (950.04 g mol^{-1}): C 60.68, H 8.28, N 17.69; found: C 60.56, H 8.50, N 17.49.

[Mg(pz^{tBu,Me})₂(thf)]₂ (3-thf). Hpz^{tBu,Me} (200.0 mg, 1.447 mmol) was dissolved in 10 mL THF and a solution of $\text{Mg}(\text{nBu})_2$ (0.58 mL, 0.58 mmol, 1 M in $\text{Et}_2\text{O}/n\text{-hexane}$) was added dropwise. After stirring overnight, the solution was concentrated under reduced pressure and stored at ambient temperature. After 7 days colorless crystals were obtained suitable for an X-ray structure analysis. The supernatant slurry solution was separated and the crystals covered with a sticky oil were washed several times with *n*-pentane. Drying the crystals under reduced pressure gave **3-thf** (180.4 mg, 243 μmol , 67%). ^1H NMR (500.13 MHz, $[\text{D}_8]\text{THF}$, 26 °C): δ = 5.78 (s, 4H, 4-*H*(pz)), 3.61 (m, 8 H, 1/4- CH_2 (thf)), 2.08 (s, 12 H, CH_3), 1.77 (m, 8 H, 2/3- CH_2 (thf)), 1.15 (s, 36 H, $\text{C}(\text{CH}_3)_3$) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (125.76 MHz, $[\text{D}_8]\text{THF}$, 26 °C): δ = 163.0 (br, 3/5- $\text{C}(\text{pz})$), 149.6 (br, 3/5- $\text{C}(\text{pz})$), 102.1 (4- $\text{C}(\text{pz})$), 68.0 (1/4- $\text{C}(\text{thf})$), 32.2 ($\text{C}(\text{CH}_3)_3$), 31.4 ($\text{C}(\text{CH}_3)_3$), 26.2 (2/3- $\text{C}(\text{thf})$), 13.0 (CH_3) ppm. IR (Nujol/CsI): $\tilde{\nu}_{\text{max}}$ = 2950 (Nujol, CH), 2928 (Nujol, CH), 2860 (Nujol, CH), 1524 (vs), 1516 (vs), 1463 (Nujol), 1416 (s), 1377 (Nujol), 1363 (vs), 1313 (s), 1235 (s), 1207 (m), 1078 (w), 1060 (m), 1030 (s), 1020 (s), 1005 (w), 983 (w), 912 (w), 892 (w), 833 (vw), 784 (s), 735 (vw), 726 (w), 697 (w), 676 (vw), 570 (vw), 506 (m), 476 (vw), 412 (vs) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{40}\text{H}_{68}\text{Mg}_2\text{N}_8\text{O}_2$ (741.65 g mol^{-1}): C 64.78, H 9.24, N 15.11; found: C 64.27, H 9.28, N 15.09.

[Mg₃(pz^{iPr,iPr})₆(Hpz^{iPr,iPr})₂] (4a-Hpz). Hpz^{iPr,iPr} (600.0 mg, 3941 μmol) was dissolved in 10 mL THF and a solution of $\text{Mg}(\text{nBu})_2$ (1.31 mL, 1.31 mmol, 1 M in $\text{Et}_2\text{O}/n\text{-hexane}$) was added dropwise. After stirring overnight, the solvent was removed under reduced pressure. After several recrystallization steps of dissolving the residue in *n*-hexane and storing it afterwards at -40 °C, **4a-Hpz** (381.0 mg, 296.5 μmol , 68%) could be obtained as colorless crystals suitable for an X-ray structure analysis. DRIFTS: $\tilde{\nu}_{\text{max}}$ = 3357 (vw), 2962 (vs), 2928 (s), 2871 (m), 2572 (vw), 1559 (vw), 1523 (m), 1506 (m), 1458 (m), 1421 (w), 1379 (w), 1363 (m), 1304 (w), 1273 (w), 1178 (w), 1141 (w), 1095 (w), 1042 (m), 1021 (w), 923 (vw), 878 (vw), 786 (m), 726 (w), 591 (w), 528 (w), 503 (w), 472 (w), 419 (w) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{72}\text{H}_{122}\text{Mg}_3\text{N}_{16}$ (1284.80 g mol^{-1}): C 67.31, H 9.57, N 17.44; found: C 67.10, H 9.52, N 17.54.

[Mg₃(pz^{iPr,iPr})₆(thf)₂] (4-thf). Hpz^{iPr,iPr} (200.0 mg, 1313 μmol) was dissolved in 10 mL THF and a solution of $\text{Mg}(\text{nBu})_2$ (0.53 mL, 0.53 mmol, 1 M in $\text{Et}_2\text{O}/n\text{-hexane}$) was added dropwise. After stirring overnight, the solvent was removed under reduced pressure. After several recrystallization steps of dissolving the residue in *n*-pentane and storing it at -40 °C, **4-thf** (101.4 mg, 90.1 μmol , 51%) could be obtained as colorless crystals suitable for an X-ray structure analysis. DRIFTS: $\tilde{\nu}_{\text{max}}$ = 3115 (vw), 2961 (vs), 2930 (vs), 2875 (s), 1526 (vs), 1508 (s), 1481 (m), 1459 (s), 1421 (w), 1380 (s), 1363 (s), 1300 (s), 1177 (m), 1141 (m), 1104 (w), 1066 (m), 1040 (vs), 1015 (s), 996 (w), 921 (w), 886 (w), 786 (s), 726 (w), 701 (vw), 591 (vw), 526 (m), 475 (m) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{62}\text{H}_{106}\text{Mg}_3\text{N}_{12}\text{O}_2$ (1124.53 g mol^{-1}): C 66.22, H 9.50, N 14.95; found: C 66.13, H 9.38, N 15.45.

[Mg₃(pz^{iPr,iPr})₄(*n*Bu)₂(thf)₂] (5). Hpz^{iPr,iPr} (200.0 mg, 1313.7 μmol) was dissolved in 10 mL THF and a solution of $\text{Mg}(\text{nBu})_2$ (0.66 mL, 0.66 mmol, 1 M in $\text{Et}_2\text{O}/n\text{-hexane}$) was added dropwise. After stirring overnight, the solvent was reduced and stored at -40 °C. Overnight, single crystals were grown suitable for an X-ray structure analysis. After separation of the supernatant solution and drying of the crystals under reduced pressure, **5** could be obtained as colorless powder (86.5 mg, 92.3 μmol , 42%). ^1H NMR (500.13 MHz, $[\text{D}_8]\text{THF}$, 26 °C): δ = 5.82 (s, 4 H, 4-*H*(pz)), 3.61 (m, 1/4- CH_2 (thf)), 3.15 (broad s, 4H, $\text{CH}(\text{CH}_3)_2$), 2.71 (broad s, 4H, $\text{CH}(\text{CH}_3)_2$), 1.77 (m, 2/3- CH_2 (thf)), 1.51 (m, 4 H, MgCH_2CH_2), 1.39–1.06 (broad s, $\text{CH}(\text{CH}_3)_2$), 1.20 (m, CH_2CH_3), 0.99–0.62 (broad s, $\text{CH}(\text{CH}_3)_2$), 0.81 (t, CH_2CH_3), -0.39 (m, 4H, MgCH_2) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (125.76 MHz, $[\text{D}_8]\text{THF}$, 26 °C): δ = 163.5 (3/5- $\text{C}(\text{pz})$), 95.6 (4- $\text{C}(\text{pz})$), 67.7 (1/4- $\text{C}(\text{thf})$), 33.6 (MgCH_2CH_2), 32.5 (CH_2CH_3), 28.8 ($\text{CH}(\text{CH}_3)_2$), 25.6 (2/3- $\text{C}(\text{thf})$), 24.5 ($\text{CH}(\text{CH}_3)_2$), 14.2 (CH_2CH_3), 9.1 (MgCH_2) ppm. IR (Nujol): $\tilde{\nu}_{\text{max}}$ = 2959 (Nujol; CH), 2923 (Nujol; CH), 2856 (Nujol; CH), 1524 (m), 1504 (m), 1481 (vs), 1460 (Nujol), 1424 (m), 1377 (Nujol), 1366 (vs), 1300 (m), 1269 (vw), 1177 (w), 1141 (vw), 1105 (s), 1061 (w), 1041 (s), 1017 (m), 990 (vw), 951 (vw), 919 (w), 886 (m), 831 (vw), 784 (vs), 725 (m), 702 (vw), 681 (vw), 590 (vw), 544 (w), 527 (m), 511 (m), 477 (m) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{52}\text{H}_{94}\text{Mg}_3\text{N}_8\text{O}_2$ (936.29 g mol^{-1}): C 66.91, H 9.87, N 12.34; found: C 66.64, H 9.96, N 12.18.

[Mg₂(pz^{CF₃,CF₃})₄(thf)₃] (6-thf). Route A: Hpz^{CF₃,CF₃} (200.0 mg, 980 μmol) was dissolved in 10 mL THF and a solution of $\text{Mg}(\text{nBu})_2$ (0.49 mL, 0.49 mmol, 1 M in $\text{Et}_2\text{O}/n\text{-hexane}$) was added dropwise. After stirring for 3 d, the solvent

was reduced and stored at $-40\text{ }^{\circ}\text{C}$. Overnight, single crystals were grown suitable for an X-ray structure analysis. After separation of the supernatant solution and drying of the crystals under reduced pressure, **6-thf** could be obtained as dark red powder (250.0 mg, $464\text{ }\mu\text{mol}$, 95%). Route B: $\text{Kpz}^{\text{CF}_3, \text{CF}_3}$ (179.4 mg, $980\text{ }\mu\text{mol}$) and MgBr_2 (68.2 mg, $370\text{ }\mu\text{mol}$) were dissolved in 10 mL THF and stirred for 7 d. After the solvent was removed under reduced pressure the residue was extracted three times with *n*-hexane. The solution was concentrated and stored at $-40\text{ }^{\circ}\text{C}$. Overnight **6-thf** (55.9 mg, $104\text{ }\mu\text{mol}$, 28%) could be obtained as dark red crystals. ^1H NMR (400.1 MHz, $[\text{D}_8]\text{THF}$, $26\text{ }^{\circ}\text{C}$): 6.84 (s, 4 H, 4-*H*(pz)), 3.62 (m, 12 H, 1/4- $\text{CH}_2(\text{thf})$), 1.78 (m, 12 H, 2/3- $\text{CH}_2(\text{thf})$) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (100.6 MHz, $[\text{D}_8]\text{THF}$, $26\text{ }^{\circ}\text{C}$): 142.7 (q, $\text{C}(\text{CF}_3)$, $^2J_{\text{C,F}}=36.58\text{ Hz}$), 123.0 (q, CF_3 , $^1J_{\text{C,F}}=267.77\text{ Hz}$), 103.3 (4- $\text{C}(\text{pz})$), 68.0 (1,4- $\text{C}(\text{thf})$), 26.2 (2,3- $\text{C}(\text{thf})$) ppm. ^{19}F NMR (282.4 MHz, $[\text{D}_8]\text{THF}$, $26\text{ }^{\circ}\text{C}$): $-60.9\text{ (CF}_3\text{)}$ ppm. IR (Nujol): $\tilde{\nu}_{\text{max}} = 3154\text{ (vw)}$, 2956 (Nujol, CH), 2924 (Nujol, CH), 2854 (Nujol, CH), 1651 (vw), 1637 (vw), 1540 (m), 1501 (w), 1462 (Nujol), 1456 (s), 1375 (Nujol), 1346 (s), 1261 (vs), 1223 (s), 1138 (vs), 1124 (vs), 1084 (s), 1022 (s), 999 (s), 963 (w), 919 (w), 876 (s), 844 (w), 819 (m), 755 (m), 737 (w), 718 (w), 684 (vw), 654 (vw), 600 (vw), 576 (w), 545 (vw), 468 (w), 425 (m) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{32}\text{H}_{28}\text{F}_{24}\text{Mg}_2\text{N}_8\text{O}_3$ ($1077.20\text{ g mol}^{-1}$): C 35.68, H 2.62, N 10.40; found: C 35.89, H 2.55, N 10.64.

[Mg(pz^{CF₃,CF₃})₂]_n (6). $\text{Kpz}^{\text{CF}_3, \text{CF}_3}$ (220.0 mg, $909\text{ }\mu\text{mol}$) and MgBr_2 (83.6 mg, $454\text{ }\mu\text{mol}$) were dissolved in 10 mL toluene and stirred for 5 d. After the solvent was removed under reduced pressure the residue was extracted three times with *n*-hexane. The solvent was removed under reduced pressure affording **6** as dark red powder (101.6 mg, $236\text{ }\mu\text{mol}$, 28%). ^1H NMR (300.1 MHz, $[\text{D}_8]\text{THF}$, $26\text{ }^{\circ}\text{C}$): 6.50 (s, 4 H, 4-*H*(pz)) ppm. ^{19}F NMR (282.4 MHz, $[\text{D}_8]\text{THF}$, $26\text{ }^{\circ}\text{C}$): $-59.8\text{ (CF}_3\text{)}$ ppm. IR (Nujol): $\tilde{\nu}_{\text{max}} = 2953\text{ (Nujol, CH)}$, 2923 (Nujol, CH), 2854 (Nujol, CH), 1547 (w), 1510 (vw), 1461 (Nujol), 1377 (Nujol), 1369 (vs), 1269 (m), 1228 (w), 1144 (s), 1113 (s), 1020 (vs), 989 (m), 886 (w), 822 (m), 759 (m), 735 (m), 722 (m), 608 (vw), 580 (w), 544 (w), 500 (w), 476 (w), 450 (m) cm^{-1} .

[Mg(pz^{Me,Me})₂]_n (7). $\text{Hpz}^{\text{Me,Me}}$ (500.0 mg, 5.201 mmol) was dissolved in 10 mL of toluene and a solution of $\text{Mg}(\text{nBu})_2$ (2.60 mL, 2.60 mmol, 1 M in $\text{Et}_2\text{O}/n\text{-hexane}$) was added dropwise. A white precipitate formed and the reaction mixture was stirred for 3 h. After the solvent was removed under reduced pressure, the white powder was washed three times with *n*-pentane. The white powder was then dried further under high vacuum for 6 h to remove excess solvent, which gave **7** (536.6 mg, 2.505 mmol, 96%) as a white powder. ^{13}C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): 152.1 (3/5- $\text{C}(\text{pz})$), 107.1 (4- $\text{C}(\text{pz})$), 12.0 (CH_3), 10.9 (CH_3) ppm. IR (Nujol): $\tilde{\nu}_{\text{max}} = 2954\text{ (Nujol, CH)}$, 2924 (Nujol, CH), 2854 (Nujol, CH), 1567 (vw), 1524 (vs), 1461 (Nujol), 1425 (vs), 1377 (Nujol), 1352 (s), 1320 (s), 1153 (vw), 1105 (w), 1073 (m), 1036 (s), 975 (w), 946 (vw), 891 (vw), 869 (vw), 837 (vw), 779 (vs), 752 (s), 724 (m), 687 (vw), 592 (vw), 537 (vw), 519 (vw), 432 (s), 413 (vs) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{10}\text{H}_{14}\text{MgN}_4$ (214.56 g mol^{-1}): C 55.98, H 6.58, N 26.11; found: C 56.87, H 6.83, N 23.59.

[Mg(pz)₂]_n (8). Pyrazole (200.0 mg, 2.938 mmol) was dissolved in 10 mL of toluene and a solution of $\text{Mg}(\text{nBu})_2$ (1.47 mL, 1.47 mmol, 1 M in $\text{Et}_2\text{O}/n\text{-hexane}$) was added dropwise. A white precipitate formed and the reaction mixture was stirred for 3 h. After the solvent was removed under reduced pressure, the white powder was washed three times with *n*-pentane. The white powder was then dried further under high vacuum for 6 h to remove excess solvent, which gave **8** (204.1 mg, 1.288 mmol, 88%) as a white powder. ^{13}C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): 141.6 (3/5- $\text{C}(\text{pz})$), 103.1 (4- $\text{C}(\text{pz})$) ppm. IR (Nujol): $\tilde{\nu}_{\text{max}} = 2952\text{ (Nujol, CH)}$, 2923 (Nujol, CH), 2854 (Nujol, CH), 1501 (s), 1460 (Nujol), 1411 (s), 1376 (Nujol), 1306 (vw), 1265 (s), 1248 (m), 1169 (m), 1156 (m), 1072 (m), 1053 (vs), 968 (w), 920 (vw), 885 (m), 778 (vs), 761 (vs), 724 (w), 627 (vs), 408 (vs) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_6\text{H}_6\text{MgN}_4$ (158.45 g mol^{-1}): C 45.48, H 3.82, N 35.36; found: C 46.65, H 4.24, N 33.25.

Mg(CO₂·pz^{tBu,tBu})₂(thf)₂ (1-CO₂,thf). A solution of $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2]_2$ (154 mg, $402\text{ }\mu\text{mol}$) in THF was stirred under 1 bar CO_2 for 30 min and stored at ambient temperature. Overnight, colorless crystals were obtained suitable for an X-ray structure analysis. The supernatant solution was separated, the residue was dried for 30 min under glovebox atmosphere and **1-CO₂,thf** was obtained as colorless crystals (235 mg, $381\text{ }\mu\text{mol}$, 95%). ^1H NMR (400.1 MHz, $[\text{D}_8]\text{THF}$, $26\text{ }^{\circ}\text{C}$): $\delta = 6.08\text{ (s, 2H, 4-}H\text{ (pz))}$, 1.48 (s, 9H; 3- $\text{C}(\text{CH}_3)_3$), 1.24 (s, 9H; 5- $\text{C}(\text{CH}_3)_3$) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (100.6 MHz, $[\text{D}_8]\text{THF}$, $26\text{ }^{\circ}\text{C}$): $\delta = 161.5\text{ (3-}C\text{ (pz))}$, 155.8 (5- $\text{C}(\text{pz})$), 149.0 (CO_2), 104.9 (4- $\text{C}(\text{pz})$), 33.9 ($\text{C}(\text{CH}_3)_3$), 32.5 ($\text{C}(\text{CH}_3)_3$), 30.1 ($\text{C}(\text{CH}_3)_3$), 29.7 ($\text{C}(\text{CH}_3)_3$) ppm. DRIFTS: $\tilde{\nu}_{\text{max}} = 3016\text{ (w)}$, 2960 (vs), 2924 (s), 2871 (s), 1745 (vs), 1699 (m), 1579 (vw), 1543 (s), 1516 (w), 1481 (m), 1465 (s), 1456 (s), 1436 (m), 1425 (m), 1393 (m), 1362 (s), 1328 (vs), 1294 (vs), 1250 (vs), 1229 (w), 1208 (m), 1170 (vs), 1143 (s), 1064 (m), 1041 (s), 1021 (m), 1009 (s), 965 (vw), 925 (m), 888 (vs), 850 (s), 815 (vs), 790 (s), 734 (vw), 699 (w), 680 (w), 566 (vw), 522 (w), 484

(w), 461 (m), 308 (w) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{32}\text{H}_{54}\text{MgN}_4\text{O}_6$ ($615.11 \text{ g mol}^{-1}$): C 62.48, H 8.85, N 9.11; found: C 62.14, H 8.89, N 9.08.

$\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{iPr},\text{iPr}})_2(\text{thf})_2$ (4- CO_2 ,thf). $[\text{Mg}_3(\text{pz}^{\text{iPr},\text{iPr}})_6(\text{thf})_2]$ (4-thf, 20 mg, $27 \mu\text{mol}$) was dissolved in 0.5 mL of $[\text{D}_8]\text{THF}$ and the atmosphere was exchanged to 1 bar CO_2 . The reaction progress was checked by ^1H NMR spectroscopy. ^1H NMR (400.1 MHz, $[\text{D}_8]\text{THF}$, 26°C): δ = 5.99 (s, 1H, 4- $H(\text{pz})$), 3.95 (broad sept., 1H; $\text{CH}(\text{CH}_3)_2$), 3.62 (m; 1/4- $H(\text{thf})$), 3.10 (broad sept., 1H; $\text{CH}(\text{CH}_3)_2$), 1.77 (m; 2/3- $H(\text{thf})$), 1.20 (broad d, 6H; $\text{CH}(\text{CH}_3)_2$), 0.96 (broad d, $^3J_{\text{H,H}}=6.08 \text{ Hz}$, 6H; $\text{CH}(\text{CH}_3)_2$) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (100.6 MHz, $[\text{D}_8]\text{THF}$, 26°C): δ = 158.7 (5- $\text{C}(\text{pz})$), 154.5 (3- $\text{C}(\text{pz})$), 149.6 (CO_2), 100.9 (4- $\text{C}(\text{pz})$), 68.0 (1/4- $\text{C}(\text{thf})$), 27.6 ($\text{CH}(\text{CH}_3)_2$), 26.8 ($\text{CH}(\text{CH}_3)_2$), 26.2 (2/3- $\text{C}(\text{thf})$), 23.0 ($\text{CH}(\text{CH}_3)_2$), 22.8 ($\text{CH}(\text{CH}_3)_2$) ppm.

$\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{tBu},\text{tBu}})_2(\text{thf})_2$ (1- CO_2 ,thf) + $\text{HOOCpz}^{\text{tBu},\text{tBu}}$. $[\text{Mg}(\text{pz}^{\text{tBu},\text{tBu}})_2(\text{Hpz}^{\text{tBu},\text{tBu}})_2]$ (1-Hpz, 20 mg, $16 \mu\text{mol}$) was dissolved in 0.5 mL of $[\text{D}_8]\text{THF}$ and the atmosphere was exchanged to 1 bar CO_2 . The reaction progress was checked by ^1H NMR spectroscopy. ^1H NMR (400.1 MHz, $[\text{D}_8]\text{THF}$, 26°C): $\text{HOOCpz}^{\text{tBu},\text{tBu}}$: δ = 11.34 (s, 1H, COOH), 5.82 (s, 1H, 4- $H(\text{pz})$), 1.28 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.24 (s, 9 H, $\text{C}(\text{CH}_3)_3$) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (100.6 MHz, $[\text{D}_8]\text{THF}$, 26°C): $\text{HOOCpz}^{\text{tBu},\text{tBu}}$: δ = 161.2 (3,5- $\text{C}(\text{pz})$), 152.6 (3,5- $\text{C}(\text{pz})$), 96.8 (4- $\text{C}(\text{pz})$), 31.2 ($\text{C}(\text{CH}_3)$), 31.0 ($\text{C}(\text{CH}_3)$), 30.6 ($\text{C}(\text{CH}_3)$) ppm.

$\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{iPr},\text{iPr}})_2(\text{thf})_2$ (4- CO_2 ,thf) + $\text{HOOCpz}^{\text{iPr},\text{iPr}}$. $[\text{Mg}_3(\text{pz}^{\text{iPr},\text{iPr}})_6(\text{Hpz}^{\text{iPr},\text{iPr}})_2]$ (4-Hpz, 20 mg, $27 \mu\text{mol}$) was dissolved in 0.5 mL of $[\text{D}_8]\text{THF}$ and the atmosphere was changed to 1 bar CO_2 . The reaction progress was checked by ^1H NMR spectroscopy. ^1H NMR (400.1 MHz, $[\text{D}_8]\text{THF}$, 26°C): $\text{HOOCpz}^{\text{iPr},\text{iPr}}$: δ = 11.22 (s, 1H; HOOC), 5.76 (s, 2H; 4- $H(\text{pz})$), 2.92 (sept., $^3J_{\text{H,H}}=6.84 \text{ Hz}$, 2H; $\text{CH}(\text{CH}_3)_2$), 2.85 (sept., $^3J_{\text{H,H}}=6.84 \text{ Hz}$, 2H; $\text{CH}(\text{CH}_3)_2$), 1.23 (d, $^3J_{\text{H,H}}=6.84 \text{ Hz}$, 12H; $\text{CH}(\text{CH}_3)_2$), 1.18 (d, $^3J_{\text{H,H}}=6.84 \text{ Hz}$; $\text{CH}(\text{CH}_3)_2$) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (100.6 MHz, $[\text{D}_8]\text{THF}$, 26°C): $\text{HOOCpz}^{\text{iPr},\text{iPr}}$: δ = 158.7 (5- $\text{C}(\text{pz})$), 154.5 (3- $\text{C}(\text{pz})$), 97.7 (4- $\text{C}(\text{pz})$), 28.7 ($\text{CH}(\text{CH}_3)_2$), 26.6 ($\text{CH}(\text{CH}_3)_2$), 23.1 ($\text{CH}(\text{CH}_3)_2$), 22.7 ($\text{CH}(\text{CH}_3)_2$) ppm.

$[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{Me},\text{Me}})_2]_n$ (7- CO_2). A Schlenk tube was loaded with solid $[\text{Mg}(\text{pz}^{\text{Me},\text{Me}})_2]_n$ (95.44 mg, $440.8 \mu\text{mmol}$) and the atmosphere changed to 1 bar CO_2 . After 3 h 7- CO_2 could be collected as a white powder in quantitative yield. ^{13}C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): 148.6 (5- $\text{C}(\text{pz})$), 142.7 (3- $\text{C}(\text{pz})$), 108.8 (4- $\text{C}(\text{pz})$), 12.3 (CH_3) ppm. 2954 (Nujol CH), 2924 (Nujol CH), 2854 (Nujol CH), 1744 (vs), 1716 (vs), 1597 (w), 1570 (m), 1523 (vw), 1459 (Nujol), 1420 (s), 1377 (Nujol), 1350 (vs), 1292 (s), 1212 (m), 1157 (w), 1133 (s), 1077 (vw), 1044 (s), 981 (s), 840 (s), 797 (vs), 765 (vs), 724 (s), 632 (w), 585 (vw), 507 (w), 420 (m) cm^{-1} . $\text{C}_{12}\text{H}_{14}\text{MgN}_4\text{O}_4$ ($302.57 \text{ g mol}^{-1}$): C 47.64, H 4.66, N 18.52; found: C 48.41, H 5.13, N 17.36.

$[\text{Mg}(\text{CO}_2 \cdot \text{pz})_2]_n$ (8- CO_2). A Schlenk tube was loaded with solid $[\text{Mg}(\text{pz})_2]_n$ (78.57 mg, $495.9 \mu\text{mmol}$) and the atmosphere was changed to 1 bar CO_2 . After 3 h 8- CO_2 could be collected as a white powder in quantitative yield. ^{13}C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): 150.2 (OCO), 139.1 (5- $\text{C}(\text{pz})$), 128.6 (3- $\text{C}(\text{pz})$), 107.2 (4- $\text{C}(\text{pz})$) ppm. IR (Nujol): $\tilde{\nu}_{\text{max}}$ = 3131 (w), 2954 (Nujol CH), 2924 (Nujol CH), 2854 (Nujol CH), 1718 (vs), 1709 (vs), 1590 (vw), 1520 (w), 1460 (Nujol), 1398 (vs), 1376 (Nujol), 1366 (vs), 1350 (vs), 1317 (vs), 1287 (vs), 1238 (m), 1198 (s), 1169 (vw), 1074 (w), 1047 (vs), 977 (m), 922 (w), 820 (vs), 793 (vs), 767 (vs), 724 (m), 654 (m), 631 (vw), 603 (w), 496 (w) cm^{-1} . $\text{C}_8\text{H}_6\text{MgN}_4\text{O}_4$ ($246.47 \text{ g mol}^{-1}$): C 38.99, H 2.45, N 22.73; found: C 40.08, H 2.85, N 22.44.

General procedure of the catalytic conversion of epoxides to cyclic carbonates. Representative example: A small Schlenk tube was charged with $[\text{Mg}(\text{pz}^{\text{tBu},\text{tBu}})_2]_2$ (10.0 mg, $26.1 \mu\text{mol}$) and TBAB (16.8 mg, $52.2 \mu\text{mol}$) and dissolved in the corresponding epoxide (5.224 mmol). The atmosphere was exchanged with 1 bar CO_2 and the reaction mixture was stirred for 24 h. The progress of the reaction was determined via ^1H NMR spectroscopy by dissolving the reaction mixture in CDCl_3 .

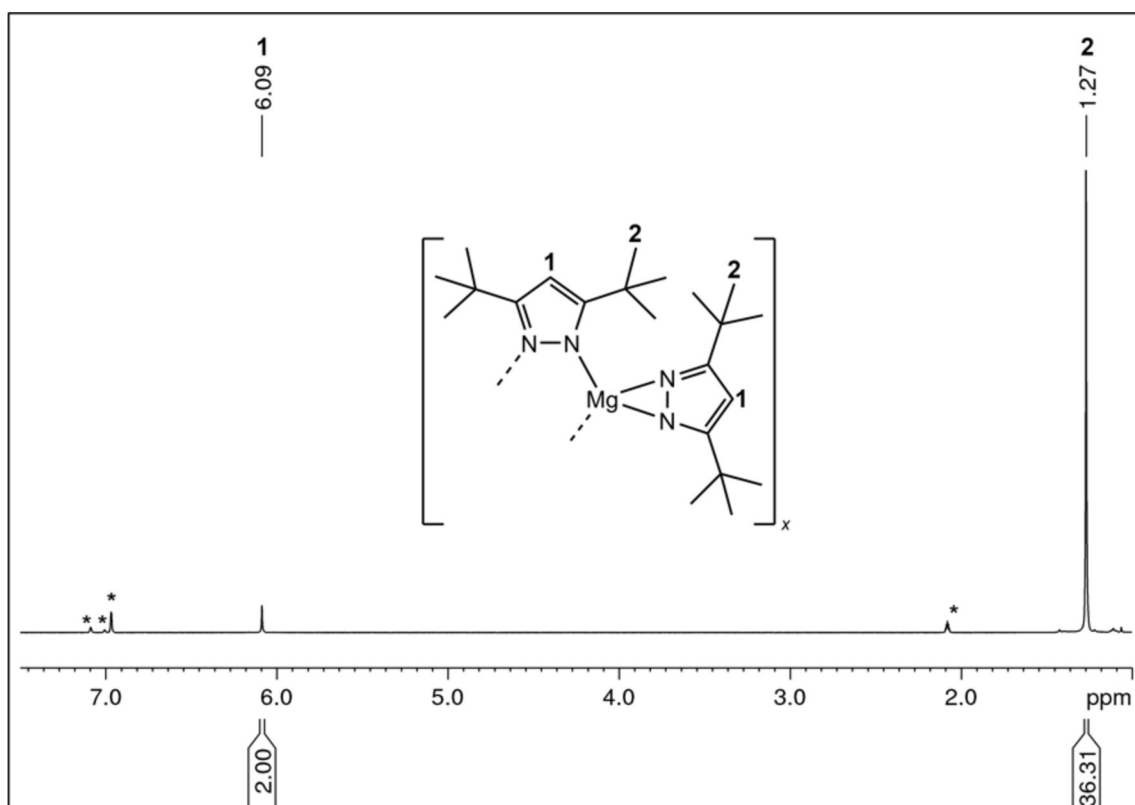


Figure S1. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2]_2$ (1).

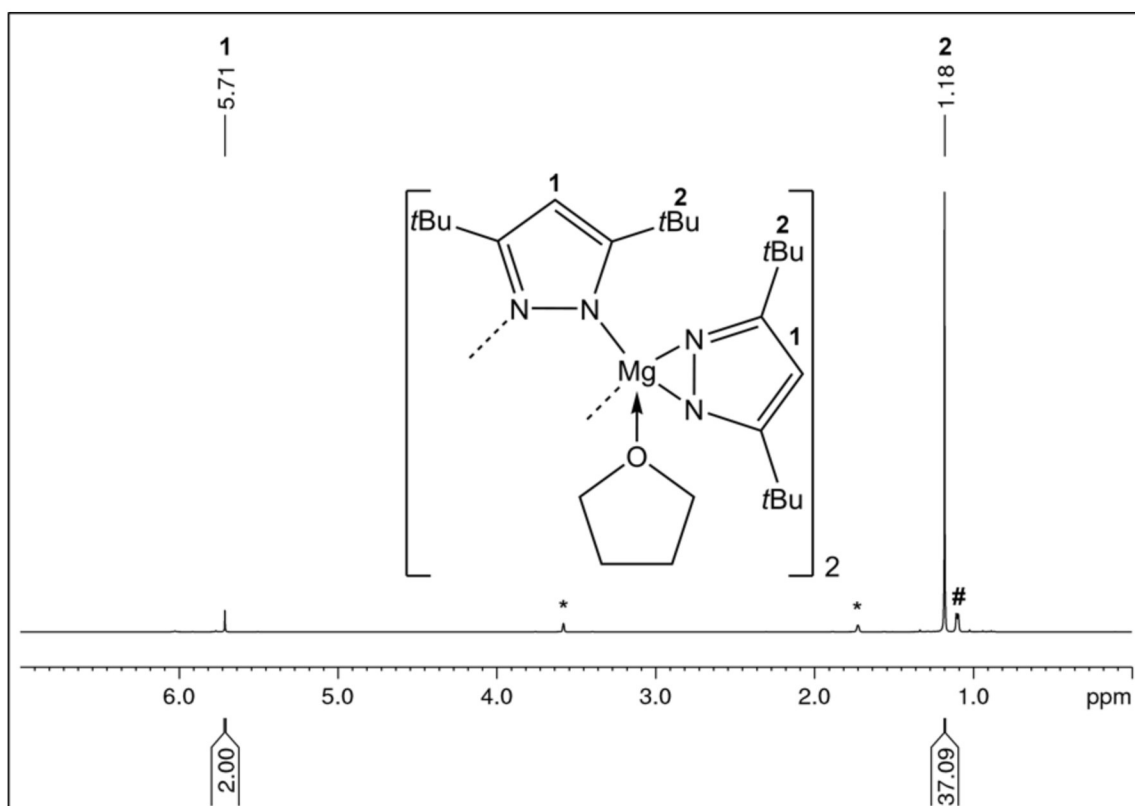


Figure S2. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2(\text{thf})]_2$ (1-thf).

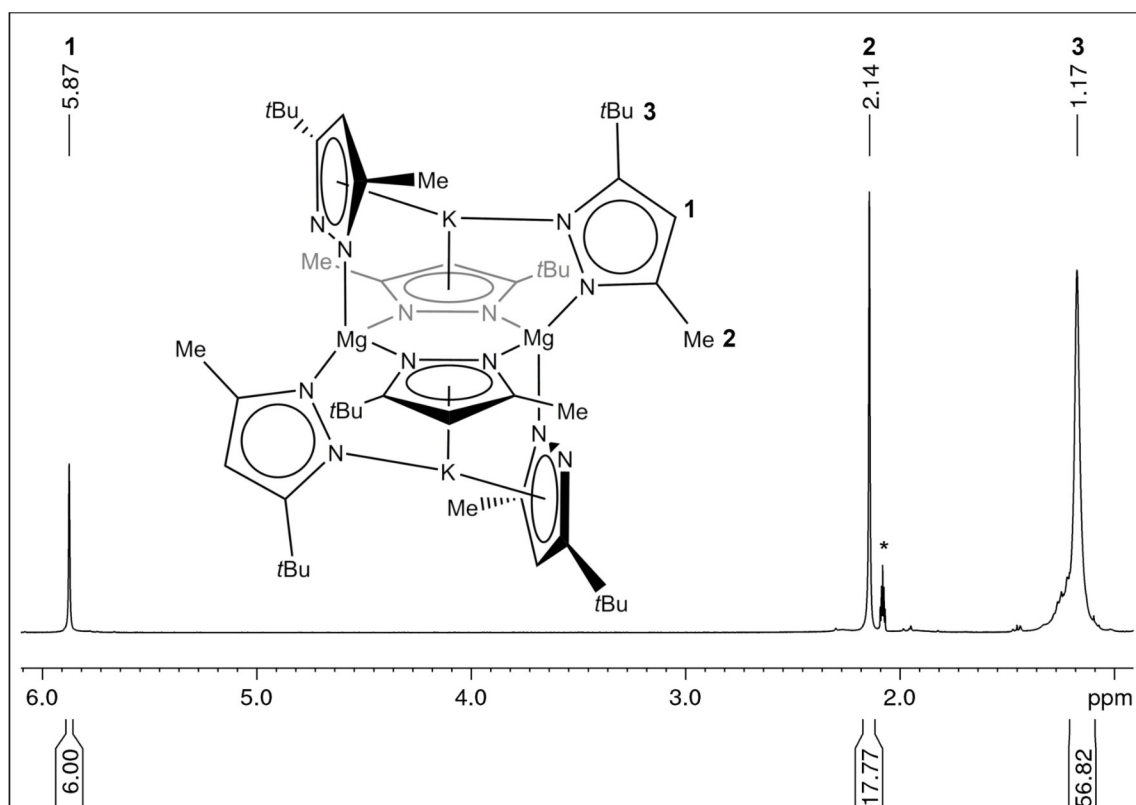


Figure S3. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{KMg}(\text{pz}^{\text{tBu},\text{Me}})_3]_2$ (**2**).

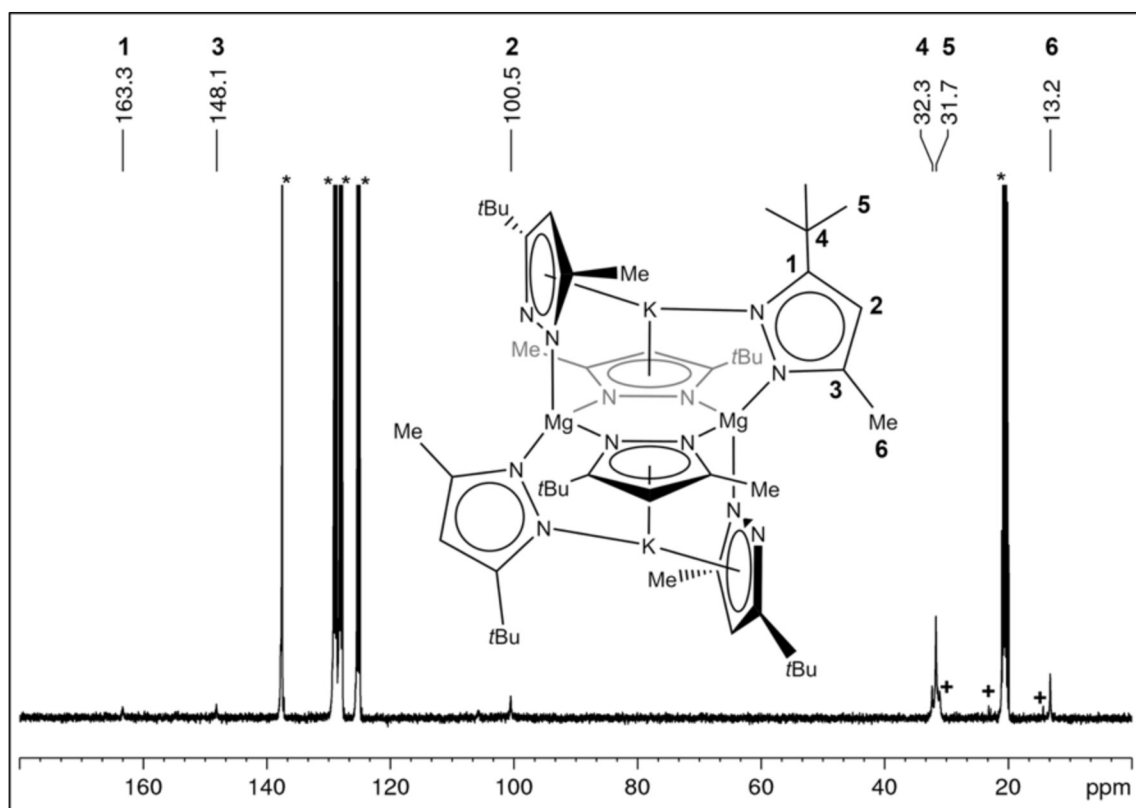


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 100.61 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{KMg}(\text{pz}^{\text{tBu},\text{Me}})_3]_2$ (**2**) (+ n -hexane).

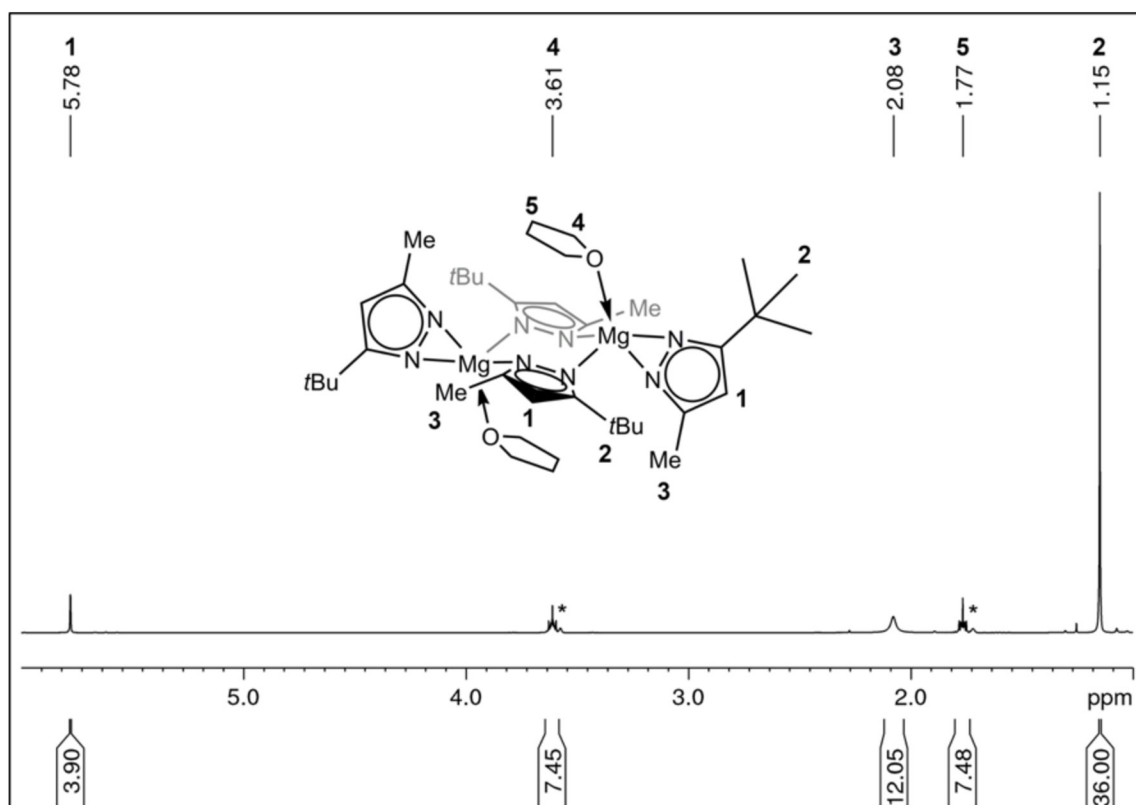


Figure S5. ¹H NMR spectrum (26 °C, 400.11 MHz, [D₈]THF) of [Mg(pz^{tBu,Me})₂(thf)]₂ (**3-thf**).

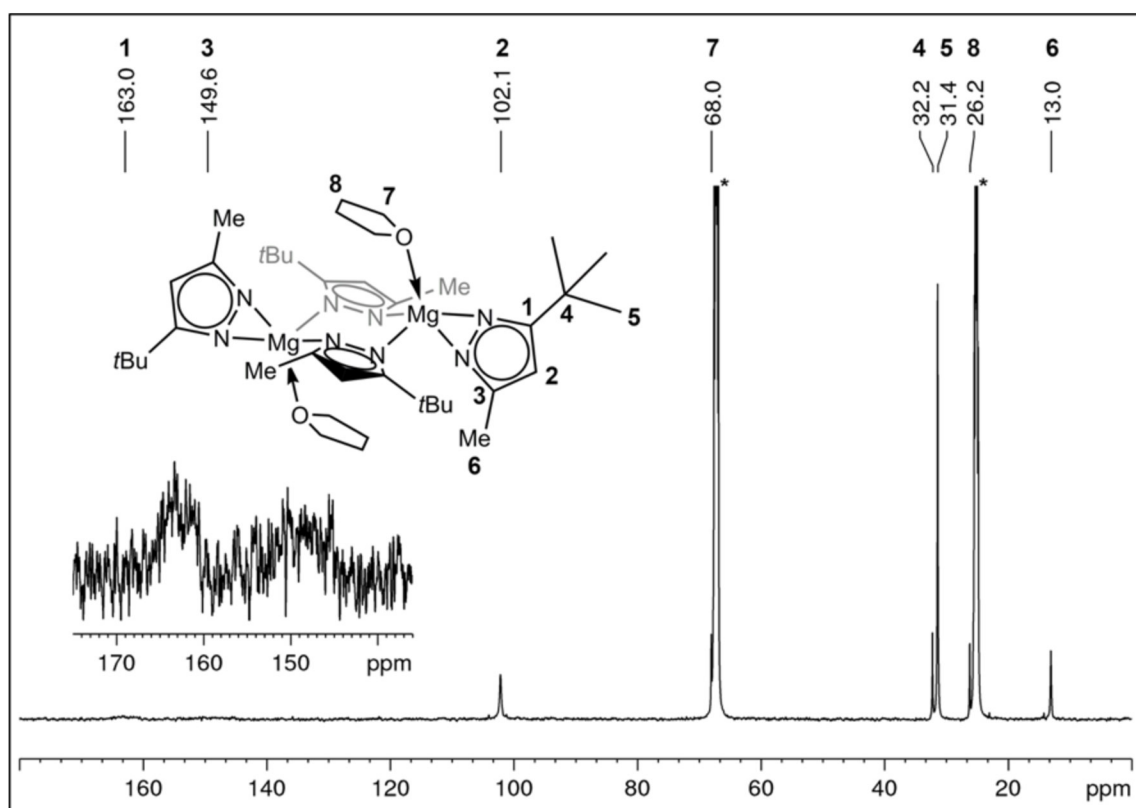


Figure S6. ¹³C{¹H} NMR spectrum (26 °C, 125.76 MHz, [D₈]THF) of [Mg(pz^{tBu,Me})₂(thf)]₂ (**3-thf**).

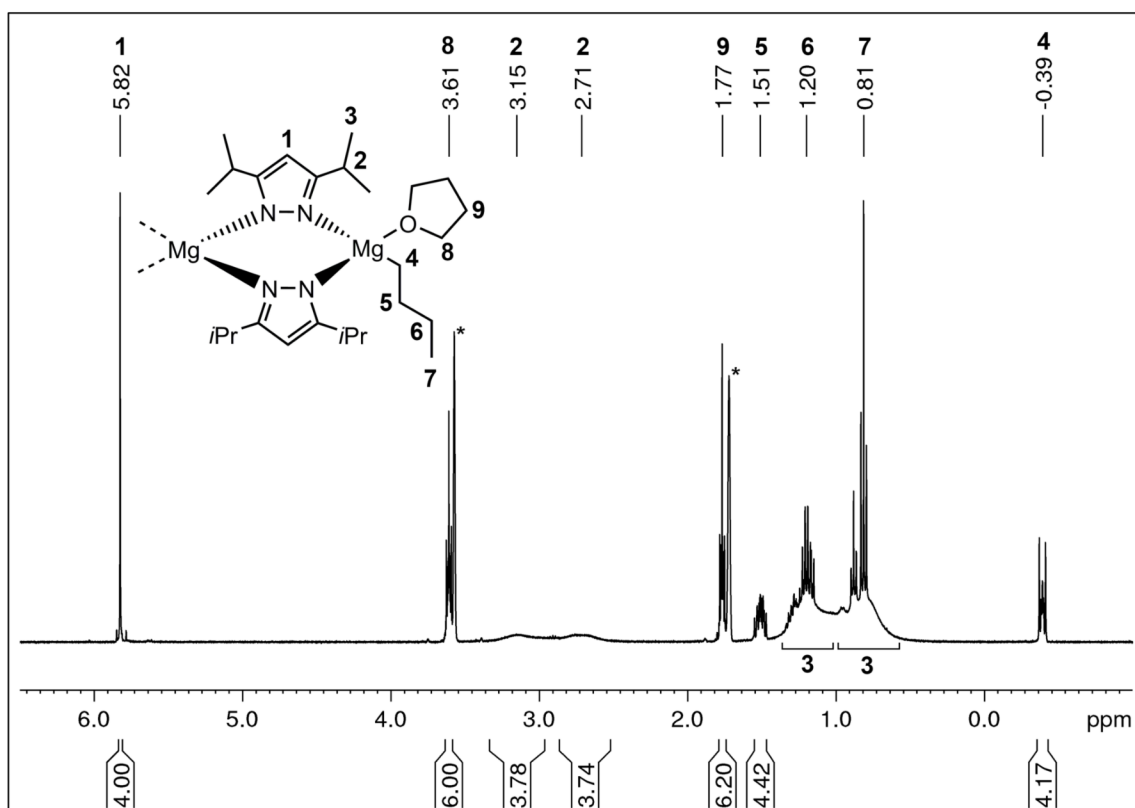


Figure S7. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_4(\text{nBu})_2(\text{thf})_2]$ (**5**).

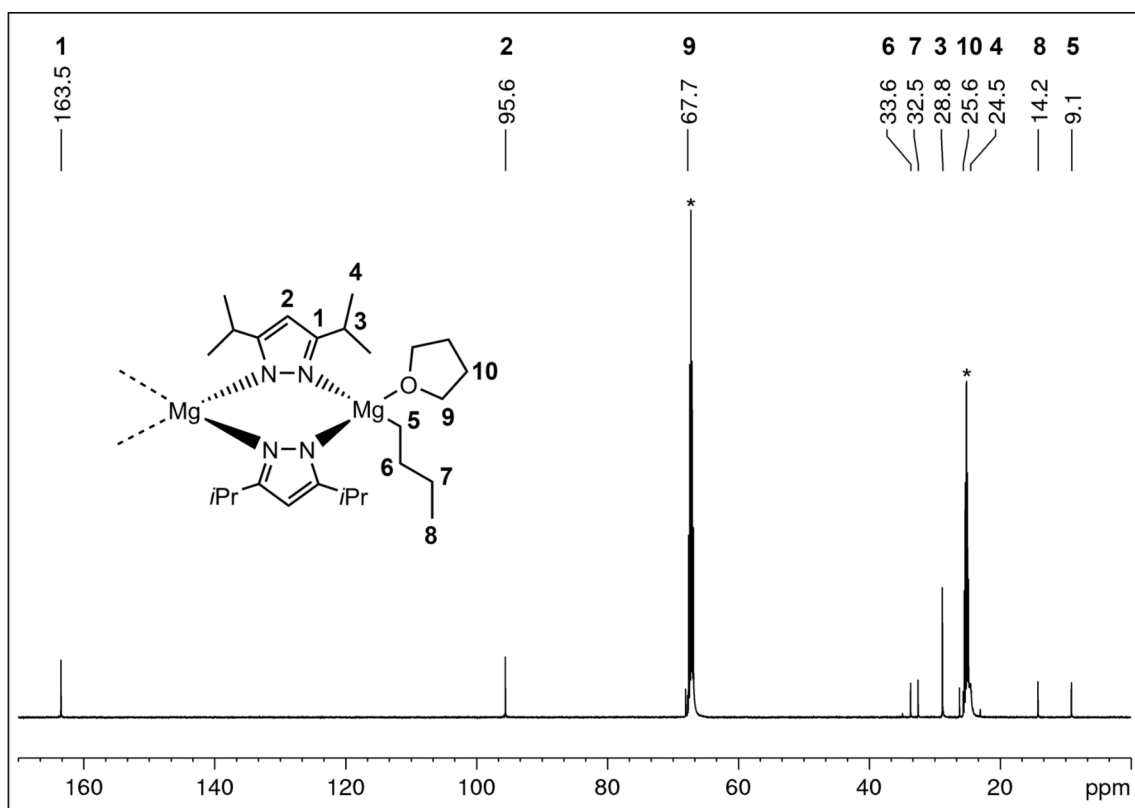


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 125.76 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_4(\text{nBu})_2(\text{thf})_2]$ (**5**).

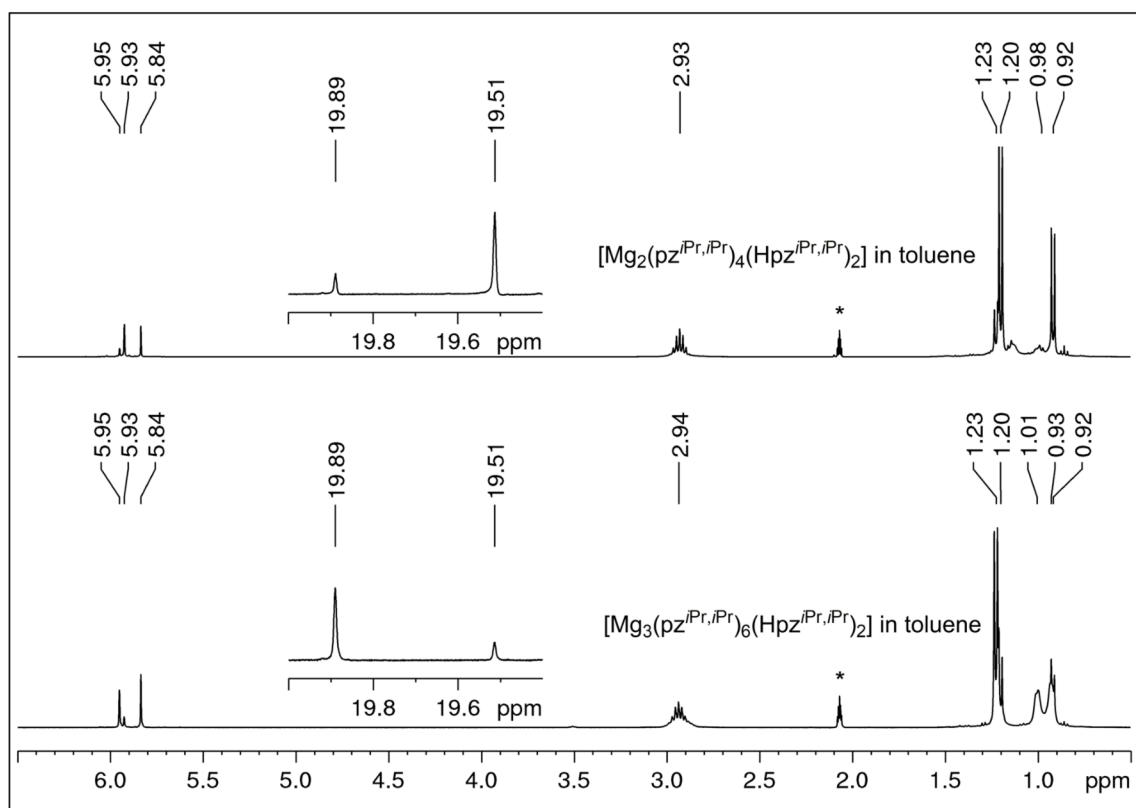


Figure S9. Comparison of ^1H NMR spectra (26 °C, 400.11 MHz, $[\text{D}_8]$ toluene) of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**, bottom) and $[\text{Mg}_2(\text{pz}^{i\text{Pr},i\text{Pr}})_4(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4-Hpz**, top).

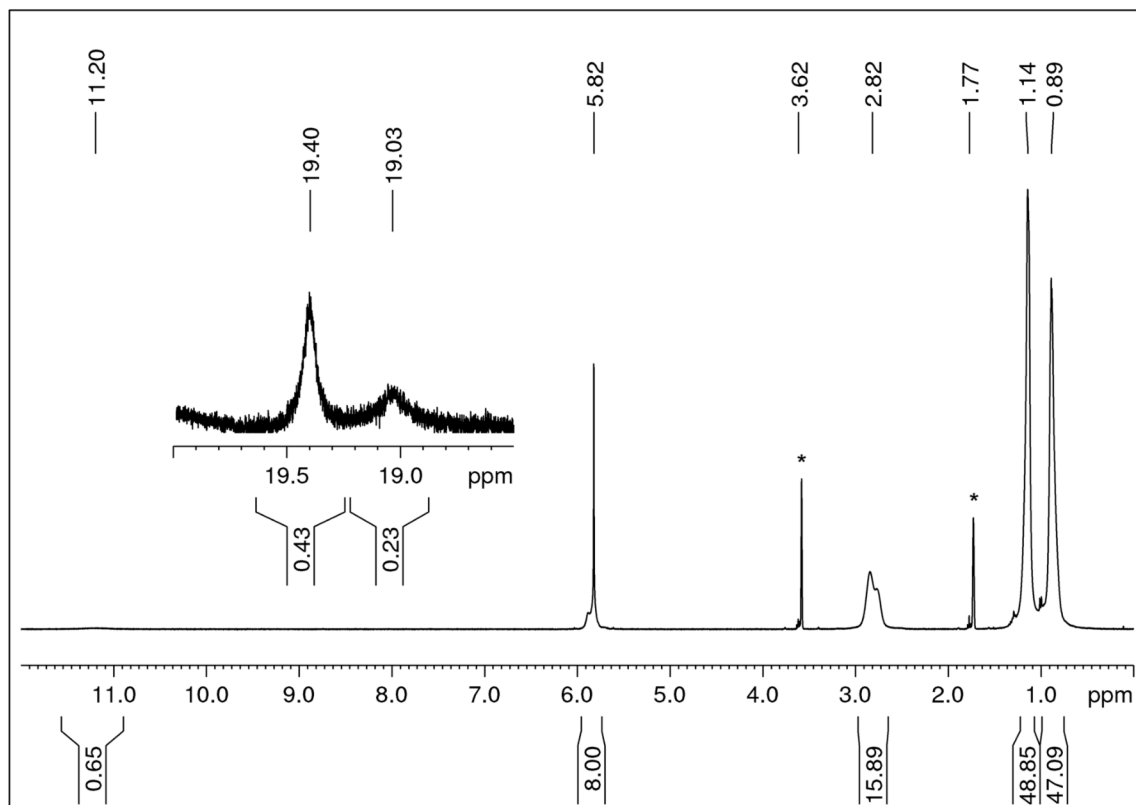


Figure S10. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]$ THF) of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**).

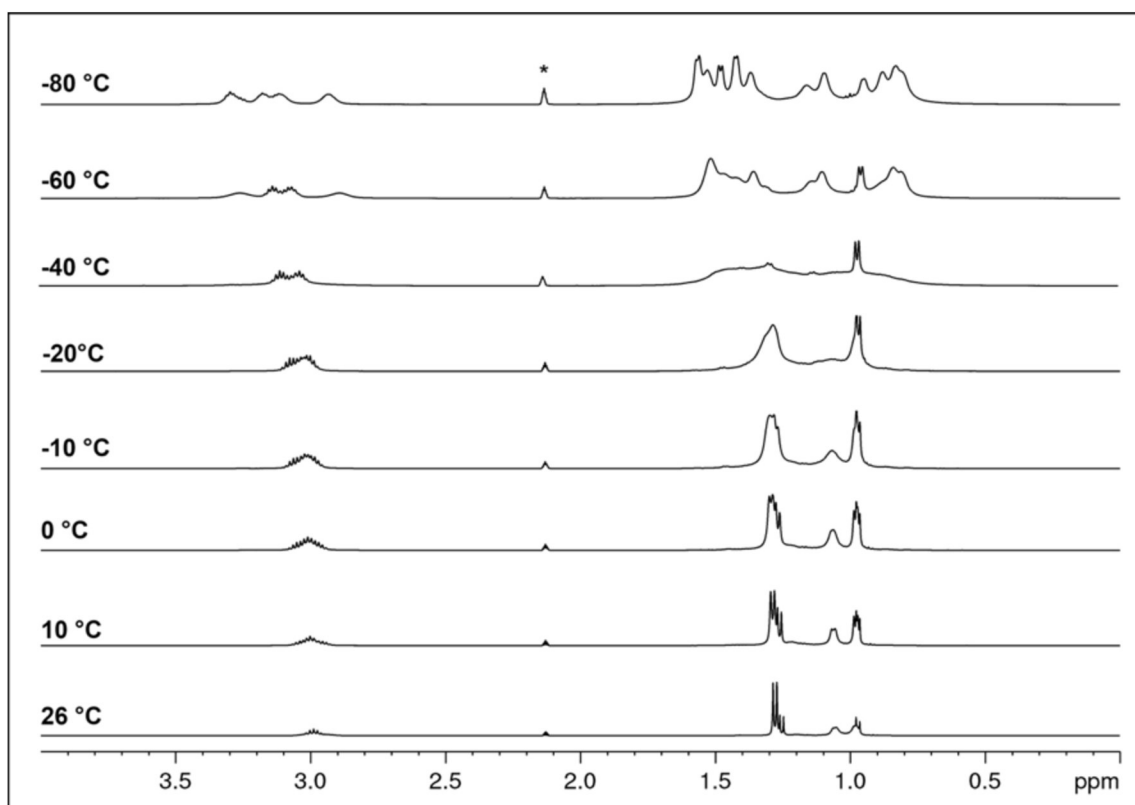


Figure S11. VT ^1H NMR spectra (500.13 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**) in the range of $26\text{ }^\circ\text{C}$ to $-80\text{ }^\circ\text{C}$.

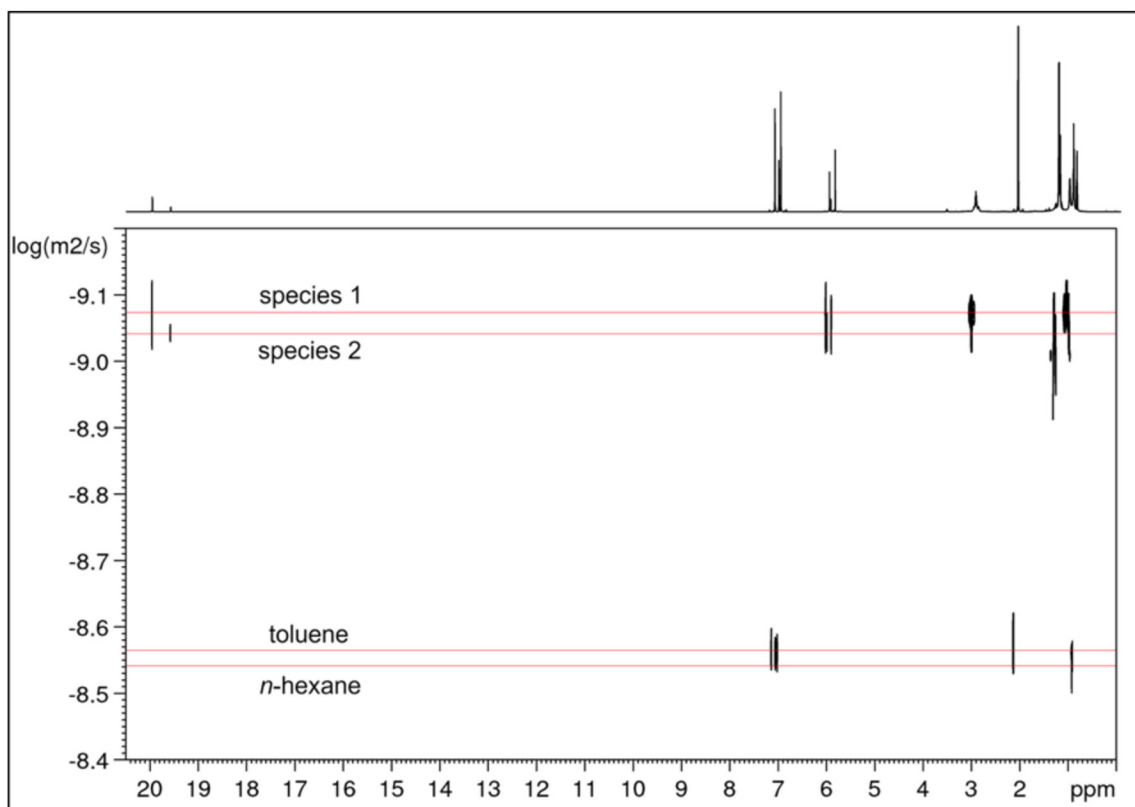


Figure S12. ^1H DOSY NMR spectrum (26 $^\circ\text{C}$, 700.29 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**). **4a-Hpz** dissociates into two different species in solution. Molecular weight calculation see below.

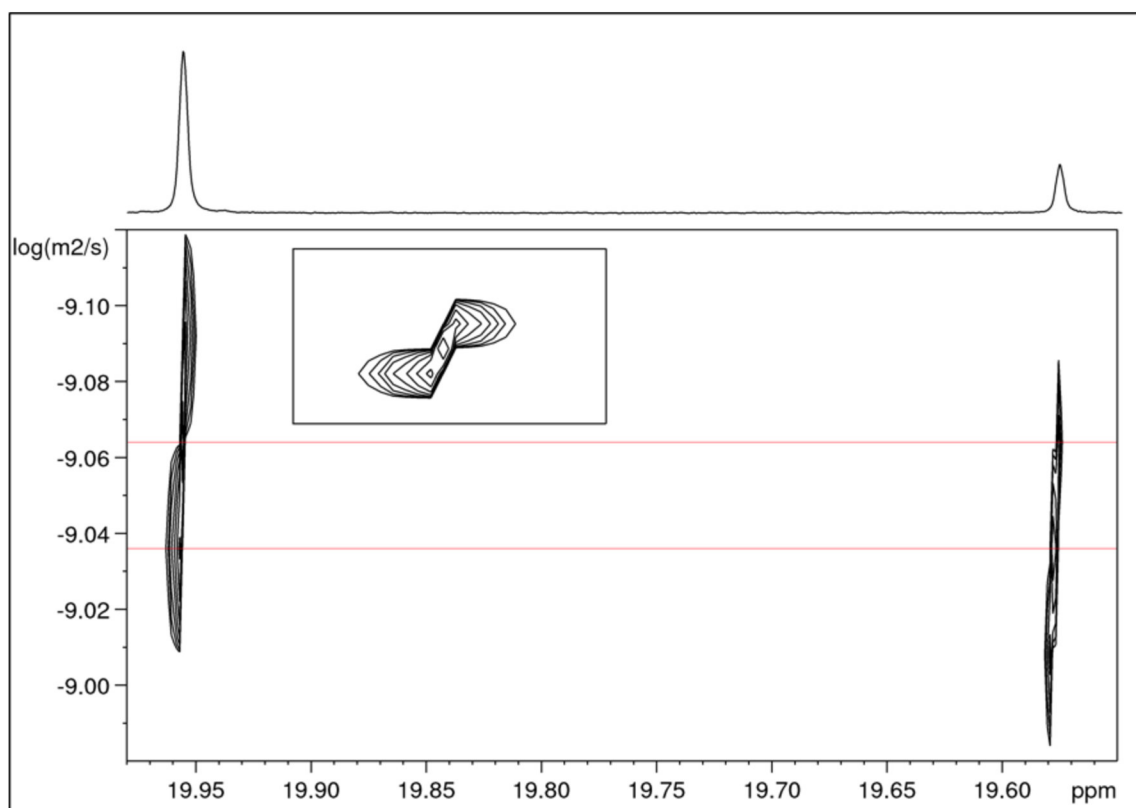


Figure S13. ^1H DOSY NMR spectrum (26 $^\circ\text{C}$, 700.29 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**) in the region of strongly low field shifted H–N signals.

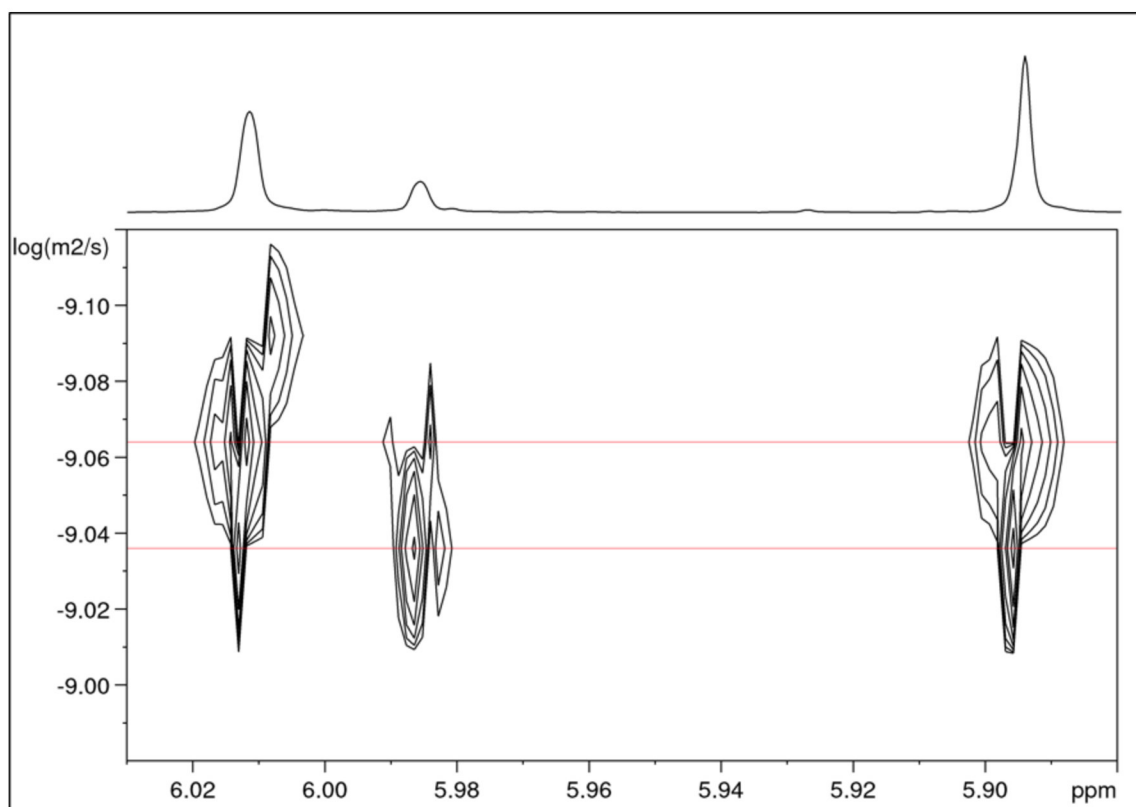


Figure S14. ^1H DOSY NMR spectrum (26 $^\circ\text{C}$, 700.29 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**) in the aromatic region.

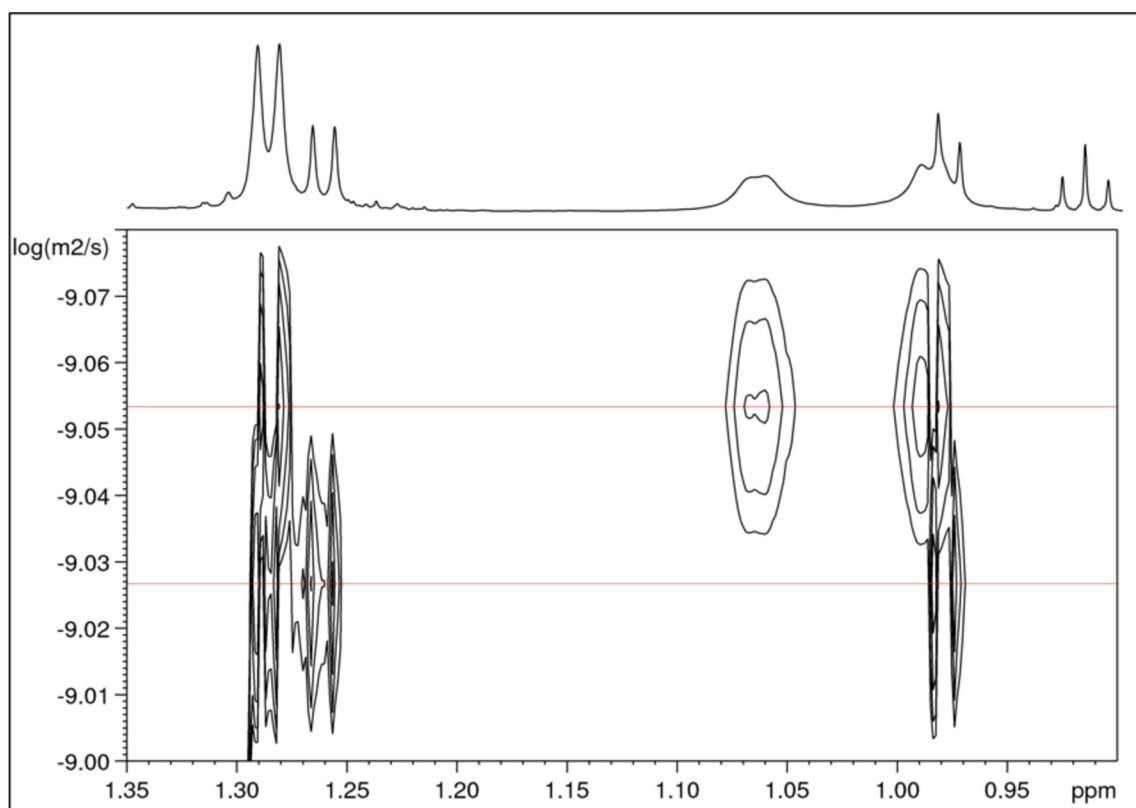


Figure S15. ¹H DOSY NMR spectrum (26 °C, 700.29 MHz, [D₈]toluene) of [Mg₃(pz^{*i*Pr,*i*Pr})₆(Hpz^{*i*Pr,*i*Pr})₂] (**4a-Hpz**) in the region of *i*Pr moities.

DOSY Experiment Data of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**)

The ^1H NMR spectrum of **4a-Hpz** revealed that dissolving **4a-Hpz** in $[\text{D}_8]\text{toluene}$ leads to fragmentation into two distinct species. The same fragmentation species were observed when **4-Hpz** was dissolved in $[\text{D}_8]\text{toluene}$ but the integrals of the two species were reversed (see Figure S7). To examine this fragmentation behavior further a ^1H DOSY NMR experiment was carried out for **4-Hpz** and **4a-Hpz**. This experiment confirmed two fragmentation species with two distinct diffusion coefficients.

Table S1. Diffusion coefficients of the fragmentation species of **4-Hpz** and **4a-Hpz** in $[\text{D}_6]\text{toluene}$ determined via ^1H DOSY NMR experiment.

4a-Hpz				4-Hpz			
Substance A	D (average)	Variance	pD (average)	Substance A	D (average)	Variance	pD (average)
T1T2	7.284E-10	0.595%	-9.1377	T1T2	8.262E-10	0.894%	-9.0829
Contin	7.445E-10	1.491%	-9.1281	Contin	7.843E-10	3.067%	-9.1055
Expt	7.843E-10	2.020%	-9.1055	Expt	8.607E-10	1.476%	-9.0651
Substance B	D (average)	Variance	pD (average)	Substance B	D (average)	Variance	pD (average)
T1T2	7.845E-10	1.31%	-9.1054	T1T2	9.050E-10	1.030%	-9.0434
Contin	8.160E-10	0.48%	-9.0883	Contin	8.979E-10	3.577%	-9.0468
Expt	8.359E-10	0.10%	-9.0778	Expt	9.649E-10	0.073%	-9.0155

The diffusion coefficients (D) were determined via three different evaluation methods provided by Topspin. The T1/T2 module uses a numeric calculation for D, whereas the contin/exponential evaluation uses manual signal picking. D was calculated from the measured pD values. The D values listed in Table S1 are averaged over all signals assigned to one species that are not overlapping with signals from another species. As expected, the DOSY revealed two species with distinct diffusion coefficient of $\log D = -9.13 \log(\text{m}^2\cdot\text{s}^{-1})$ (**A**) and $-9.09 \log(\text{m}^2\cdot\text{s}^{-1})$ (**B**). The signal at 5.84 ppm is an overlapping signal from both species hence the unchanged intensity between the spectra of the reaction of **4-Hpz** and **4a-Hpz**.

Table S2. Molecular weight calculation via the measured diffusion coefficients of the fragmentation species of **6** and **4a-Hpz** with an approximation of a highly compact sphere.

4a-Hpz				4-Hpz		
Substance A	M (calc.)	M(found)	Deviation	M (calc.)	M(found)	Deviation
T1T2	958.02	934	3%	805.78	794	1%
Contin	958.02	960	0%	805.78	902	-12%
Expt	958.02	888	7%	805.78	802	0%
Substance B	M (calc.)	M(found)	Deviation	M (calc.)	M(found)	Deviation
T1T2	805.78	804	0%	631.25	662	-5%
Contin	805.78	800	1%	631.25	688	-9%
Expt	805.78	781	3%	631.25	639	-1%

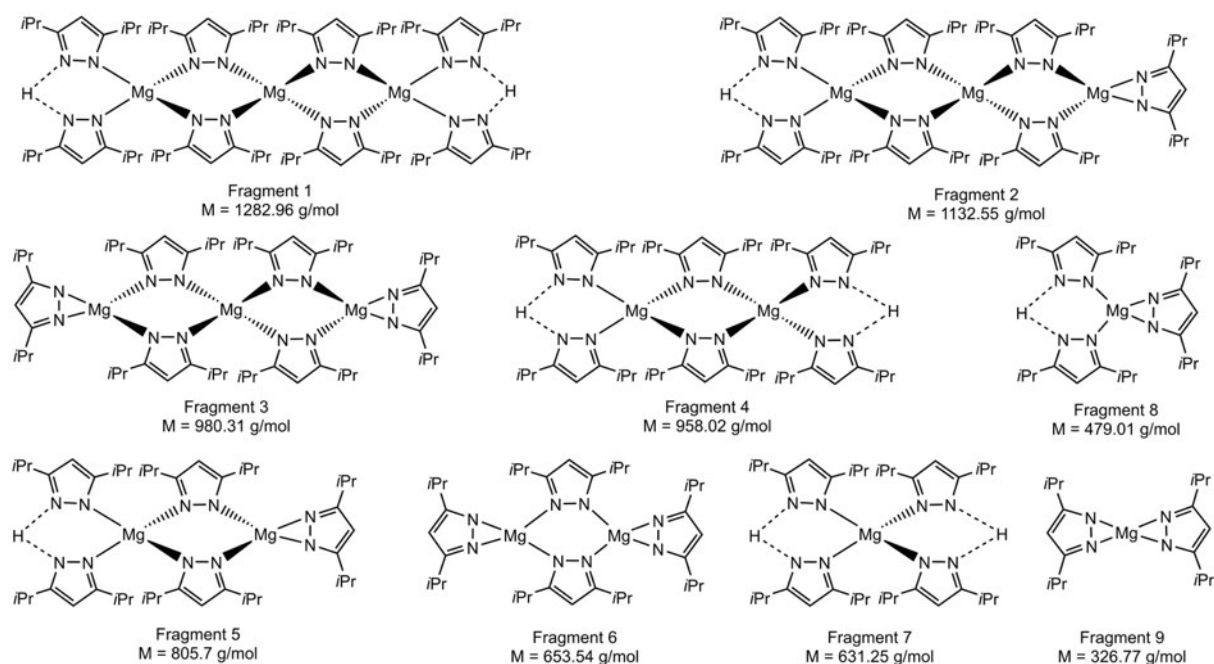
For the molecular weight calculation the method described by Stalke was used.^[11] There are nine different fragments possible for **4a-Hpz** and six for **4-Hpz** (see Scheme S1). Because there must be at least one hydrogen bond, three fragments could be eliminated for **4a-Hpz** and two for **4-Hpz**. Using an approximation of a highly compact sphere all three evaluation methods led to the same two fragments 4 ($M = 958.02 \text{ g/mol}$) and 5 ($M = 805.78 \text{ g/mol}$) for complex **4a-Hpz** (see Table S2). In all six cases the deviation lies within the methods error of 9%. However, calculating the molecular weight of the fragmentation species of **4-Hpz** led to the fragments 5 ($M = 805.78 \text{ g/mol}$) and 7 ($M = 631.25 \text{ g/mol}$). This indicates that either **4a-Hpz** and **4-Hpz** fragment into different species with a comparable chemical shift or the method varies with the used substrate.

Table S3. Molecular weight calculation via the measured diffusion coefficients of the fragmentation species of **4-Hpz** and **4a-Hpz** with an approximation of an ellipsoid.

	4a-Hpz			4-Hpz		
Substance A	M (calc.)	M(found)	Deviation	M (calc.)	M(found)	Deviation
T1T2	631.25	603	4%	631.25	599	5%
Contin	631.25	668	-6%	631.25	665	-5%
Expt	631.25	636	-1%	631.25	604	4%
Substance B	M (calc.)	M(found)	Deviation	M (calc.)	M(found)	Deviation
T1T2	479.01	554	-16%	479.01	516	-8%
Contin	479.01	588	-23%	479.01	533	-11%
Expt	479.01	565	-18%	479.01	501	-5%

Using an approximation of an ellipsoid leads to higher deviations for species 2. For complex **4a-Hpz**, the deviation is too high to assign it to one of the six possible fragments. For complex **4-Hpz**, the T1/T2 and exponential evaluation of species 2 could be assigned to fragment 8 ($M = 479.01$ g/mol). In the case of species 1 both complexes **4a-Hpz** and **4-Hpz** led to fragment 7 ($M = 631.25$ g/mol).

Depending on the approximation method for the molecular weight calculation the fragments are either fragment 4, 5 and 7 for a highly compact sphere or 7 and 8 for an ellipsoid.



Scheme S1. Possible fragmentation species for **4a-Hpz** dissolved in toluene.

Since a crystal structure of any fragmentation product of **4-Hpz** or **4a-Hpz** could not be obtained, a comparison of the calculated and measured hydrodynamic radii was not possible.

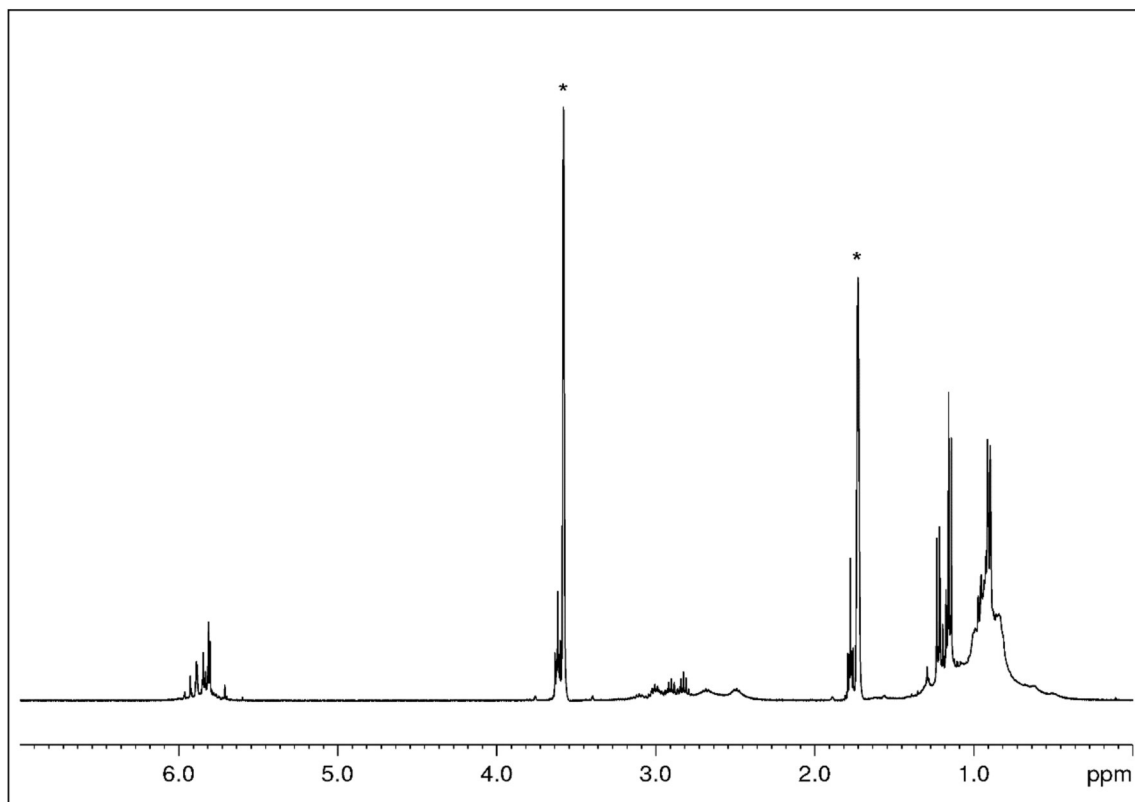


Figure S16. ^1H NMR spectrum (26 °C, 400.12 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{thf})_2]$ (**4-thf**).

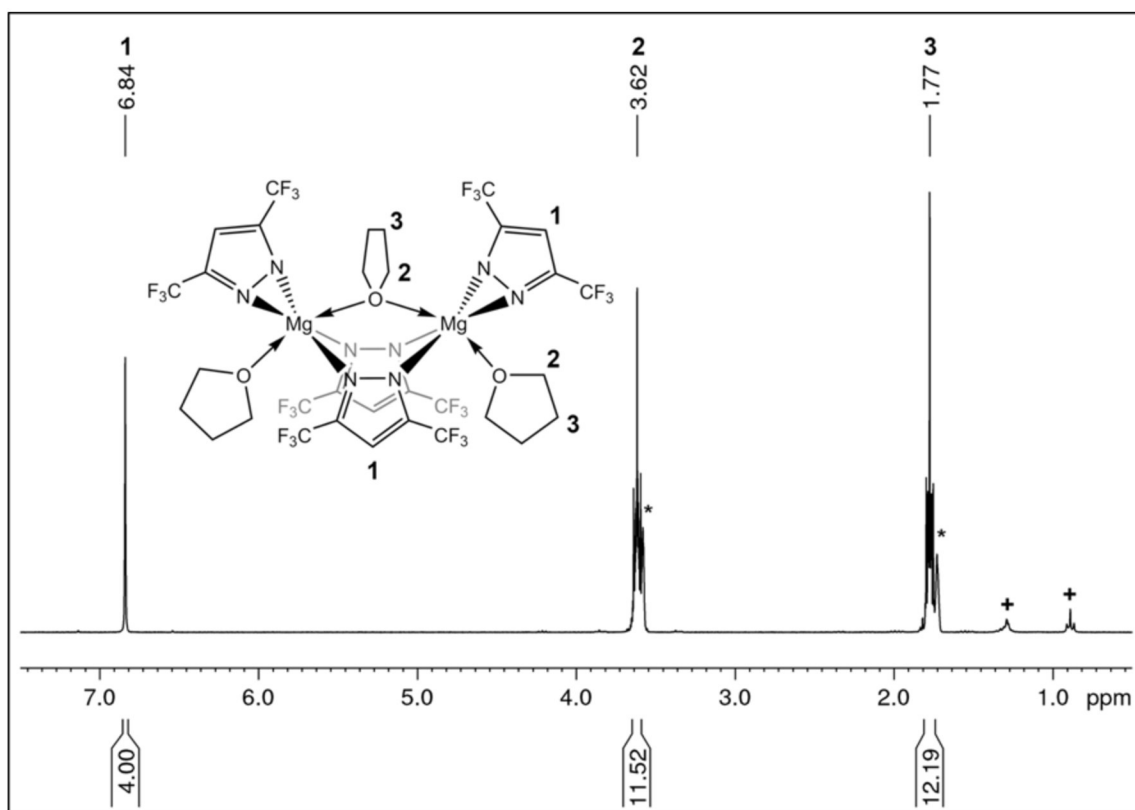


Figure S17. ^1H NMR spectrum (26 °C, 300.13 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}_2(\text{pz}^{\text{CF}_3,\text{CF}_3})_4(\text{thf})_3]$ (**6-thf**) (+ *n*-hexane).

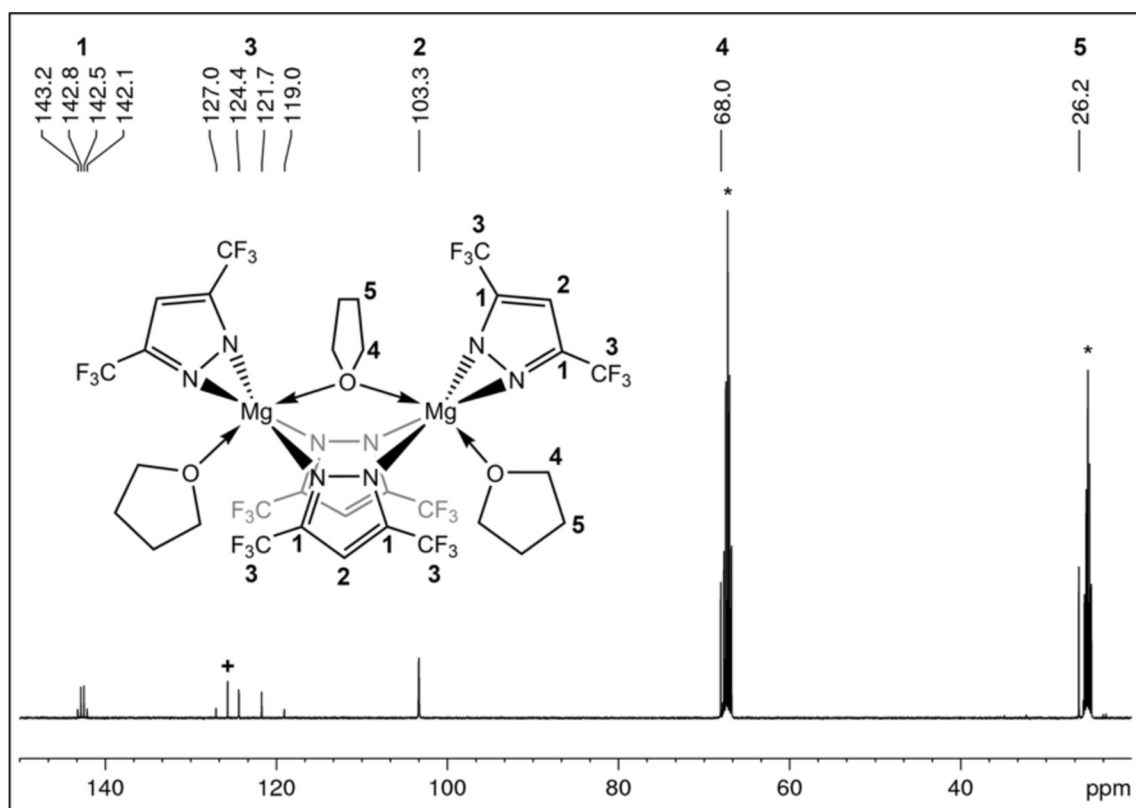


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 100.61 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}_2(\text{pz}^{\text{CF}_3, \text{CF}_3})_4(\text{thf})_3]$ (**6-thf**) (+ solv. CO_2).

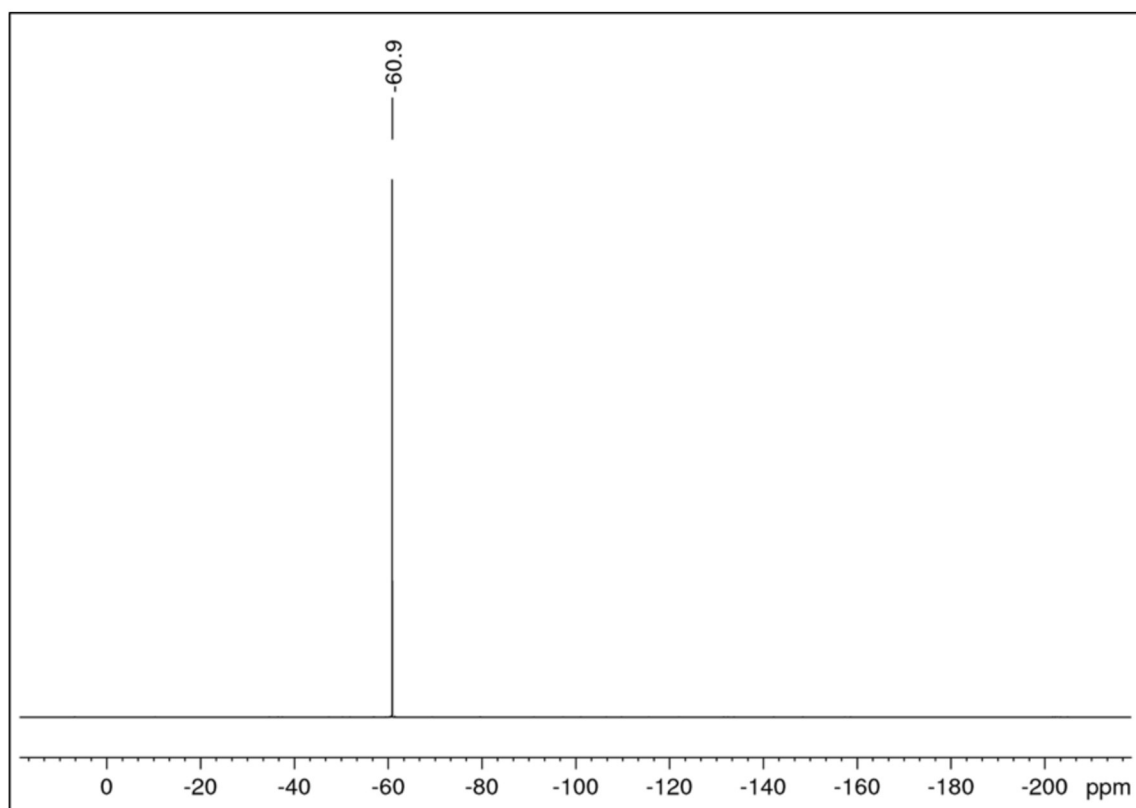


Figure S19. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (26 °C, 282.40 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}_2(\text{pz}^{\text{CF}_3, \text{CF}_3})_4(\text{thf})_3]$ (**6-thf**).

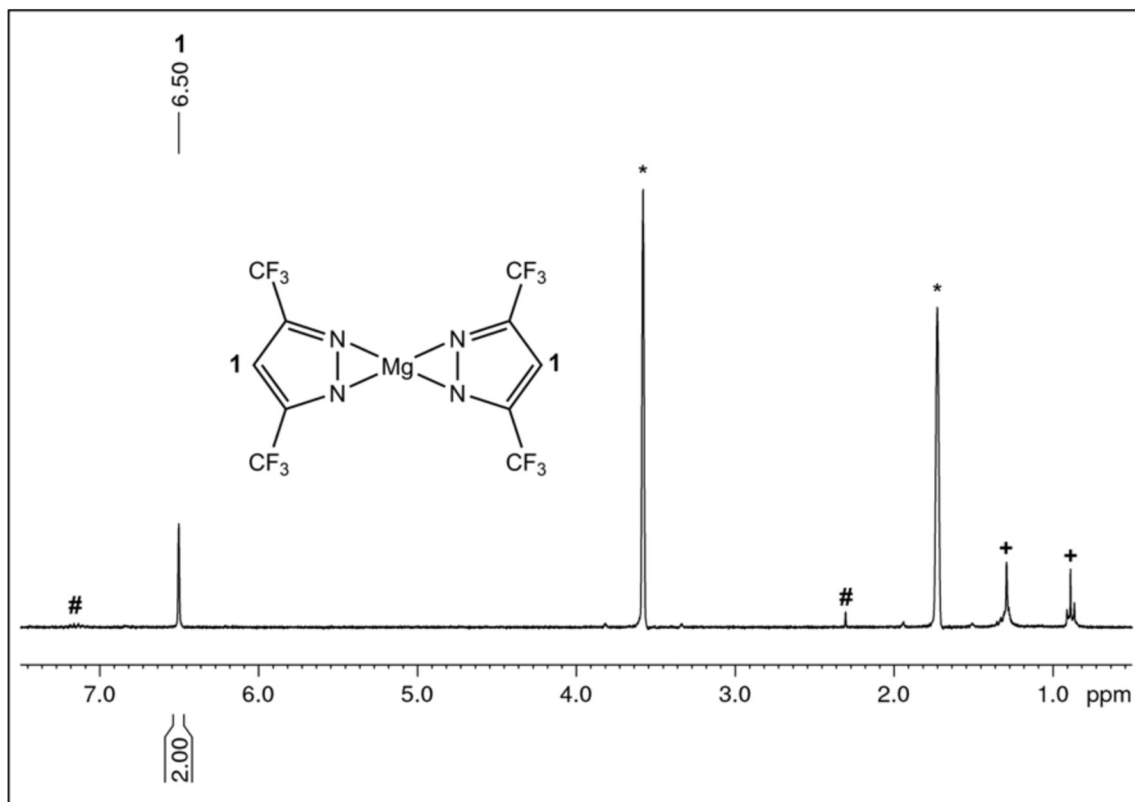


Figure S20. ^1H NMR spectrum (26 °C, 300.13 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}(\text{pz}^{\text{CF}_3, \text{CF}_3})_2]_n$ (**6**) (+ *n*-hexane/# impurities).

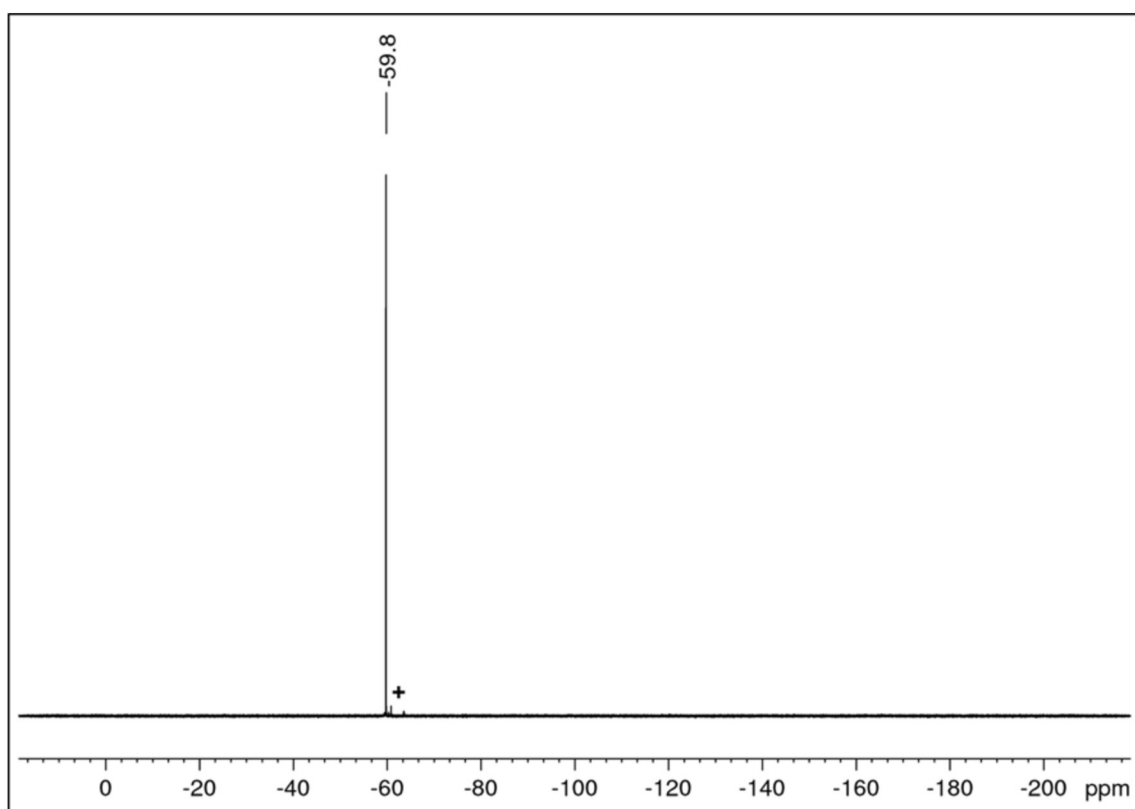


Figure S21. ^{19}F NMR spectrum (26 °C, 282.40 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}(\text{pz}^{\text{CF}_3, \text{CF}_3})_2]_n$ (**6**) (+ impurities).

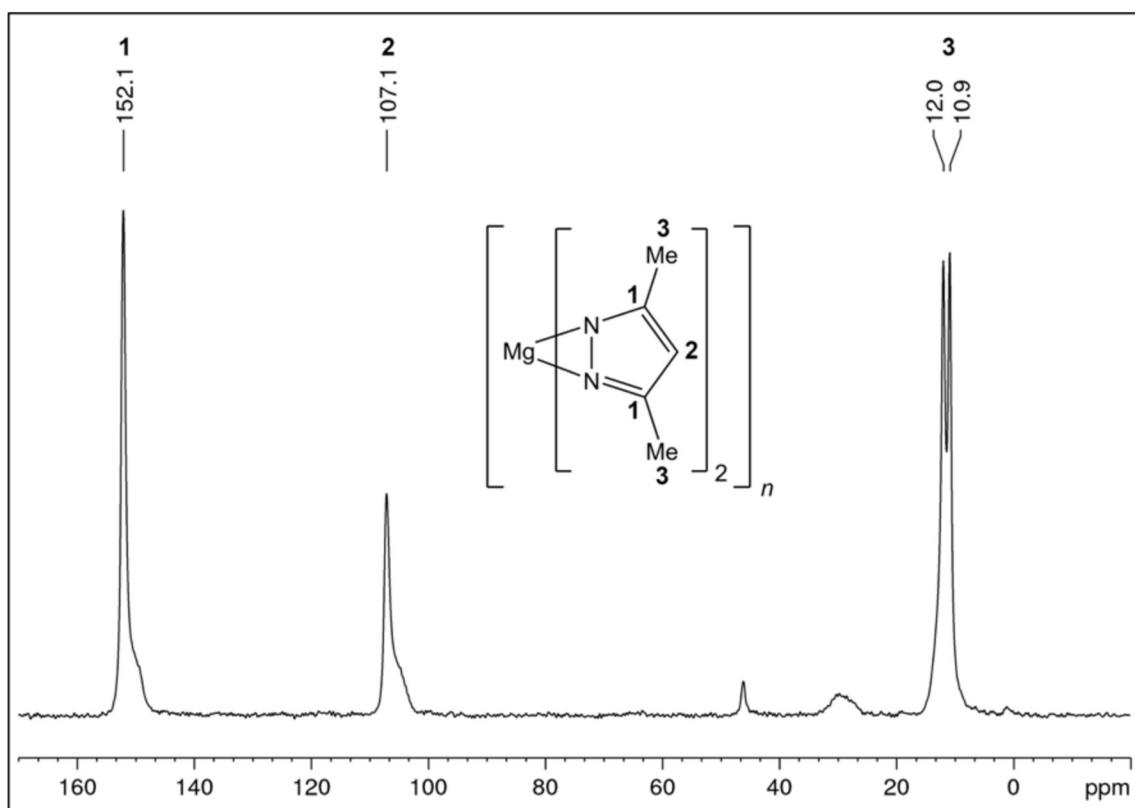


Figure S22. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $[\text{Mg}(\text{pz}^{\text{Me,Me}})_2]_n$ (**7**).

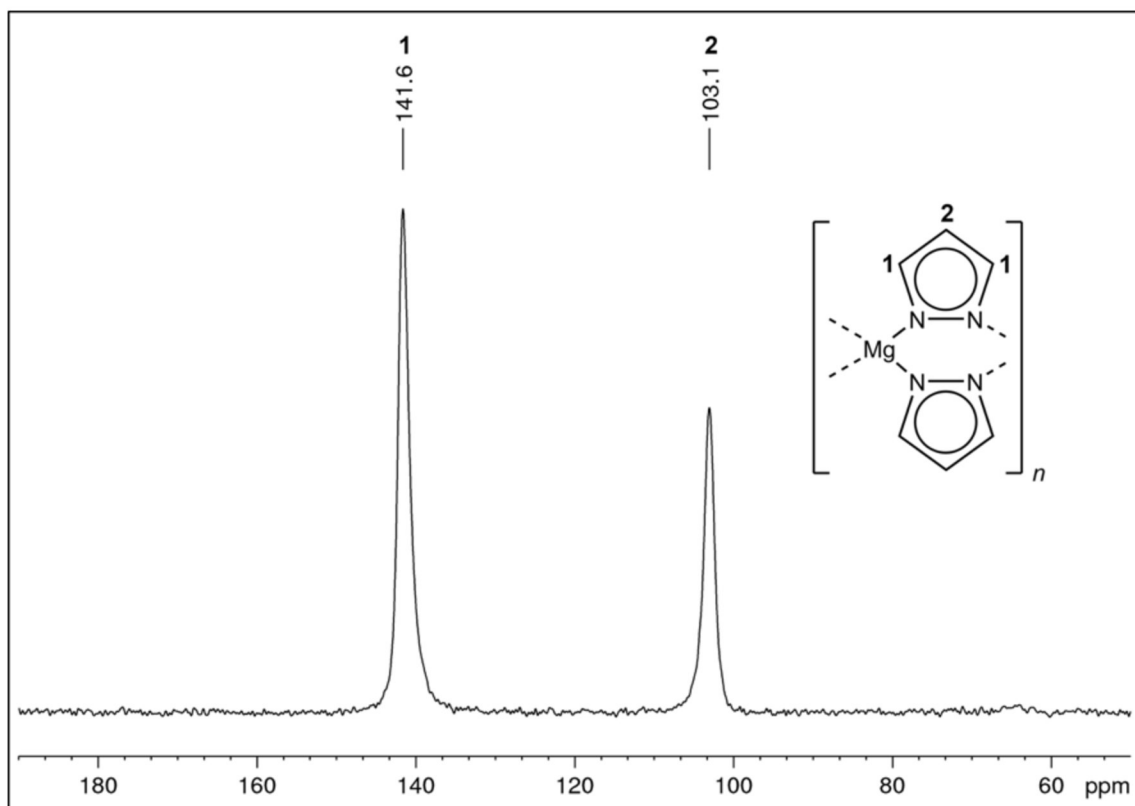


Figure S23. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $[\text{Mg}(\text{pz})_2]_n$ (**8**).

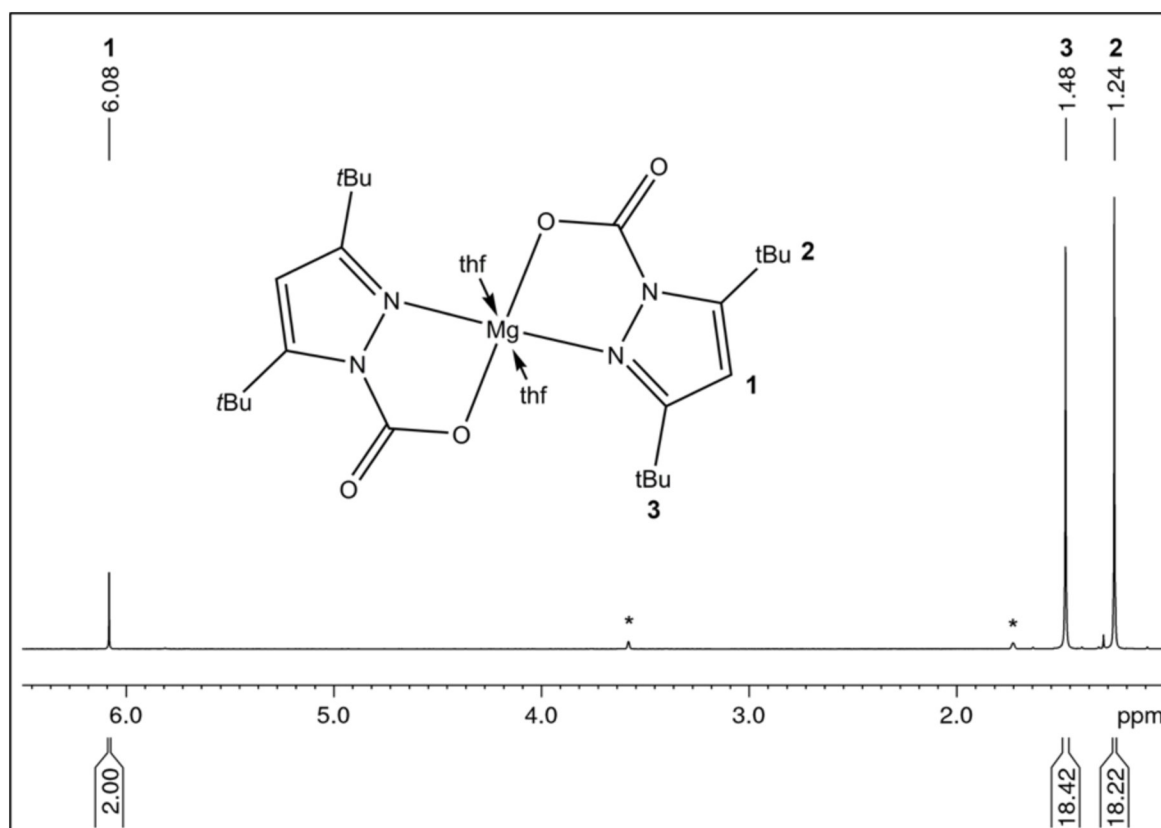


Figure S24. ^1H NMR spectrum (26 °C, 400.12 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (**1-CO₂,thf**).

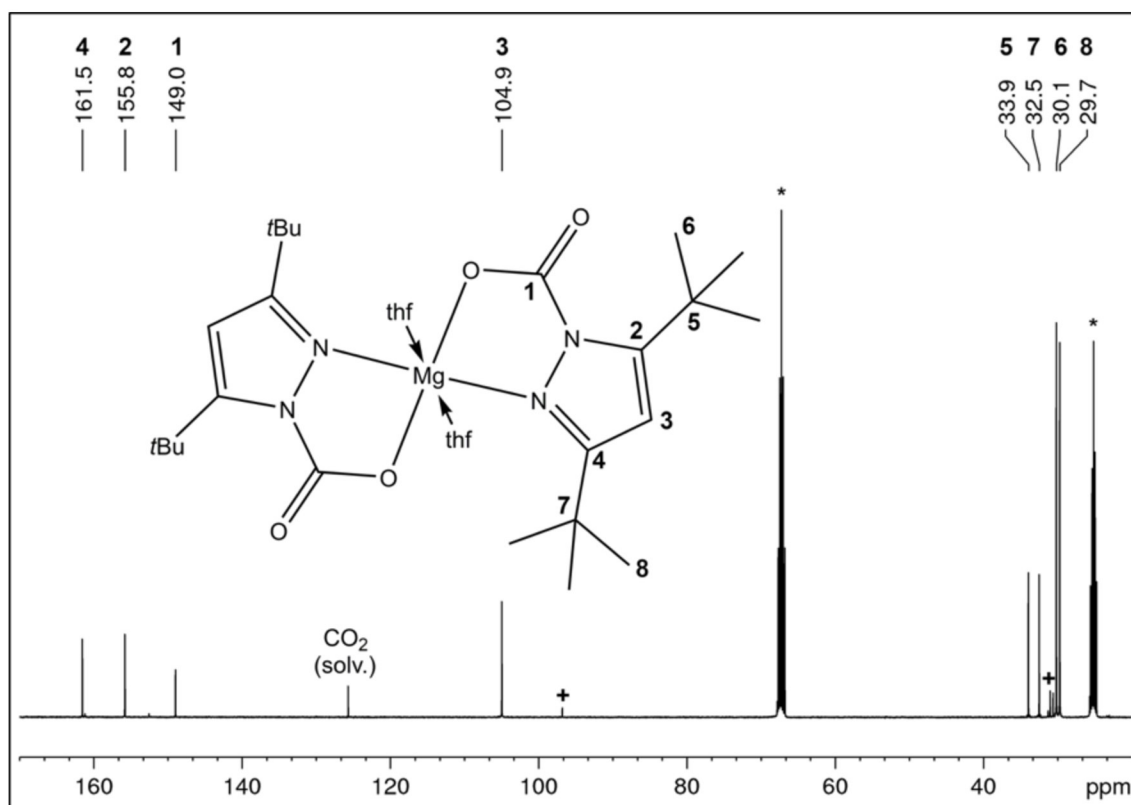


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 100.60 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (**1-CO₂,thf**) (+ impurities).

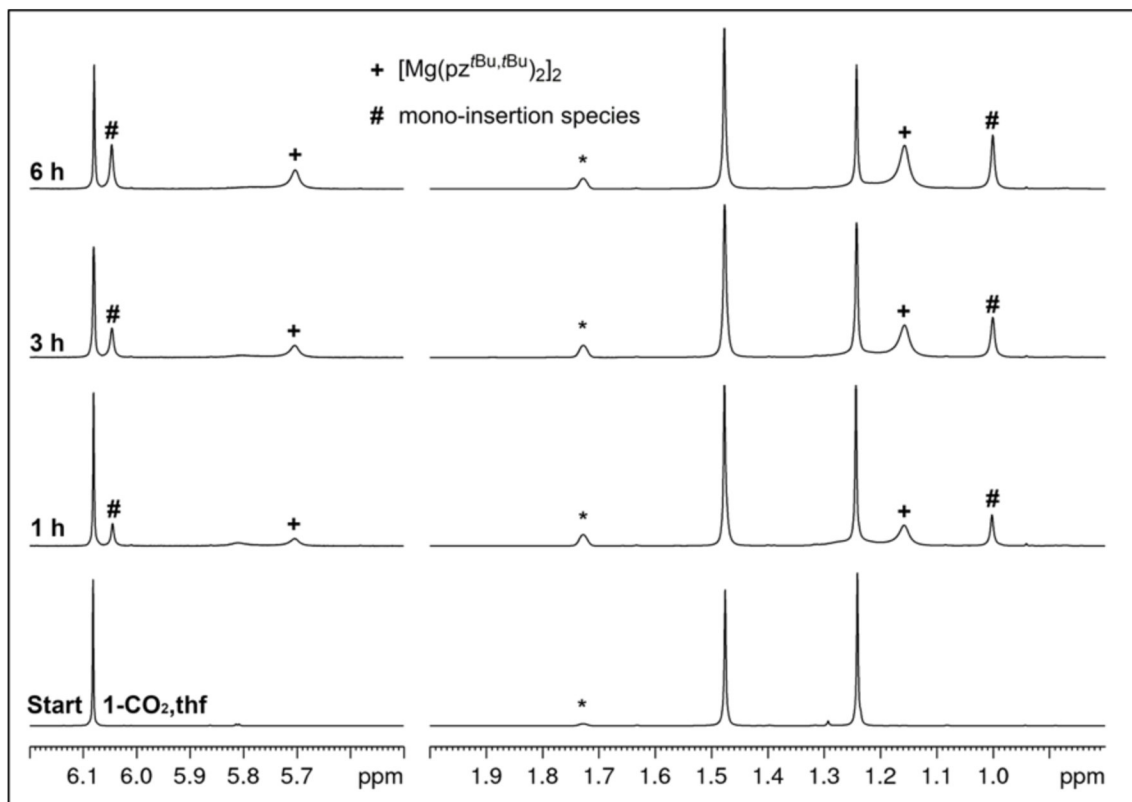


Figure S26. Comparison of ^1H NMR spectra (26 °C, 400 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (**1-CO₂,thf**) after exposure to reduced pressure over different time periods showing the formation of $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (**1-thf**, +) and proposed $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})(\text{pz}^{\text{tBu,tBu}})(\text{thf})_x]$ (#).

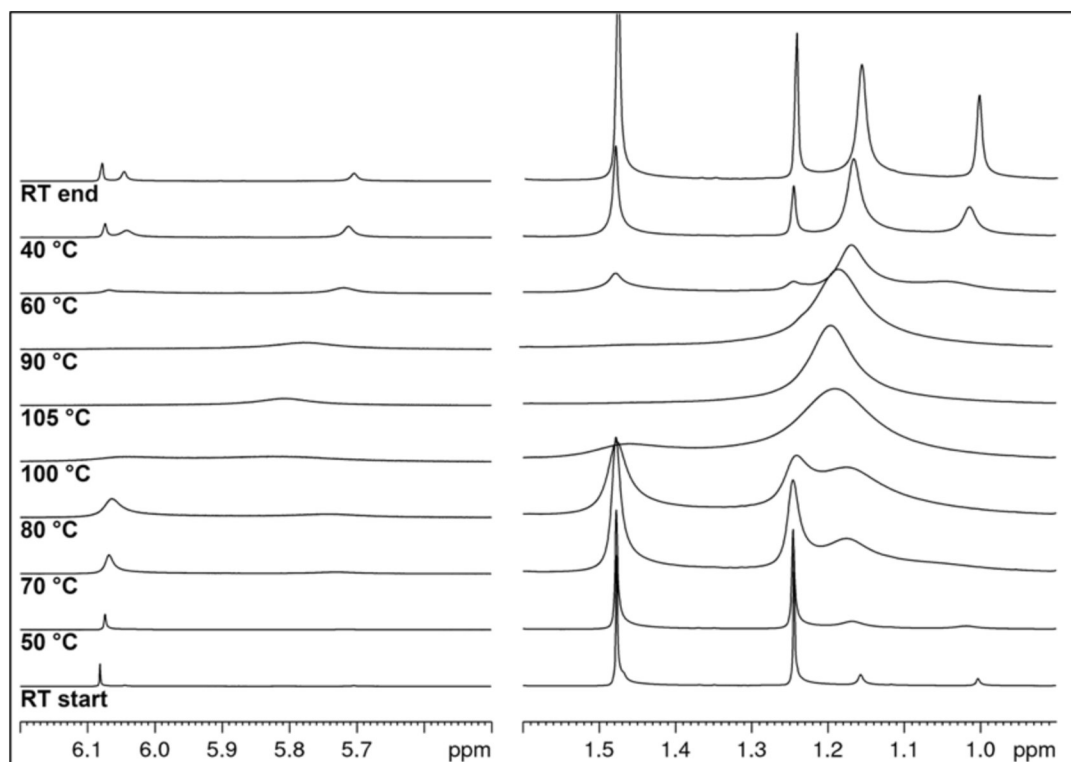


Figure S27. VT ^1H NMR spectra (500.13 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (**1-CO₂,thf**) in the range of 26 °C to 105 °C showing the formation of $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (**1-thf**) and proposed $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})(\text{pz}^{\text{tBu,tBu}})(\text{thf})_x]$.

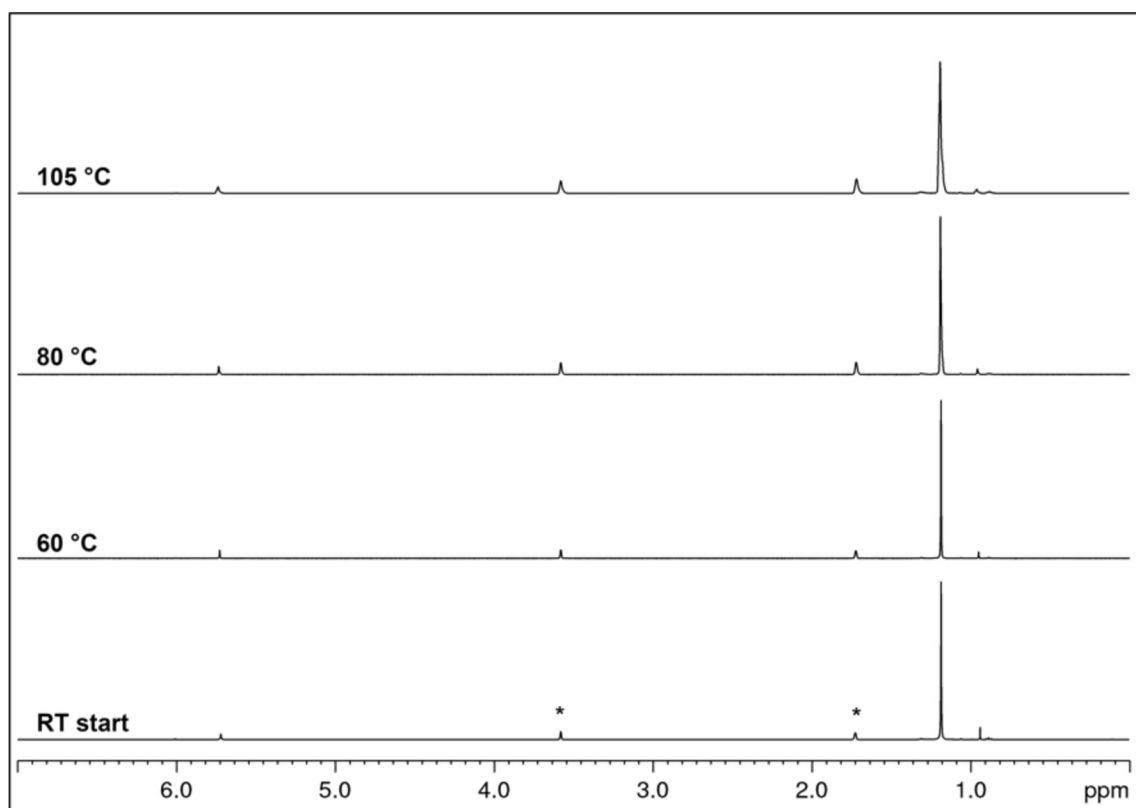


Figure S28. VT ^1H NMR spectra (500.13 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (**1-thf**) in the range of 26 °C to 105 °C.

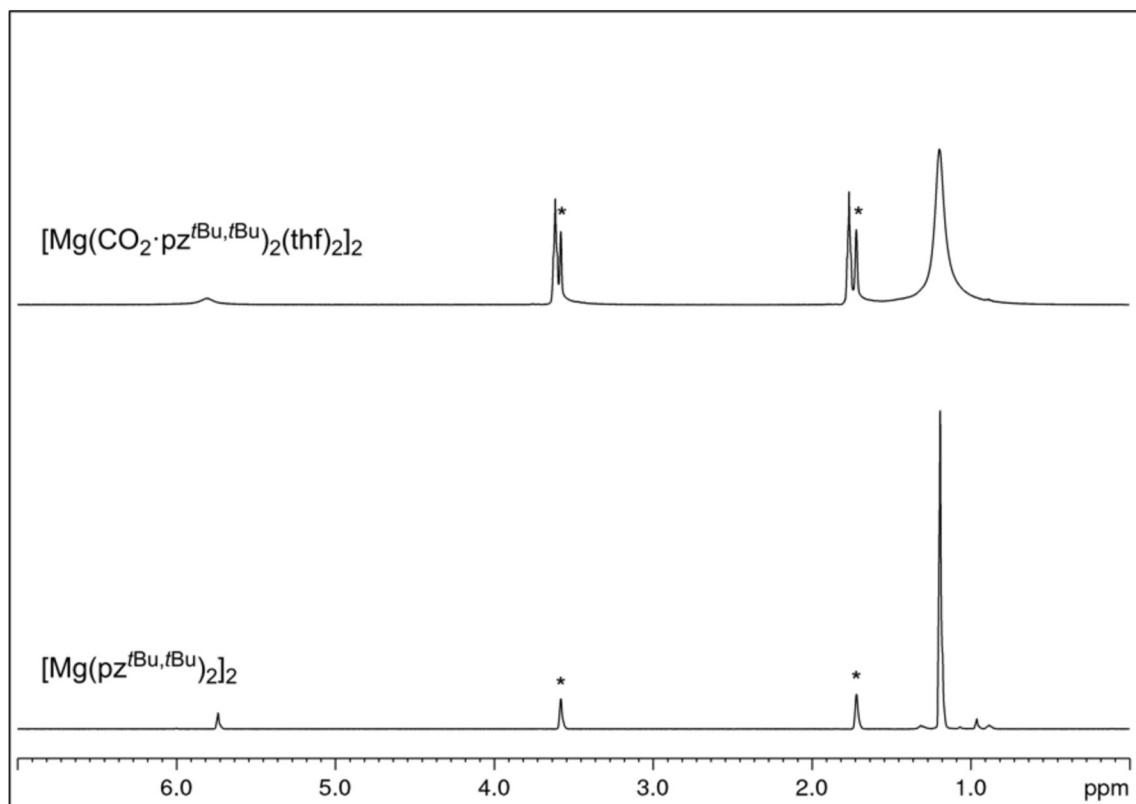


Figure S29. Comparison of ^1H NMR spectra (500.13 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (**1-thf**) and $[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]_2$ (**1-CO₂,thf**) at 105 °C.

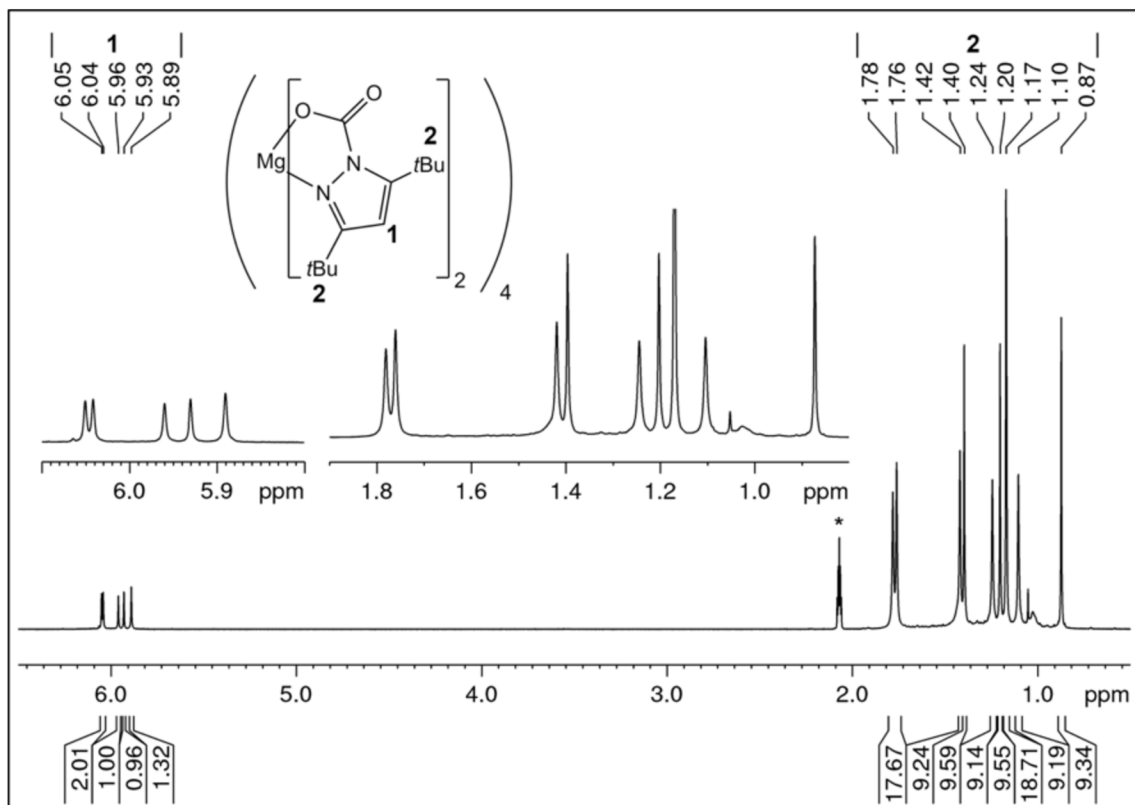


Figure S30. ¹H NMR spectrum (26 °C, 400.11 MHz, [D₈]toluene) of $[Mg(CO_2 \cdot pz^{tBu,tBu})_2]_4$ (1-CO₂).

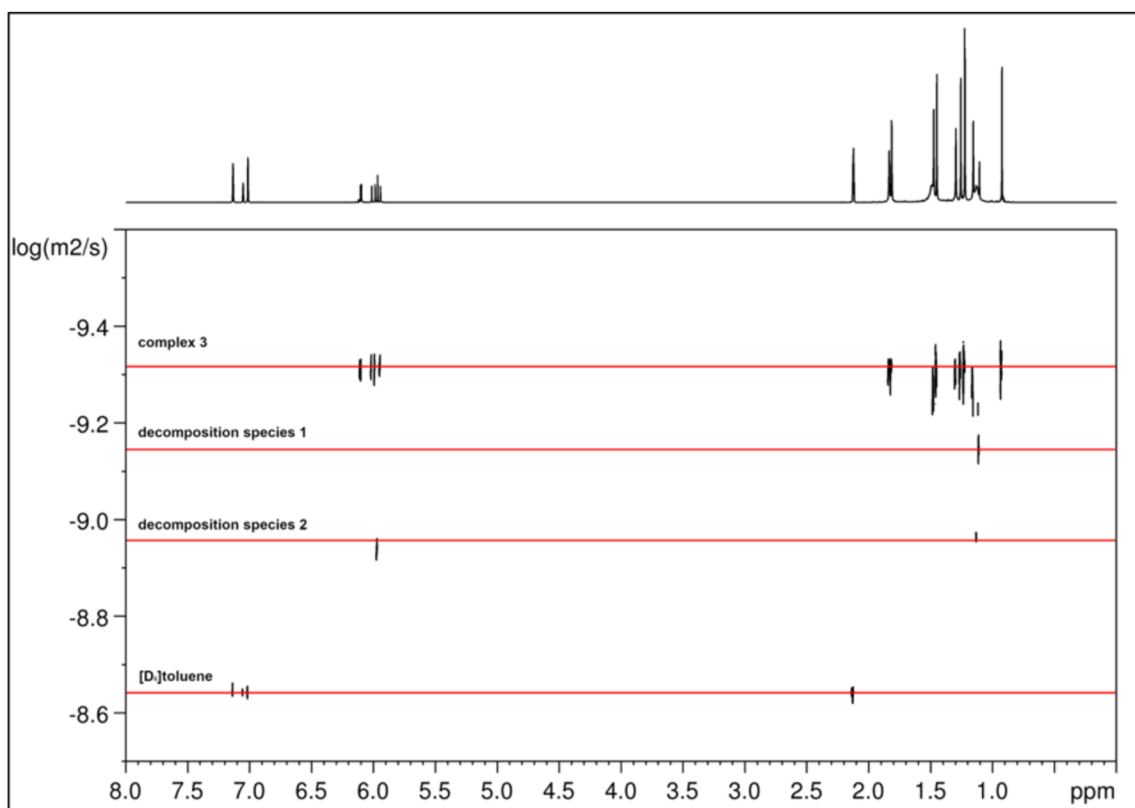


Figure S31. ¹H DOSY NMR spectrum (26 °C, 700.29 MHz, [D₈]toluene) of $[Mg(CO_2 \cdot pz^{tBu,tBu})_2]_4$ (1-CO₂). Decomposition species 2 is most likely HO₂Cpz^{tBu,tBu} but a molecular weight calculation was not possible due to overlapping of the signals with 1-CO₂. Decomposition species 1 could not be assigned to a specific product.

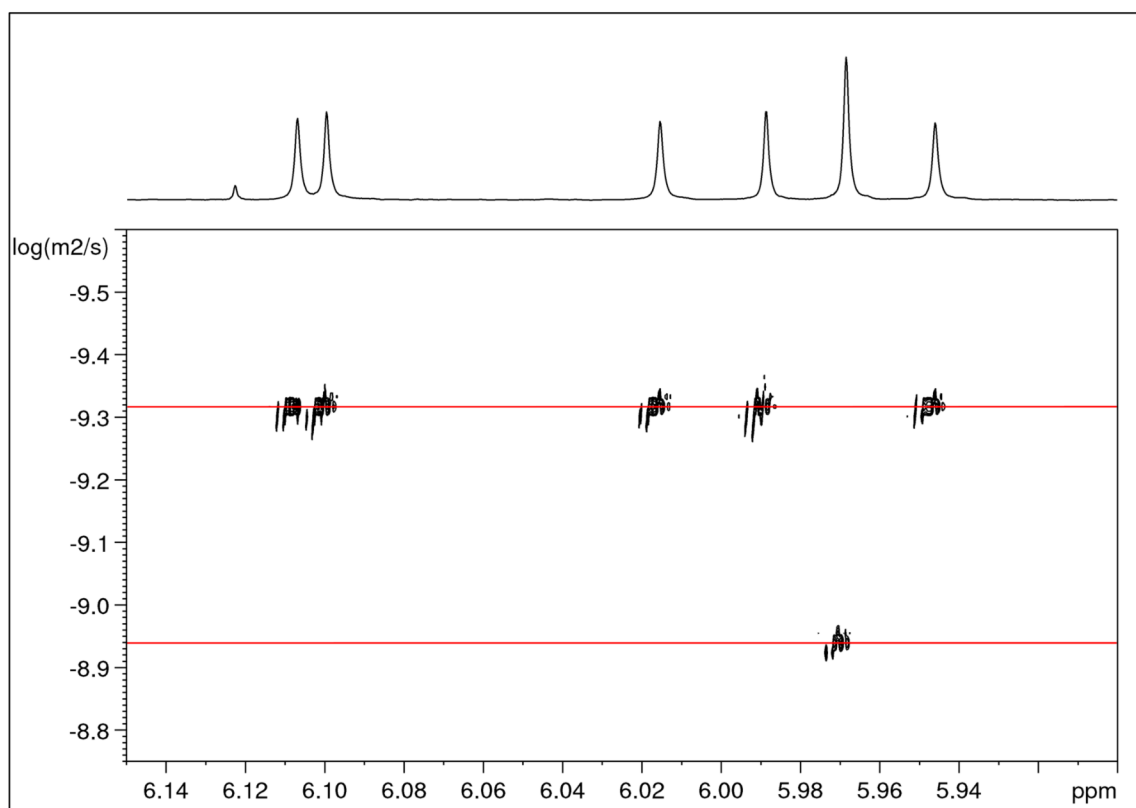


Figure S32. ^1H DOSY NMR spectrum (26 °C, 700.29 MHz, $[\text{D}_8]$ toluene) of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})_2]_4$ (**1-CO₂**, top red line) and decomposition product 2 (bottom red line) in the aromatic region.

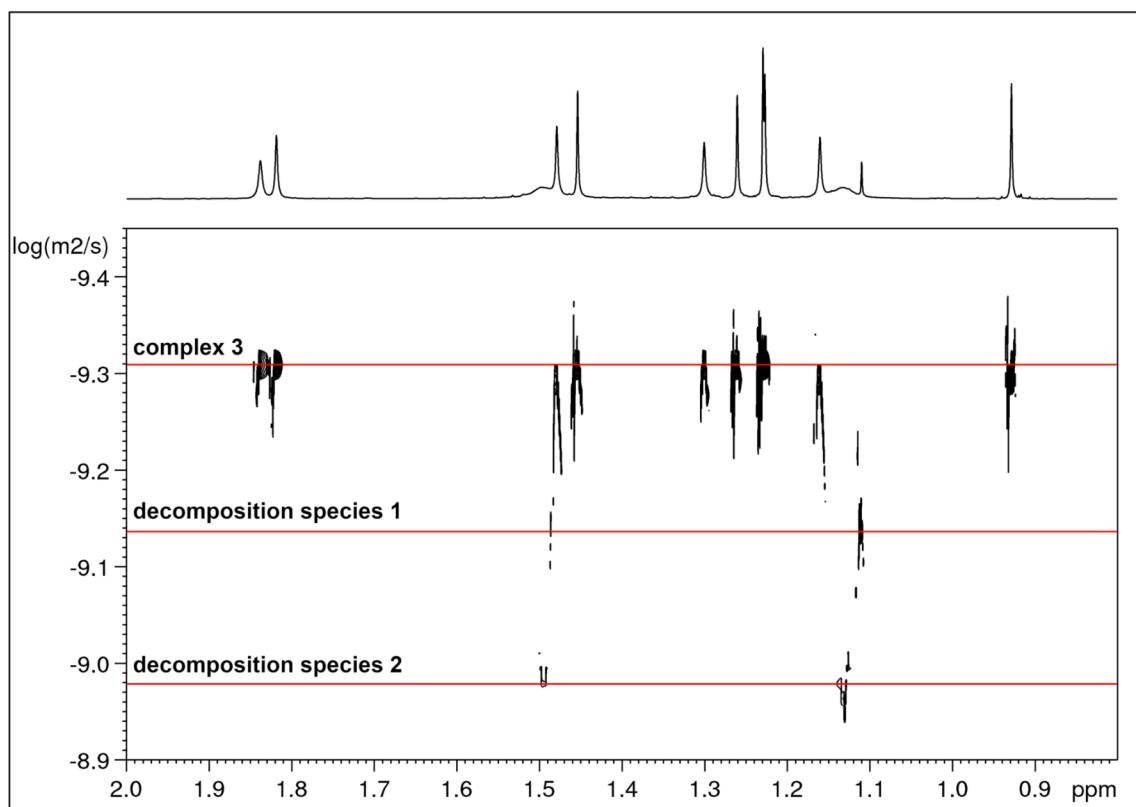


Figure S33. ^1H DOSY NMR spectrum (26 °C, 700.29 MHz, $[\text{D}_8]$ toluene) of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})_2]_4$ (**1-CO₂**) in the region of tBu moieties. Abbreviations of the signals of **1-CO₂** at 1.48 and 1.16 ppm of the diffusion coefficient of **1-CO₂** are due to overlapping with signals of decomposition product 2.

¹H DOSY NMR Experiment Data of [Mg(CO₂·pz^{tBu,tBu})₂]₄ (1-CO₂)

The ¹H DOSY NMR measurement was performed to determine whether **1-CO₂** is an oligomeric species as indicated by the ¹H NMR spectrum. Indeed, the DOSY experiment showed only one species with one diffusion coefficient for all 15 signals of **1-CO₂**. In the period between recording the initial ¹H NMR spectrum and performing the DOSY experiment two decomposition products formed which are marked in Figures S27-S29. Each of these decomposition products has a specific diffusion coefficient. According to its chemical shift, decomposition product 2 is most likely the carbamic acid HO₂Cpz^{tBu,tBu}. However, a molecular weight calculation was not possible, due to overlapping of the signals with other species.

Table S4. Diffusion coefficients in [D₆]toluene determined via ¹H DOSY NMR experiment

Evaluation	D (average)	Variance	Variance%	pD (average)
T1T2	1.0323E-09	9.393E-11	9.099E-02	-898.620%
Contin	1.171E-09	1.335E-12	1.140E-03	-893.145%
Expt	1.0955E-09	6.816E-11	6.222E-02	-896.039%

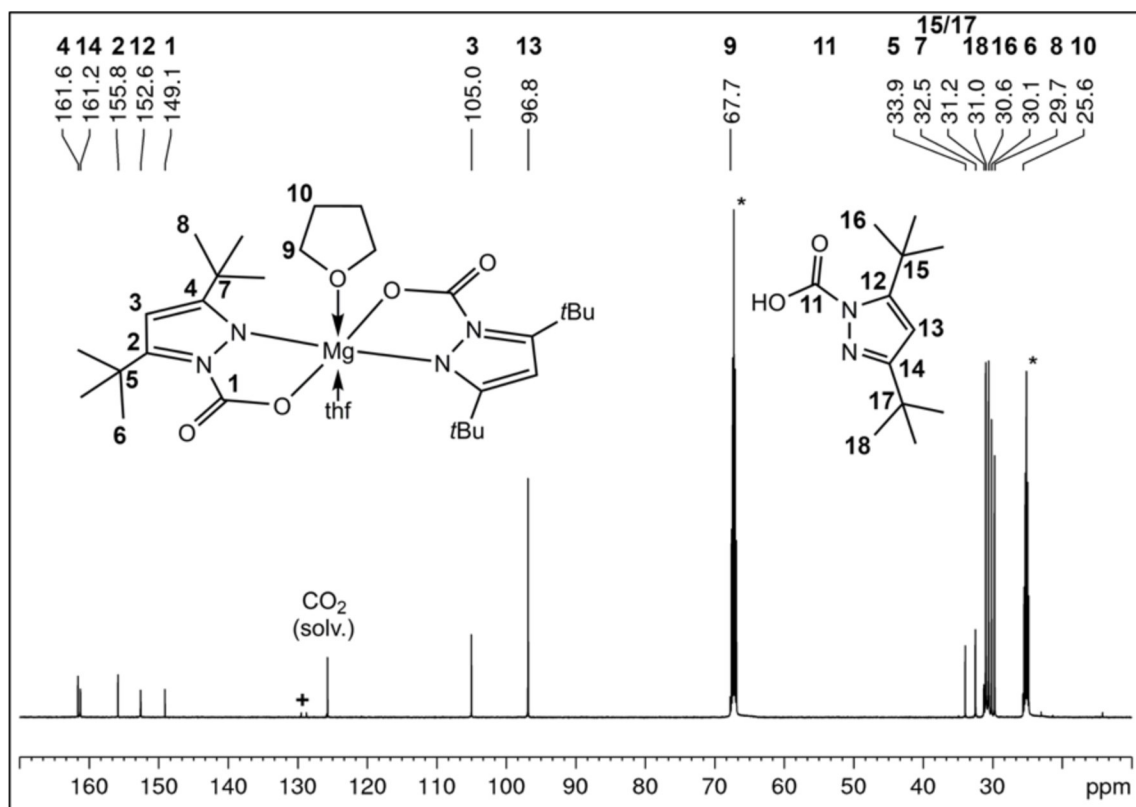
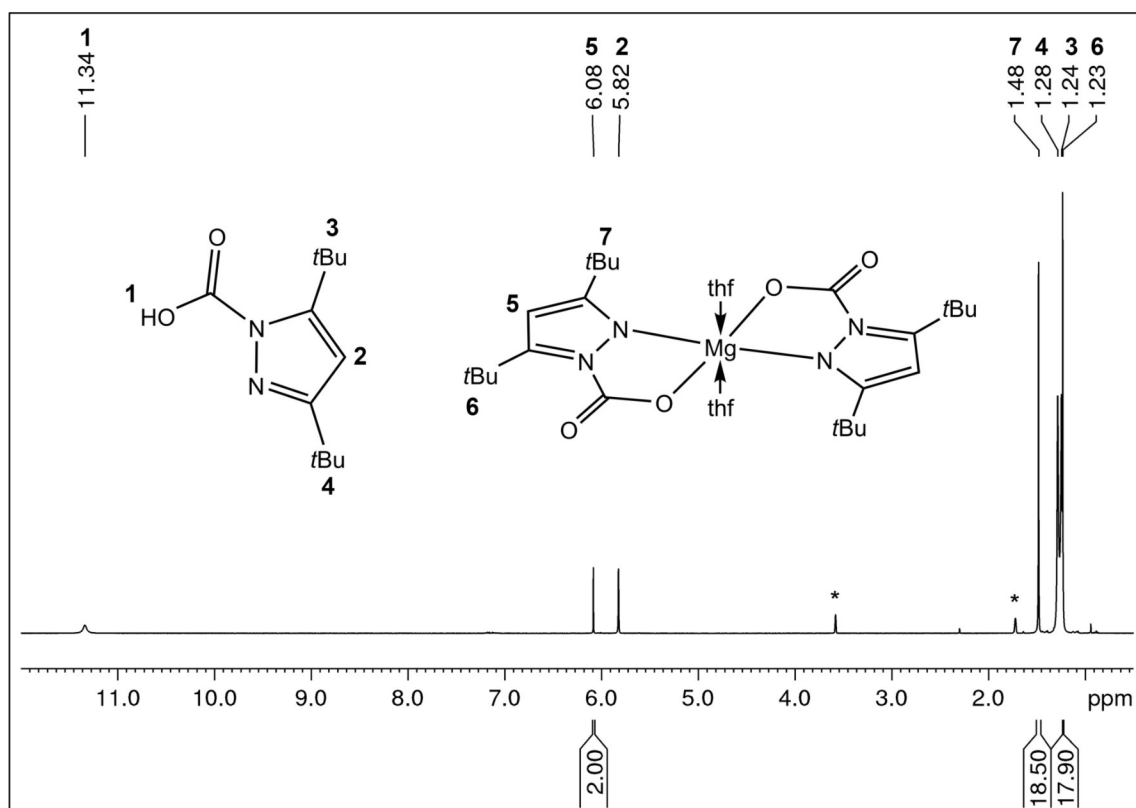
The diffusion coefficients (D) were determined via three different evaluation methods provided by Topspin. The T1/T2 module uses a numeric calculation for D, whereas the contin/exponential evaluation uses manual signal picking. D was calculated from the measured pD values. The D values listed in Table S4 are averaged overall signals assigned to one species that are not overlapping with signals from another species.

Table S5. Molecular weight calculation via the measured diffusion coefficients

Evaluation	Sphere			Ellipsoid			Merged		
	M(calc.)	M(found)	Deviation	M(calc.)	M(found)	Deviation	M(calc.)	M(found)	Deviation
T1T2	1883.59	1721	9%	1280.66	1133	12%	1280.66	1104	14%
Contin	1883.59	1911	-1%	1280.66	1234	4%	1280.66	1200	6%
Expt	1883.59	1875	0%	1280.66	1215	5%	1280.66	1182	8%

For the molecular weight calculation the method described by Stalke was used.^[11] The approximation of a highly compacted sphere is probably the best way to describe such a oligomer due to the molecular rotation and vibration. Using this approximation, molecular weights between 1721 and 1911 g/mol were found applying the three evaluation methods. This fits good to the tetrameric species [Mg(CO₂·pz^{tBu,tBu})₂]₄ with a molecular weight of 1883.59 g/mol. All three evaluation methods are within the methods error of 9 % with the exponential evaluation being the closet with 1875 g/mol. Changing the approximation from a sphere to an ellipsoid or a less accurately merged one, the deviation from an oligomer of the form [Mg(CO₂·pz^{tBu,tBu})₂]_n is too big for an accordance. The found molecular weights are between 1104 and 1234 g/mol, which does not fit for any oligomeric species with complete CO₂ insertion. However, given that a highly compact sphere is the most likely state in solution over the NMR timescale and the solid-state experiments speaks for a complete CO₂ insertion, **1-CO₂** is most likely the tetrameric species [Mg(CO₂·pz^{tBu,tBu})₂]₄.

Since a crystal structure of **1-CO₂** could not be obtained, a comparison of the calculated and measured hydrodynamic radii was not possible.



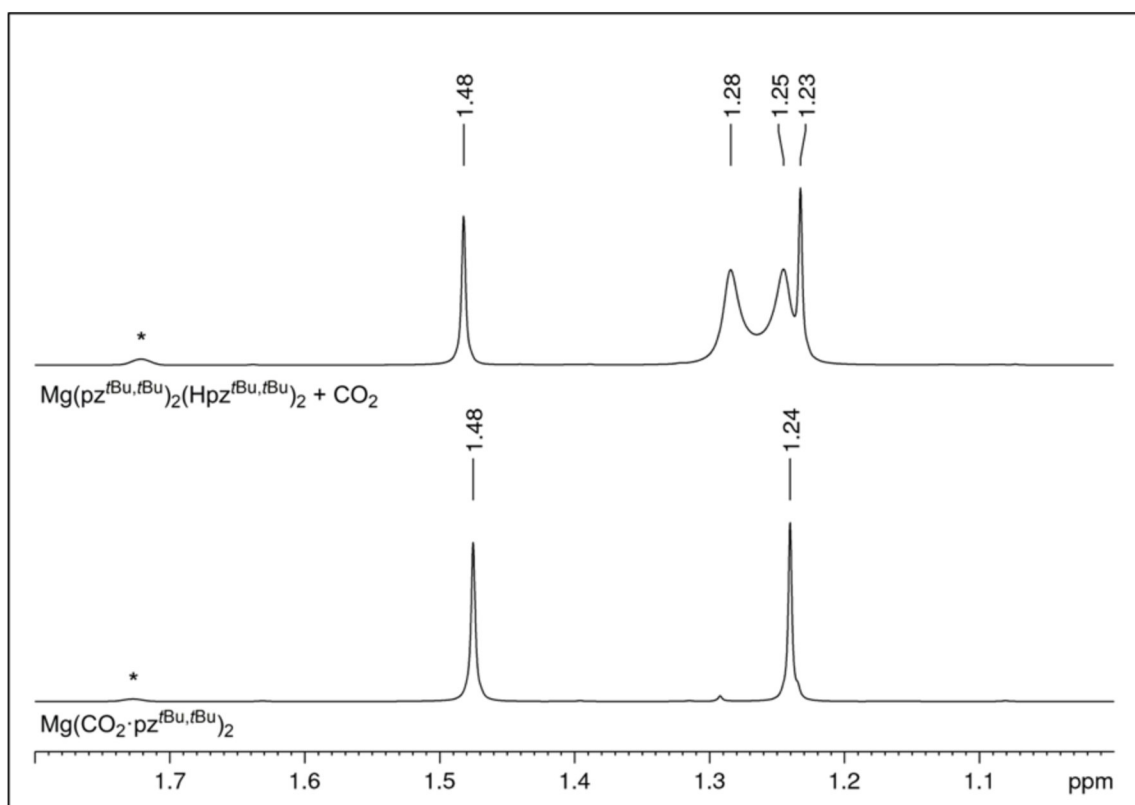


Figure S36. Comparison of the ^1H NMR spectra (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of the reaction of $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2]_2$ (**1**, bottom) and $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2(\text{Hpz}^{\text{tBu,tBu}})_2]$ (**1-Hpz**, top) with CO_2 in $[\text{D}_8]\text{THF}$.

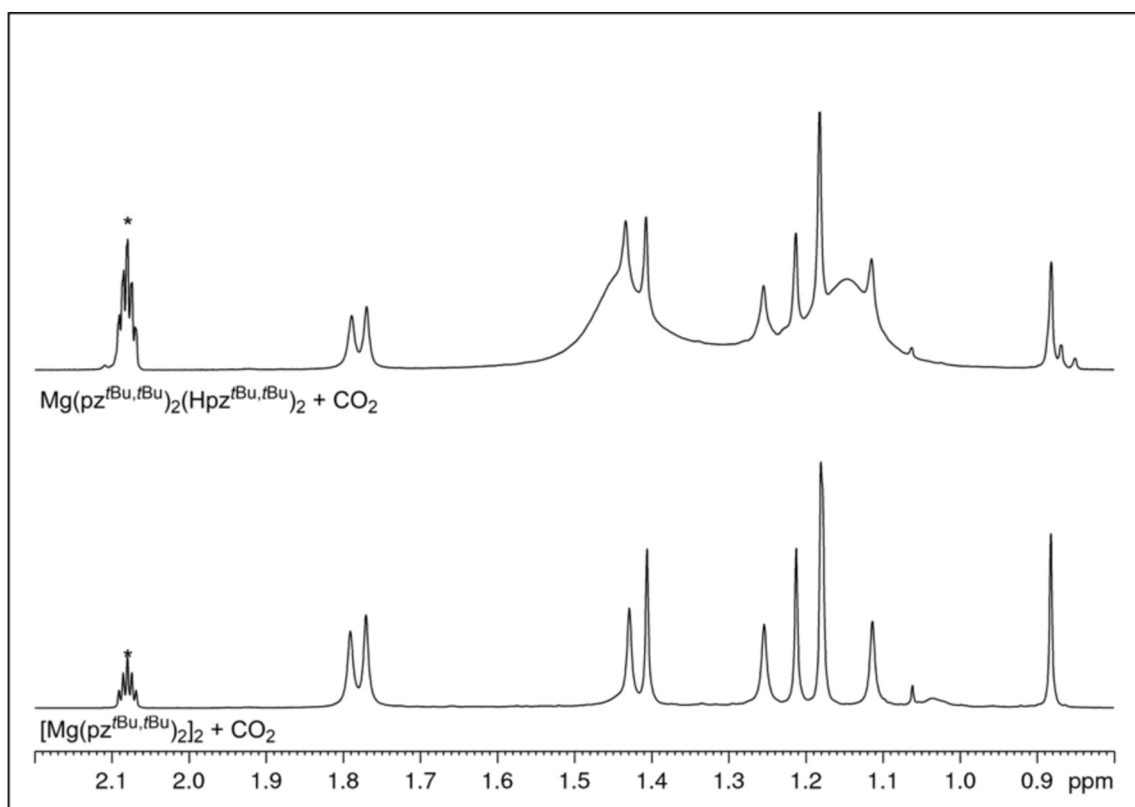


Figure S37. Comparison of the ^1H NMR spectra (26 °C, 400.11 MHz, $[\text{D}_8]\text{toluene}$) of the reaction of $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2]_2$ (**1**, bottom) and $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2(\text{Hpz}^{\text{tBu,tBu}})_2]$ (**1-Hpz**, top) with CO_2 in $[\text{D}_8]\text{toluene}$.

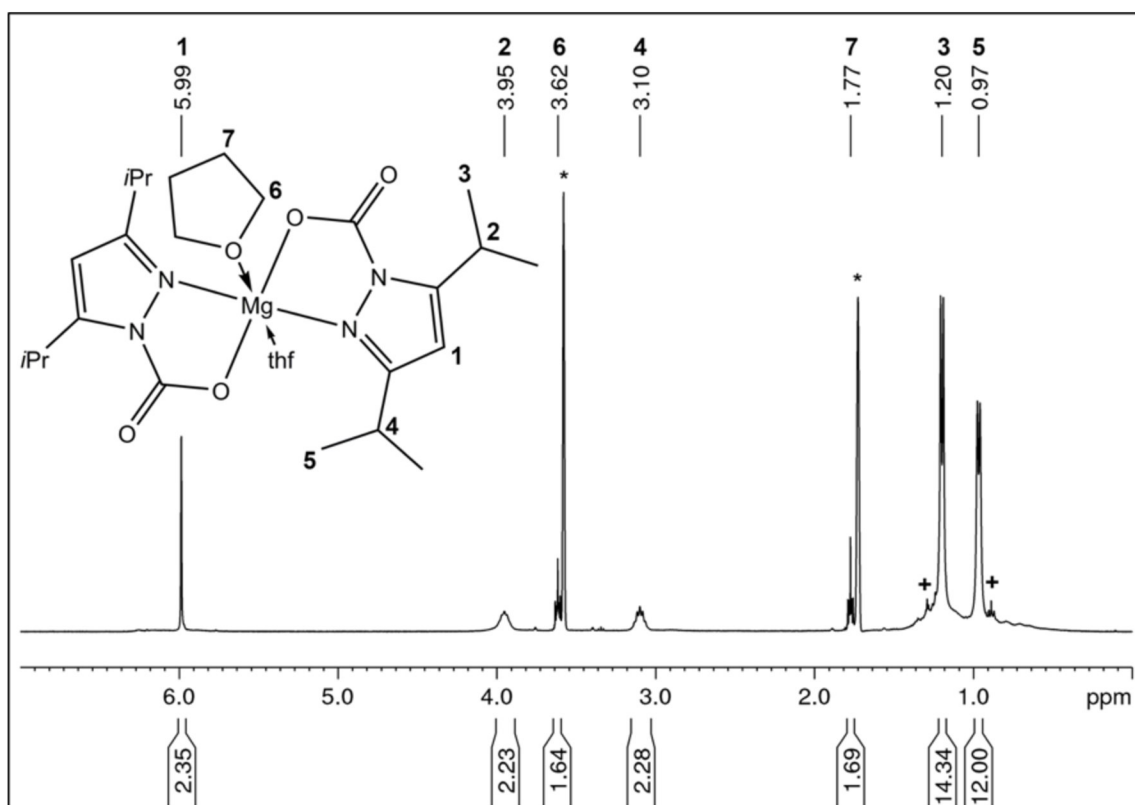


Figure S38. ¹H NMR spectrum (26 °C, 400.11 MHz, [D₈]THF) of [Mg(CO₂·pz^{iPr,iPr})₂(thf)₂] (4-CO₂,thf) (+ *n*-hexane).

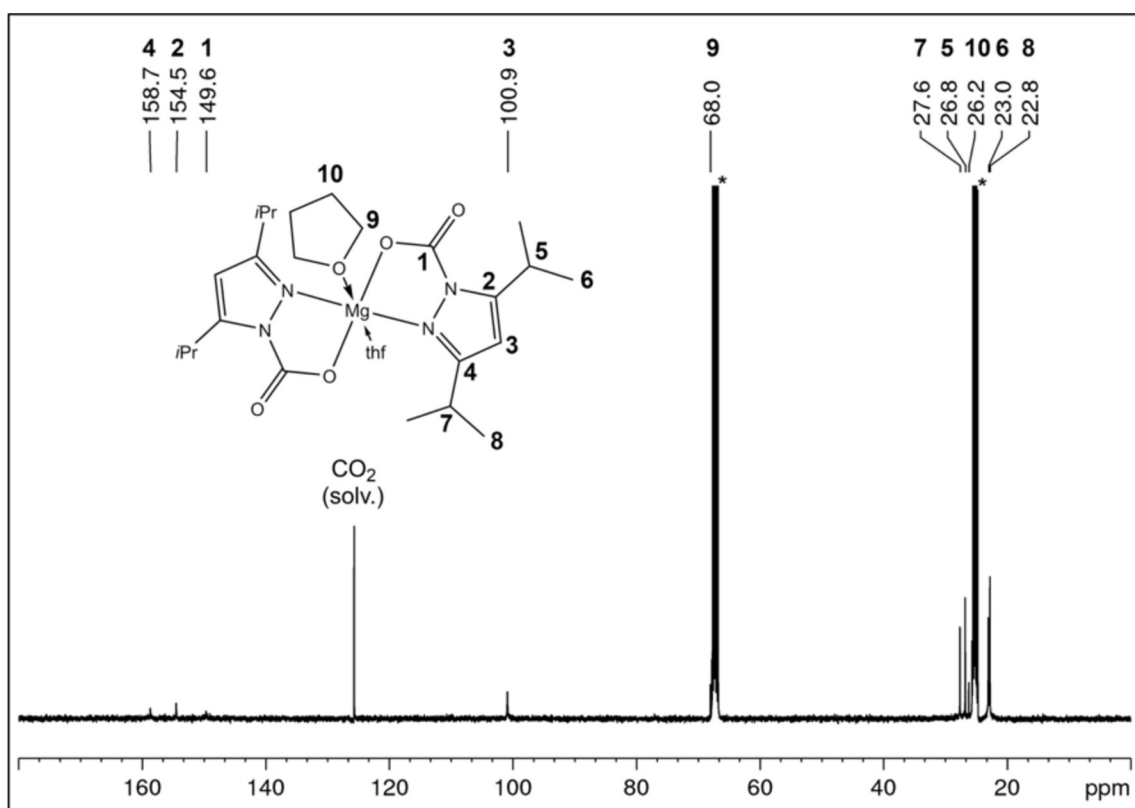


Figure S39. ¹³C{¹H} NMR spectrum (26 °C, 100.61 MHz, [D₈]THF) of [Mg(CO₂·pz^{iPr,iPr})₂(thf)₂] (4-CO₂,thf).

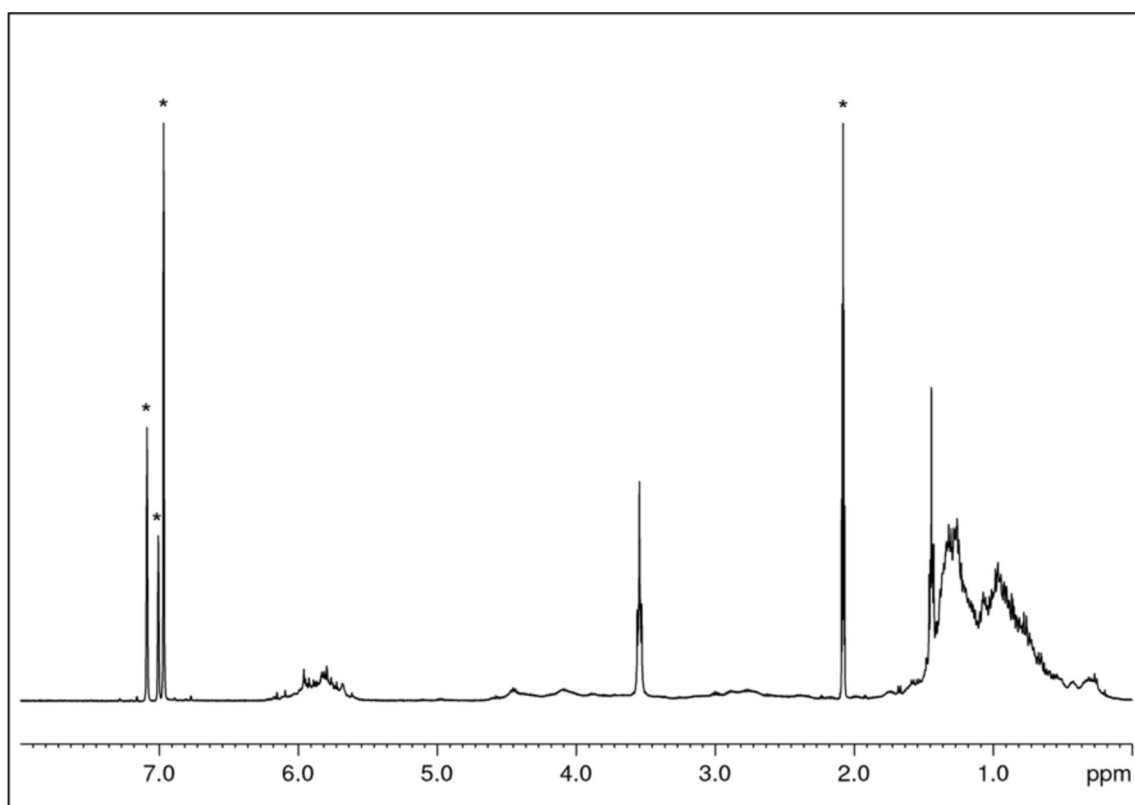


Figure S40. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{i\text{Pr},i\text{Pr}})_2]_4$ (**4-CO₂**).

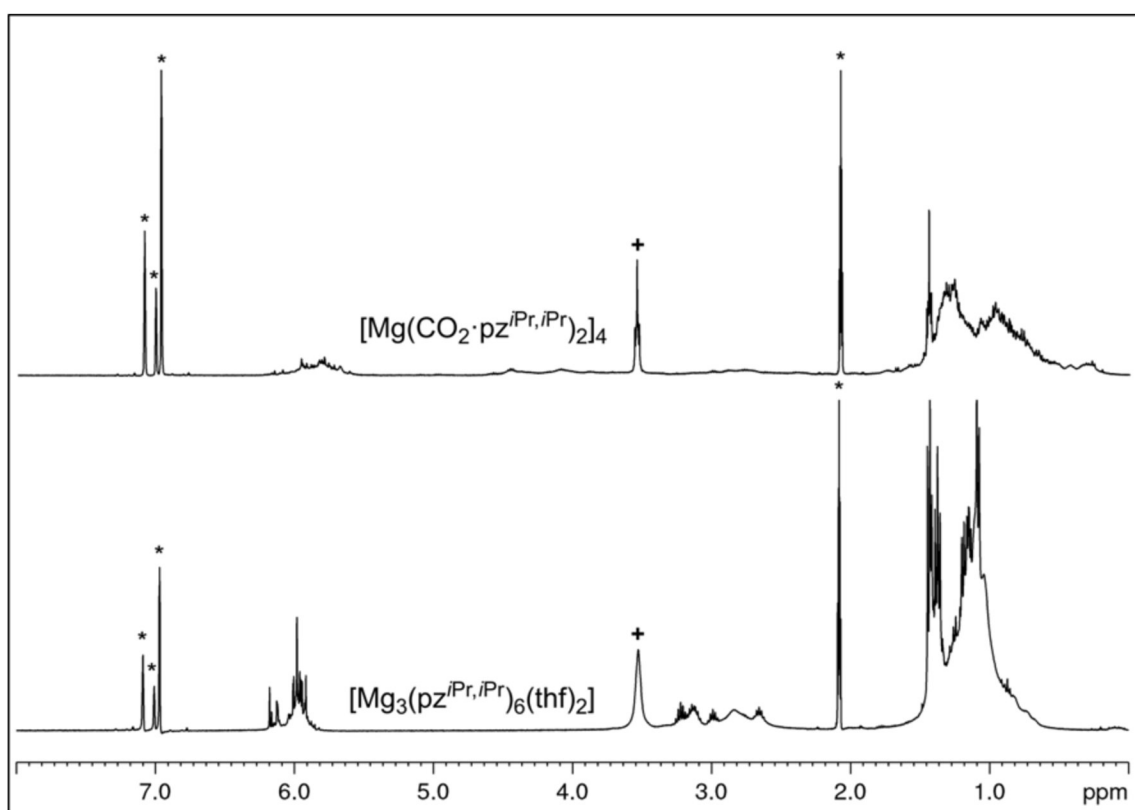


Figure S41. Comparison of the ^1H NMR spectra (26 °C, 100.61 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{thf})_2]$ (**4-thf**, bottom) and $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{i\text{Pr},i\text{Pr}})_2]_4$ (**4-CO₂**, top) (+ residual THF).

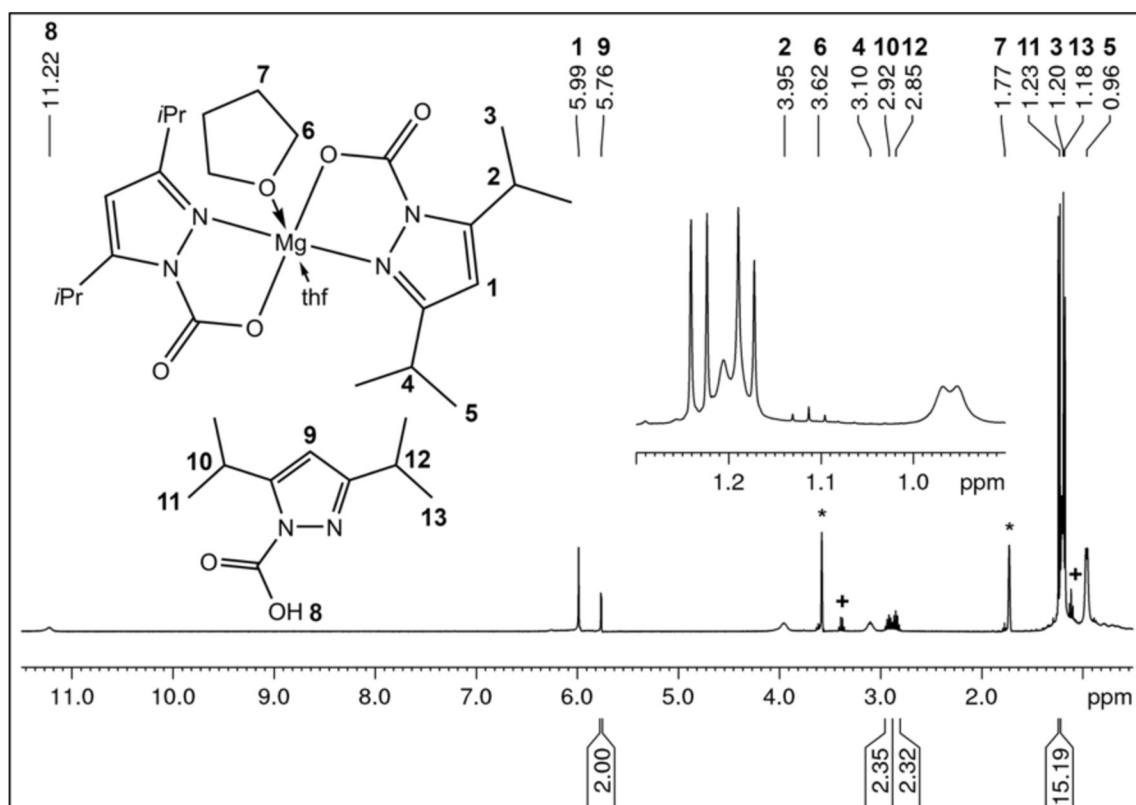


Figure S42. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of the reaction of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**) with CO_2 and the formation of $[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{i\text{Pr},i\text{Pr}})_2(\text{thf})_2]$ (**4-CO₂**) and $\text{HO}_2\text{Cpz}^{i\text{Pr},i\text{Pr}}$ (+ Et_2O).

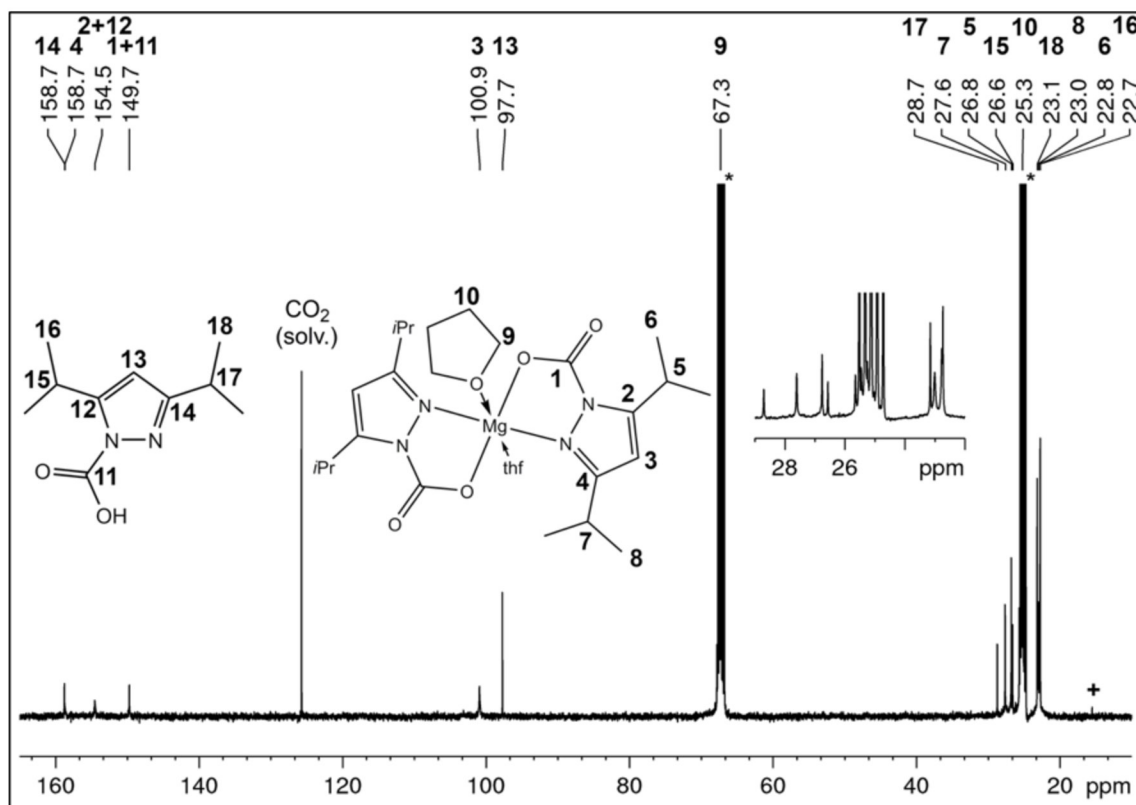


Figure S43. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 100.61 MHz, $[\text{D}_8]\text{THF}$) of the reaction of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**) with CO_2 and the formation of $[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{i\text{Pr},i\text{Pr}})_2(\text{thf})_2]$ (**4-CO₂**) and $\text{HO}_2\text{Cpz}^{i\text{Pr},i\text{Pr}}$ (+ Et_2O).

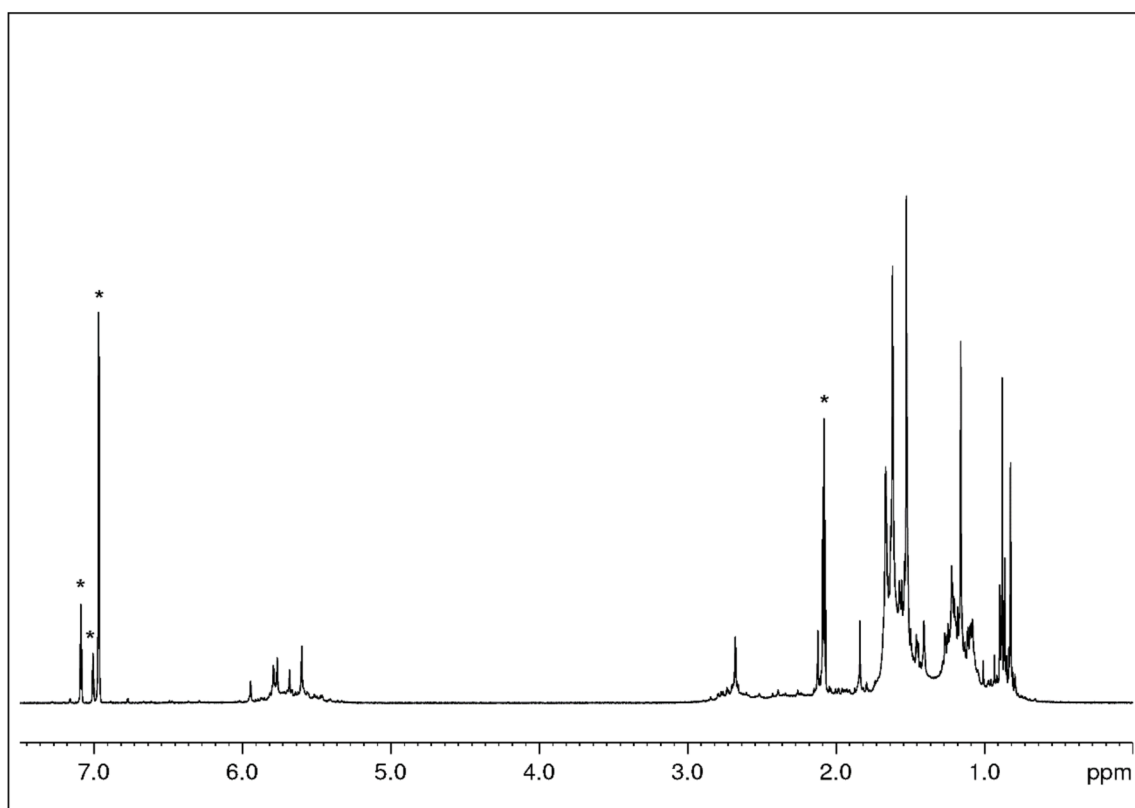


Figure S44. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]$ toluene) of the reaction of $[\text{KMg}(\text{pz}^{\text{tBu,Me}})_3]_2$ (**2**) with CO_2 .

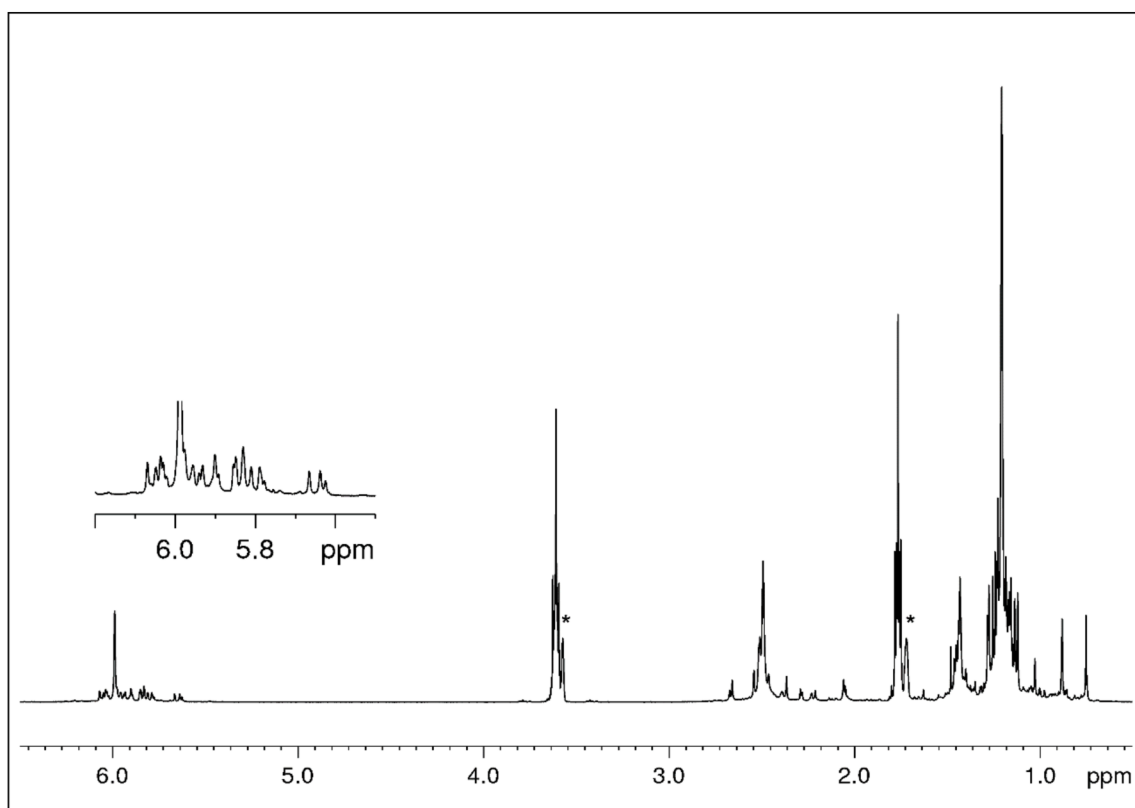


Figure S45. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]$ THF) of the reaction of $[\text{Mg}(\text{pz}^{\text{tBu,Me}})_2(\text{thf})]_2$ (**3**) with CO_2 .

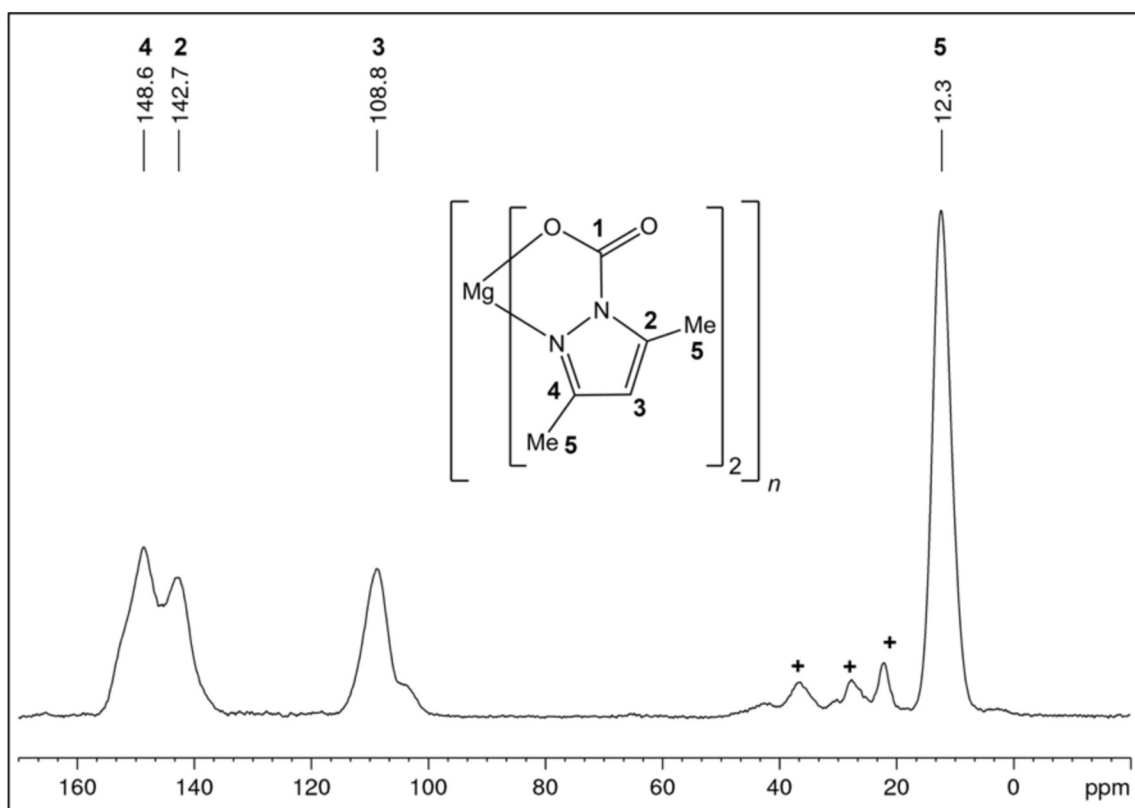


Figure S46. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $[Mg(CO_2 \cdot pz^{Me,Me})_2]_n$ (**7-CO₂**) (+ *n*-hexane).

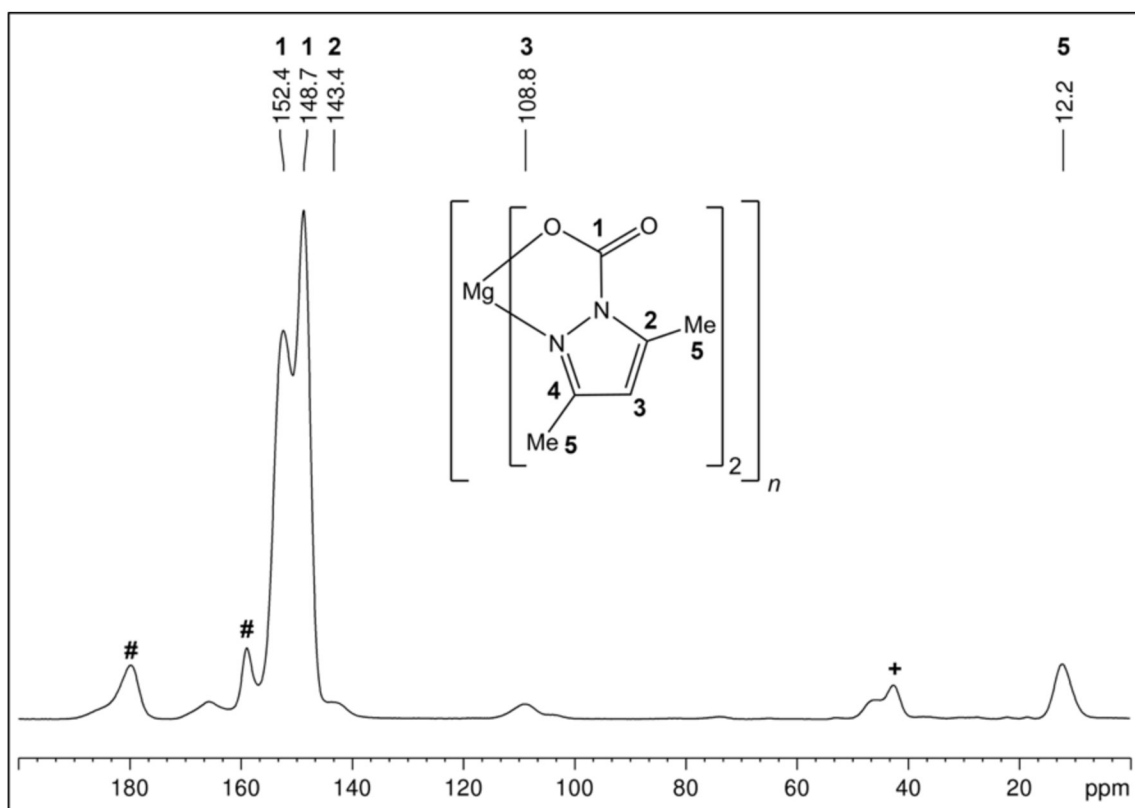


Figure S47. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $[Mg(^{13}CO_2 \cdot pz^{Me,Me})_2]_n$ (**7-CO₂**) (+ rotation side band; # $^{13}CO_2$ unknown side product).

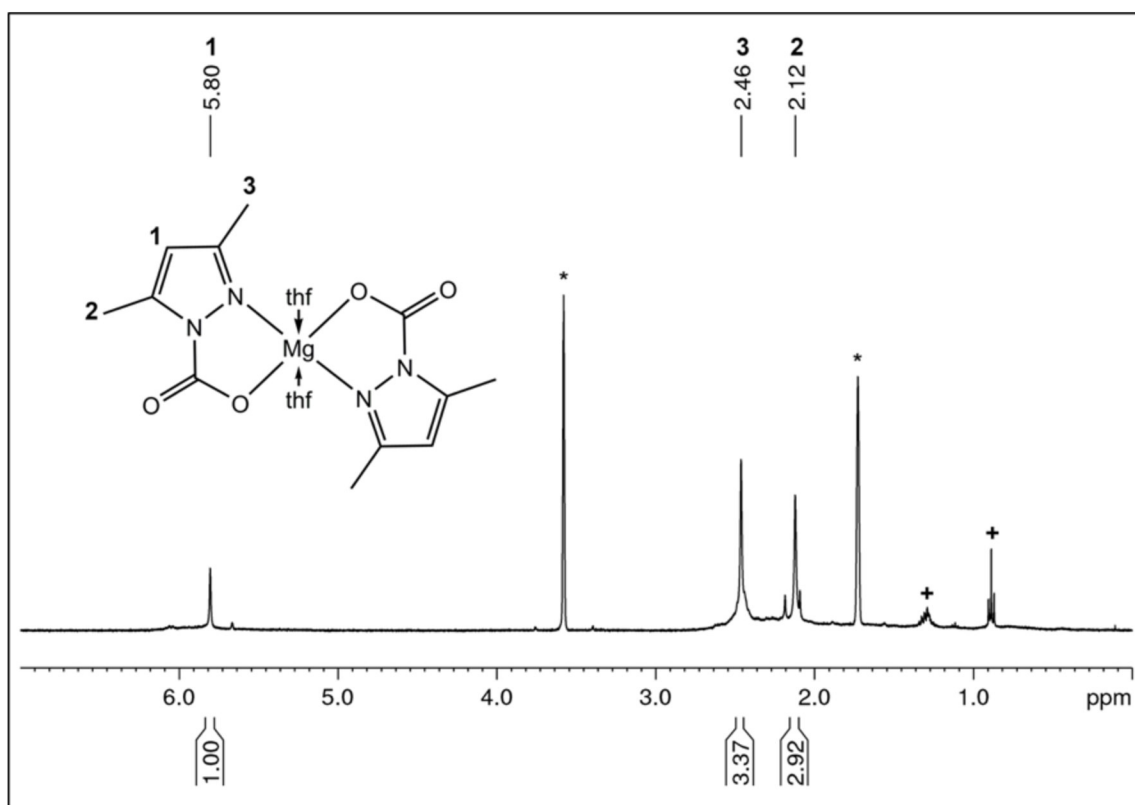


Figure S48. ¹H NMR spectrum (26 °C, 400.11 MHz, [D₈]THF) of [Mg(CO₂·pz^{Me,Me})₂]_n (7-CO₂,thf) (+ *n*-hexane).

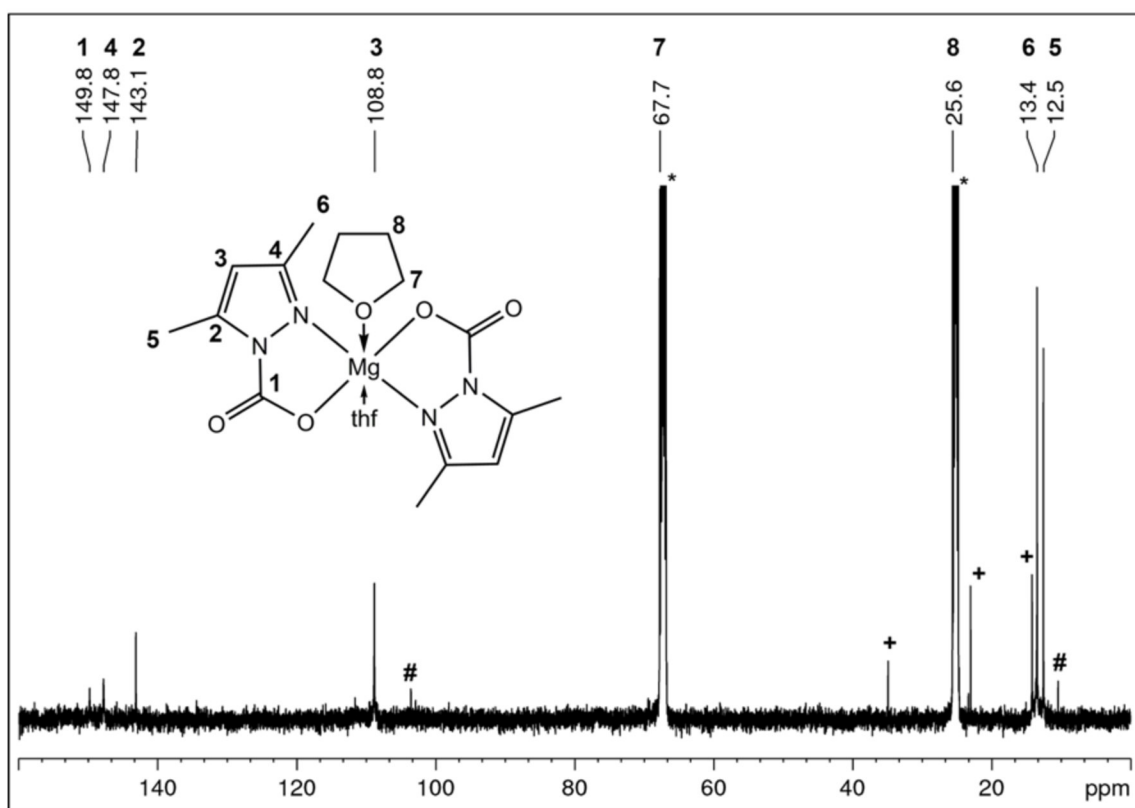


Figure S49. ¹³C NMR spectrum (26 °C, 125.76 MHz, [D₈]THF) of [Mg(CO₂·pz^{Me,Me})₂]_n (7-CO₂,thf) (+ *n*-hexane/# impurities).

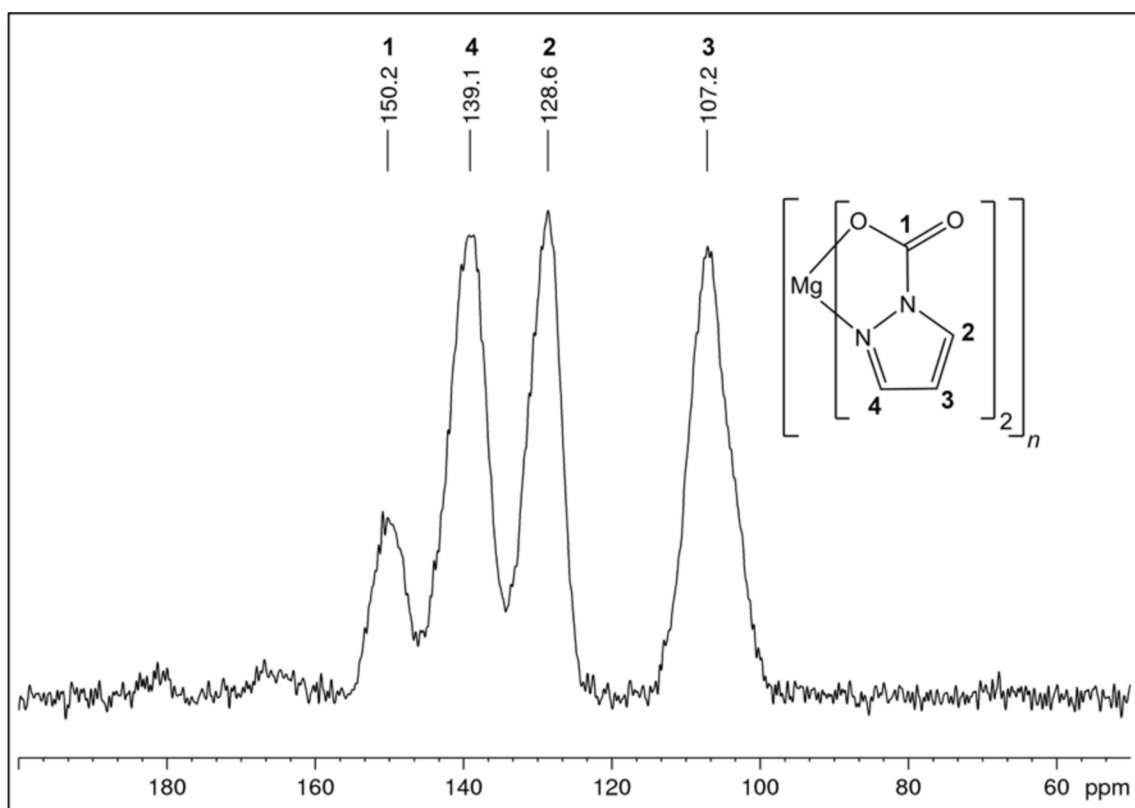


Figure S50. ^{13}C CP/MAS NMR spectrum (75.47 MHz, MAS at 8 kHz) of $[\text{Mg}(\text{CO}_2\cdot\text{pz})_2]_n$ (**8-CO₂**).

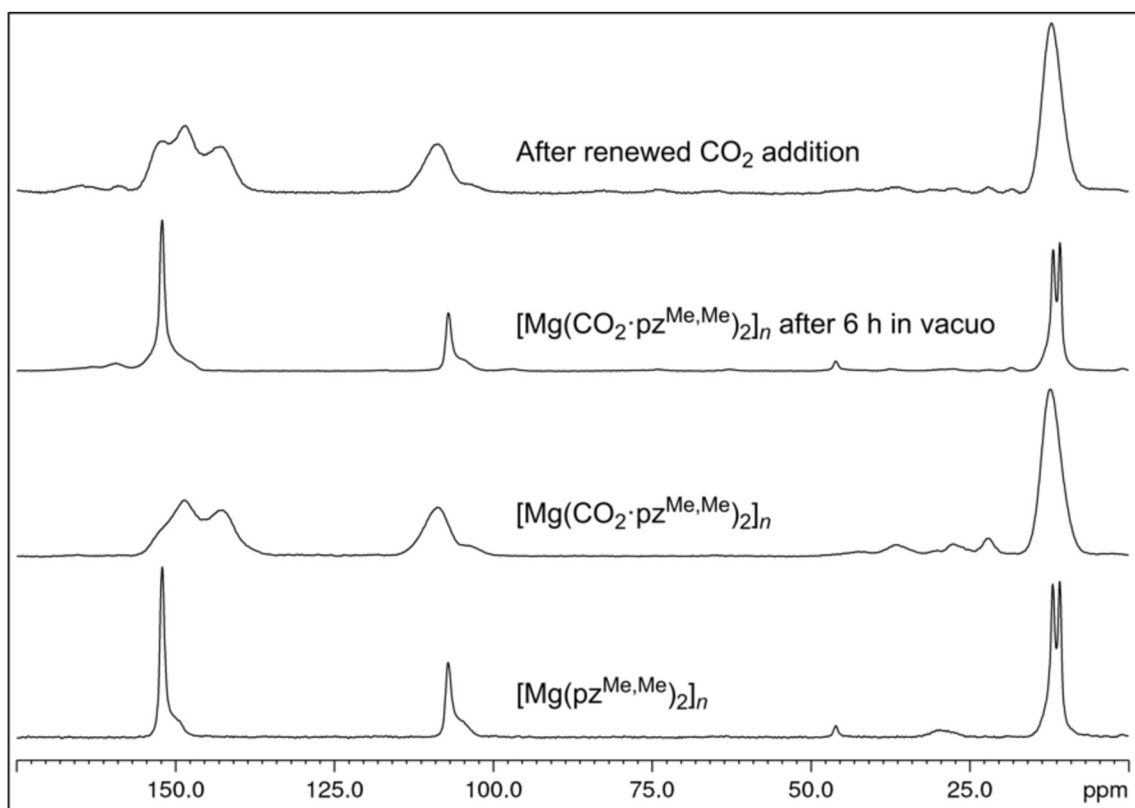


Figure S51. CO_2 insertion and release behavior of $[\text{Mg}(\text{pz}^{\text{Me,Me}})_2]_n$ (**7**) and $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{Me,Me}})_2]_n$ (**7-CO₂**) monitored by ^{13}C CP/MAS NMR spectra (75.47 MHz, MAS at 8 kHz).

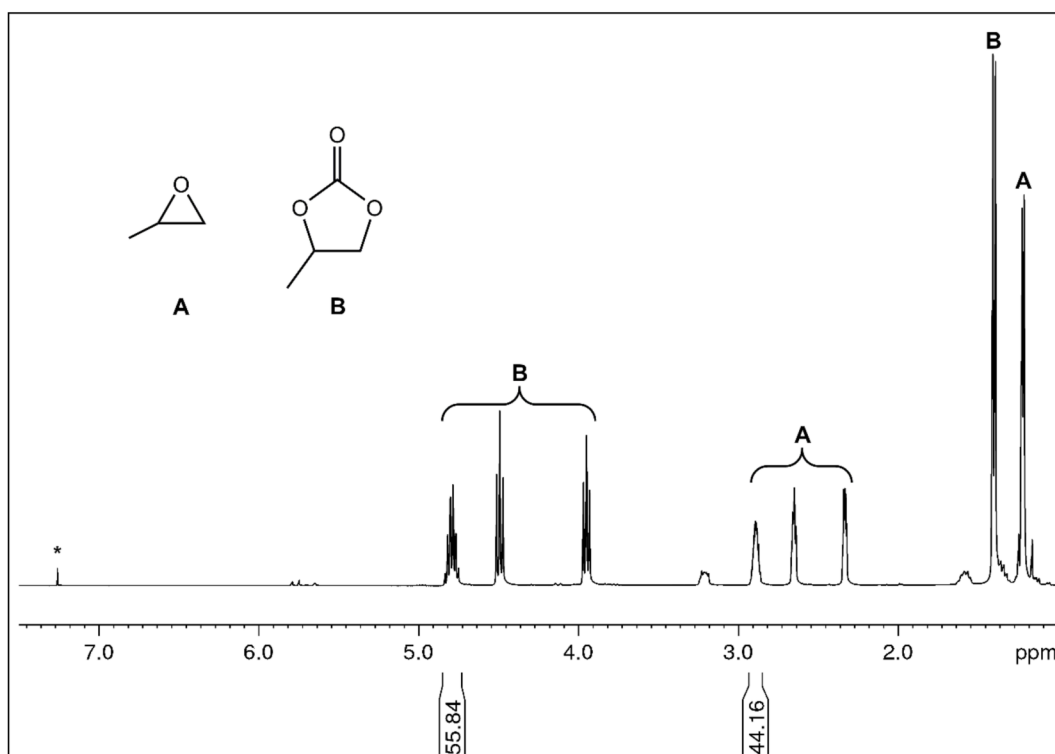


Figure S52. ^1H NMR spectrum (26 °C, 400 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% (in relation to Mg) of $[\text{Mg}(\text{pz}^{\text{tBu},\text{tBu}})_2]_2$ (**1**).

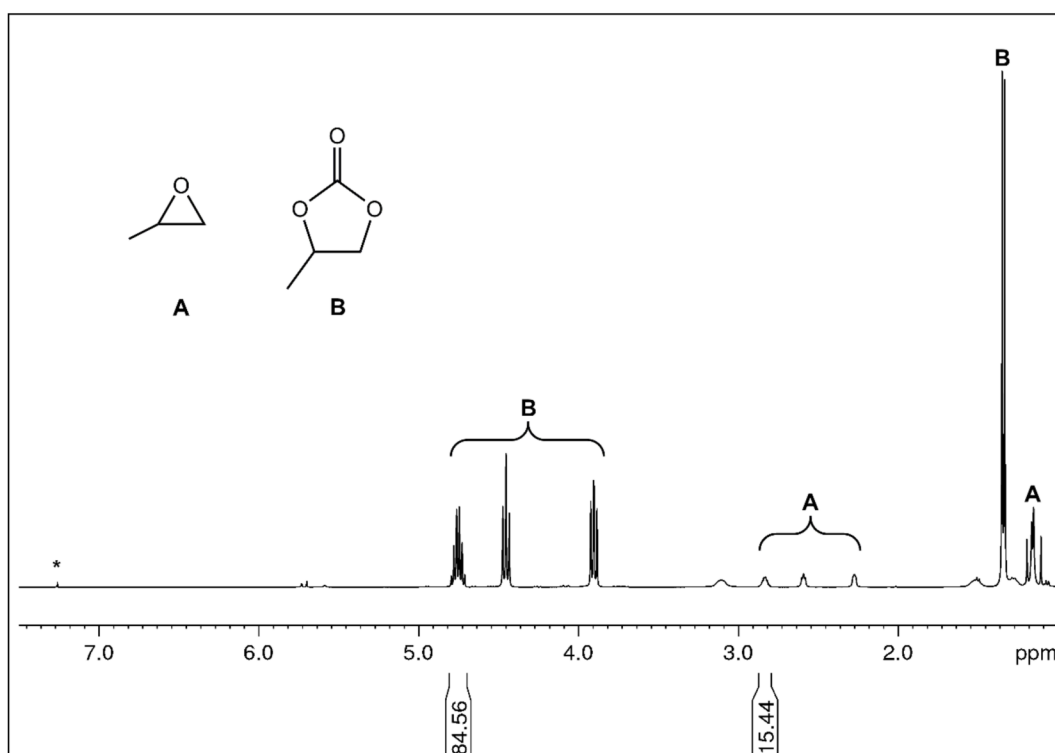


Figure S53. ^1H NMR spectrum (26 °C, 400 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 1 mol% (in relation to Mg) of $[\text{Mg}(\text{pz}^{\text{tBu},\text{tBu}})_2]_2$ (**1**).

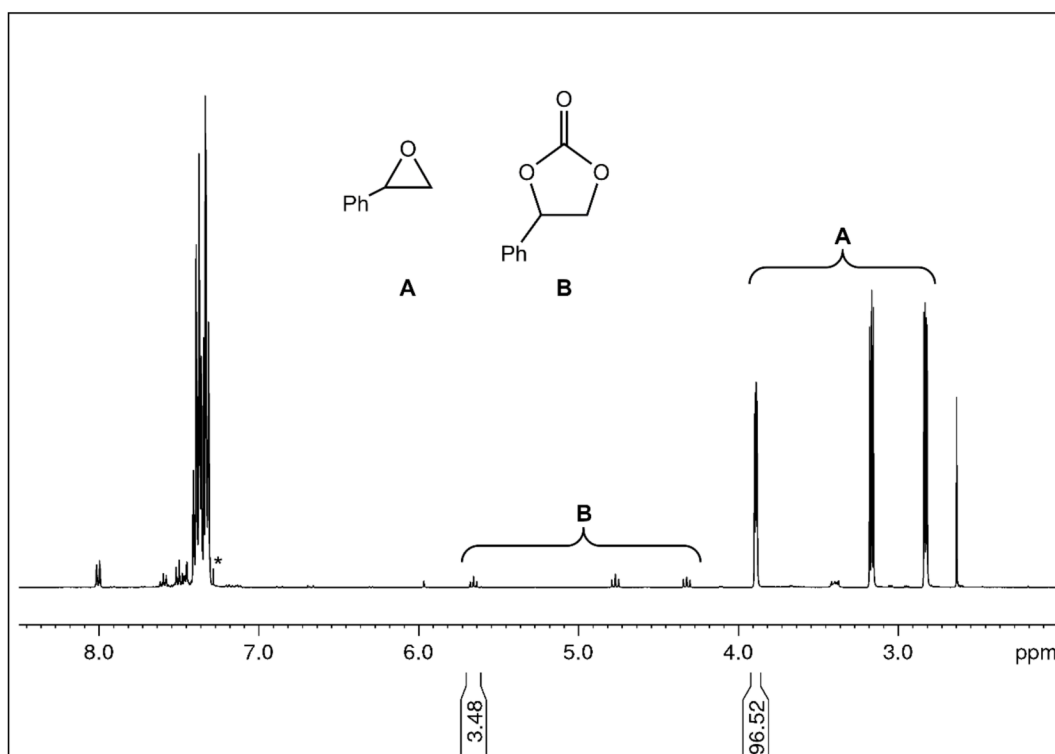


Figure S54. ^1H NMR spectrum (26 °C, 400 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of styrene oxide and CO_2 to styrene carbonate by using 0.5 mol% (in relation to Mg) of $[\text{Mg}(\text{pz}^{\text{tBu},\text{tBu}})_2]_2$ (**1**).

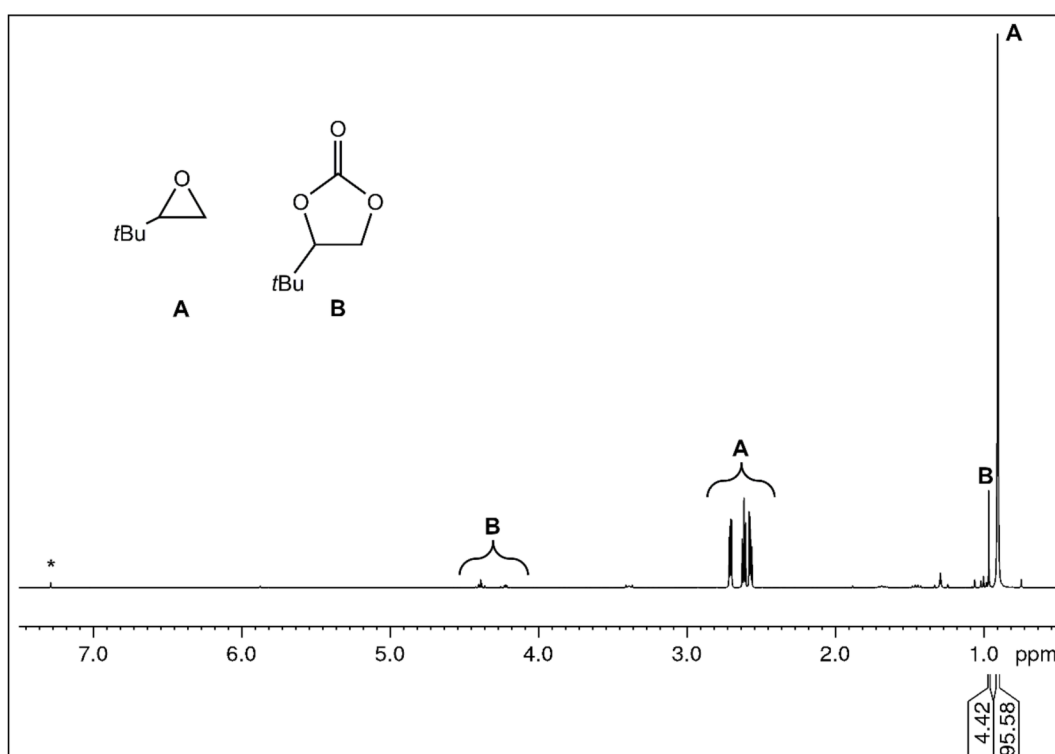


Figure S55. ^1H NMR spectrum (26 °C, 400 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of 2-*tert*-butyl oxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% (in relation to Mg) of $[\text{Mg}(\text{pz}^{\text{tBu},\text{tBu}})_2]_2$ (**1**).

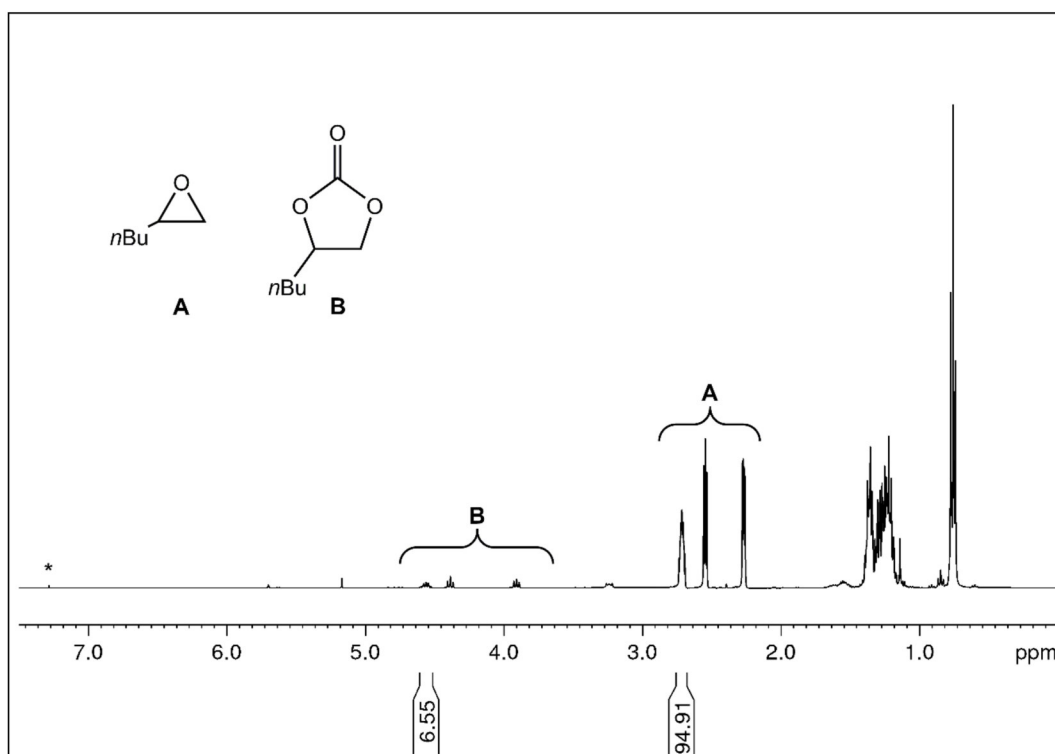


Figure S56. ^1H NMR spectrum (26 °C, 400 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO_2 to 1,2- n -hexylene carbonate by using 0.5 mol% (in relation to Mg) of $[\text{Mg}(\text{pz}^{t\text{Bu},t\text{Bu}})_2]_2$ (**1**).

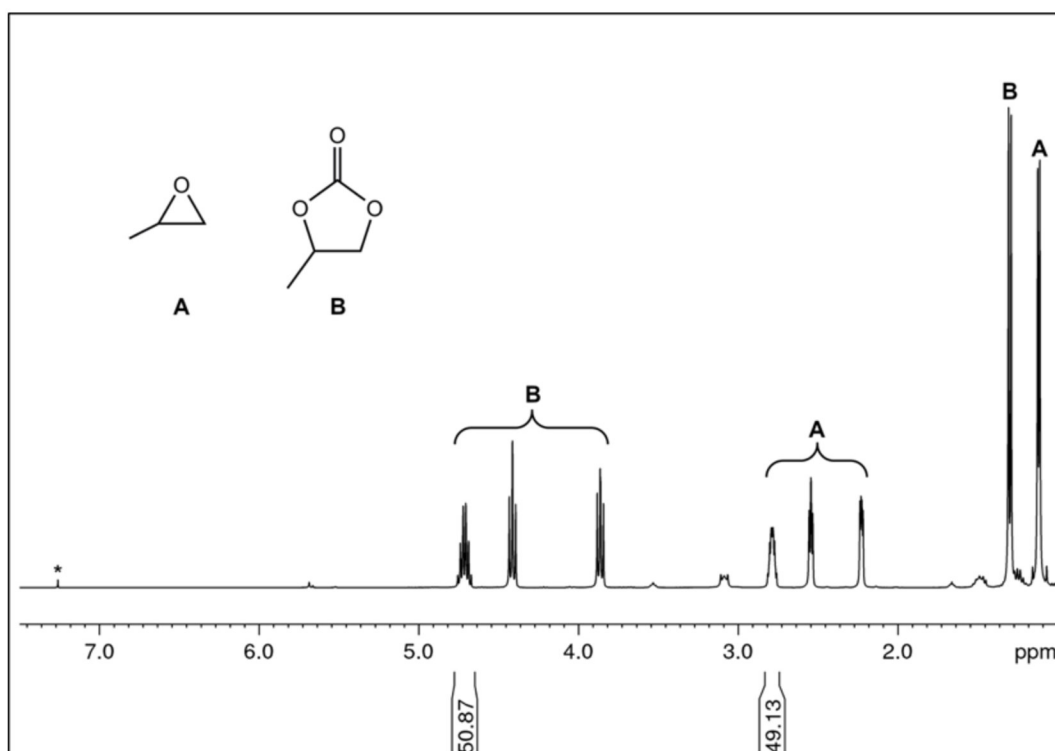


Figure S57. ^1H NMR spectrum (26 °C, 400 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% (in relation to Mg) of $[\text{Mg}(\text{pz}^{t\text{Bu},t\text{Bu}})_2(\text{thf})]_2$ (**1-thf**).

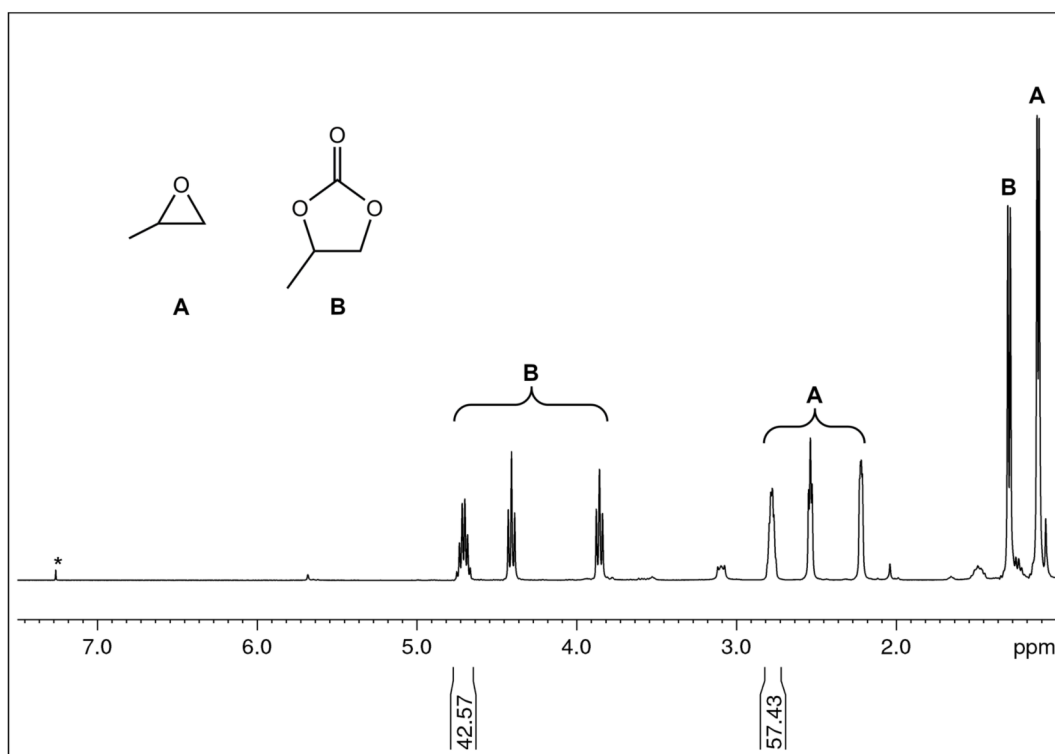


Figure S58. ¹H NMR spectrum (26 °C, 400 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.5 mol% (in relation to Mg) of [Mg(pz^{tBu,Me})₂(thf)]₂ (**3-thf**).

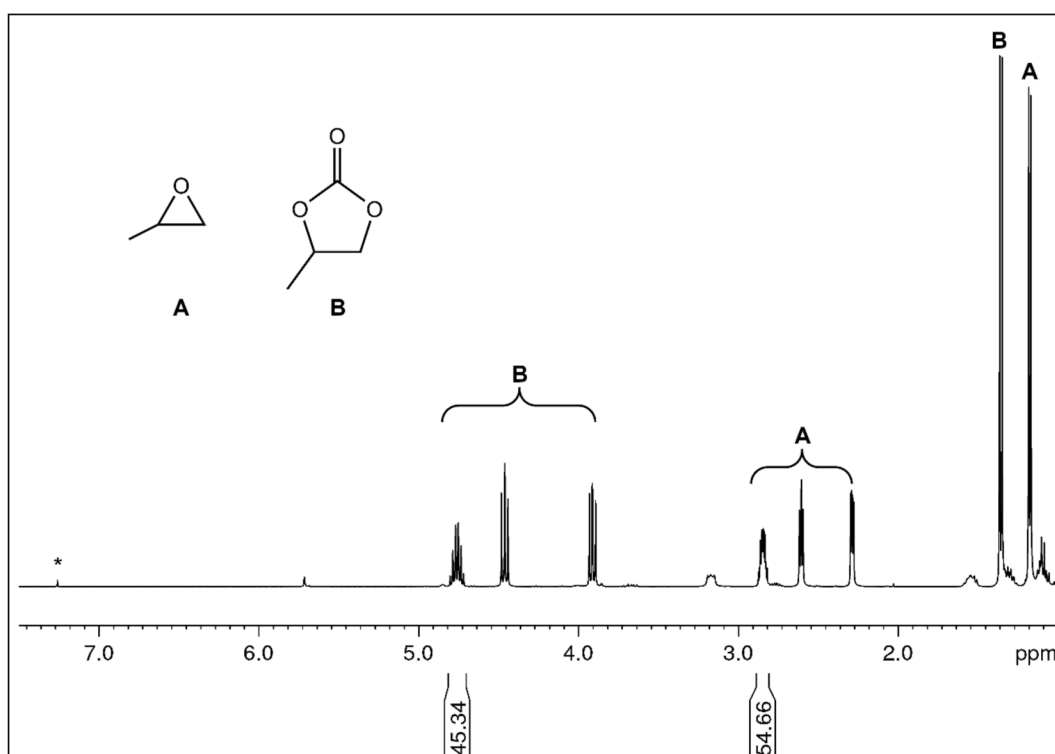


Figure S59. ¹H NMR spectrum (26 °C, 400 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.5 mol% (in relation to Mg) of [Mg₃(pz^{iPr,iPr})₆(Hpz^{iPr,iPr})₂] (**4a-Hpz**).

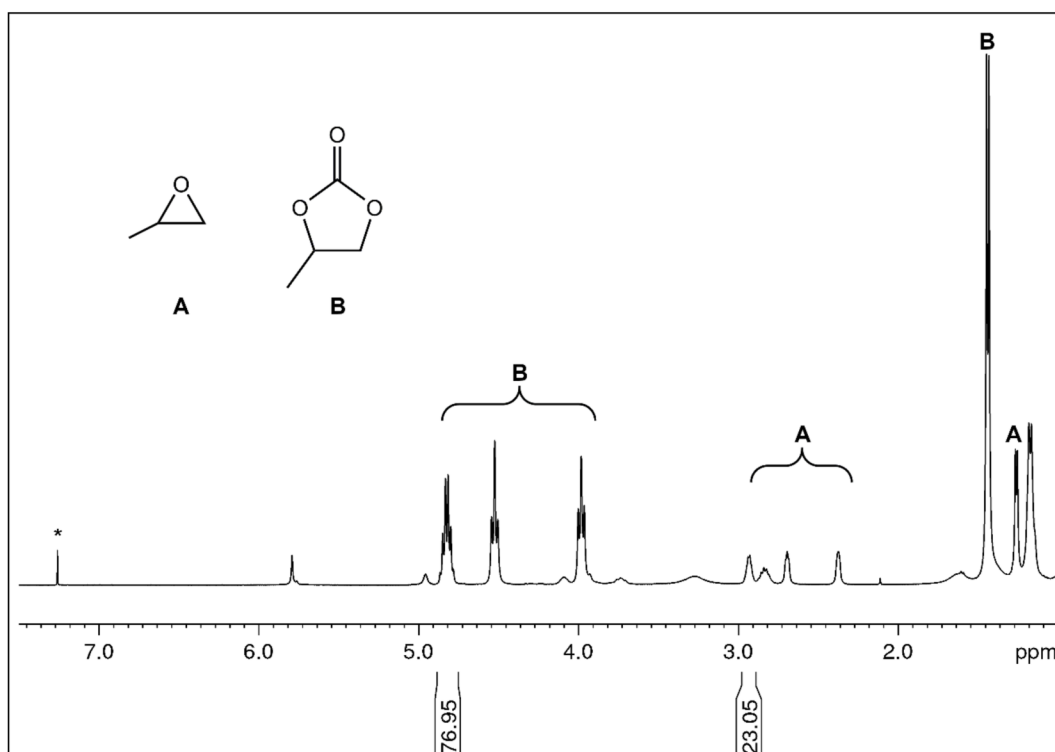


Figure S60. ¹H NMR spectrum (26 °C, 400 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 1 mol% (in relation to Mg) of [Mg₃(pz^{*i*Pr,*i*Pr})₆(Hpz^{*i*Pr,*i*Pr})₂] (**4a**-Hpz).

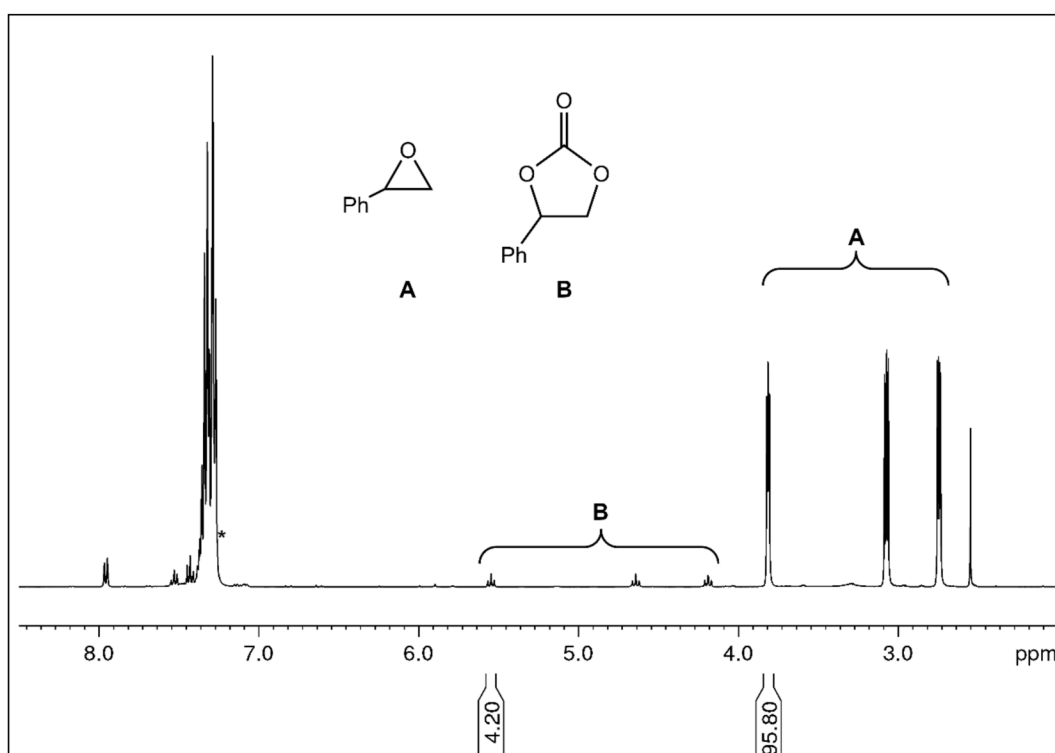


Figure S61. ¹H NMR spectrum (26 °C, 400 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of styrene oxide and CO₂ to styrene carbonate by using 0.5 mol% (in relation to Mg) of [Mg₃(pz^{*i*Pr,*i*Pr})₆(Hpz^{*i*Pr,*i*Pr})₂] (**4a**-Hpz).

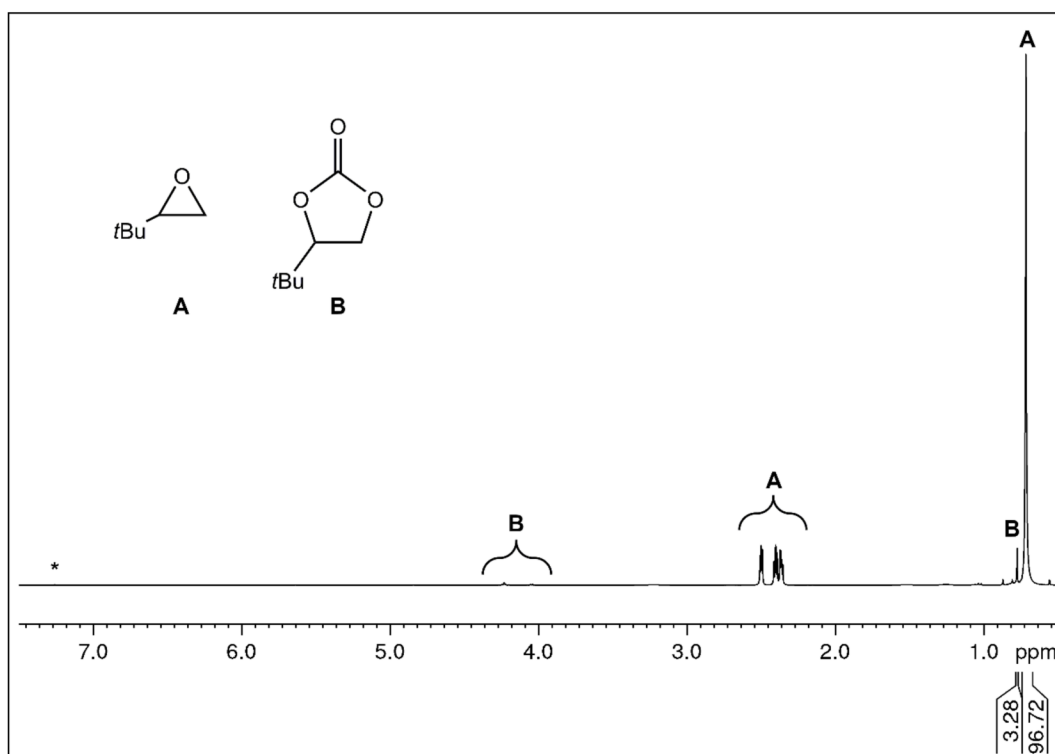


Figure S62. ^1H NMR spectrum (26 °C, 400 MHz, CDCl_3) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% (in relation to Mg) of $[\text{Mg}_3(\text{pz}^{\text{iPr}}, \text{iPr})_6(\text{Hpz}^{\text{iPr}}, \text{iPr})_2]$ (**4a-Hpz**).

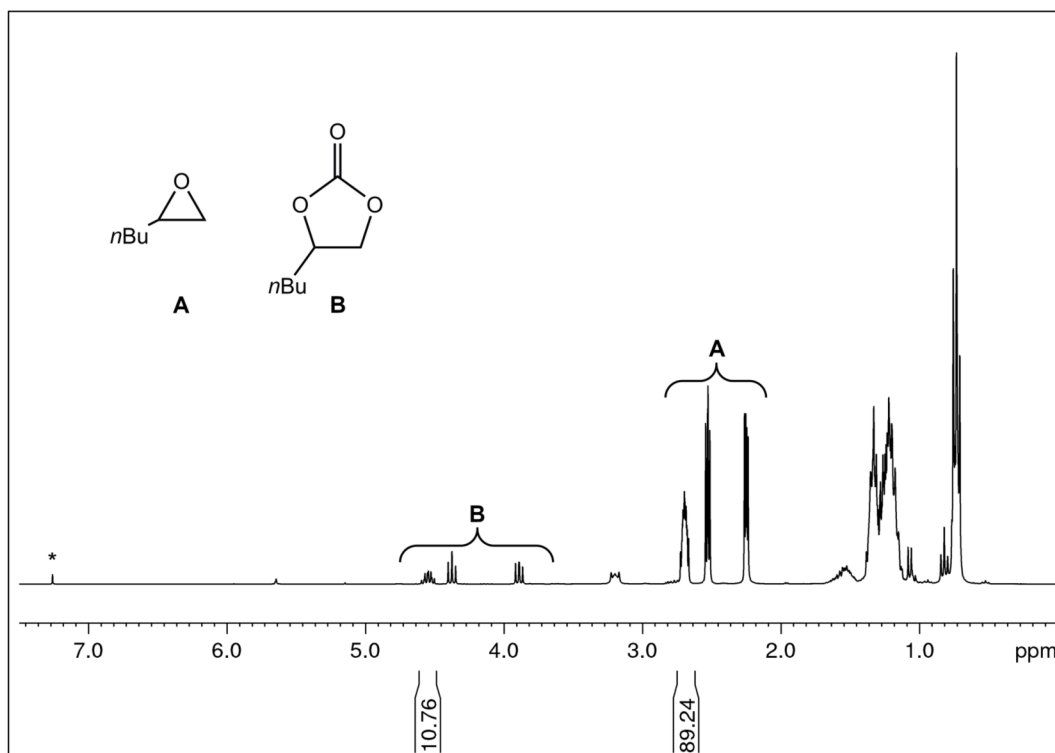


Figure S63. ^1H NMR spectrum (26 °C, 400 MHz, CDCl_3) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO_2 to 1,2-*n*-hexylene carbonate by using 0.5 mol% (in relation to Mg) of $[\text{Mg}_3(\text{pz}^{\text{iPr}}, \text{iPr})_6(\text{Hpz}^{\text{iPr}}, \text{iPr})_2]$ (**4a-Hpz**).

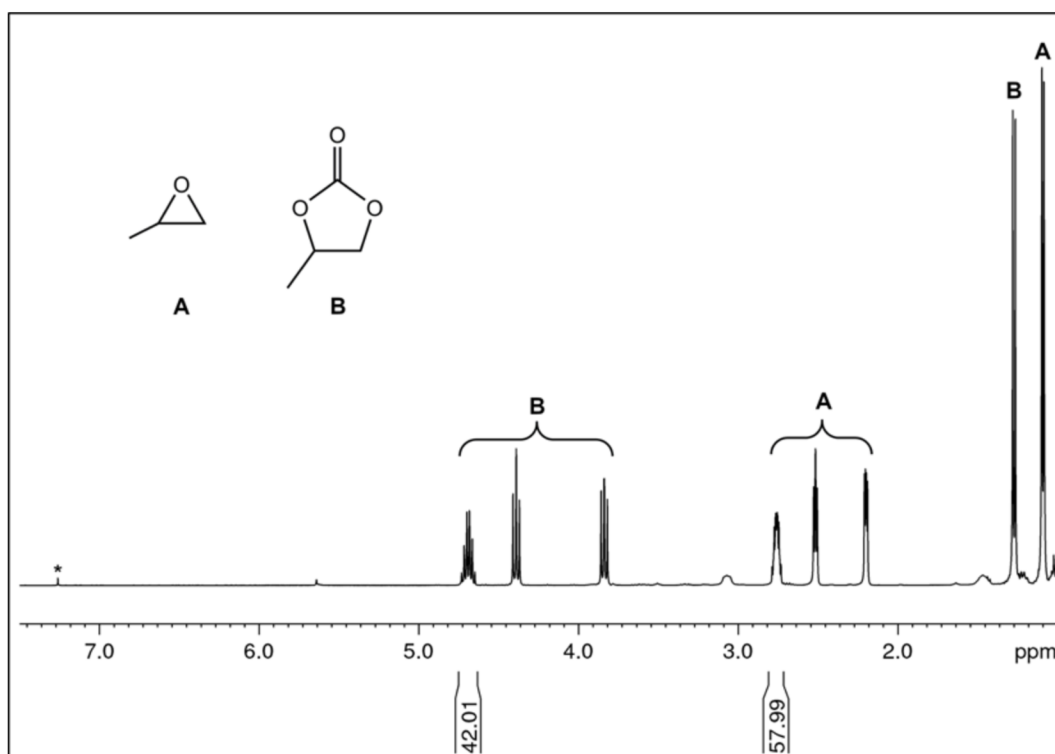


Figure S64. ^1H NMR spectrum (26 °C, 400 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% (in relation to Mg) of $[\text{Mg}_3(\text{pz}^{\text{iPr,iPr}})_6(\text{thf})_2]$ (**4-thf**).

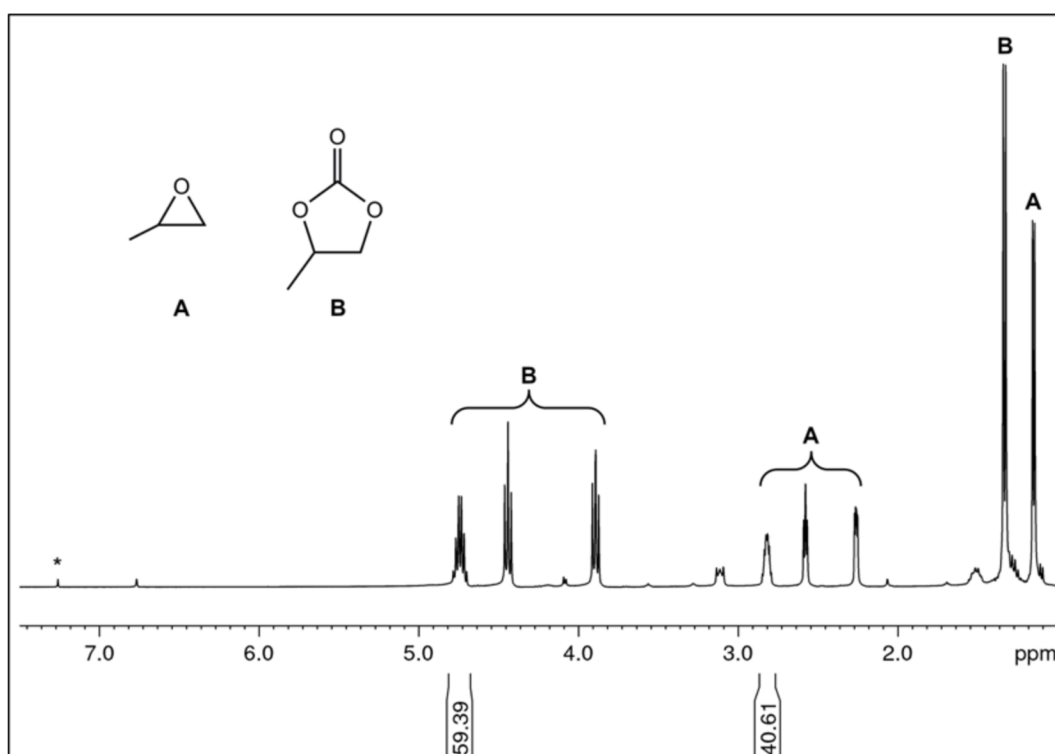


Figure S65. ^1H NMR spectrum (26 °C, 400 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% (in relation to Mg) of $[\text{Mg}_2(\text{pz}^{\text{CF}_3,\text{CF}_3})_4(\text{thf})_3]$ (**6-thf**).

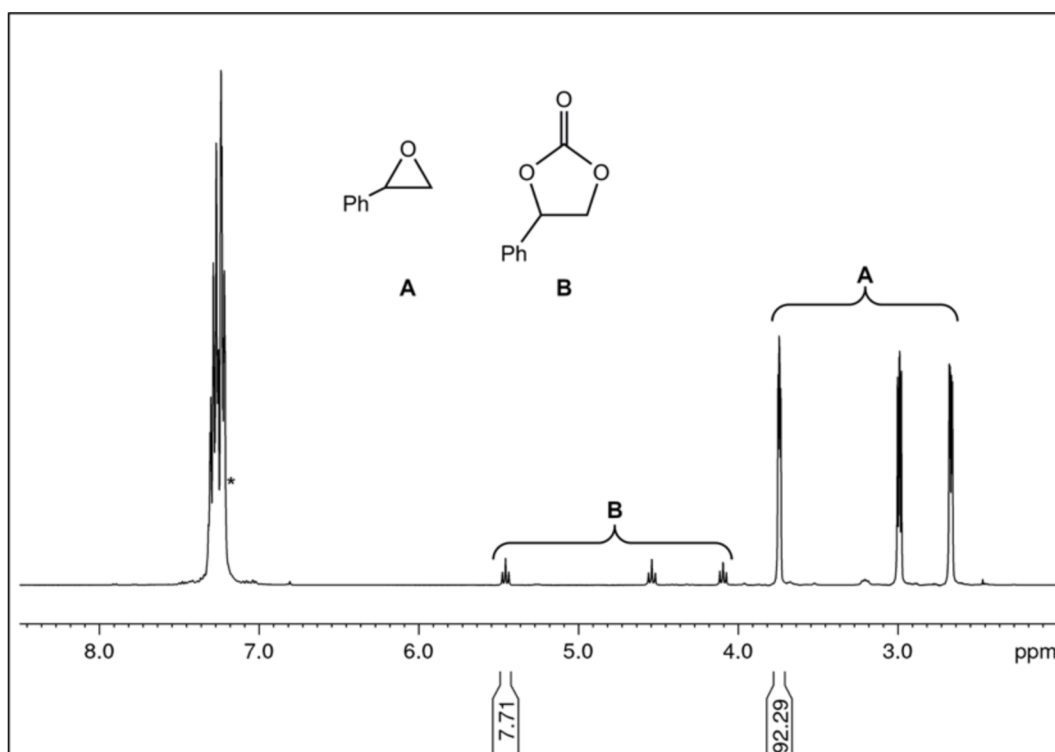


Figure S66. ¹H NMR spectrum (26 °C, 400 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of styrene oxide and CO₂ to styrene carbonate by using 0.5 mol% (in relation to Mg) of [Mg₂(pz^{CF₃,CF₃})₄(thf)₃] (**6-thf**).

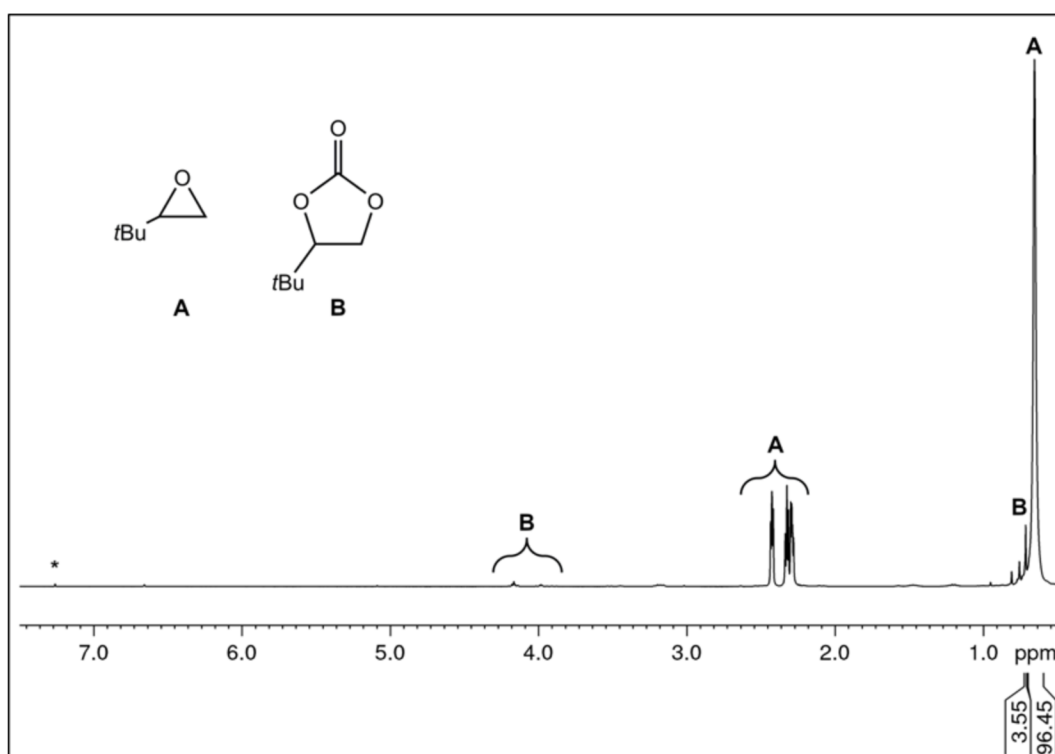


Figure S67. ¹H NMR spectrum (26 °C, 400 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO₂ to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% (in relation to Mg) of [Mg₂(pz^{CF₃,CF₃})₄(thf)₃] (**6-thf**).

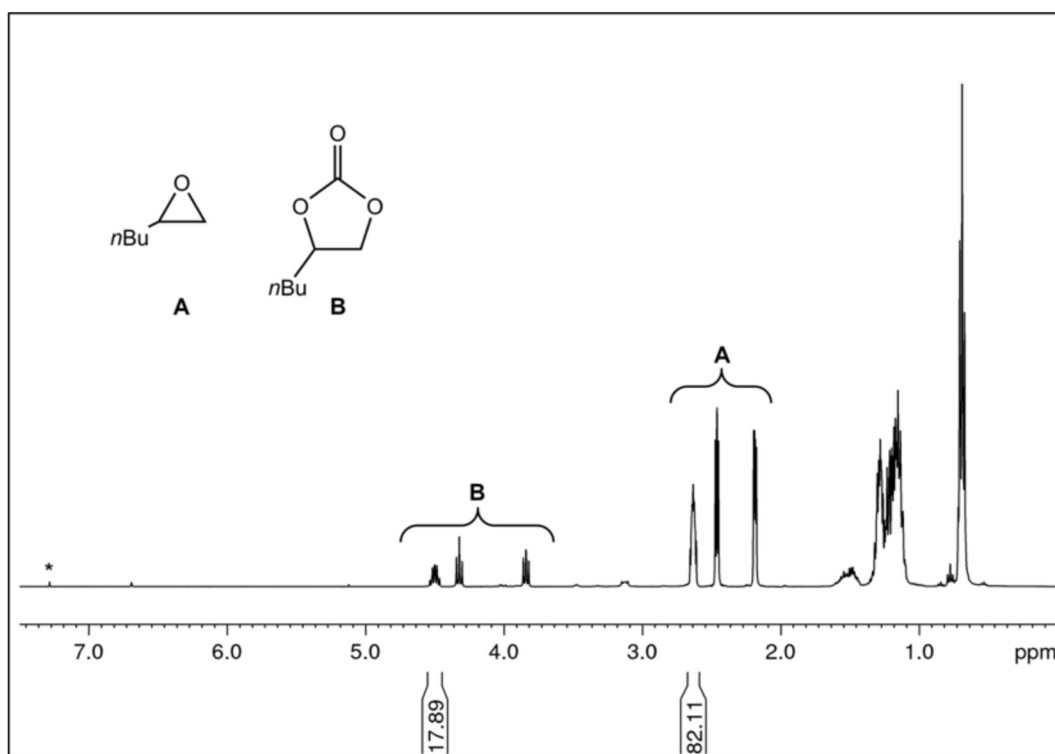


Figure S68. ¹H NMR spectrum (26 °C, 400 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO₂ to 1,2-*n*-hexylene carbonate by using 0.5 mol% (in relation to Mg) of [Mg₂(pz^{CF₃,CF₃})₄(thf)₃] (**6-thf**).

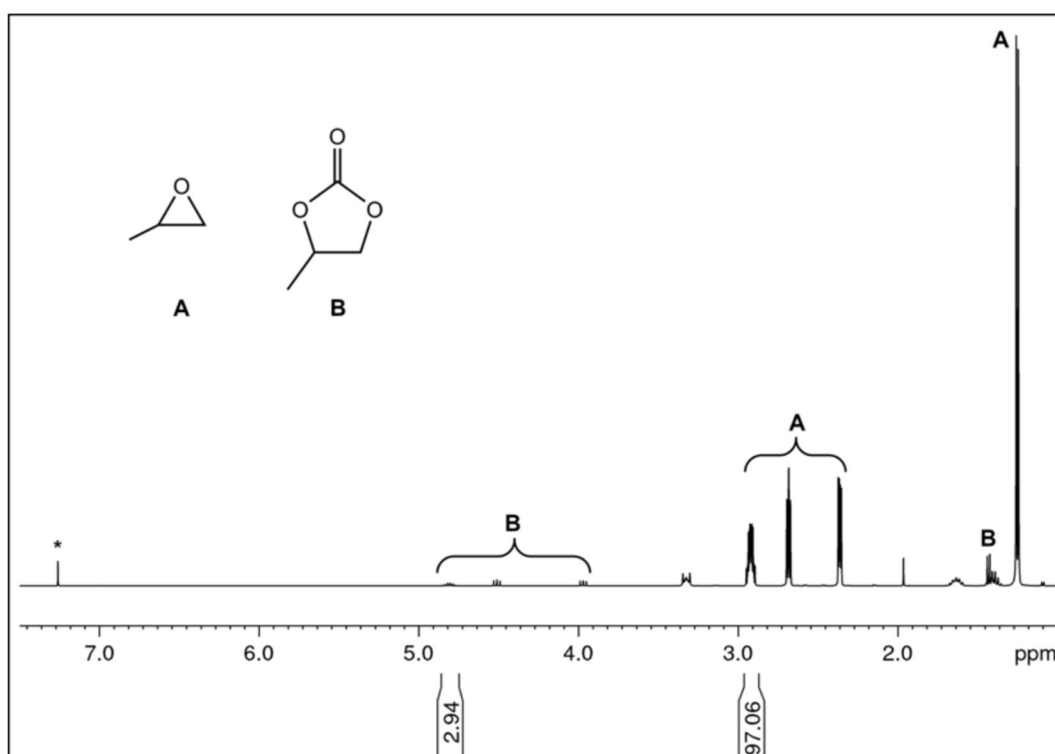


Figure S69. ¹H NMR spectrum (26 °C, 400 MHz, chloroform-*d*) of the reaction mixture of the conversion of propylene oxide and CO₂ to propylene carbonate in the absence of magnesium pyrazlate, by using only 1 mol% TBAB as catalyst.

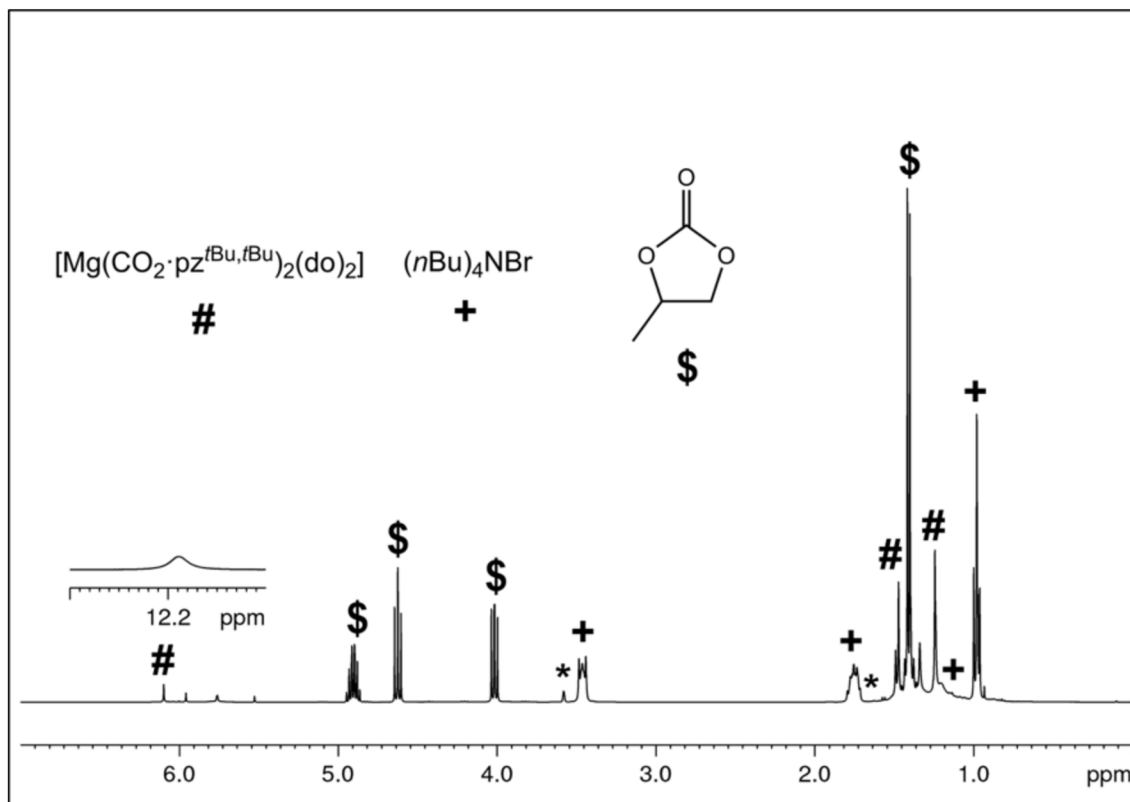
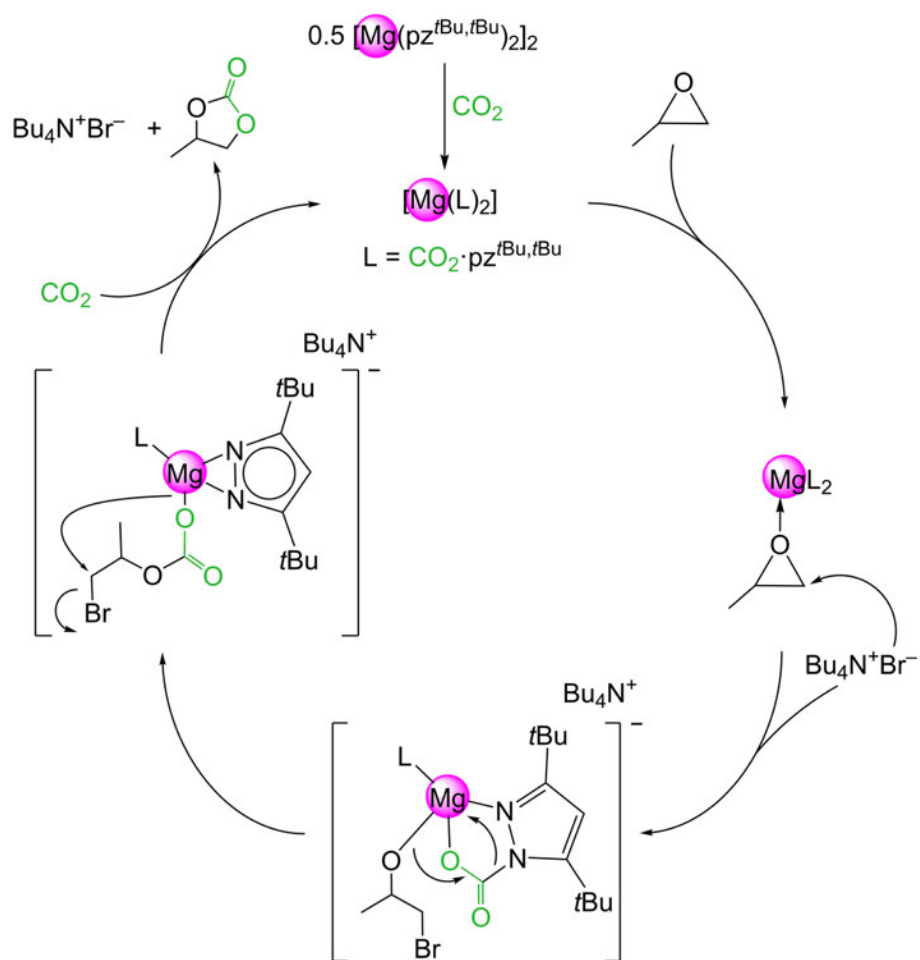


Figure S70. ^1H NMR spectrum (26 °C, 400 MHz, $[\text{D}_8]\text{THF}$) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 10 mol% (in relation to Mg) of $[\text{Mg}(\text{pz}^{\text{tBu,tBu}})_2]$ (**1**). Visible products are $[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (#), propylene carbonate (\$), and TBAB (+).



Scheme S2. Proposed mechanism for the catalytic conversion of propylene oxide to propylene carbonate with **1** as an exemplary catalyst.

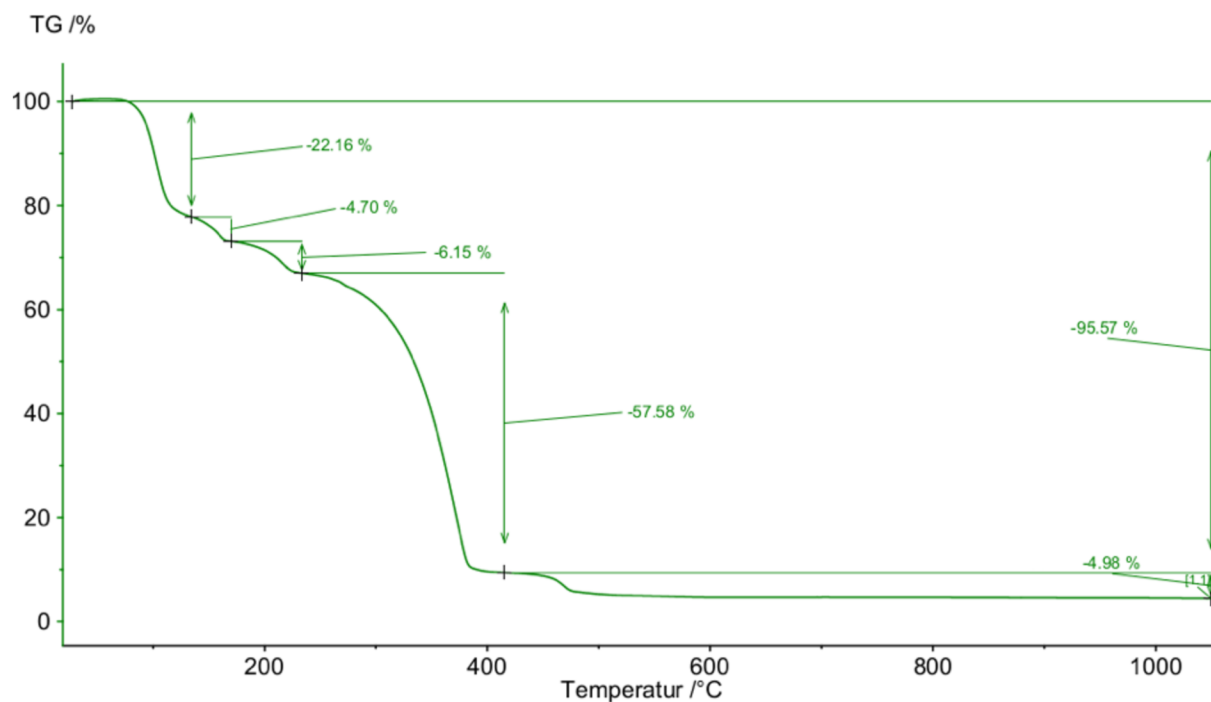


Figure S71. TGA of $[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (1-CO₂,thf). Sample was heated from 28 °C to 1000 °C with a heating ratio of 1 Kmin⁻¹ under constant Ar flow.

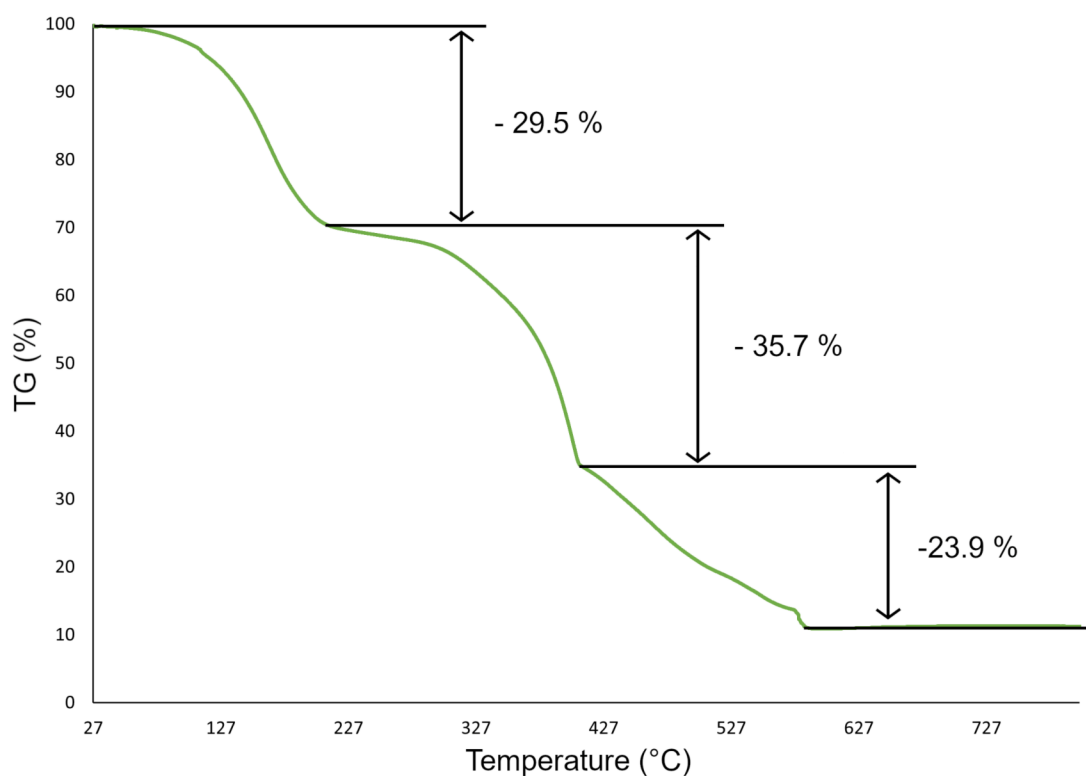


Figure S72. TGA of $[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{Me,Me}})_2]$ (7-CO₂). Sample was heated from 28 °C to 1000 °C with a heating ratio of 1 Kmin⁻¹ under constant Ar flow.

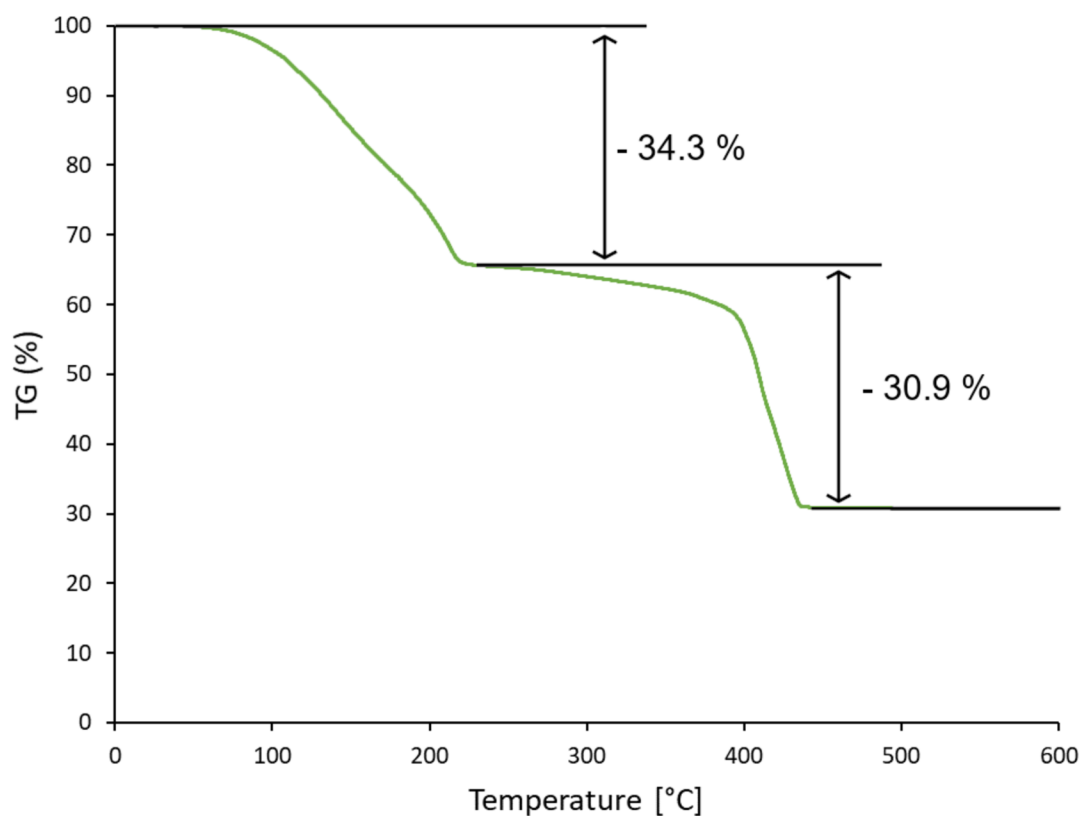


Figure S73. TGA of $[\text{Mg}(\text{CO}_2 \cdot \text{pz})_2]_n$ (8- CO_2). Sample was heated from 28 °C to 1000 °C with a heating ratio of 1 Kmin^{-1} under constant Ar flow.

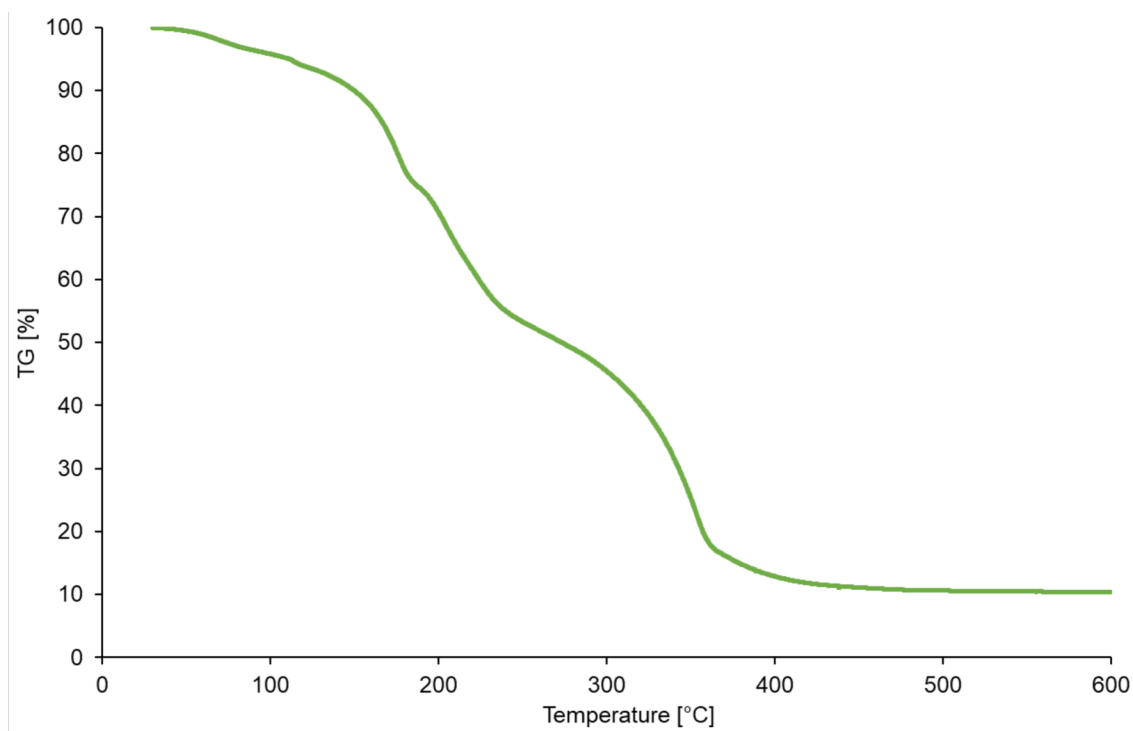


Figure S74. TGA of $[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{tBu,tBu}})_2]_4$ (1- CO_2). Sample was heated from 28 °C to 1000 °C with a heating ratio of 1 Kmin^{-1} under constant Ar flow.

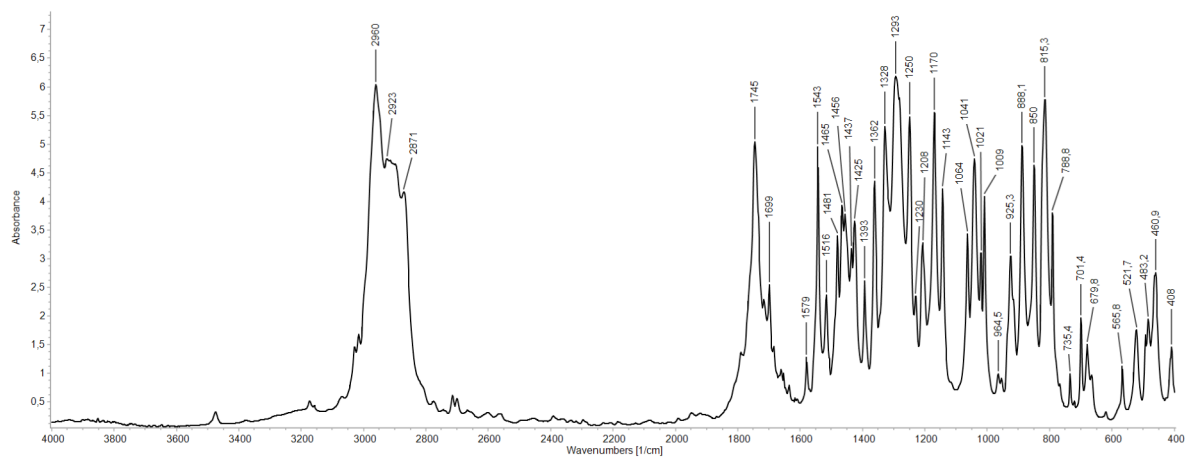


Figure S75. DRIFT spectrum of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{tBu,tBu}})_2(\text{thf})_2]$ (**1-CO₂,thf**) at 25 °C.

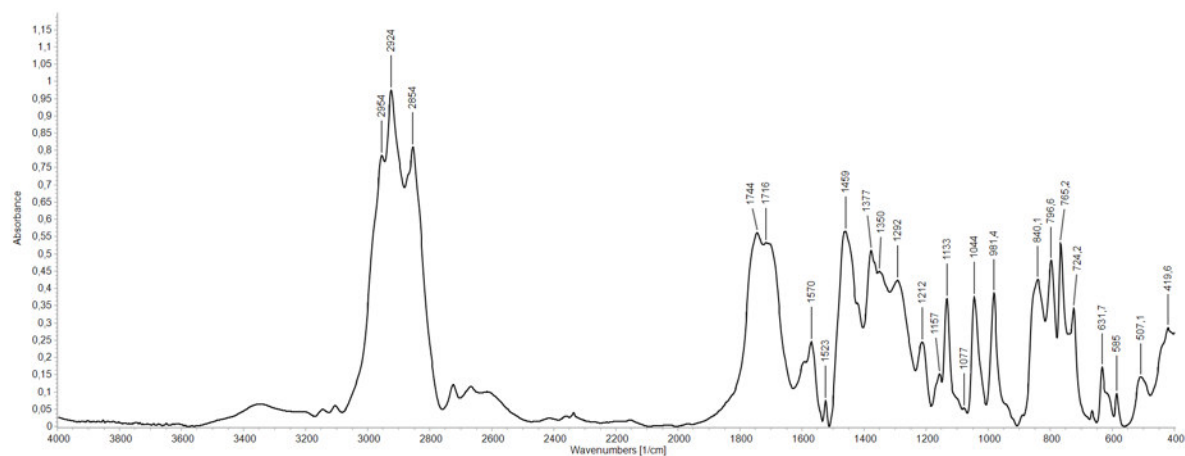


Figure S76. IR (Nujol) spectrum of $[\text{Mg}(\text{CO}_2\cdot\text{pz}^{\text{Me,Me}})_2]_n$ (**7-CO₂**) at 25 °C.

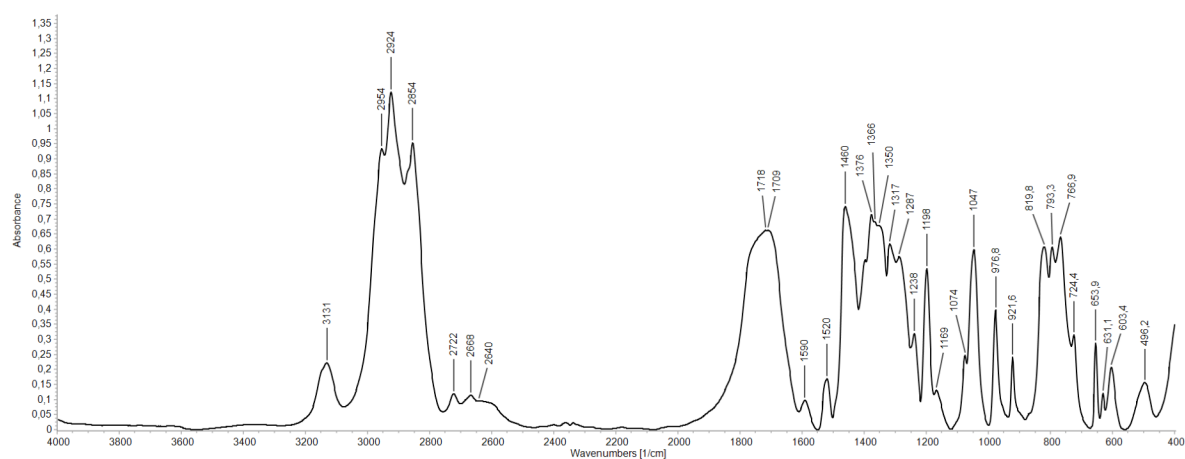


Figure S77. IR (Nujol) spectrum of $[\text{Mg}(\text{CO}_2\cdot\text{pz})_2]_n$ (**8-CO₂**) at 25 °C.

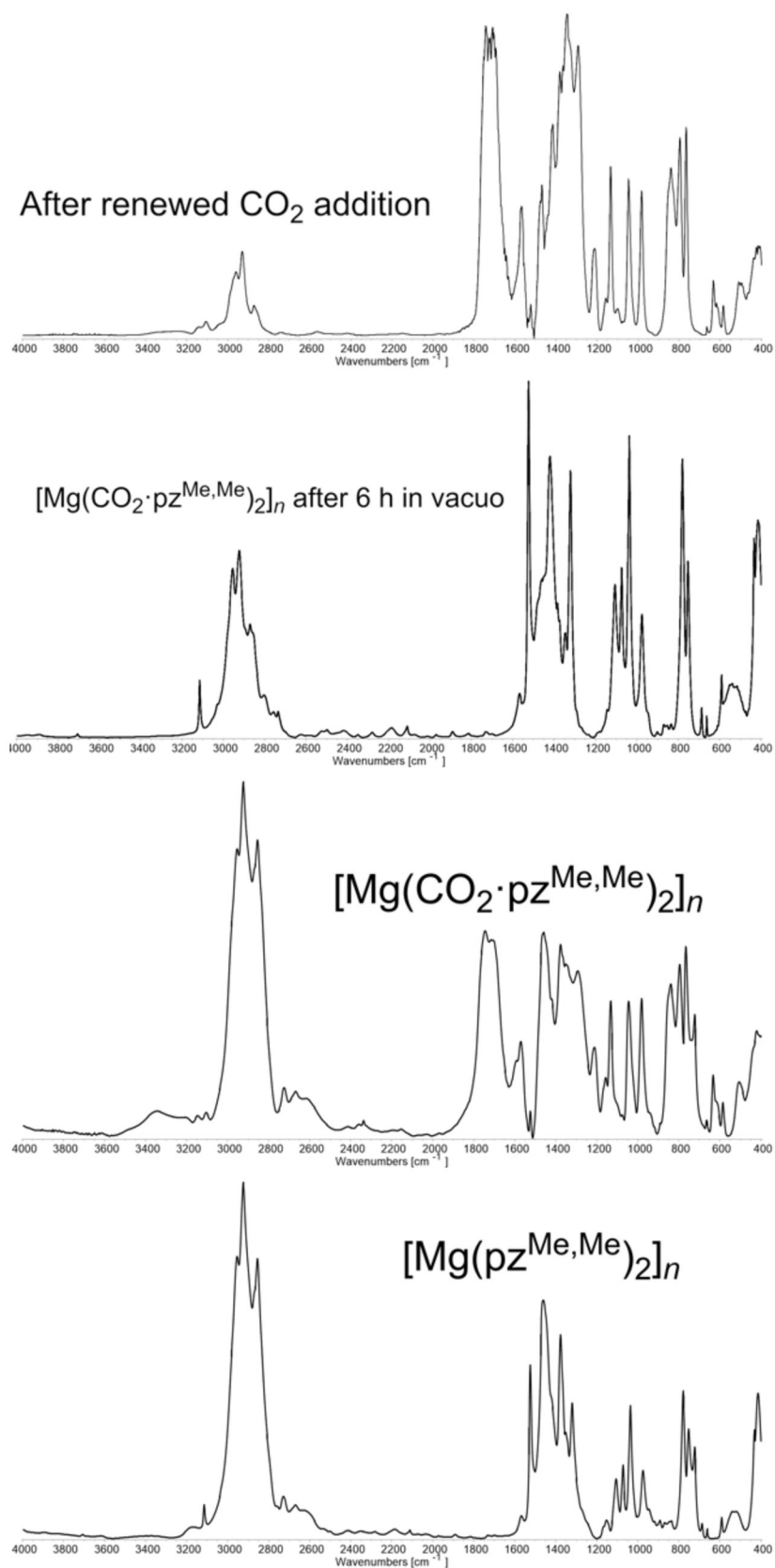


Figure S78. CO₂ insertion and release behavior of $[\text{Mg}(\text{pz}^{\text{Me,Me}})_2]_n$ (**7**) and $[\text{Mg}(\text{CO}_2 \cdot \text{pz}^{\text{Me,Me}})_2]_n$ (**7-CO₂**) monitored by IR spectra (Nujol bottom two, DRIFT top two).

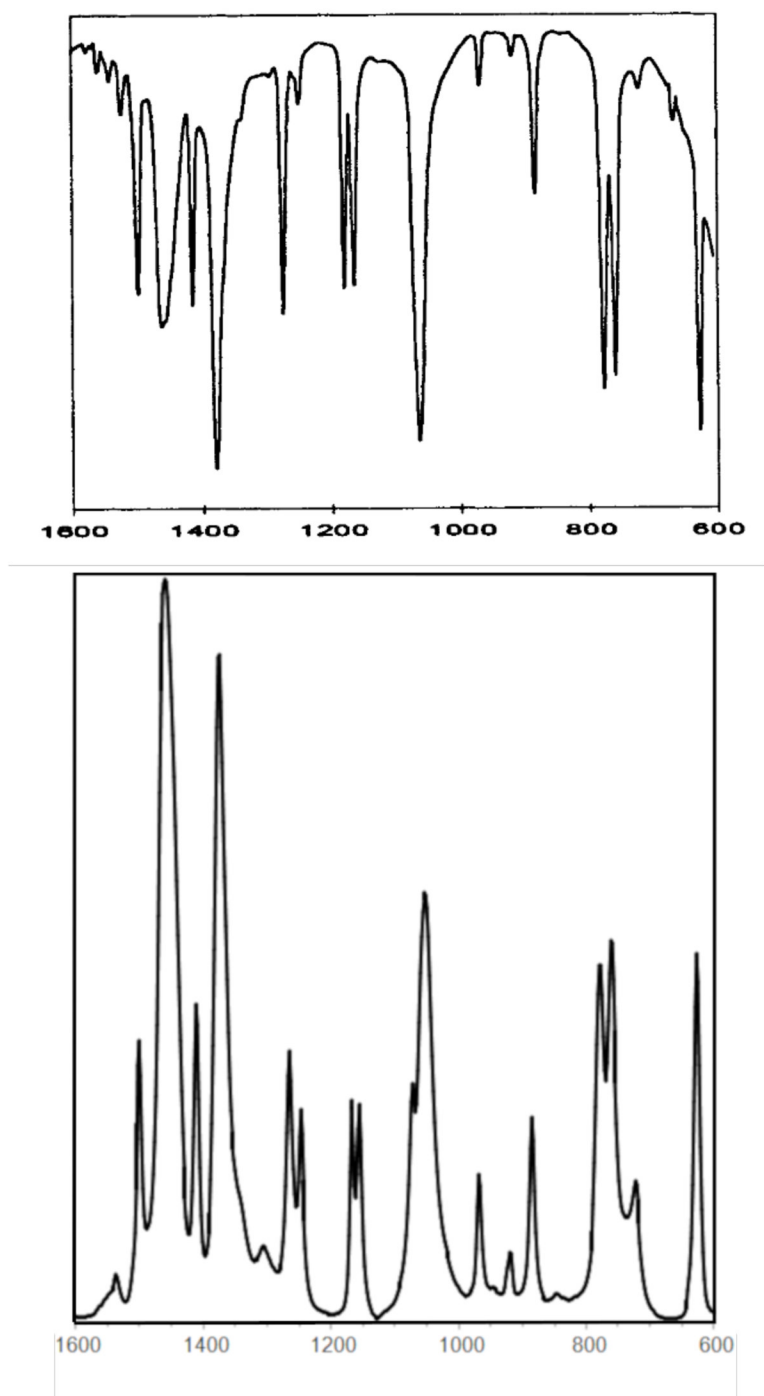


Figure S79. Comparison of the DRITF spectra of $[\text{Mg}(\text{pz})_2]_n$ (**8**, bottom) and $[\text{Zn}(\text{pz})_2]_n$ (top).^[12]

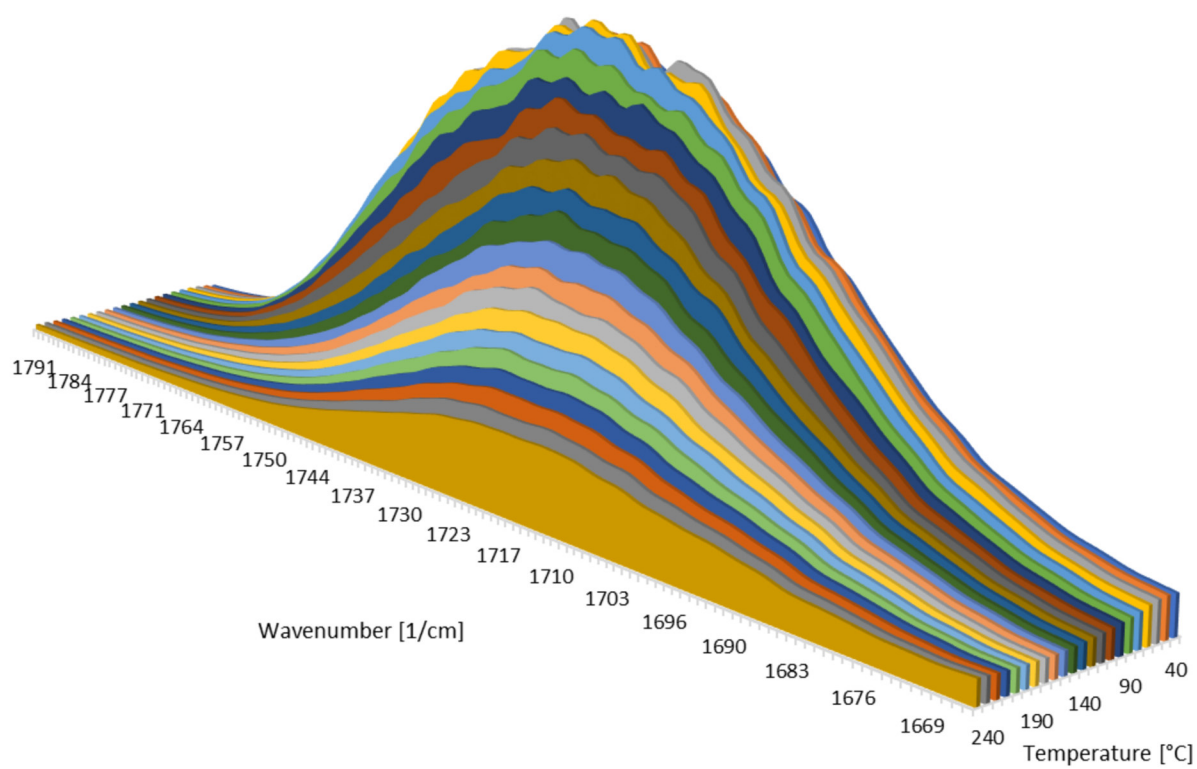


Figure S80. In situ VT DRIFT spectra of $[\text{Mg}(\text{CO}_2\cdot\text{pz})_2]_n$ (**8-CO₂**) after the atmosphere was changed from CO₂ to Ar.

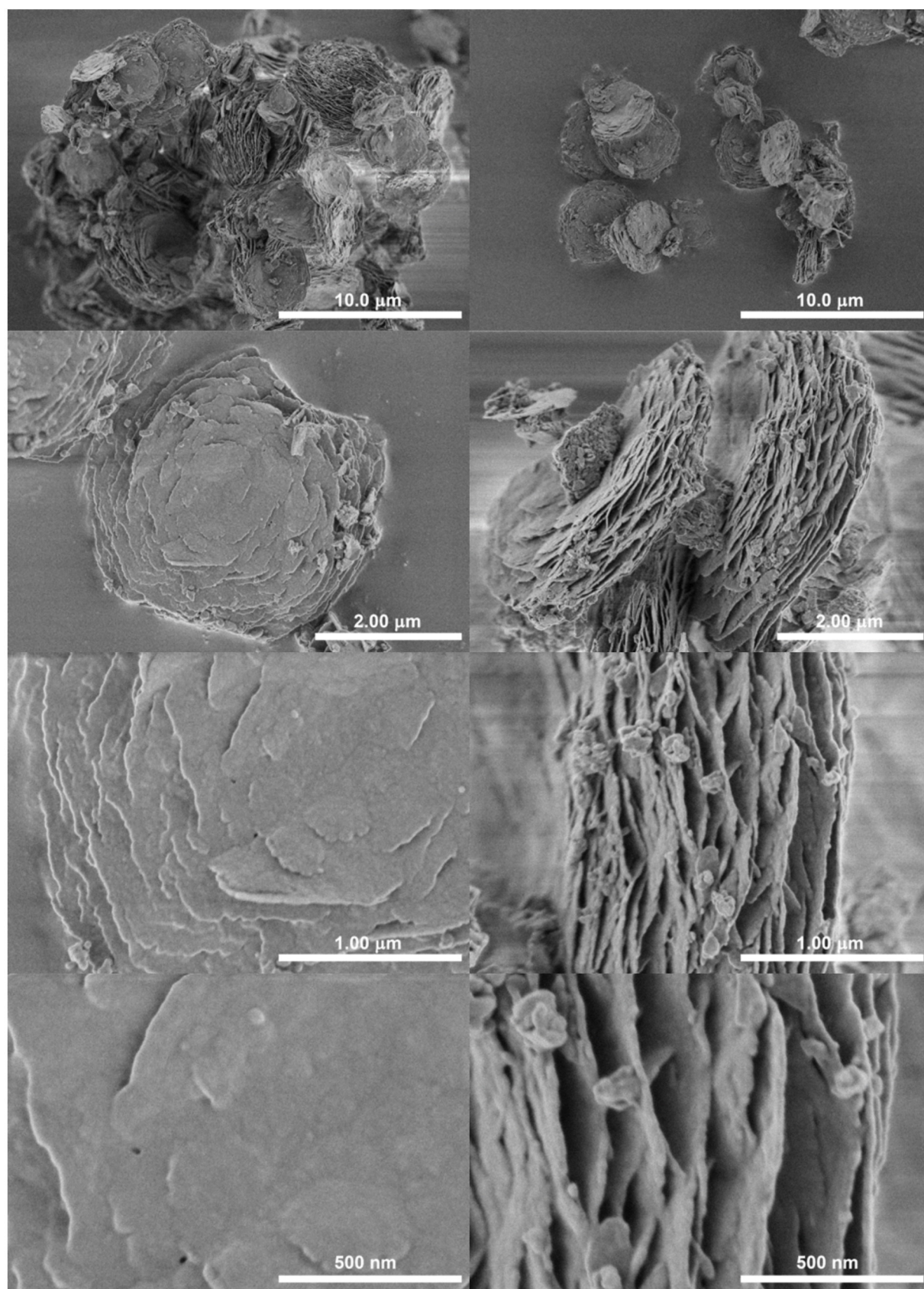


Figure S81. SEM images of $[\text{Mg}(\text{pz})_2]_n$ (**8**). The overall morphology of **8** features thin layers (10-20 nm) of round platelets (3-6 μm). SEM images of **8**- CO_2 were infeasible, due to immediate CO_2 release in high vacuum.

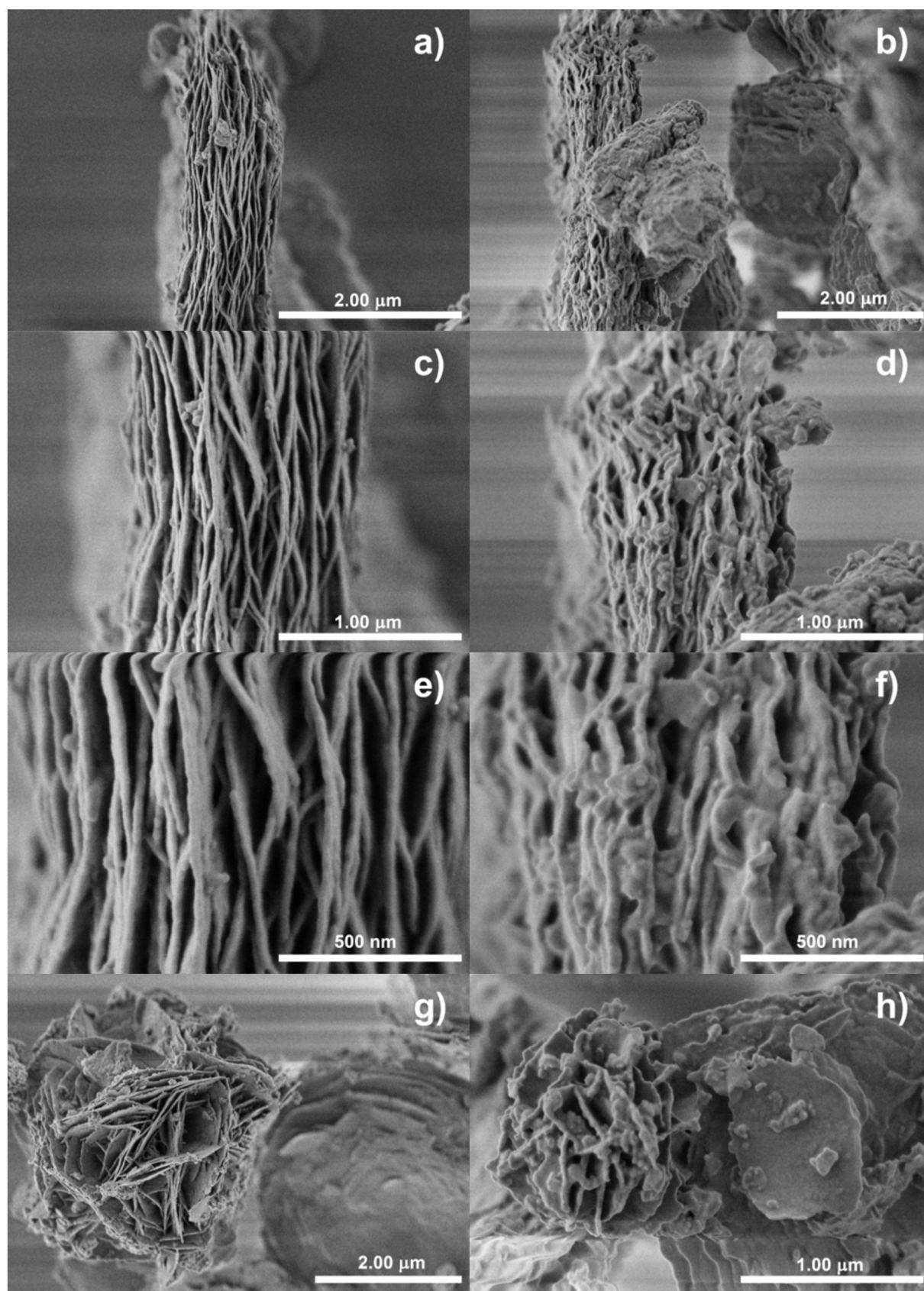


Figure S82. SEM images of $[\text{Mg}(\text{pz})_2]_n$ (**8**, a), c), e), g)) and **8** after one week exposure to ambient atmosphere (b), d), f), h)).

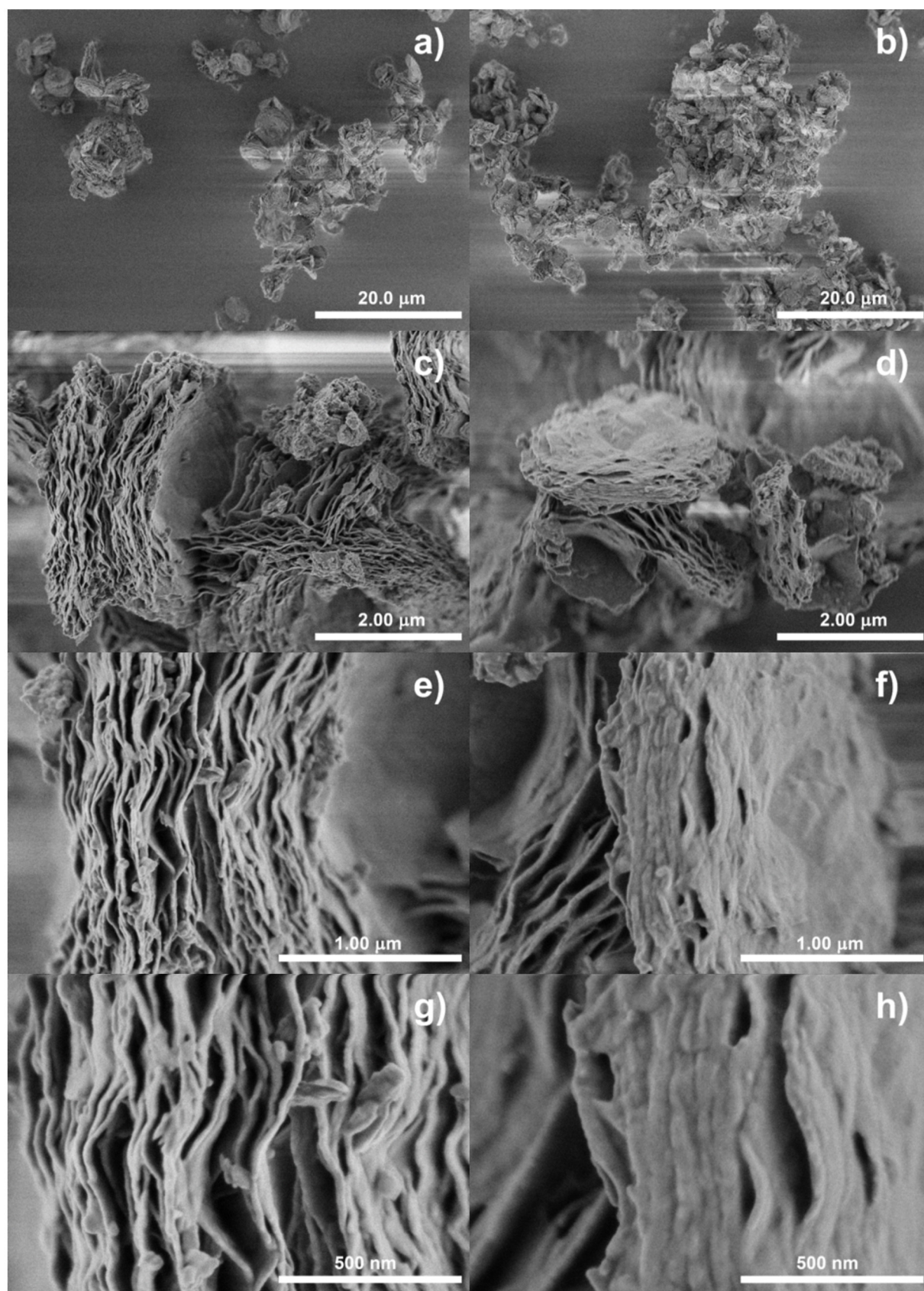


Figure S83. SEM images of $[\text{Mg}(\text{pz})_2]_n$ (**8**, a), c), e), g)) and **8** after one week exposure to ambient atmosphere (b), d), f), h)).

Table S6. Crystallographic Data for **2**, **3-thf**, **5** and **4a-Hpz**

	2	3-thf	5	4a-Hpz
formula	C ₄₈ H ₇₈ K ₂ Mg ₂ N ₁₂	C ₄₀ H ₆₈ Mg ₂ N ₈ O ₂	C ₅₂ H ₉₄ Mg ₃ N ₈ O ₂	C ₇₂ H ₁₂₂ Mg ₃ N ₁₆
CCDC	2342200	2342196	2342195	2342199
M [g mol ⁻¹]	950.04	741.64	936.28	1284.78
color/shape	colorless/prism	colorless/block	colorless/block	colorless/column
Crystal dimensions [mm]	0.137 x 0.114 x 0.076	0.251 x 0.204 x 0.101	0.249 x 0.129 x 0.101	0.437 x 0.184 x 0.139
cryst. system	triclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2/ <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	9.844(2)	10.6846(7)	16.1661(13)	21.9180(10)
<i>b</i> [Å]	11.547(3)	10.7816(7)	10.4304(8)	18.1705(8)
<i>c</i> [Å]	13.742(3)	11.3605(8)	18.4158(15)	20.3234(9)
[°]	71.277(4)	66.078(2)	90	90
[°]	74.381(4)	68.914(2)	112.411(2)	103.1070(10)
[°]	66.942(4)	73.097(2)	90	90
<i>V</i> [Å ³]	1342.7(5)	1099.96(13)	2870.7	7883.2(6)
<i>Z</i>	1	1	2	4
<i>T</i> [K]	173(2)	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.175	1.120	1.083	1.083
μ [mm ⁻¹]	0.243	0.096	0.096	0.087
<i>F</i> (000)	512	404	1028	2808
θ range [°]	1.586/28.734	2.041/28.723	1.430/26.375	1.472/28.334
unique reflns	6953	5697	10731	18652
observed reflns	53540	34062	5742	86840
<i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> > 2 σ) ^[a]	0.0426/0.0990	0.0426/0.1102	0.0722/0.1555	0.0522/0.1170
<i>R</i> ₁ / <i>wR</i> ₂ (all data) ^[a]	0.0617/0.1100	0.0530/0.1179	0.1148/0.1773	0.0913/0.1355
GOF ^[b]	1.037	1.031	1.036	1.017

^[a] $R_1 = \sum(|F_o| - |F_c|) / \sum F_o$, $F_o > 4\sigma(F_o)$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]\}^{1/2}$. ^[b]GOF = $[\sum w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$.

Table S7. Crystallographic Data for **4-thf**, **6-thf** and **1-CO₂,thf**, and **LiMg₄(CO₂·Pz^{iPr,iPr})₉**

	4-thf*	6-thf	1-CO₂,thf	LiMg₄(CO₂·Pz^{iPr,iPr})₉*
formula	C ₆₂ H ₁₀₆ Mg ₃ N ₁₂ O ₂	C ₃₂ H ₂₈ F ₂₄ Mg ₂ N ₈ O ₃	C ₃₂ H ₅₄ MgN ₄ O ₆	2 C ₉₀ H ₁₃₅ LiMg ₄ N ₁₈ O ₁₈ , 5·C ₇ H ₈
CCDC	2342201	2342198	2342197	2352312
M [g mol ⁻¹]	1124.51	1077.24	615.10	4183.33
color/shape	colorless/block	yellow/column	colorless/column	colorless/plate
Crystal dimensions [mm]	0.088 x 0.038 x 0.035	0.391 x 0.143 x 0.120	0.303 x 0.138 x 0.105	0.148 x 0.118 x 0.045
cryst. system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
<i>a</i> [Å]	32.802(3)	27.807(3)	8.6250(7)	21.2556(7)
<i>b</i> [Å]	10.5871(11)	9.5838(9)	10.9218(9)	22.0236(8)
<i>c</i> [Å]	19.763(2)	18.5235(17)	17.9314(14)	50.9504(16)
[°]	90	90	90	90
[°]	103.477(7)	123.1410(10)	93.313(2)	90
[°]	90	90	90	90
<i>V</i> [Å ³]	6674.3(12)	4133.4(7)	1686.3(2)	23851.2(14)
<i>Z</i>	4	4	2	4
<i>T</i> [K]	100(2)	100(2)	100(2)	100
wavelength [Å]	1.54184	0.71073	0.71073	1.54178
ρ_{calcd} [g cm ⁻³]	1.119	1.731	1.211	1.165
μ [mm ⁻¹]	0.789	0.213	0.100	0.832
<i>F</i> (000)	2456	2160	668	8968
θ range [°]	2.770/50.221	2.221/28.724	2.184/29.552	2.707/50.501
unique reflns	6222	5336	4700	12499
observed reflns	79269	32769	42441	94548
<i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> > 2 σ) ^[a]	0.0888/0.1572	0.0372/0.0911	0.0375/0.0958	0.0848/ 0.2006
<i>R</i> ₁ / <i>wR</i> ₂ (all data) ^[a]	0.2489/0.2221	0.0490/0.0998	0.0446/0.1021	0.1520/ 0.2395
GOF ^[a]	1.015	1.041	1.037	1.046

^[a] $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $F_o > 4\sigma(F_o)$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]\}^{1/2}$. ^[b]GOF = $[\sum w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$.

* Connectivity structure only.

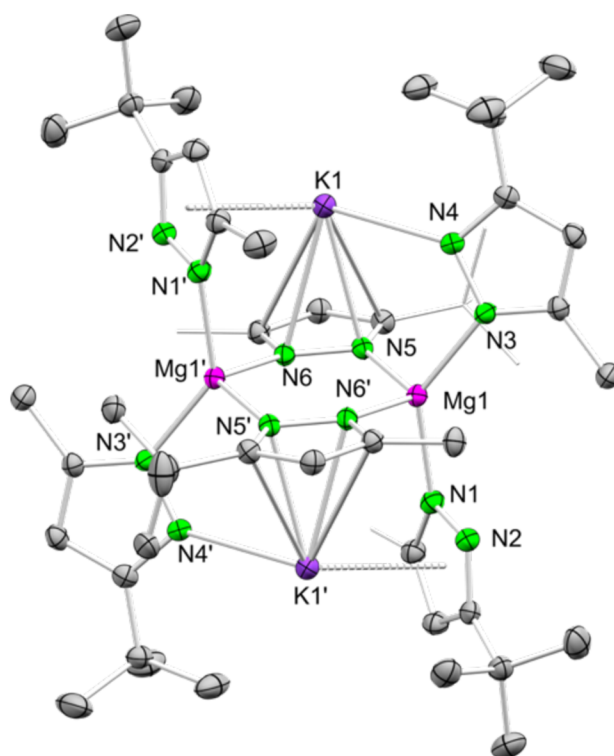


Figure S84. Crystal structure of $[\text{Mg}(\text{pz}^{\text{tBu,Me}})_2(\text{Kpz}^{\text{tBu,Me}})]_2$ (**2**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted and some Me/tBu moieties are displayed as wireframe for clarity. Selected interatomic distances [Å]: Mg1–N1 2.0541(14), Mg1–N3 2.0414(14), Mg1–N5 2.0759(14), Mg1–N6' 2.1061(14), K1–N4 2.8419(14), K1–N5 2.7940(14), K1–N6 2.9040(14), K1–Ct 2.800, N(pz)–C(pz(3/5-position)) 1.340(2)–1.3567(19), C(pz(4-position))–C(pz(3/5-position)) 1.381(2)–1.406(2). Selected angles [°]: N3–Mg1–N1 135.24(6), N3–Mg1–N5 104.92(6), N1–Mg1–N5 99.90(6), N3–Mg1–N6' 103.18(6), N1–Mg1–N6' 99.59(5), N5–Mg1–N6' 114.27(5). ' = -x+1, -y+1, -z+1

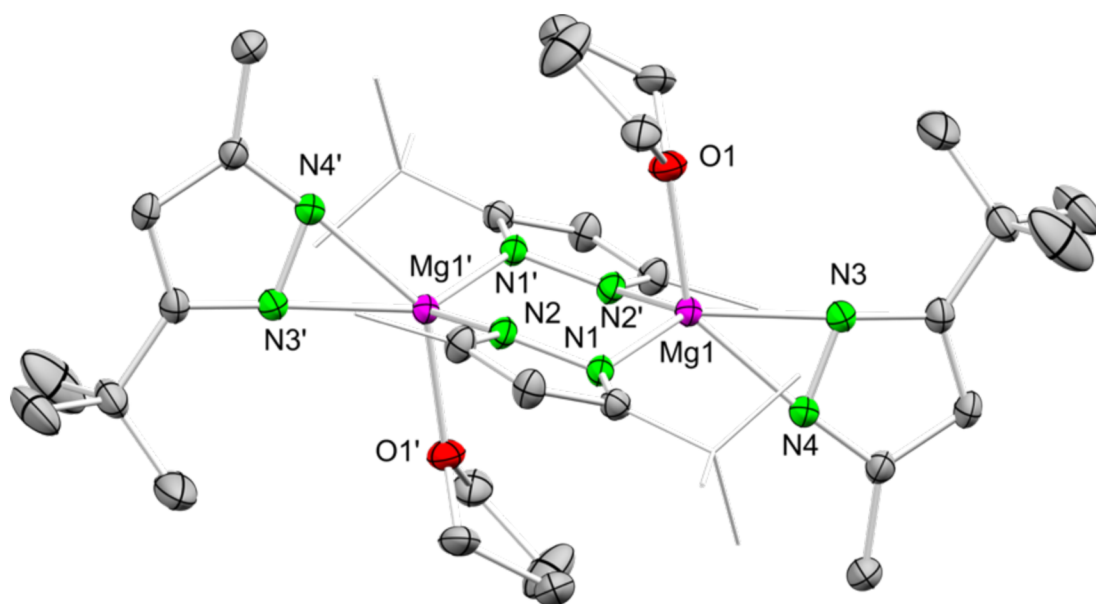


Figure S85. Crystal structure of $[\text{Mg}(\text{pz}^{\text{tBu,Me}})_2(\text{thf})]_2$ (**3-thf**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted and some Me/tBu moieties are displayed as wireframe for clarity. Selected interatomic distances [Å]: Mg1–N1 2.0783(10), Mg1–N2' 2.0890(11), Mg1–N3 2.0454(11), Mg1–N4 2.0965(11), N(pz)–C(pz(3/5-position)) 1.3377(15)–1.3530(15), C(pz(4-position))–C(pz(3/5-position)) 1.3898(17)–1.3970(17). Selected angles [°]: N3–Mg1–O1 101.22(4), N3–Mg1–N2' 114.10(4), O1–Mg1–N2' 93.98(4), N3–Mg1–N4 39.25(4), O1–Mg1–N4 140.35(4), N2'–Mg1–N4 104.89(4), O1–Mg1–N1 92.42(4), N1–Mg1–N2' 113.83(4), N1–Mg1–N4 110.40(4), N3–Mg1–N2' 114.10(4). ' = -x+1, -y, -z+1

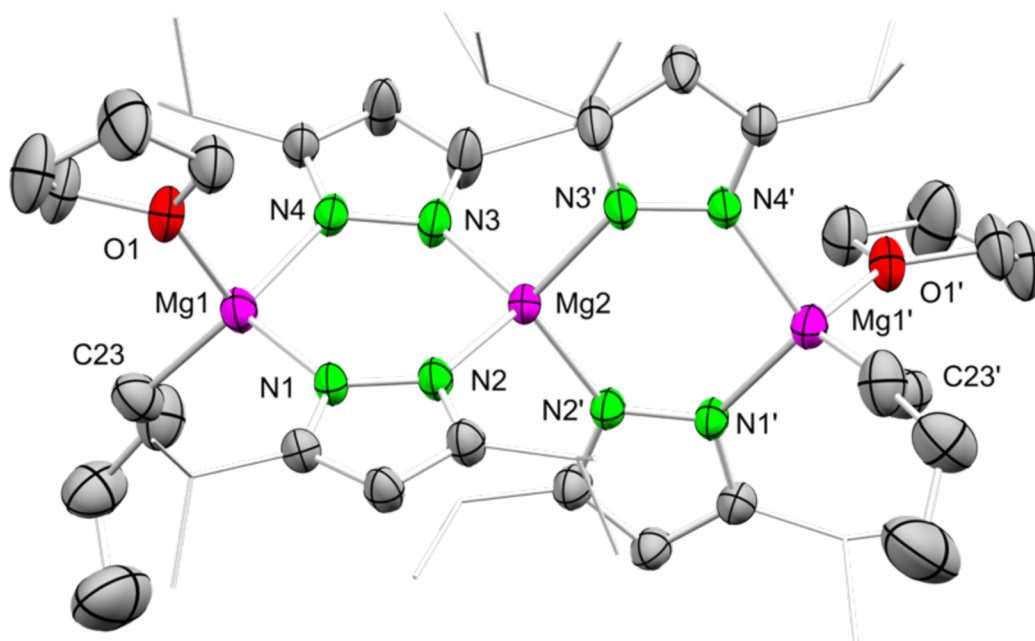


Figure S86. Crystal structure of $[\text{Mg}_3(\text{pz}^{\text{iPr,Pr}})_4(\text{nBu})_2(\text{thf})_2]$ (**5**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted and *iPr* moieties are displayed as wireframe for clarity. Selected interatomic distances [Å]: Mg1–N1 2.081(3), Mg1–N4 2.071(3), Mg2–N2 2.059(3), Mg2–N3 2.055(3), Mg1–O1 2.051(3), Mg1–C23/C23A 2.140(13)/2.09(2)*, N(pz)–C(pz(3/5-position)) 1.338(5)–1.347(4), C(pz(4-position))–C(pz(3/5-position)) 1.376(5)–1.392(5). Selected angles [°]: O1–Mg1–N4 102.97(12), O1–Mg1–N1 99.40(12), N4–Mg1–N1 106.52(11), O1–Mg1–C23A 100.3(6), N4–Mg1–C23 121.0(7), N1–Mg1–C23 122.0(8), O1–Mg1–C23 113.0(3), N4–Mg1–C23 114.5(4), N1–Mg1–C23 118.4(4), N3'–Mg2–N3 108.63(19), N3'–Mg2–N2' 109.12(11), N3'–Mg2–N2 110.92(11), N3–Mg2–N2 110.92(11), N2'–Mg2–N2 108.15(18). ' = -x+1/2, y, -z+3/2 *disorder

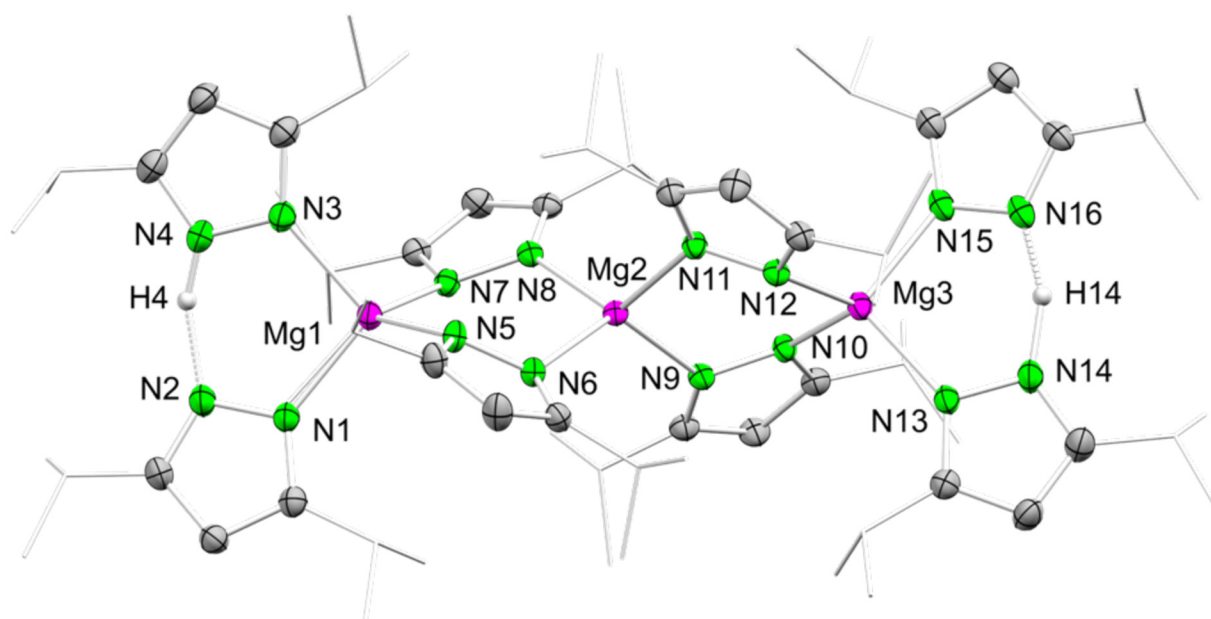


Figure S87. Crystal structure of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{Hpz}^{i\text{Pr},i\text{Pr}})_2]$ (**4a-Hpz**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted and *iPr* moieties are displayed as wireframe for clarity. Selected interatomic distances [Å]: Mg1–N 2.0485(15)–2.1000(16), Mg2–N 2.0846(15)–2.1008(15), Mg3–N 2.0374(15)–2.0915(16), N2–H4A 1.61(3), N4–H4A 1.05(3), N14–H14 1.06(3), N16–H14 1.60(3). Selected angles [°]: N5–Mg1–N7 102.25(6), N5–Mg1–N1 109.91(6), N7–Mg1–N1 121.34(6), N5–Mg1–N3 118.44(6), N7–Mg1–N3 106.26(6), N1–Mg1–N3 99.66(6), N8–Mg2–N11 122.50(6), N8–Mg2–N6 101.06(6), N11–Mg2–N6 101.74(6), N8–Mg2–N9 105.56(6), N11–Mg2–N9 102.95(6), N6–Mg2–N9 124.94(6), N12–Mg3–N10 103.85(6), N12–Mg3–N15 108.94(6), N10–Mg3–N15 118.91(6), N12–Mg3–N13 114.92(6), N10–Mg3–N13 110.26(6), N15–Mg3–N13 100.48(6).

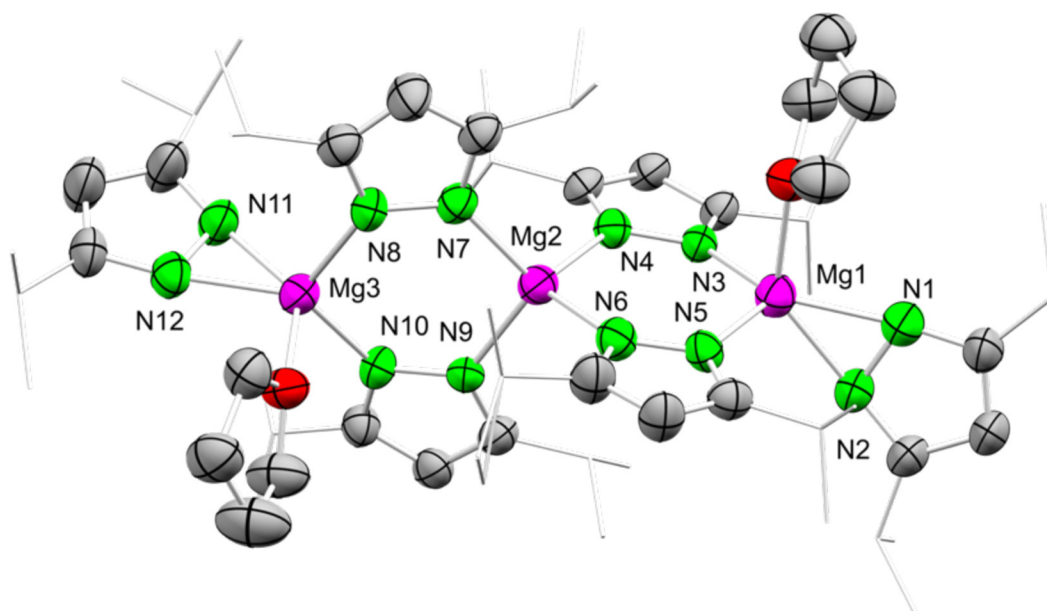


Figure S88. Crystal structure of $[\text{Mg}_3(\text{pz}^{i\text{Pr},i\text{Pr}})_6(\text{thf})_2]$ (**4-thf**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted and *iPr* moieties are displayed as wireframe for clarity (connectivity structure only).

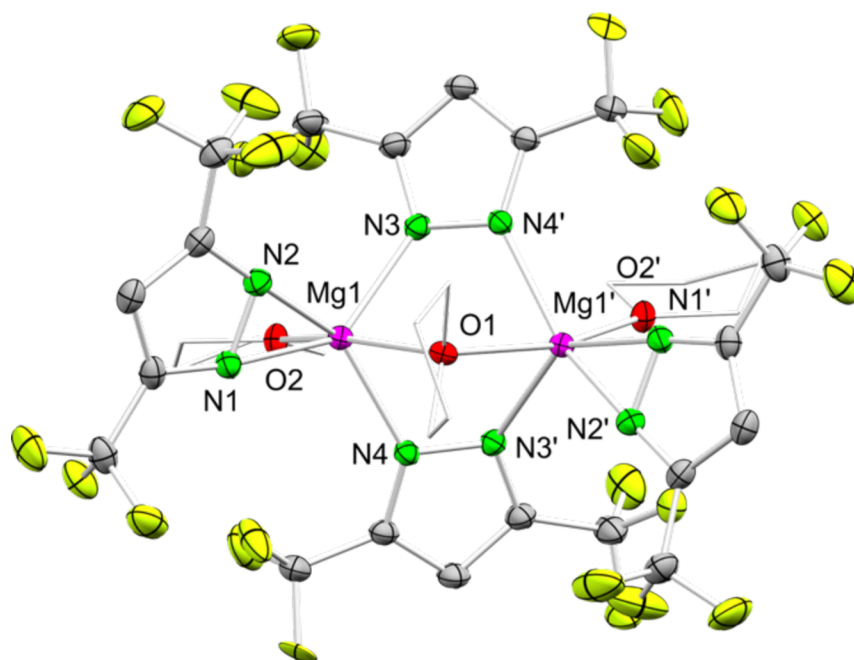


Figure S89. Crystal structure of $[\text{Mg}_2(\text{pz}^{\text{CF}_3, \text{CF}_3})_4(\text{thf})_3]$ (**6-thf**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted and THF donors are displayed as wireframe for clarity. Selected interatomic distances [Å]: Mg1–N1 2.1533(13), Mg1–N2 2.0939(13), Mg1–N3 2.1577(12), Mg1–N4 2.1386(12), Mg1–O1 2.2979(10), Mg1–O2 2.0554(11). Selected angles [°]: O2–Mg1–N2 107.94(5), O2–Mg1–N4 88.27(4), N2–Mg1–N4 145.30(5), O2–Mg1–N1 95.86(5), N2–Mg1–N1 37.44(5), N4–Mg1–N1 112.47(5), O2–Mg1–N3 92.92(5), N2–Mg1–N3 101.02(5), N4–Mg1–N3 108.74(5), N1–Mg1–N3 138.02(5), O2–Mg1–O1 163.32(4), N2–Mg1–O1 88.73(4), N4–Mg1–O1 77.58(4), N1–Mg1–O1 97.68(4), N3–Mg1–O1 83.47(4).

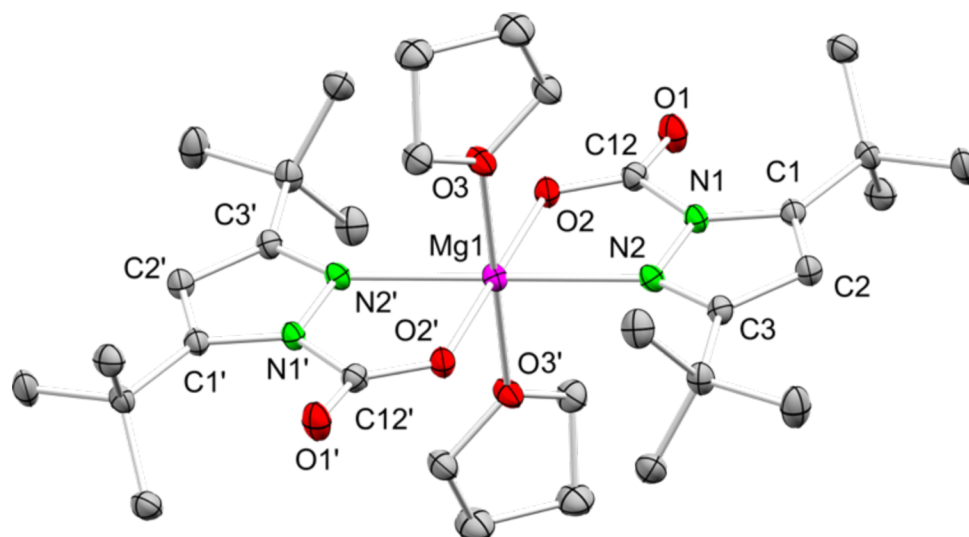


Figure S90. Crystal structure of $[\text{Mg}(\text{CO}_2\text{-pz}^{\text{tBu}, \text{tBu}})_2(\text{thf})_2]$ (**1-CO₂,thf**). Ellipsoids are set at the 50% probability level. Hydrogen atoms as well as disorder in the thf ligands are omitted for clarity. Selected interatomic distances [Å]: Mg1–O2 1.9917(7), Mg1–N2 2.2273(8), Mg1–O3 2.1095(7), C12–O1 1.2165(12), C12–O2 1.2621(11), C12–N1 1.4773(12), C2–C1 1.3788(13), C2–C3 1.4073(13), N1–C1 1.3800(12), N2–C3 1.3310(12). Selected angles [°]: O1–C12–O2 129.23(9), O2–Mg1–N2 75.33(3), O2–Mg1–O3 90.95(3), O2–Mg1–N2 75.33(3), O2'–Mg1–N2 104.67(3), O2–Mg1–O2' 180.0. ' = -x+1, -y+1, -z+1

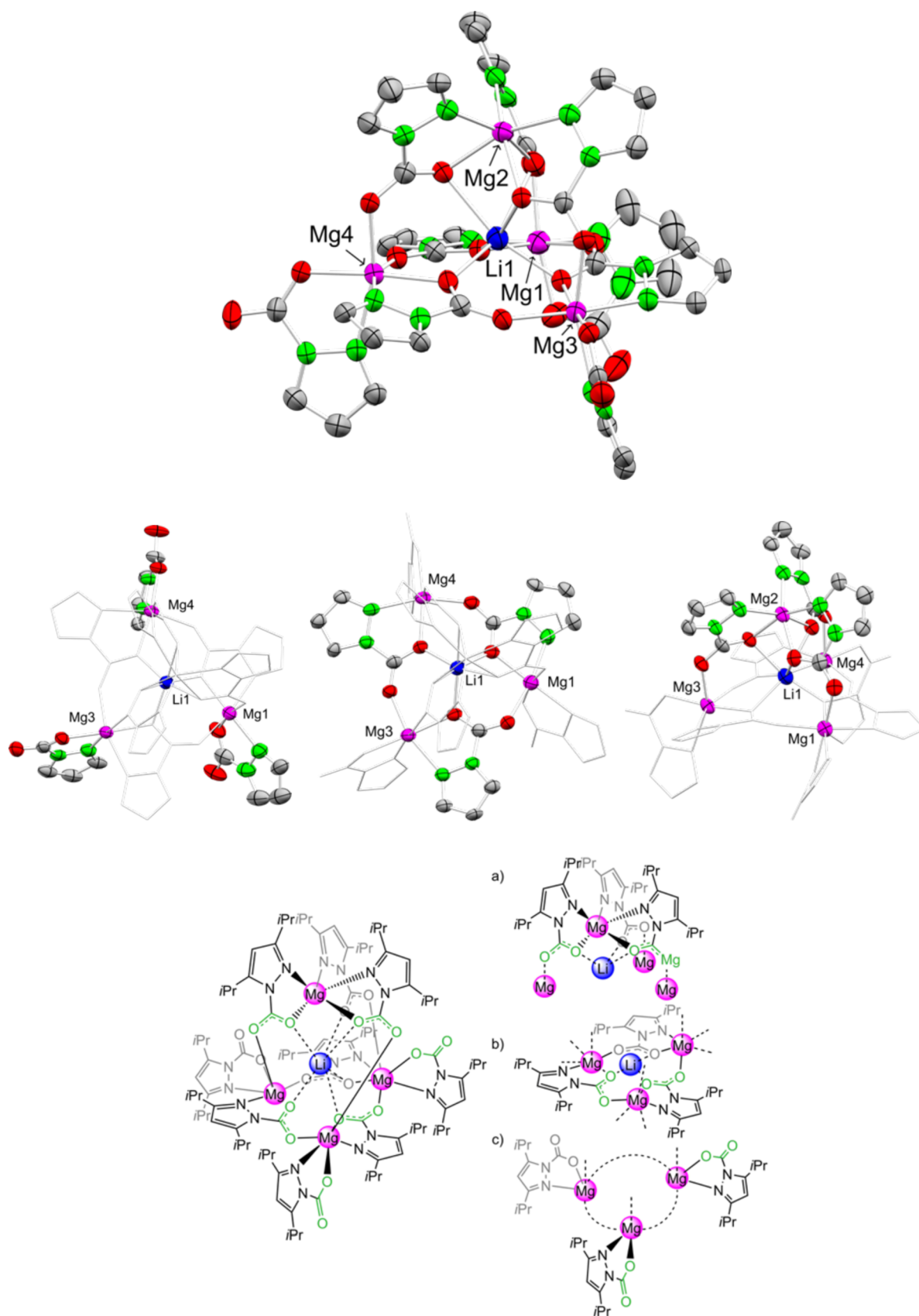
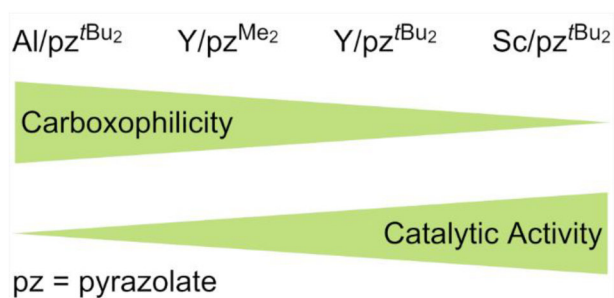


Figure S91. Crystal structure of $[\text{LiMg}_4(\text{CO}_2\cdot\text{pz}^{\text{iPr,iPr}})_9]$ (connectivity). Ellipsoids are set at the 50% probability level. Hydrogen atoms as well as lattice solvent toluene and THF are omitted for clarity. For a better description of the molecular structure, sections of the distinct metal-carbamate coordination are highlighted and further clarified by ChemDraw representations.

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Carbon dioxide affinity ("carboxophilicity") of trivalent light metal pyrazolates



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Carbon dioxide affinity (“carboxophilicity”) of trivalent light metal pyrazolates†

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Trivalent group 3 and 13 light metal pyrazolates were synthesised and their reactivity towards CO₂ was investigated. The homoleptic complex Al(pz^{tBu})₃ reversibly inserts two molecules of CO₂ to afford Al(CO₂·pz^{tBu})₂(pz^{tBu}), exhibiting CO₂ release only at elevated temperatures (>100 °C). In contrast, donor-stabilised Sc(pz^{tBu})₃(thf) forms mono-inserted species [Sc(μ-CO₂·pz^{tBu})(pz^{tBu})₂]₂, which already releases CO₂ at ambient temperature and pressure and hence is isolable only at low temperature. For the yttrium complex Y(pz^{tBu})₃(thf)₂, insertion of CO₂ is not observable at ambient temperature. The new homoleptic aluminium diisopropyl pyrazolate complex [Al(pz^{iPr})₃]₂ shows exhaustive CO₂ insertion, while dimethyl pyrazolate could be isolated as the separated ion pair [Al(N,N',N''-Al(pz^{Me})₃Me)₂][Al(pz^{Me})₃Me]. The scandium complex Sc(pz^{tBu})₃(thf) performed best in the catalytic cycloaddition reaction of CO₂ and epoxides, unveiling an inverse correlation of carboxophilicity (=CO₂ affinity) and catalytic activity. Carboxophilicity is assessed using CO₂-release temperature (via VT ¹H NMR spectroscopy and thermogravimetric analysis).

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Introduction

Anthropogenic greenhouse gases, in particular carbon dioxide, are the main reason for global climate change. Consequently, combating CO₂ build-up has developed into the most important and compelling research field in the chemical sciences.^{1–11} Carbon dioxide capture and storage (CCS) from flue gas or directly from air (DAC) are industrially realised with aqueous amine scrubbers; this technology, however, is affected by low capacities (<15 wt% CO₂), sensitivity to oxygen and high regeneration energies (high “energy penalty”).^{8,9} Academic research has focused on amino-functionalized porous materials such as mesoporous silica, zeolites or metal-organic frameworks, with the latter showing promising results under simulated flue gas.^{5,12–17} Moreover, a detailed molecular understanding of metal-ligand interactions with carbon dioxide seems crucial for developing efficient (catalytic) processes for its chemical valorization.¹⁸ Here, metal-N(ligand) cooperativity has proven particularly effective in CO₂ transformations together with a synergistic interplay to reversibly insert this heteroallene.¹⁸ Any reversible insertion/de-insertion process will rely on a fine balance of metal-centred oxophilicity

and ligand-nitrogen nucleophilicity, which we have termed carboxophilicity (Fig. 1, top).

Recently, we found that CO₂ reversibly inserts into metal-pyrazolato bonds involving oxophilic metal centres. It was revealed that tetravalent dimeric [Ce(pz^{Me})₄]₂ and the trivalent cluster [Ce(pz^{Me})₃]₄ can accommodate 25 wt% CO₂.¹⁹ Adapting this approach to the environmentally friendlier earth-abundant light metal magnesium, parent pyrazolate [Mg(pz)₂]_n achieved an exceptionally high reversible CO₂ uptake of up to 35.7 wt%.²⁰ Structurally authenticated complexes include tetravalent Ce(CO₂·pz^{Me})₄ (A)¹⁹ and divalent Mg(CO₂·pz^{tBu})₂(thf)₂ (B),²⁰ showing exclusive κ²(N,O) carbamate coordination (Fig. 1,

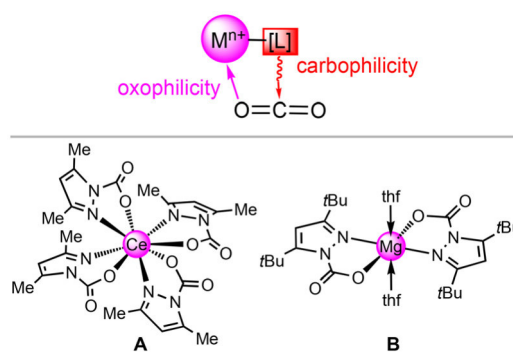


Fig. 1 Top: Carboxophilicity of metal-ligand entities as driven by the oxophilicity of the metal centre and nucleo(carbo)philicity of the ligand. Bottom: Examples of tetravalent (cerium, A)¹⁹ and divalent (magnesium, B) carbamate complexes,²⁰ which feature fully reversible CO₂ insertion.

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† Electronic supplementary information (ESI) available. CCDC 2358935–2358943. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4qi01656d>



bottom). Moreover, all pyrazolate complexes displayed moderate catalytic activity in the conversion of CO₂ and epoxides to their corresponding cyclic carbonates. In this work, we report on the reactivity of trivalent pyrazolates of highly oxophilic group 3 and 13 light metals aluminium, scandium and yttrium towards CO₂. In addition, we discuss CO₂ release temperature as a quantifiable measure for assessing carboxophilicity.

The reactivity of organoaluminium complexes towards carbon dioxide was described by Ziegler in 1960 and expanded on later in 1970 by Weidlein.^{21,22} Accordingly, CO₂ inserts irreversibly into trialkyl aluminium compounds to afford tertiary alkoxides or carboxylates, which upon hydrolysis, produced their corresponding alcohols or carboxylic acids. Dimeric [Al(μ-CO₂-N(iPr)₂)(CO₂-N(iPr)₂)₂]₂ features the first structurally characterised aluminium carbamate complex, accessed from AlBr₃/HN(iPr)₂/CO₂.²³ Moreover, dimeric heteroleptic carbamate [Me₂Al(μ-CO₂-N(iPr)₂)₂]₂ was obtained (among others) *via* CO₂ insertion into [Me₂Al(μ-N(iPr)₂)₂Mg(μ-Me)]_n.²⁴ More recently, compound [Al(κ²-N,N-2-{methylamino}pyridine)₂R] (R = Et, iBu) was shown to insert CO₂ not only into the Al-C(alkyl) bond but also in one of the two Al-N bonds of each pyridine ligand.^{25,26} Furthermore, the frustrated Lewis acid pair 9,9-dimethylxanthene(PPh₂-AlMe₂Cl-AlMeCl) engaged in reversible CO₂ insertion.²⁷ In addition, aluminium compounds supported by a rigid ligand backbone, such as porphyrinato, salen or amino-tris(phenolato), are active in the cycloaddition of CO₂ with epoxides, with the latter displaying a promising performance with low catalyst loads.^{28–36} The porphyrinate complex (TPP)Al(OMe) showed reversible insertion behaviour towards CO₂ in the presence of 1-methylimidazole.²⁸

For rare-earth metals, a rich CO₂-insertion chemistry is already existent.^{19b} However, for most metal–ligand entities, CO₂ insertion turned out to be irreversible, forming carboxylates/formate from alkyls/hydrides,^{37–42} carbonates from alkoxide/aryloxide^{43,44} or carbamates from amide complexes.^{45–48} Scandocene [(C₅Me₅)₂Sc(CO₂-*p*-tolyl)] features the first structurally characterised organoscandium CO₂ insertion complex.³⁷ Evans *et al.* described the first yttrium carbamate complex, [(C₅Me₅)₂Y(CO₂-ε-caprolactam)]₂, obtained by CO₂ insertion into the Y–N bond of (C₅Me₅)₂Y(O,N-ε-caprolactam).⁴⁷ Rare-earth-metal complexes also gained attention for their catalytic performance in the co-polymerisation of CO₂ and epoxides to polycarbonates,^{43,49–52} as well as the cycloaddition of both compounds to the cyclic carbonates with amino-tris(phenolates) as the most promising catalysts.^{52–59} Particularly thanks to the works of the groups of Deacon, Junk, and Winter, there exists a vast variety of rare-earth-metals pyrazolates, featuring distinct coordination modes.^{60–64} We were mostly interested in diamagnetic scandium and yttrium pyrazolates, such as Sc(pz^{tBu})₃,⁶¹ [Y(pz^{Me})₃(thf)]₂⁶² and Y(pz^{tBu})₃(do)₂.⁶⁰

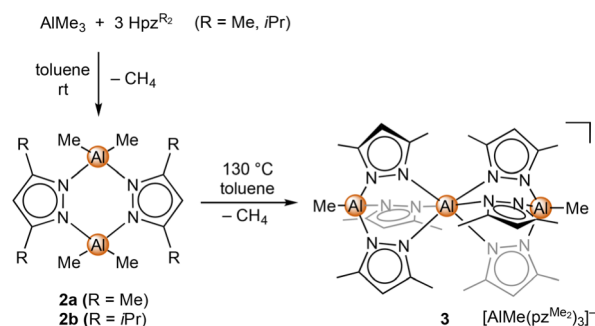
Results and discussion

Selection and CO₂ insertion of group 13 pyrazolates

Aluminium pyrazolates. Deacon *et al.* obtained discrete Al(pz^{tBu})₃ (**1**) *via* a salt-metathesis reaction of AlCl₃ and K(pz^{tBu})

in THF as the first and so far only known homoleptic aluminium pyrazolate complex.⁶⁵ In addition to *tert*-butyl-substituted pyrazolate complex **1**, we probed the feasibility of new derivatives bearing smaller, “lighter” methyl and isopropyl substituents. Since the salt-metathesis reactions of AlCl₃ and Kpz^{Me} led to no isolable product, a protonolysis protocol with AlMe₃ and Hpz^{Me} was applied. Even though a ratio of 1 : 3 of both compounds was used, only a single methane elimination occurred at ambient temperature, affording the well-known [Me₂Alpz^{Me}]₂ (**2a**) (Scheme 1).^{66,67}

Complex **2a** features a recurring structural motif,^{68–70} which was also observed for the new diisopropyl derivative [Me₂Alpz^{iPr}]₂ (**2b**). Refluxing a 1 : 3 mixture in toluene gave a more extensive but still incomplete ligand exchange. The crystalline material gained overnight revealed the solid-state structure of the separated ion pair [Al(N,N',N''-Al{pz^{Me}}₃Me)₂][MeAl(pz^{Me})₃] (**3**) (Fig. S102†). The mono-cationic fragment revealed an aluminium(III) centre coordinated by two mono-anionic [MeAl(pz^{Me})₃][−] ligands. The latter are reminiscent of the tris(pyrazolyl)hydroborato ligand Tp^{Me,Me}, while the Tp analogous aluminium ligand is accessed *via* a protonolysis reaction of LiAlH₄ with pyrazole.^{71–74} The separated anion in complex **3** is another [MeAl(pz^{Me})₃][−] entity. The central aluminium atom of the cationic fragment features a slightly distorted octahedral geometry (N–Al–N angles ±3° off). The aluminium centres of the tridentate “scorpionato”-type ligand adopt a slightly distorted tetrahedral geometry with N–Al–N angles around 100° and C–Al–N angles around 117°. The respective angles in the separated [MeAl(pz^{Me})₃][−] anion are 103° and 112° and hence are closer to tetrahedral. The three aluminium centres of the cationic fragment are almost linearly arranged (∠Al, Al, Al 1.5°), with the outer Al1/Al3–N (av. 1.874 Å and 1.893 Å) and inner Al2–N distances (av. 2.035 Å and 2.048 Å) reflecting the distinct coordination numbers. The trinuclear complex [AlMe({N,N'-3,3'-bipyrazolate}₂AlMe₂)₂], obtained from bispyrazole and AlMe₃ (1 : 1.5),⁷⁵ shows a similar structural motif. The ²⁷Al NMR spectrum of compound **3** revealed only two signals at δ = 75.7 ppm and 0.3 ppm, assignable to 4- and 6-coordinated aluminium centres, respectively.



Scheme 1 Protonolysis reactions of AlMe₃ with three equivalents HpzR₂ (R = Me and iPr), to form [Me₂Alpz^{Me}]₂ (**3**) at ambient temperature and separated ion pair [Al(N,N',N''-Al{pz^{Me}}₃Me)₂][MeAl(pz^{Me})₃] (**4**) by refluxing at 130 °C.



Further heating a 1 : 3 mixture of AlMe_3 and Hpz^{Me} in mesitylene to 180 °C, in order to achieve full methyl elimination, did not lead to any isolable product, and thus the homoleptic $[\text{Al}(\text{pz}^{\text{Me}})_3]$ remains elusive.

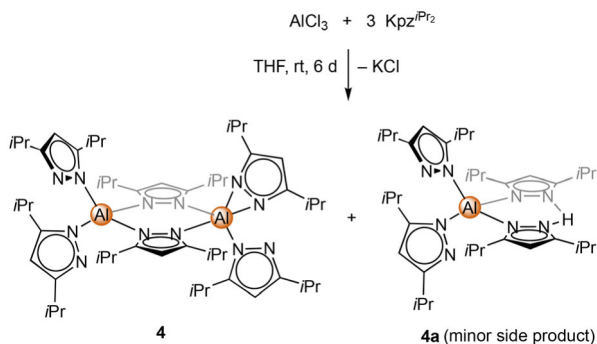
Unlike the dimethyl derivative, potassium diisopropyl pyrazolate reacted smoothly with aluminium chloride *via* a salt-metathesis route (Scheme 2). The crystal structure revealed the homoleptic bimetallic complex $[\text{Al}(\text{pz}^{\text{iPr}})_3]_2$ (**4**) (Fig. 2), with two bridging pyrazolato ligands arranged in an approximate boat conformation with the aluminium atoms. Interestingly, the terminal pyrazolato ligands show different coordination modes. One aluminium centre features terminal pyrazolatos coordinated exclusively in a κ^1 coordination mode, while the other one accommodates the N-ligand in both κ^1 and κ^2 fashion. The ^1H and ^{13}C NMR spectra of **4** show the bridging and terminal pyrazolatos as two different signal sets in a ratio of 1 : 2. The ^{27}Al NMR resonance was detected at $\delta = 68.1$ ppm. Some reactions gave ^1H NMR spectra with an additional slightly shifted signal set. We were able to fractionally crystallize this side product, and the solid-state structure revealed the monomeric mixed pyrazole/pyrazolato complex $\text{Al}(\text{pz}^{\text{iPr}})_3(\text{Hpz}^{\text{iPr}})$ (**4a**) (Fig. S104†). The structure of **4a** is quite similar to that of **4** with one $\text{Al}(\text{pz}^{\text{iPr}})_2$ fragment replaced by a

proton, which forms a hydrogen bond with the pyrazolyl moieties. Most likely, the pyrazole originated from partial hydrolysis caused by residual moisture in the solvent THF.

Attempts at homoleptic gallium pyrazolates. Since CO_2 insertion/de-insertion into metal–ligand bonds crucially depends on the bond polarization, we also aimed at employing gallium pyrazolates. Surprisingly, homoleptic gallium pyrazolates have not been reported yet.^{73,76–79} Given that $[\text{Al}(\text{pz}^{\text{R}2})_3]$ ($\text{R} = \text{iPr}, \text{tBu}$) could be readily obtained by salt metathesis, we used similar protocols to access putative gallium derivatives. However, the reactions of GaX_3 ($\text{X} = \text{Cl}, \text{Br}$) with $\text{Kpz}^{\text{R}2}$ ($\text{R} = \text{Me}, \text{tBu}$) turned out very unsatisfactorily, and only a small amount of crystalline material could be obtained (Scheme 3).

An X-ray structural analysis revealed the formation of the dimeric complex $[\text{Ga}(\text{pz}^{\text{tBu}})(\mu\text{-N,N,C-pz}^{\text{tBu,C(CH}_3)_2\text{CH}_2})_2]_2$ (**5**) (Fig. 3). C–H-bond activation at one *t*Bu moiety under release of pyrazole generated a dianionic pyrazolato ligand, bridging with both nitrogen atoms and one CH_2 group between the gallium atoms.

The molecular structure of complex **5** indicates a rather complex reactivity of gallium pyrazolates. Such distinct behaviour of aluminium and gallium in salt-metathesis reactions is not unknown, as previously shown for $\text{MCl}_3/\text{LiN}(\text{SiMe}_3)_2$ or $\text{MCl}_3/\text{LiN}(\text{SiHMe}_2)_2$ mixtures ($\text{M} = \text{Al}, \text{Ga}$). There, gallium also engaged in extensive Si–X-bond activation ($\text{X} = \text{C}, \text{H}$).⁸⁰ Application of a protonolysis protocol employing a 1 : 3 mixture of GaMe_3 and Hpz^{tBu} led to the known $[\text{Me}_2\text{Ga}$



Scheme 2 Synthesis of homoleptic $[\text{Al}(\text{pz}^{\text{iPr}})_3]_2$ (**4**) *via* salt metathesis of AlCl_3 and Kpz^{iPr} . The side product $\text{Al}(\text{pz}^{\text{iPr}})_3(\text{Hpz}^{\text{iPr}})$ (**4a**) is formed in the presence of residual moisture.

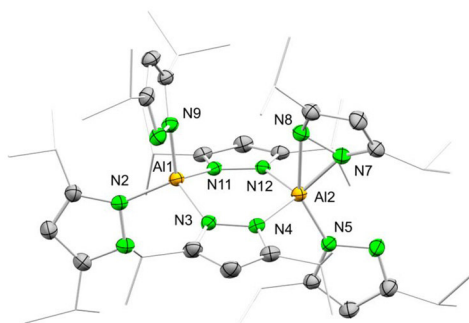
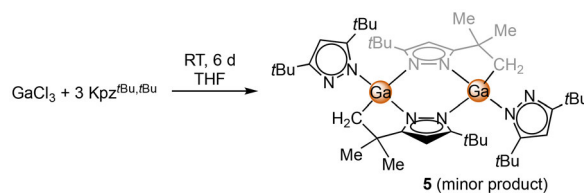


Fig. 2 Crystal structure of $[\text{Al}(\text{pz}^{\text{iPr}})_3]_2$ (**4**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. See ESI† for selected interatomic distances and angles.



Scheme 3 Reaction of GaCl_3 with Kpz^{tBu} to yield $[\text{Ga}(\text{pz}^{\text{tBu}})(\mu\text{-N,N,C-pz}^{\text{tBu,C(CH}_3)_2\text{CH}_2})_2]_2$ (**5**) as a side product.

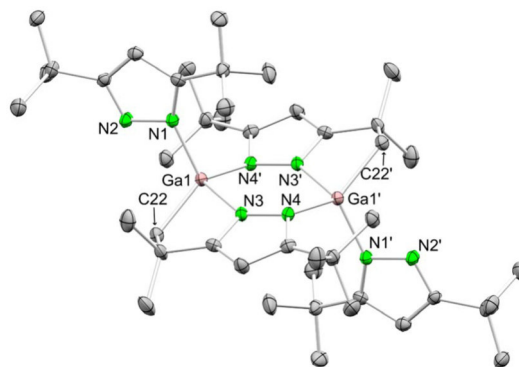


Fig. 3 Crystal structure of $[\text{Ga}(\text{pz}^{\text{tBu}})(\mu\text{-N,N,C-pz}^{\text{tBu,C(CH}_3)_2\text{CH}_2})_2]_2$ (**5**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. See ESI† for selected interatomic distances and angles.



(pz^{tBu})₂,⁸¹ analogous to the aluminium-based reactions displayed in Scheme 1.

Reactivity of aluminium pyrazolates towards CO₂. Reacting Deacon's Al(pz^{tBu})₃ (**1**) with an excess of CO₂ in THF led to heteroallene insertion into two of the three pyrazolato ligands forming the bis(carbamato) complex Al(CO₂·pz^{tBu})₂(pz^{tBu}) (**1-CO₂**) (Scheme 4). The CO₂ content in **1-CO₂** corresponds to 13.5 wt% CO₂ or 3.1 mmol CO₂ per gram. Performing an NMR-scale reaction revealed the formation of a mono-inserted intermediate prior to full conversion into **1-CO₂**. This contrasts with our observations with magnesium and cerium pyrazolates showing such an intermediate only in the CO₂-releasing steps.^{19,20}

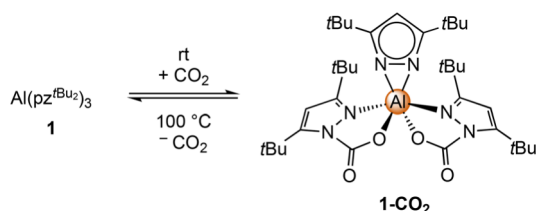
The crystal structure of **1-CO₂** revealed a strongly distorted octahedral geometry (see Fig. 4). The aluminium centre is coordinated with two carbamato moieties in the κ²(N,O) mode and one pyrazolato ligand in the terminal κ²(N,N) mode. Because of the sterically demanding *t*Bu moieties, all three ligands are twisted against each other, which gives the complex a propeller-like overall geometry. Both stereoisomers (Λ,Δ) can be found in the unit-cell which is further corroborated by the centrosymmetric space group *Pbca*. The solid-state structure might also explain the non-occurrence of an exhaustive CO₂ insertion, since the bulky *t*Bu moieties hinder a vital tilt of the third pyrazolato ligand. The inserted CO₂ moieties exhibit an angle around 127.5°, along with localized C–O double (1.199–1.203 Å) and single bonds (1.285–1.288 Å). Such

bond localization is also found in the pyrazolato rings. The 4C–3/5C and the 1/2N–3/5C distances of the non-inserted pyrazolato ring differ slightly by 0.005 Å, whereas, for the carbamate pyrazolato rings, the differences are significantly larger at 0.031–0.034 Å and 0.047 Å, respectively.

DRIFTS measurements further validate this behaviour, displaying strong absorption bands at $\tilde{\nu}$ = 1774/1763 cm^{−1} and $\tilde{\nu}$ = 1328 cm^{−1} for the C=O and C–O stretching vibrations, respectively. The ¹H NMR spectrum of **1-CO₂** shows two singlets for the pyrazolato backbone proton at δ = 6.32 and 6.00 ppm in a 1 : 2 ratio. Additionally, three singlets with an integral of 18 protons each, one at δ = 1.50 and two at δ = 1.05 ppm, are detected, in accordance with three distinct *t*Bu moieties. Further, the ¹³C NMR spectrum of **1-CO₂** shows a signal at δ = 146.9 ppm, assignable to inserted CO₂, while the ²⁷Al resonance at δ = 17.0 ppm appears slightly shifted, broadened and less intense (due to loss of symmetry) compared to that of precursor **1** (δ = 23.3 ppm).

Unlike the previously examined cerium and magnesium pyrazolates, solid **1-CO₂** does not show any CO₂ release at ambient temperature, not even under reduced pressure. This high carboxophilicity was further revealed by a variable-temperature (VT) NMR study in THF-*d*₈ (see S15), revealing prominent CO₂ release only at 90 °C. At this temperature, the formation of small amounts of the mono-inserted complex [Al(CO₂·pz^{tBu})(pz^{tBu})₂] can be detected, while increasing the temperature to 100 °C led to small amounts of **1**. This is in contrast to the CO₂-inserted magnesium pyrazolates which fully de-insert the heteroallene in this temperature range.¹⁹ Cooling the sample which was heated to 100 °C to ambient temperature shows the re-formation of **1-CO₂** as the predominant species, along with small amounts of the mono-inserted complex and **1**. Retreatment of this mixture with an excess of CO₂ fully restores compound **1-CO₂**. A thermogravimetric analysis (TGA) of **1-CO₂** revealed CO₂ release in the temperature range between 114 °C and 196 °C, with a mass loss of 15.8% which is in good agreement with the calculated 13.5%. A single CO₂-release step like in solution could not be observed.

Treatment of [Al(pz^{iPr})₃] (**4**) with 1 bar CO₂ gave no crystalline material; however, the NMR data suggest an exhaustive insertion into every pyrazolato ligand (see S16–S18†). Three signals for the pyrazolato backbone protons appear in the ¹H NMR spectrum in a 1 : 1 : 1 integral ratio. Furthermore, four septets for the tertiary *i*Pr proton are detected in a 3 : 1 : 1 : 1 integral ratio. This indicates the expected asymmetry of the *i*Pr groups resulting from CO₂ insertion, in accordance with distinct signals for the *i*Pr moieties adjacent to the inserted CO₂ and one signal for *i*Pr distant to the inserted CO₂. This assignment is further strengthened by the ¹³C NMR spectrum, which shows three signals for inserted CO₂ ranging from δ = 147.0 to 146.6 ppm. A ¹H–¹³C HMBC experiment revealed that each of the three pyrazolato backbone proton signals couples with two carbon signals in the shift region for 3/5-pyrazolato carbon atoms, lending more evidence for the new asymmetry. The isopropyl CH₃ groups appear as one multiplet with 24 protons and four doublets with 3 protons. This suggests a hindered



Scheme 4 Reaction of Al(pz^{tBu})₃ (**1**) with excess CO₂ in toluene.

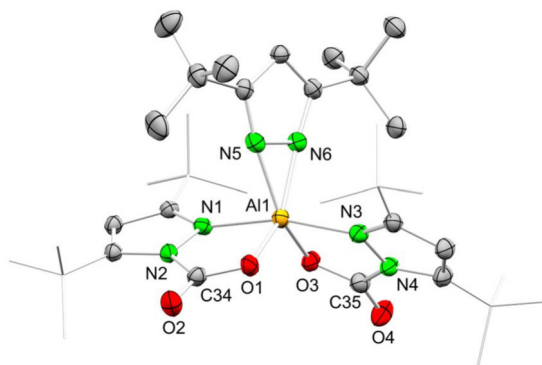


Fig. 4 Crystal structure of Al(CO₂·pz^{tBu})₂(pz^{tBu}) (**1-CO₂**). Ellipsoids are set at the 50% probability level. Hydrogen atoms and disorder in the *t*Bu moieties are omitted for clarity. See ESI† for selected interatomic distances and angles.



rotation of the *i*Pr moieties as a result of the three inserted CO₂. Upon CO₂ insertion, the ²⁷Al NMR signal shifted to higher field, from $\delta = 68.1$ ppm in **4** to $\delta = 12.1$ ppm. The putative [Al(CO₂·pz^{*t*Bu})₃] (**4**-CO₂) would infer a capacity of 21.6 wt% CO₂.

Reactivity of group 3 metal pyrazolates towards CO₂

The scandium pyrazolate Sc(pz^{*t*Bu})₃(thf) (**7**) was synthesized by applying the salt-metathesis protocol described by Deacon for aluminium pyrazolate Al(pz^{*t*Bu})₃ (**1**, *vide supra*). Accordingly, the mercury-free synthesis using THF-activated scandium chloride and Kpz^{*t*Bu} gave **7** in a good yield (see Scheme 5).

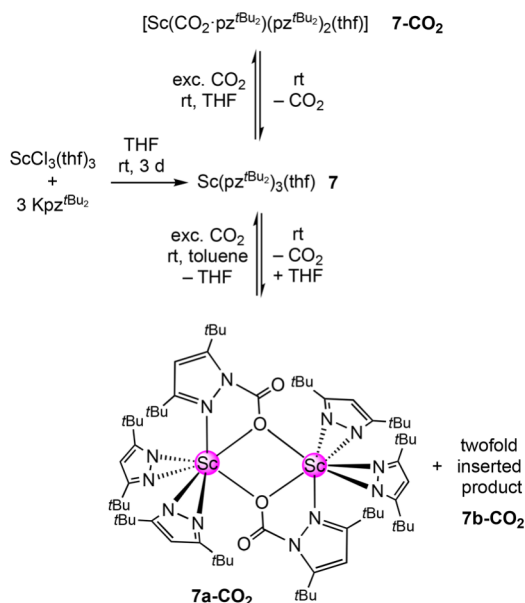
The crystal structure of **7** revealed one THF donor molecule bound to the scandium centre and three κ^2 (N,N)-coordinated pyrazolato ligands (see Fig. S107†). Unsurprisingly, the Sc–N distances are slightly longer than those in donor-free Sc(pz^{*t*Bu})₃.⁶¹ The scope of group 3 metal pyrazolates was extended to the literature known complex [Y(pz^{*Me*})₃(thf)]₂ (**9**) obtained *via* protonolysis of YCp₃ with Hpz^{*Me*}.⁶² Dimeric **9** contains two bridging and four terminal pyrazolato ligands which appear in solution ¹H and ¹³C NMR experiments as only one signal set due to fast ligand exchange. A ¹³C CP/MAS NMR experiment revealed separated signal sets for the terminal and bridging ligands (see S26†). The quaternary carbon atoms of the terminal pyrazolates even appear as four well separated signals. Applying the synthesis protocol as used for scandium complex **7**, monomeric [Y(pz^{*t*Bu})₃(thf)]₂ (**10**) was obtained. The solid-state structure of **10** revealed two THF donor molecules

bound to the metal centre, isostructural to the pyridine-stabilized derivative [Y(pz^{*t*Bu})₃(Py)₂] (see S108†).⁶⁰

Treatment of Sc(pz^{*t*Bu})₃(thf) (**7**) with 1 bar CO₂ in THF-*d*₈ gave immediate CO₂ insertion, as evidenced by ¹H NMR spectroscopy. Three signals for *t*Bu moieties appeared at $\delta = 1.51$, 1.24 and 0.77 ppm, with an integral ratio of 9:36:9, respectively, as well as two signals for pyrazolato backbone protons at $\delta = 6.15$ ppm and $\delta = 6.04$ ppm with an integral ratio of 2:1, respectively. In addition, two signals of coordinated THF were observed. These signals can be assigned to the mono-inserted donor-stabilized complex [Sc(CO₂·pz^{*t*Bu})(pz^{*t*Bu})₂(thf)] (**7**-CO₂). The ¹³C NMR spectrum shows the resonance for the inserted CO₂ at $\delta = 149.7$ ppm. The CO₂ insertion can be also tracked by ⁴⁵Sc NMR spectroscopy, since the sharp resonance of **7** at $\delta = 41.6$ ppm shifts slightly towards lower field at $\delta = 69.1$ ppm for **7**-CO₂, also involving signal broadening. Unfortunately, we were not able to isolate any crystalline material of **7**-CO₂, due to immediate complete CO₂ release in the absence of solvent, already at ambient temperature and pressure. This effective and immediate reversibility of **7**/**7**-CO₂ is a stark contrast to the aluminium derivative **1**-CO₂, where CO₂ release only occurred at elevated temperature and was not observed at reduced pressure. To further confirm CO₂ insertion into scandium pyrazolate **7**, *in situ* DRIFTS experiments were pursued. At 1 bar CO₂ atmosphere, the immediate formation of a single strong band at $\tilde{\nu} = 1759$ was observed, indicative of a C=O bond stretching vibration (see S98 and S99†). Replacing the carbon dioxide atmosphere by argon resulted in complete CO₂ deinsertion and back-formation of **7**. A VT ¹H NMR experiment uncovered a fully dynamic equilibrium between **7** and **7**-CO₂ in solution inside a closed vessel (see S31†). Starting with **7**-CO₂, even at ambient temperature, traces of **7** were detected. By gradually increasing the temperature, the conversion of **7**-CO₂ into **7** became more and more prominent and *vice versa*. Cooling the mixture to ambient temperature resulted in an almost identical ¹H NMR spectrum as that at the outset of the VT NMR experiment.

Treatment of **7** with 1 bar CO₂ in toluene-*d*₈ instead of THF-*d*₈ resulted in immediate CO₂ insertion as well. However, this time, the ¹H NMR spectrum revealed the formation of two distinct insertion products, **7a**-CO₂ and **7b**-CO₂. One species shows three signals for *t*Bu moieties (9:36:9) with chemical shifts close to **7**-CO₂, while the second species gives four *t*Bu proton signals at $\delta = 1.69$, 1.49, 0.74 and 0.49 ppm with an integral ratio of 18:9:18:9. This second species appeared to be a product with a higher degree of inserted CO₂. Correspondingly, the pyrazolato backbone protons appeared as two sets of two singlets with an integral ratio of 2:1. Furthermore, the ⁴⁵Sc NMR spectrum showed two resonances at $\delta = 165.7$ ppm and $\delta = 39.1$ ppm.

This time, single-crystalline **7a**-CO₂ could be obtained from the solution; however, like observed for **7**-CO₂, solid **7a**-CO₂ showed immediate CO₂ release at ambient temperature. Therefore, permanent cooling at –40 °C was essential for setting up and performing a successful XRD measurement. The crystal structure revealed the dimeric donor-free mono-



Scheme 5 Salt-metathesis reaction of ScCl₃(thf)₃ and Kpz^{*t*Bu} to yield donor-stabilised Sc(pz^{*t*Bu})₃(thf) (**7**). Treatment with an excess of CO₂ produces the donor-stabilised mono-insertion product [Sc(CO₂·pz^{*t*Bu})(pz^{*t*Bu})₂(thf)] (**7**-CO₂) in THF and a mixture of the mono-inserted species [Sc(CO₂·pz^{*t*Bu})(pz^{*t*Bu})₂]₂ (**7a**-CO₂) and a higher inserted species **7b**-CO₂ in toluene.



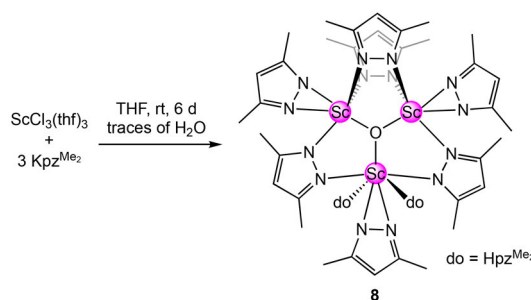
inserted species $[\text{Sc}(\text{CO}_2\cdot\text{pz}^{\text{tBu}})(\text{pz}^{\text{tBu}})_2]_2$ (**7a-CO₂**) bearing the two carbamate ligands in a $[\mu-1\kappa^2(\text{N},\text{O}):2\kappa(\text{O})]$ bridging fashion (Fig. 5). Moreover, the scandium centres accommodate two terminal $\kappa^2(\text{N},\text{N}')$ pyrazolatos. As indicated by the ^1H NMR spectrum, coordinated THF from the starting material was displaced.

The overall reversibility of the CO_2 insertion of **7a-CO₂** is akin to that of **7-CO₂**. The original NMR solution as well as isolated **7a-CO₂** redissolved in toluene- d_8 , giving similar ^1H NMR spectra, both showing small amounts of the second species **7b-CO₂**. In the absence of a CO_2 atmosphere, **7b-CO₂** seems to be unstable in solution at ambient pressure, which is why no crystalline **7b-CO₂** could be isolated. Given the *t*Bu proton signal set (integral ratio of 18 : 9 : 18 : 9), representing two carbamate ligands and one pyrazolato ligand, species **7b-CO₂** likely features the twofold CO_2 -inserted compound $[\text{Sc}(\text{CO}_2\cdot\text{pz}^{\text{tBu}})_2(\text{pz}^{\text{tBu}})]$.

Our attempts to synthesize the homoleptic scandium dimethyl pyrazolate *via* a salt-metathesis protocol $[\text{ScCl}_3(\text{thf})_3 + 3\text{Kpz}^{\text{Me}_2}]$ were unsuccessful. However, on one occasion, the trimetallic oxo-centred cluster $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2]$ (**8**) was obtained as the main product in a crystalline yield of 74% (see Scheme 6, Fig. 6).⁸²

Two scandium centres in **8** are coordinated by four pyrazolato ligands each, and one is coordinated by three pyrazolatos and two donor pyrazoles. Each scandium centre bears one terminal $\kappa^2(\text{N},\text{N}')$ pyrazolato ligand, while two scandium centres are bridged twice by $\mu-1\kappa(\text{N}):2\kappa(\text{N}')$ pyrazolatos. The scandium centre being single-bridged to the other two accommodates the two pyrazole donors. Overall, a total of one equivalent H_2O is formally required to yield complex **8**, which most likely originated from residual water in the solvent THF.

The ^1H NMR spectrum of compound **8** displays the methyl groups and the backbone protons of the pyrazolato and pyrazole ligands as one signal each, at $\delta = 2.13$ ppm and $\delta = 5.73$ ppm, respectively, which indicates rapid exchange of the ligands in solution. The two NH-protons appear as one broad



Scheme 6 Synthesis of the oxo-centred cluster $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2]$ (**8**).

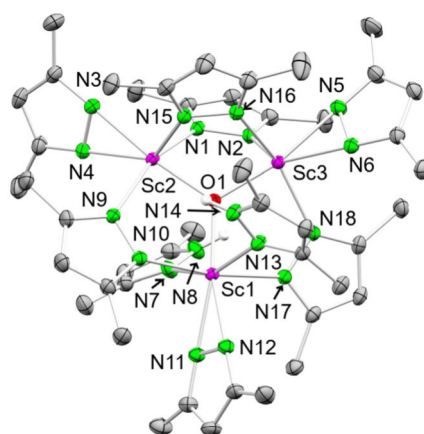


Fig. 6 Crystal structure of $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2]$ (**8**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. See ESI† for selected interatomic distances and angles.

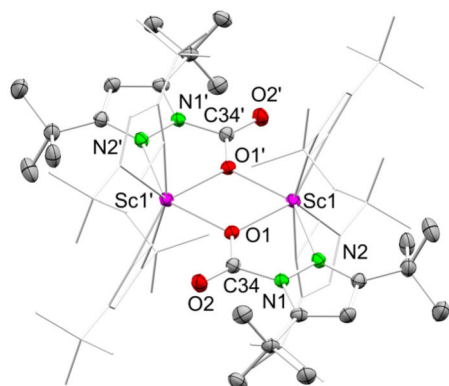


Fig. 5 Crystal structure of $[\text{Sc}(\text{CO}_2\cdot\text{pz}^{\text{tBu}})(\text{pz}^{\text{tBu}})_2]_2$ (**7a-CO₂**). Ellipsoids are set at the 50% probability level. Hydrogen atoms and disorder in the *t*Bu moieties are omitted for clarity. See ESI† for selected interatomic distances and angles.

signal at $\delta = 11.82$ ppm. As expected, the ^{45}Sc NMR spectrum features two resonances at $\delta = 153.2$ ppm and $\delta = 45.1$ ppm in a ratio of 1 : 2. More surprisingly, treatment of **8** with 1 bar CO_2 led to two well-defined products as suggested by NMR spectroscopy. One product presents the carbamic acid $\text{HO}_2\text{Cpz}^{\text{Me}_2}$ with typically broad proton and carbon signals, which we reported lately as a co-product of the reaction of mixed pyrazolato/pyrazole magnesium complexes with CO_2 or as a hydrolysis product of the carbamate complexes.²⁰ The second product **8-CO₂** appeared as three sharp signals in the ^1H NMR spectrum at $\delta = 5.95$, 2.26 and 2.18 ppm. This pattern indicates exhaustive CO_2 insertion into the oxo-cluster. This is further implied by the ^{45}Sc NMR spectrum, featuring only one signal at $\delta = 53.6$ ppm. The ^{13}C NMR spectrum revealed two signals for inserted CO_2 at $\delta = 151.2$ ppm and $\delta = 150.2$ ppm, assignable to the carbamic acid and the CO_2 -functionalized oxo cluster, respectively. However, no crystalline material of **8-CO₂** could be obtained yet, and attempts to reproduce **8** by using an equimolar amount of water in the reaction depicted in Scheme 5 were unsuccessful.

The CO_2 -inserted product of $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (**9**) shows the typical splitting of the methyl groups in the ^1H NMR spectrum (THF- d_8), resonating at $\delta = 2.18$ ppm and $\delta = 2.09$ ppm, indica-



tive of the formation of $Y(CO_2pz^{Me})_3(thf)$ (**9-CO₂**). However, several other non-assignable signals were detected along with that of putative **9-CO₂** (see Fig. S45†), most likely representing a rather complex cluster species. A VT 1H NMR study revealed that **9-CO₂** fully back-converts into **9** at 70 °C, while the unknown species remains unchanged (see Fig. S48†). Recently, we introduced a solvent-free procedure, in which the pyrazolate compound is reacted with CO₂ neat as a solid.²⁰ By using this procedure for **9**, the resulting **9-CO₂** exhibited a mass gain of 15.6 wt%. This is slightly higher than the expected value for a two-fold insertion (14.5 wt%) and lower than that for a complete insertion (20.3 wt%). Correspondingly, the ^{13}C CP/MAS spectrum of **9-CO₂** revealed two signal sets. One can be assigned to unreacted **9** and the other to putative **9-CO₂**. The chemical shifts are comparable to those observed for $[Mg(CO_2pz^{Me})_2]_n$ with a resolved signal for inserted CO₂ at 152.1 ppm. A final statement on the amount of inserted CO₂ in **9-CO₂** cannot be made. In contrast, $Y(pz^{tBu})_3(thf)_2$ (**10**) did not show any traceable CO₂ insertion into the Y–N bond at ambient temperature. Only traces of the carbamic acid HO_2Cpz^{tBu} could be detected in the 1H NMR spectrum, pointing to some Hpz^{tBu} impurities in **10** (see Fig. S51†). Overall, this indicates that yttrium complex **10** has an even less pronounced capability to bind CO₂ than the scandium congener **7**. This is also in agreement with the CO₂-insertion capability of homoleptic ceric pyrazolates $Ce(pz^{RR'})_4$ which was found to decrease in the order of $pz^{Me_2} > pz^{tBu,Me} > pz^{Ph} > pz^{tBu}$.^{8,3}

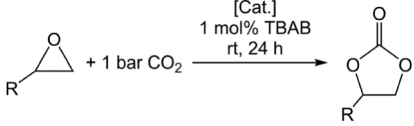
Synthesis and reactivity of unsubstituted “parent” pyrazolates of aluminium and scandium

Since the parent pyrazolate $[Mg(pz)_2]_n$ displayed an exceptionally high reversible CO₂ uptake of up to 35.7 wt%,²⁰ it was of interest to examine such reaction behaviour for the trivalent light metals. The trivalent parent pyrazolates $[Al(pz)_3]_n$ (**11**) and $[Sc(pz)_3]_n$ (**12**) were accessed *via* transamination of $Al(pz^{tBu})_3$ (**1**) and $Sc(pz^{tBu})_3(thf)$ (**7**) with Hpz in toluene, as indicated by the instant formation of a white precipitate. The ^{13}C CP/MAS spectra of amorphous **11** and **12** showed the expected signal sets (Fig. S52/S54†). The ^{27}Al CP/MAS experiment revealed a signal at 5.2 ppm (Fig. S53†) featuring the most high-field shifted signal observed for a homoleptic aluminium pyrazolate. For polymeric **12**, the ^{45}Sc resonance was resolved at 156.0 ppm (Fig. S55†). Not unexpectedly, the CO₂-uptake behaviours of **11** and **12** were in line with those of the discrete substituted pyrazolates (*vide supra*). When exposing the solids in a very simple manner to an atmosphere of 1 bar CO₂ for three hours, mass gains of 8.2 wt% for **11** and 6.9 wt% for **12** were found. However, these materials rapidly release CO₂ at atmospheric pressure, as indicated by FTIR spectroscopy.

Catalytic cycloaddition of epoxides and CO₂

Given our previous works on metal pyrazolates, we were interested in the behaviour of trivalent metal pyrazolates as catalysts in the cycloaddition of epoxides and CO₂ (Table 1). Applying the standard protocol (0.5 mol% catalyst, 1 mol% cocatalyst tetra-*n*-butylammonium bromide (TBAB), epoxide as

Table 1 Catalytic activities of trivalent metal pyrazolates in the conversion of epoxides to cyclic carbonates^{a,b}

					
Entry	Catalyst	R = Me	R = Ph	R = <i>t</i> Bu	R = <i>n</i> Bu
1	1-Al	65%	5%	2%	7%
2	4-Al	43%	8%	3%	11%
3	7-Sc	>99%	27%	24%	29%
4	9-Y	84%	20%	5%	22%
5	10-Y	97%	22%	8%	18%
6	13-Ce^{III}	96%	13%	5%	9%
7	14-Ce^{IV}	88%	23%	13%	25%

^a Reaction conditions: 1 bar CO₂, 0.5 mol% metal centre of the catalyst, 1 mol% TBAB at ambient temperature for 24 h. ^b Conversion determined by comparison of the integral protons at the α -position of the epoxide and the corresponding cyclic carbonate (expect for 3,3-dimethyl-1,2-butene carbonate where the integral of the *t*Bu moieties was used).

solvent), the catalysis was performed under 1 bar CO₂ at ambient temperature. After 24 h, the conversion was determined from the 1H NMR spectra. Pyrazolates $Al(pz^{tBu})_3$ (**1**) [$Al(pz^{iPr})_3$] (**4**), $Sc(pz^{tBu})_3(thf)$ (**7**), $[Y(pz^{Me})_3(thf)]_2$ (**9**) and $Y(pz^{tBu})_3(thf)_2$ (**10**) were employed as catalysts in addition to tetrametallic cluster $[Ce(pz^{Me})_3]_4$ (**13**) and the tetravalent $[Ce(pz^{Me})_4]_2$ (**14**) for comparison. Propylene oxide, styrene oxide, 2-*tert*-butyloxirane and 1,2-epoxyhexane were employed as substrates. Aluminium complex **1** showed only moderate catalytic activity, converting 65% of propylene oxide to the cyclic carbonate (entry 1). The sterically more demanding epoxides were only minimally converted by complex **1**, which achieved the highest conversion for 1,2-epoxyhexane (7%).

Dimeric complex **4** displayed an even lower conversion of 43% for propylene oxide, but performed slightly better in the cases of styrene oxide (8%) and 1,2-epoxyhexane (11%) (entry 2). This can be ascribed to the smaller *i*Pr groups of **4** (versus *t*Bu of **1**) in agreement with the observations made for magnesium pyrazolates.²⁰

Scandium complex **7** performed best in this cycloaddition reaction, affording 99% conversion of propylene oxide with only traces of the starting material left (entry 3). Complex **7** also exhibited the highest catalytic activity of the metal pyrazolates under study for the three other epoxides, ranging from 24 to 29%. The yttrium-based catalysts **9** and **10** provided similar results, with monomeric **10** achieving slightly higher conversions than dimeric **9**, except for 1,2-epoxyhexane (entry 4 and 5). The results obtained for the cerium-based catalysts were in line with our earlier report, showing only slight deviations.¹⁹ Strikingly, there seems to be a negative correlation between the carboxophilicity of the metal pyrazolate and its catalytic activity (Table 2). As described above, scandium carbamate **7-CO₂** releases CO₂ readily in the absence of a solvent or when placed in an open vessel. Also, under the applied conditions, mono-



Table 2 Correlation of catalytic conversion and CO₂ release temperatures (from VT ¹H NMR studies and TG measurements)

Catalyst	CO ₂ -release temperature [°C]		Catalytic convers. [%]	Oxophilicity M [Θ] ^b
	¹ H NMR start → end	TGA start → end		
15-Mg ^a	70–105	134–233	56	0.6
1-Al	100–120 ^c	114–196	65	0.8
9-Y	rt–70	60–154	84	0.8
14-Ce ^{IV}	10–60 ^a	55–95 ^a	88	0.9
13-Ce ^{III}		52–90 ^a	96	0.9
10-Y		—	97	0.8
7-Sc	rt	rt	>99	0.8

^a Previous work Mg,²⁰ Ce.¹⁹ ^b Ref. 84. ^c De-insertion not complete at this temperature, which is the upper limit of the VT NMR setup.

meric yttrium pyrazolate **10** did not insert any significant amount of CO₂, while dimeric yttrium pyrazolate **9** did insert CO₂ and displayed a CO₂-releasing step at 70 °C. Since the CO₂-release temperature range of complexes that reversibly insert CO₂ is an approximate measure of their carboxophilicity, comparison with the respective catalytic conversions clearly show that the lower the carboxophilicity, the higher the catalytic activity (Table 2). On the other hand, the carboxophilicity does not reflect the trends in the extent of the (calculated) oxophilicity (Table 2)⁸⁴ and electronegativity (Pauling scale)⁸⁵ and might be affected further by the Lewis acidity of the metal centre (Al³⁺ > Sc³⁺ > Y³⁺), as well as the carbophilicity,⁸⁶ sterics and coordination mode (terminal *versus* bridging) of the carbamate ligand. For further comparison, the average N–C(CO₂) distance in complexes **1-Al**–CO₂ (1.444(3) Å), **7-Sc**–CO₂ (1.436(2) Å), [Ce(CO₂·pz^{Me})₃]₄ (**13**–CO₂) (1.432(12) Å), [Ce(CO₂·pz^{Me})₄] (**14**–CO₂ = **A**, Fig. 1 bottom) (1.436(3) Å) and [Mg(CO₂·pz^{Me})₂(thf)₂] (**B**, Fig. 1 bottom) (1.477(1) Å) were detected in a close range.

Finally, the best-performing scandium complex **7** was examined for the cycloaddition of propylene oxide and CO₂ under varying conditions (Table 3). The aforementioned performance using the standard procedure (conversion of >99%) corresponds to a TON of >199 (entry 1). Decreasing the catalyst concentration to 0.25 mol% lowered the overall catalytic conversion to 71, but increased the TON to 284 (entry 2). Employing only 0.01 mol% of **7** at harsher reaction conditions (10 bar CO₂ and 90 °C), further increased the TON to 4600 (entry 3).

Table 3 Catalytic activity of **7** in the conversion of propylene oxide and CO₂ to cyclic carbonate under different conditions^a

Entry	<i>T</i> [°C]/ <i>p</i> [bar]	<i>C</i> (Cat.) [mol%]	Conversion ^b [%]	TON ^c
1	24/1	0.5	>99%	199
2	24/1	0.25	71%	284
3	90/10	0.01	45%	4600

^a 24 h in neat epoxide. ^b Conversion determined by comparison of the integrals protons at the α-position of the epoxide and the corresponding cyclic carbonate. ^c ((epoxide/Mg) × conversion)/100.

The TOF of **7** was determined at 120 h^{−1} over the progress of the reaction applying our standard procedure (Fig. S86 and Table S1†).

Accordingly, complete conversion (>99%) was already detected after 12 h, but already after 6 h, the conversion was noted at 96%. Using half the amount of catalyst (entry 2) did not give similarly high conversions after 6 or 10 h, pointing to the catalyst load as the determining factor. Overall, a mechanism/catalytic cycle as described for the cerium and magnesium congeners is proposed.^{19,20} To put the present catalytic results into a proper perspective, even the most active catalysts under study show only moderate catalytic activity in comparison to systems described in literature. For example, the chlorinated tetraphenyl porphyrin aluminium complex (tetra(2,4-chloro)phenylporphyrin)AlCl reaches TOFs of up to 185 200 h^{−1}.³⁶ For the rare-earth metals, the scorpionate complex [La{N(SiHMe₂)₂}₂κ³-(1-[2,2-bis(pz^{Me})-1,1-Ph₂Et]-1,3-Cp)] was noted at TOFs of 15 000 h^{−1} and TONs of up to 306 667.⁵⁷

Conclusions

The scope and feasibility of reversible metal-pyrazolate CO₂-insertion chemistry is expandable to the trivalent light metals of groups 3 and 13. The reaction behaviors of monomeric aluminium(III) and scandium(III) pyrazolates are strikingly distinct under identical conditions. While homoleptic Al(pz^{tBu})₃, bearing the comparatively small metal centre, inserts two CO₂ molecules to form Al(CO₂·pz^{tBu})₂(pz^{tBu}), Sc(pz^{tBu})₃(thf) accommodates only one molecule CO₂ per scandium, affording the dimeric complex [Sc(μ-CO₂·pz^{tBu})(pz^{tBu})₂]₂. Both complexes feature completely reversible heteroallene insertion, as revealed by FTIR and VT ¹H NMR spectroscopy and thermogravimetric analysis (TGA). Again, strikingly, the aluminium complex releases the CO₂ only at temperatures >100 °C, while the scandium complex undergoes CO₂ de-insertion at ambient temperature and pressure. The implications of the pyrazolato substituents for the extent of CO₂ insertion was demonstrated for the new homoleptic complex [Al(pz^{iPr})₃]₂, which gave exhaustive CO₂ insertion, marking a capacity of 21.6 wt% CO₂. Applying the metal pyrazolates under study as catalysts in the cycloaddition of CO₂ and epoxides to cyclic carbonates revealed an inverse correlation of the catalytic activity and carboxophilicity (=CO₂ affinity): the higher the carboxophilicity, the lower the catalytic activity. Given the reversible CO₂ insertion into metal pyrazolates, the carboxophilicity can be assessed by the CO₂-release temperature (*via* VT ¹H NMR spectroscopy and TGA). The scandium complex Sc(pz^{tBu})₃(thf) performed best, with a maximum TOF of 120 h^{−1} and a TON of 284 at ambient conditions.

Data availability

The data that support the findings of this study are available in the ESI† of this article.



Conflicts of interest

There are no conflicts of interest.

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Supporting Information

Carbon dioxide affinity (“carboxophilicity”) of trivalent light metal pyrazolates

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Experimental Section

General Considerations. All manipulations were performed under rigorous exclusion of air and moisture under argon atmosphere (< 0.1 ppm O_2 , < 0.1 ppm of H_2O) in a MB200B glovebox (MBraun) or according to standard Schlenk techniques and in oven-dried glassware. Solvents (THF, *n*-hexane and toluene) were purified by using SPS Grubbs type columns (MBraun SPS-800, solvent purification system) and stored inside a glovebox. THF was dried further over molecular sieves. $[D_8]$ toluene and $[D_8]$ THF were obtained from Sigma Aldrich and dried over Na/K alloy and filtered prior to use. $AlCl_3$ (99%), 3,5-Dimethyl pyrazole (99%), $GaCl_3$ (99%), $GaBr_3$ (99%), hydrazine hydrate and 2,2,6,6-tetramethylheptane-3,5-dione were purchased from Sigma Aldrich and used as received. Trimethylaluminium (98%) was purchased from abcr and used as received. 3,5-Di-*tert*-butylpyrazole,¹ di-*iso*-propyl pyrazole,¹ $[Ce(pz^{Me_2})_4]_2$ (ref. 2) and $[Ce(pz^{Me_2})_3]_4$ (ref. 3) and were synthesised according to procedures known in the literature. $ScCl_3(thf)_3$ was synthesised according to procedures known in the literature by using the route via Sc_2O_3 and $SOCl_2$.⁴ Argon and CO_2 were supplied by Westfalen AG. Solution 1H , ^{13}C , ^{27}Al and ^{45}Sc NMR spectra were recorded on a Bruker AVII+400 spectrometer (1H : 400.11 MHz; ^{13}C : 100.61 MHz, ^{27}Al : 104.26 MHz; ^{45}Sc : 97.19 MHz) at 299 K. The chemical shifts listed in the experimental section are referenced to solvent residual resonances in parts per million in relation to tetramethylsilane. The variable temperature 1H NMR spectra and 1H , ^{13}C , ^{27}Al and ^{45}Sc NMR spectra were recorded in a J. Young valve NMR tube on a Bruker AVII+500 spectrometer (1H : 500.13 MHz; ^{13}C : 125.76 MHz; ^{27}Al : 130.3 MHz; ^{45}Sc : 121.5 MHz). For ^{27}Al NMR spectra in general, the probe head itself gives a broad signal at around 64 ppm for the 400 MHz spectrometer and around 12 ppm for the 500 MHz spectrometer. Solid-state NMR spectra were obtained at ambient temperature on a Bruker AVIIIHD-300WB spectrometer (1H NMR 300.13 MHz, ^{13}C 75.47 MHz, ^{27}Al 78.20 MHz, ^{45}Sc 72.90 MHz) equipped with MAS (magic angle spinning) hardware using a ZrO_2 rotor with an outside diameter of 4 mm. IR spectra were recorded on a NICOLET 6700 FTIR spectrometer (Thermo Fisher Scientific). The samples were mixed with KBr powder and measured in a DRIFT cell with KBr windows. DRIFT data were converted by using the Kubelka-Munk refinement. *In situ* IR spectra were recorded on a Bruker Invenio R spectrometer with a praying mantis unit. Elementary analyses were performed on an Elementar vario MICRO cube. Single crystals were grown from saturated solutions of *n*-hexane, toluene, THF, or $[D_8]$ THF by standard techniques. Suitable single crystals from **1-CO₂**, **3**, **4**, **4a**, **5**, **7**, **7-CO₂**, **8** and **10** for X-ray structure studies were selected in a glovebox and coated with Parabar 10312 (Hampton research). Crystallographic data were measured on a Bruker APEX II DUO instrument equipped with μS micro focus sealed tube and QUAZAR optics for MoK_α radiation ($\lambda = 0.71073$ Å). The data collection strategy was determined using COSMO⁵ employing ω - and ϕ scans. Raw data were processed using APEX⁶ and SAINT,⁷ corrections for absorption effects were applied using SADABS.⁸

$Al(pz^{tBu_2})_3$ (1). The procedure and the analytical data are consistent with the literature (ref. 9). ^{27}Al NMR (130.3 MHz, $[D_8]$ THF, 26 °C): $\delta = 23.3$ ppm.

$[AlMe_2(pz^{iPr_2})]_2$ (2b). To a solution of Hpz^{iPr_2} (200.0 mg, 1.314 mmol) in 10 mL toluene a solution of $AlMe_3$ (32.6 mg, 437.9 μ mol) in 2 mL toluene was added dropwise and stirred for 24 h. The solvent was removed under reduced pressure and washed three times with 10 mL *n*-hexane. After removing the solvent under reduced pressure **2b** (60.0 mg, 144.0 μ mol, 66%) was obtained as a colourless powder. 1H NMR (400.1 MHz, $[D_8]$ THF, 26 °C): $\delta = 6.36$ (s, 2 H, 4-*H*(*pz*)), 3.36 (sept., $^3J_{H,H} = 6.73$ Hz, 4 H, *CH*(CH_3)₂), 1.31 (d, $^3J_{H,H} = 6.73$ Hz, 24 H, *CH*(CH_3)₂), -0.62 (s, 12 H, *Al*(CH_3)₂) ppm. Elemental analysis calcd. (%) for $C_{22}H_{42}Al_2N_4$ (416.57 g mol⁻¹): C 63.43, H 10.16, N 13.45; found: C 63.68, H 10.16, N 13.68.

$[Al(N,N',N''-Al\{pz^{Me_2}\}_3Me)_2][Al(pz^{Me_2})_3Me]$ (3). To a solution of Hpz^{Me_2} (200.0 mg, 2.081 mmol) in 10 mL toluene a solution of $AlMe_3$ (50.0 mg, 693.5 μ mol) in 2 mL toluene was added dropwise in a pressure tube. The solution was heated to 130 °C and stirred for 4 d. After cooling to ambient temperature colourless crystals were grown suitable for an X-ray structure analysis. The supernatant solution was separated and the crystalline material was dried under reduced pressure. Compound **3** was obtained as a colourless powder in a quantitative yield. ^{27}Al NMR (104.3 MHz, $[D_8]$ THF, 26 °C): $\delta = 75.7$ (Me $Al(pz_3)$), 0.3 (*Al*(pz_3)₂) ppm. DRIFTS: $\tilde{\nu}_{max} = 3118$ (m, *CH*(aryl)), 3052 (w), 2978 (m), 2954 (m), 2928 (s), 2867 (m), 2814 (vw), 2744 (vw), 1577 (w), 1541 (vs), 1506 (m), 1419 (vs), 1370 (m), 1328 (s), 1316 (vs), 1208 (vw), 116 (s), 1124 (vs), 1090 (m), 1055 (vs), 1042 (s), 1015 (s), 988 (m), 971 (s), 821 (s), 791 (vs), 776 (s), 756 (m), 746 (s), 671 (m), 595 (m), 530 (s), 505 (s), 482 (s), 461 (m), 411 (m), 402 (m) cm⁻¹. $C_{48}H_{72}Al_4N_{18}$ (1009.16 g mol⁻¹): C 58.21, H 7.57, N 23.96; found: C 58.27, H 6.87, N 26.74. The hydrogen and nitrogen results are outside the range for analytical purity, but no better elemental analysis could be obtained to current date, due to co-crystallization of excess Hpz^{Me_2} and the high nitrogen content.

[Al(pz^{iPr₂})₃]₂ (4). AlCl₃ (87.0 mg, 653 μmol) and Kpz^{iPr₂} (372.5 mg, 1.958 mmol) were dissolved in 15 mL THF and stirred for 6 d. The solvent was removed under reduced pressure and the residue was extracted three times with *n*-hexane. The solution was concentrated and stored at –40 °C. Overnight single crystals formed suitable for an X-ray structure analysis. After separation of the supernatant solution and drying of the crystals under reduced pressure, **4** could be obtained as a colourless powder (142.8 mg, 149 μmol, 46%). ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 6.27 (s, 2 H, 4-*H*(μ-pz)), 5.89 (s, 4 H, 4-*H*(pz)), 2.99 (sept., ³J_{H,H}=6.77 Hz, 4 H, CH(CH₃)₂(μ-pz)), 2.68 (sept., ³J_{H,H}=6.89 Hz, 8 H, CH(CH₃)₂(pz)), 1.04 (d, ³J_{H,H}=6.89 Hz, 48 H, CH(CH₃)₂(pz)), 1.04 (d, ³J_{H,H}=6.77 Hz, 24 H, CH(CH₃)₂(μ-pz)) ppm. ¹³C{H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 167.3 (3/5-C (μ-pz)), 161.5 (3/5-C (pz)), 101.7 (4-C (μ-pz)), 99.4 (4-C (pz)), 27.8 (CH(CH₃)₂ (pz)), 27.7 (CH(CH₃)₂ (μ-pz)), 24.0 (CH(CH₃)₂ (pz)), 23.4 (CH(CH₃)₂ (μ-pz)) ppm. ²⁷Al NMR (104.26 MHz, [D₈]THF, 26 °C): δ = 68.1 ppm. $\tilde{\nu}_{\text{max}}$ = 2963 (vs), 2928 (s), 2908 (m), 2868 (m), 1534 (s), 1518 (w), 1495 (w), 1459 (m), 1423 (w), 1380 (m), 1360 (m), 1300 (w), 1283 (w), 1266 (w), 1179 (w), 1167 (w), 1141 (m), 1107 (m), 1071 (w), 1054 (m), 1030 (w), 991 (w), 926 (vw), 879 (vw), 800 (w), 731 (w), 720 (w), 693 (vw), 596 (w), 561 (w), 540 (m), 504 (w), 483 (w), 440 (w) cm⁻¹. C₅₄H₉₀Al₂N₁₂ (961.36 g mol⁻¹): C 67.47, H 9.44, N 17.48; found: C 67.80, H 9.44, N 17.65.

[Al(pz^{iPr₂})₃(Hpz^{iPr₂})]₂ (4a). Compound **4b** was obtained as a crystalline side product in the synthesis of **4** due to residual water in the solvent THF. ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 5.99 (s, 4 H, 4-*H*(pz)), 2.75 (sept., ³J_{H,H}=6.89 Hz, 8 H, CH(CH₃)₂), 1.12 (d, ³J_{H,H}=6.89 Hz, 48 H, CH(CH₃)₂) ppm.

[Ga(pz^{tBu₂})(μ-N,N,C-pz^{tBu,C(CH₃)₂CH₂)]₂ (5).} GaCl₃ (31 mg, 178 μmol) and Kpz^{tBu₂} (125 mg, 534 μmol) were dissolved in 15 mL THF and stirred for 6 d. The solvent was removed under reduced pressure and the residue was extracted three times with THF. The solution was concentrated and stored at –40 °C. Overnight a few colourless single crystals of **5** formed suitable for an X-ray structure analysis. NMR studies showed a complicated product mixture.

[GaMe₂(pz^{tBu₂})]₂. To a solution of Hpz^{tBu₂} (236 mg, 1.306 mmol) in 10 mL toluene a solution of GaMe₃ (50 mg, 435 μmol) in 2 mL toluene was added dropwise and stirred overnight. The solvent was removed under reduced pressure and washed three times with 10 mL *n*-hexane. After removing the solvent under reduced pressure [GaMe₂(pz^{tBu₂})]₂ was obtained as colourless crystals in a quantitative yield. ¹H NMR (400.1 MHz, [D₈]Tol, 26 °C): δ = 6.19 (s, 2 H, 4-*H*(pz)), 1.33 (s, 36 H, C(CH₃)₃), –0.23 (s, 6 H, Ga(CH₃)₂) ppm.

Al(CO₂·pz^{tBu₂})₂(pz^{tBu₂}) (1-CO₂). A solution of Al(pz^{tBu₂})₃ (300.0 mg, 531 μmol) in THF was stirred under 1 bar CO₂ for 16 h and stored under ambient temperature. By evaporating the solvent slowly under glovebox atmosphere colourless crystals were obtained suitable for an X-ray structure analysis. The supernatant solution was separated, the residue was dried for 2 h at glove box atmosphere and **1-CO₂** was obtained as a white powder (304.0 mg, 465 μmol, 88%). ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 6.32 (s, 2 H, 4-*H* (CO₂·pz)), 6.00 (s, 1 H, 4-*H* (pz)), 1.50 (s, 18 H, 3-C(CH₃)₃ (CO₂·pz)), 1.05 (s, 18 H, 3-C(CH₃)₃ (CO₂·pz)), 1.05 (s, 18 H, 3/5-C(CH₃)₃ (pz)) ppm. ¹³C{H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 161.9 (5-C (CO₂·pz)), 161.8 (5-C (pz)), 156.7 (3-C (CO₂pz)), 146.9 (CO₂), 108.2 (4-C (CO₂pz)), 102.5 (4-C (pz)), 34.0 (3-C(CH₃)₃ (CO₂·pz)), 33.2 (5-C(CH₃)₃ (CO₂·pz)), 32.5 (3/5-C(CH₃)₃ (pz)), 31.0 (3/5-C(CH₃)₃ (pz)), 30.3 (5-C(CH₃)₃ (CO₂·pz)), 29.2 (3-C(CH₃)₃ (CO₂·pz)) ppm. ²⁷Al NMR (130.3 MHz, [D₈]THF, 26 °C): δ = 17.0 ppm. DRIFT: $\tilde{\nu}_{\text{max}}$ = 3144 (vw), 2968 (s), 2912 (w), 2871 (w), 1774 (vs), 1763 (vs), 1722 (w), 1543 (w), 1508 (w), 1480 (w), 1462 (m), 1431 (m), 1397 (vw), 1363 (m), 1328 (vs), 1314 (s), 1289 (vs), 1253 (s), 1233 (w), 1215 (w), 1191 (m), 1159 (m), 1066 (s), 1018 (s), 999 (w), 931 (w), 880 (vs), 866 (s), 835 (vs), 822 (w), 805 (w), 779 (m), 720 (vw), 699 (w), 632 (vw), 575 (vs), 562 (vs), 539 (w), 512 (vs), 482 (w), 428 (m) cm⁻¹. Elemental analysis calcd. (%) for C₃₅H₅₇AlN₆O₄ (652.84 g mol⁻¹): C 64.39, H 8.80, N 12.87; found: C 64.19, H 8.15, N 13.10.

[Al(CO₂·pz^{iPr₂})₃]_x (4-CO₂). A solution of [Al(pz^{iPr₂})₃]₂ (**4**). (20 mg, 21 μmol) in 0.5 mL THF-d₈ placed in a J.Young NMR tube was put under 1 bar CO₂ atmosphere. A complete CO₂ insertion was observed in the ¹H NMR. However, **4-CO₂** could not be isolated as a solid. ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 6.50 (4-*H* (pz)), 6.35 (4-*H* (pz)), 6.31 (4-*H* (pz)), 3.86 (CH(CH₃)₂), 3.58 (CH(CH₃)₂), 3.35 (CH(CH₃)₂), 1.96 (CH(CH₃)₂), 1.27 (CH(CH₃)₂), 1.14 (CH(CH₃)₂), 0.92 (CH(CH₃)₂), 0.86 (CH(CH₃)₂), 0.79 (CH(CH₃)₂) ppm. ¹³C{H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 162.3 (3-C(pz)), 160.9 (3-C(pz)), 159.5 (3-C(pz)), 156.5 (5-C(pz)), 155.8 (5-C(pz)), 155.6 (5-C(pz)), 147.0 (CO₂), 146.6 (CO₂), 146.6 (CO₂), 105.7 (4-C(pz)), 104.6 (4-C(pz)), 103.9 (4-C(pz)), 26.8 (CH(CH₃)₂), 26.7 (CH(CH₃)₂), 26.5 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 23.1 (CH(CH₃)₂), 22.5 (CH(CH₃)₂), 22.4 (CH(CH₃)₂), 22.2 (CH(CH₃)₂), 21.8 (CH(CH₃)₂), 21.3 (CH(CH₃)₂) ppm. ²⁷Al NMR (130.3 MHz, [D₈]THF, 26 °C): δ = 12.1 ppm.

Sc(pz^{tBu₂})₃(thf) (7). ScCl₃(thf)₃ (143.8 mg, 391 μmol) and Kpz^{tBu₂} (275.1 mg, 1.173 mmol) were dissolved in 15 mL THF and stirred for 3 d. The solvent was removed under reduced pressure and the residue was extracted three times with *n*-hexane. The solution was concentrated and stored under –40 °C. Overnight single crystals were grown suitable for an X-ray structure analysis. After separation of the supernatant solution and drying of the crystals under reduced pressure, **7** could be obtained as a colourless powder (210.0 mg, 321 μmol, 82%). ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 6.06 (s, 3 H, 4-*H*(pz)), 3.62 (m, 4 H, 1,4-CH₂(thf)), 1.77 (m, 4 H, 2,3-CH₂(thf)), 1.20 (s, 54 H, C(CH₃)₃) ppm. ¹³C{H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 158.9 (3/5-*C*(pz)), 103.0 (4-*C*(pz)), 67.7 (1,4-CH₂(thf)), 32.4 (C(CH₃)₃), 31.5 (C(CH₃)₃), 25.6 (3,4-*C*(thf)) ppm. ⁴⁵Sc NMR (121.5 MHz, [D₈]THF, 26 °C): δ = 41.6 ppm. DRIFTS: $\tilde{\nu}_{\text{max}}$ = 3115 (vw, CH(aryl)), 2963 (vs), 2929 (s), 2902 (s), 2867 (s), 1520 (m), 1505 (s), 1459 (s), 1434 (m), 1415 (w), 1387 (w), 1359 (s), 1310 (w), 1252 (m), 1229 (m), 1205 (w), 1108 (vw), 1020 (m), 997 (m), 952 (vw), 919 (w), 871 (m), 825 (vw), 796 (m), 724 (w), 682 (vw), 628 (vw), 562 (vw), 538 (w), 478 (m) cm⁻¹. C₃₇H₆₅N₆O₅Sc (654.92 g mol⁻¹): C 67.86, H 10.00, N 12.83; found: C 67.12, H 9.70, N 12.42. The carbon value is outside the range for analytical purity, but no better elemental analysis could be obtained to date, due to residual THF.

[Y(pz^{Me₂})₃(thf)]₂ (9). YCl₃(thf)_{2.5} (200.0 mg, 446 μmol) and Kpz^{tBu₂} (179.9 mg, 1340 μmol) were dissolved in 15 mL THF and stirred for 3 d. The solvent was removed under reduced pressure and the residue was extracted three times with *n*-hexane. The solution was concentrated and stored under –40 °C. Overnight single crystals were grown suitable for an X-ray structure analysis. After separation of the supernatant solution and drying of the crystals under reduced pressure **9** could be obtained as a colourless powder (138.1 mg, 309 μmol, 69%). ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 5.86 (s, 3 H, 4-*H*(pz)), 3.62 (m, 4 H, 1,4-CH₂(thf)), 2.18 (s, 18 H, CH₃), 1.77 (m, 4 H, 2,3-CH₂(thf)) ppm. ¹³C{H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 144.9 (3/5-*C*(pz)), 107.4 (4-*C*(pz)), 68.0 (1,4-CH₂(thf)), 26.2 (2,3-CH₂(thf)), 13.2 (CH₃) ppm. ¹³C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): 148.8 (3/5-*C*(pz)), 145.6 (3/5-*C*(pz)), 144.9 (3/5-*C*(pz)), 143.7 (3/5-*C*(pz)), 111.3 (4-*C*(η-pz)), 105.0 (4-*C*(μ-pz)), 72.2 (1,4-CH₂(thf)), 24.5 (2,3-CH₂(thf)), 15.5 (CH₃(μ-pz)), 15.0 (CH₃(μ-pz)), 13.6 (CH₃(η-pz)) ppm.

[Y(pz^{tBu₂})₃(thf)₂] (10). YCl₃(thf)_{2.5} (100.0 mg, 266 μmol) and Kpz^{tBu₂} (174.4 mg, 799 μmol) were dissolved in 15 mL THF and stirred for 3 d. The solvent was removed under reduced pressure and the residue was extracted three times with *n*-hexane. The solution was concentrated and stored under –40 °C. Overnight single crystals were grown suitable for an X-ray structure analysis. After separation of the supernatant solution and drying of the crystals under reduced pressure **10** could be obtained as a colourless powder (171.1 mg, 189 μmol, 71%). ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 6.05 (s, 3 H, 4-*H*(pz)), 3.62 (m, 4 H, 1,4-CH₂(thf)), 1.77 (m, 4 H, 2,3-CH₂(thf)), 1.22 (s, 54 H, C(CH₃)₃) ppm. ¹³C{H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 159.2 (3/5-*C*(pz)), 101.6 (4-*C*(pz)), 68.0 (1,4-CH₂(thf)), 32.4 (C(CH₃)₃), 31.6 (C(CH₃)₃), 26.2 (2,3-CH₂(thf)) ppm. C₄₁H₇₃N₆O₂Y (770.98 g mol⁻¹): C 63.87, H 9.54, N 10.90; found: C 64.42, H 9.32, N 11.05.

[Sc(CO₂·pz^{tBu₂})(pz^{tBu₂})₂(thf)]₂ (7-CO₂). A solution of Sc(pz^{tBu₂})₃(thf) (**7**) (20 mg, 34 μmol) in 0.5 mL THF-d₈ in a J.Young NMR tube was put under 1 bar CO₂ atmosphere. While, a CO₂ insertion was observed in the ¹H NMR spectrum, **7-CO₂** could not be isolated as a solid, due to immediate CO₂ release in the absence of a solvent. ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 6.15 (s, 2 H, 4-*H*(pz)), 6.04 (s, 1 H, 4-*H*(CO₂pz)), 3.62 (m, 4 H, 1,4-CH₂(thf)), 1.77 (m, 4 H, 2,3-CH₂(thf)), 1.51 (s, 9 H, C(CH₃)₃(CO₂pz)), 1.24 (s, 36 H, C(CH₃)₃(pz)), 0.77 (s, 9 H, C(CH₃)₃(CO₂pz)) ppm. ¹³C{H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 160.5 (3/5-*C* (CO₂·pz)), 159.4 (3/5-*C* (pz)), 157.0 (3/5-*C* (CO₂·pz)), 149.7 (CO₂), 104.9 (4-*C*(pz)), 104.6 (4-*C*(CO₂·pz)), 68.2 (1,4-*C*(thf)), 34.1 (C(CH₃)₃(CO₂·pz)), 32.6 (C(CH₃)₃(pz)), 32.4 (C(CH₃)₃(CO₂·pz)), 31.5 (C(CH₃)₃(pz)), 30.2 (C(CH₃)₃(CO₂·pz)), 29.7 (C(CH₃)₃(CO₂·pz)), 26.4 (2,3-*C*(thf)) ppm. ⁴⁵Sc NMR (121.5 MHz, [D₈]THF, 26 °C): δ = 69.1 ppm. For an IR spectrum, see S99. Elemental analysis was not feasible due to immediate CO₂ release upon drying the CO₂-inserted compound.

[Sc(CO₂·pz^{tBu₂})(pz^{tBu₂})₂]₂ (7a-CO₂). A solution of Sc(pz^{tBu₂})₃(thf) (**7**) (20 mg, 34 μmol) in 0.5 mL toluene-d₈ in a J.Young NMR tube was put under 1 bar CO₂ atmosphere. A complete insertion was observed in the ¹H NMR spectrum. Overnight single crystals of **7a-CO₂** were grown suitable for an X-ray structure analysis. ¹H NMR (500.1 MHz, [D₈]Tol, 26 °C): δ = 6.29 (s, 4 H, 4-*H*(pz)), 5.92 (s, 2 H, 4-*H*(CO₂·pz)), 1.67 (s, 18 H, 5-*C*(CH₃)₃(CO₂·pz)), 1.39 (s, 72 H, C(CH₃)₃(pz)), 0.78 (s, 18 H, 3-*C*(CH₃)₃(CO₂·pz)) ppm. ¹³C{H} NMR (100.6 MHz, [D₈]Tol, 26 °C): δ = 159.9 (3-*C* (CO₂·pz)), 159.1 (3/5-*C* (pz)), 156.9 (5-*C* (CO₂·pz)), 148.6 (CO₂), 104.7 (4-*C*(pz)), 103.9 (4-*C*(CO₂·pz)), 33.9 (5-CC(CH₃)₃(CO₂·pz)), 31.9 (3CC(CH₃)₃(CO₂·pz)), 31.4 (3/5-CC(CH₃)₃(pz)), 30.6 (C(CH₃)₃(pz)), 30.0 (3-CC(CH₃)₃(CO₂·pz)), 29.3 (5-CC(CH₃)₃(CO₂·pz)) ppm. ⁴⁵Sc NMR (97.19 MHz, [D₈]Tol, 26 °C): δ = 39.1 ppm. For an IR

spectrum, see S99. Elemental analysis was not feasible due to immediate CO₂ release upon drying the CO₂-inserted compound.

[Sc₃O(pz^{Me₂})₇(Hpz^{Me₂})₂] (8). ScCl₃(thf)₃ (113.8 mg, 310 μmol) and Kpz^{Me₂} (124.7 mg, 929 μmol) were dissolved in 15 mL THF and stirred for 6 d. The solvent was removed under reduced pressure and the residue was extracted three times with THF. The solution was concentrated and stored under -40 °C. Overnight single crystals were grown suitable for an X-ray structure analysis. After separation of the supernatant solution and drying of the crystals under reduced pressure, **8** could be obtained as a colourless powder (75.4 mg, 75 μmol, 72%). ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 12.38 (s, 2 H, NH), 5.74 (s, 9 H, 4-H(pz)), 2.14 (s, 54 H, C(CH₃)₃) ppm. ¹³C{H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 143.6 (3/5-C(pz)), 105.3 (4-C(pz)), 11.7 (CH₃) ppm. ⁴⁵Sc NMR (121.5 MHz, [D₈]THF, 26 °C): δ = 153.2 (ScO(pz)₃(Hpz)₂), 45.1 (ScO(pz)₄) ppm.

[Y(CO₂·pz^{Me₂})₃(thf)]₂ (9-CO₂). Route A: A solution of [Y(pz^{Me₂})₃(thf)]₂ (**9**) (30 mg, 40 μmol) in 0.5 mL THF-d₈ placed in a J.Young NMR tube was put under 1 bar CO₂ atmosphere. A complete insertion was observed in the ¹H NMR spectrum. However, a crystalline material of **9-CO₂** could not be isolated. Route B: A Schlenk tube was loaded with solid [Y(pz^{Me₂})₃(thf)]₂ (**9**) and the atmosphere changed to 1 bar CO₂. After 3 h **9-CO₂** could be collected as a white powder in quantitative yield. ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 5.66 (s, 3 H, 4-H(pz)), 3.62 (m, 4 H, 1,4-CH₂(thf)), 2.18 (s, 9 H, CH₃), 2.09 (s, 9 H, CH₃), 1.77 (m, 4 H, 2,3-CH₂(thf)) ppm. ¹³C{H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 148.4 (3-C (pz)), 138.6 (5-C (pz)), 103.4 (4-C (pz)), 68.0 (1,4-C(thf)), 26.2 (2,3-CH₂(thf)), 13.1 (5-CCH₃ (pz)), 10.4 (3-CCH₃ (pz)) ppm. ¹³C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz): δ = 152.1 (CO₂), 149.6 (5-C(pz)), 143.8 (3-C(pz)), 109.5 (4-C(pz)), 67.2 (1,4-C(thf)), 25.1 (2,3-CH₂(thf)), 12.8 (CH₃) ppm. DRIFTS: $\tilde{\nu}_{\max}$ = 3327 (vw), 3145 (vw), 3107 (vw), 2981 (w), 2926 (w) 2870 (w), 1729 (vs), 1702 (vs), 1686 (vs), 1561 (m), 1521 (vw), 1467 (m), 1415 (m), 1368 (s), 1341 (s), 1300 (s), 1213 (m), 1158 (vw), 1133 (m), 1068 (w), 1042 (s), 983 (m), 913 (vw), 834 (s), 791 (m), 727 (vw), 663 (vw), 632 (w), 607 (vw), 577 (vw), 477 (w), 456 (w), 426 (w), 407 (vw) cm⁻¹.

[Al(pz)₃]_n (10). To a solution of Al(pz^{tBu₂})₃ (**1**) (228 mg, 404 μmol) in 8 mL toluene a solution of Hpz (83 mg, 121 μmol) in 8 mL toluene was added dropwise. An immediate formation of a white precipitate was observed. The reaction mixture was stirred for an additional 4 h. The solvent was removed under reduced pressure and the residue was washed three times with *n*-hexane. After drying the residue under reduced pressure **10** could be obtained as a white powder (71 mg, 310 μmol, 77%). ¹³C CP/MAS (75.47 MHz, MAS at 8 kHz): δ = 139.8 (3/5-C(pz)), 102.4 (4-C(pz)) ppm. ²⁷Al CP/MAS (78.20 MHz, MAS at 8 kHz): δ = 5.2 ppm. DRIFTS: $\tilde{\nu}_{\max}$ = 1502 (m), 1425 (w), 1411 (vw), 1397 (s), 1354 (vw), 1278 (m), 1252 (vw), 1184 (w), 1172 (w), 1066 (vs), 976 (vw), 945 (vw), 927 (vw), 894 (vw), 764 (s), 628 (s), 480 (m), 444 (m) cm⁻¹. C₉H₉N₆Al (228.19 g mol⁻¹): C 47.37, H 3.98, N 36.83; found: C 50.12, H 4.68, N 33.93. The values are outside the range for analytical purity, but no better elemental analysis could be obtained to date, due to the high nitrogen content and residual **1**, which is visible in the solid-state NMR spectra.

[Sc(pz)₃]_n (11). To a solution of Sc(pz^{tBu₂})₃(thf) (**7**) (200 mg, 270 μmol) in 8 mL toluene a solution of Hpz (84 mg, 124 μmol) in 8 mL toluene was added dropwise. An immediate formation of a white precipitate was observed. The reaction mixture was stirred for an additional 4 h. The solvent was removed under reduced pressure and the residue was washed three times with *n*-hexane. After drying the residue under reduced pressure **11** could be obtained as a white powder in quantitative yield. ¹³C CP/MAS (75.47 MHz, MAS at 8 kHz): δ = 139.5 (3/5-C(pz)), 102.9 (4-C(pz)) ppm. ⁴⁵Sc CP/MAS (72.90 MHz, MAS at 8 kHz): δ = 156.0 ppm. DRIFTS: $\tilde{\nu}_{\max}$ = 1493 (vs), 1444 (w), 1412 (vs), 1367 (vs), 1257 (vs), 1240 (m), 1156 (vs), 1074 (m), 1041 (vs), 962 (s), 920 (m), 882 (w), 762 (vs), 730 (w), 695 (vw), 619 (vs), 465 (vw) cm⁻¹. C₉H₉N₆Sc (246.17 g mol⁻¹): C 43.91, H 3.69, N 34.14; found: C 48.35, H 4.52, N 28.83. The values are outside the range for analytical purity, but no better elemental analysis could be obtained to date, due to the high nitrogen content and residual **7**, which is visible in the solid-state NMR spectra.

[Al(CO₂·pz)_x(pz)_{3-x}]_n (10-CO₂). A Schlenk tube was loaded with solid [Al(pz)₃]_n (78.57 mg, 495.9 μmmol) and the atmosphere was changed to 1 bar CO₂. Overnight **10-CO₂** could be collected as a white powder in quantitative yield. DRIFTS: $\tilde{\nu}_{\max}$ = 1767 (w), 1503 (vw), 1425 (vw), 1397 (m), 1353 (vw), 1278 (m), 1185 (vw), 1173 (vw), 1067 (vs), 977 (vw), 956 (vw), 838 (vw), 762 (m), 627 (m), 480 (vw), 446 (vw) cm⁻¹.

General procedure of the catalysis of epoxides to cyclic carbonates. As a representative example: a small Schlenk tube was charged with Al(pz^{tBu₂})₃ (10.0 mg, 17 μmol) and TBAB (11.4 mg, 35 μmol) and dissolved in the

corresponding epoxide (3.541 mmol). The atmosphere was exchanged with 1 bar CO₂ and the reaction mixture was stirred for 24 h. The state of the conversion from the epoxide to the cyclic carbonate was determined via ¹H NMR by dissolving the reaction mixture in CDCl₃.

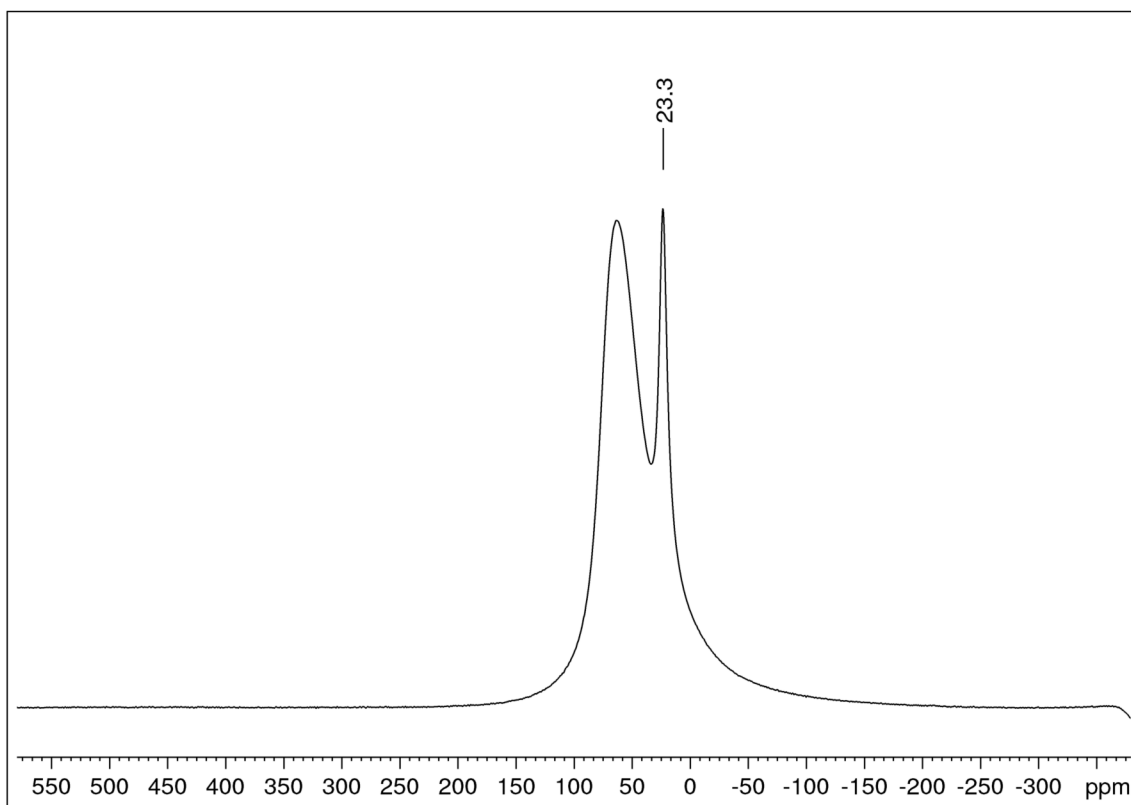


Figure S1. ^{27}Al NMR spectrum (26 °C, 130.32 MHz, $[\text{D}_8]\text{THF}$) of $\text{Al}(\text{pz}^{\text{tBu}_2})_3$ (**1**).

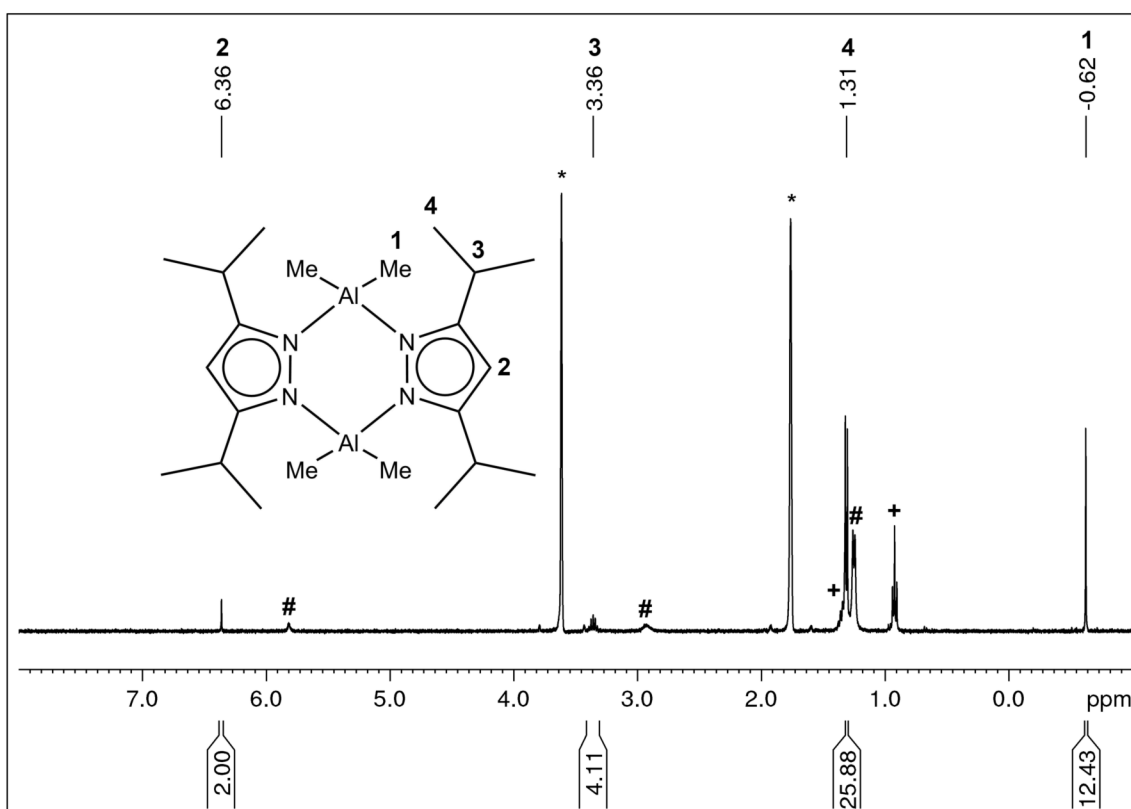


Figure S2. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{AlMe}_2\text{pz}^{\text{iPr}_2}]_2$ (**2b**) (*n*-hexane, H_2O).

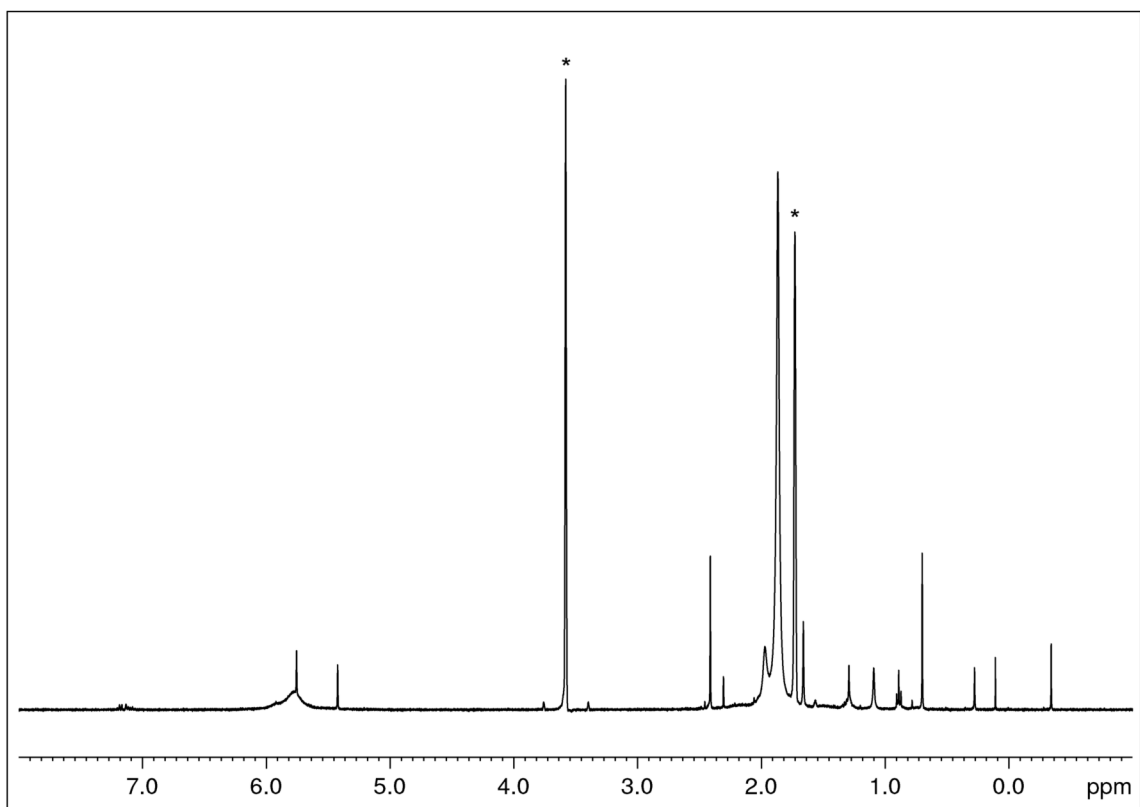


Figure S3. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Al}(\text{N},\text{N}',\text{N}''\text{-Al}\{\text{pz}^{\text{Me}_2}\}_3\text{Me})_2][\text{Al}(\text{pz}^{\text{Me}_2})_3\text{Me}]$ (**3**).

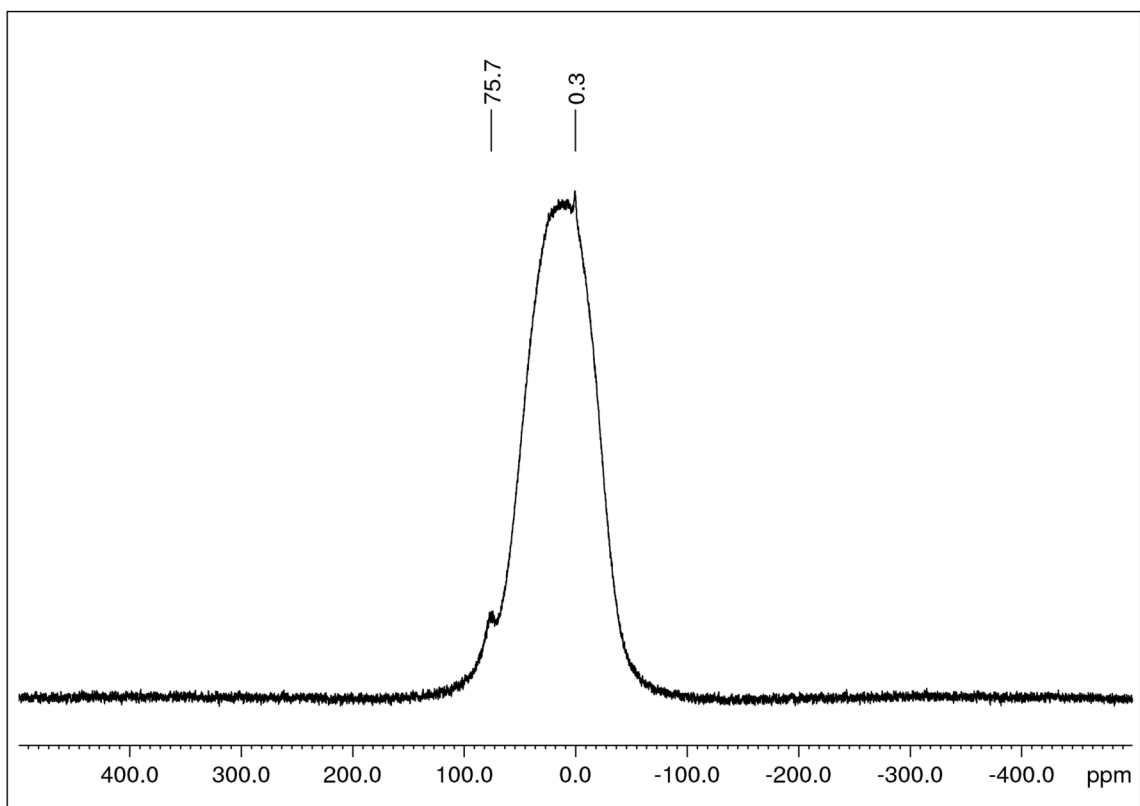


Figure S4. ^{27}Al NMR spectrum (26 °C, 104.26 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Al}(\text{N},\text{N}',\text{N}''\text{-Al}\{\text{pz}^{\text{Me}_2}\}_3\text{Me})_2][\text{Al}(\text{pz}^{\text{Me}_2})_3\text{Me}]$ (**3**).

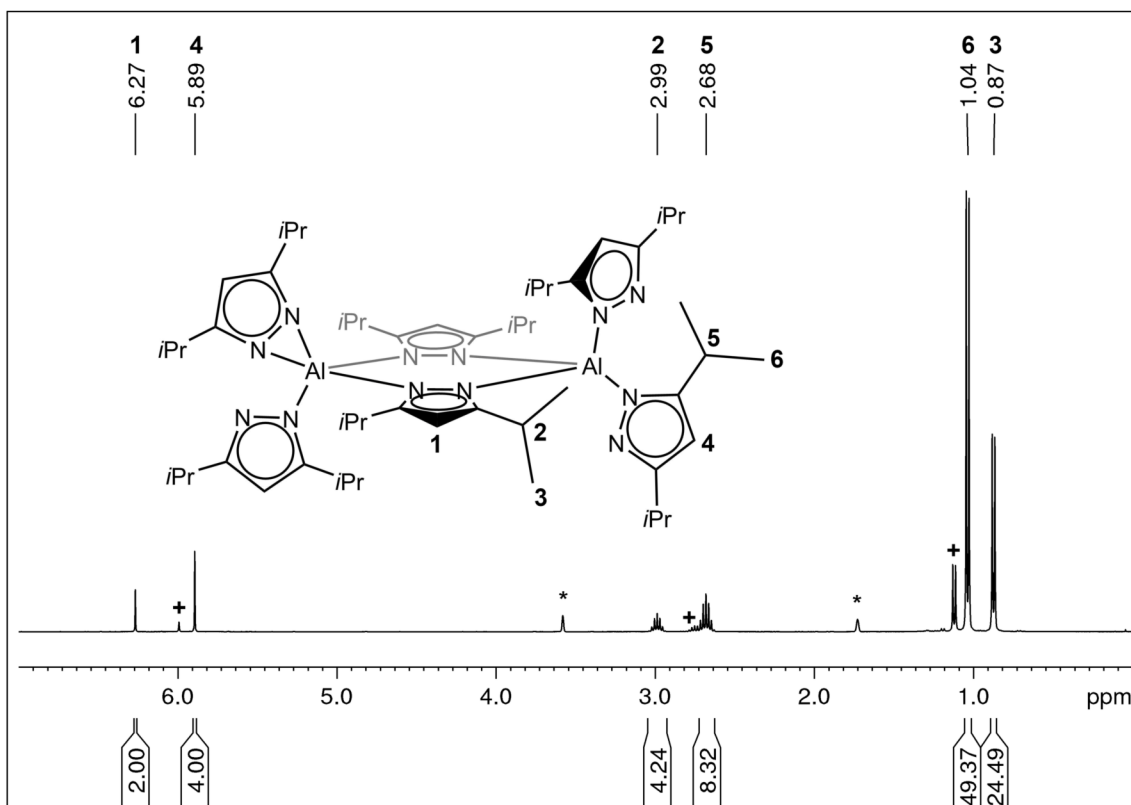


Figure S5. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Al}(\text{pz}^{\text{iPr}_2})_3]_2$ (**4**) (+ $\text{Al}(\text{pz}^{\text{iPr}_2})_3(\text{Hpz}^{\text{iPr}_2})$ (**4a**)).

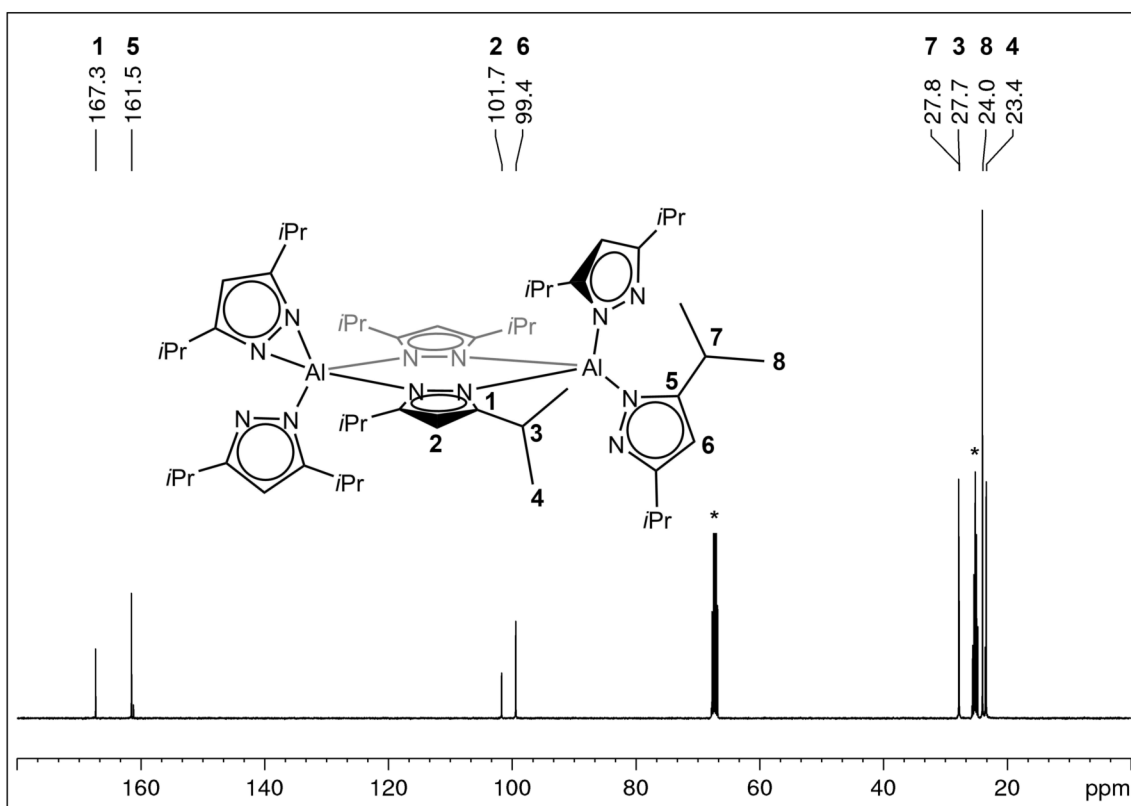


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 100.61 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Al}(\text{pz}^{\text{iPr}_2})_3]_2$ (**4**).

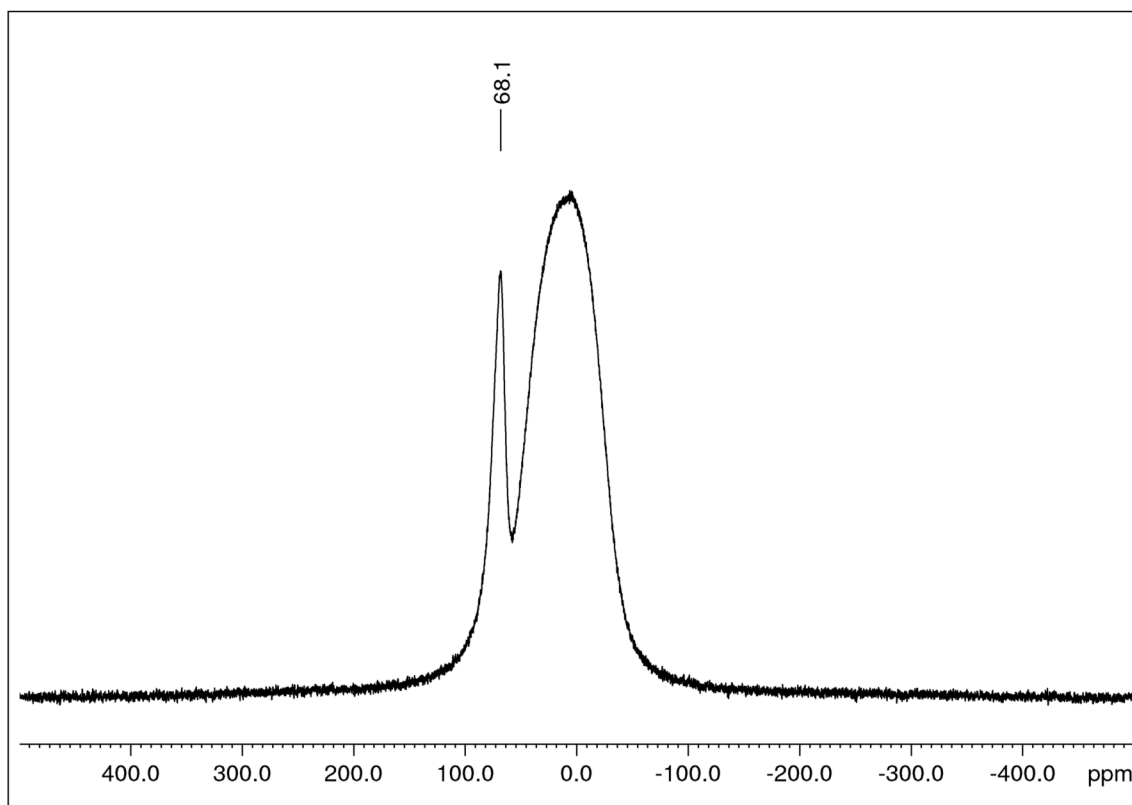


Figure S7. ^{27}Al NMR spectrum (26 °C, 104.26 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Al}(\text{pz}^{\text{iPr}_2})_3]_2$ (**4**).

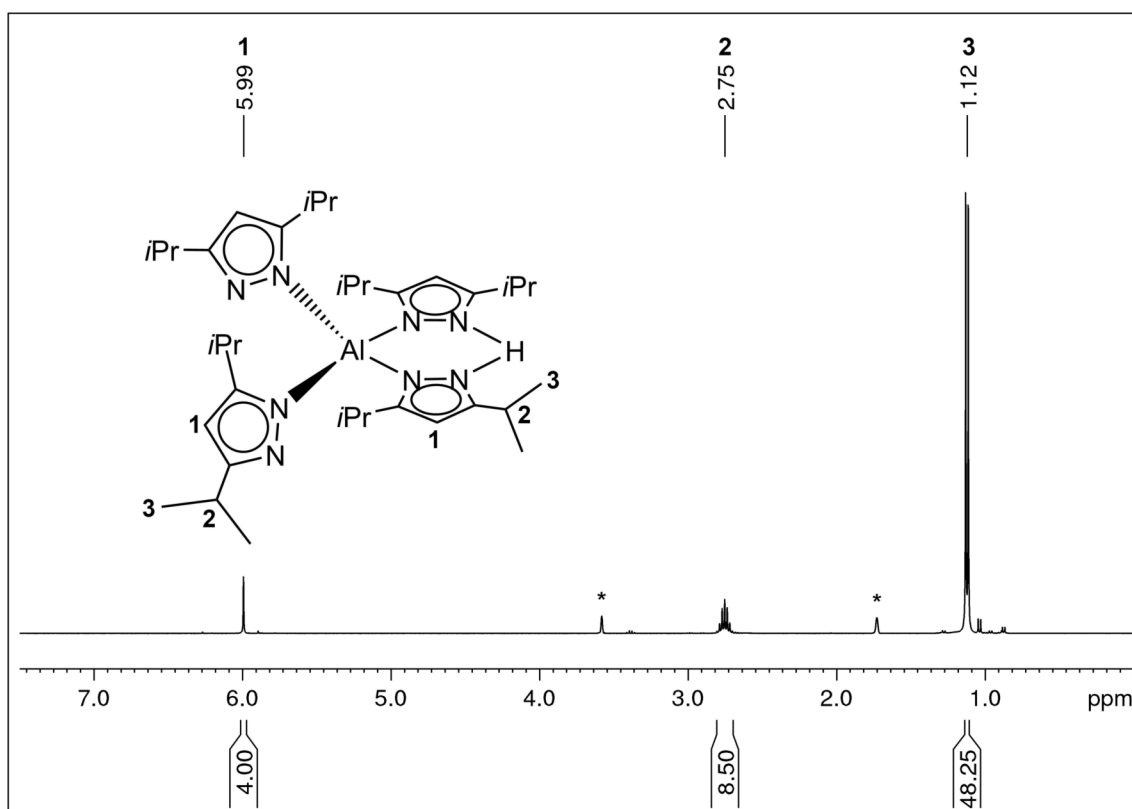


Figure S8. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $\text{Al}(\text{pz}^{\text{iPr}_2})_3(\text{Hpz}^{\text{iPr}_2})$ (**4a**).

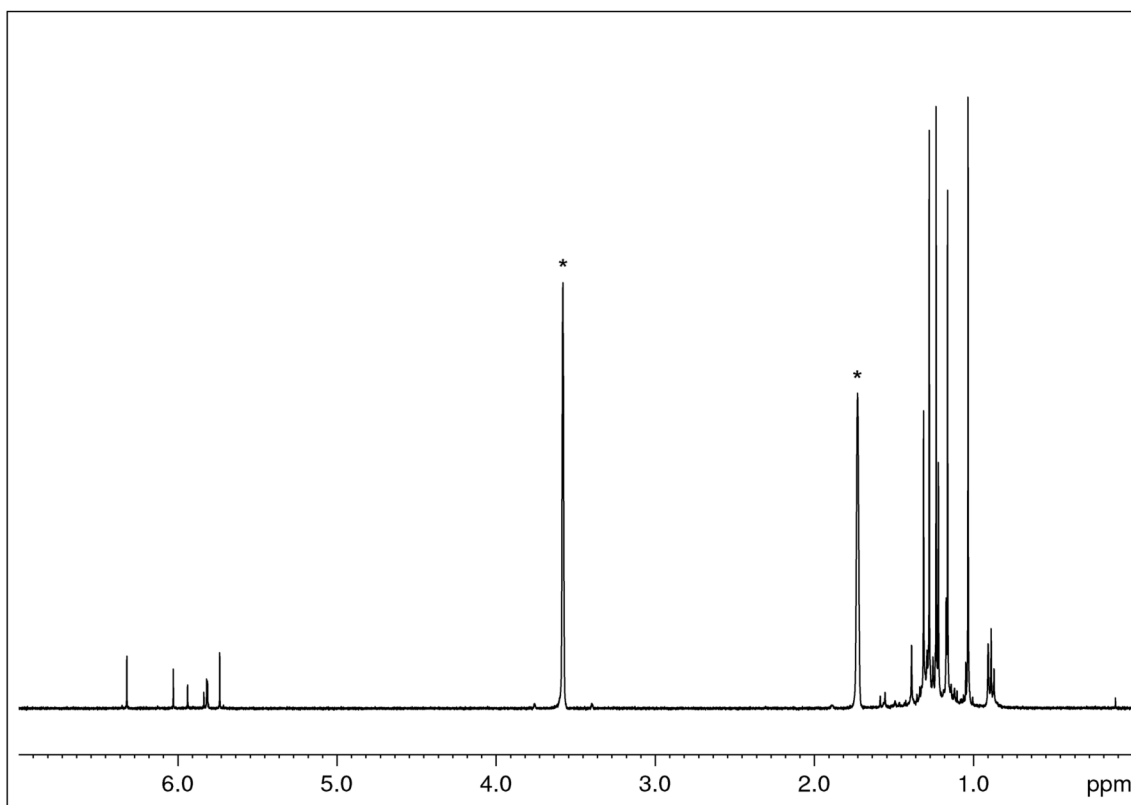


Figure S9. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of the reaction mixture resulting in $[\text{Ga}(\text{pz}^{\text{tBu}_2})(\mu\text{-N,N,C-pz}^{\text{tBu,C(CH}_3)_2\text{CH}_2})_2]$ (**5**) as a side product.

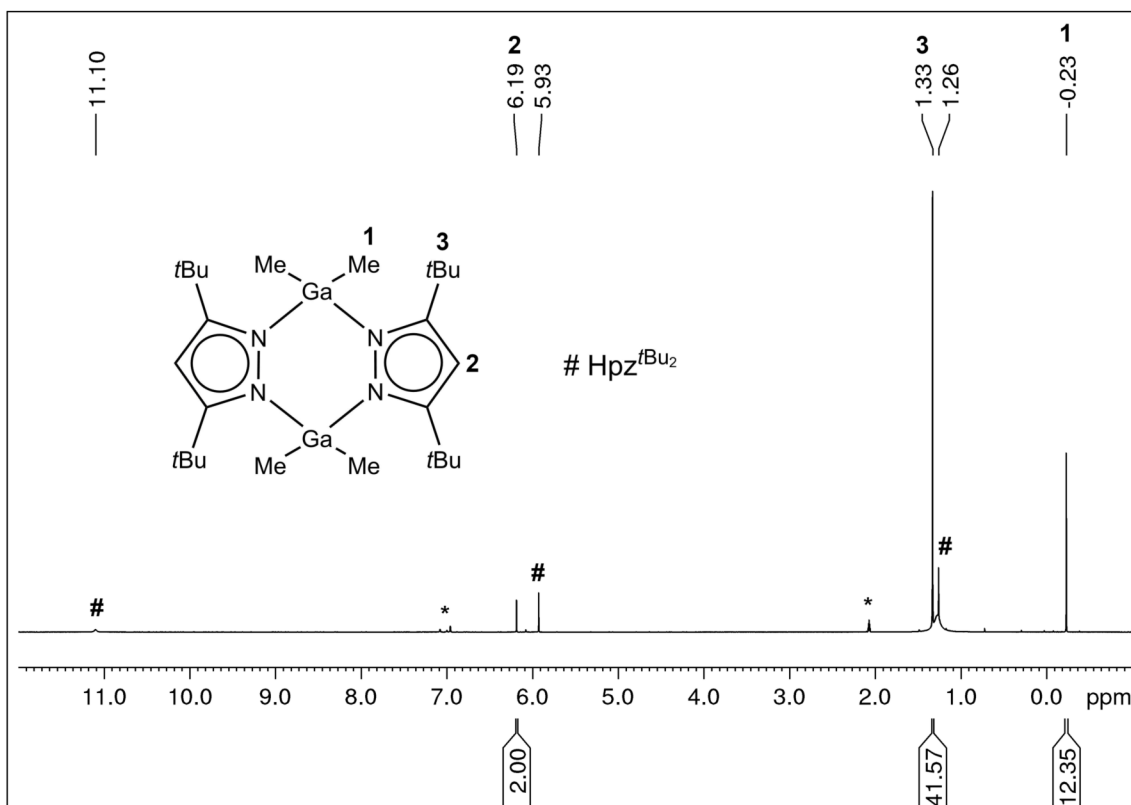


Figure S10. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{GaMe}_2\text{pz}^{\text{tBu}_2}]_2$ (# excess HpztBu_2).

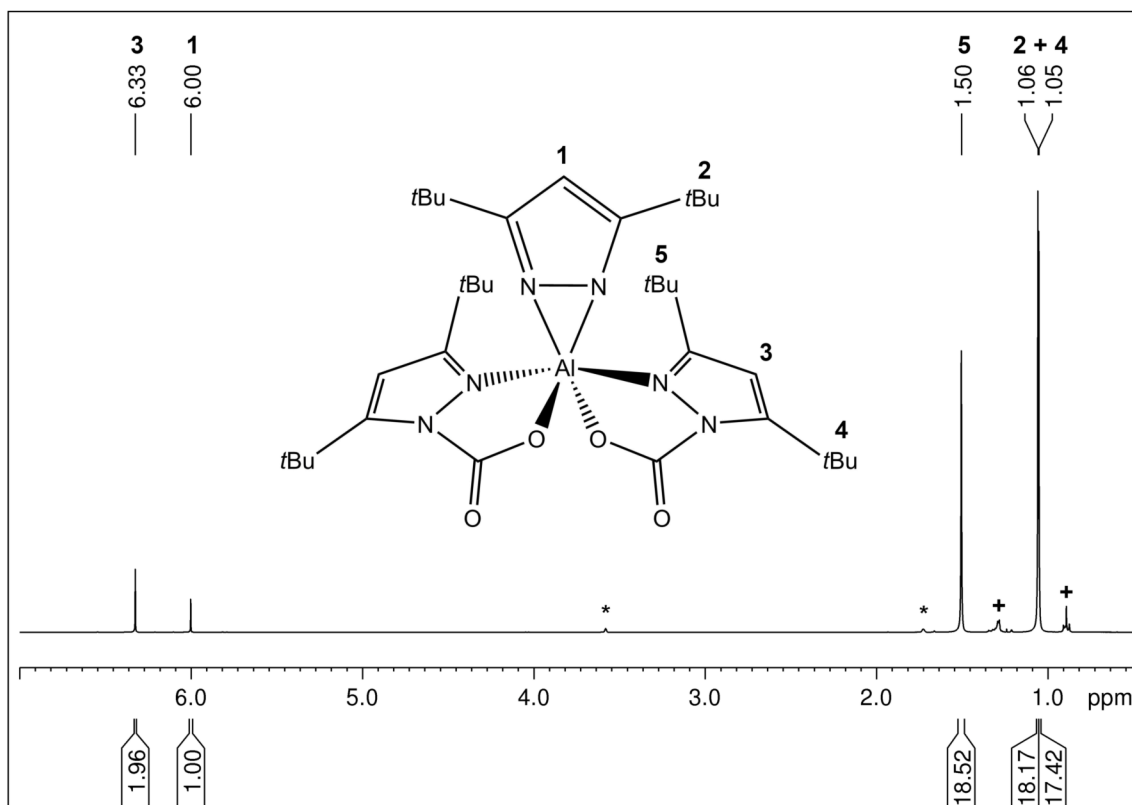


Figure S11. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $\text{Al}(\text{CO}_2\cdot\text{pz}^{\text{tBu}})_2(\text{pz}^{\text{tBu}})$ (**1-CO₂**) (+ *n*-hexane).

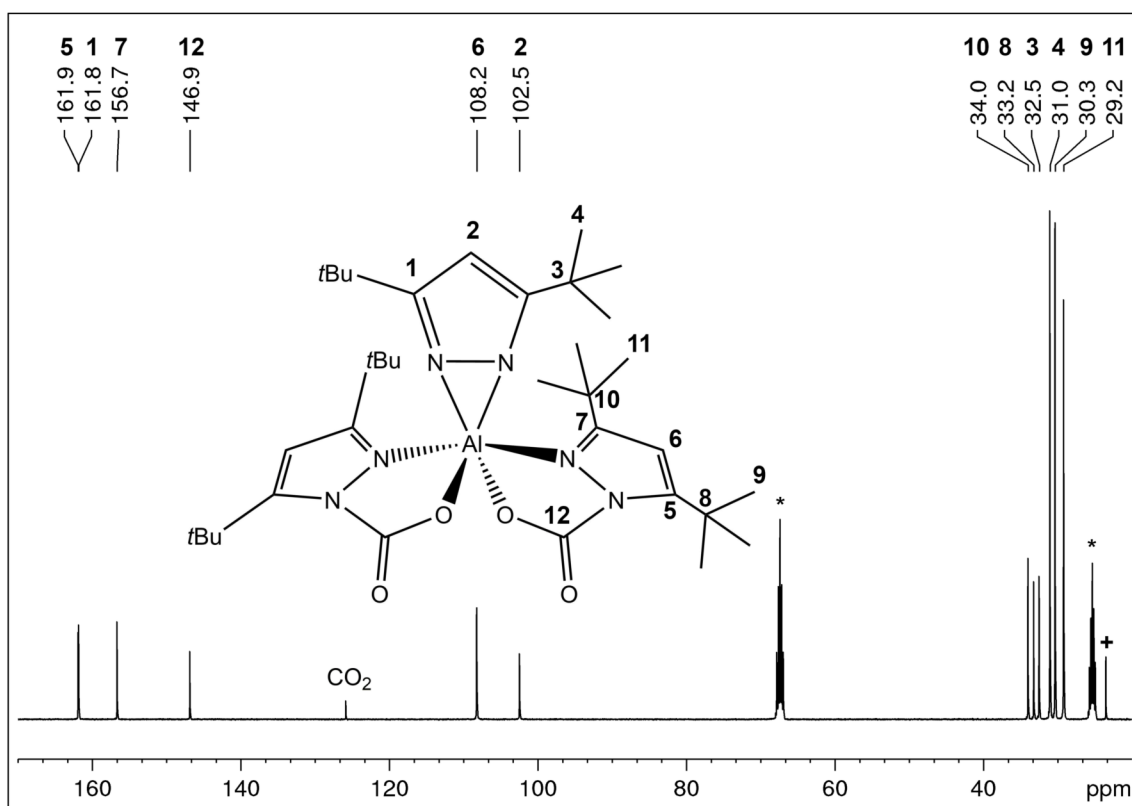


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 100.61 MHz, $[\text{D}_8]\text{THF}$) of $\text{Al}(\text{CO}_2\cdot\text{pz}^{\text{tBu}})_2(\text{pz}^{\text{tBu}})$ (**1-CO₂**) (+ *n*-hexane).

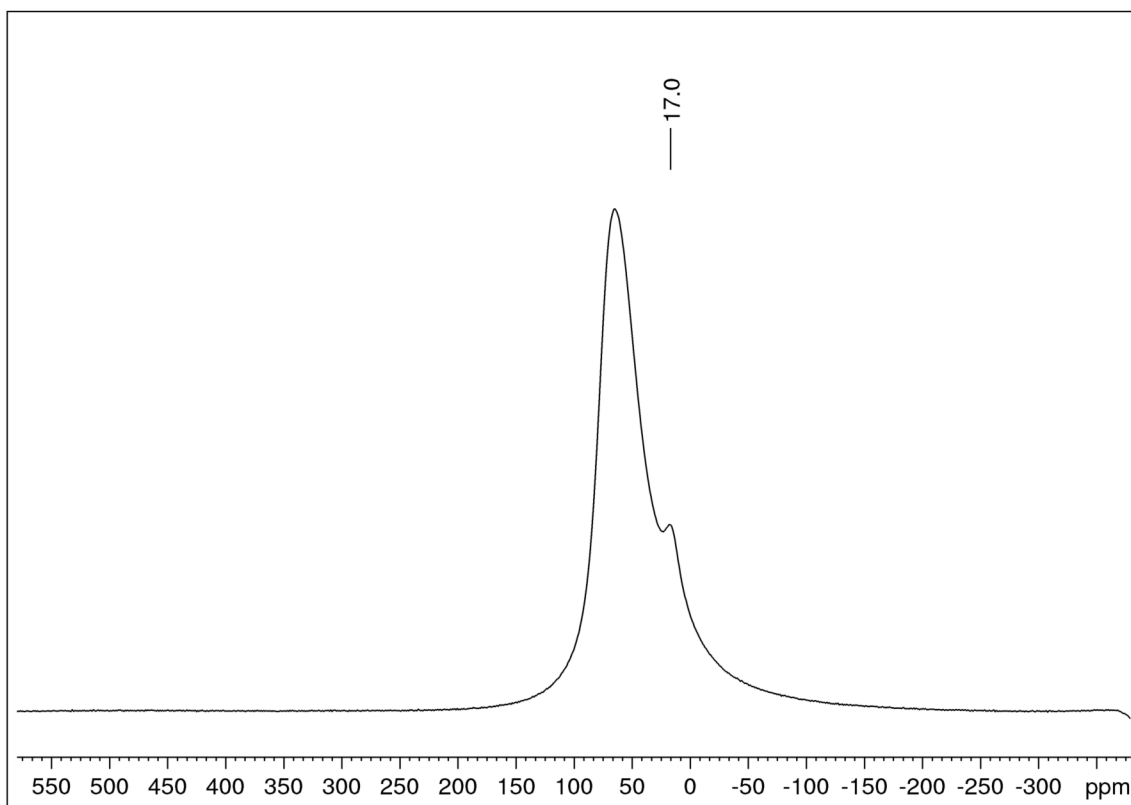


Figure S13. ^{27}Al NMR spectrum (26 °C, 130.32 MHz, $[\text{D}_8]\text{THF}$) of $\text{Al}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (**1-CO₂**).

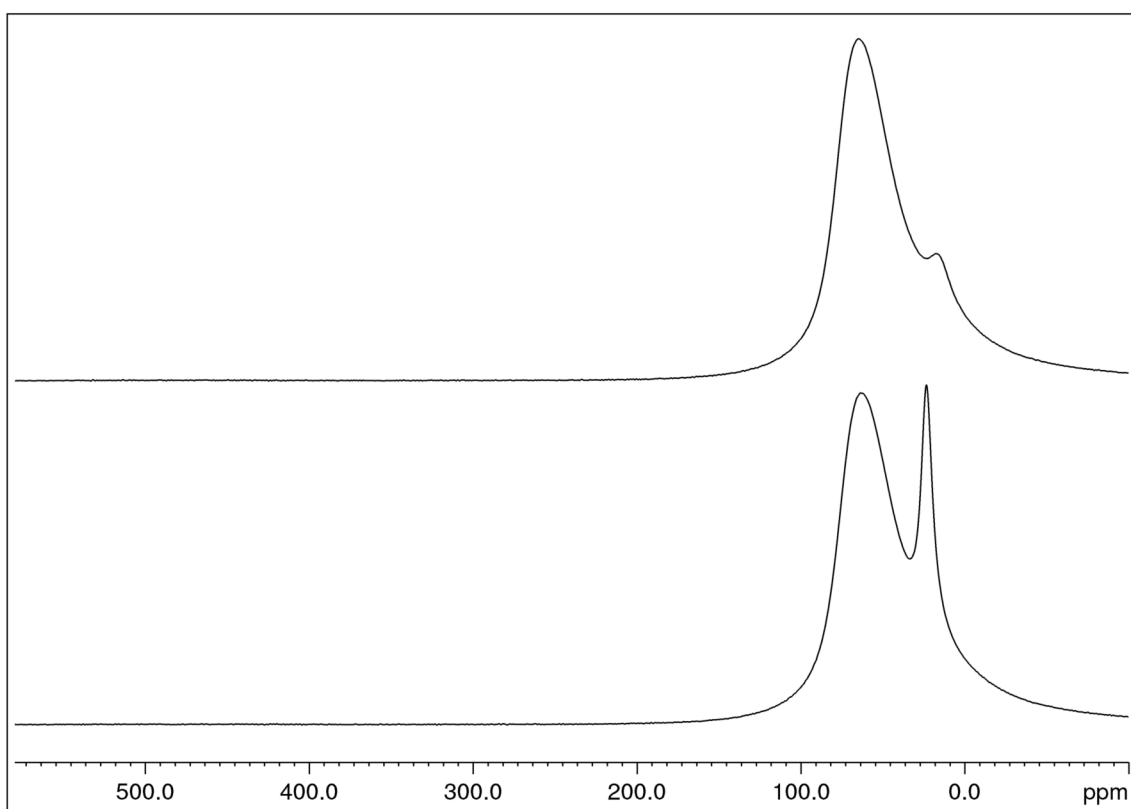


Figure S14. Comparison of the ^{27}Al NMR spectra (26 °C, 130.32 MHz, $[\text{D}_8]\text{THF}$) of $\text{Al}(\text{pz}^{\text{tBu}_2})_3$ (**1**, bottom) and $\text{Al}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (**1-CO₂**, top).

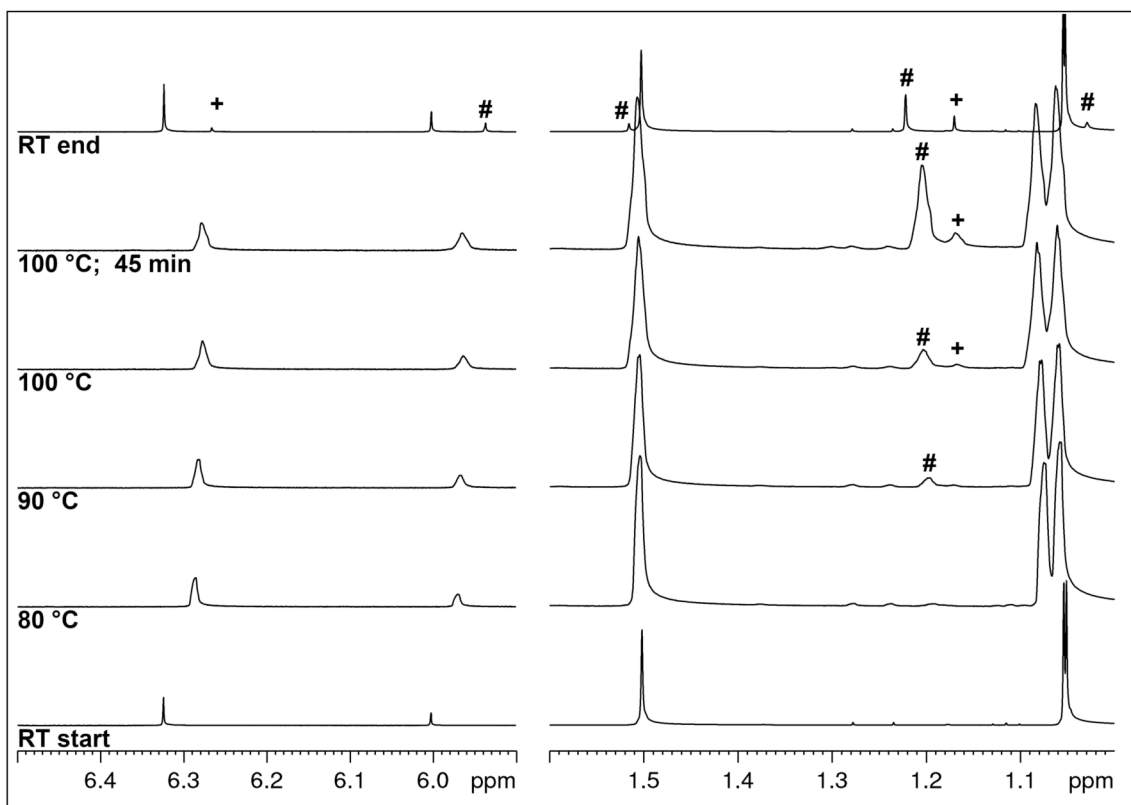


Figure S15. VT ^1H NMR spectra (500.13 MHz, $[\text{D}_8]\text{THF}$) of $\text{Al}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (**1-CO₂**) in the range of 26 °C to 100 °C and back to 26 °C showing the formation of + $\text{Al}(\text{pz}^{\text{tBu}_2})_3$ (**1**) and # $\text{Al}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2$.

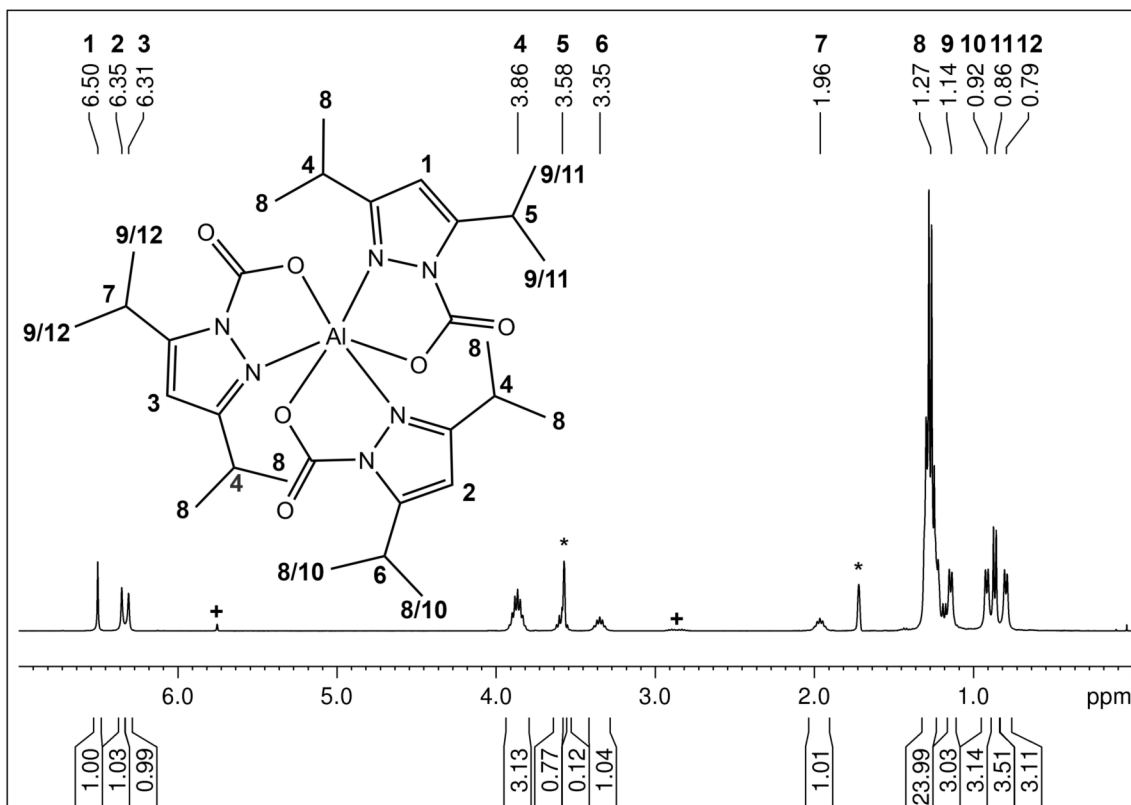


Figure S16. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Al}(\text{CO}_2\cdot\text{pz}^{\text{IPr}_2})_3]_2$ (**4-CO₂**).

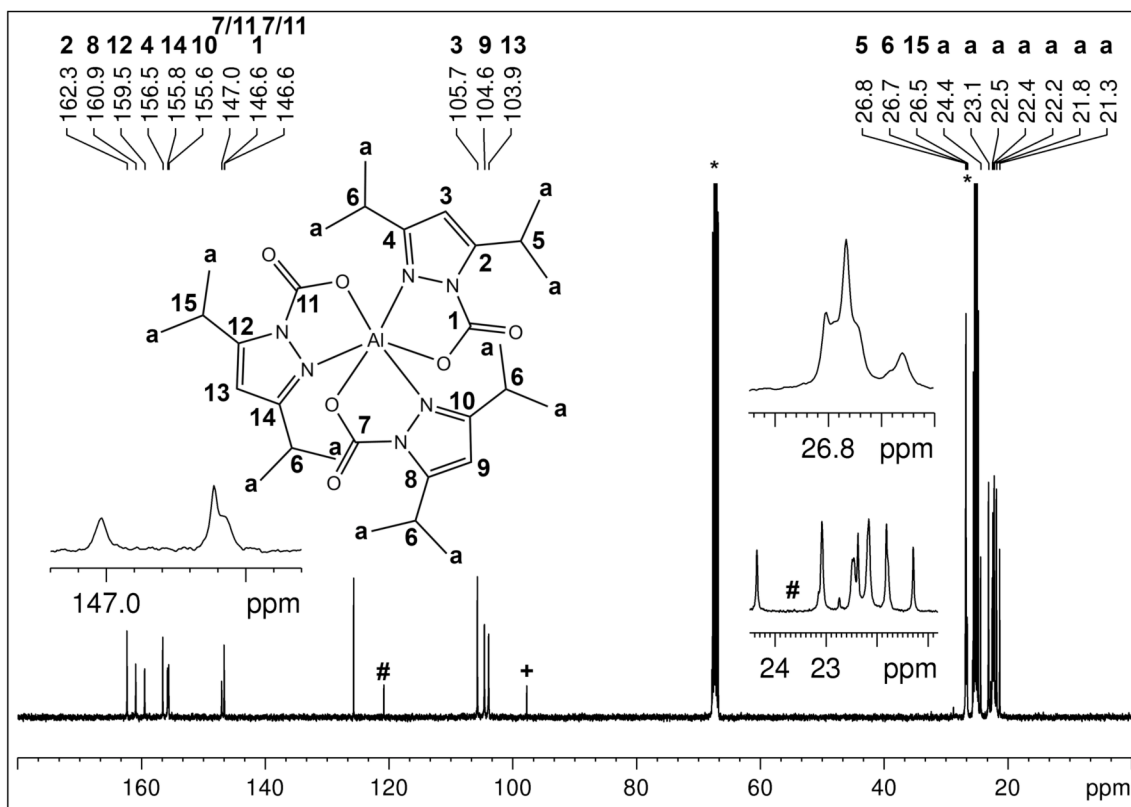


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 100.61 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Al}(\text{CO}_2\text{-pz}^{\text{iPr}_2})_3]_2$ (**4-CO₂**).

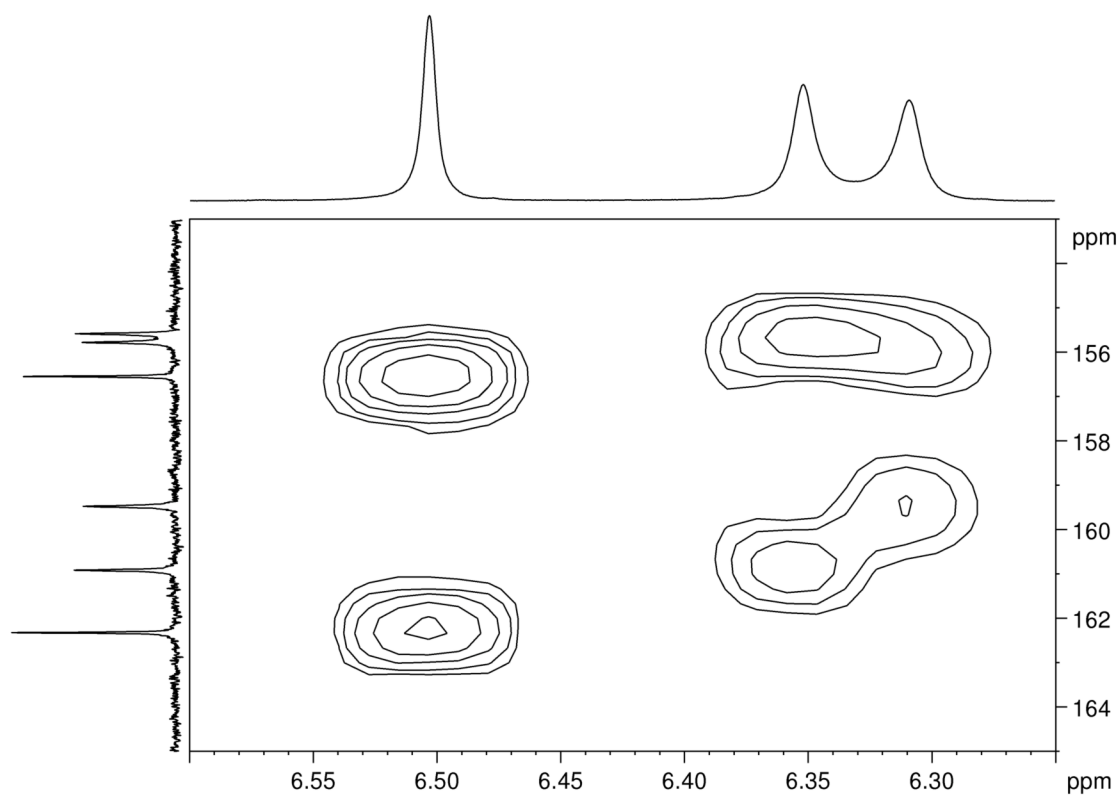


Figure S18. ^1H - ^{13}C HMBC NMR spectrum (26 °C, 100.61 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Al}(\text{CO}_2\text{-pz}^{\text{iPr}_2})_3]_2$ (**4-CO₂**).

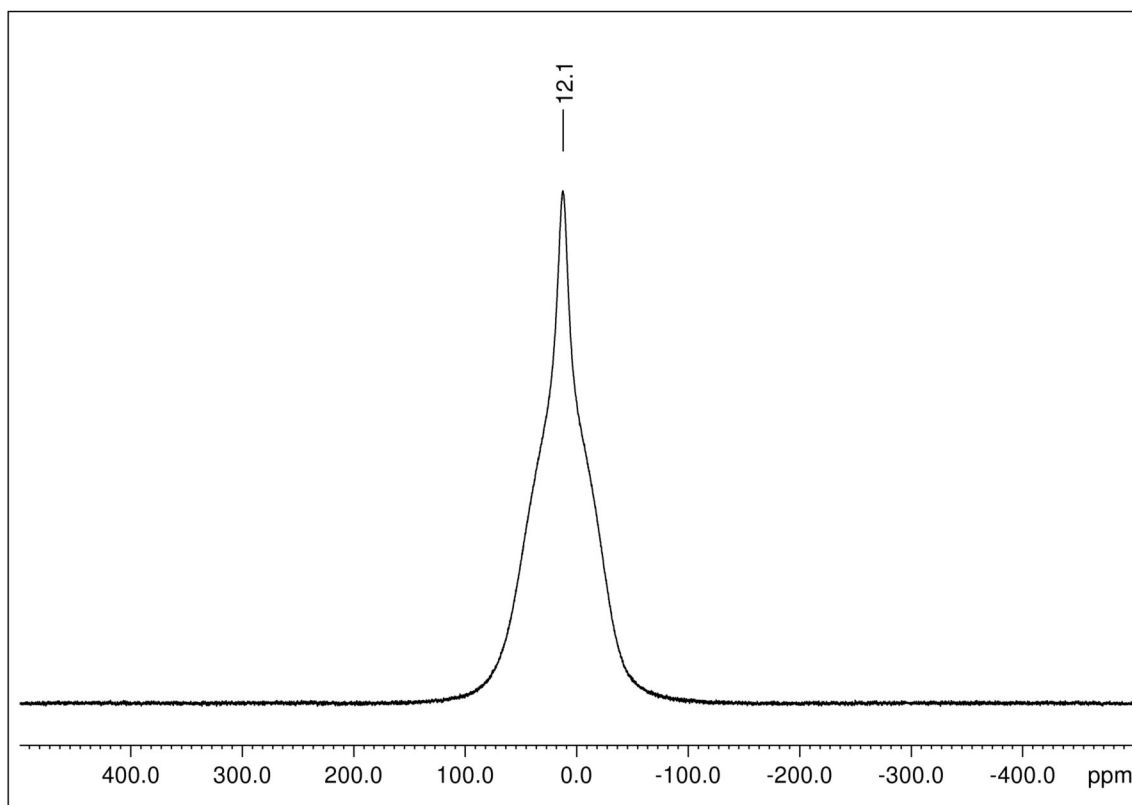


Figure S19. ^{27}Al NMR spectrum (26 °C, ^1H : 400.11 MHz/ ^{13}C : 104.26 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Al}(\text{CO}_2\cdot\text{pz}^{\text{iPr}_2})_3]_2$ (**4-CO₂**).

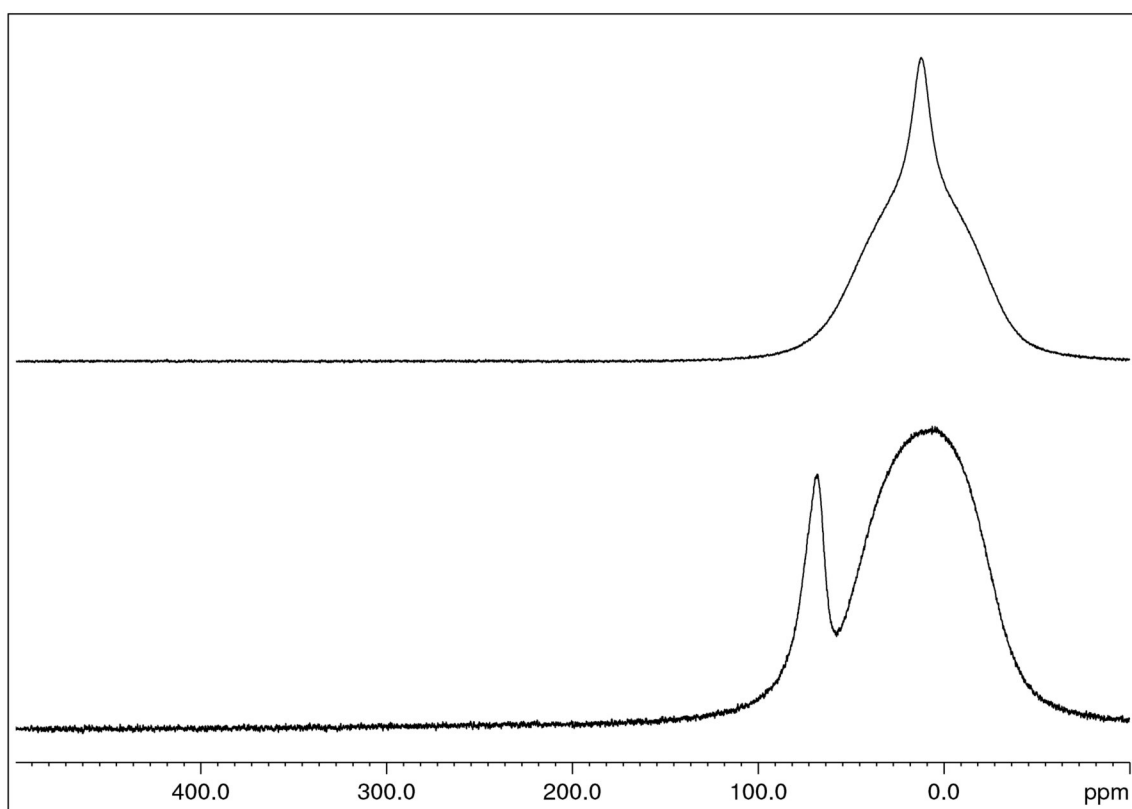


Figure S20. Comparison of the ^{27}Al NMR spectra (26 °C, 130.32 MHz, $[\text{D}_8]\text{THF}$) of $\text{Al}(\text{pz}^{\text{iPr}_2})_3$ (**5**, bottom) and $[\text{Al}(\text{CO}_2\cdot\text{pz}^{\text{iPr}_2})_3]_2$ (**4-CO₂**, top).

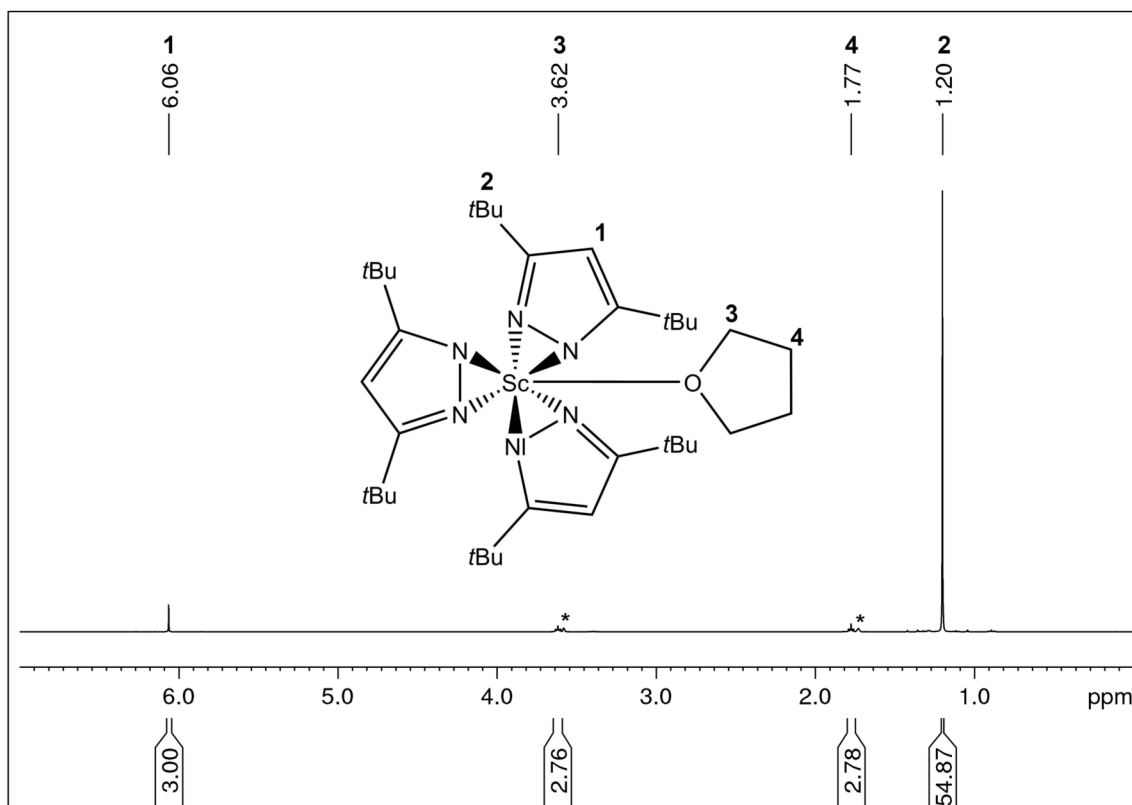


Figure S21. ¹H NMR spectrum (26 °C, 400.11 MHz, [D₈]THF) of Sc(pz^{tBu}₂)₃(thf) (**7**).

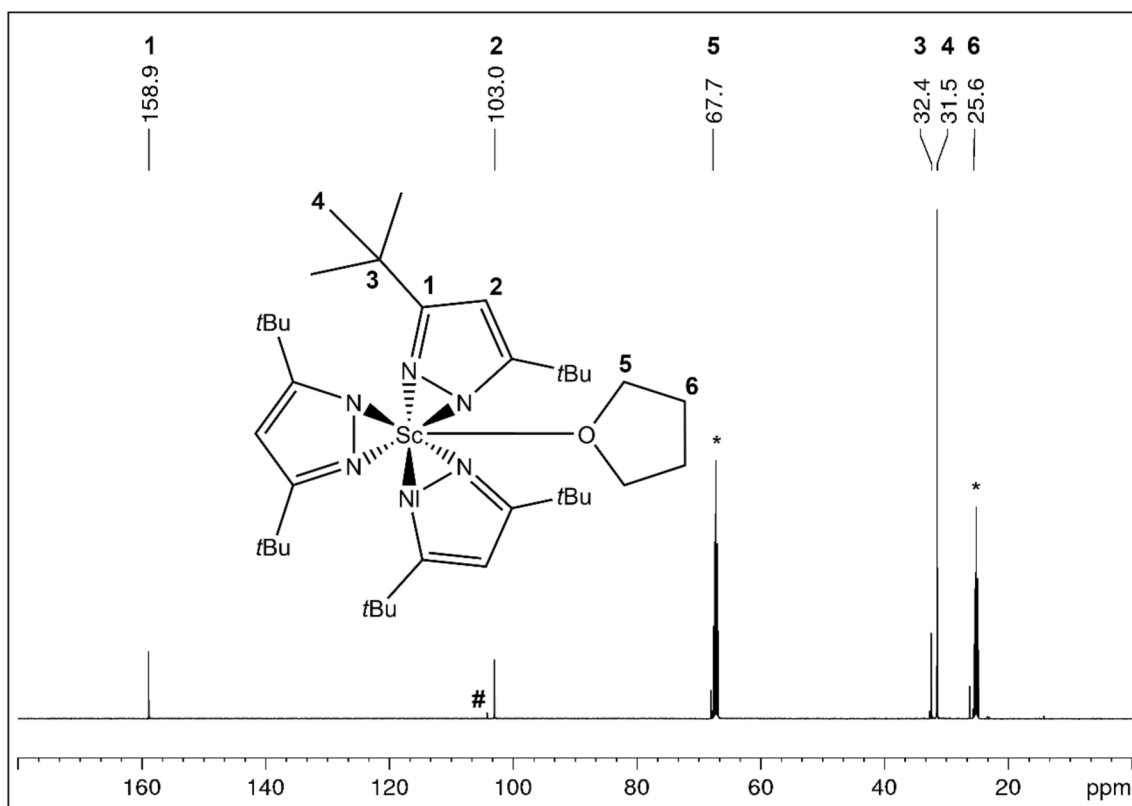


Figure S22. ¹³C{¹H} NMR spectrum (26 °C, 125.76 MHz, [D₈]THF) of Sc(pz^{tBu}₂)₃(thf) (**7**).

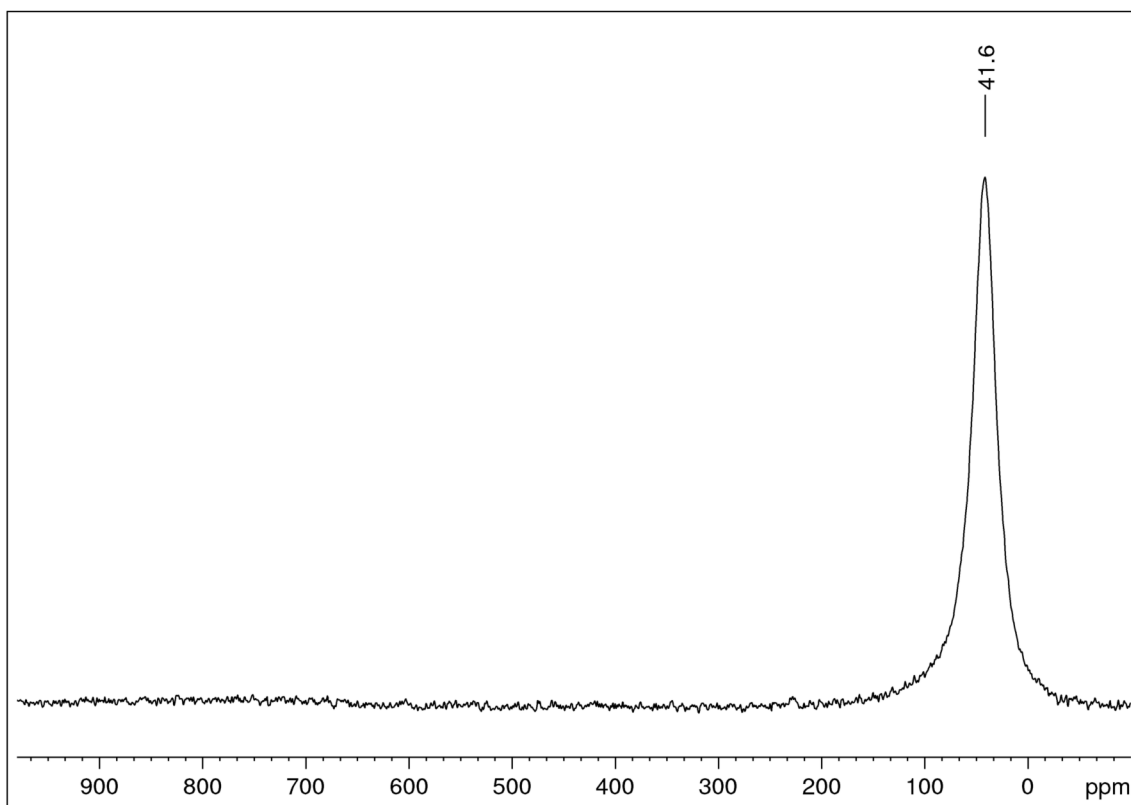


Figure S23. ^{45}Sc NMR spectrum (26 °C, 121.49 MHz, $[\text{D}_8]\text{THF}$) of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**).

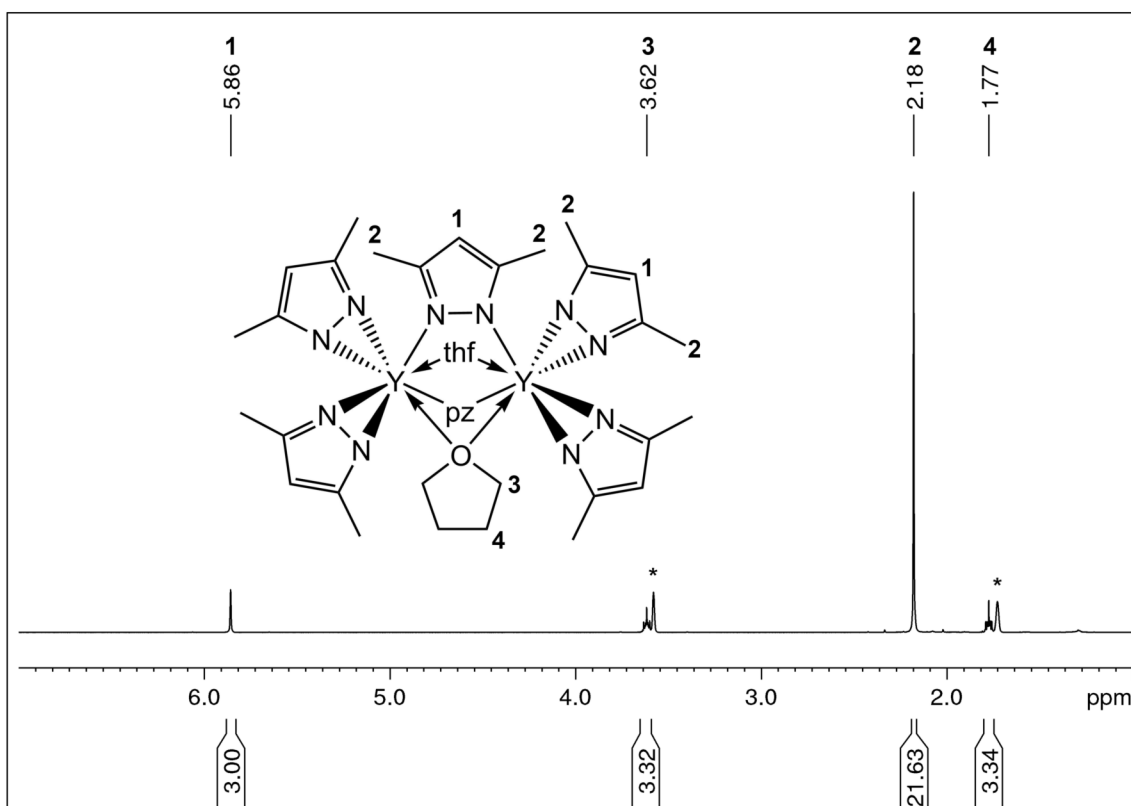


Figure S24. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})_2]$ (**9**).

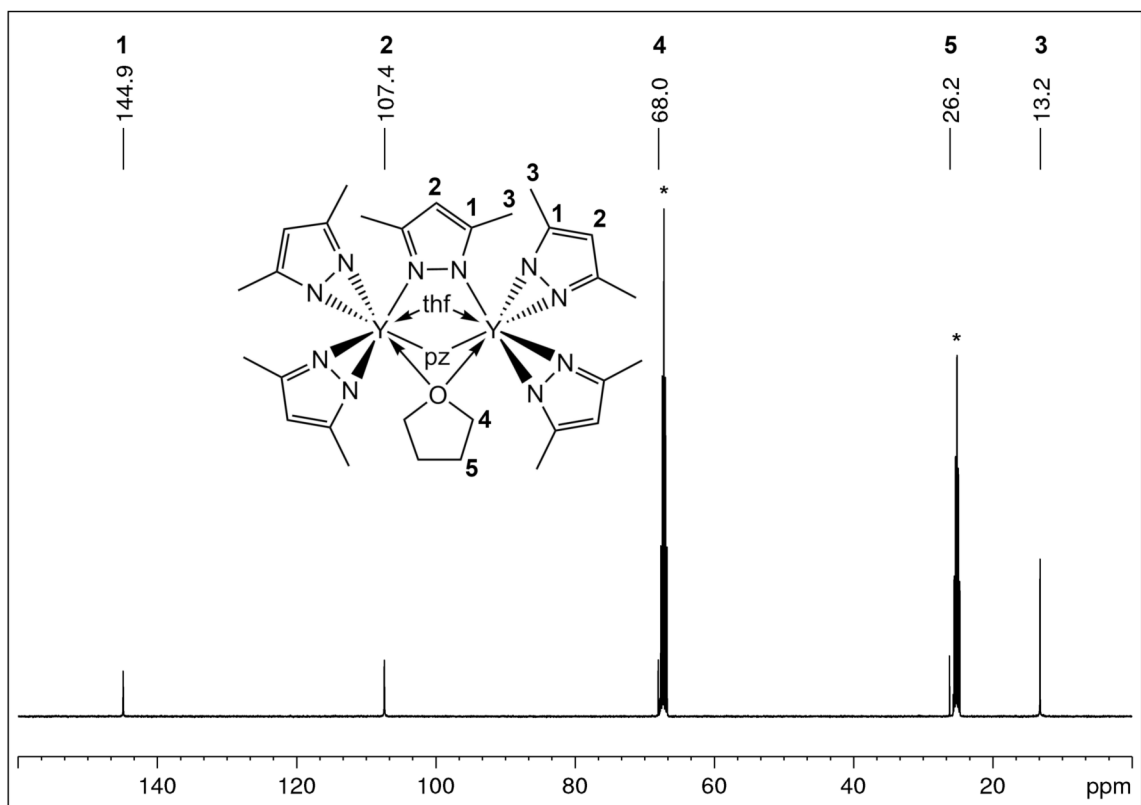


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 100.61 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (**9**).

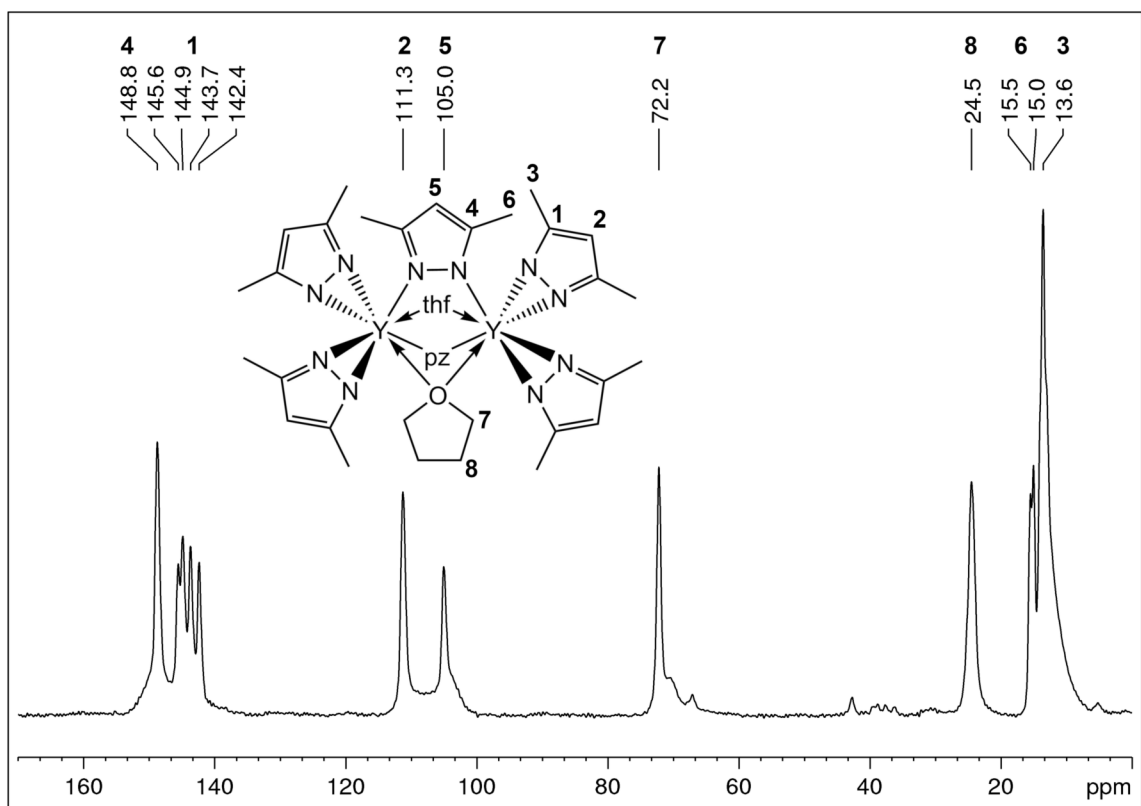
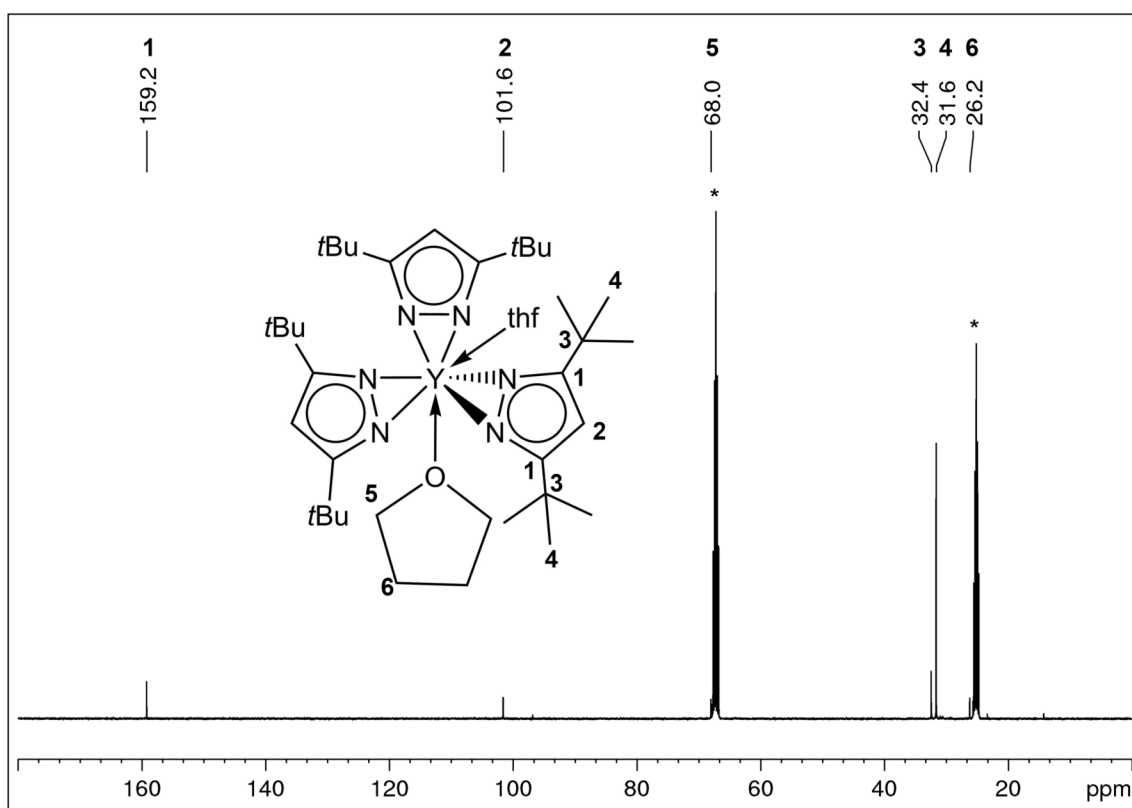
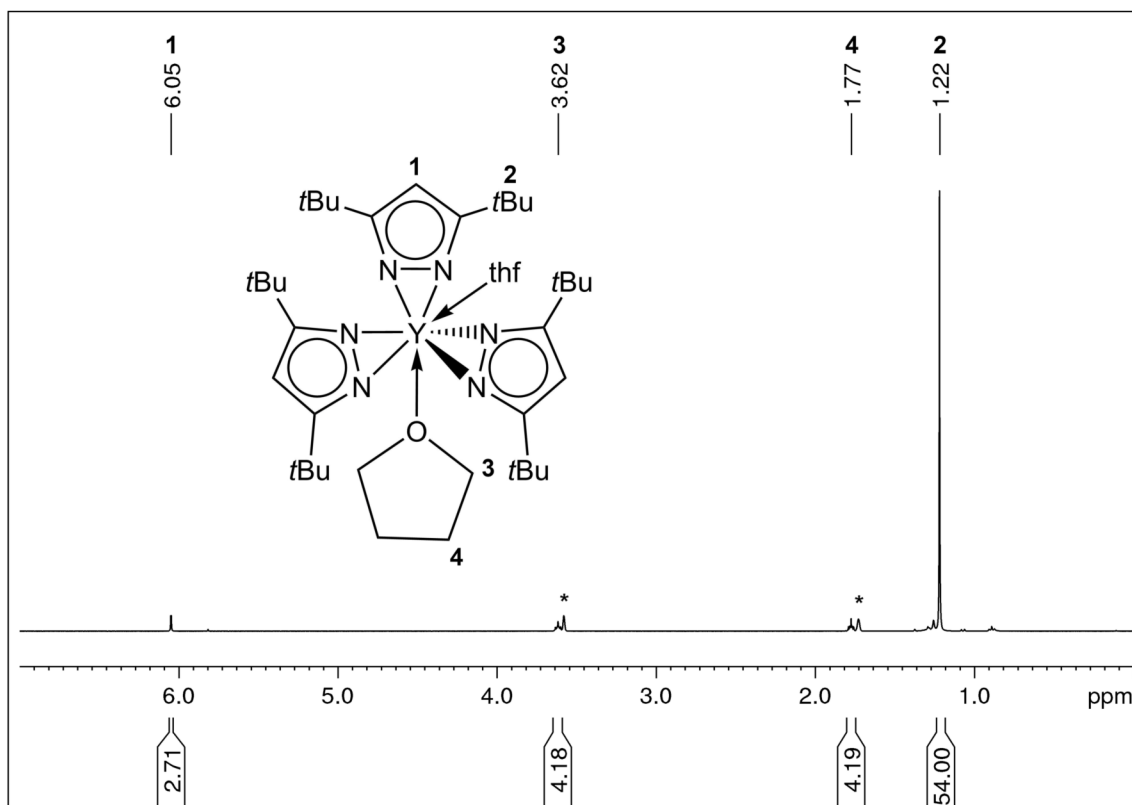


Figure S26. ^{13}C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz) of $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (**9**).



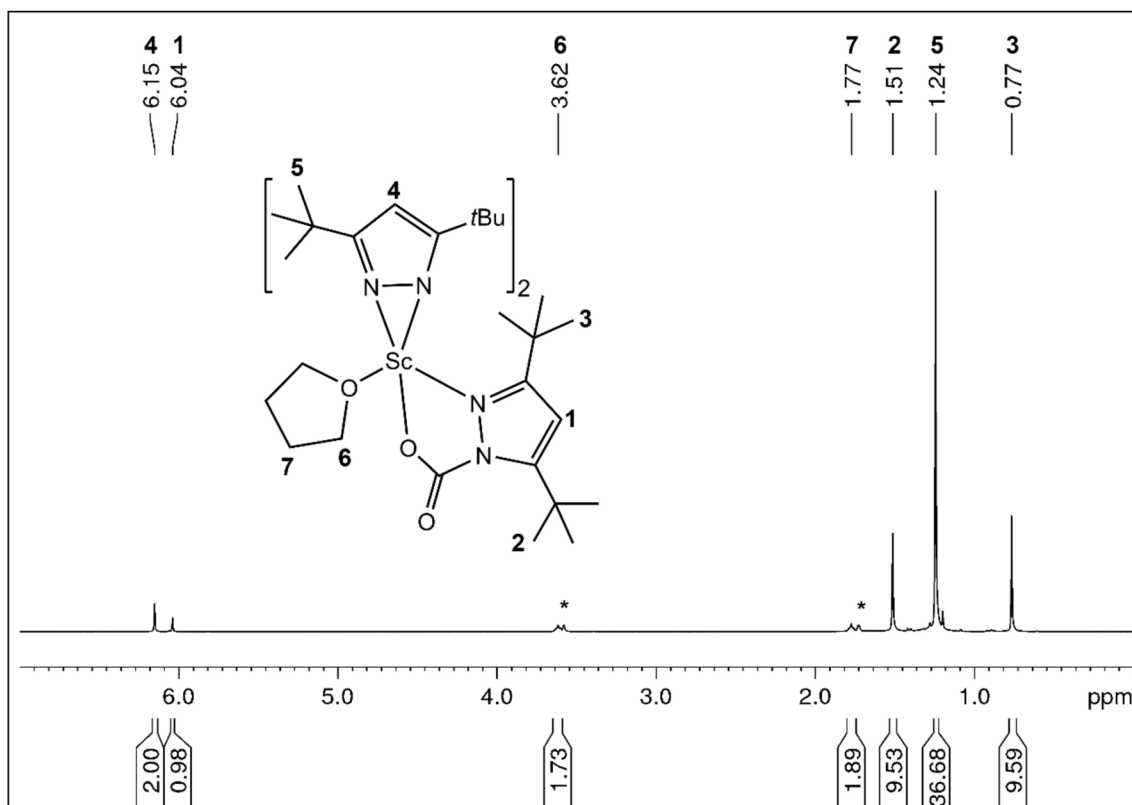


Figure S29. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Sc}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2(\text{thf})]$ (**7-CO₂**).

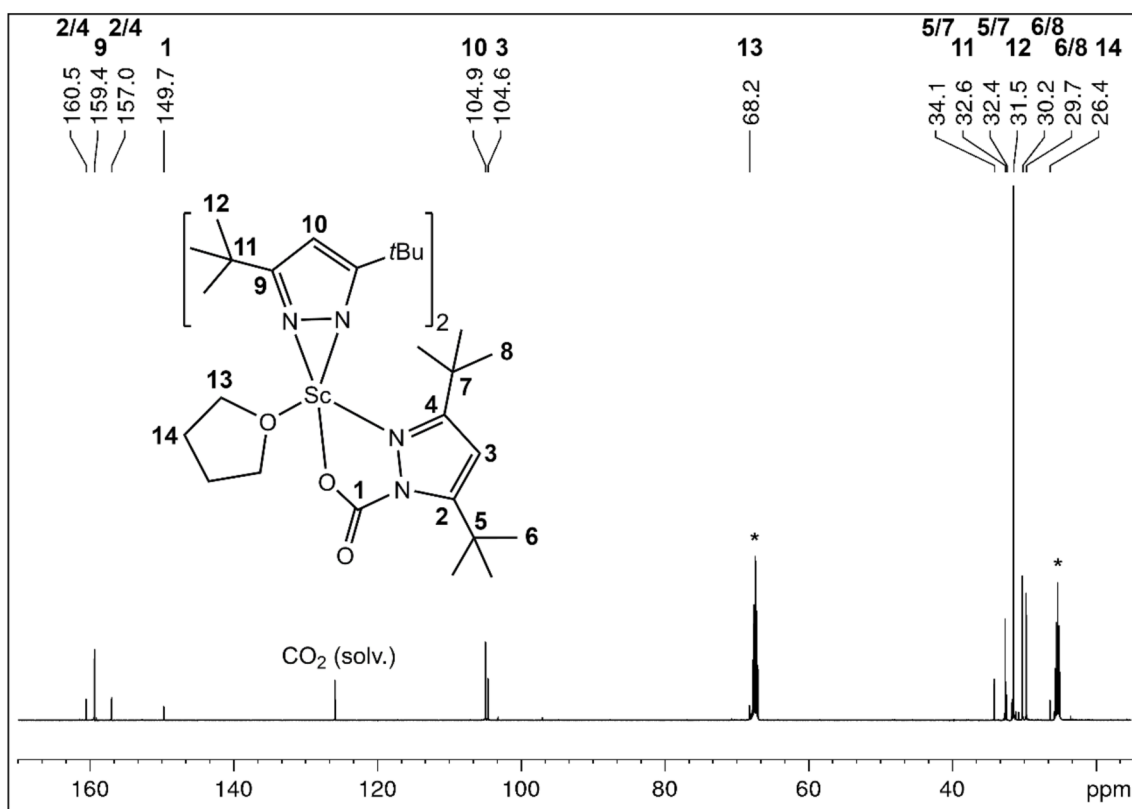


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 125.76 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Sc}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2(\text{thf})]$ (**7-CO₂**).

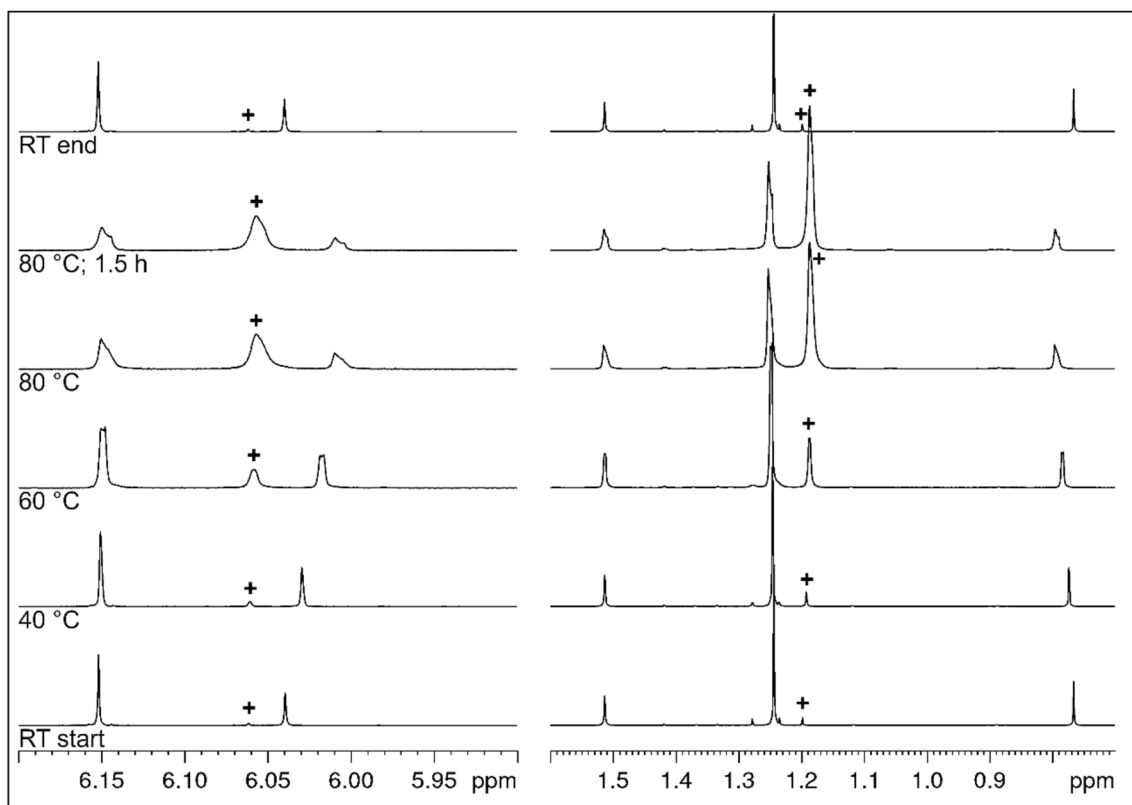


Figure S31. VT ^1H NMR spectra (500.13 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Sc}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2(\text{thf})]$ (**7-CO₂**) in the range of 26 °C to 80 °C and back to 26 °C showing the formation of + $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**).

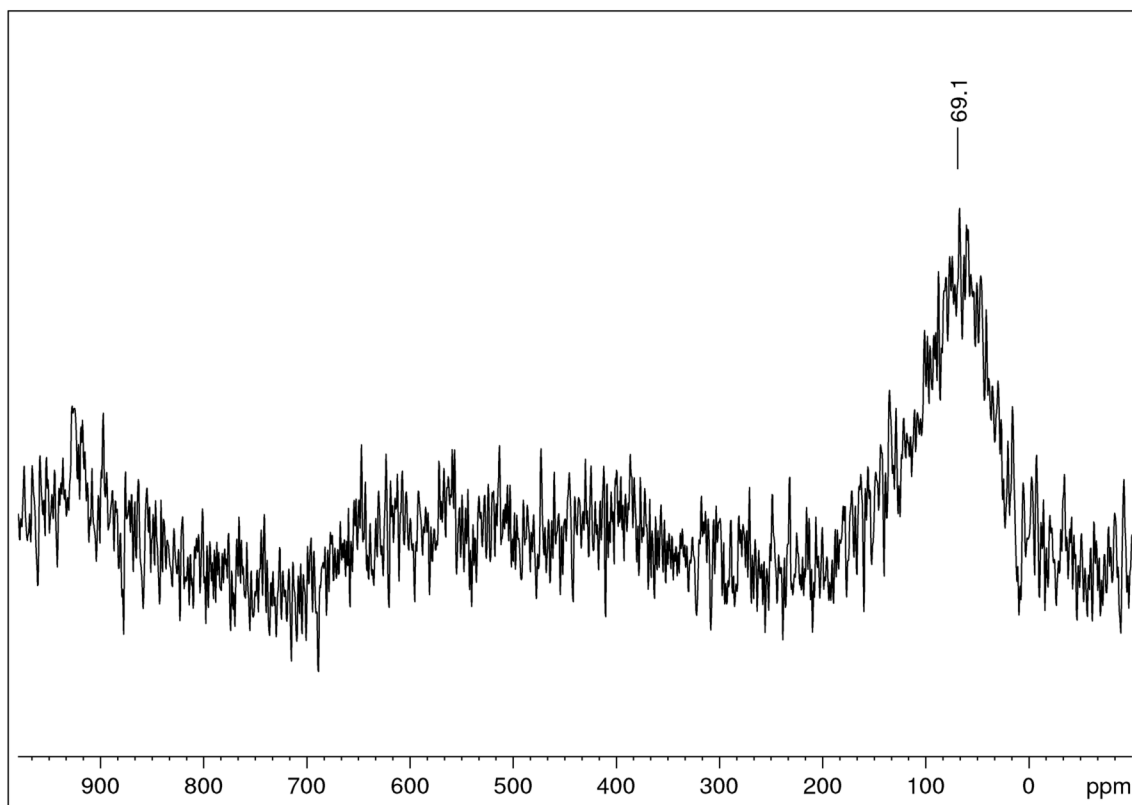


Figure S32. ^{45}Sc NMR spectrum (26 °C, 121.49 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Sc}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2(\text{thf})]$ (**7-CO₂**).

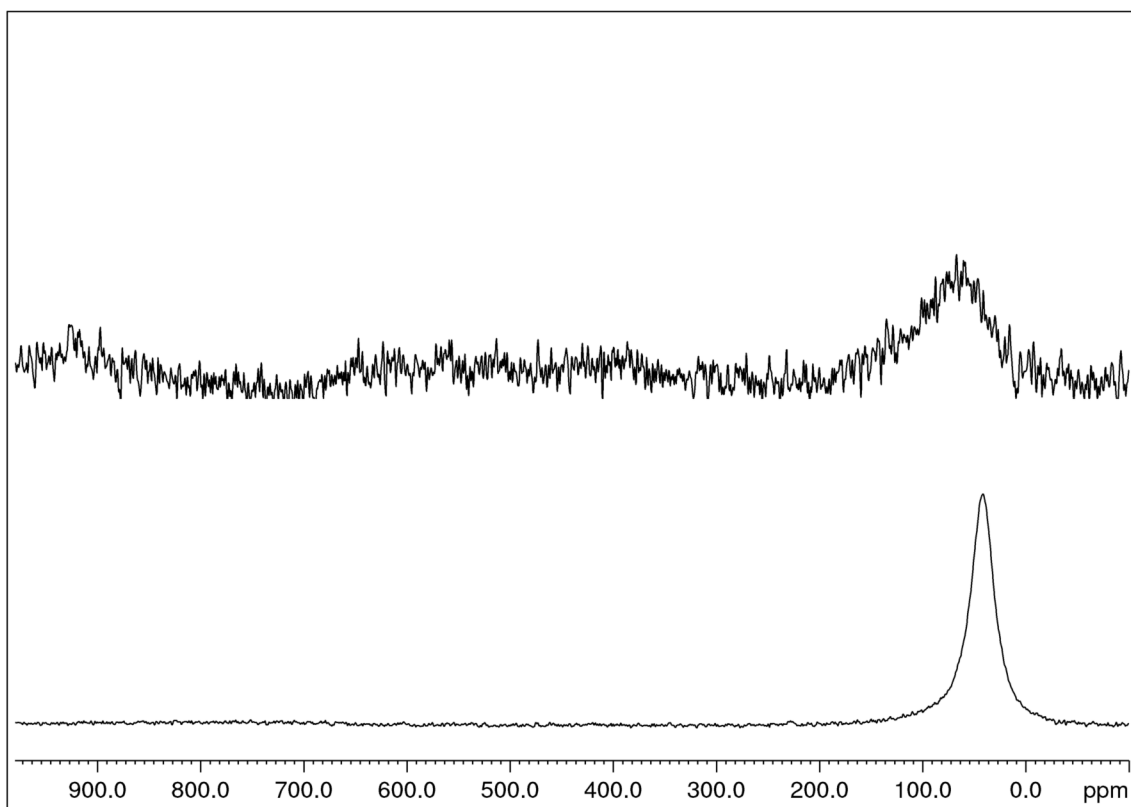


Figure S33. Comparison of the ^{45}Sc NMR spectra (26 °C, 121.49 MHz, $[\text{D}_8]\text{THF}$) of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**, bottom) and $\text{Sc}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2(\text{thf})$ (**7-CO₂**, top).

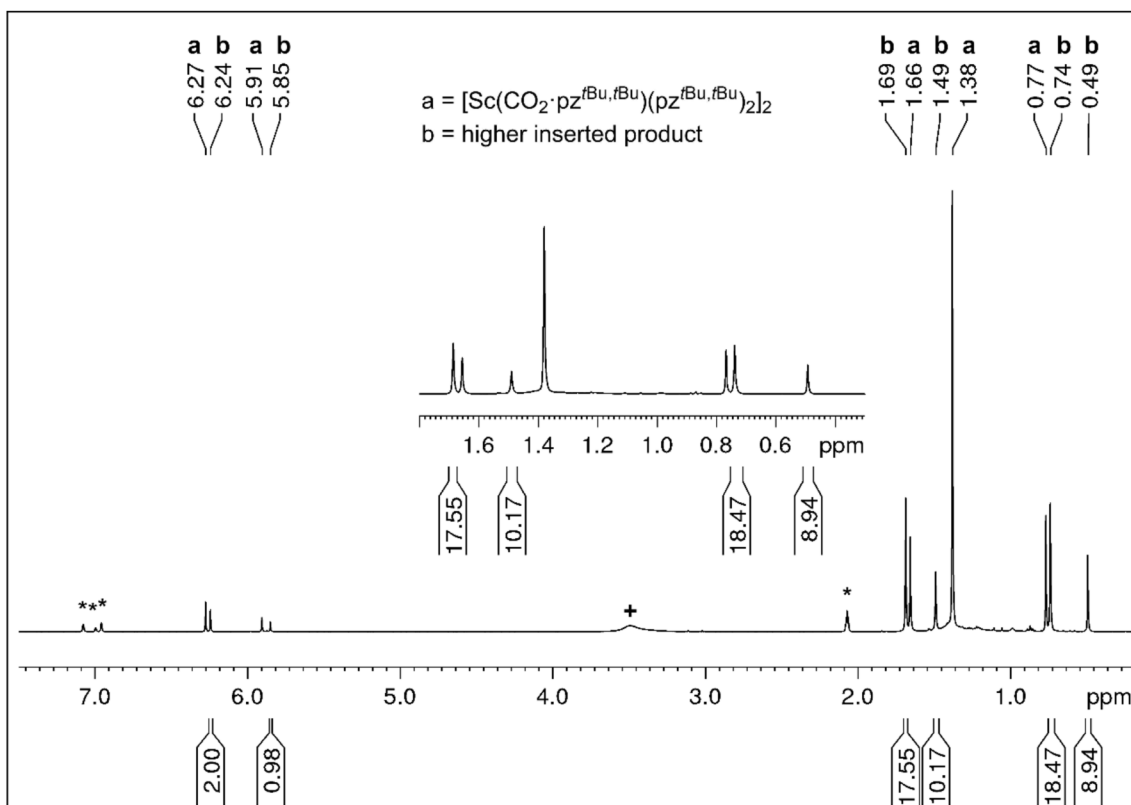


Figure S34. ^1H NMR spectrum (26 °C, 400.12 MHz, $[\text{D}_8]\text{toluene}$) of **a** $[\text{Sc}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2]_2$ (**7a-CO₂**) and **b** **a** higher inserted product (**7b-CO₂**, + free THF).

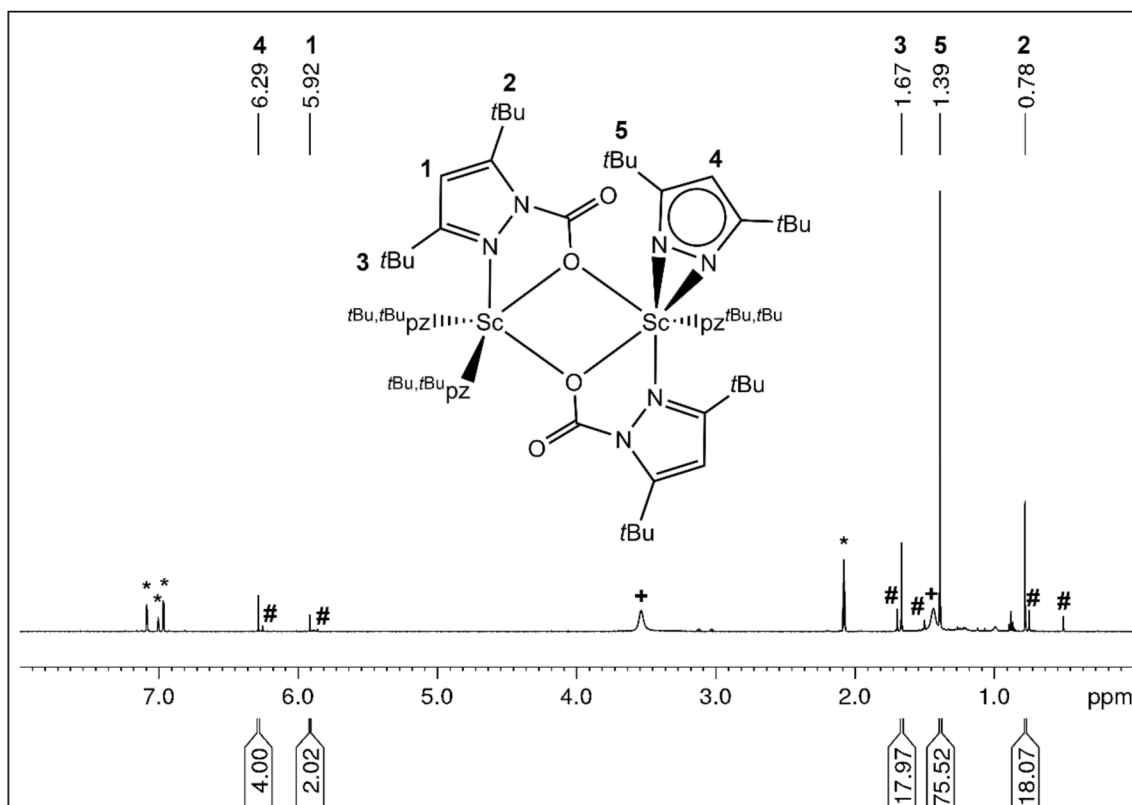


Figure S35. ^1H NMR spectrum (26 °C, 500.13 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Sc}(\text{CO}_2\text{-pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2]_2$ (**7a-CO₂**) (# a higher inserted product **7b-CO₂**; + free THF).

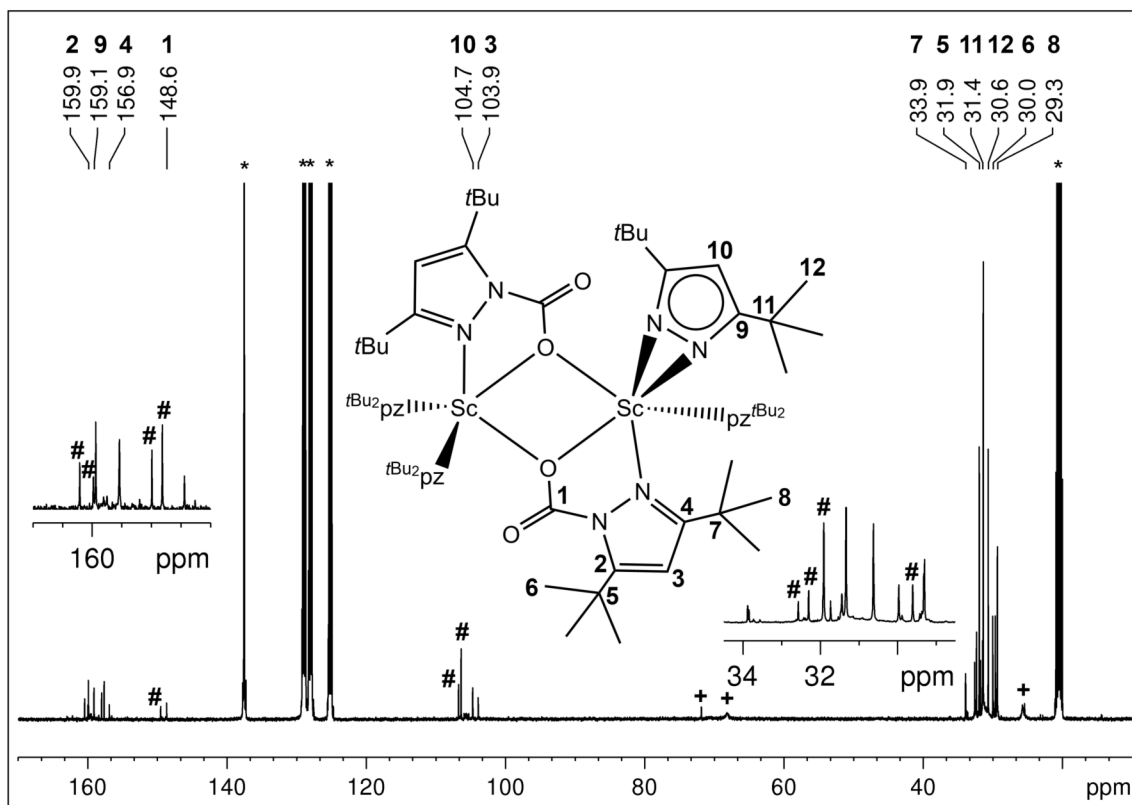


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 125.76 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Sc}(\text{CO}_2\text{-pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2]_2$ (**7a-CO₂**) (+ free/coordinated THF; # higher inserted species **7b-CO₂**).

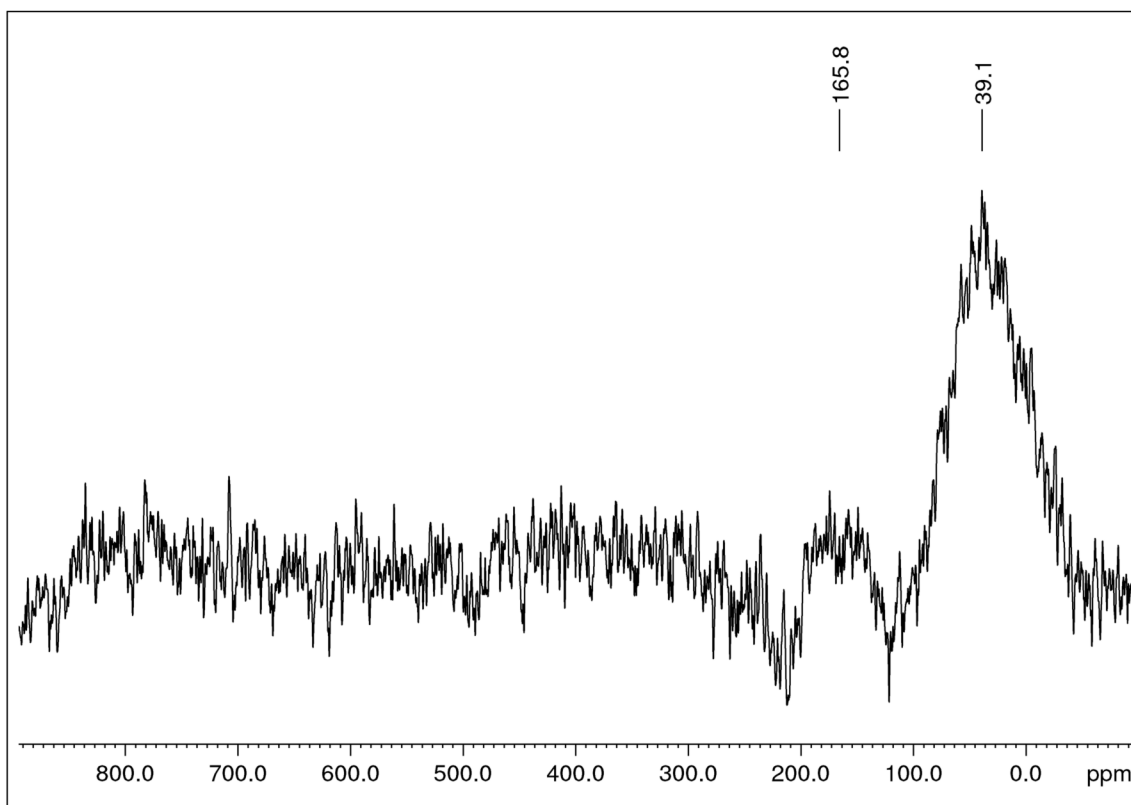


Figure S37. ^{45}Sc NMR spectrum (26 °C, 97.19 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Sc}(\text{CO}_2\text{-pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2]_2$ (**7a-CO₂**) at $\delta = 39.1$ ppm and higher inserted species **7b-CO₂** at $\delta = 165.8$ ppm.

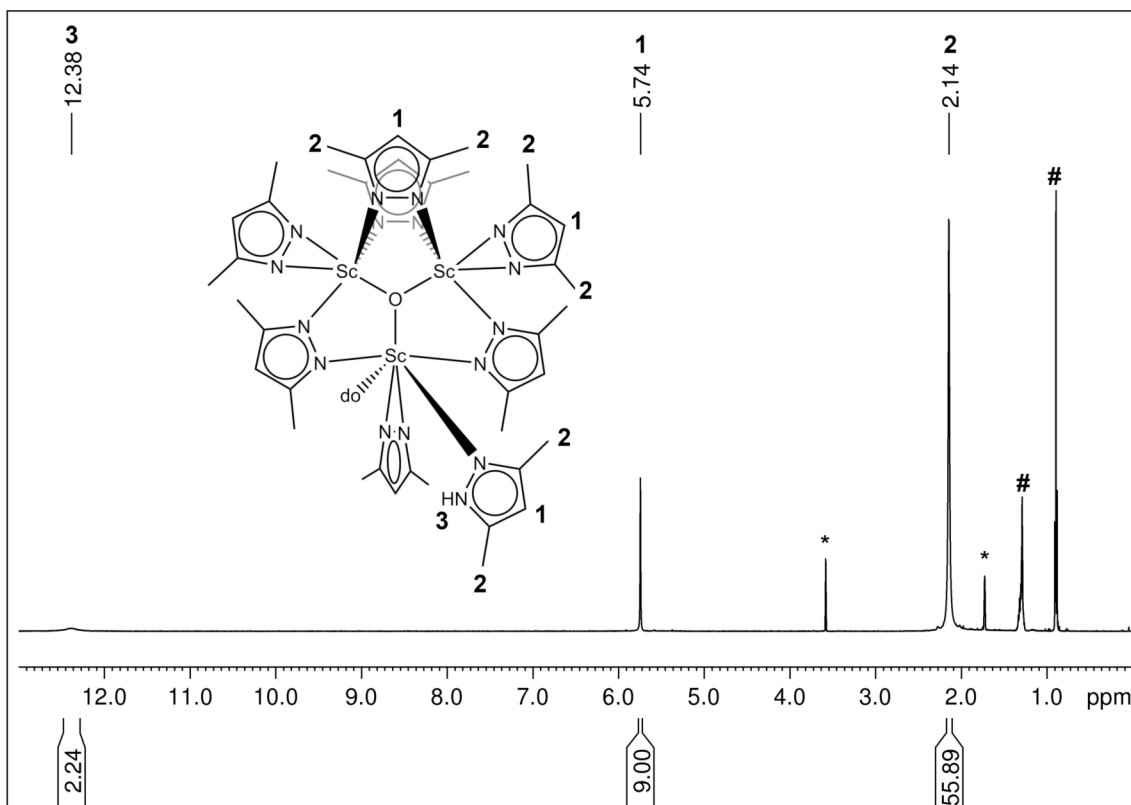


Figure S38. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2]$ (**8**) (# *n*-hexane, do = Hpz^{Me_2}).

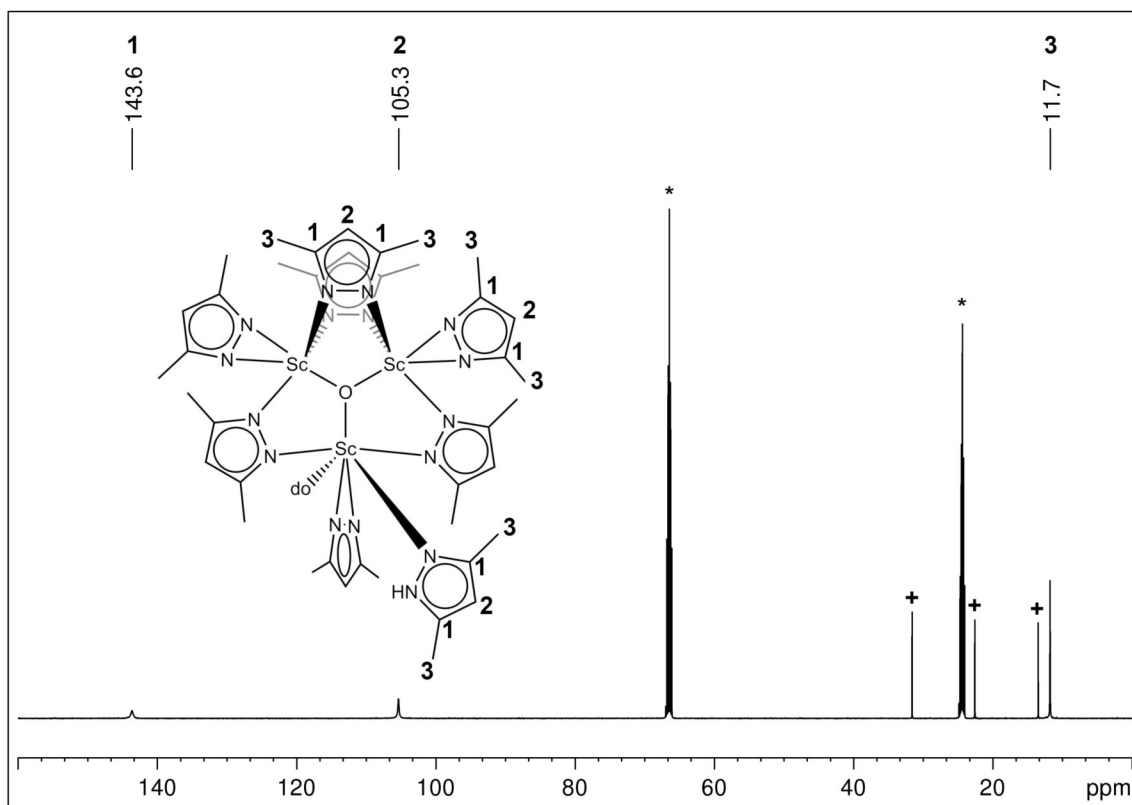


Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 125.76 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2]$ (8) (+ *n*-hexane).

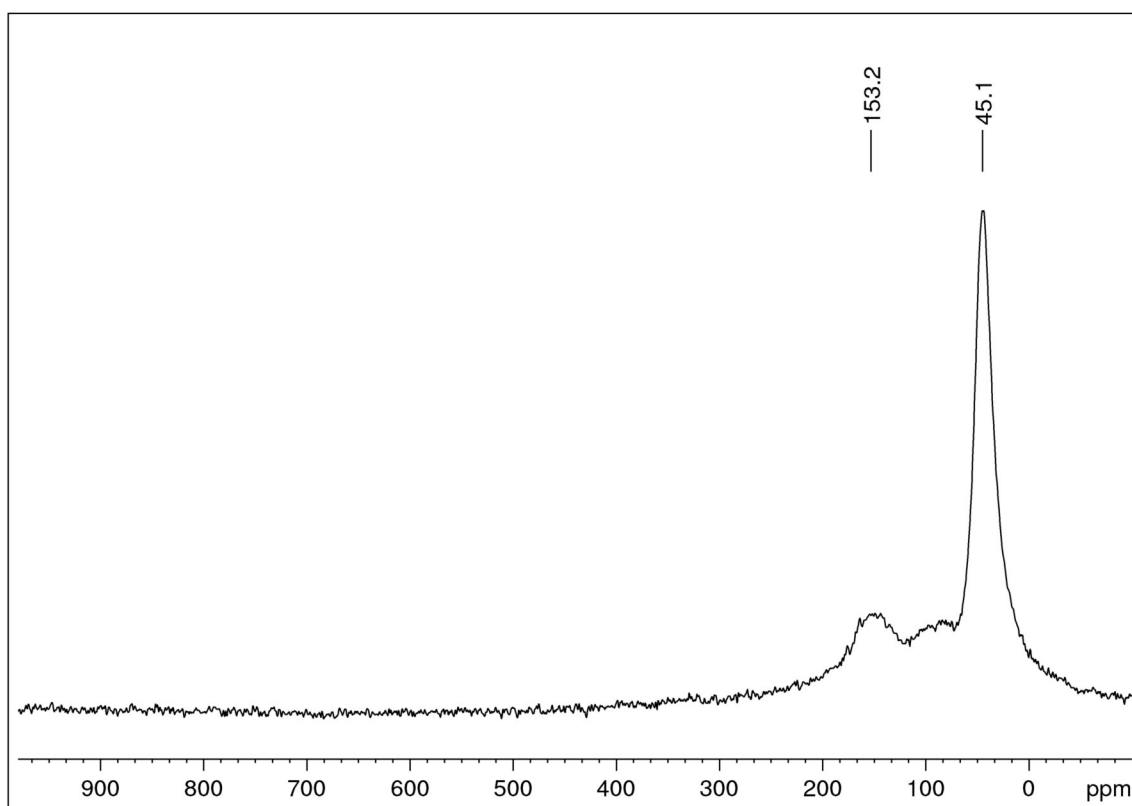


Figure S40. ^{45}Sc NMR spectrum (26 °C, 121.49 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2]$ (8).

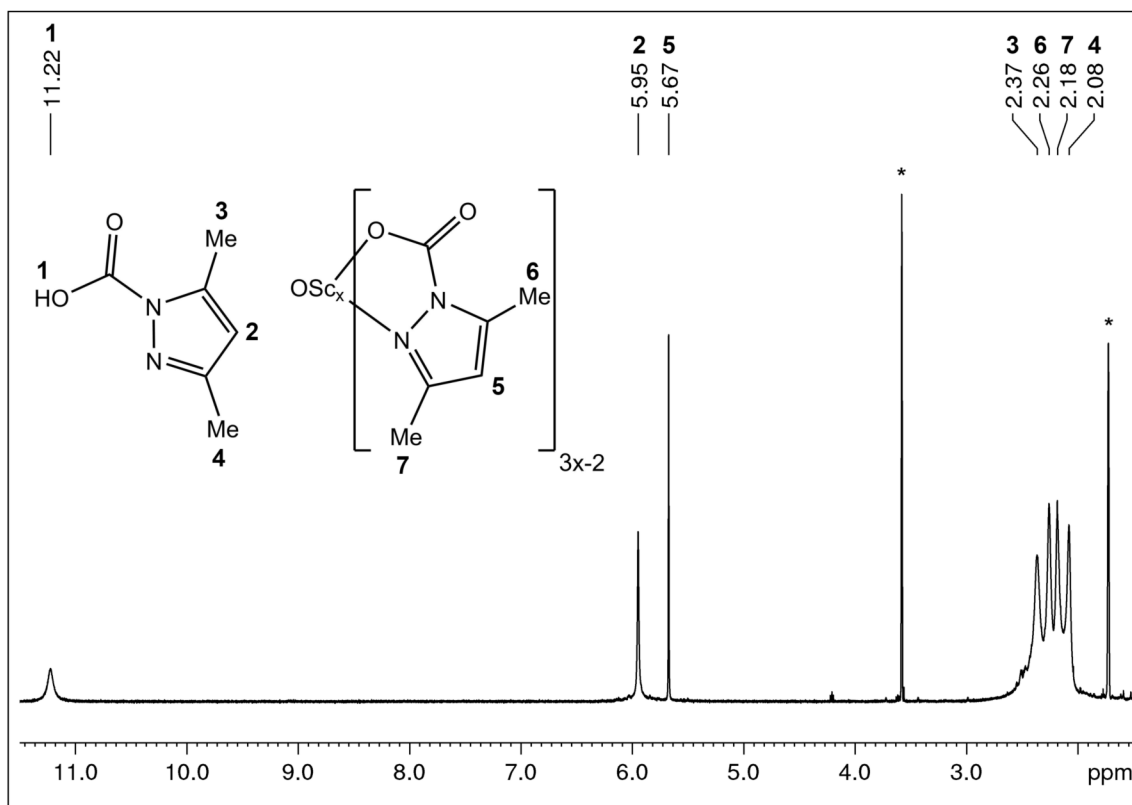


Figure S41. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of the product from $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2] + \text{CO}_2$ (**8-CO₂**).

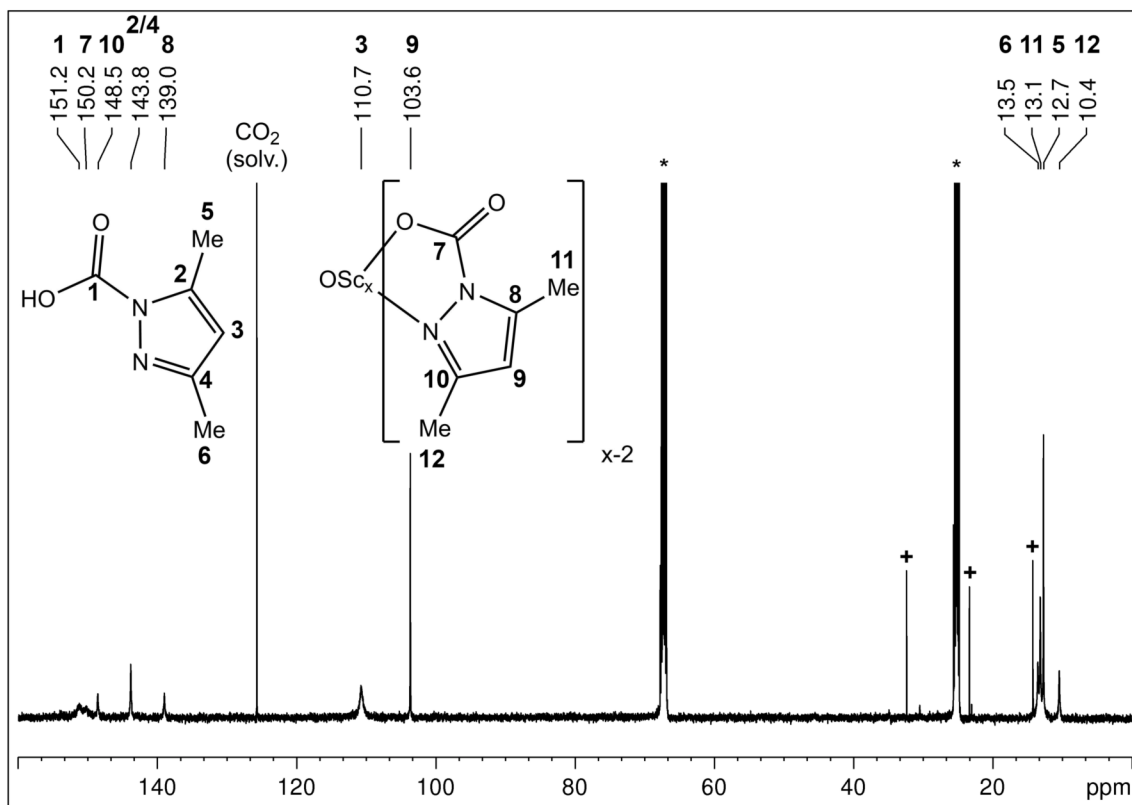


Figure S42. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (26 °C, 125.76 MHz, $[\text{D}_8]\text{THF}$) of the product from $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2] + \text{CO}_2$ (**8-CO₂**) (+ *n*-hexane).

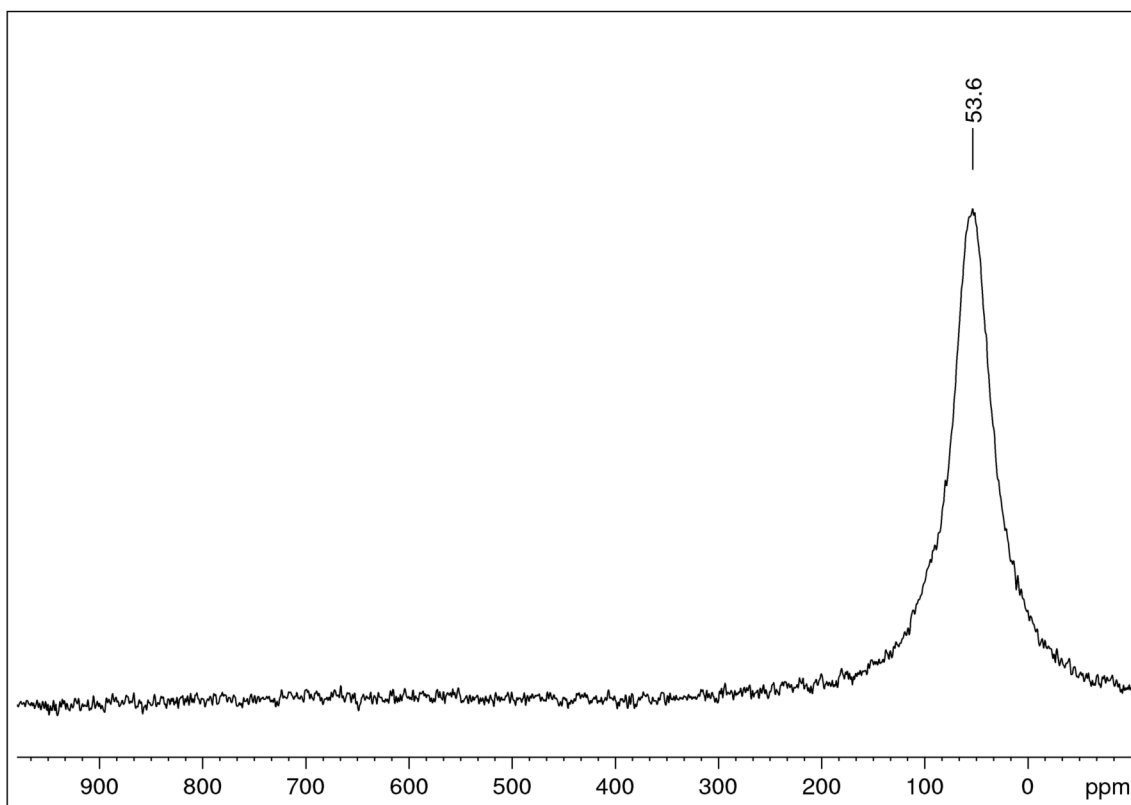


Figure S43. ^{45}Sc NMR spectrum (26 °C, 121.49 MHz, $[\text{D}_8]\text{THF}$) of the product from $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2] + \text{CO}_2$ (**8-CO₂**).

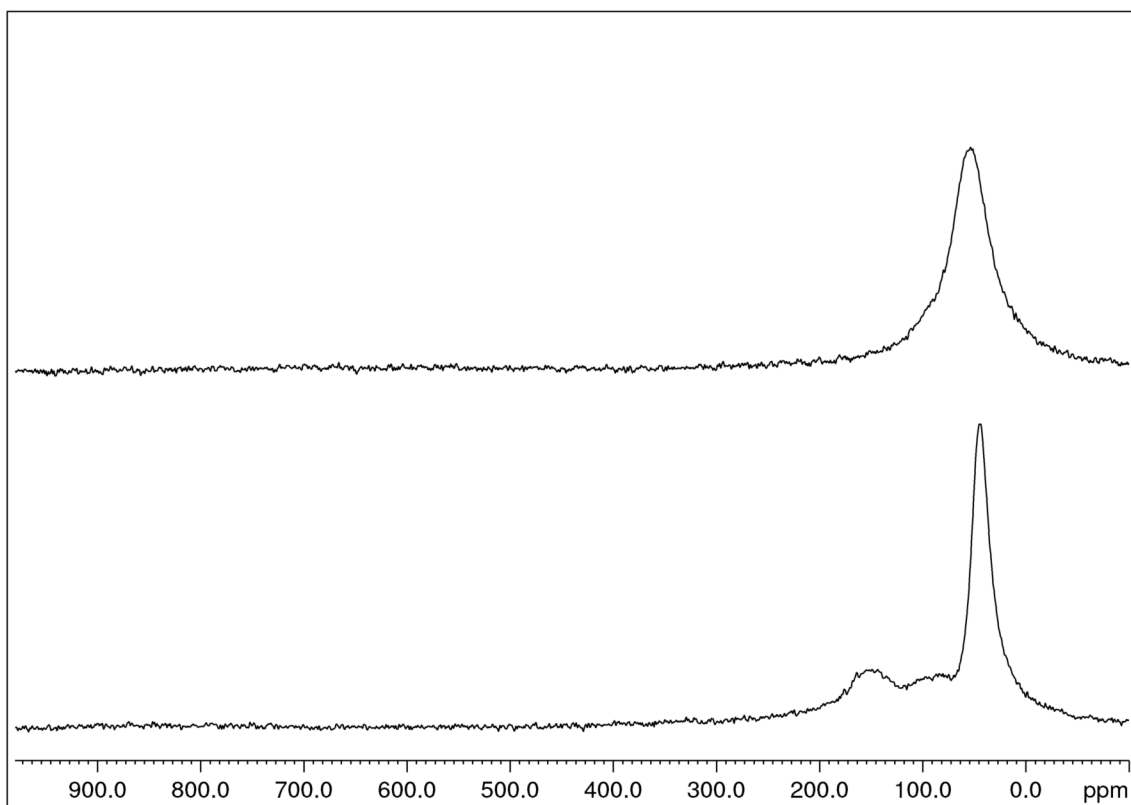


Figure S44. Comparison of the ^{45}Sc NMR spectra (26 °C, 121.49 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2]$ (**8**, bottom) and of the product from $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2] + \text{CO}_2$ (**8-CO₂**, top).

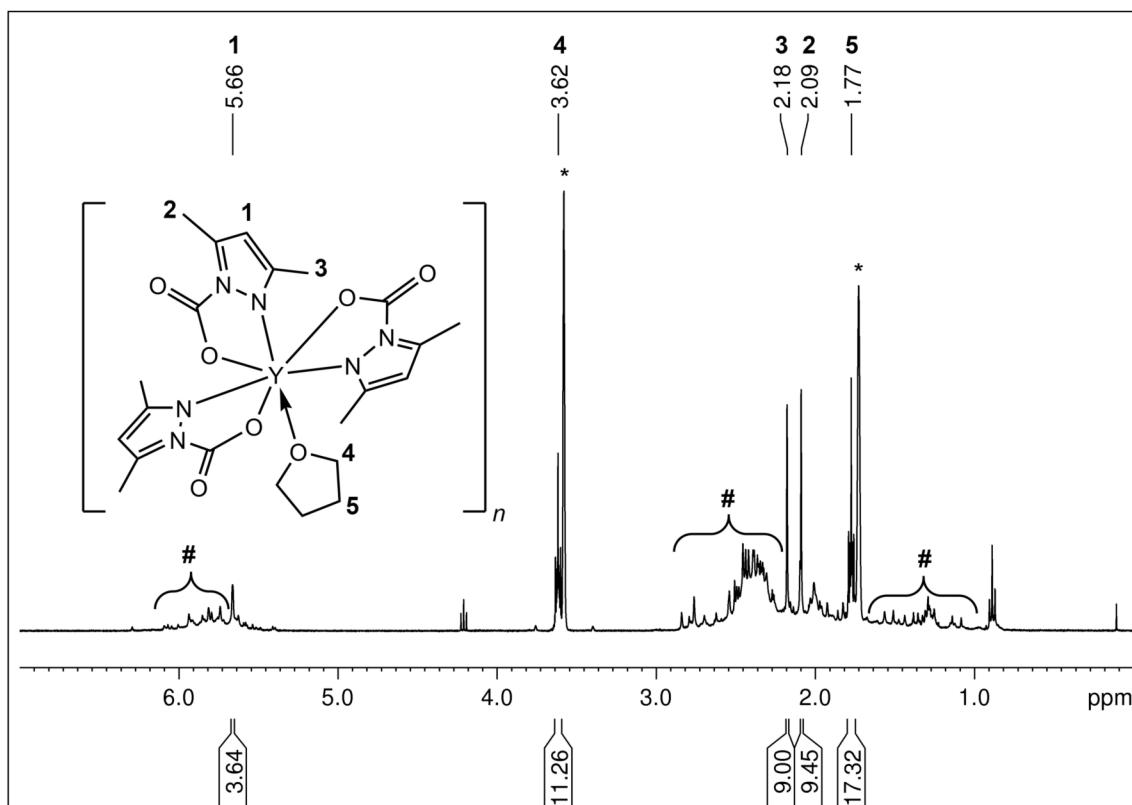


Figure S45. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Y}(\text{CO}_2\text{-pz}^{\text{Me}_2})_3(\text{thf})_x]_n$ (**9-CO₂**) (# cluster insertion species).

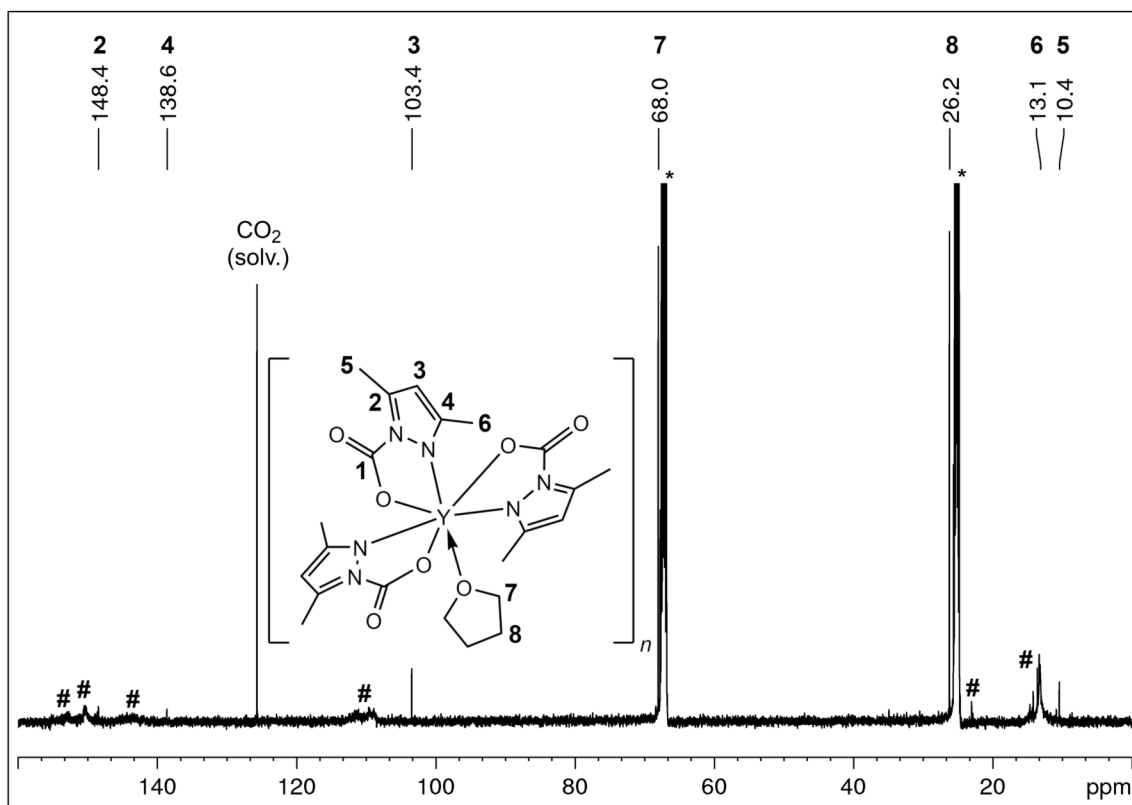


Figure S46. ^{13}C NMR spectrum (26 °C, 125.76 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Y}(\text{CO}_2\text{-pz}^{\text{Me}_2})_3(\text{thf})_x]_n$ (**9-CO₂**) (# cluster insertion species).

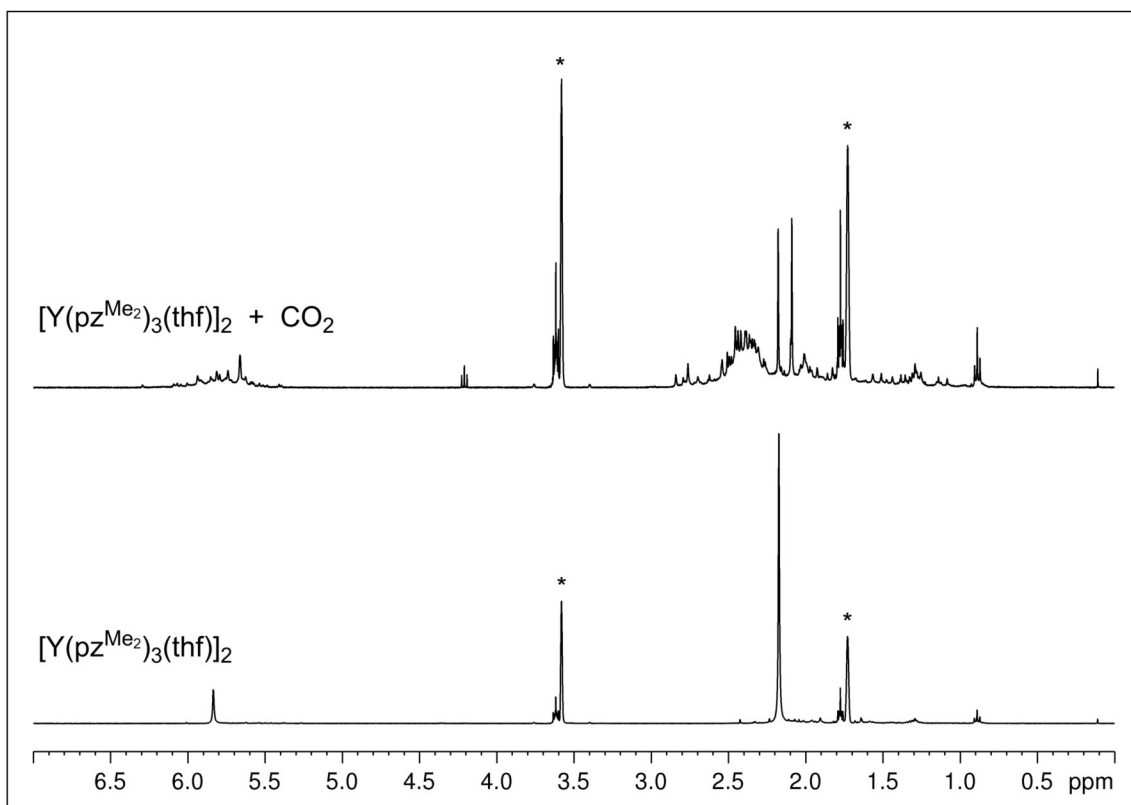


Figure S47. Comparison of the ^1H NMR spectra (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (**9**, bottom) and $[\text{Y}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_3(\text{thf})_x]_n$ (**9-CO₂**, top).

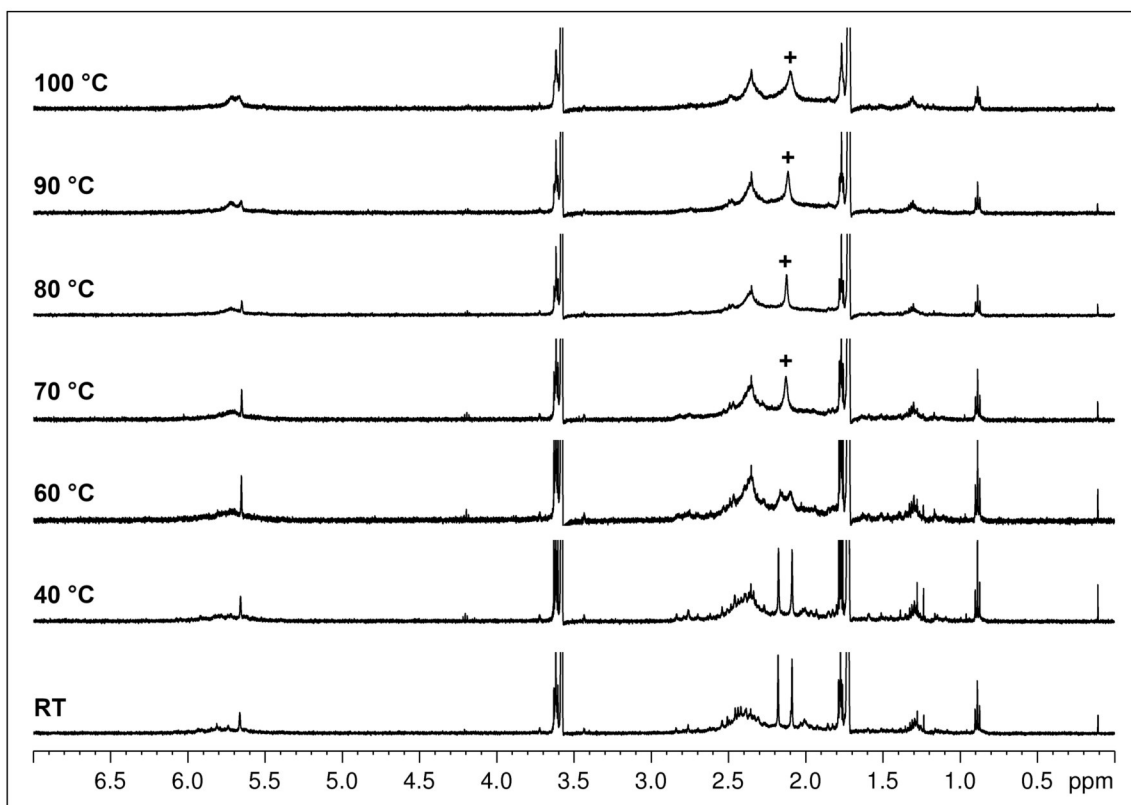


Figure S48. VT ^1H NMR spectra (500.13 MHz, $[\text{D}_8]\text{THF}$) of $[\text{Y}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_3(\text{thf})_x]_n$ (**9-CO₂**) in the range of 26 °C to 100 °C (+ showing CO_2 release and formation of $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (**9**)).

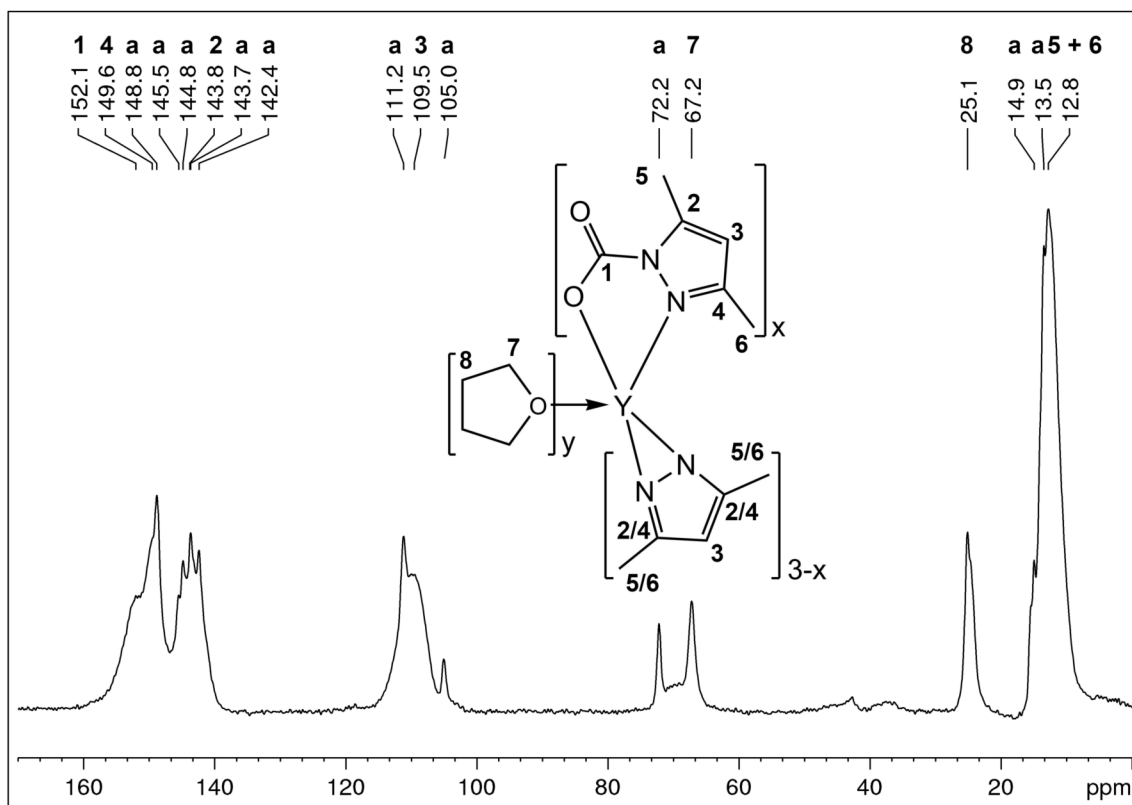


Figure S49. ^{13}C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz) of $[\text{Y}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_x(\text{pz}^{\text{Me}_2})_{3-x}(\text{thf})_y]_n$ (**9-CO₂**) (a = $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (**9**)).

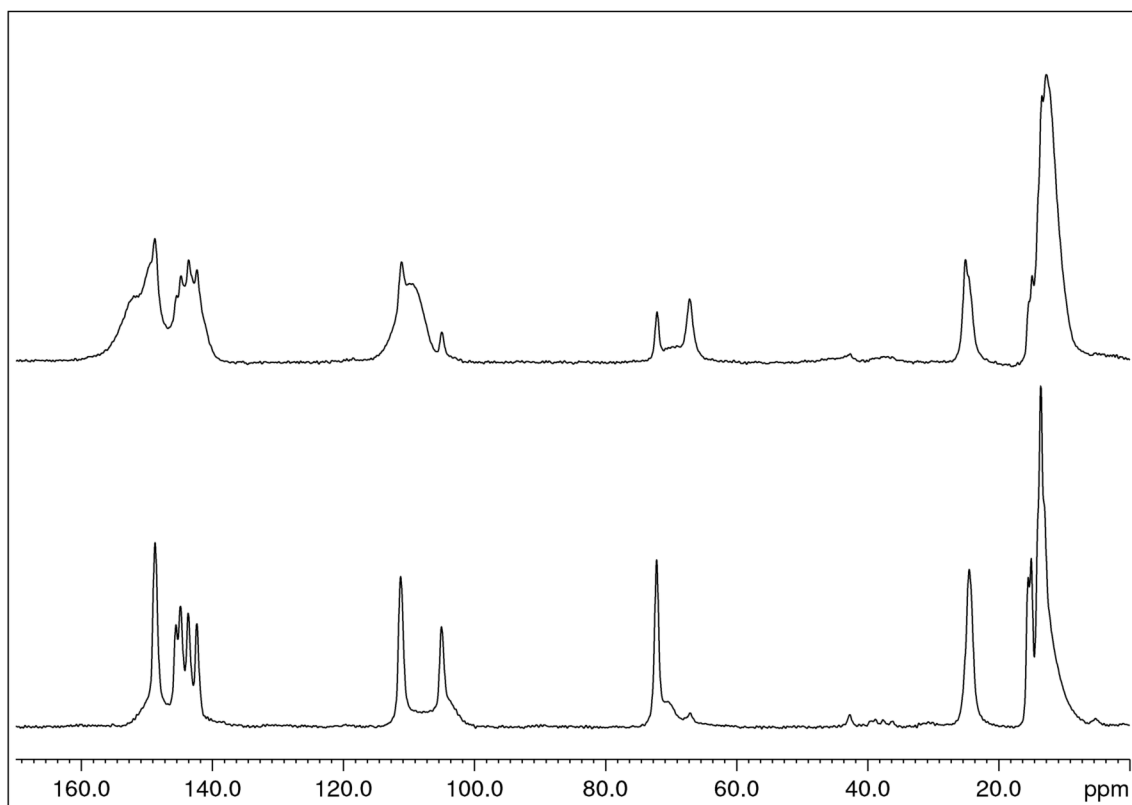


Figure S50. Comparison of ^{13}C CP/MAS spectra (75.47 MHz, MAS at 8 kHz) of $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (**9**, bottom) and $[\text{Y}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_x(\text{pz}^{\text{Me}_2})_{3-x}(\text{thf})_y]_n$ (**9-CO₂**, top).

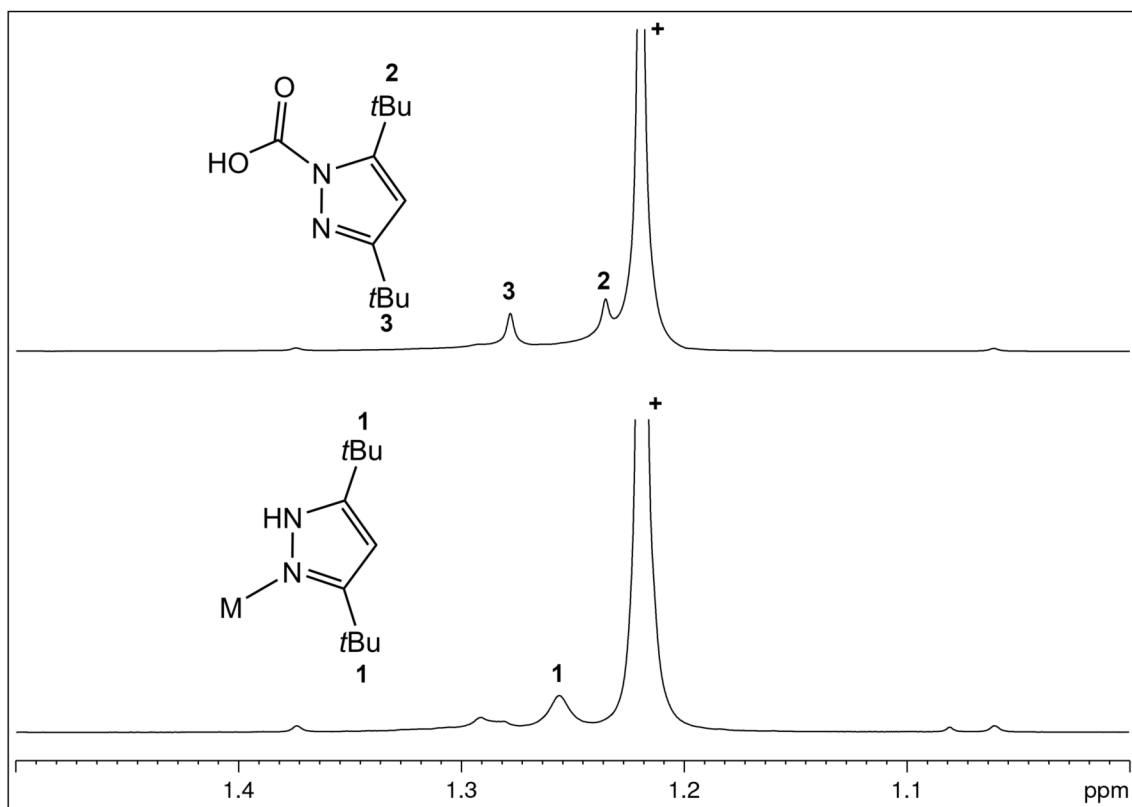


Figure S51. ^1H NMR spectrum (26 °C, 400.11 MHz, $[\text{D}_8]\text{THF}$) of $\text{Y}(\text{pz}^{\text{tBu}_2})_3(\text{thf})_2$ (**10**) reacted with 1 bar CO_2 .

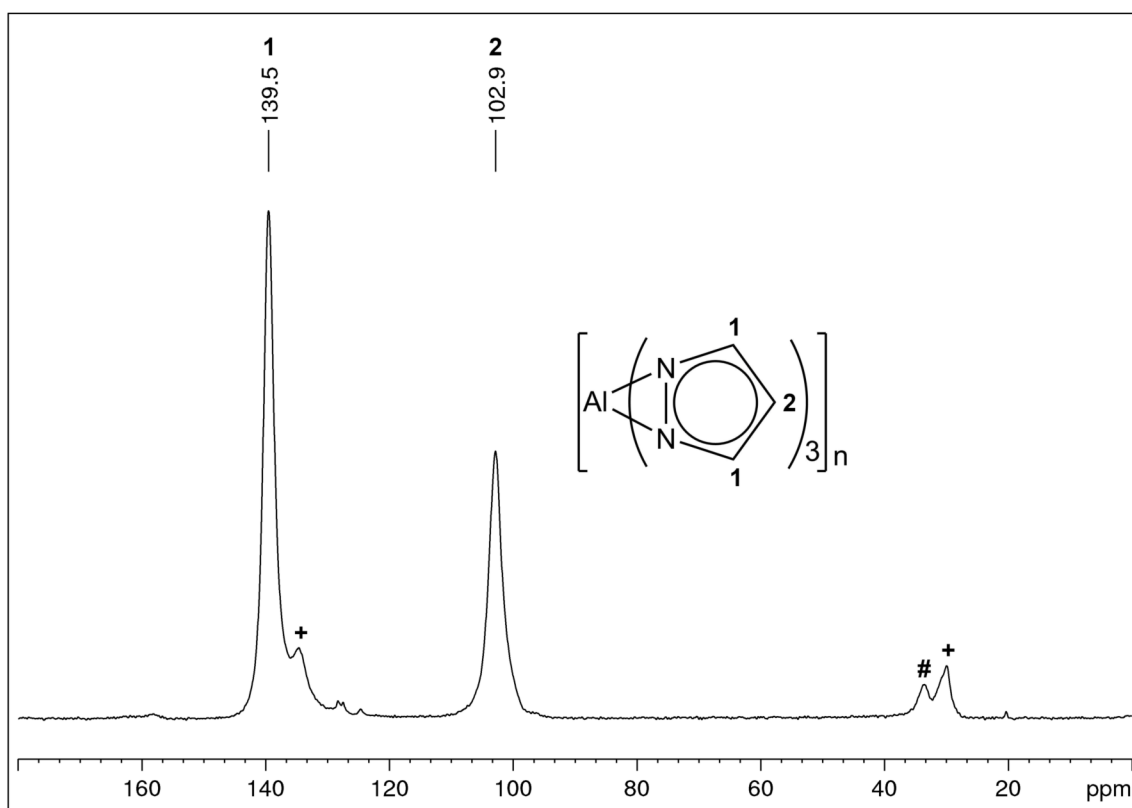


Figure S52. ^{13}C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz) of $[\text{Al}(\text{pz})_3]_n$ (**10**) (+ residual $\text{Al}(\text{pz}^{\text{tBu}_2})_3$ (**1**); # rotation side band).

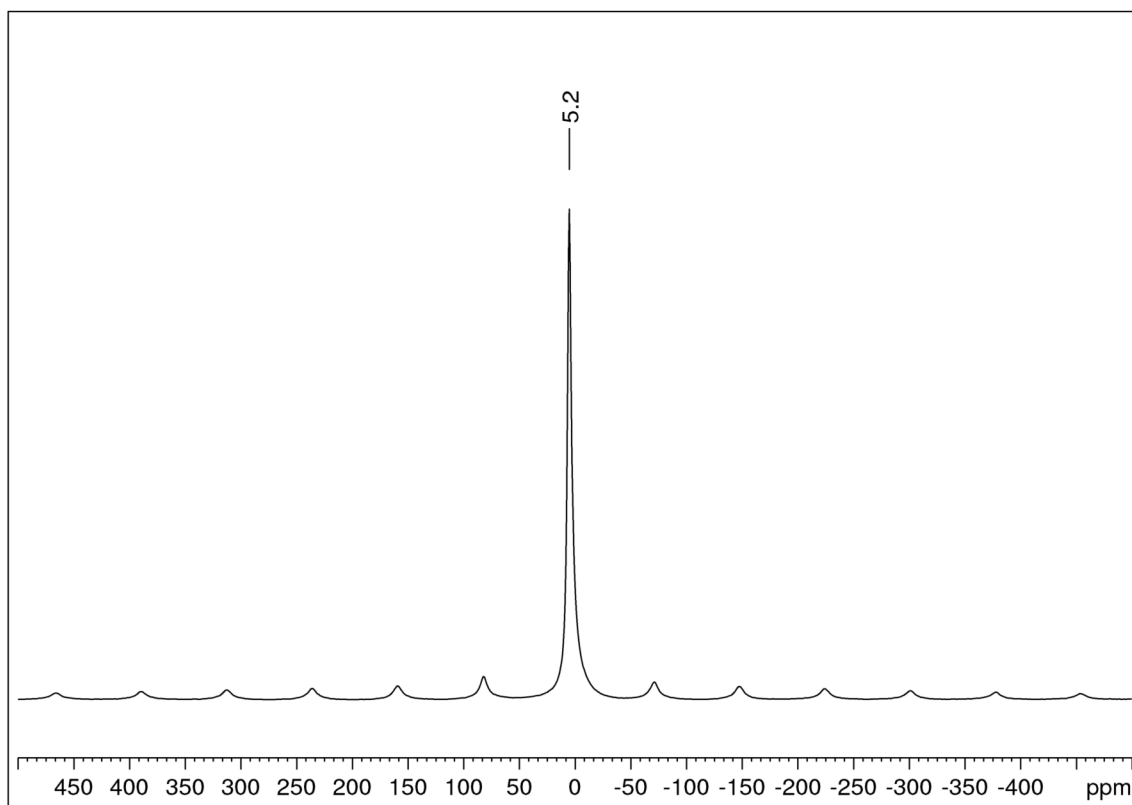


Figure S53. ^{27}Al CP/MAS spectrum (78.20 MHz, MAS at 8 kHz) of $[\text{Al}(\text{pz})_3]_n$ (**10**).

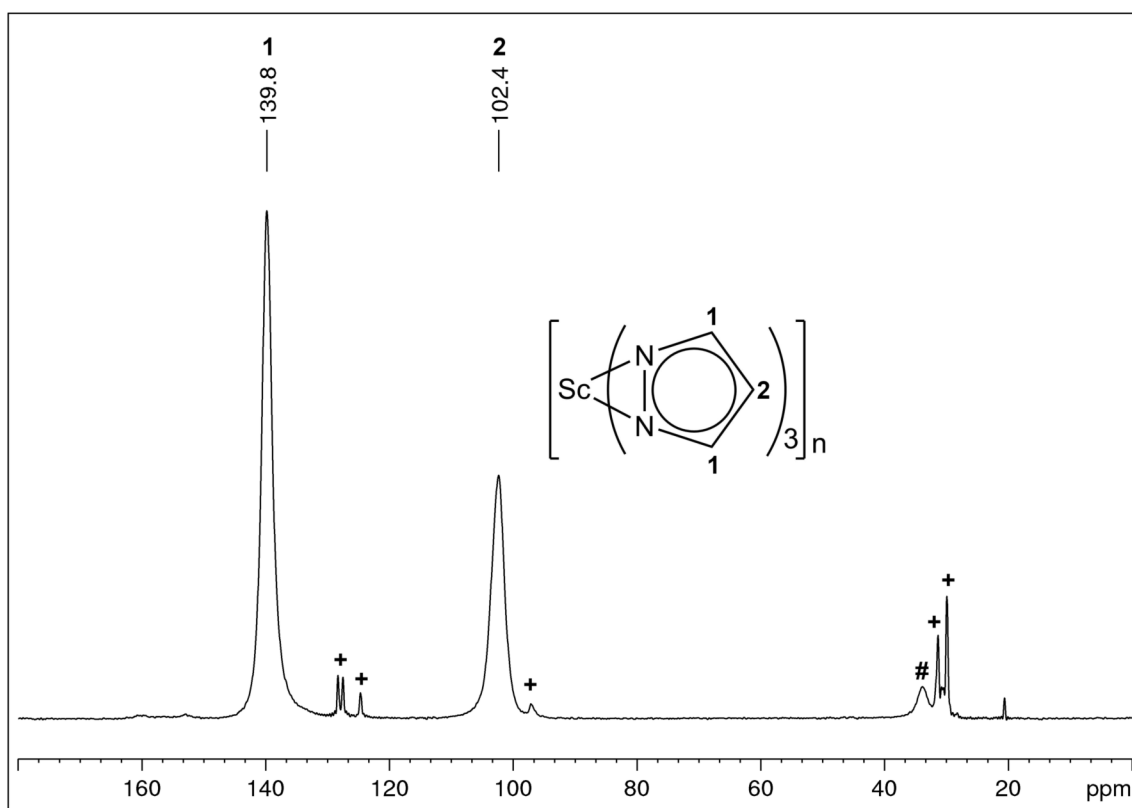


Figure S54. ^{13}C CP/MAS spectrum (75.47 MHz, MAS at 8 kHz) of $[\text{Sc}(\text{pz})_3]_n$ (**11**) (+ residual $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**); # rotation side band).

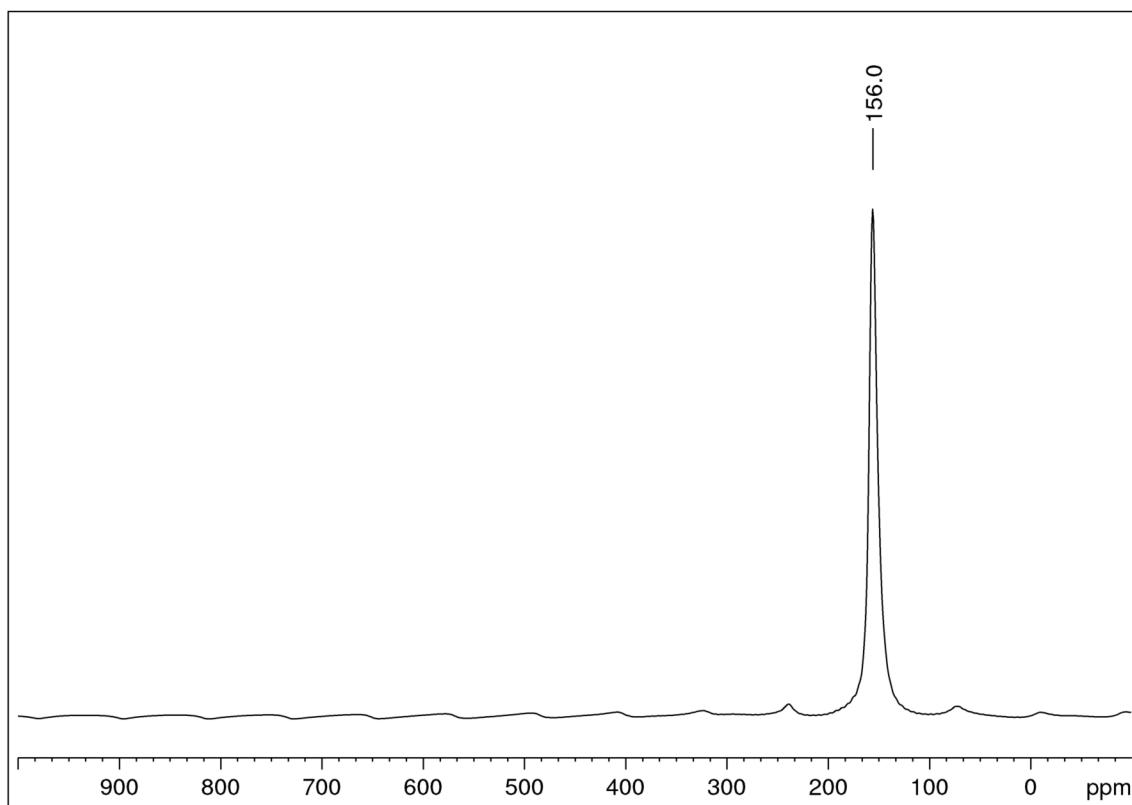


Figure S55. ^{45}Sc CP/MAS spectrum (72.90 MHz, MAS at 8 kHz) of $[\text{Sc}(\text{pz})_3]_n$ (**11**).

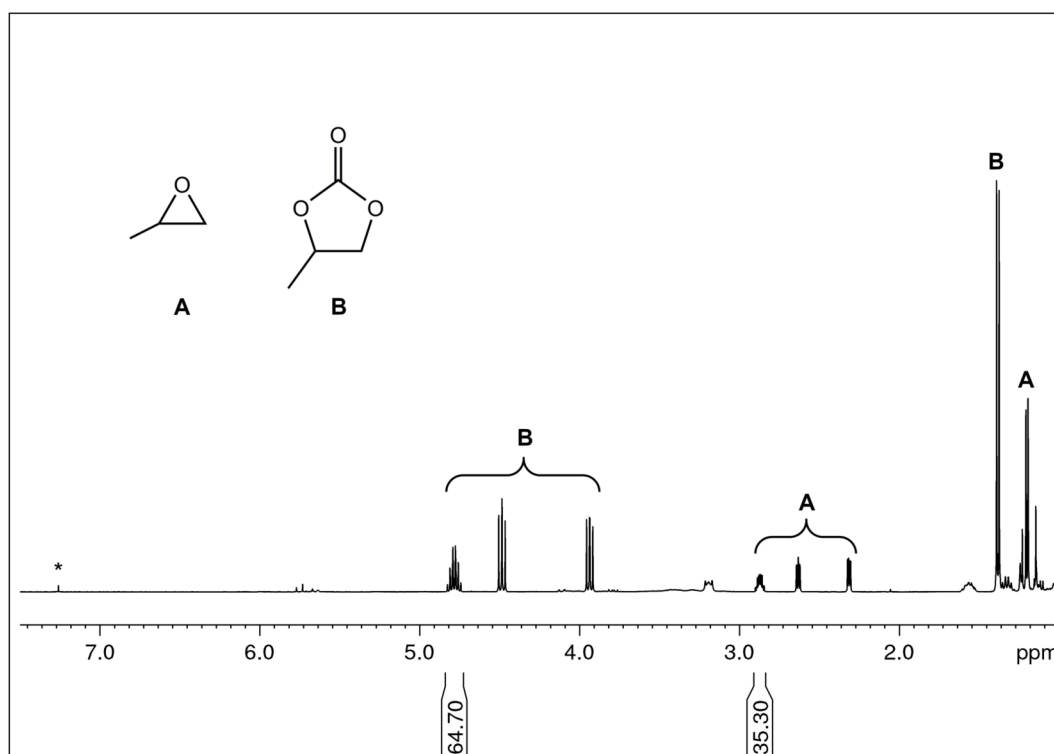


Figure S56. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Al}(\text{pz}^{\text{tBu}_2})_3$ (**1**) as a catalyst.

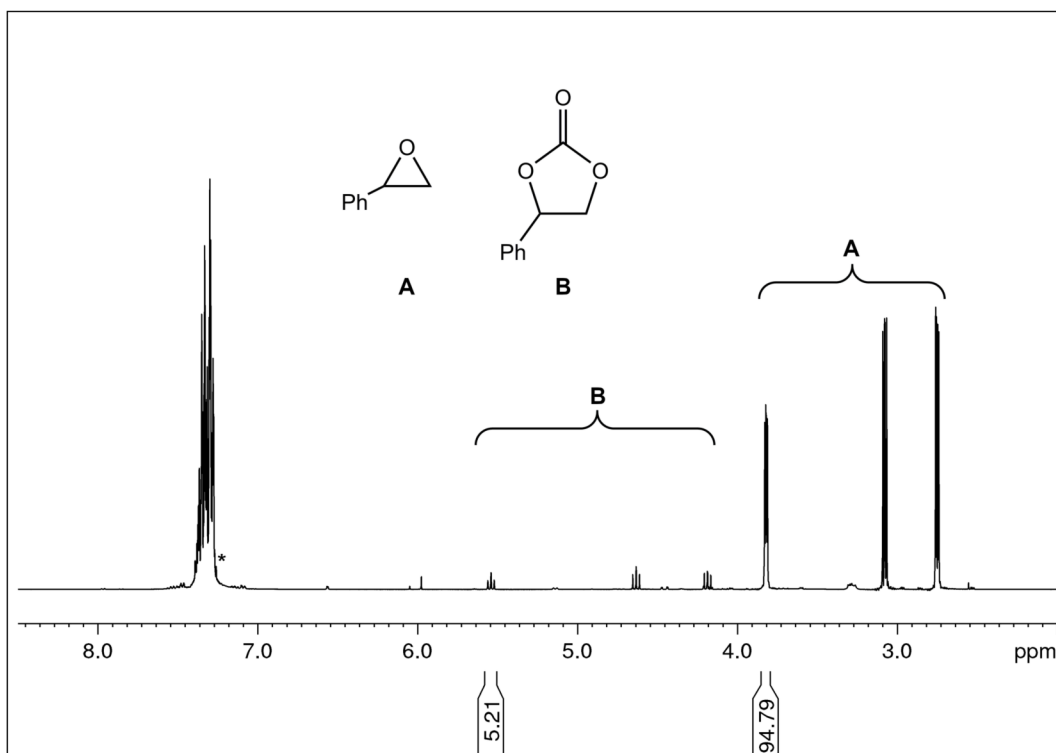


Figure S57. ^1H NMR spectrum (26 °C, 400.11 MHz, $\text{chloroform-}d$) of the reaction mixture of the catalytic conversion of styrene oxide and CO_2 to styrene carbonate by using 0.5 mol% of $\text{Al}(\text{pz}^{t\text{Bu}_2})_3$ (**1**) as a catalyst.

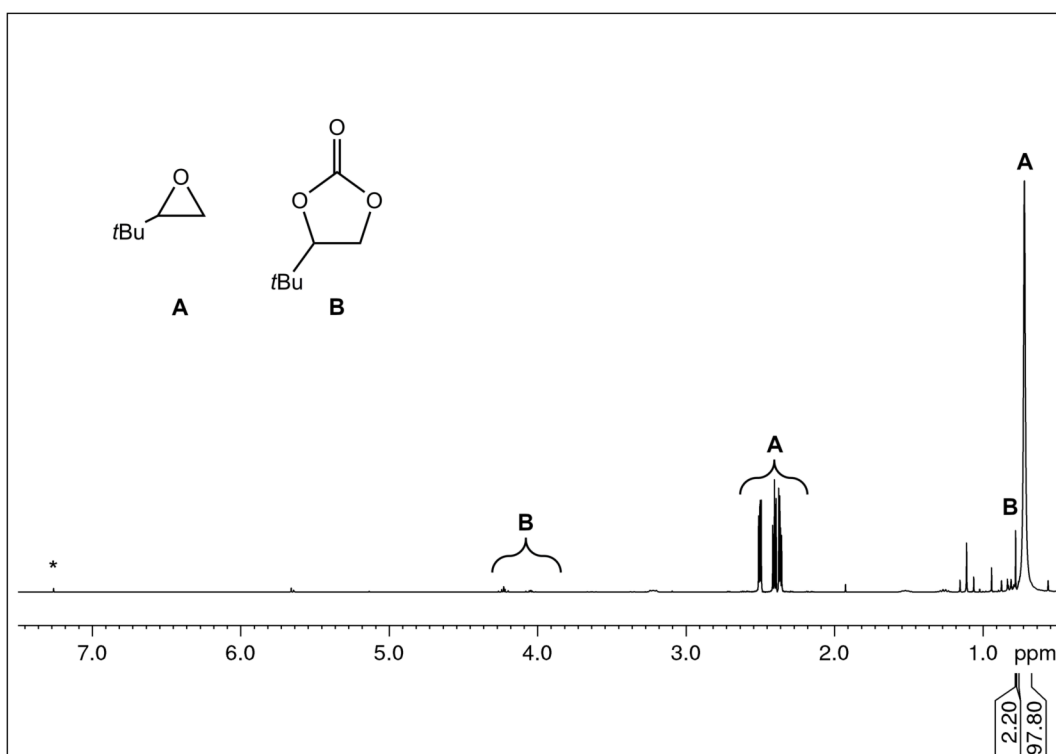


Figure S58. ^1H NMR spectrum (26 °C, 400.11 MHz, $\text{chloroform-}d$) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% of $\text{Al}(\text{pz}^{t\text{Bu}_2})_3$ (**1**) as a catalyst.

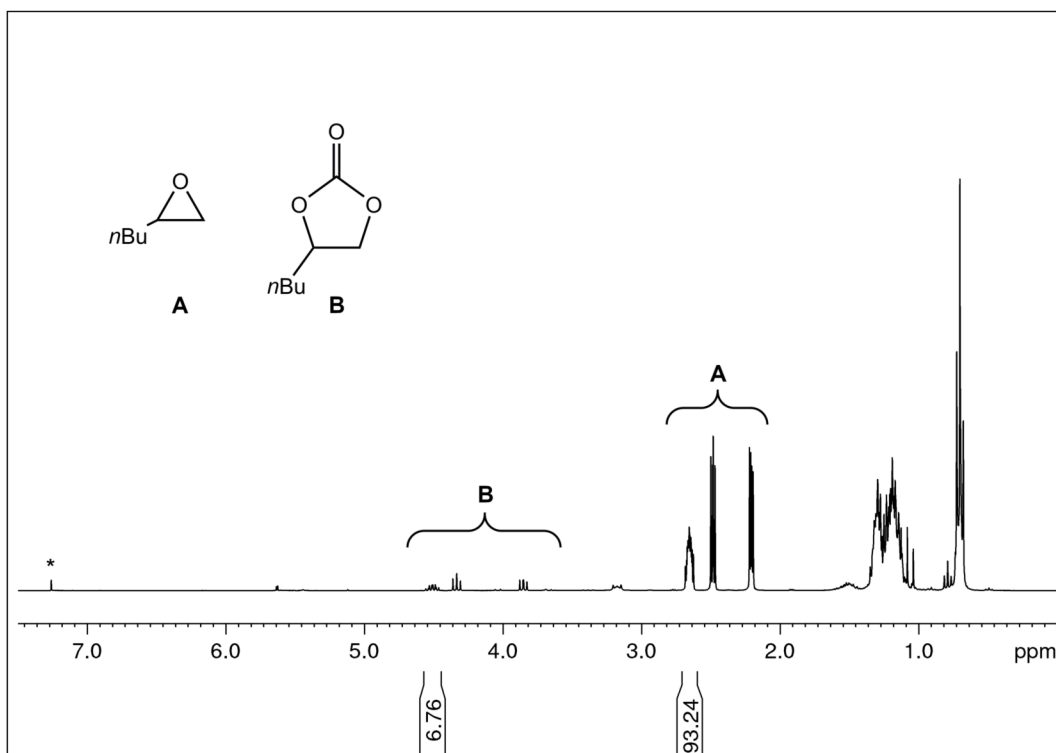


Figure S59. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO₂ to 1,2-*n*-hexylene carbonate by using 0.5 mol% of Al(pz^{tBu})₃ (**1**) as a catalyst.

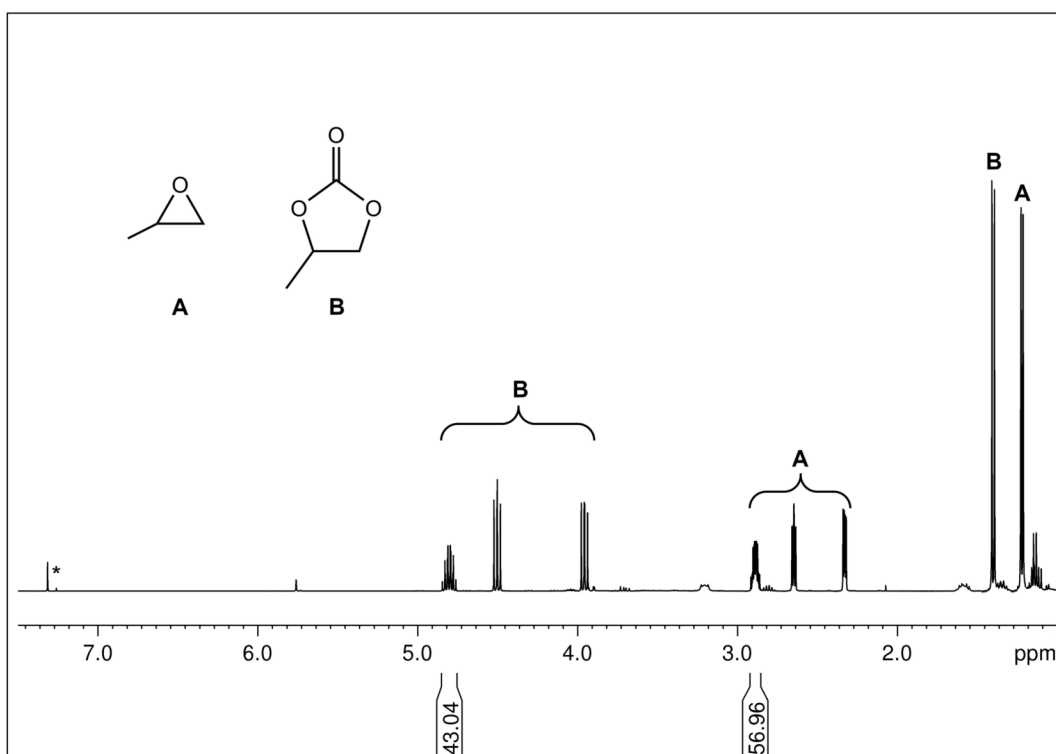


Figure S60. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.5 mol% of [Al(pz^{iPr})₃]₂ (**4**) as a catalyst.

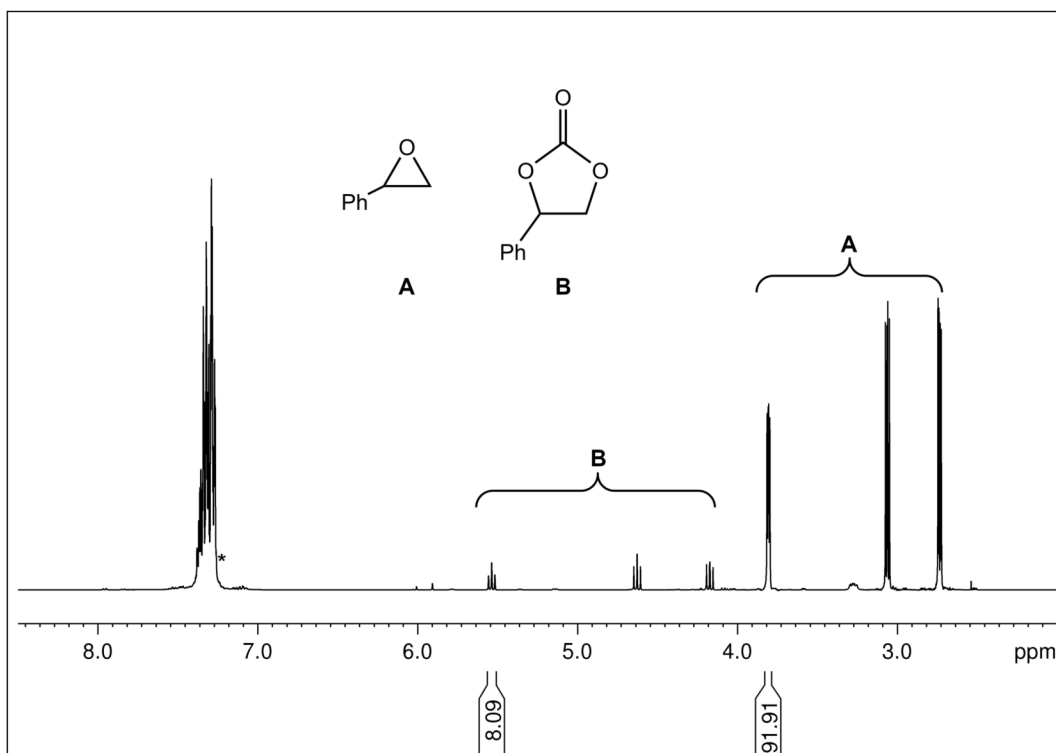


Figure S61. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of styrene oxide and CO_2 to styrene carbonate by using 0.5 mol% of $[\text{Al}(\text{pz}^{i\text{Pr}_2})_3]_2$ (**4**) as a catalyst.

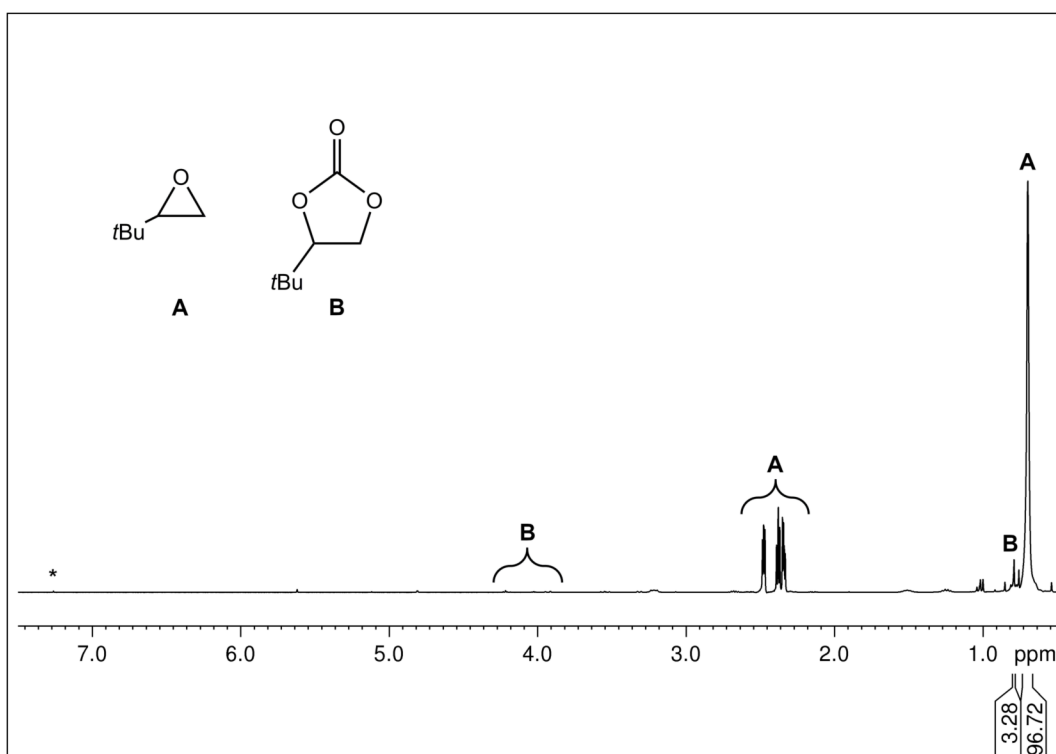


Figure S62. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% of $[\text{Al}(\text{pz}^{i\text{Pr}_2})_3]_2$ (**4**) as a catalyst.

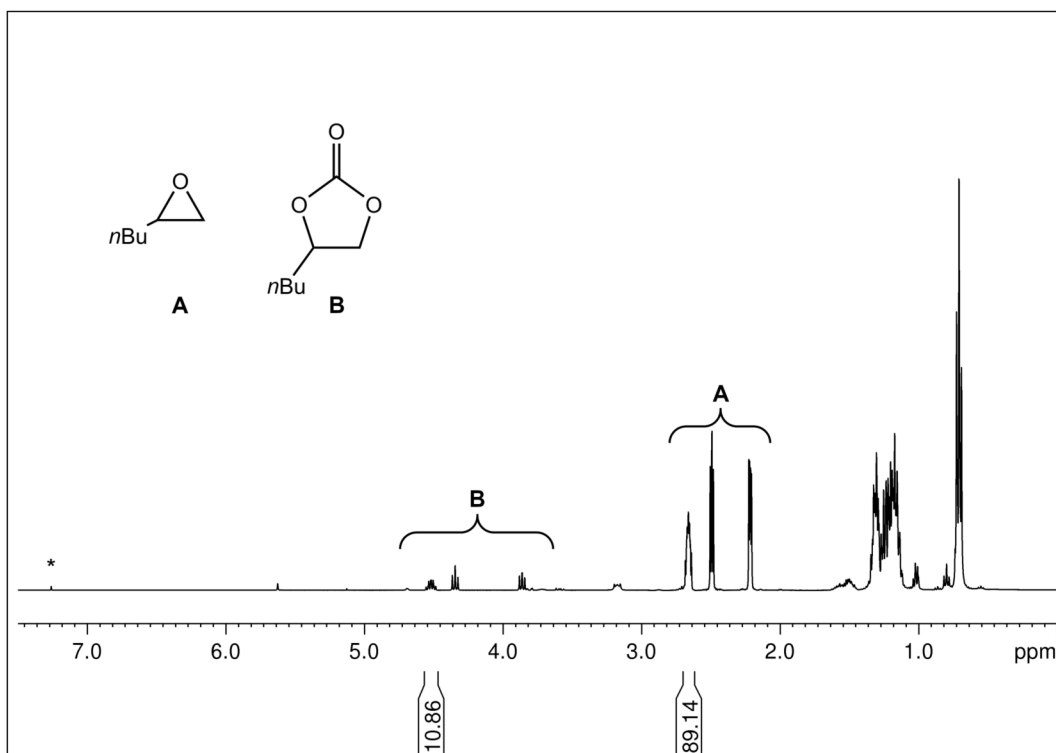


Figure S63. ^1H NMR spectrum (26 °C, 400.11 MHz, CHCl_3) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO_2 to 1,2-*n*-hexylene carbonate by using 0.5 mol% of $[\text{Al}(\text{pz}^{\text{iPr}_2})_3]_2$ (**4**) as a catalyst.

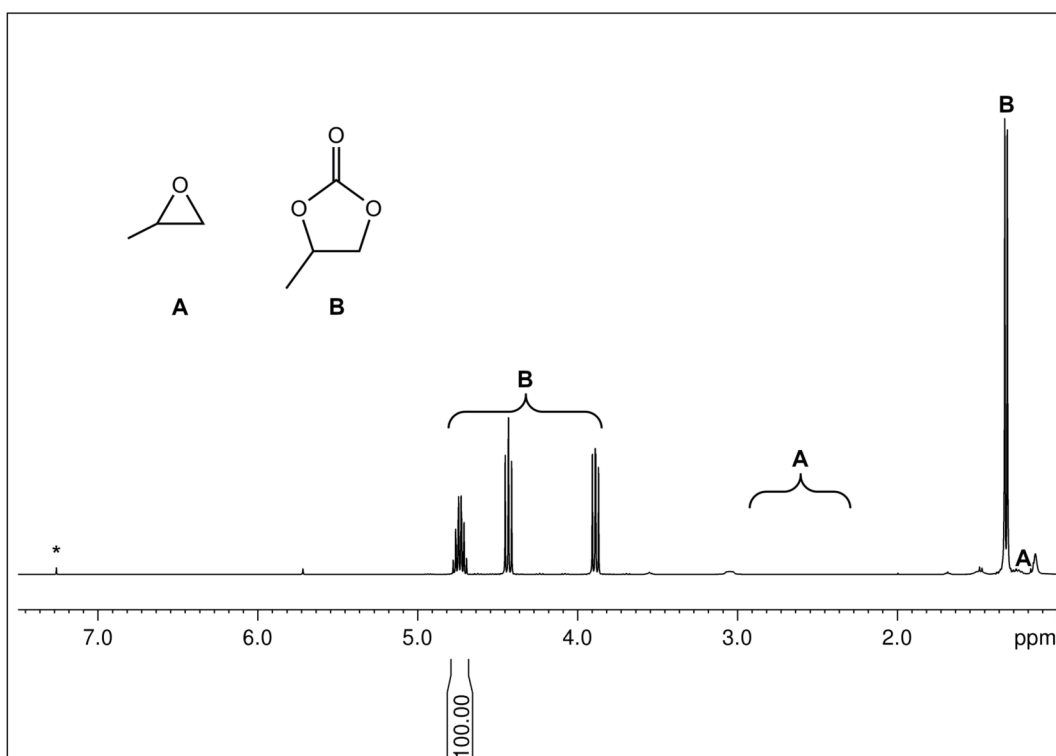


Figure S64. ^1H NMR spectrum (26 °C, 400.11 MHz, CHCl_3) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) as a catalyst.

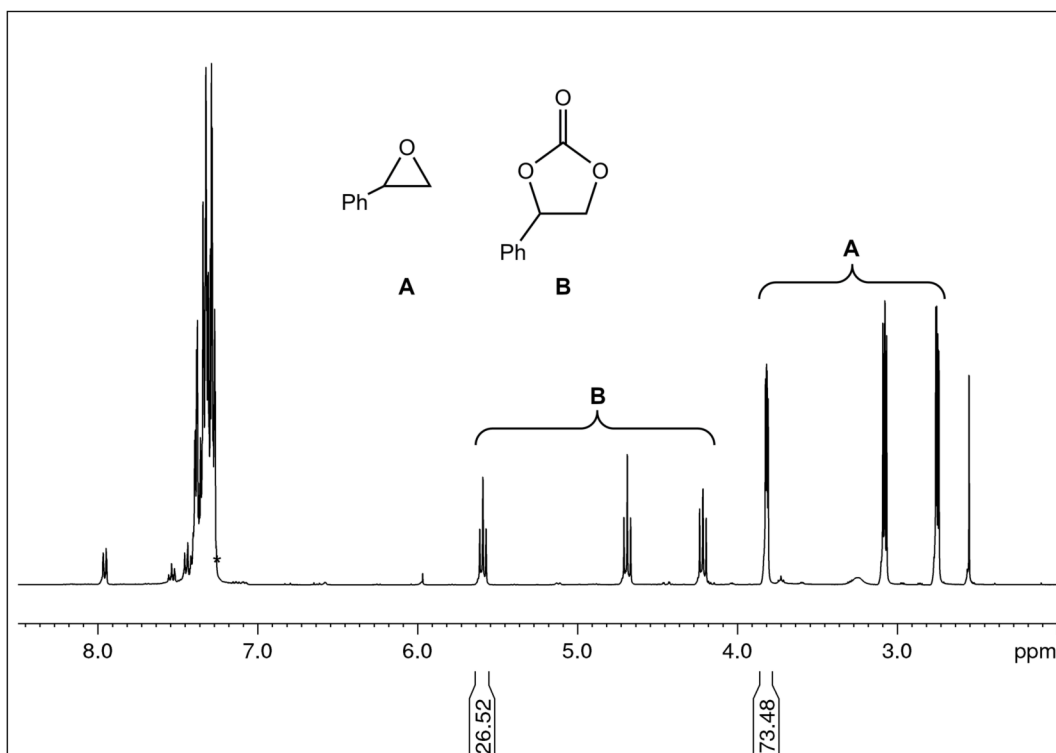


Figure S65. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of styrene oxide and CO_2 to styrene carbonate by using 0.5 mol% of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) as a catalyst.

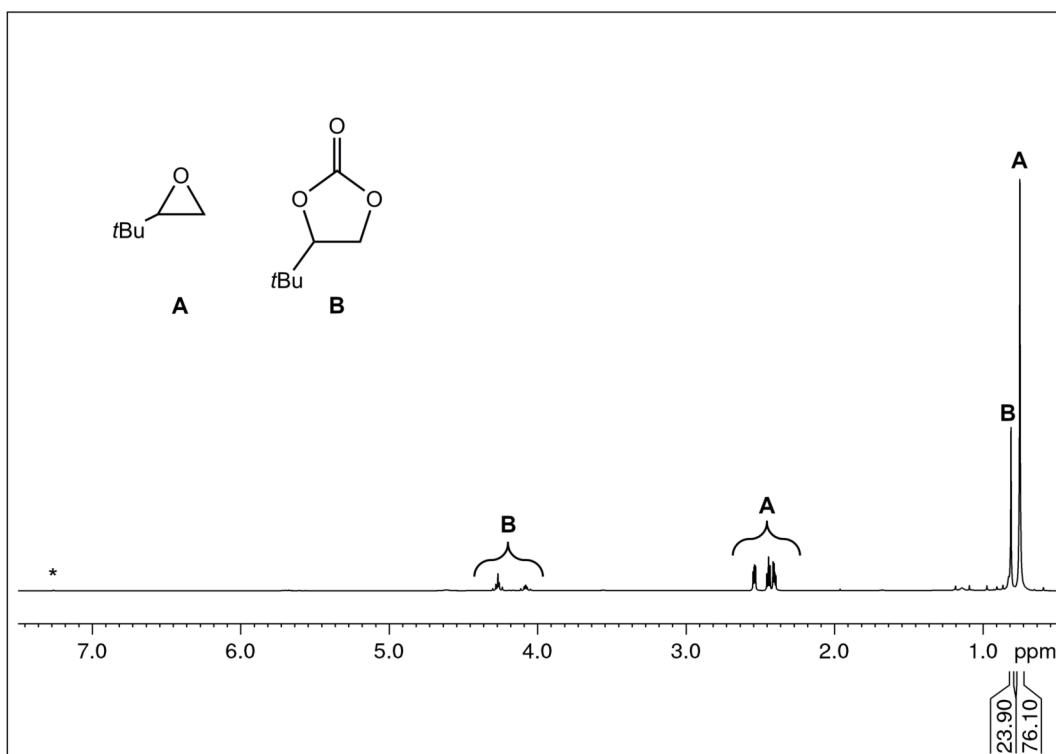


Figure S66. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) as a catalyst.

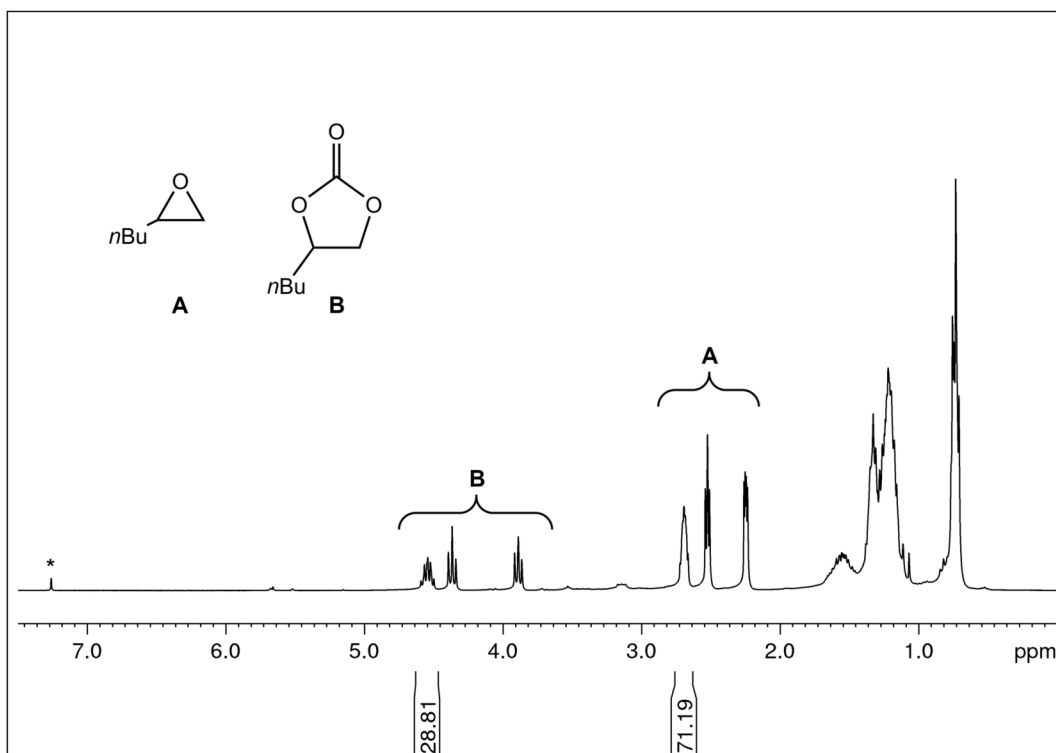


Figure S67. ^1H NMR spectrum (26 °C, 400.11 MHz, CHCl_3 - d) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO_2 to 1,2-*n*-hexylene carbonate by using 0.5 mol% of $\text{Sc}(\text{pz}^{t\text{Bu}_2})_3(\text{thf})$ (**7**) as a catalyst.

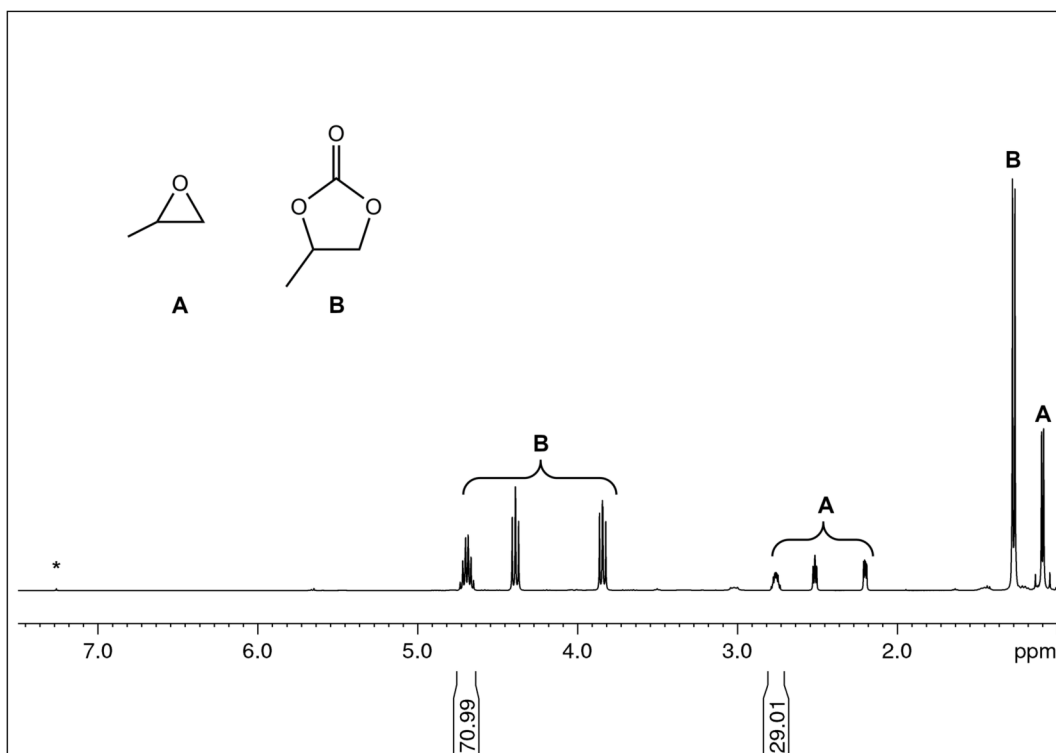


Figure S68. ^1H NMR spectrum (26 °C, 400.11 MHz, CHCl_3 - d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.25 mol% of $\text{Sc}(\text{pz}^{t\text{Bu}_2})_3(\text{thf})$ (**7**) as a catalyst.

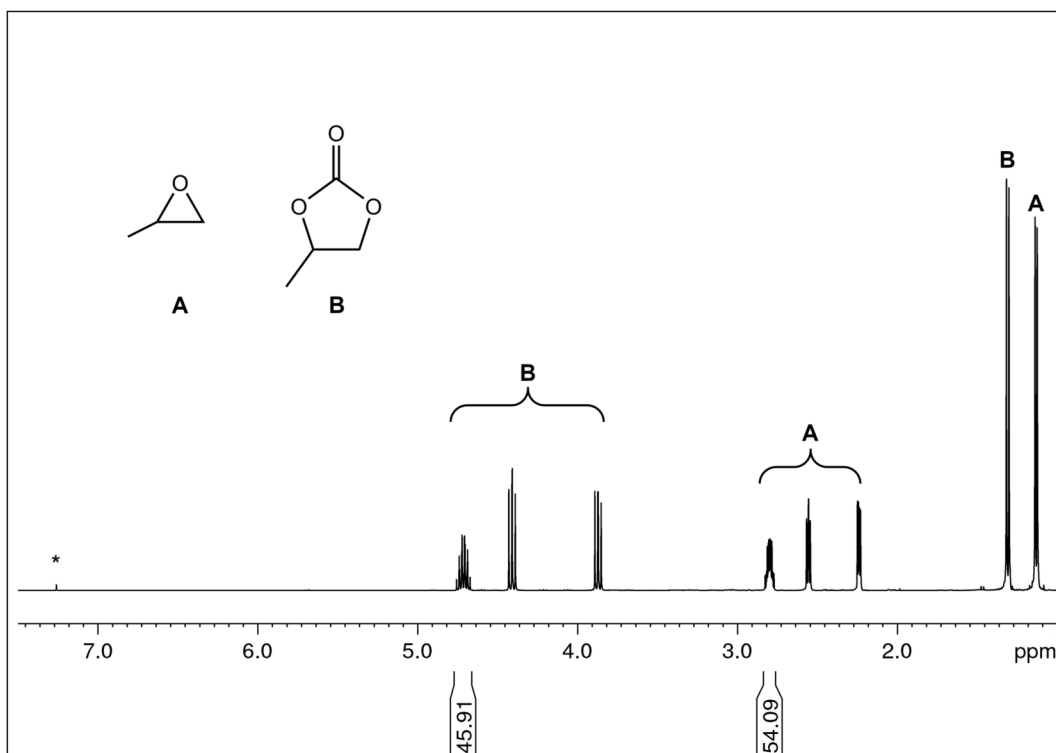


Figure S69. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.01 mol% of Sc(pz^{tBu₂})₃(thf) (**7**) as a catalyst at 90 °C and 10 bar CO₂.

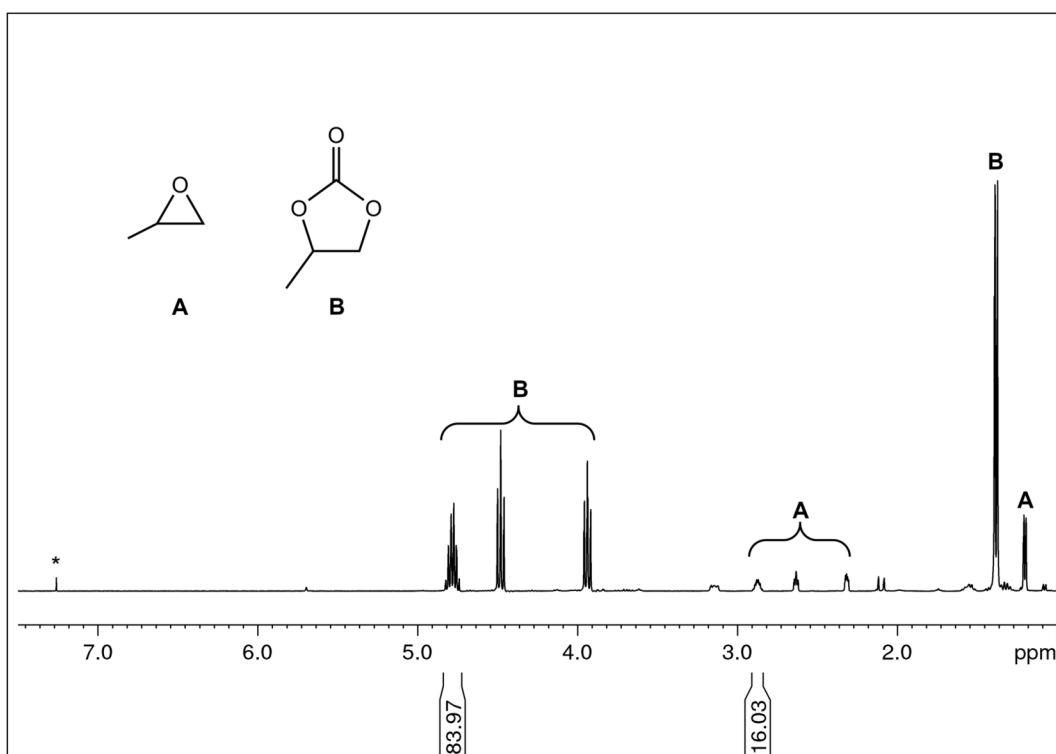


Figure S70. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.5 mol% of [Y(pz^{Me₂})₃(thf)]₂ (**9**) as a catalyst.

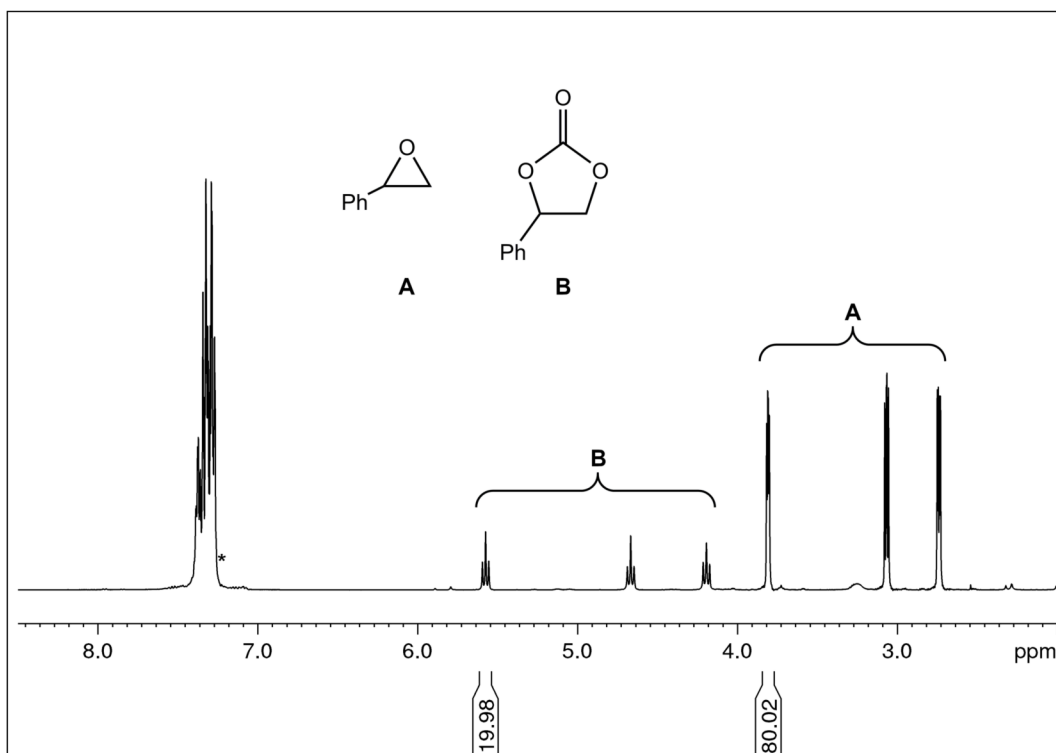


Figure S71. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of styrene oxide and CO_2 to styrene carbonate by using 0.5 mol% of $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (**9**) as a catalyst.

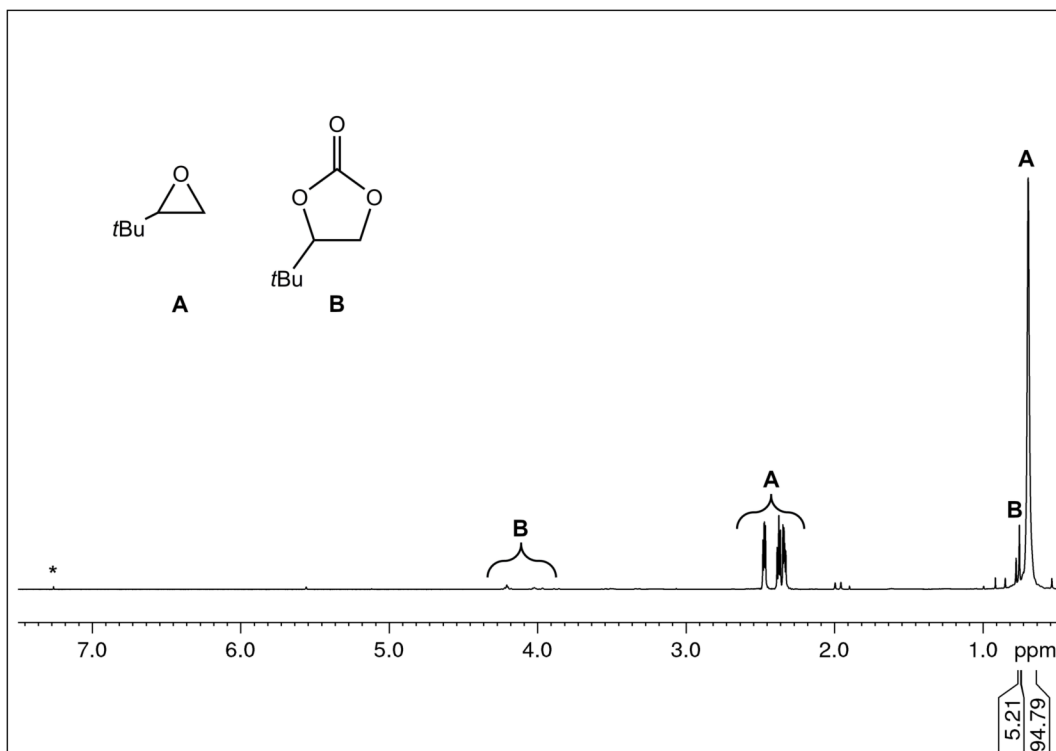


Figure S72. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% of $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (**9**) as a catalyst.

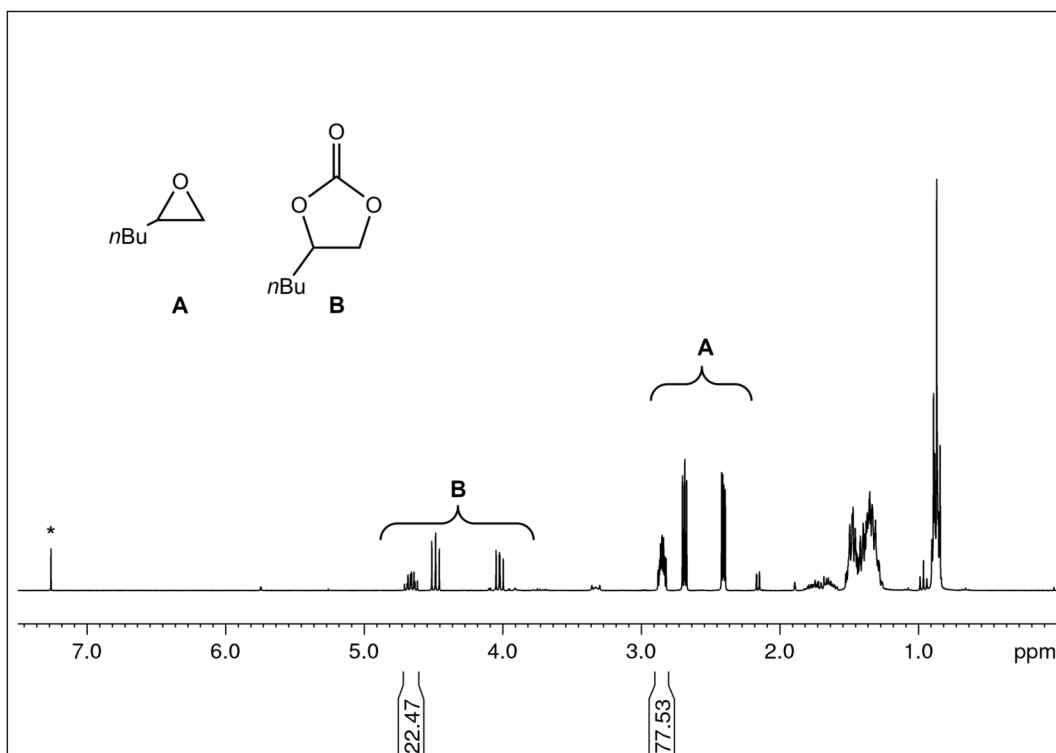


Figure S73. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO_2 to 1,2- n -hexylene carbonate by using 0.5 mol% of $[\text{Y}(\text{pz}^{\text{Me}_2})_3(\text{thf})]_2$ (**9**) as a catalyst.

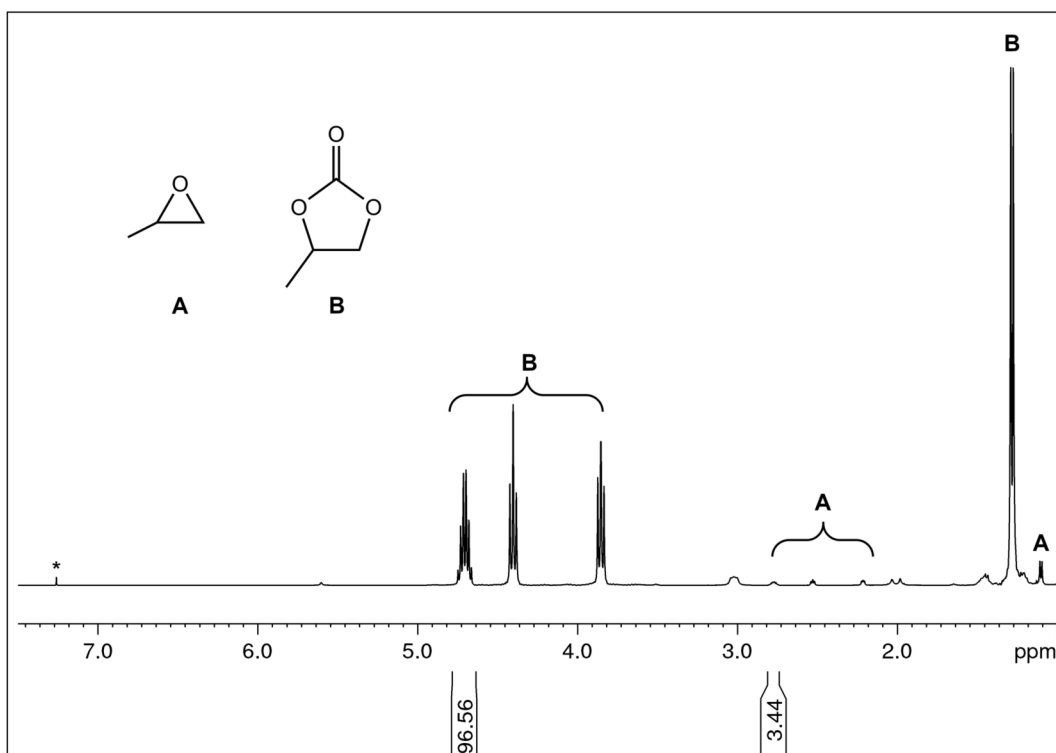


Figure S74. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $[\text{Y}(\text{pz}^{\text{tBu}_2})_3(\text{thf})]_2$ (**10**) as a catalyst.

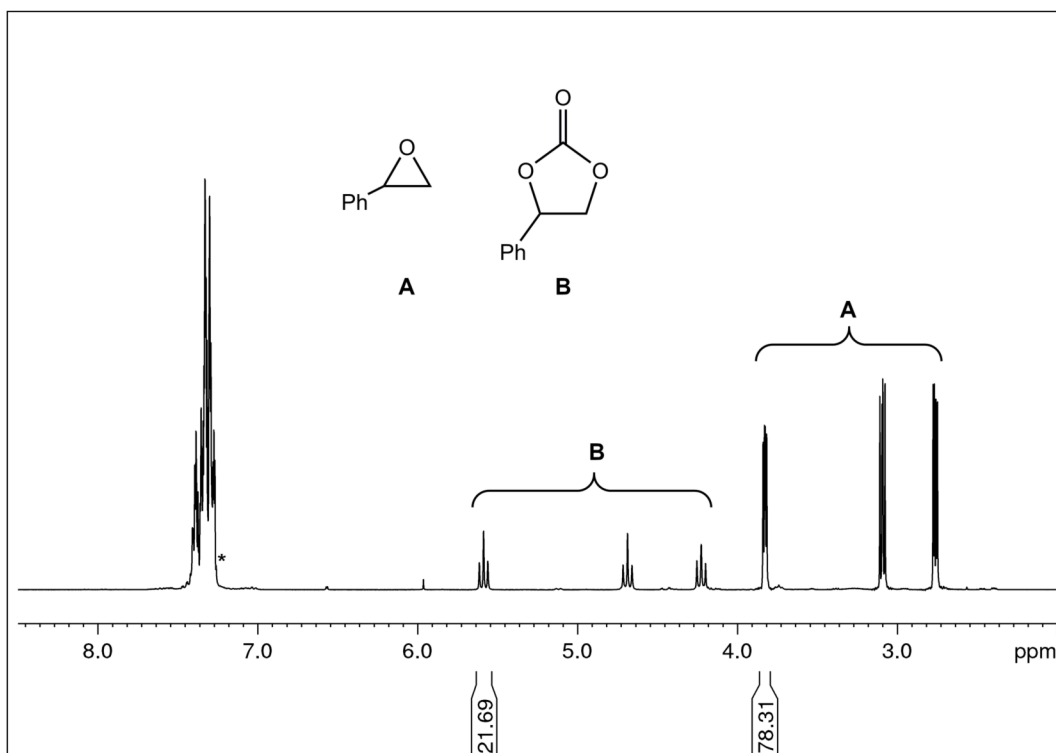


Figure S75. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of styrene oxide and CO_2 to styrene carbonate by using 0.5 mol% of $[\text{Y}(\text{pz}^{\text{tBu}_2})_3(\text{thf})]_2$ (**10**) as a catalyst.

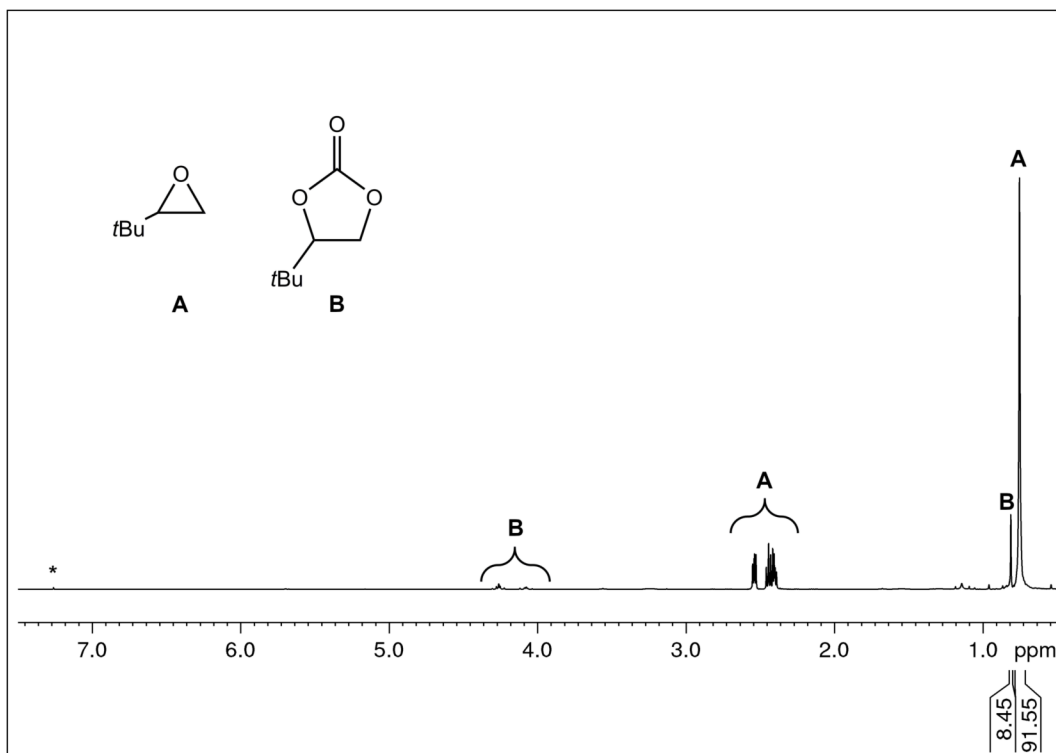


Figure S76. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% of $[\text{Y}(\text{pz}^{\text{tBu}_2})_3(\text{thf})]_2$ (**10**) as a catalyst.

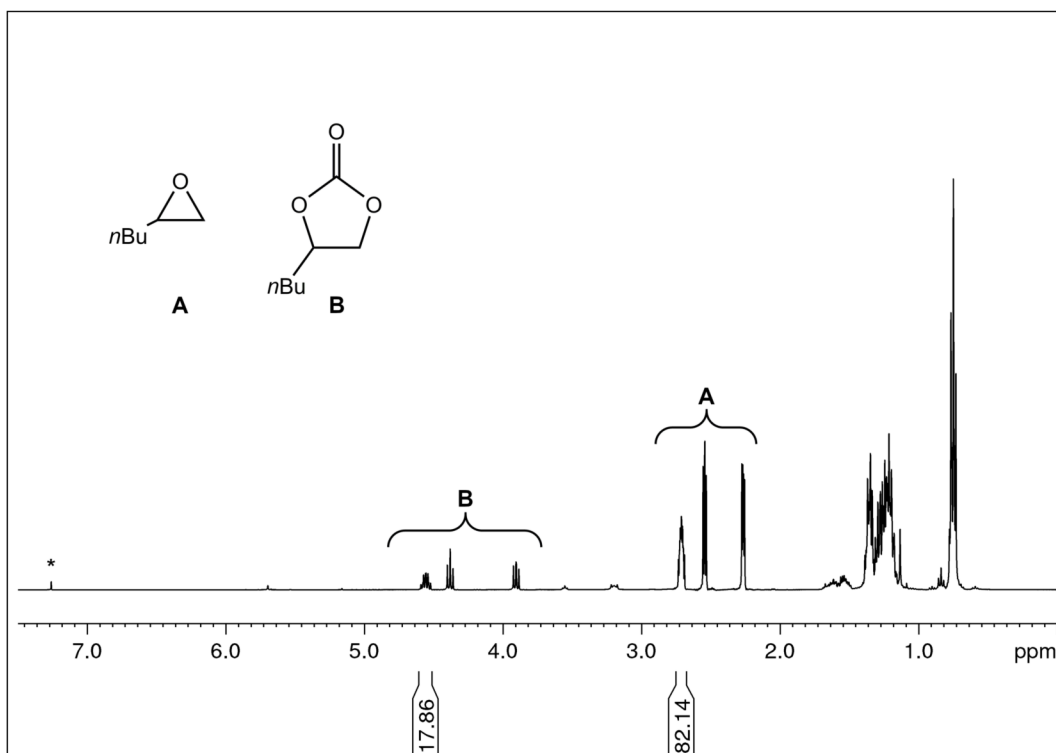


Figure S77. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO_2 to 1,2- n -hexylene carbonate by using 0.5 mol% of $[\text{Y}(\text{pz}^{\text{tBu}_2})_3(\text{thf})_2]$ (**10**) as a catalyst.

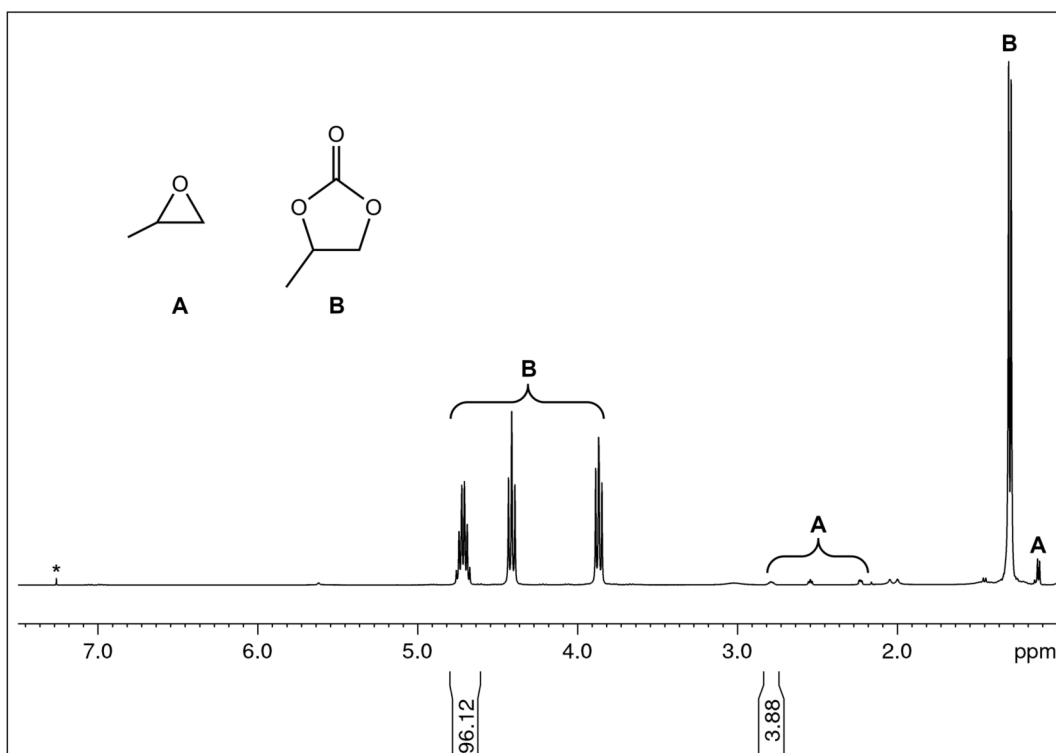


Figure S78. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $[\text{Ce}(\text{pz}^{\text{Me}_2})_3]_4$ (**13**) as a catalyst.

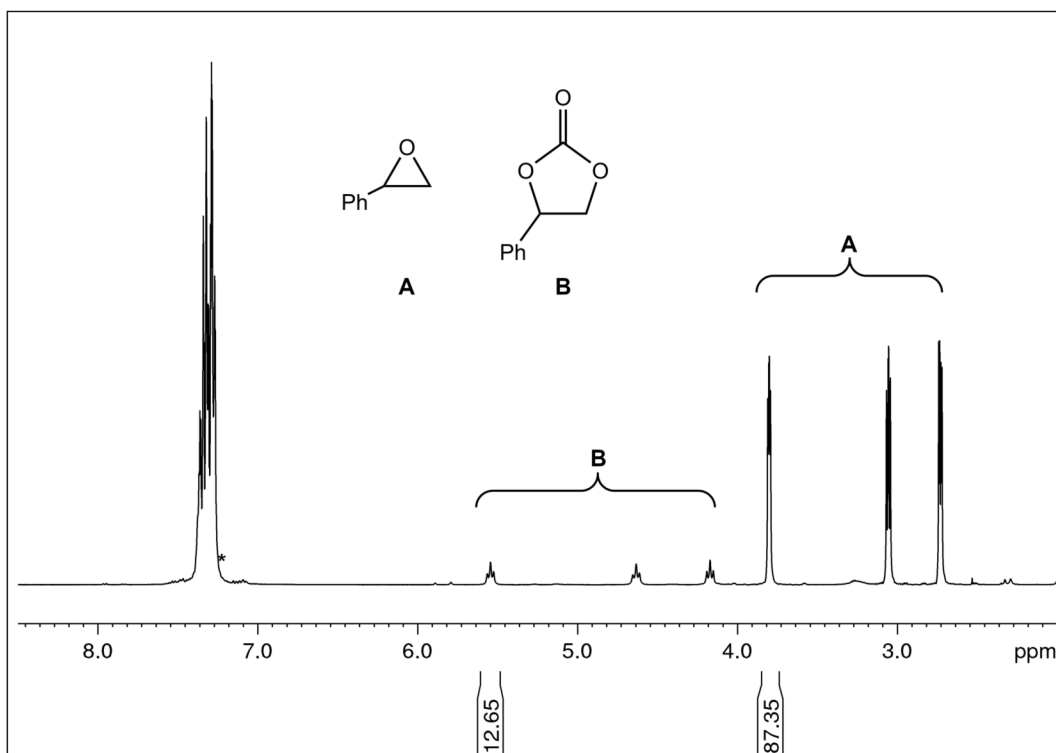


Figure S79. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of styrene oxide and CO_2 to styrene carbonate by using 0.5 mol% of $[\text{Ce}(\text{pz}^{\text{Me}_2})_3]_4$ (**13**) as a catalyst.

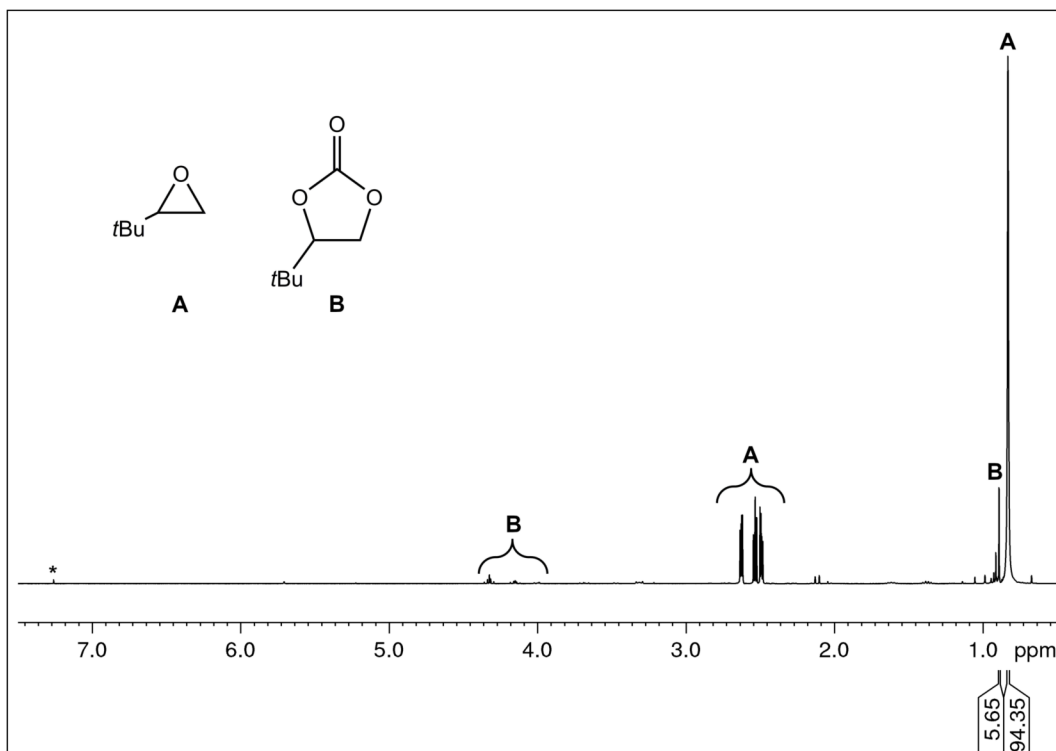


Figure S80. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% of $[\text{Ce}(\text{pz}^{\text{Me}_2})_3]_4$ (**13**) as a catalyst.

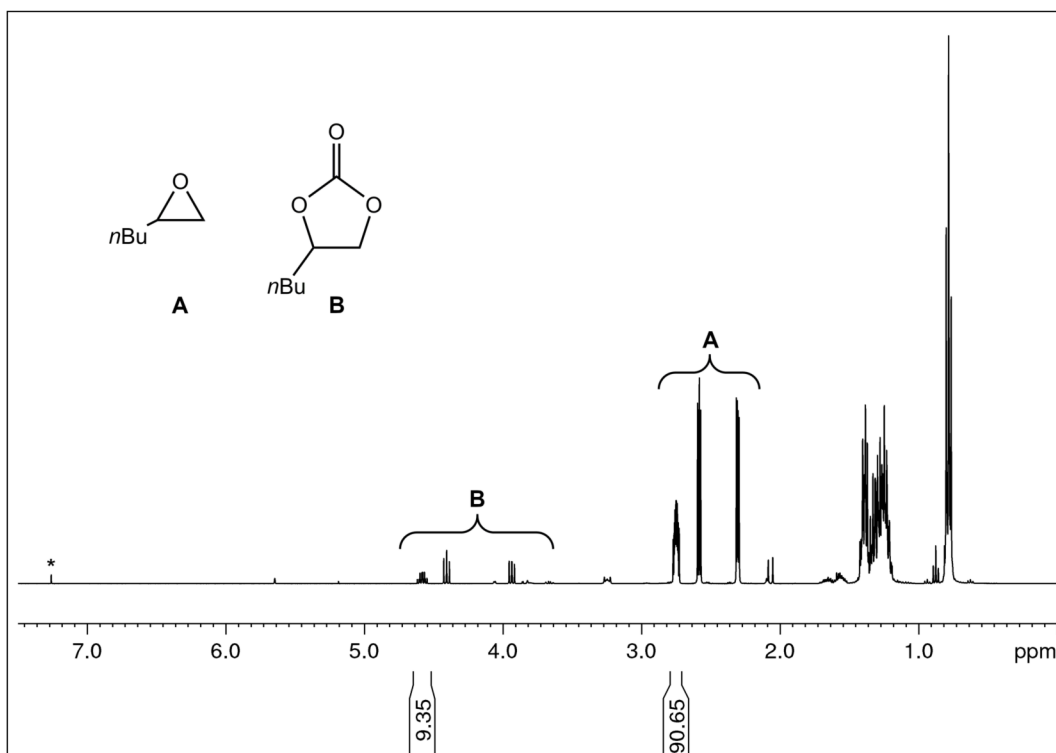


Figure S81. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO₂ to 1,2-*n*-hexylene carbonate by using 0.5 mol% of [Ce(pz^{Me₂})₃]₄ (**13**) as a catalyst.

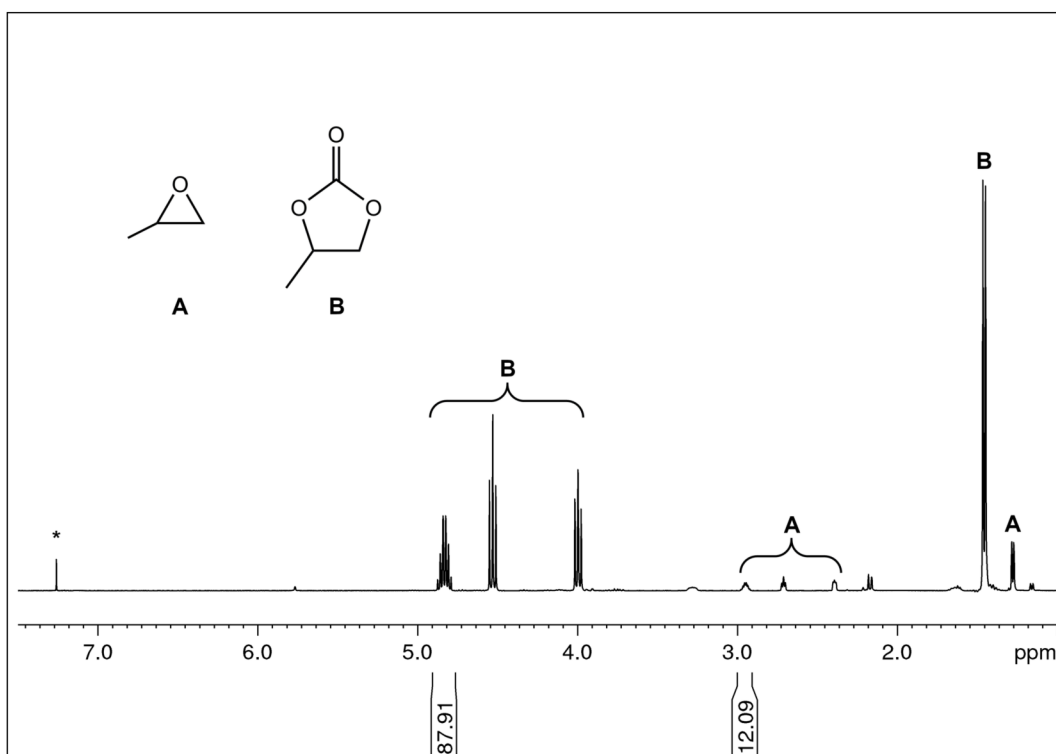


Figure S82. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.5 mol% of [Ce(pz^{Me₂})₄]₂ (**14**) as a catalyst.

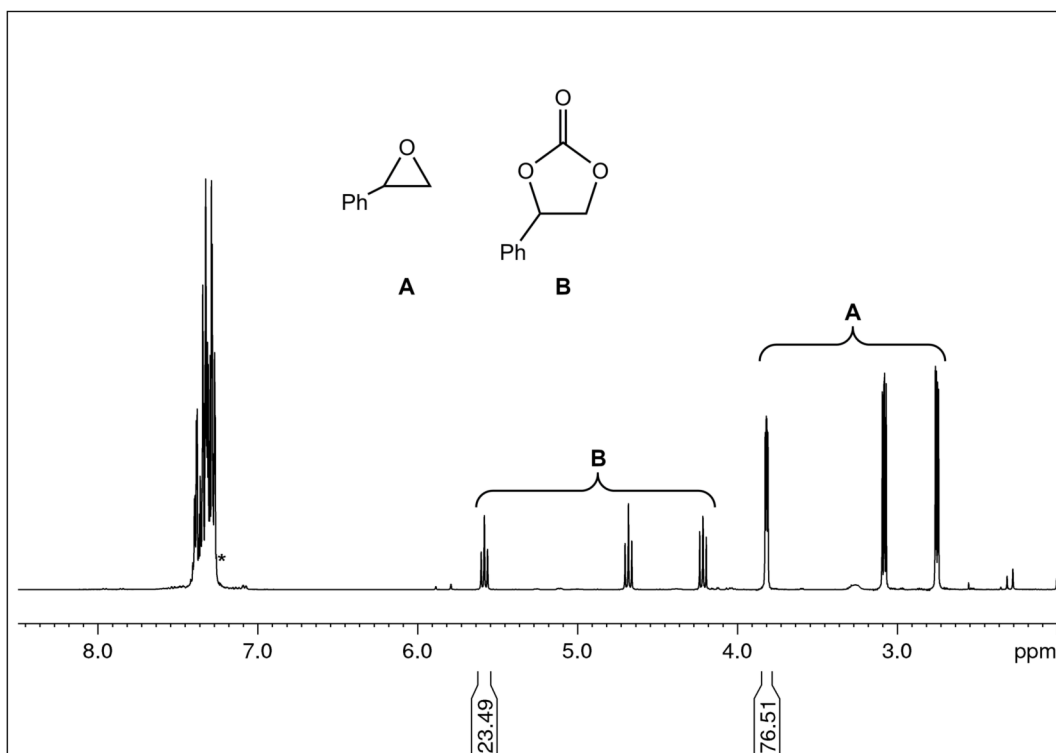


Figure S83. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of styrene oxide and CO_2 to styrene carbonate by using 0.5 mol% of $[\text{Ce}(\text{pz}^{\text{Me}_2})_4]_2$ (**14**) as a catalyst.

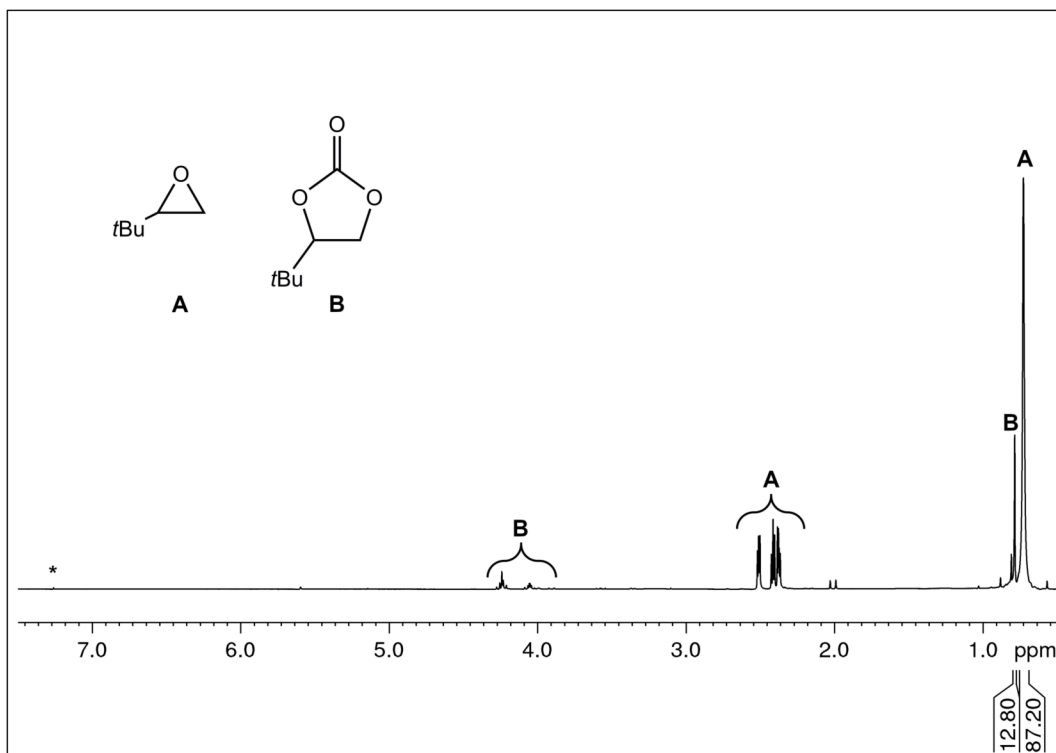


Figure S84. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO_2 to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% of $[\text{Ce}(\text{pz}^{\text{Me}_2})_4]_2$ (**14**) as a catalyst.

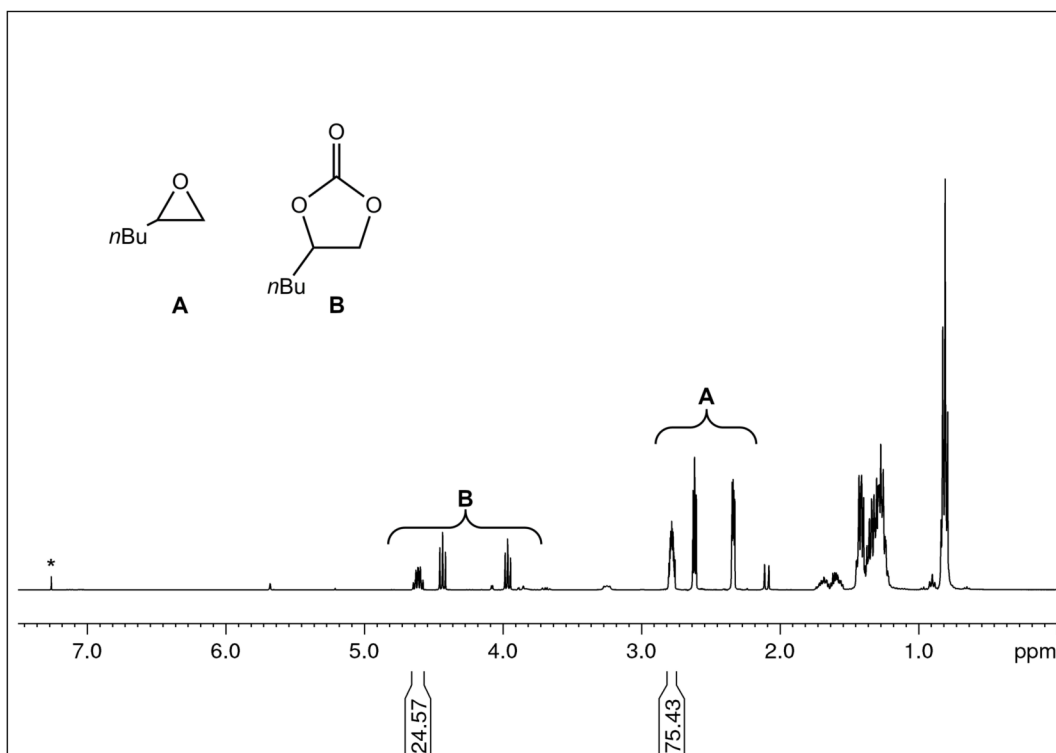


Figure S85. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO₂ to 1,2-*n*-hexylene carbonate by using 0.5 mol% of [Ce(pz^{Me₂})₄]₂ (**14**) as a catalyst.

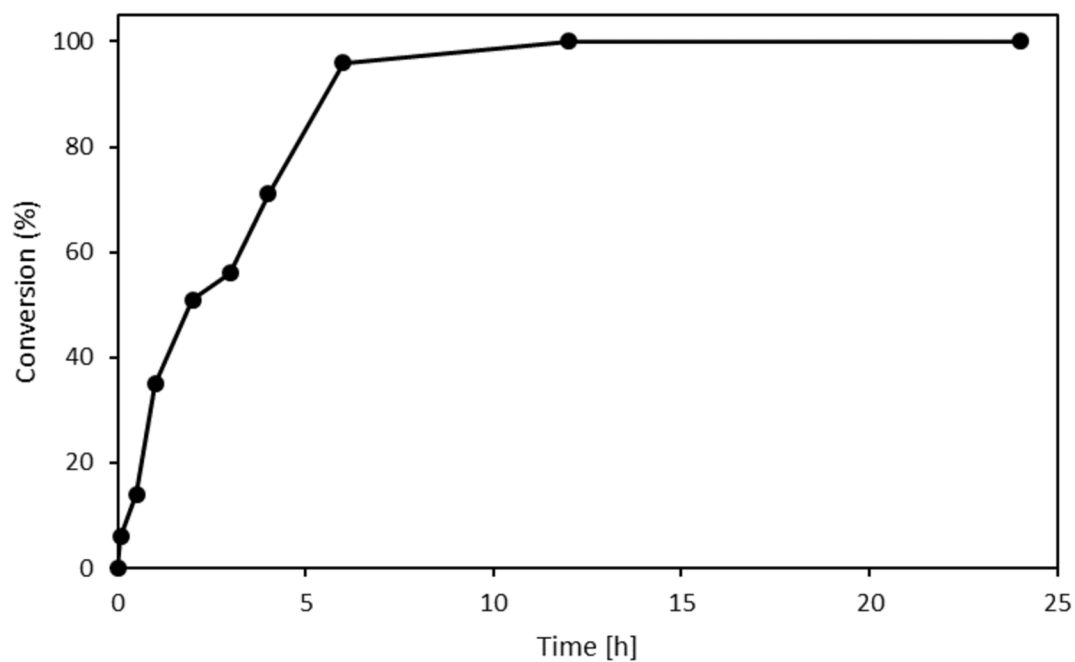


Figure S86. Conversion of propylene oxide to the corresponding cyclic carbonate with $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) as a catalyst, plotted against the reaction time.

Table S1. TOF determination of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) with 1 bar CO_2 at ambient temperature

Entry	Time [h]	Conversion [%]	TON	TOF [h^{-1}]
1	0	0	0	0
2	5 min	5	12	120
3	0.5	14	28	43
4	1	35	70	84
5	2	51	102	32
6	3	56	112	10
7	4	71	142	30
8	6	96	192	25
9	12	100	200	1.3
10	24	100	200	0

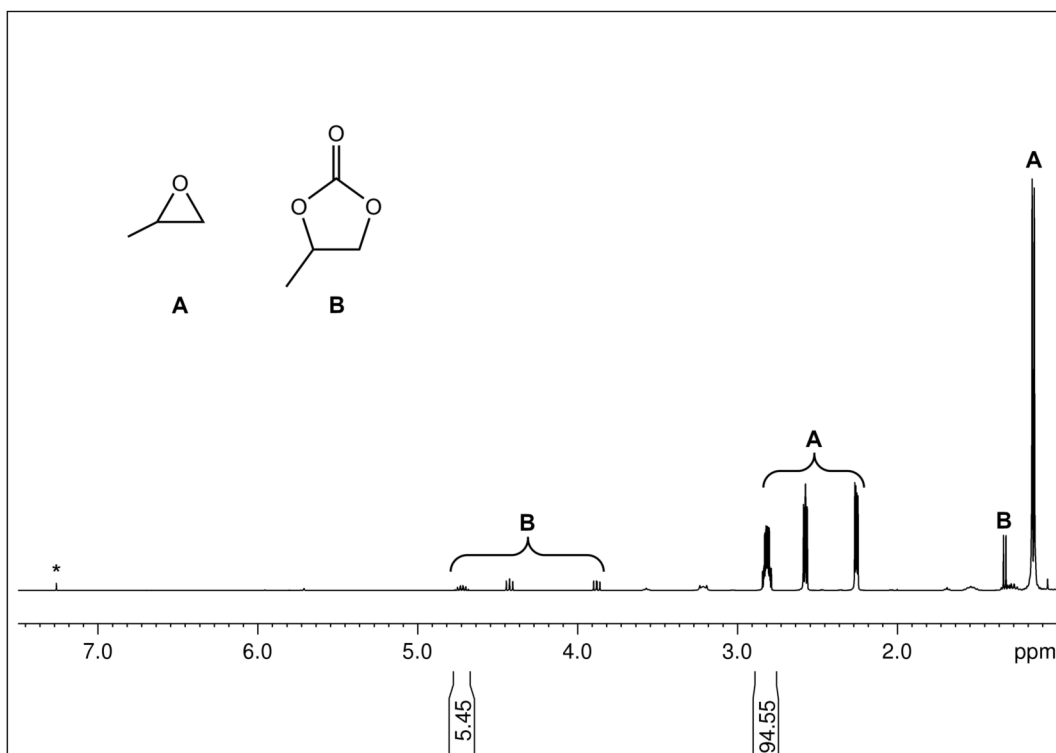


Figure S87. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) as a catalyst after 5 min.

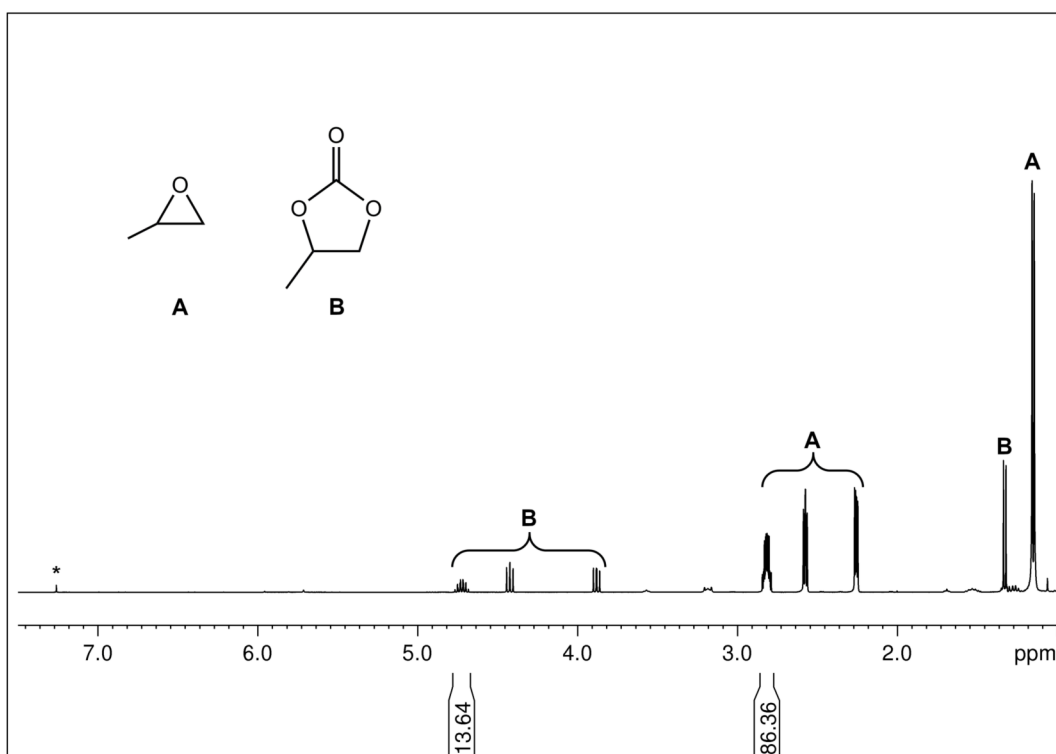


Figure S88. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) as a catalyst after 30 min.

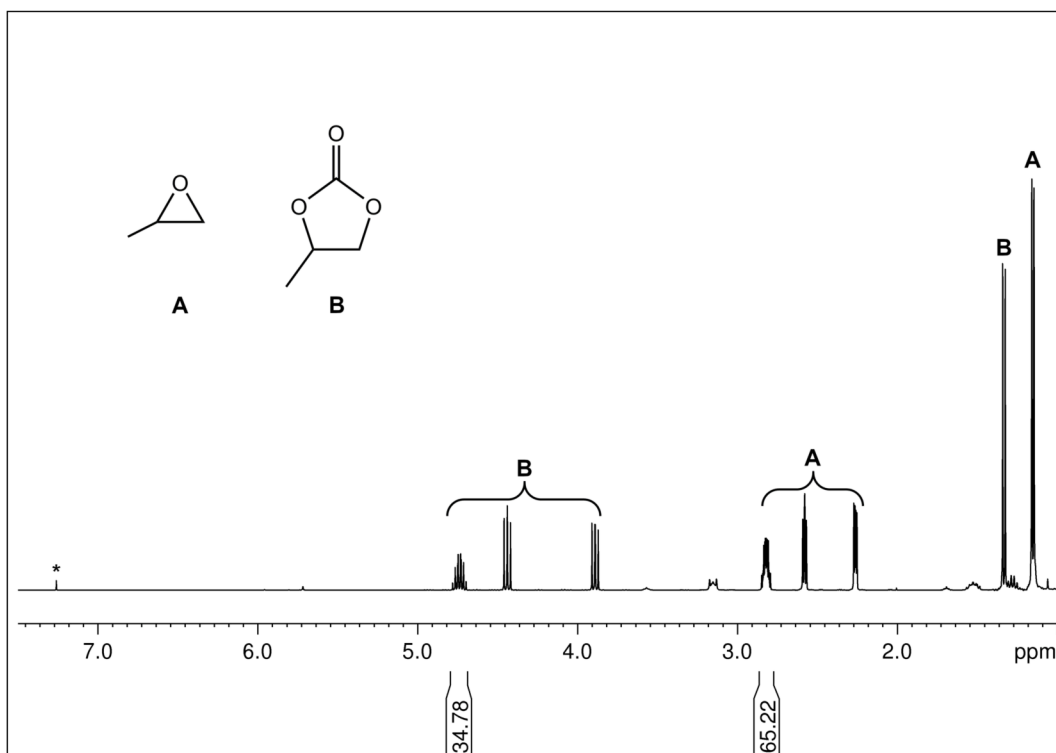


Figure S89. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) as a catalyst after 1 h.

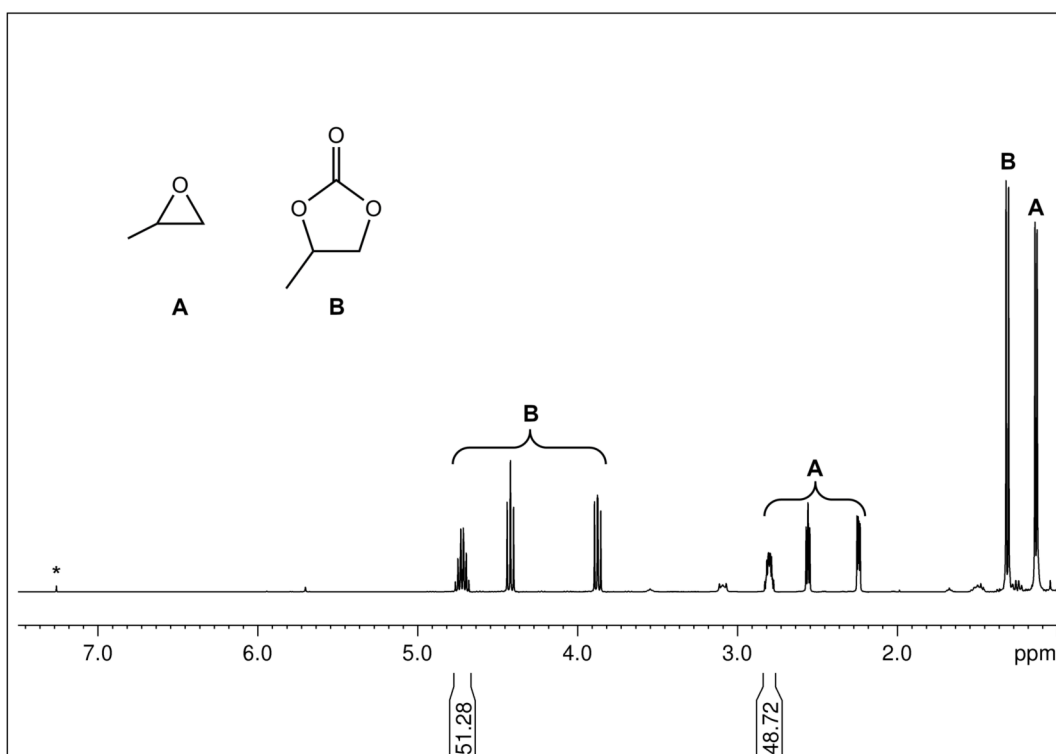


Figure S90. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) as a catalyst after 2 h.

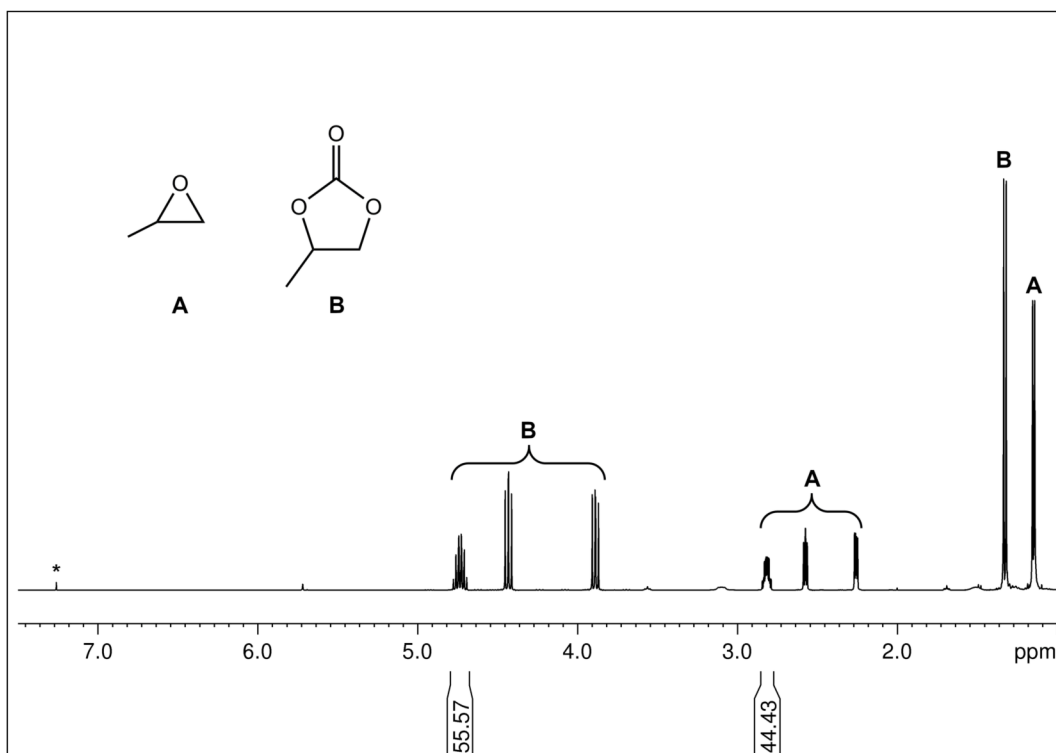


Figure S91. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) as a catalyst after 3 h.

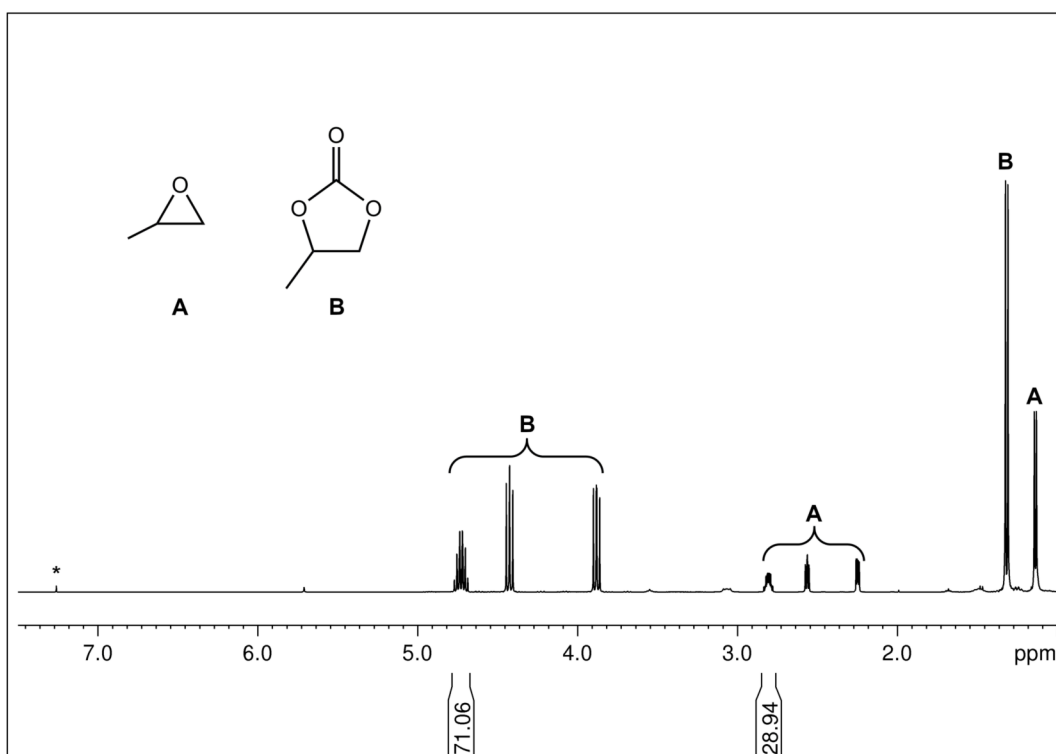


Figure S92. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) as a catalyst after 4 h.

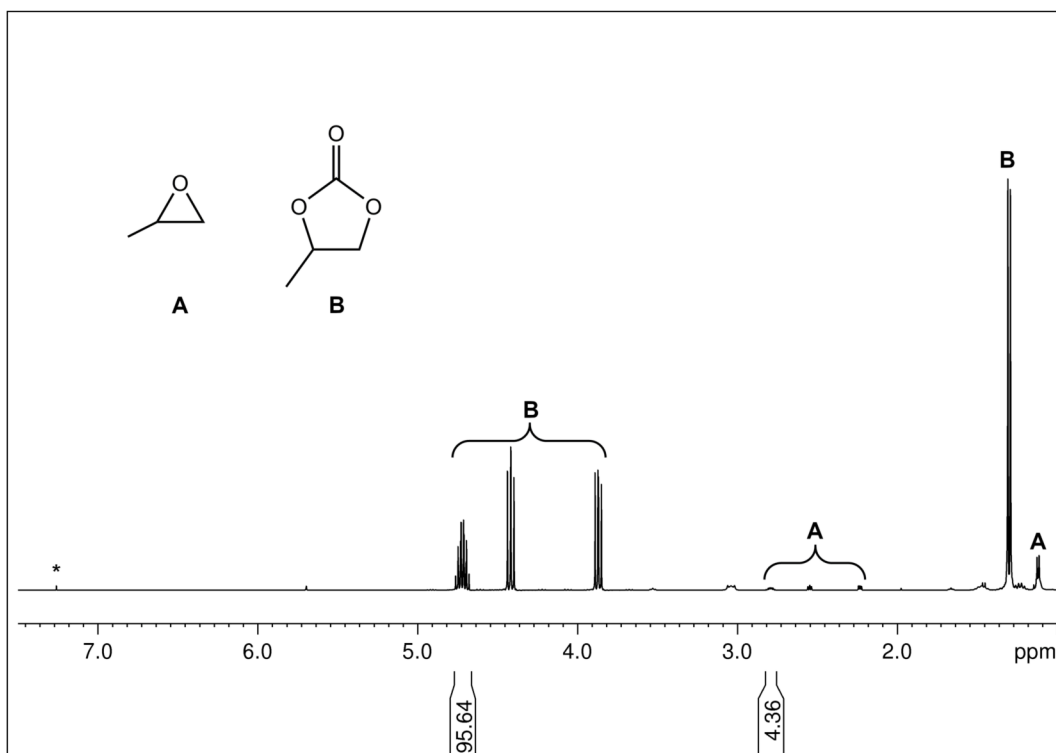


Figure S93. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.5 mol% of Sc(pz^{tBu₂})₃(thf) (**7**) as a catalyst after 6 h.

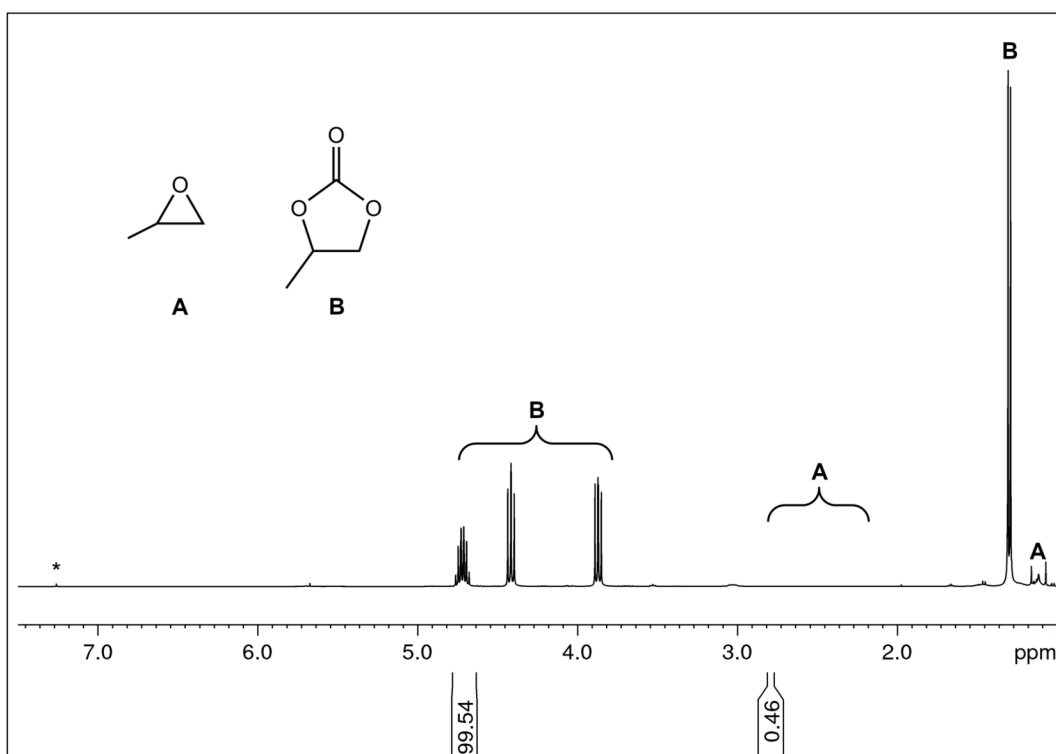


Figure S94. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO₂ to propylene carbonate by using 0.5 mol% of Sc(pz^{tBu₂})₃(thf) (**7**) as a catalyst after 12 h.

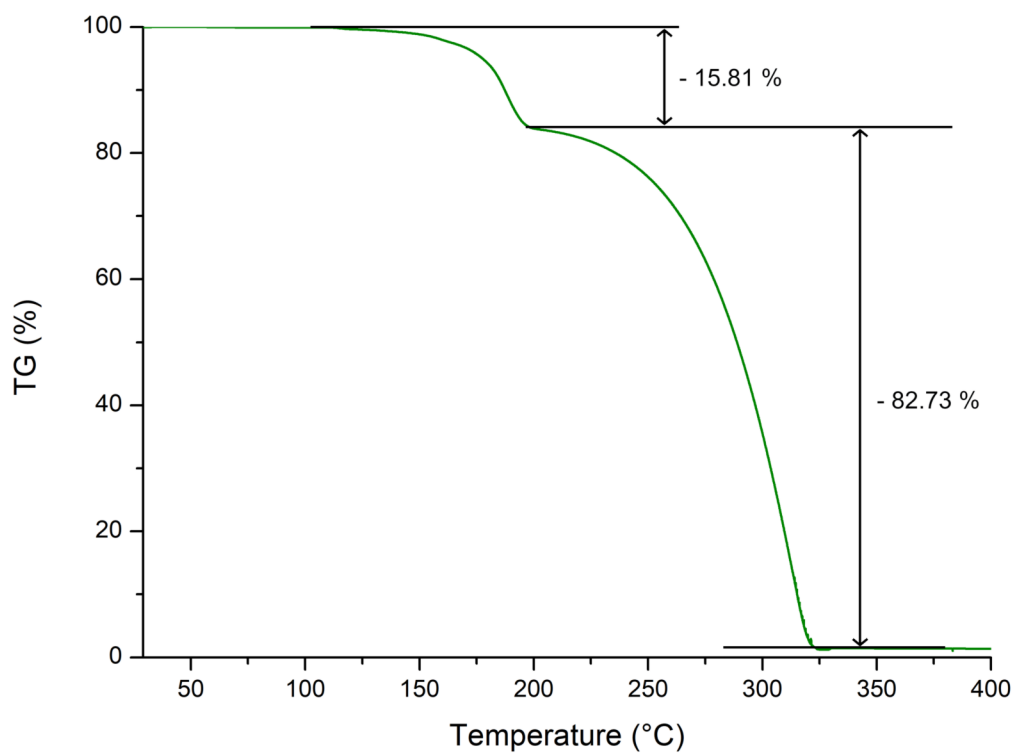


Figure S95. TGA of $\text{Al}(\text{CO}_2\cdot\text{pz}^{\text{tBu}})_2(\text{pz}^{\text{tBu}})_2$ (**1-CO₂**). Sample was heated from 28 °C to 1000 °C with a heating ratio of 1 K/min⁻¹ under constant Ar flow.

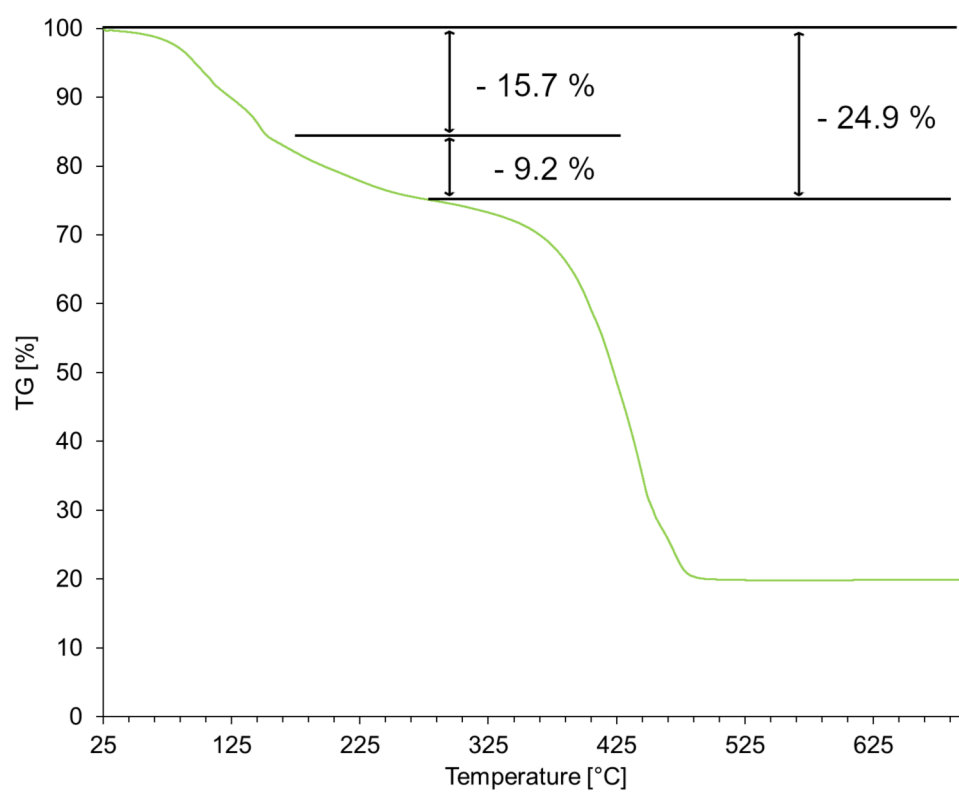


Figure S96. TGA of $\text{Y}(\text{CO}_2\cdot\text{pz}^{\text{Me}})_3(\text{thf})_2$ (**9-CO₂**). Sample was heated from 28 °C to 1000 °C with a heating ratio of 1 K/min⁻¹ under constant Ar flow.

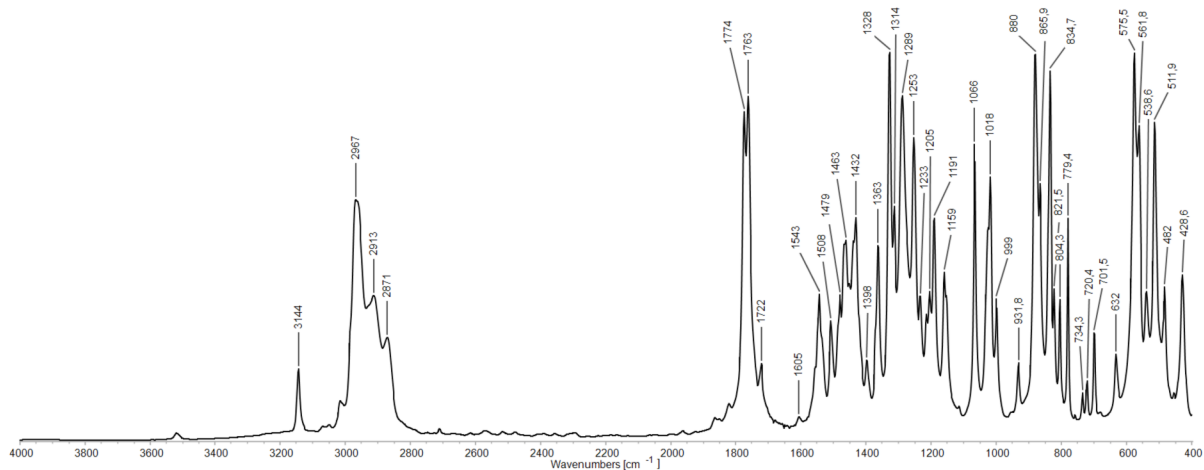


Figure S97. DRIFT spectrum of $\text{Al}(\text{CO}_2\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (**1-CO₂**) at 25 °C.

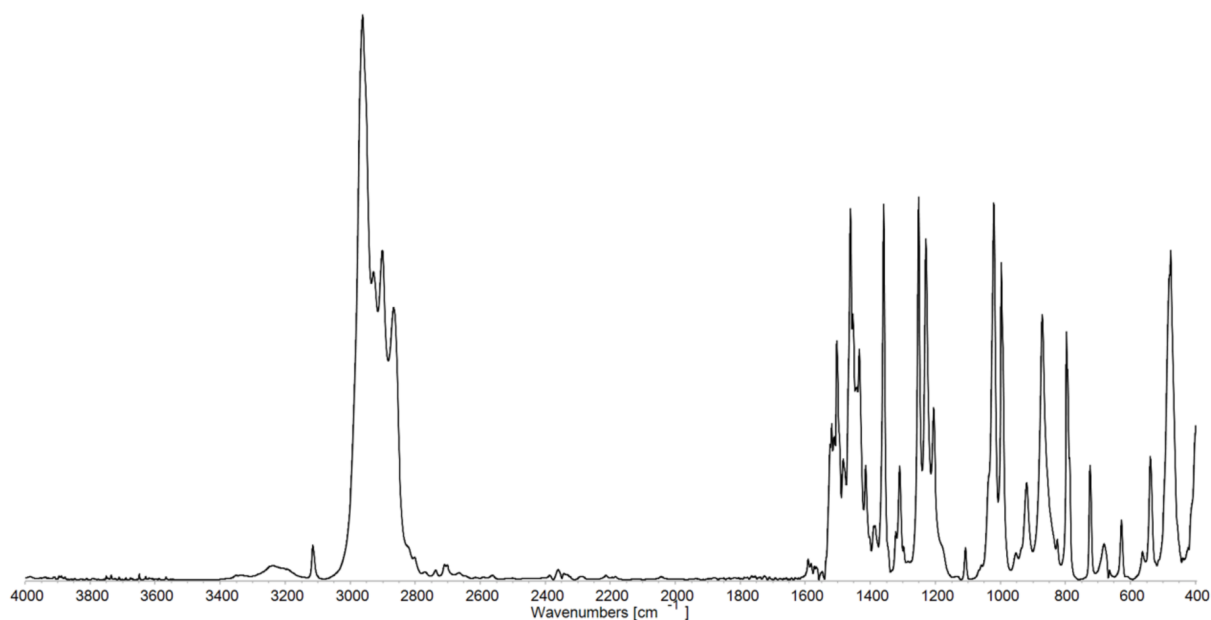


Figure S98. DRIFT spectrum of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7**) at 25 °C.

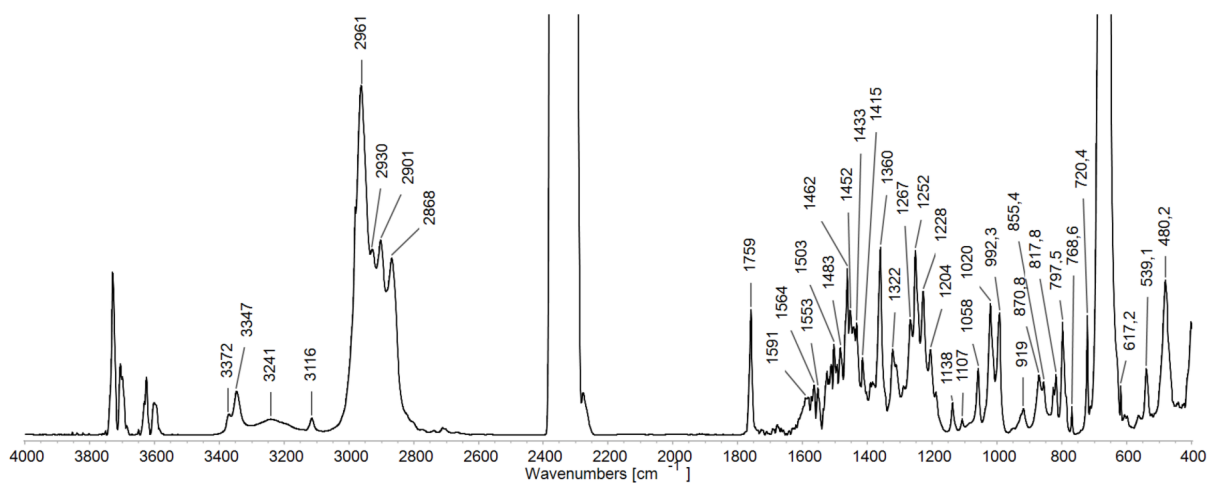


Figure S99. DRIFT spectrum of $\text{Sc}(\text{pz}^{\text{tBu}_2})_3(\text{thf})$ (**7-CO₂**) under 1 bar CO₂ at 25 °C.

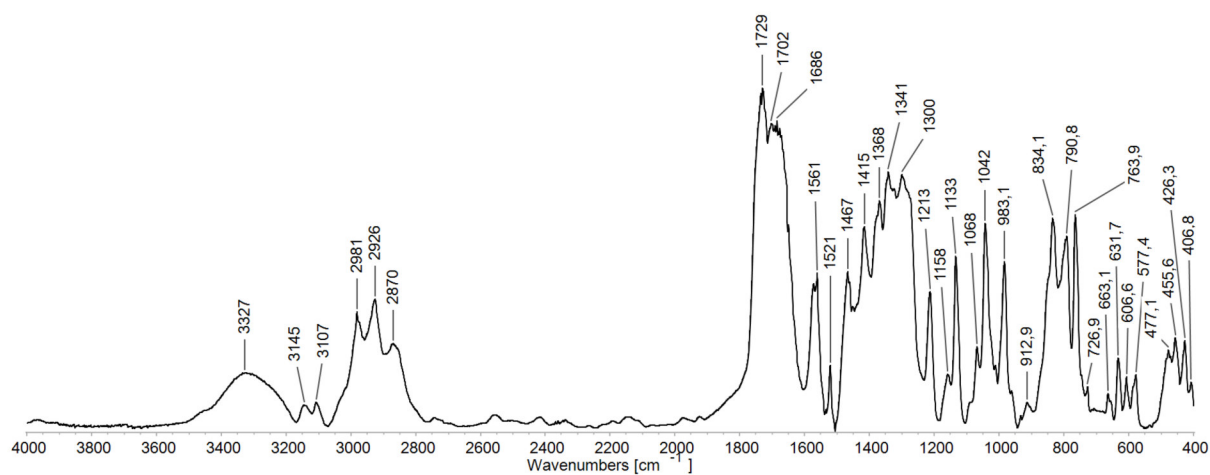


Figure S100. DRIFT spectrum of $\text{Y}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_3(\text{thf})_2$ (**9-CO₂**) at 25 °C.

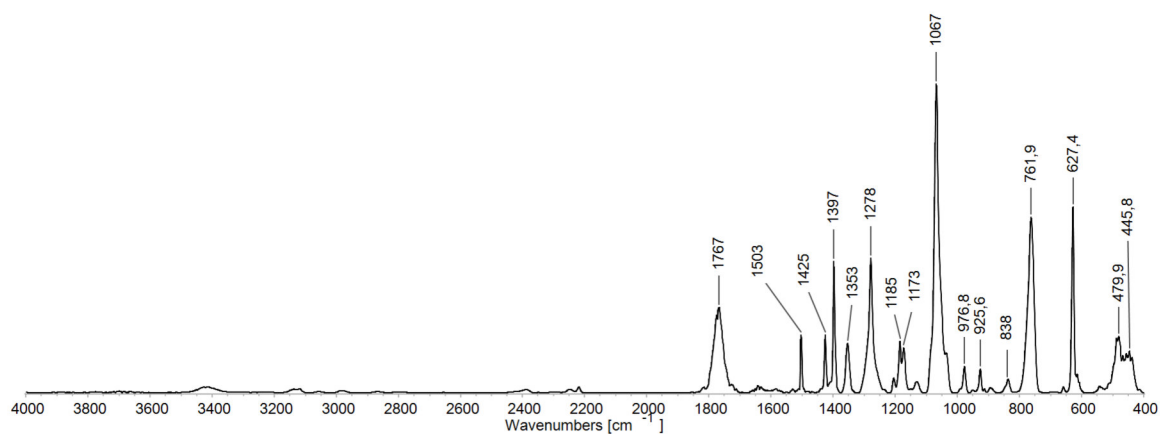


Figure S101. DRIFT spectrum of $[\text{Al}(\text{CO}_2\cdot\text{pz})_x(\text{pz})_{3-x}]_n$ (**10-CO₂**) at 25 °C.

Table S2. Crystallographic data for compounds **3**, **4**, **4a** and **5**

	3	4	4a	5
Formula	C ₄₈ H ₇₂ Al ₄ N ₁₈	C ₅₄ H ₉₀ Al ₂ N ₁₂	C ₃₆ H ₆₁ AlN ₈	C ₄₄ H ₇₄ Ga ₂ N ₈
CCDC	2358936	2358938	2358937	2358935
M [g mol ⁻¹]	1009.15	961.33	632.90	854.55
colour/shape	colourless/cube	colourless/block	colourless/block	colourless/needle
Crystal dimensions [mm]	0.251 x 0.214 x 0.208	0.260 x 0.257 x 0.216	0.259 x 0.226 x 0.128	0.201 x 0.086 x 0.071
cryst. system	orthorhombic	triclinic	triclinic	monoclinic
space group	<i>Cmc</i> 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	13.5515(8)	11.9641(18)	10.0806(6)	11.4112(11)
<i>b</i> [Å]	17.0956(11)	14.235(2)	18.8650(11)	8.8769(9)
<i>c</i> [Å]	22.4553(13)	18.584(3)	21.4540(13)	22.888(2)
α [°]	90	89.358(3)	70.659(2)	90
β [°]	90	89.130(3)	85.157(2)	98.730(2)
γ [°]	90	67.655(3)	83.751(2)	90
<i>V</i> [Å ³]	5202.2(5)	2927.1(8)	3821.7(4)	2291.6(4)
<i>Z</i>	4	2	4	2
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.288	1.091	1.100	1.238
μ [mm ⁻¹]	0.143	0.094	0.088	1.214
<i>F</i> (000)	2152	1048	1384	912
θ range [°]	1.814/30.517	1.547/24.881	1.756/25.049	1.806/27.527
unique reflns	8255	10026	13486	5194
observed reflns	37775	53177	55907	32488
[a] <i>R</i> ₁ /[b] <i>wR</i> ₂ (>2 σ) ^[a]	0.0389/0.0976	0.0452/0.1076	0.0466/0.1009	0.0401/0.0864
[a] <i>R</i> ₁ /[b] <i>wR</i> ₂ (all data)	0.0438/0.1020	0.0651/0.1214	0.0774/0.1158	0.0648/0.0973
GOF ^[c]	1.027	1.026	1.018	1.034

[a] $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $F_o > 4\sigma(F_o)$, [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2 / \sum(w(F_o^2)^2)]\}^{1/2}$. [c] $GOF = [\sum w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$

Table S3. Crystallographic data for compounds **1-CO₂**, **7**, **10** and **7-CO₂**

	1-CO₂	7	10	7-CO₂
formula	C ₃₅ H ₅₇ AlN ₆ O ₄	C ₃₇ H ₆₅ N ₆ O ₅ Sc	C ₄₉ H ₈₉ N ₆ O ₄ Y	C ₈₂ H ₁₃₀ N ₁₂ O ₄ Sc ₂
CCDC	2358942	2358939	2358941	2358943
M [g mol ⁻¹]	652.84	654.91	915.17	1437.89
colour/shape	colourless/block	colourless/block	colourless/column	colourless/cube
Crystal dimensions [mm]	0.193 x 0.121 x 0.119	0.297 x 0.181 x 0.116	0.268 x 0.077 x 0.064	0.339 x 0.220 x 0.176
cryst. system	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>Pna2₁</i>	<i>P2₁/n</i>
<i>a</i> [Å]	12.7837(12)	9.7097(5)	22.7827(11)	14.3516(15)
<i>b</i> [Å]	21.0258(19)	22.2896(11)	9.7252(5)	17.1001(19)
<i>c</i> [Å]	28.522(3)	18.4502(9)	23.6286(12)	18.145(2)
α [°]	90	90	90	90
β [°]	90	102.3030(10)	90	109.058(2)
γ [°]	90	90	90	90
<i>V</i> [Å ³]	7666.2(12)	3901.4(3)	5235.3(5)	4209.0(8)
<i>Z</i>	8	4	4	2
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.131	1.115	1.161	1.135
μ [mm ⁻¹]	0.095	0.223	1.159	0.214
<i>F</i> (000)	2832	1432	1984	1560
θ range [°]	1.428/25.024	1.453/26.205	2.265/30.519	1.581/28.299
unique reflns	6769	7822	15927	10457
observed reflns	57763	52769	70066	62529
^[a] <i>R</i> ₁ / ^[b] <i>wR</i> ₂ (<i>I</i> > 2 σ) ^[a]	0.0451/0.0993	0.0417/0.0988	0.0521/ 0.1227	0.0472/0.1190
^[a] <i>R</i> ₁ / ^[b] <i>wR</i> ₂ (all data)	0.0786/0.1178	0.0576/0.1097	0.1024/0.1427	0.0688/0.1332
GOF ^[c]	1.012	1.018	1.032	1.053

[a] $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$, $F_o > 4\sigma(F_o)$, [b] $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$. [c] $GOF = [\sum w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$

Table S4. Crystallographic data for compound **8**

8	
formula	C ₄₅ H ₆₅ N ₁₈ OSc ₃
CCDC	2358940
M [g mol ⁻¹]	1009.03
colour/shape	colourless/block
Crystal dimensions [mm]	0.399 x 0.328 x 0.128
cryst. system	triclinic
space group	<i>P</i> $\bar{1}$
<i>a</i> [Å]	11.6097(7)
<i>b</i> [Å]	13.0389(7)
<i>c</i> [Å]	18.9316(11)
α [°]	97.154(2)
β [°]	96.121(2)
γ [°]	111.919(2)
<i>V</i> [Å ³]	2601.2(3)
<i>Z</i>	2
<i>T</i> [K]	100(2)
wavelength [Å]	0.71073
ρ_{calcd} [g cm ⁻³]	1.288
μ [mm ⁻¹]	0.432
F(000)	1064
θ range [°]	1.711/28.699
unique reflns	13459
observed reflns	103615
^[a] R ₁ / ^[b] wR ₂ (<i>I</i> > 2 σ) ^[a]	0.0376/0.0931
^[a] R ₁ / ^[b] wR ₂ (all data)	0.0481/0.1005
GOF ^[c]	1.026

[a] $R_1 = \sum (|F_0| - |F_c|) / \sum |F_0|$, $F_0 > 4\sigma(F_0)$ [b] $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2 / \sum [w(F_0^2)^2]]^{1/2}$. [c] $GOF = [\sum w(F_0^2 - F_c^2)^2 / (n_0 - n_p)]^{1/2}$

The structures were solved by direct methods and refined against all data by full-matrix least-squares methods on F^2 using ShelXTL¹⁰ and ShelXL¹¹. All the non-hydrogen atoms were refined anisotropically. Disorder models for **1**-CO₂ and **7** were calculated using RIGU and SIMU restraints. For **7**-CO₂ and **10** DSR¹² was used, a program for refining disordered structures in SHELXL. Complex **10** was refined in an orthorhombic space group $Pna2_1$ and shows disorder of the whole complex. Attempts to do the calculation in the monoclinic system ($P2_1/n$) using a twin law (-1 0 0 0 -1 0 0 0 1), did not result in a better refinement. All this data can be obtained free of charge from The Cambridge Crystallographic Data Centre via: <https://www.ccdc.cam.ac.uk/structures/>

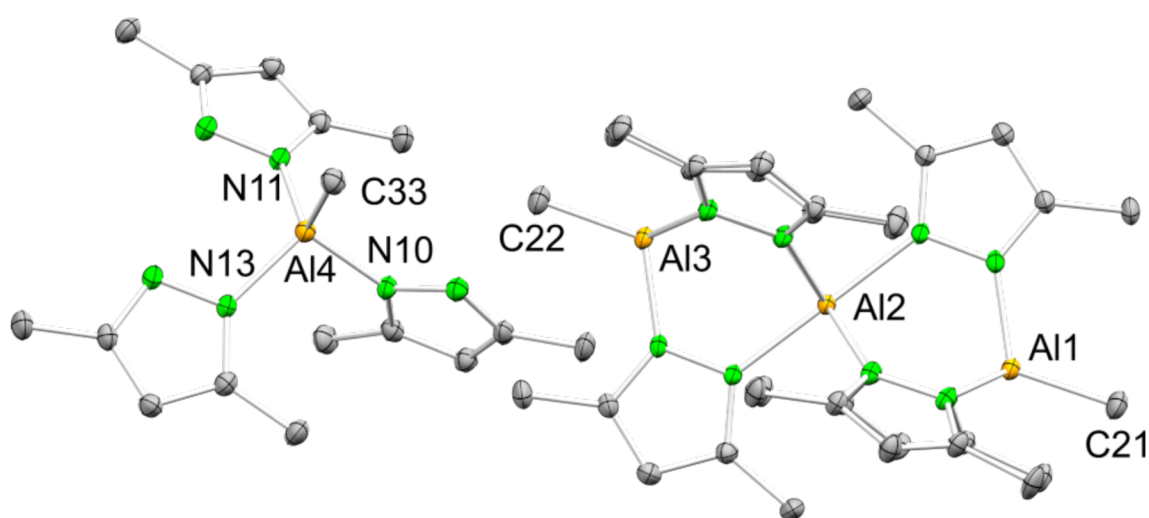


Figure S102. Crystal structure of $[\text{Al}(\text{N},\text{N}',\text{N}''\text{-Al}\{\text{pz}^{\text{Me}_2}\}_3\text{Me})_2][\text{Al}(\text{pz}^{\text{Me}_2})_3\text{Me}]$ (**3**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Al1–N1 1.875(3), Al1–N3 1.8816(19), Al1–C21 1.945(3), Al2–N2 2.043(3), Al2–N4 2.0483(18), Al2–N5 2.0348(18), Al2–N7 2.037(3), Al3–N6 1.8861(18), Al3–N8 1.892(3), Al3–C22 1.938(3), Al4–N10 1.887(3), Al4–N11 1.9026(18), Al4–C33 1.952(4).

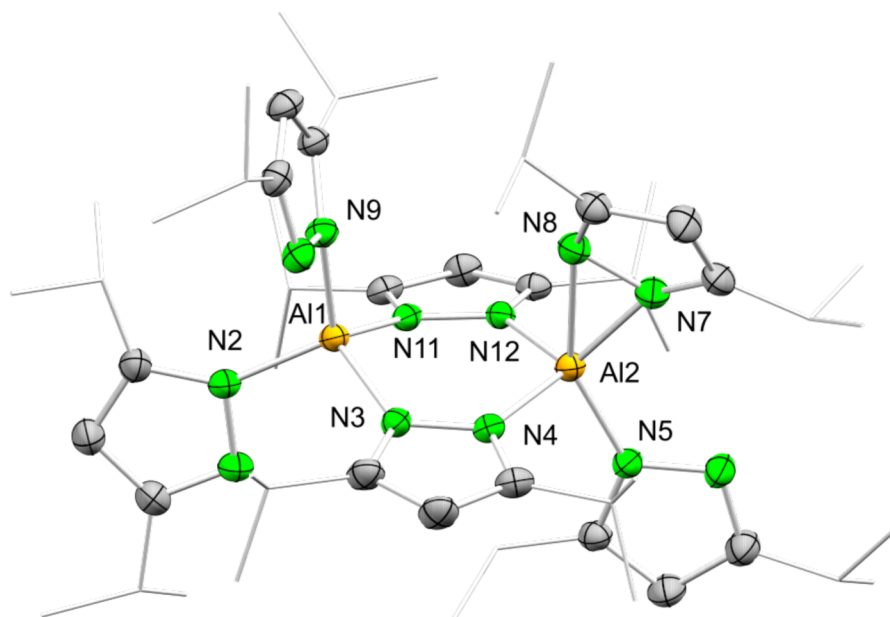


Figure S103. Crystal structure of $[\text{Al}(\text{pz}^{\text{Pr}_2})_3]_2$ (**4**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Al1–N2 1.8358(17), Al1–N3 1.8904(16), Al1–N9 1.8417(16), Al1–N11 1.9093(17), Al2–N4 1.8926(17), Al2–N5 1.8672(16), Al2–N7 1.8288(17), Al2–N8 2.1461(17), Al2–N12 1.8901(16).

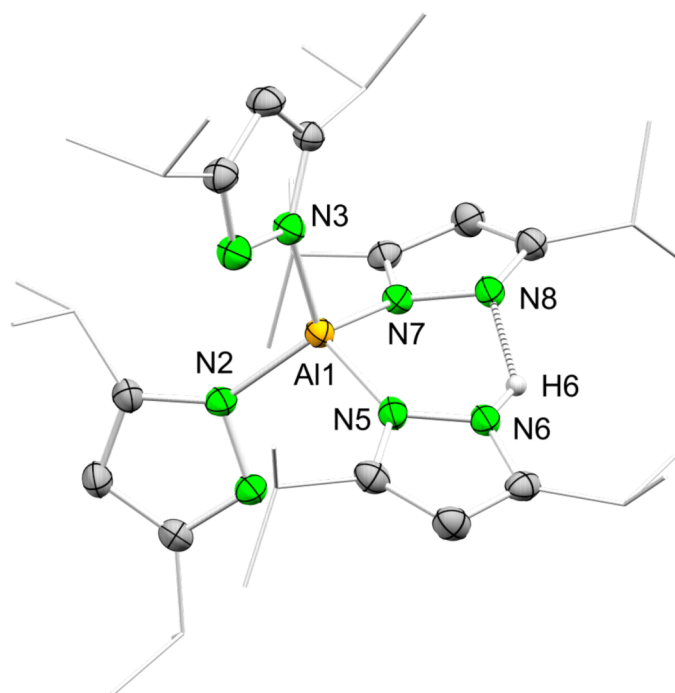


Figure S104. Crystal structure of $\text{Al}(\text{pz}^{\text{Pr}_2})_3(\text{Hpz}^{\text{Pr}_2})$ (**4a**). Ellipsoids are set at the 50% probability level. Hydrogen atoms as well as a second complex in the unit cell are omitted for clarity. Selected interatomic distances [Å]: Al1–N2 1.8365(17), Al1–N3 1.8513(17), Al1–N5 1.9085(17), Al1–N7 1.8716(16), N6–H6 0.8800, N8–H6 1.946.

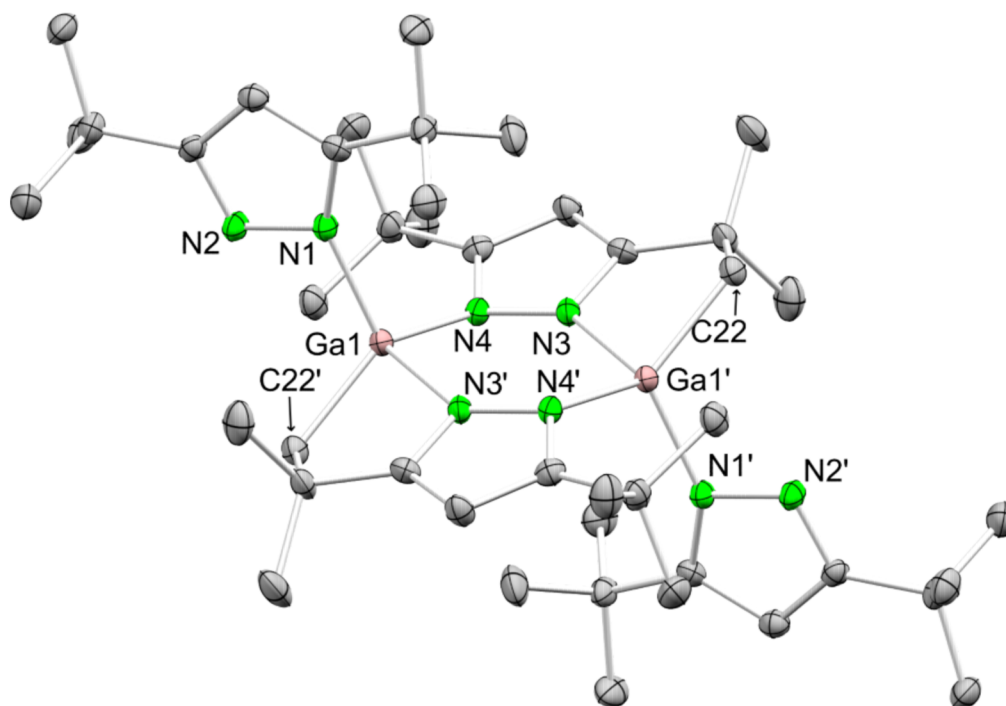


Figure S105. Crystal structure of $[\text{Gapz}^{\text{tBu}_2}(\mu\text{-N,N,C-pz}^{\text{tBu,C(CH}_3)_2\text{CH}_2})]_2$ (**5**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Ga1–N1 1.9197(19), Ga1–N3' 1.9848(19), Ga1–N4 1.950(2), Ga1–C22' 1.957(2).

' = -x+1, -y+1, -z+1

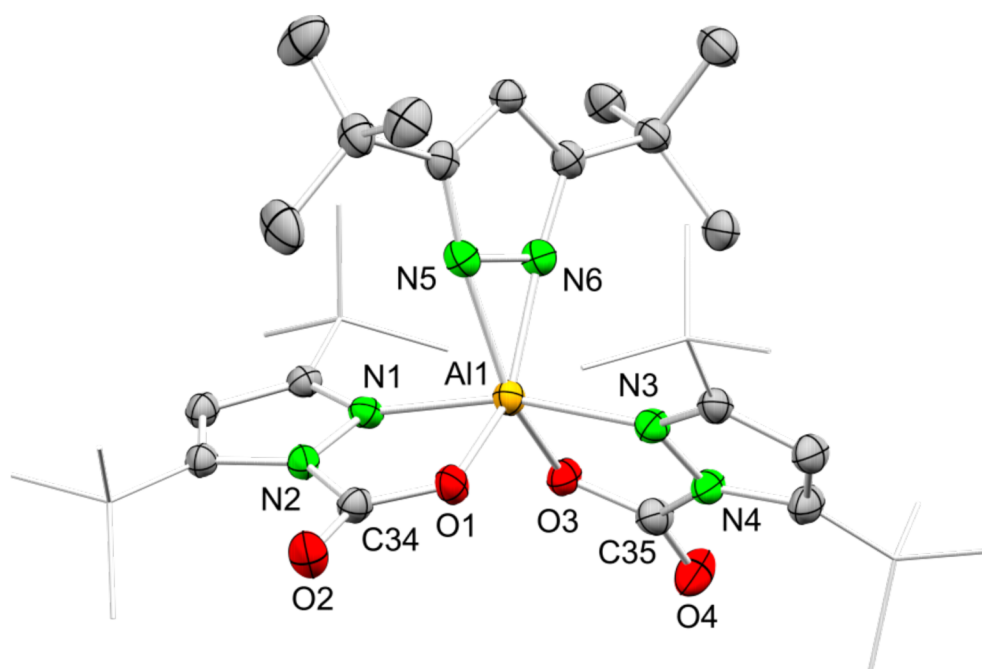


Figure S106. Crystal structure of $\text{Al}(\text{CO}_2\text{-pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (**1-CO}_2**). Ellipsoids are set at the 50% probability level. Hydrogen atoms as well as disorder in the tBu moieties are omitted for clarity. Selected interatomic distances [Å]: Al1–N1 2.0633(17), Al1–N3 2.0713(18), Al1–N5 2.0188(19), Al1–N6 1.8881(18), Al1–O1 1.8025(15), Al1–O3 1.8043(15), C34–O1 1.288(2), C34–O2 1.199(2), C35–O3 1.285(2), C35–O4 1.203(3).

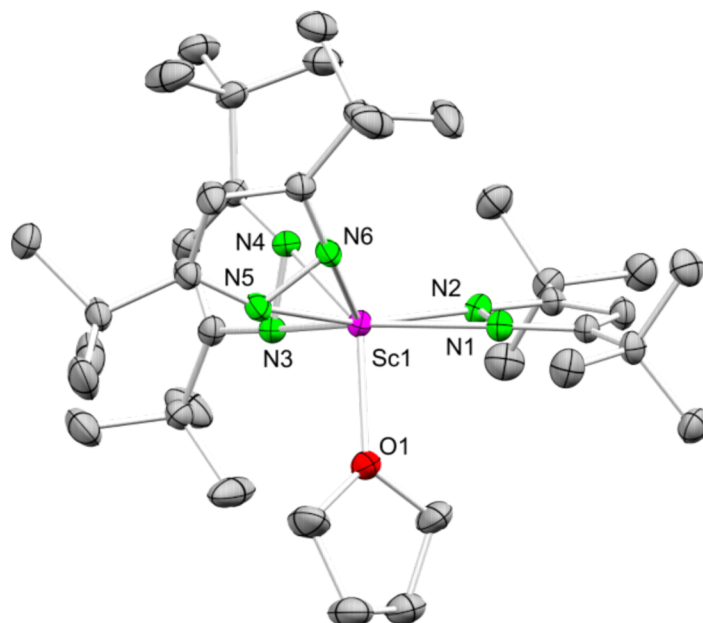


Figure S107. Crystal structure of $\text{Sc}(\text{pz}^{\text{tBu}})_3(\text{thf})$ (**7**). Ellipsoids are set at the 50% probability level. Hydrogen atoms as well as disorder in *t*Bu moieties and the coordinated THF are omitted for clarity. Selected interatomic distances [Å]: Sc1–N1 2.1663(14), Sc1–N2 2.1338(14), Sc1–N3 2.1634(14), Sc1–N4 2.1306(14), Sc1–N5 2.1772(14), Sc1–N6 2.1368(14), Sc1–O1 2.1928(12).

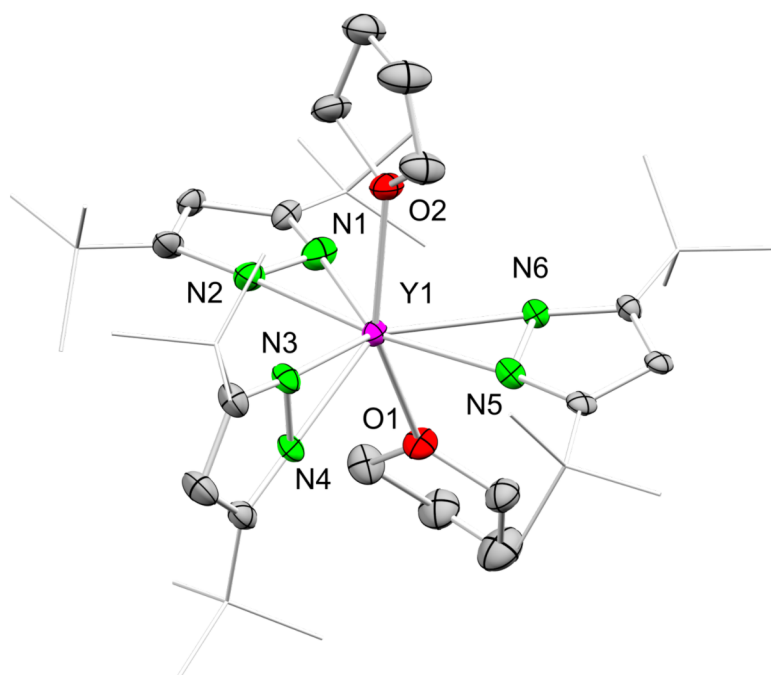


Figure S108. Crystal structure of $[\text{Y}(\text{pz}^{\text{tBu}})_3(\text{thf})_2]$ (**10**). Ellipsoids are set at the 50% probability level. Hydrogen atoms as well as disorder in both pyrazolate and THF ligands omitted for clarity. Selected interatomic distances [Å]: Y1–N1 2.385(7), Y1–N2 2.284(7), Y1–N3 2.345(11), Y1–N4 2.281(11), Y1–N5 2.340(11), Y1–N6 2.406(10), Y1–O1 2.427(8), Y1–O2 2.397(2).

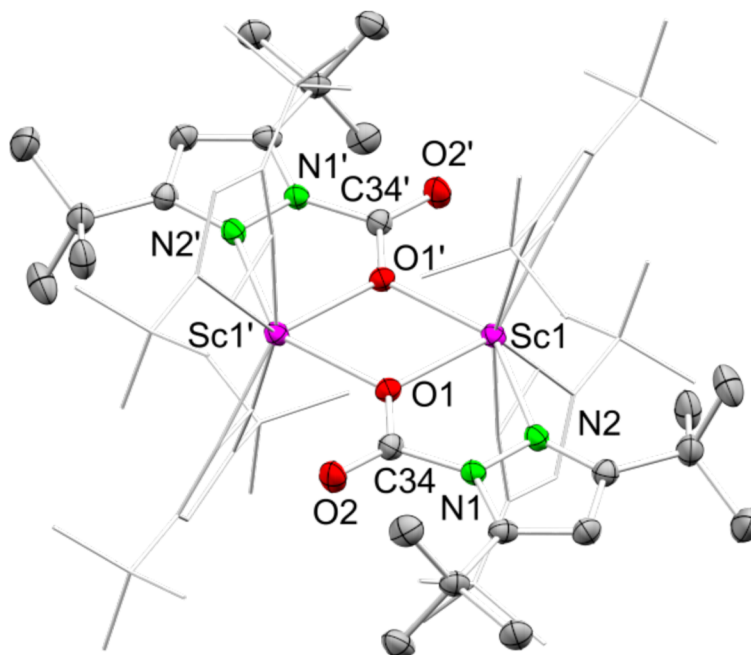


Figure S109. Crystal structure of $\text{Sc}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2$ (**7-CO₂**). Ellipsoids are set at the 50% probability level. Hydrogen atoms as well as disorder in *t*Bu moieties and one solvent toluene are omitted for clarity. Selected interatomic distances [Å]: Sc1–N2 2.3188(13), Sc1–N3 2.1854(13), Sc1–N4 2.1394(13), Sc1–N5 2.1383(14), Sc1–N6 2.1672(13), Sc1–O1 2.1713(10), Sc1–O1' 2.1604(11), C34–O1 1.2991(18), C34–O2 1.2035(19).

' = -x+1, -y+1, -z+1

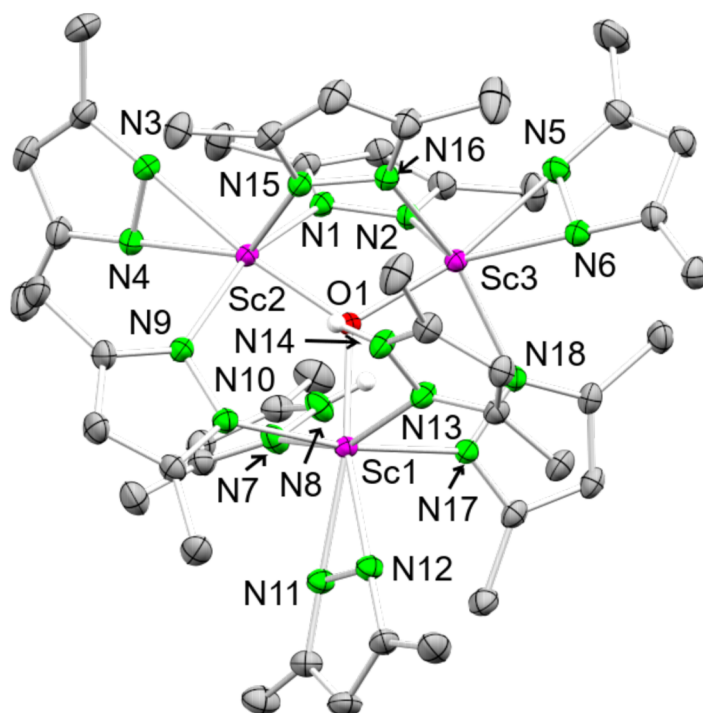
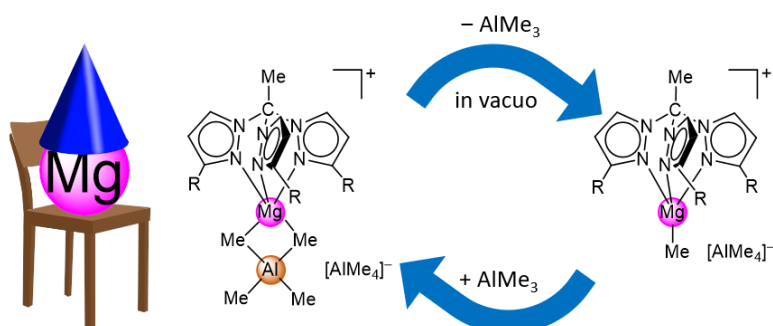


Figure S110. Crystal structure of $[\text{Sc}_3\text{O}(\text{pz}^{\text{Me}_2})_7(\text{Hpz}^{\text{Me}_2})_2]$ (**8**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Sc1–N7 2.3496(13), Sc1–N10 2.2535(12), Sc1–N11 2.1921(13), Sc1–N12 2.1884(12), Sc1–N13 2.3716(13), Sc1–N17 2.2667(12), Sc1–O1 2.0132(10), Sc2–N1 2.2926(12), Sc2–N3 2.1755(12), Sc2–N4 2.1585(13), Sc2–N9 2.2624(13), Sc2–N15 2.2173(13), Sc2–O1 1.9886(10), Sc3–N2 2.2103(13), Sc3–N5 2.1652(13), Sc3–N6 2.1834(13), Sc3–N16 2.2786(13), Sc3–N18 2.2570(12), Sc3–O1 1.9886(10).

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Reactivity of $\text{Mg}(\text{AlMe}_4)_2$ towards neutral Tris(pyrazolyl)alkanes



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Various new tris(pyrazolyl)alkanes of the class $\text{R}'\text{CTp}^{3-\text{R}}$ ($\text{R}' = \text{Me}, \text{Et}, n\text{Pr}, i\text{Bu}$; $\text{R} = \text{Et}, \text{cyPr}, \text{Cy}, p\text{-tBuPh}, \text{Ph}$; $\text{cyPr} = \text{cyclopropyl}$, $\text{Cy} = \text{cyclohexyl}$, $p\text{-tBuPh} = \text{para-tert-butylphenyl}$) were synthesised and their reactivity towards $\text{Mg}(\text{AlMe}_4)_2$ was examined. Along with new examples of recurring structural motifs, such as separated ion pairs and “metal in a box” complexes, e.g., $[(\text{MeCTp}^{3-\text{Et}})_2\text{Mg}][\text{AlMe}_4]_2$, several magnesium complexes with new structural features/compositions were obtained. Treatment of the “metal in a box” species $[(\text{MeCTp}^{3-\text{R}})\text{Mg}][\text{AlMe}_4]_2$ with THF donor gave the terminal methyl complex $[(\text{MeCTp}^{3-\text{cyPr}})\text{MgMe}(\text{thf})_2][\text{AlMe}_4]$. Variation of the backbone alkyl substituent R' in the tris(pyrazolyl)alkane $\text{R}'\text{CTp}^{3-\text{Ph}}$ gave ionic liquids ($\text{R}' = \text{Et}, n\text{Pr}$) and the methyl-bridged dimagnesium complex $[(i\text{BuCTp}^{3-\text{Ph}})_2\text{Mg}][\text{AlMe}_4]_2(\mu\text{-Me})[\text{AlMe}_4]$. The bulky Cy and $p\text{-tBuPh}$ moieties at the pyrazolyl 3 position gave the new structural motif $[(\text{MeCTp}^{3-\text{R}}\text{Mg}(\eta^1\text{-AlMe}_4))][\text{AlMe}_4]$ (η^3 , $\text{R} = \text{Cy}$; η^2 , $\text{R} = p\text{-tBuPh}$), stabilising a “[$\text{Mg}(\text{AlMe}_4)]^+$ ” entity. The AlMe_3 group can be reversibly displaced under reduced pressure affording the new separated ion pair $[(\text{MeCTp}^{3-p\text{-tBuPh}})\text{MgMe}][\text{AlMe}_4]$ with a terminal “[MgMe] $^+$ ” moiety. Moderate thermal treatment of both $[(\text{MeCTp}^{3-p\text{-tBuPh}})\text{MgMe}][\text{AlMe}_4]$ and $[(\text{MeCTp}^{3-p\text{-tBuPh}})\text{Mg}(\eta^2\text{-AlMe}_4)][\text{AlMe}_4]$ resulted in selective C–H-bond activation in the 5 position of one of the pyrazolyl moieties and the formation of an AlMe_3 -modified anionic tris(pyrazolyl)alkane and hence the neutral complex $[\text{MeC}(\text{pz}^{3-p\text{-tBuPh}})_2(\text{pz}^{3-p\text{-tBuPh},5\text{-AlMe}_3})]\text{MgMe}$.

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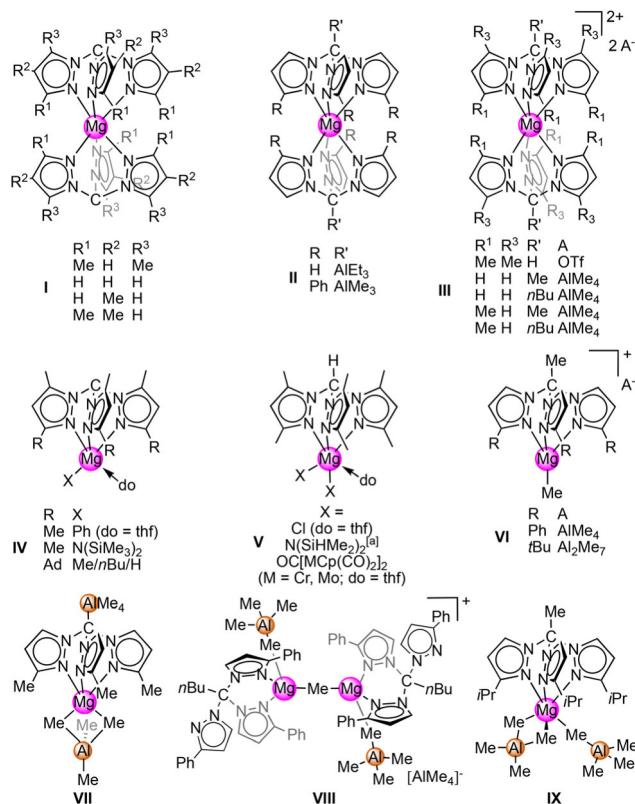
Introduction

While Grignard compounds RMgX ($\text{R} = \text{hydrocarbyl}$; $\text{X} = \text{Br}, \text{Cl}$) are among the most eminent reagents in organic synthesis,^{1–8} the elucidation of the Schlenk equilibrium has clearly opened new avenues in organometallic chemistry. Crucially, manipulation of the Schlenk equilibrium by donor solvents features a viable path to dialkyl and diaryl magnesium species.^{9,10} As early as 1964 Weiß structurally characterised $[\text{MgMe}_2]_n$, which was obtained in this way.¹¹ Since then, several donor-stabilised monomeric and dimeric complexes of $[\text{MgMe}_2]_n$ have been reported (e.g., donor = quinuclidine, THF, TMEDA).^{12–17}

The seminal discoveries of tris(pyrazolyl)methane (HCTp) by Hückel und Bretschneider in 1935 (ref. 18) and subsequently of the trispyrazolylborato (Tp) scorpionate ligands in 1966 by Trofimenko paved the way for a new class of highly versatile ancillary ligands applicable in various areas of coordination chemistry.^{19–27} Such polypyrazolyl scorpionate ligands

can be easily modified both at the pyrazole carbon atoms ($\text{Tp}^{3-\text{R},5-\text{R}}$) and in the case of HCTp additionally at the apical carbon atom ($\text{R}'\text{CTp}^{3-\text{R},4-\text{R},5-\text{R}}$). Neutral $\text{R}'\text{CTp}$ ($\text{R} = \text{H}, \text{alkyls}$) have been repeatedly used to stabilise highly reactive magnesium alkyl species.²⁸ Also, several complexes of magnesium bearing a mono-anionic CTP ligand have been structurally characterised (see Scheme 1).^{29–34} “Metal in a box” complexes such as $(\text{CTp}^{3-\text{R},4-\text{R},5-\text{R}})_2\text{Mg}$ (**I**) were first described by Mountford and Breher in 2008.²⁹ Here, the application of magnesium dialkyl species led to the deprotonation of the backbone hydrogen. Similarly, such carbanion formation can be triggered in the presence of highly basic $[\text{AlMe}_4]$ moieties, which can subsequently form trialkylaluminium adducts (or heteroaluminato-type species) to afford complexes $(\text{R}_3\text{AlCTp}^{3-\text{R}})_2\text{Mg}$ (**II**).^{30,35} By using an alkylated backbone or by protonating the apical carbanion with HOTf, separated ion pair “metal in a box” complexes $[(\text{R}'\text{CTp}^{3-\text{R},5-\text{R}})_2\text{Mg}][\text{A}]_2$ (**III**, $\text{A} = \text{OTf}, \text{AlMe}_4$) can be obtained.^{29,35–37} When HCTp is reacted with a bulky magnesium base MgR_2 ($\text{R} = \text{Ph}$ or $[\text{N}(\text{SiMe}_3)_2]$) or has a bulky substituent at the 3 position (adamantyl), deprotonation occurs as well but only one monoanionic CTP ligand coordinates at the magnesium centre to yield $(\text{CTp}^{3-\text{Me},5-\text{R}})\text{MgR}$ (do) (**IV**).^{29,30,34,35} Re-protonation of complexes of the type **IV** afforded $(\text{HCTp}^{\text{Me,Me}})\text{MgX}_2(\text{do})$ (**V**) with the neutral HCTp donor.^{29,30,32}

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† Electronic supplementary information (ESI) available. CCDC 2386219–2386230. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4dt02722a>



Scheme 1 Structural motifs of reported magnesium tris(pyrazolyl)alkane and methanide complexes^a $\kappa^2(\text{N}, \text{N}')$.

We have recently reported on several new magnesium tris(pyrazolyl)alkane complexes that resulted from the treatment of homoleptic tetramethylaluminate $\text{Mg}(\text{AlMe}_4)_2$ with differently substituted $\text{R}'\text{CTp}^{3-\text{R}}$.³⁵ The isolated complexes revealed species of types **II** and **III** as recurring structural motifs. Sterically demanding $\text{MeCTp}^{3-\text{R}}$ ($\text{R} = t\text{Bu}, \text{Ph}$) ligands were able to stabilise a $[\text{MgMe}]^+$ fragment in compounds $[(\text{MeCTp}^{3-\text{R}})\text{MgMe}][\text{A}]$ (**VI**, $\text{A} = \text{AlMe}_4, \text{Al}_2\text{Me}_7$). Use of silyl-substituted Me_3SiCTp resulted in SiMe_4 elimination and formation of a monoanionic heteroaluminate species “ Me_3AlCTp ”. Accordingly, a “metal in a box” complex could be prevented and the neutral $\text{Me}_3\text{AlCTp}^{3-\text{Me}}\text{Mg}(\text{AlMe}_4)$ (**VII**) was isolated with one $[\text{AlMe}_4]$ unit remaining at the magnesium centre. Longer alkyl chains in the backbone led to the dimagnesium complex $[(\text{nBuCTp}^{3-\text{Ph}})\text{Mg}\{\text{AlMe}_4\}_2(\mu\text{-Me})][\text{AlMe}_4]$ (**VIII**) with the rare $\kappa^2(\text{N}, \text{N}')$ coordination mode of the RCTp ligand. Finally, the $\text{MeCTp}^{3-\text{iPr}}$ ligand provided the appropriate steric bulk to accommodate two $[\text{AlMe}_4]$ units at the magnesium centre, namely $\text{MeCTp}^{3-\text{iPr}}\text{Mg}(\text{AlMe}_4)_2$ (**IX**).³⁵

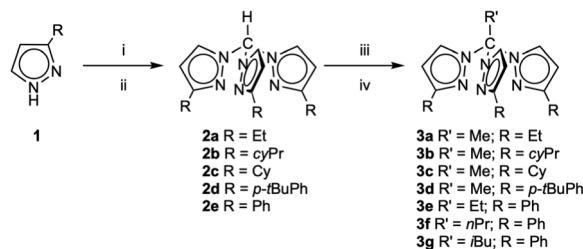
In the present study, we further expanded the tris(pyrazolyl)alkane ligand library $[\text{R}'\text{CTp}^{3-\text{R}}]$ to gain an even better understanding of the steric influence of both the position 3 substituents on the pyrazolyl groups and the apical carbon atom substitution on the stabilisation of magnesium alkyl fragments.

Results and discussion

$\text{R}'\text{CTp}^{3-\text{R}}$ ligand synthesis

Several new $\text{R}'\text{CTp}^{3-\text{R}}$ derivatives were synthesized to investigate the feasibility of additional bis(aluminate) complexes of the favoured type **IX** (Scheme 1). The $\text{HCTp}^{3-\text{R}}$ derivatives **2** were obtained from the corresponding 3-R-pyrazoles **1** applying the phase-transfer catalysis reaction of Elguero *et al.*, which was optimised by Reger *et al.*^{38,39} To separate the desired product from the three other formed isomers, the mixture was refluxed with *p*-toluenesulfonic acid (Scheme 2). The apical carbon atom was alkylated in a one-pot synthesis by initial lithiation of the carbon atom with $\text{Li}[\text{N}(\text{SiMe}_3)_2]$, followed by the addition of alkyl halides, which gives the neutral tris(pyrazolyl)alkane $\text{R}'\text{CTp}^{3-\text{R}}$ (**3**, Scheme 2 and Fig. 1).

Considering the successful formation of the donor-stabilised bis(tetramethyl)aluminate magnesium complex **IX** employing $\text{MeCTp}^{3-\text{iPr}}$, tris(pyrazolyl)alkanes **3a–c** were synthesised to examine the steric demand of pyrazolyl substituents ($\text{R} = \text{Et}, \text{cyPr}, \text{Cy}$) comparable to the *iPr* group and to complete the series of previously employed substituents *Me* and *iPr*.³⁵ The bulky **3d** ($\text{R} = 3\text{-}p\text{-}t\text{BuPh}$) was selected not only to prevent the formation of a “metal in a box” complex but also to assess the feasibility of methyl activation and hence the formation of a methylidene species. For comparison, the potassium salt of isoelectronic monoanionic $\text{Tp}^{3-\text{p-}t\text{BuPh}}$ formed the neutral complex $\text{Tp}^{3-\text{p-}t\text{BuPh}}\text{MgMe}$ when reacted with MgMe_2 .⁴⁰ We previously noticed a pronounced variability of the reactivity of monomeric $\text{Mg}(\text{AlMe}_4)_2$ ^{41,42} towards $\text{R}'\text{CTp}^{3-\text{Ph}}$ depending



Scheme 2 Preparation of ligands $\text{R}'\text{CTp}^{3-\text{R}}$ **3a–g**. (i) $(n\text{Bu})_4\text{NBr}$, CHCl_3 , Na_2CO_3 , H_2O , reflux, 3–7 d. (ii) *pTosOH*, toluene, 120 °C, 1 d. (iii) $\text{Li}[\text{N}(\text{SiMe}_3)_2]$, THF, –78 °C, 30 min. (iv) $\text{R}'\text{X}$, THF, –78 °C to rt, 16 h.

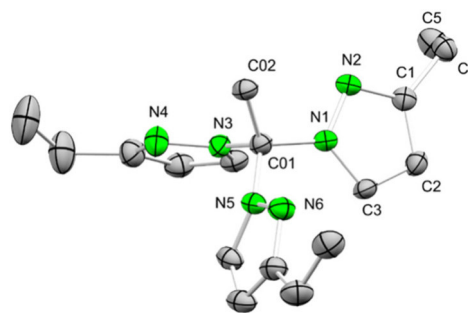
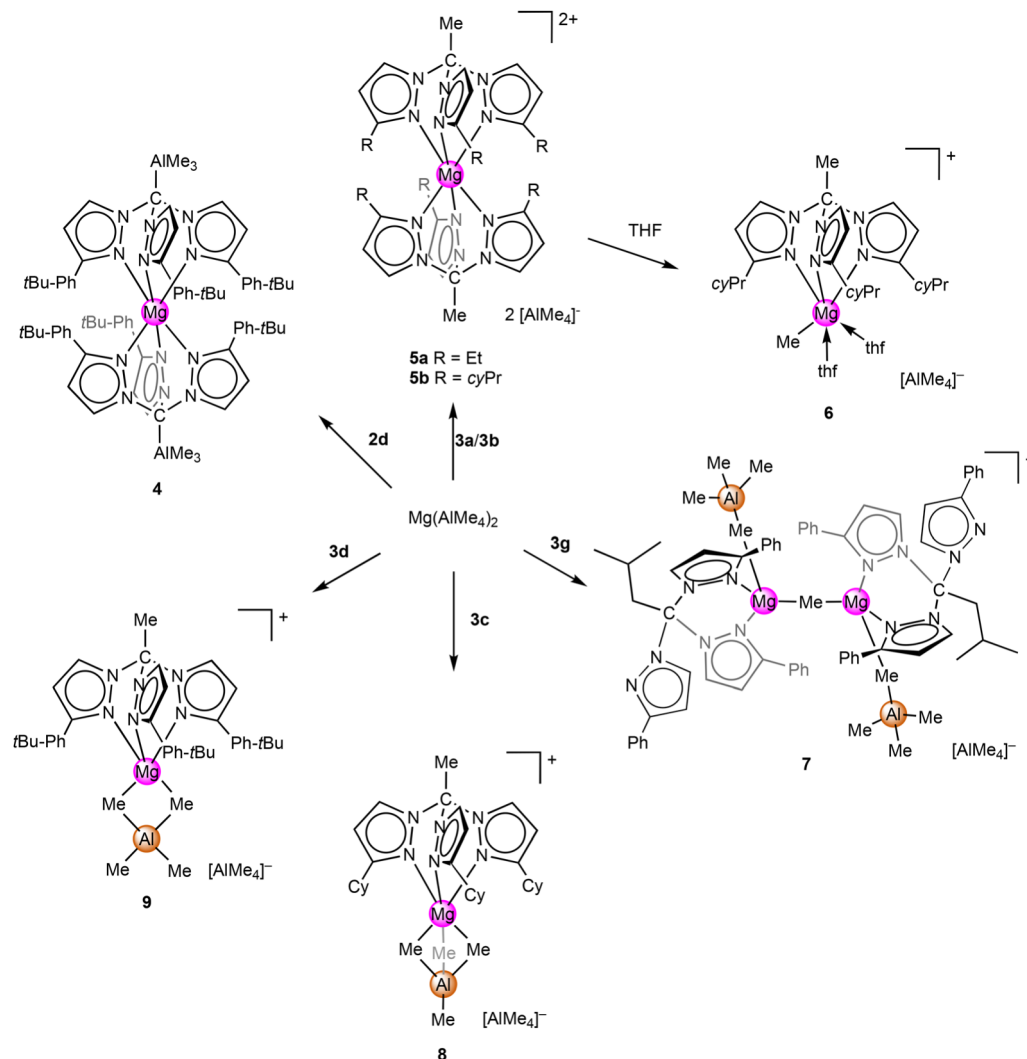


Fig. 1 Representative solid-state structure of **3a**. For the crystal structures of compounds **3b**, **3c** (connectivity) and **3e–g**, see the ESI.†



Scheme 3 Reaction of $\text{Mg}(\text{AlMe}_4)_2$ with **2d**, **3a–d** and **3g** in a toluene/*n*-hexane mixture.

on the chain length of R' , affording either separated ion pairs **VI** or the unusual methyl-bridged dimagnesium complex **VIII**. To further examine the effect of distinct backbone alkylation, the tris(pyrazolyl)alkanes **3e–g** ($\text{R}' = \text{Et}, n\text{Pr}, i\text{Bu}$) were targeted. All ligands were purified by recrystallization or column chromatography. Solid-state structures for **3a–c** and **3e–g** could be determined by single-crystal X-ray diffraction (SCXRD) analysis (Fig. 1 or ESI†). Tris(pyrazolyl)alkane backbone moieties other than alkyl chains (*e.g.* H , SiMe_3 or $\text{Bn} = \text{benzyl}$) were ruled out since we found previously that their reaction with $\text{Mg}(\text{AlMe}_4)_2$ either led to decomposition or carbanion formation *via* the displacement of the hydrogen atom at the apical carbon atom with an AlMe_3 moiety.

Magnesium $\text{R}'\text{CTp}^{3-\text{R}}$ complexes

Homoleptic $\text{Mg}(\text{AlMe}_4)_2$ was previously identified as a suitable precursor preventing the decomposition of $\text{R}'\text{CTp}^{3-\text{R}}$ ligands as observed in the case of MgMe_2 .³⁵ For the synthesis of the new discrete magnesium complexes, a solution of $\text{Mg}(\text{AlMe}_4)_2$ in

n-hexane was added dropwise to a solution of **2d** or **3a–g** in toluene (for an overview see Scheme 3).

To assess whether the sterically demanding $\text{HCTp}^{3-p-t\text{BuPh}}$ (**2d**) can prevent methanide formation and any concomitant functionalization of the apical carbon atom, $\text{Mg}(\text{AlMe}_4)_2$ was treated with the crude product of **2d**. However, SCXRD analysis of the crystallized product revealed the recurring structural motif of the neutral “metal in a box” bis(methanide) complex ($\text{Me}_3\text{AlCTp}^{3-p-t\text{BuPh}})_2\text{Mg}$ (**4**) (see the ESI†). Even the bulky *p*-*t*BuPh groups protrude into the coordination sphere of the other scorpionate ligand and thus cannot prevent the accommodation of two monoanionic heteroaluminato ligands. The magnesium centre in **4** is coordinated by the six nitrogen atoms of the two methanide ligands in a distorted octahedral fashion with N–Mg–N angles in the range of 85.45(9) to 102.49(14)°. The apical carbon–magnesium–apical carbon axis is close to linear (178.58°).

Treatment of $\text{Mg}(\text{AlMe}_4)_2$ with **3a/b** instantly gave a white precipitate indicative of the formation of a separated ion pair



with a “metal in a box” structure. This very structural motif could be confirmed by the solid-state structure of complex $[(\text{MeCTp}^{3-\text{Et}})_2\text{Mg}][\text{AlMe}_4]_2$ (**5a**) (Fig. 2). Two $\text{MeCTp}^{3-\text{Et}}$ ligands coordinate the magnesium centre in the $\kappa^3(\text{N},\text{N}',\text{N}'')$ mode forming a dicationic entity with two $[\text{AlMe}_4]^-$ anions as counter ions. The six-coordinated magnesium centre adopts a slightly distorted octahedral geometry with longer distances to the equatorial nitrogen atoms (Mg1–N2, 2.1666(10) Å; Mg1–N4, 2.1676(10) Å; Mg1–N6, 2.1458(10) Å). All observed Mg–N distances are in the expected range of magnesium complexes bearing two tris(pyrazolyl)methane ligands (2.113(1)–2.196(1) Å).^{29–31,33,35} The CH_2 groups of the ethyl moiety are almost coplanar with the magnesium centre and the CH_3 groups are displaced only marginally from this plane. The apical carbon atom (C01) adopts an almost ideal tetrahedral geometry (109.21(9)–109.93(9)°). The NMR spectra of **5a** match those found in the reference literature, with ligand signals only slightly shifted.

In the ^{13}C NMR spectrum, the two $[\text{AlMe}_4]^-$ ions appear as a non-binominal sextet at $\delta = -4.2$ ppm due to the interaction with the ^{27}Al nucleus ($I = 5/2$, $^1J(\text{Al},\text{C}) = 70.4$ Hz) (Fig. S29†).⁴³ In the ^1H NMR spectrum, the proton signals of the $[\text{AlMe}_4]^-$ moieties appear at $\delta = -1.28$ ppm but the expected sextet is not fully resolved (Fig. S28†).

Given the similar reaction behaviour of the $\text{Mg}(\text{AlMe}_4)_2/3\text{b}$ mixture involving product precipitation, the formation of putative complex $[(\text{MeCTp}^{3-\text{cyPr}})_2\text{Mg}][\text{AlMe}_4]_2$ (**5b**) seemed obvious. However, a crystalline material could only be obtained by heating a solid sample in a J. Young valve NMR tube to 150 °C in toluene. The structural motif of a separated ion pair

$[(\text{MeCTp}^{3-\text{cyPr}})_2\text{Mg}][\text{AlMe}_4]_2$ could be confirmed by a connectivity structure of crystals obtained under these harsh conditions (Fig. S6†). The formation of the “metal in a box” complex came as a surprise since the steric difference of *cyPr* and *iPr* is marginal. It is likely that the conformational/rotational flexibility of the *iPr* methyl moieties counteracts the coordination of a second MeCTp ligand. Because of the high insolubility of the precipitated product in aliphatic and aromatic solvents, THF was used as a solvent for NMR measurements. The ^1H NMR spectrum indicated that the separated ion pair converted to a complex of the type $[(\text{MeCTp}^{3-\text{R}})\text{MgMe}(\text{thf})_2][\text{AlMe}_4]$ as proposed previously by NMR spectroscopy.³⁵ Crystallisation could be achieved by cooling the THF solution to -40 °C revealing the solid-state structure of methyl complex $[\text{MeCTp}^{3-\text{cyPr}}\text{MgMe}(\text{thf})_2][\text{AlMe}_4]$ (**6**) (Fig. 3). The $[\text{MgMe}]^+$ fragment is coordinated by one $\text{MeCTp}^{3-\text{cyPr}}$ ligand and two THF donor molecules, which are fully separated from the charge-balancing $[\text{AlMe}_4]^-$ counter ion. The magnesium centre adopts a distorted octahedral geometry with angles ranging from 78.18(10) to 105.39(17)°.

Unsurprisingly, the Mg1–C001 distance of 2.182(4) Å is slightly longer than those of 4-coordinate terminal methyl magnesium complexes $[\text{MeCTp}^{3-\text{R}}\text{MgMe}][\text{AlMe}_4]$ ($\text{R} = t\text{Bu}$: 2.115(2) Å and $\text{R} = \text{Ph}$: 2.091(2) Å) and $\text{Tp}^{\text{R,Me}}\text{MgMe}$ ($\text{R} = \text{Me}$: 2.097(4) Å and $\text{R} = t\text{Bu}$: 2.119(3) Å) but distinctly shorter than the Mg–C distance involving the bridging position of MgMe_2 with 2.234(2) and 2.24(3) Å.^{11,35,44,45} However, the Mg1–C001 distance in **6** is in line with other six-coordinate terminal methyl complexes $[\text{MeMg}(\text{15-crown-5})][\text{A}]$ ($\text{A} = \text{Me}_5\text{Mg}_2$: 2.140(7) Å and $\text{A} = \text{Cp}$: 2.124(2) Å) and $[\text{MeMg}(\text{thf})(\text{dme})_2]\text{I}$ (2.162(6) Å).^{46–48} It appears that the *cyPr* substituents of **6** provide enough steric flexibility so that the magnesium centre can accommodate two THF molecules, which is in contrast to complexes $[\text{MeCTp}^{3-\text{R}}\text{MgMe}][\text{AlMe}_4]$ (**VI**; $\text{R} = t\text{Bu}, \text{Ph}$) mentioned above, in which the THF solvent is not coordinated to magnesium.

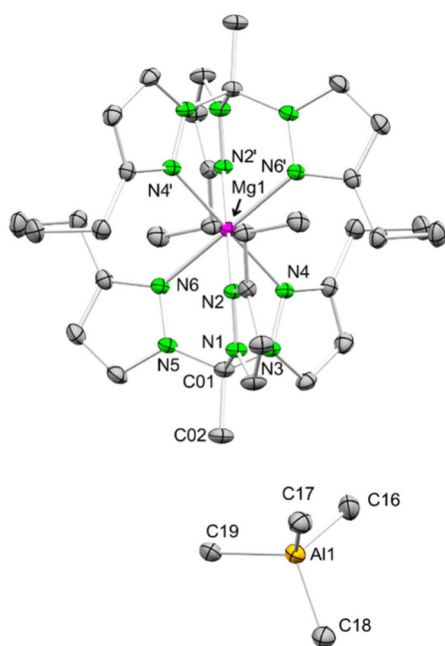


Fig. 2 Crystal structure of **5a**. Hydrogen atoms, one lattice THF molecule and the second $[\text{AlMe}_4]^-$ are omitted for clarity and atomic displacements are set at a 50% probability level.

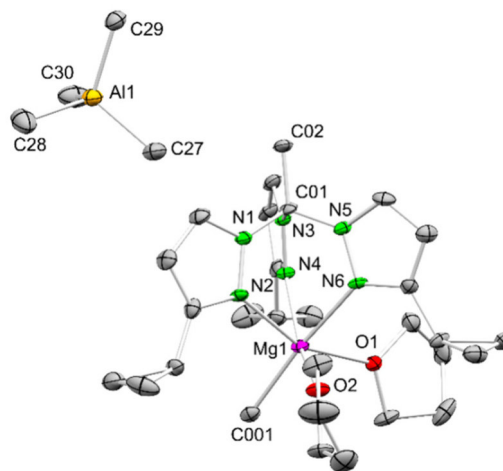


Fig. 3 Crystal structure of **6**. Hydrogen atoms are omitted for clarity and atomic displacements are set at a 50% probability level.



For further probing the impact of the apical carbon substitution, $\text{Mg}(\text{AlMe}_4)_2$ was reacted with $\text{R}'\text{CTp}^{3-\text{Ph}}$ ($\text{R}' = \text{Et}$ (**3e**), $n\text{Pr}$ (**3f**), and $i\text{Bu}$ (**3g**)). Note that complexes $[\text{MeCTp}^{3-\text{Ph}}\text{MgMe}][\text{AlMe}_4]$ ($\text{R}' = \text{Me}$, type **VI**) and $[(\{n\text{BuCTp}^{3-\text{Ph}}\}\text{Mg}\{\text{AlMe}_4\})_2(\mu\text{-Me})][\text{AlMe}_4]$ ($\text{R}' = n\text{Bu}$, **VIII**) were identified previously.³⁵ Accordingly, instant oil formation was observed in the case of tris(pyrazolyl)alkanes **3e** and **3f**. The crude products showed characteristic behaviour of an ionic liquid, impeding their crystallographic characterization. Moreover, the ^1H NMR spectra showed broadened signals that were not indicative of any structural motif detected so far. However, the $\text{Mg}(\text{AlMe}_4)_2/3\text{g}$ reaction produced colourless crystals suitable for SCXRD analysis. The connectivity structure revealed that the methyl-bridged dimagnesium complex $[(\{i\text{BuCTp}^{3-\text{Ph}}\}\text{Mg}\{\text{AlMe}_4\})_2(\mu\text{-Me})][\text{AlMe}_4]$ (**7**, Fig. S8†) is isostructural to the previously identified n -butyl derivative **VIII**.

Further increasing the steric demand of the substituent in the 3 position of the pyrazole rings (compared to $\text{R}' = i\text{Pr}$, compound **IX**), $\text{Mg}(\text{AlMe}_4)_2$ was reacted with **3c** bearing cyclohexyl (Cy) groups. Crystals suitable for SCXRD analysis were obtained by recrystallisation in 1,2-difluorobenzene. The solid-state structure revealed the new structural motif of the separated ion pair $[(\text{MeCTp}^{3-\text{Cy}})\text{Mg}(\text{AlMe}_4)][\text{AlMe}_4]$ (**8**) (Fig. 4).

The $\text{MeCTp}^{3-\text{Cy}}$ ligand stabilises a $[\text{Mg}(\text{AlMe}_4)]^+$ fragment via $\kappa^3(\text{N},\text{N}',\text{N}'')$ coordination while the $[\text{AlMe}_4]$ ligand interacts with the magnesium centre in an η^3 fashion. The monoanionic $[\text{AlMe}_4]$ counter ion is fully separated. The magnesium centre adopts a slightly distorted octahedral geometry with both ligands coordinating in a facial manner. The C01-Mg1-Al1 axis running through the ligand backbone is almost linear (176.45°). As expected the cyclohexyl groups adopt the chair conformation pointing away from the magnesium centre just like the cyPr groups in **6** and the $i\text{Pr}$ groups in **IX**.³⁵

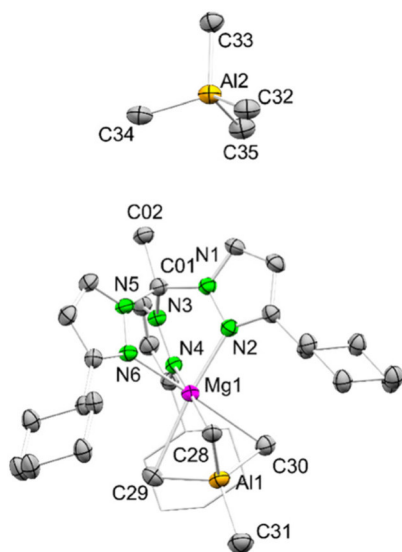


Fig. 4 Crystal structure of **8**. Hydrogen atoms are omitted for clarity and atomic displacements are set at a 50% probability level.

Crystallisation of the reaction product formed by the treatment of $\text{Mg}(\text{AlMe}_4)_2$ with the bulky **3d** (with $\text{R}' = p\text{-}t\text{BuPh}$) was achieved by redissolving the residue in benzene and dropwise addition of n -pentane to the solution at 40°C . As detected for **8**, the solid-state structure revealed the formation of a monocationic complex entity in $[(\text{MeCTp}^{3-p\text{-}t\text{BuPh}})\text{Mg}(\text{AlMe}_4)][\text{AlMe}_4]$ (**9**) (Fig. 5) with the magnesium centre also coordinated with one tris(pyrazolyl)ethane ligand in the $\kappa^3(\text{N},\text{N}',\text{N}'')$ mode. However, due to the enhanced steric demand of **3d** compared to **3c**, this time the $[\text{AlMe}_4]$ unit is η^2 -coordinated. The now 5-coordinate magnesium centre adopts a strongly distorted square pyramidal geometry with two nitrogen atoms (N2 and N4) of the scorpionate ligand and two carbon atoms of the $[\text{AlMe}_4]$ unit (C40 and C41) located in the equatorial and one ligand nitrogen (N6 , the “sting”) in the apical position. Hence, the coordination of the $\text{MeCTp}^{3-p\text{-}t\text{BuPh}}$ ligand itself appears highly asymmetrical, very much scorpionate-like with two pincers and one sting. The putative sixth coordination position for octahedral geometry is approached by *ortho*-carbon atoms of two different phenyl rings (C18 : 3.592 , C9 : 3.700 Å). The overall asymmetric coordination of the scorpionate ligand is also seen in the distance of the phenyl rings, measured by the distance of the *ortho*-carbon atoms closest to each other (C9-C18 4.118 Å, C5-C31 6.187 Å, and C22-C35 8.567 Å) and furthermore in the N-N distances between the three coordinating nitrogen atoms (N2-N4 2.717 Å, N2-N6 2.877 Å, and N4-N6 3.110 Å), as well as by the N-Mg-N angles (N2-Mg1-N4 $76.64(5)^\circ$, N2-Mg1-N6 $83.24(6)^\circ$, and N4-Mg1-N6 $91.91(6)^\circ$). Finally, the C01-Mg1-Al1 axis deviates considerably from linearity (165.43°).

The pronounced asymmetric tris(pyrazolyl)ethane coordination in complex **9** is not detected in the ambient tempera-

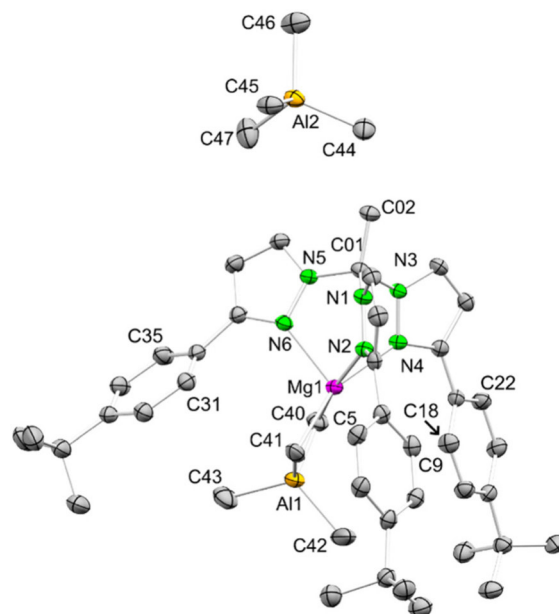


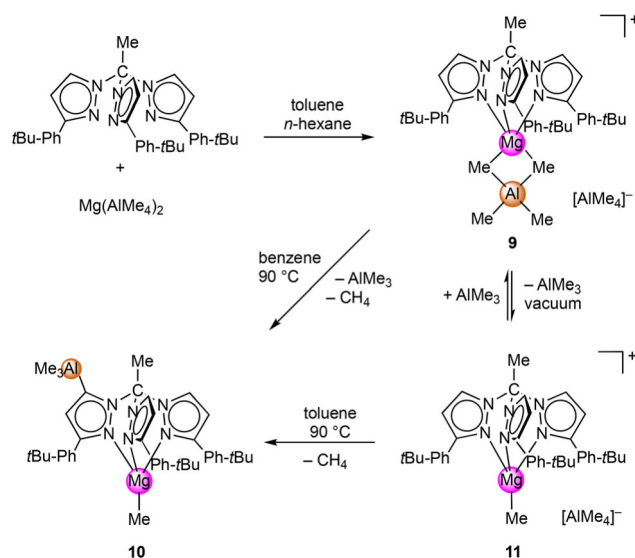
Fig. 5 Crystal structure of **9**. Hydrogen atoms, the lattice $[\text{D}_6]\text{benzene}$ molecules and the disorder in one $t\text{Bu}$ group are omitted for clarity and atomic displacements are set at a 50% probability level.



ture ^1H NMR spectrum, which is similar to that of complex **8**. The two pyrazole hydrogen atoms in the 4- and 5 positions appear as multiplets in the aromatic region at $\delta = 8.03/7.84$ ppm and $\delta = 6.28/5.80$ ppm, respectively, with an integral of each being three. Also, there is only one sharp signal found for the bridging and terminal methyl groups of the coordinated $[\text{AlMe}_4]$ unit and for the methyl groups of the displaced $[\text{AlMe}_4]$ at $\delta = -0.19$ (**8**)/ -0.34 ppm (**9**), which indicates fast exchange of the coordinated and free tetramethylaluminato groups. Because of this dynamic behaviour VT ^1H NMR spectroscopy experiments were performed on both complexes **8** and **9** (Fig. S34/38†). Accordingly, the signals at $\delta = -0.19$ ppm and $\delta = -0.34$ ppm broaden as the temperature decreases. For **8**, the signal splits into two separated singlets at -50 °C while for **9** this behaviour is detected at -60 °C. At -80 °C, these two signals are located at $\delta = 0.18$ and -0.06 ppm (**8**) and at $\delta = 0.24$ and -0.79 ppm (**9**), both in a ratio of 2:1. All other signals ascribed to **8** split into two signals at -80 °C even that of the backbone methyl group, which means that the $[\text{AlMe}_4]$ group exchange is more complicated. The same signal splitting is observed for **9** (at -80 °C) except that the signal of the backbone methyl group appears as a very broad signal. This could indicate that for **9** only one $\text{R}'\text{CTp}^{3-\text{R}}$ ligand species is present during the exchange of the $[\text{AlMe}_4]$ groups, but acts in a hemilabile fashion with one arm off. The splitting of the signals is completely reversible for both complexes upon warming the solutions to ambient temperatures. Complex **9** also remains intact when heated to 80 °C and re-cooled to ambient temperature.

Behaviour of $[(\text{MeCTp}^{3-p-t\text{BuPh}})\text{Mg}(\text{AlMe}_4)][\text{AlMe}_4]$ (**9**) at elevated temperatures and under vacuum

As revealed by ^1H NMR spectroscopy, further heating of complex **9** to 90 °C led to a selective activation of the scorpionate ancillary ligand. Full conversion was indicated by a new set of signals showing the pyrazolyl moieties in a ratio of 1:2 along with the backbone methyl group, which appeared slightly shifted to lower field. Slow evaporation of the solvent generated crystals suitable for SCXRD analysis. The solid-state structure revealed C–H-bond activation of one pyrazole ring at the 5 position forming the neutral complex $[\text{MeC}(\text{pz}^{3-p-t\text{BuPh}})_2(\text{pz}^{3-p-t\text{BuPh},5-\text{AlMe}_3})]\text{MgMe}$ (**10**) (Scheme 4 and Fig. 6). Notably, heating a solution of **10** to 100 °C resulted in complete decomposition. Complex **10** adopts a distorted tetrahedral geometry with the magnesium centre accommodating the new scorpionate ligand in the routine η^3 fashion and a terminal methyl group. The $\text{Mg1}–\text{C43}$ distance of $2.090(2)$ Å matches other terminal $\text{Mg}–\text{C}$ distances of tetrahedral magnesium methyl complexes.^{35,44} Due to the metalation of one pyrazolyl ring the scorpionate ligand is monoanionic. Because of this and the less bulkier methyl group the overall geometry of the ligand scaffold is more symmetrical in comparison with that of complex **9**. As a consequence, the N–N distances of the three coordinating nitrogen atoms lie between 2.842 and 2.873 Å (*cf.*, **9** $\Delta_{\text{max}} = 0.393$ Å) and the $\text{C01}–\text{Mg1}–\text{C43}$ axis is close to linear (177.65°). Since the scorpionate ligand in **10** is



Scheme 4 Thermal activation and reversible coordination of AlMe_3 in complex **9**. $\text{R} = p\text{-tBuPh}$.

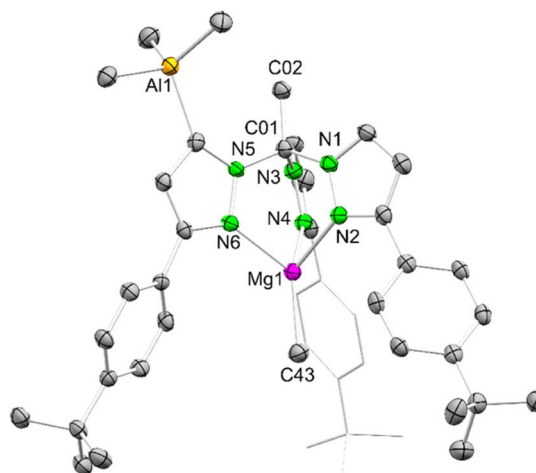


Fig. 6 Crystal structure of **10**. Hydrogen atoms and two solvent toluene molecules are omitted for clarity and atomic displacements are set at a 50% probability level.

monoanionic, complex **10** is now comparable to the $\text{Tp}^{3-p-t\text{BuPh}}\text{MgMe}$ complex proposed by Parkin.⁴⁰ A striking feature of the ^1H NMR spectrum of **10** is the considerable low-field shift at $\delta = 7.32$ ppm of the singlet of the hydrogen atom in the 4 position of the activated pyrazolyl ring. In contrast, the doublet signal of the hydrogen atom in the 4 position of the non-activated pyrazolyl rings appears at $\delta = 5.90$ ppm. The methyl ligand and the AlMe_3 group were detected at $\delta = -0.99$ ppm and 0.16 ppm, respectively.

By applying reduced pressure, AlMe_3 can be displaced from complex **9** forming the new separated ion pair $[(\text{MeCTp}^{3-p-t\text{BuPh}})\text{MgMe}][\text{AlMe}_4]$ (**11**) (Scheme 4). The ^1H NMR spectrum of **11** shows slightly shifted signals of the ancillary ligand while the counter ion $[\text{AlMe}_4]$ and the methyl group co-



ordinated to the magnesium centre appear as two distinct signals at $\delta = -0.09$ ppm and -1.04 ppm, respectively (Fig. S42†). Adding a stoichiometric amount of AlMe_3 to **11** reformed complex **9** quantitatively, thus proving full reversibility. This behaviour is reminiscent of the $\text{Tp}^{\text{Me,Me}}\text{Mg}(\text{AlMe}_4)/\text{Tp}^{\text{Me,Me}}\text{MgMe}$ system engaging in donor-induced tetraalkylaluminate cleavage.⁴² Heating complex **11** to 90 °C also led to the formation of complex **10**, suggesting that the C–H-bond activation in the 5 position of the pyrazolyl moiety is caused by the attack of the separated $[\text{AlMe}_4]$ anion *via* the release of methane.

Cone angle calculations

The mathematically exactly calculated cone angles⁴⁹ of the scorpionate ligands of the newly synthesised complexes are shown in Table 1. The cone angles featured by $[(\text{MeCTp}^{3-\text{Et}})_2\text{Mg}][\text{AlMe}_4]_2$ (**5a**, $\theta^\circ = 247.95^\circ$) and $[\text{MeCTp}^{3-\text{CyPr}}\text{MgMe}(\text{thf})_2][\text{AlMe}_4]$ (**6**, $\theta^\circ = 250.80^\circ$) are very close to that observed for the bis(tetramethylaluminate) complex $[(\text{MeCTp}^{3-\text{iPr}})\text{Mg}(\text{AlMe}_4)_2]$ ($\theta = 248.76^\circ$).³⁵ Despite this similarity, completely different coordination environments exist even though all complexes exhibit a coordination number of six. It seems that the slightly higher steric demand of the iPr group in comparison to Et and CyPr, caused by the flexibility of the two Me groups, is sufficient to prevent the formation of the “metal in a box” complex. As expected the cone angle calculated for $[(\text{MeCTp}^{3-\text{Cy}})\text{Mg}(\text{AlMe}_4)][\text{AlMe}_4]$ (**8**) ($\theta^\circ = 260.64^\circ$) is distinctly higher than that enforced by the iPr, Et or CyPr substituents, which allows the stabilization of the $\text{Mg}(\eta^3\text{-AlMe}_4)^+$ fragment with three methyl groups coordinated to the metal centre. The tentative cone angles of the two disordered species of **9** are determined as $\theta^\circ = 289.60^\circ$ and $\theta^\circ = 291.34^\circ$. The only magnesium complexes with a cone angle comparable to **9** are $[(\text{MeCTp}^{3-\text{Ph}})\text{MgMe}][\text{AlMe}_4]$ ($\theta^\circ = 282.84^\circ$) and the extremely bulky $[(\text{CTp}^{\text{Ad,Me}})\text{MgMe}]$ ($\theta^\circ = 301.47^\circ$).^{35,50} Upon thermal C–H-bond activation and formation of $[\text{MeC}(\text{pz}^{3-p-t\text{BuPh}})_2(\text{pz}^{3-p-t\text{BuPh},5-\text{AlMe}_3})]\text{MgMe}$ (**10**), the cone angle increased even further to $\theta^\circ = 299.10^\circ$. Now that the scorpionate ligand has a negative charge it is better comparable to the adamantyl methanide complex $[(\text{CTp}^{\text{Ad,Me}})\text{MgMe}]$ and both angles are indeed very close. Comparing the cone angles of $(\text{Me}_3\text{AlCTp}^{3-p-t\text{BuPh}})_2\text{Mg}$ (**4**) and **10**, which both feature anionic scorpionate ligands with *p*-tBuPh moieties in the 3 position, there is a difference of 11.08° . Therefore, the ligand coordinated to the metal centre opposite to the examined/calculated $\text{R}'\text{CTp}^{3-\text{R}}$ ligand has a vast influence on the cone angle too.

Table 1 Overview of the mathematically exactly calculated cone angle θ° of the magnesium tris(pyrazolyl)alkane complexes under study (see the ESI† for calculations)

4	5a	6	8	9	10
288.02	247.95	250.80	260.64	289.60 291.34	299.10

Conclusions

The scope of the tris(pyrazolyl)alkane $\text{R}'\text{CTp}^{3-\text{R}}$ library, here with varying substituents in the pyrazolyl 3 position and at the apical carbon atom, could be successfully expanded by derivatives $\text{MeCTp}^{3-\text{Et}}$, $\text{MeCTp}^{3-\text{CyPr}}$, $\text{MeCTp}^{3-\text{Cy}}$, $\text{MeCTp}^{3-p-t\text{BuPh}}$, $\text{EtCTp}^{3-\text{Ph}}$, $n\text{PrCTp}^{3-\text{Ph}}$ and $i\text{BuCTp}^{3-\text{Ph}}$ (CyPr = cyclopropyl, Cy = cyclohexyl, *3-p*-tBuPh = *para-tert*-butylphenyl). As anticipated, the reaction of bis(tetramethylaluminate) magnesium $\text{Mg}(\text{AlMe}_4)_2$ with neutral tris(pyrazolyl)alkanes $\text{R}'\text{CTp}^{3-\text{R}}$ is strongly dependent on the steric effect of such scorpionate ligands, resulting in the partial or full displacement of the aluminate ligands. The smaller Et and CyPr substituents in the 3 position favour the formation of the recurring “undesired” structural motifs of a “metal in a box” complex $[(\text{MeCTp}^{3-\text{R}})_2\text{Mg}][\text{AlMe}_4]_2$ (R = Et, CyPr). The bulky Cy and *p*-tBuPh moieties led to the separated ion pairs $[(\text{MeCTp}^{3-\text{R}})\text{Mg}(\text{AlMe}_4)][\text{AlMe}_4]$ (R = Cy, *p*-tBuPh) with distinct η^2 - and η^3 -coordination modes of the AlMe_4 moiety. Variation of the alkyl substituent R' at the apical carbon atom of $\text{R}'\text{CTp}^{3-\text{Ph}}$ (R' = Et, *n*Pr, *i*Bu) led to the isolation of the dimagnesium species $[(i\text{BuCTp}^{3-\text{Ph}})\text{Mg}\{\text{AlMe}_4\}_2(\mu\text{-Me})][\text{AlMe}_4]$ with a $\kappa^2(\text{N},\text{N}')$ coordination mode of the tris(pyrazolyl)alkane ligand. Separated ion pairs of the type $[(\text{MeCTp}^{3-\text{R}})\text{Mg}(\text{AlMe}_4)][\text{AlMe}_4]$ are prone to AlMe_3 separation, when exposed to a vacuum, and a selective pyrazolyl deprotonation, upon thermal treatment. The latter C–H-bond activation is triggered by the non-coordinating $[\text{AlMe}_4]$ anion and generates a new monoanionic scorpionate ligand in $[\text{MeC}(\text{pz}^{3-p-t\text{BuPh}})_2(\text{pz}^{3-p-t\text{BuPh},5-\text{AlMe}_3})]\text{MgMe}$ featuring a terminal Mg-CH_3 moiety.

Experimental

General considerations

All manipulations were performed under rigorous exclusion of air and moisture under an argon atmosphere (<1 ppm O_2 , <1 ppm of H_2O) in an MB200B glovebox (MBraun) or according to standard Schlenk techniques and in oven-dried glassware. Solvents (THF, *n*-pentane, *n*-hexane, Et_2O and toluene) were purified by using Grubbs-type columns (MBraun SPS-800, solvent purification system) and stored inside a glovebox. THF was dried further over molecular sieves. $[\text{D}_6]$ Benzene, $[\text{D}_8]$ toluene and $[\text{D}_8]$ THF were obtained from Sigma Aldrich and dried over a Na/K alloy and filtered prior to use. 1,4-Dioxane was dried over sodium metal, distilled and degassed and stored inside a glovebox. 1,2-Difluorobenzene was purchased from Sigma Aldrich, dried over CaH_2 , distilled and degassed prior to use. Acetophenone (>98%), benzophenone (>98%), *n*-BuLi (2.5 M in *n*-hexane), cyclopropyl methyl ketone (99%), 1,4-dihydro-2H-pyran (>97%), ethyl bromide (>99%), ethyl iodide (99%, copper stabilized), hexamethyldisilazane (>99%), hydrazine dihydrochloride (>98%), methylmagnesium bromide (3 M in Et_2O), *n*-propyl iodide (99%), 1-iodo-2-methylpropane (97%, copper stabilized), pyrazole (>98%) and tetra-*n*-butylammonium bromide (98%) were purchased from Sigma



Aldrich and used as received. Iodomethane (>99%) and methyl *tert*-butyl ether (MTBE) were purchased from Acros Organics and used as received. *N,N*-Dimethylformamide dimethylacetate (>97%), 4'-*tert*-butylacetophenone (98%) and trimethyl-aluminium (98%) were purchased from abcr and used as received. Cyclohexyl methyl ketone (95%) was purchased from Alfa Aesar and used as received. $\text{Li}[\text{N}(\text{SiMe}_3)_2]$,⁵¹ MgMe_2 ,^{9,10} and $\text{Mg}(\text{AlMe}_4)_2$ ⁴¹ were synthesized according to the literature procedures. The 3-*R*-pyrazoles **1** were synthesized according to standard procedures (*R* = Et,⁵² *cyPr*,⁵³ Cy,⁵³ Ph,⁵³ *p*-*t*BuPh⁵³). Argon was supplied by Westfalen AG. ¹H and ¹³C NMR spectra were recorded on a Bruker AVII+400 spectrometer (¹H: 400.11 MHz; ¹³C: 100.61 MHz) at 299 K. The chemical shifts compiled in the Experimental section are referenced to solvent residual resonances in parts per million relative to tetramethylsilane. The variable temperature ¹H NMR spectra of **8** and **9** were recorded in a J. Young valve NMR tube on a Bruker AVII+500 spectrometer (¹H: 500.13 MHz; ¹³C: 125.76 MHz) at 299 K. IR spectra were recorded on a NICOLET 6700 FTIR spectrometer (Thermo Fisher Scientific). The samples were mixed with KBr powder and measured in a DRIFT cell with KBr windows. DRIFT data were converted by using the Kubelka–Munk refinement. Elemental analyses were performed on an Elementar Vario MICRO cube. Single crystals were grown from saturated solutions of [D₆]benzene, 1,2-difluorobenzene, Et₂O, MTBE, *n*-pentane, or THF by standard techniques. Suitable single crystals for X-ray structure studies were selected in a glovebox and coated with Parabar 10312 (Hampton Research). Crystallographic data were measured on a Bruker APEX II DUO instrument equipped with an I μ S micro focus sealed tube and QUAZAR optics for MoK α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXT software packages and refined on *F*² (with all independent reflections) using the SHELXL software package. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms of C–H bonds were located using a riding model at the expected position for hydrogen with a fixed interatomic distance.

General procedure for the synthesis of 2. The synthesis of tris(pyrazolyl)alkanes **2** was achieved according to the literature procedure by Reger.³⁹ In a 1 L three-necked flask with a KPG stirrer the corresponding 3-alkylpyrazole (1 equiv.), Na₂CO₃ (20 equiv.) and (*n*-Bu)₄NBr (0.05 equiv.) were dissolved in 350 mL each of water and CHCl₃. The reaction mixture was heated to 95 °C and was stirred vigorously until completeness (3–7 days). After cooling to ambient temperature, water was added to dissolve excess Na₂CO₃. The organic layer was separated and the solvent was removed under reduced pressure. After redissolving the residue in Et₂O and combining all layers the aqueous layer was washed three times with Et₂O. The combined organic layers were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The residual dark red oil was redissolved in 200 mL of toluene in a 500 mL round bottom flask. After adding 400 mg of *p*TsOH the mixture was heated to reflux for 1 d. After cooling to ambient temperature, the reaction mixture was washed with brine and the aqueous layer was extracted three times with Et₂O. The

combined organic layers were dried with Na₂SO₄ and filtered. After removal of the solvent *in vacuo* an oil was obtained. Unreacted pyrazole could be separated by sublimation. The ¹H NMR spectra showed that the oil was a mixture of the desired product **2** (HC(pz^{3-R})₃) and the undesired isomer (HC(pz^{3-R})₂(pz^{5-R})) with one flipped pyrazolyl moiety. The isomer ratio depended on the steric bulk of the corresponding pyrazole and was determined by comparison of the backbone hydrogen *H*-CTp^{3-R} signal integrals. Used quantities and yields for **2**:

HCTp^{3-Et} (2a). 3-Ethylpyrazole (27.2 g, 282 mmol), Na₂CO₃ (180 g, 1.697 mol), and (*n*-Bu)₄NBr (4.56 g, 14 mmol). Reaction time: 7 d. **2a** was obtained as a dark red oil (88%, 24.7 g, 82.9 mmol). The ratio of the crude product mixture: **2a**: undesired isomer = 1 : 0.4.

HCTp^{3-cyPr} (2b). 3-Cyclopropylpyrazole (25.0 g, 231 mmol), Na₂CO₃ (143 g, 1.350 mol), and (*n*-Bu)₄NBr (3.62 g, 11 mmol). Reaction time: 7 d. **2b** was obtained as a dark brown oil (81%, 21.1 g, 63 mmol). The ratio of the crude product mixture: **2b**: undesired isomer = 1 : 0.6.

HCTp^{3-Cy} (2c). 3-Cyclohexylpyrazole (24.0 g, 160 mmol), Na₂CO₃ (102 g, 960 mmol), and (*n*-Bu)₄NBr (2.58 g, 8.0 mmol). Reaction time: 5 d. **2c** was obtained as a dark red oil in a quantitative yield. The ratio of the crude product mixture: **2c**: undesired isomer = 1 : 0.2.

HCTp^{3-p-tBuPh} (2d). 3-*para-tert*-Butylphenylpyrazole (25.0 g, 124 mmol), Na₂CO₃ (79.4 g, 749 mmol), and (*n*-Bu)₄NBr (2.0 g, 6.2 mmol). Reaction time: 7 d. **2d** was obtained as a dark red oil (50%, 11.4 g, 19 mmol). The ratio of the crude product mixture: **2d**: undesired isomer = 1 : 0.1.

HCTp^{3-Ph} (2e). 3-Phenylpyrazole (25.0 g, 173 mmol), Na₂CO₃ (110 g, 1.040 mol), and (*n*-Bu)₄NBr (2.80 g, 8.7 mmol). Reaction time: 3 d. **2e** was obtained as a dark red oil (45%, 11.5 g, 26 mmol). The ratio of the crude product mixture: **2e**: undesired isomer = 1 : 0.1.

Preparation and characterization of compounds **3**, **4**, **5**, **6**, **8**, **9**, **10** and **11**

MeCTp^{3-Et} (3a). The crude product of HCTp^{3-Et} (**2a**) (3.00 g, 10.1 mmol) was dissolved in 80 mL of THF. After cooling to –78 °C, a solution of Li[N(SiMe₃)₂] (2.52 g, 15.1 mmol) in THF was added dropwise. The reaction mixture was allowed to warm to ambient temperature and stirred for another hour. After re-cooling to –78 °C, MeI (0.94 mL, 15.1 mmol) was added dropwise and the mixture was allowed to warm to ambient temperature. After stirring at ambient temperature overnight, water (50 mL) was added, THF was removed under reduced pressure and the aqueous solution was extracted three times with Et₂O (50 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The obtained dark red oil was chromatographed on a silica gel column that was packed and flushed with a mixture of 3 : 1 petroleum ether and Et₂O. The fractions containing the desired product were combined and the solvent was removed under reduced pressure, which gave **3a** as a colourless powder (670 mg, 2.14 mmol, 28%). Crystals suitable



for SCXRD analysis could be obtained by recrystallization from MTBE. ^1H NMR (400.1 MHz, CDCl_3 , 26 °C): δ = 6.52 (d, 3H, $^3J_{\text{HH}}$ = 2.5 Hz; 5-*H*(pz)), 6.09 (d, 3H, $^3J_{\text{HH}}$ = 2.5 Hz; 4-*H*(pz)), 2.91 (s, 3H; CH_3CTp), 2.67 (q, 6H, $^3J_{\text{HH}}$ = 7.6 Hz; CH_2CH_3), 1.24 ppm (t, 3H, $^3J_{\text{HH}}$ = 7.6 Hz; CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , 26 °C): δ = 156.7 (3-*C*(pz)), 129.6 (5-*C*(pz)), 104.8 (4-*C*(pz)), 90.1 (CH_3CTp), 25.9 (CH_3CTp), 21.6 (CH_2CH_3), 13.8 ppm (CH_2CH_3). DRIFTS: $\tilde{\nu}_{\text{max}}$ = 3134w, 3115w, 2969s, 2935m, 2873m, 2641vw, 1703vw, 1526s, 1467m, 1454m, 1371s, 1312m, 1260s, 1209s, 1112m, 1049s, 1008w, 976m, 952w, 796s, 759s, 659w, 632w, 578vw, 439vw cm^{-1} . Elemental analysis calcd (%) for $\text{C}_{17}\text{H}_{24}\text{N}_6$ (312.42 g mol^{-1}): C 65.36, H 7.74, N 26.90; found: C 65.49, H 7.47, N 26.94.

MeCTp^{3-CyPr} (3b). Following the procedure described for **3a**, the crude product of **2b** (3.00 g, 8.89 mmol), $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ (1.95 g, 11.7 mmol) and MeI (1.50 mL, 11.2 mmol) yielded **3b** as a brownish oil as the crude product. Further purification was achieved by flash column chromatography with a 3 : 1 mixture of petroleum ether and Et_2O with subsequent recrystallization from Et_2O to afford **3b** as colourless crystals (983 mg, 2.82 mmol, 31%) suitable for SCXRD analysis. ^1H NMR (400.1 MHz, CDCl_3 , 26 °C): δ = 6.46 (d, 3H, $^3J_{\text{HH}}$ = 2.6 Hz, 5-*H*(pz)), 5.85 (d, 3H, $^3J_{\text{HH}}$ = 2.6 Hz, 4-*H*(pz)), 2.84 (s, 3H, CH_3CTp), 1.92 (m, 3H, $(\text{CH}_2)_2\text{CH}$), 0.88 (m, 6H, $(\text{CH}_2)_2\text{CH}$), 0.67 ppm (m, 6H, $(\text{CH}_2)_2\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , 26 °C): δ = 157.2 (3-*C*(pz)), 129.7 (5-*C*(pz)), 102.7 (4-*C*(pz)), 90.1 (CTp), 25.8 (CH_3CTp), 9.4 ($(\text{CH}_2)_2\text{CH}$), 8.2 ppm ($(\text{CH}_2)_2\text{CH}$). DRIFTS: $\tilde{\nu}_{\text{max}}$ = 3142w, 3124w, 3087vw, 3003m, 2952w, 2852vw, 2469vw, 2075vw, 1708w, 1613vw, 1531vs, 1480m, 1444m, 1397s, 1371s, 1305s, 1259vs, 1220s, 1208vs, 1177s, 1113m, 1045s, 988s, 883m, 763s, 709vw, 561vw, 631vw, 488vw cm^{-1} . Elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{24}\text{N}_6$ (348.21 g mol^{-1}): C 68.94, H 6.94, N 24.12; found C 68.86, H 6.85, N 23.99.

MeCTp^{3-Cy} (3c). Following the procedure described for **3a**, the crude product of **2c** (2.65 g, 5.75 mmol), $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ (1.93 g, 11.5 mmol) and MeI (0.72 mL, 11.5 mmol) yielded a mixture of a dark red oil and small cubic crystals. After recrystallization from methyl *tert*-butyl ether and washing with MeOH, **3c** could be obtained as cubic colourless crystals (344 mg, 0.72 mmol, 13%). ^1H NMR (400.1 MHz, CDCl_3 , 26 °C): δ = 6.39 (m, 3H; 5-*H*(pz)), 6.05 (m, 3H; 4-*H*(pz)), 2.90 (s, 3H; CH_3CTp), 2.68 (m, 3H; 1-*H*(Cy)), 1.96–1.94 (m, 6H; 2,6-*H*(Cy)), 1.80–1.77 (m, 6H; 3,5-*H*(Cy)), 1.73–1.69 (m, 3H; 4-*H*(Cy)), 1.45–1.31 (m, 12H; 2,6-; 3,5-*H*(Cy)), 1.30–1.20 ppm (m, 3H; 4-*H*(Cy)). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , 26 °C): δ = 160.3 (3-*C*(pz)), 129.4 (5-*C*(pz)), 103.4 (4-*C*(pz)), 90.3 (CH_3CTp), 37.7 (1-*C*(Cy)), 33.2 (2,6-*C*(Cy)), 26.3 (3,5-*C*(Cy)), 26.1 (4-*C*(Cy)), 25.7 ppm (CH_3CTp). DRIFTS: $\tilde{\nu}_{\text{max}}$ = 2922s, 2849m, 1522m, 1447w, 1370w, 1347vw, 1289vw, 1260m, 1232w, 1213w, 1132vw, 1106vw, 1058w, 1033vw, 977w, 891vw, 817vw, 793m, 768w, 752m, 640vw cm^{-1} . Elemental analysis calcd (%) for $\text{C}_{29}\text{H}_{42}\text{N}_6$ (474.70 g mol^{-1}): C 73.38, H 8.92, N 17.70; found: C 73.23, H 8.73, N 17.42.

MeCTp^{3-*p*-tBuPh} (3d). Following the procedure described for **3a**, the crude product of **2d** (2.00 g, 3.27 mmol), $\text{Li}[\text{N}(\text{SiMe}_3)_2]$

(822 mg, 4.91 mmol) and MeI (0.31 mL, 4.91 mmol) yielded a mixture of a dark red oil and a colourless solid. The solid was washed five times with *n*-pentane. Further purification was achieved by flash column chromatography with a 5 : 1 mixture of petroleum ether and Et_2O to afford **3d** as a colourless powder (671 mg, 10.7 mmol, 33%). ^1H NMR (400.1 MHz, CDCl_3 , 26 °C): δ = 7.79 (m, 6H; *o*-*H*(Ph)), 7.45 (m, 6H; *m*-*H*(Ph)), 6.82 (d, 3H, $^3J_{\text{HH}}$ = 2.5 Hz; 5-*H*(pz)), 6.58 (d, 3H, $^3J_{\text{HH}}$ = 2.5 Hz; 4-*H*(pz)), 3.16 (s, 3H; CH_3CTp), 1.36 ppm (s, 27H; $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , 26 °C): δ = 153.2 (3-*C*(pz)), 151.3 (*p*-*C*(Ph)), 130.5 (5-*C*(pz)), 130.1 (*i*-*C*(Ph)), 125.7 (*o*-*C*(Ph)), 125.5 (*m*-*C*(Ph)), 103.8 (4-*C*(pz)), 91.1 (MeCTp), 34.6 ($\text{C}(\text{CH}_3)_3$), 31.3 ($\text{C}(\text{CH}_3)_3$), 26.0 ppm (CH_3CTp). DRIFTS: $\tilde{\nu}_{\text{max}}$ = 3127vw, 2963m, 2902w, 2865w, 1719vw, 1668vw, 1605vw, 1501m, 1450w, 1387w, 1365w, 1268m, 1232s, 1124w, 1089vw, 1047w, 1017vw, 978vw, 948vw, 839m, 793m, 763m, 742w, 700vw, 642vw, 560w, 501vw cm^{-1} . Elemental analysis calcd (%) for $\text{C}_{41}\text{H}_{48}\text{N}_6$ (624.88 g mol^{-1}): C 78.81, H 7.74, N 13.45; found: C 79.01, H 7.85, N 13.35.

EtCTp^{3-Ph} (3e). Following the procedure described for **3a**, the crude product of **2e** (2.00 g, 4.52 mmol), $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ (983 mg, 5.88 mmol) and EtI (542 μL , 6.78 mmol) yielded **3e** as a pale yellow solid as the crude product. Further purification was achieved by recrystallization from a 1 : 1 mixture of *n*-hexane and MTBE to afford **3e** as colourless crystals (1.55 g, 3.28 mmol, 73%) suitable for SCXRD analysis. ^1H NMR (400.1 MHz, CDCl_3 , 26 °C): δ = 7.86 (m, 6H, *o*-*H*(Ph)), 7.38 (m, 9H, *m*-*H*(Ph), *p*-*H*(Ph)), 7.07 (d, 3H, $^3J_{\text{HH}}$ = 2.8 Hz, 5-*H*(pz)), 6.62 (d, 3H, $^3J_{\text{HH}}$ = 2.7 Hz, 4-*H*(pz)), 3.54 (q, 2H, $^3J_{\text{HH}}$ = 7.2 Hz, CH_2CTp), 1.38 ppm (t, 3H, $^3J_{\text{HH}}$ = 7.2 Hz, $\text{CH}_3\text{CH}_2\text{C}(\text{pz})_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , 26 °C): δ = 153.1 (3-*C*(pz)), 133.1 (*i*-*C*(Ph)), 131.6 (5-*C*(pz)), 128.8 (*m*-*C*(Ph)), 128.3 (*p*-*C*(Ph)), 126.1 (*o*-*C*(Ph)), 103.7 (4-*C*(pz)), 93.1 (CTp), 34.1 (CH_2CTp), 9.3 ppm (CH_3CH_2). DRIFTS: $\tilde{\nu}_{\text{max}}$ = 3145vw, 3064vw, 3004vw, 2982vw, 2951vw, 2953w, 1604vw, 1582vw, 1528m, 1497m, 1457s, 1390s, 1358m, 1298m, 1275w, 1247w, 1217vs, 1180vw, 1160vw, 1100w, 1075m, 1051m, 1028m, 859s, 758s, 750s, 520vw cm^{-1} . Elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{26}\text{N}_6$ (470.22 g mol^{-1}): C 76.57, H 5.57, N 17.86; found C 76.30, H 5.97, N 17.62.

***n*PrCTp^{3-Ph} (3f).** Following the procedure described for **3a**, the crude product of **2e** (2.00 g, 4.52 mmol), $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ (983 mg, 5.88 mmol) and *n*PrI (553 μL , 5.88 mmol) yielded **3f** as a pale yellow solid as the crude product. Further purification was achieved by recrystallization from a 1 : 1 mixture of *n*-hexane and MTBE to afford **3f** as colourless crystals (2.13 g, 4.40 mmol, 97%) suitable for SCXRD analysis. ^1H NMR (400.1 MHz, CDCl_3 , 26 °C): δ = 7.87 (m, 6H, *o*-*H*(Ph)), 7.39 (m, 9H, *m*-*H*(Ph), *p*-*H*(Ph)), 7.06 (d, 3H, $^3J_{\text{HH}}$ = 2.7 Hz, 5-*H*(pz)), 6.62 (d, 3H, $^3J_{\text{HH}}$ = 2.7 Hz, 4-*H*(pz)), 3.46 (m, 2H, CH_2CTp), 1.89 (m, 2H, $\text{CH}_2\text{CH}_2\text{CTp}$), 1.08 (t, 3H, $^3J_{\text{HH}}$ = 7.4 Hz, CH_3CH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , 26 °C): δ = 153.1 (3-*C*(pz)), 133.1 (*i*-*C*(Ph)), 131.5 (5-*C*(pz)), 128.8 (*m*-*C*(Ph)), 128.3 (*p*-*C*(Ph)), 126.1 (*o*-*C*(Ph)), 103.7 (4-*C*(pz)), 92.8 ($\text{C}(\text{pz})_3$), 42.5 (CH_2CTp), 17.8 ($\text{CH}_2\text{CH}_2\text{CTp}$), 14.4 (CH_3CH_2) ppm. DRIFTS: $\tilde{\nu}_{\text{max}}$ = 3059vw, 2961w, 2869vw, 1604vw, 1528m, 1499vs, 1455vs,



1435s, 1385s, 1357s, 1301s, 1279w, 1210vs, 1100w, 1074w, 1044w, 1028w, 946vw, 903m, 855m, 800w, 752s, 695s, 686m, 659vw, 627w, 511vw cm⁻¹. Elemental analysis calcd (%) for C₃₁H₂₈N₆ (484.2 g mol⁻¹): C 76.83, H 5.82, N 17.34; found C 76.35, H 5.69, N 17.43.

iBuCTp^{3-Ph} (3g). Following the procedure described for **3a**, the crude product of **2e** (2.00 g, 4.52 mmol), Li[N(SiMe₃)₂] (983 mg, 5.88 mmol) and iBuI (676 μL, 5.88 mmol) yielded a pale yellow solid as the crude product. Further purification was achieved by recrystallization from MTBE to afford **3g** as colourless crystals (1.99 g, 3.98 mmol, 88%) suitable for SCXRD analysis. ¹H NMR (400.1 MHz, CDCl₃, 26 °C): δ = 7.85 (m, 6H, *o*-H(Ph)), 7.38 (m, 9H, *m*-H(Ph), *p*-H(Ph)), 7.02 (d, 3H, ³J_{HH} = 2.7 Hz, 5-H(pz)), 6.61 (d, 3H, ³J_{HH} = 2.7 Hz, 4-H(pz)), 3.45 (d, 2H, ³J_{HH} = 5.4 Hz, CH₂CTp), 2.55 (m, 1H, (CH₃)₂CHCH₂CTp), 1.00 (d, 6H, ³J_{HH} = 6.7 Hz, (CH₃)₂CH₂) ppm. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 26 °C): δ = 152.8 (3-C(pz)), 133.1 (i-C(Ph)), 131.6 (5-C(pz)), 128.8 (*m*-C(Ph)), 128.3 (*p*-C(Ph)), 126.1 (*o*-C(Ph)), 103.9 (4-C(pz)), 93.3 (CTp), 47.6 (CH₂CTp), 24.5 ((CH₃)₂CHCH₂CTp), 24.1 ((CH₃)₂CH) ppm. DRIFTS: $\tilde{\nu}_{\max}$ = 3145vw, 3060vw, 2992vw, 2955w, 2867w, 1954vw, 1713vw, 1605vw, 1528m, 1499vs, 1456vs, 1387s, 1356s, 1288m, 1219s, 1208vs, 1102m, 1075m, 1045w, 1028vw, 975vw, 946w, 924w, 915w, 885w, 822w, 777w, 756s, 697s, 686w, 661vw, 627vw, 513 cm⁻¹. Elemental analysis calcd (%) for C₃₂H₃₀N₆ (498.3 g mol⁻¹): C 77.08, H 6.06, N 16.85; found C 76.53, H 5.92, N 16.49.

[(AlMe₃CTp^{3-*p*-tBuPh})₂Mg] (4). A solution of Mg(AlMe₄)₂ (16.3 mg, 81.9 μmol) in 5 mL of *n*-hexane was added dropwise to a stirred suspension of the crude product of **2d** (100 mg, 164 μmol) in 5 mL of toluene. After stirring for 2 h the solvent was removed under reduced pressure yielding a white solid. Recrystallization from toluene gave **4** (47.8 mg, 34.5 μmol, 42%) as colourless crystals suitable for SCXRD analysis. ¹H NMR (400.1 MHz, [D₈]toluene, 26 °C): δ = 8.92 (d, 6H, ³J_{HH} = 2.8 Hz, 5-H(pz)), 6.88 (m, 12H, *o*-H(Ph)), 6.69 (m, 12H, *m*-H(Ph)), 5.78 (d, 6H, ³J_{HH} = 2.8 Hz, 4-H(pz)), 1.14 (s, 54H, C(CH₃)₃), 0.20 ppm (s, 18H, Al(CH₃)₃). ¹³C{¹H} NMR (100.6 MHz, [D₈]toluene, 26 °C): δ = 156.3 (3-C(pz)), 151.5 (*p*-C(Ph)), 138.5 (3-C(pz)), 129.2 (i-C(Ph)), 128.3 (*m*-C(Ph)), 124.0 (*o*-C(Ph)), 105.0 (4-C(pz)), 87.6 (CAlMe₃), 34.4 (C(CH₃)₃), 31.2 (C(CH₃)₃), -2.2 ppm (Al(CH₃)₃). DRIFTS: $\tilde{\nu}_{\max}$ = 3163w, 2964s, 2922m, 2868w, 1912vw, 1614w, 1568vw. 1505m, 1474m, 1420w, 1378m, 1363w, 1344w, 1309vw, 1270w, 1248w, 1186s, 1020vw, 1005vw, 991vw, 949vw, 839m, 812s, 775vs, 744m, 731m, 695vs, 644w, 618vw, 561w, 523vw, 501w, 463vw, 429vw cm⁻¹. Elemental analysis calcd (%) for C₈₆H₁₀₈Al₂MgN₁₂·0.5C₇H₈ (1434.37 g mol⁻¹): C 74.95 H 7.87 N 11.72; found: C 75.61 H 8.28 N 10.90. The carbon result is outside the range for analytical purity, but no better elemental analysis could be obtained to date, due to solvent molecules in the lattice and due to the highly air- and moisture-sensitive nature of compound **4**.

[(MeCTp^{3-Et})₂Mg][AlMe₄]₂ (5a). A solution of Mg(AlMe₄)₂ (31.7 mg, 0.16 mmol) in 5 mL of *n*-hexane was added dropwise to a stirred suspension of **3a** (100 mg, 0.32 mmol) in 5 mL of toluene and a white precipitate formed immediately. After stir-

ring for 2 h the solvent was removed under reduced pressure and the residual solid was washed three times with *n*-pentane. **5a** was obtained as a white powder (121 mg, 0.14 mmol, 92%). Colourless crystals of **5a** suitable for SCXRD analysis were grown from THF at -40 °C. ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 8.58 (d, 6H, ³J(H,H) = 2.8 Hz; 5-H(pz)), 6.60 (d, 6H, ³J_{HH} = 2.9 Hz; 4-H(pz)), 3.55 (s, 6H; CH₃CTp), 1.86 (q, 12H, ³J_{HH} = 7.6 Hz; CH₂CH₃), 1.01 (t, 18H, ³J_{HH} = 7.6 Hz; CH₂CH₃), -1.28 ppm (m, 24H; [Al(CH₃)₄]). ¹³C{¹H} NMR (100.6 MHz, [D₈]THF, 26 °C): δ = 161.1 (3-C(pz)), 134.8 (5-C(pz)), 106.7 (4-C(pz)), 85.1 (MeCTp), 24.8 (CH₃CTp), 20.94 (CH₂CH₃), 12.15 (CH₂CH₃), -4.2 ppm (sext, ¹J(Al,C) = 70.4 Hz; [Al(CH₃)₄]). DRIFTS: $\tilde{\nu}_{\max}$ = 3160vw, 2975vw, 2898m, 2798vw, 1528m, 1478w, 1436vw, 1411vw, 1386s, 1357w, 1314vw, 1298vw, 1212s, 1150w, 1080m, 1058w, 1025w, 994vw, 951vw, 796vw, 775m, 696s, 687m, 596vw, 546w, 488vw cm⁻¹. Elemental analysis calcd (%) for C₄₂H₇₂Al₂MgN₆ (823.39 g mol⁻¹): C 61.27, H 8.81, N 20.41; found: C 60.84, H 8.76, N 20.10.

[(MeCTp^{3-CyPr})₂Mg][AlMe₄]₂ (5b) and [MeCTp^{3-CyPr}MgMe(thf)₂][AlMe₄] (6). A solution of **3b** (100 mg, 287 μmol) in 2 mL of toluene was added dropwise to a solution of Mg(AlMe₄)₂ (57.0 mg, 287 μmol) in 5 mL of toluene and a white precipitate formed immediately. After removing the solvent under reduced pressure, the crude product was washed with *n*-pentane (3 × 3 mL) to yield [(MeCTp^{3-CyPr})₂Mg][AlMe₄]₂ (**5b**) as a white powder. Colourless crystals suitable for SCXRD analysis could be obtained by heating the solid in a J. Young valve NMR tube to 150 °C in toluene. Elemental analysis calcd (%) for C₄₈H₇₂Al₂MgN₁₂·C₈H₂₄MgAl₂ (1094.01 g mol⁻¹): C 61.48 H 8.85 N 15.36; found: C 61.16 H 8.52 N 15.11 (crude product). Because of the high insolubility of **5b** in aliphatic and aromatic solvents, no satisfactory NMR spectra could be obtained. Redissolving **5b** in THF and cooling to -40 °C led to the formation of colourless crystals of **6** suitable for SCXRD analysis. ¹H NMR (400.1 MHz, [D₈]THF, 26 °C): δ = 8.36 (d, 3H, ³J_{HH} = 2.7 Hz, 5-H(pz)), 6.09 (d, 3H, ³J_{HH} = 2.4 Hz, 4-H(pz)), 3.40 (s, 3H, CH₃C(pz)₃), 1.12 (m, 3H, (CH₂)₂CH), 0.67 (m, 12H, (CH₂)₂CH) ppm. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 26 °C): δ = 163.2 (3-C(pz)), 133.9 (5-C(pz)), 101.3 (4-C(pz)), 84.1 (C(pz)₃), 23.8 (CH₃C(pz)₃), 10.9 ((CH₂)₂CH), 9.40 ((CH₂)₂CH), -4.8 (sext, ¹J_{C,Al} = 70.4 Hz, Al(CH₃)₄) ppm.

[(MeCTp^{3-Cy})₂Mg(AlMe₄)]₂ (8). A solution of Mg(AlMe₄)₂ (42.0 mg, 0.21 mmol) in 5 mL of *n*-hexane was added dropwise to a stirred suspension of **3c** (100 mg, 0.21 mmol) in 5 mL of toluene. After stirring for 2 h, the solvent was removed under reduced pressure yielding a white solid. Redissolving the solid in anhydrous 1,2-difluorobenzene and cooling to -40 °C afforded colourless crystals of **8** (66.5 mg, 0.10 mmol, 46%) suitable for SCXRD analysis. ¹H NMR (400.1 MHz, [D₈]toluene, 26 °C): δ = 7.84 (m, 3H; 5-H(pz)), 5.80 (m, 3H; 4-H(pz)), 3.11 (s, 3H; CH₃CTp), 2.69 (m, 3H; 1-CH(Cy)), 1.59 (m, 12H; 2,6-; 3,5-CH₂(Cy)), 1.52 (m, 3H; 4-CH₂(Cy)), 1.21 (m, 6H; 3,5-CH₂(Cy)), 1.06 (m, 9H; 2,6-; 3,5-CH₂(Cy)), -0.19 ppm (s, 24H; [Al(CH₃)₄]/Mg(CH₃)₂Al(CH₃)). ¹³C{¹H} NMR (100.6 MHz, [D₈]toluene/1,2-difluorobenzene, 26 °C): δ = 164.4 (3-C(pz)), 133.1 (5-C(pz)), 105.1 (4-C(pz)), 83.5 (MeCTp), 37.5 (1-C(Cy)),



33.4 (2,6-*C*(Cy)), 26.3 (3,5-*C*(Cy)), 25.7 (4-*C*(Cy)), 24.9 (CH_3CTp), -4.2 ppm ($[\text{Al}(\text{CH}_3)_4]/\text{Mg}(\text{CH}_3)_2\text{Al}(\text{CH}_3)_2$). DRIFTS: $\tilde{\nu}_{\text{max}} = 3147\text{w}$, 2922vs , 2850m , 2797w , 1530s , 1507vw , 1479w , 1447m , 1414w , 1397w , 1378w , 1360m , 1346w , 1303vw , 1290vw , 1268vw , 1211vs , 1185w , 1142m , 1078vs , 1031m , 996vw , 967vw , 890vw , 851vw , 812vw , 791w , 767vs , 743w , 723s , 705vs , 694vs , 613s , 548w , 419w cm^{-1} . Elemental analysis calcd (%) for $\text{C}_{37}\text{H}_{66}\text{Al}_2\text{MgN}_6$ (689.29 g mol^{-1}): C 66.01, H 9.88, N 12.48; found: C 65.96 H 10.10 N 12.37.

[(MeCTp)^{3-*p*-tBuPh}]₂Mg(AlMe₄)](AlMe₄) (9). A solution of Mg(AlMe₄)₂ (42.8 mg, 0.22 mmol) in 5 mL of *n*-hexane was added dropwise to a stirred suspension of **3d** (135 mg, 0.22 mmol) in 5 mL of toluene. After stirring for 2 h the solvent was removed under reduced pressure yielding a yellow oil. Redissolving the oil in anhydrous benzene and adding *n*-pentane dropwise under stirring at 40 °C afforded colourless crystals of **9** (134 mg, 0.16 mmol, 79%) suitable for SCXRD analysis. ¹H NMR (400.1 MHz, [D₈]toluene, 26 °C): δ = 8.03 (m, 3H; 5-*H*(pz)), 7.31 (m, 6H; *o*-*H*(Ph)), 7.23 (m, 6H; *m*-*H*(Ph)), 6.28 (m, 3H; 4-*H*(pz)), 3.27 (s, 3H; CH_3CTp), 1.12 (s, 27H; $\text{C}(\text{CH}_3)_3$), -0.34 ppm (s, 24H; $[\text{Al}(\text{CH}_3)_4]/\text{Mg}(\text{CH}_3)_2\text{Al}(\text{CH}_3)_2$). ¹³C{¹H} NMR (100.6 MHz, [D₈]toluene/1,2-difluorobenzene, 26 °C): δ = 158.7 (3-*C*(pz)), 154.4 (*p*-*C*(Ph)), 133.4 (5-*C*(pz)), 129.2 (*ipso*-*C*(Ph)), 128.3 (*o*-*C*(Ph)), 126.5 (*m*-*C*(Ph)), 107.5 (4-*C*(pz)), 84.6 (MeCTp), 34.8 ($\text{C}(\text{CH}_3)_3$), 31.0 ($\text{C}(\text{CH}_3)_3$), 25.2 (CH_3CTp), -4.5 ppm ($[\text{Al}(\text{CH}_3)_4]/\text{Mg}(\text{CH}_3)_2\text{Al}(\text{CH}_3)_2$). DRIFTS: $\tilde{\nu}_{\text{max}} = 3147\text{w}$, 2962m , 2906m , 2870w , 2800w , 1615w , 1541w , 1505m , 1468w , 1383m , 1364w , 1304vw , 1260w , 1212m , 1153vw , 1127vw , 1098vw , 1066m , 1017vw , 991vw , 947vw , 839w , 775s , 698m , 688s , 623w , 541vw , 501vw cm^{-1} . Elemental analysis calcd (%) for $\text{C}_{49}\text{H}_{72}\text{Al}_2\text{MgN}_6$ (823.43 g mol^{-1}): C 71.47, H 8.81, N 10.21; found: C 71.97, H 8.13, N 10.94. The hydrogen result is outside the range for analytical purity, but no better elemental analysis could be obtained to date due to solvent molecules in the lattice and the highly air- and moisture-sensitive nature of compound **9**.

[MeC(pz^{3-*p*-tBuPh})₂(pz^{3-*p*-tBuPh},5-*AlMe*₃)]MgMe (10). A solution of **9** (144.2 mg, 0.18 mmol) in benzene was heated in a pressure tube to 90 °C for 1 d. The mixture was allowed to cool to ambient temperature and the solvent was removed under reduced pressure. Redissolving the obtained solid in toluene and slow evaporation of the solvent led to colourless crystals of **10** (84.9 mg, 0.12 mmol, 66%) suitable for SCXRD analysis. ¹H NMR (400.1 MHz, [D₈]benzene, 26 °C): δ = 7.45 (m, 2H, *o*-*H*(Ph, pz^{3-*p*-tBuPh},5-*AlMe*₃)), 7.41 (m, 4H, *o*-*H*(Ph, pz^{3-*p*-tBuPh})), 7.32 (s, 1H, 4-*H*(pz, pz^{3-*p*-tBuPh},5-*AlMe*₃)), 7.18 (m, 6H, 5-*H*(pz, pz^{3-*p*-tBuPh}) and *m*-*H*(Ph, pz^{3-*p*-tBuPh})), 7.06 (m, 2H, *m*-*H*(Ph, pz^{3-*p*-tBuPh},5-*AlMe*₃)), 5.90 (d, 2H, 4-*H*(pz, pz^{3-*p*-tBuPh})), 3.35 (s, 3H, CH_3), 1.08 (s, 18H, $\text{C}(\text{CH}_3)_3(\text{pz}^{3-*p*-t\text{BuPh}})$), 1.06 (s, 9H, $\text{C}(\text{CH}_3)_3(\text{pz}^{3-*p*-t\text{BuPh},5-*AlMe}_3})*$), 0.16 (s, 9H, $\text{Al}(\text{CH}_3)_3$), -0.99 ppm (s, 3H, MgCH_3). ¹³C{¹H} NMR (100.6 MHz, [D₈]toluene/1,2-difluorobenzene, 26 °C): δ = 156.7 (3-*C*(pz, pz^{3-*p*-tBuPh})), 156.5 (3-*C*(pz, pz^{3-*p*-tBuPh},5-*AlMe*₃)), 153.7 (*p*-*C*(Ph, pz^{3-*p*-tBuPh})), 152.2 (*p*-*C*(Ph, pz^{3-*p*-tBuPh},5-*AlMe*₃)), 132.1 (5-*C*(pz, pz^{3-*p*-tBuPh})), 128.2 (4-*C*(pz, pz^{3-*p*-tBuPh},5-*AlMe*₃)), 128.0 (*o*-*C*(Ph, pz^{3-*p*-tBuPh})), 126.3 (*m*-*C*(Ph, pz^{3-*p*-tBuPh})), 126.0 (*m*-*C*(Ph, pz^{3-*p*-tBuPh},5-*AlMe*₃)), 105.7 (4-

C(pz, pz^{3-*p*-tBuPh})), 87.4 (MeCTp), 34.7 ($\text{C}(\text{CH}_3)_3(\text{pz}^{5-*H*})$), 34.6 ($\text{C}(\text{CH}_3)_3(\text{pz}^{3-*p*-t\text{BuPh},5-*AlMe}_3})*$), 31.1 ($\text{C}(\text{CH}_3)_3(\text{pz}^{3-*p*-t\text{BuPh}})$), 31.1 ($\text{C}(\text{CH}_3)_3(\text{pz}^{3-*p*-t\text{BuPh},5-*AlMe}_3})*$), 26.7 (CH_3CTp), -4.6 ppm (AlMe_3). The ¹³C NMR resonances for Mg-CH₃, both quaternary *ipso*-Ph carbons, the *o*-Ph carbon of the pz^{3-*p*-tBuPh},5-*AlMe*₃ and the 5-*C*(pz^{5-*AlMe*₃) could not be detected due to overlap with the solvent signal or insufficient resolution. Elemental analysis calcd (%) for $\text{C}_{45}\text{H}_{59}\text{AlMgN}_6$ (735.3 g mol^{-1}): C 73.54, H 8.45, N 11.19; found: C 74.88, H 8.44, N 10.11.}

[(MeCTp)^{3-*p*-tBuPh}]₂MgMe(AlMe₄) (11). Solid **9** converted to complex **11**, either over 6 months at ambient temperature or after 4 d under reduced pressure. Compound **11** was obtained quantitatively as a white solid. ¹H NMR (400.1 MHz, [D₈]toluene, 26 °C): δ = 8.28 (m, 3H; 5-*H*(pz)), 7.34 (m, 6H; *o*-*H*(Ph)), 7.16 (m, 6H; *m*-*H*(Ph)), 6.33 (m, 3H; 4-*H*(pz)), 3.54 (s, 3H; CH_3CTp), 1.08 (s, 27H; $\text{C}(\text{CH}_3)_3$), -0.09 (s, 12H; $\text{Al}(\text{CH}_3)_4$), -1.04 ppm (s, 3H, MgCH_3). ¹³C{¹H} NMR (100.6 MHz, [D₈]toluene/1,2-difluorobenzene, 26 °C): δ = 158.2 (3-*C*(pz)), 153.9 (*p*-*C*(Ph)), 134.3 (5-*C*(pz)), 129.2 (*ipso*-*C*(Ph)), 128.3 (*o*-*C*(Ph)), 126.2 (*m*-*C*(Ph)), 107.1 (4-*C*(pz)), 85.0 (MeCTp), 34.7 ($\text{C}(\text{CH}_3)_3$), 31.0 ($\text{C}(\text{CH}_3)_3$), 25.6 ppm (CH_3CTp). The carbon signal of the methyl group coordinated to the magnesium centre could not be detected. Elemental analysis calcd (%) for $\text{C}_{45}\text{H}_{59}\text{AlMgN}_6$ (735.3 g mol^{-1}): C 73.51, H 8.09, N 11.43; found: C 73.40, H 8.14, N 10.62. The nitrogen result is outside the range for analytical purity, but no better elemental analysis could be obtained to date due the highly air- and moisture-sensitive nature of compound **11**.

Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for the compounds have been deposited in the Cambridge Crystallographic Data Centre (2386219–2386230).†

Conflicts of interest

There are no conflicts of interest.

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Supporting Information

Reactivity of $\text{Mg}(\text{AlMe}_4)_2$ towards neutral Tris(pyrazolyl)alkanes

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Table S1. Crystallographic Data for Compounds **3a**, **3b**, **3c** and **3e**

	3a	3b	3c*	3e
formula	C ₁₇ H ₂₄ N ₆	C ₂₀ H ₂₄ N ₆	C ₂₉ H ₄₂ N ₆	C ₃₀ H ₂₆ N ₆
CCDC	2386227	2386220	2386219	2386222
M [g mol ⁻¹]	312.42	348.39	474.68	470.57
color/shape	colorless/needle	colorless/rod	colorless/block	colorless/block
Crystal dimensions [mm]	0.232 x 0.176 x 0.088	0.389 x 0.235 x 0.186	0.360 x 0.340 x 0.280	0.549 x 0.256 x 0.216
cryst. system	orthorhombic	hexagonal	trigonal	triclinic
space group	<i>Pca</i> 2 ₁	<i>P</i> 6 ₃	<i>R</i> 3 <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	10.2106(6)	12.7968(10)	13.0173(14)	11.6713(8)
<i>b</i> [Å]	30.7802(17)	12.7968(10)	13.0173(14)	13.0857(9)
<i>c</i> [Å]	11.0809(6)	6.5617(5)	27.493(5)	17.0523(12)
α [°]	90	90	90	92.633(2)
β [°]	90	90	90	97.331(2)
γ [°]	90	120	120	100.998(2)
<i>V</i> [Å ³]	3482.6(3)	930.57(16)	4034.5(11)	2529.0(3)
<i>Z</i>	8	2	6	4
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.192	1.243	1.172	1.236
μ [mm ⁻¹]	0.075	0.078	0.071	0.076
<i>F</i> (000)	1344	372	1548	992
θ range [°]	1.323/26.361	3.184/30.049	2.336/28.774	1.795/28.282
unique reflns	7074	1824	2338	12609
observed reflns	76630	25103	10181	12609
^[a] <i>R</i> ₁ / ^[b] <i>wR</i> ₂ (<i>I</i> > 2 σ) ^[a]	0.0406/0.0923	0.0404/0.0914	0.0832/0.2389	0.0517/0.01166
^[a] <i>R</i> ₁ / ^[b] <i>wR</i> ₂ (all data)	0.0513/0.0989	0.0486/0.0989	0.0989/0.2587	0.0689/0.1279
GOF ^[c]	1.034	1.054	1.077	1.042

^[a]*R*₁ = $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, *F*₀ > 4 σ (*F*₀), ^[b]*wR*₂ = $\{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, ^[c]GOF = $[\Sigma w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$ *connectivity only.

Table S2. Crystallographic data for compounds **3f**, **3g**, **4** and **5a**

	3f	3g	4	5a
formula	C ₃₁ H ₂₈ N ₆	C ₃₂ H ₃₀ N ₆	C ₈₆ H ₁₀₈ Al ₂ MgN ₁₂ ·0.5(C ₇ H ₈)	C ₄₂ H ₇₂ Al ₂ MgN ₆ ·2(C ₄ H ₈ O)
CCDC	2386225	2386224	2386228	2386223
M [g mol ⁻¹]	484.59	498.62	1434.17	967.59
color/shape	colorless/block	colorless/block	colorless/block	colorless/plate
Crystal dimensions [mm]	0.390 x 0.263 x 0.209	0.232 x 0.174 x 0.169	0.263 x 0.259 x 0.196	0.348 x 0.153 x 0.110
cryst. system	triclinic	triclinic	tetragonal	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>I</i> $\bar{4}$ 2d	<i>P</i> $\bar{1}$
a [Å]	10.0945(6)	9.9371(2)	34.119(3)	9.7777(12)
b [Å]	10.6005(6)	10.2888(2)	34.119(3)	12.1692(14)
c [Å]	14.4819(8)	14.6512(4)	15.6274(12)	13.3741(16)
α [°]	68.975(2)	71.1880(10)	90	111.897(2)
β [°]	84.913(2)	87.3140(10)	90	103.651(2)
γ [°]	66.2510(10)	68.6040(10)	90	97.092(2)
<i>V</i> [Å ³]	1321.17(13)	1315.95(5)	18192(3)	1394.8(3)
<i>Z</i>	2	2	8	1
<i>T</i> [K]	101(2)	101(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.218	1.258	1.047	1.152
μ [mm ⁻¹]	0.074	0.077	0.086	0.111
F (000)	512	528	6168	526
θ range [°]	1.510/27.102	1.473/28.700	3.470/28.350	2.205/29.026
unique reflns	5840	6810	11311	7374
observed reflns	47758	47259	77626	34685
[^a] <i>R</i> ₁ /[^b] <i>wR</i> ₂ (<i>I</i> > 2 σ) [^a]	0.0520/0.1240	0.0414/0.1039	0.0570/0.1290	0.0406/0.0961
[^a] <i>R</i> ₁ /[^b] <i>wR</i> ₂ (all data)	0.0600/0.1317	0.0518/0.1113	0.0774/0.1392	0.0540/0.1045
GOF [^c]	1.040	1.022	1.044	1.060

$$^{\text{[a]}}R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|, F_o > 4\sigma(F_o), ^{\text{[b]}}wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}, ^{\text{[c]}}GOF = [\Sigma w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$$

Table S3. Crystallographic Data for Compounds **5b**, **6**, **7** and **8**

	5b*	6	7*	8
formula	C ₄₈ H ₇₂ Al ₂ MgN ₁₂ · 1.5(C ₇ D ₈)	C ₃₃ H ₅₅ AlMgN ₆ O ₂ · 2(C ₄ H ₈ O)	C ₇₇ H ₉₉ Al ₃ Mg ₂ N ₁₂	C ₃₇ H ₆₆ Al ₂ MgN ₆
CCDC		2386221		2386230
M [g mol ⁻¹]	1045.72	763.32	1322.24	673.22
color	colorless/plate	colorless/plate	colorless/block	colorless/plate
crystal dimensions [mm]	0.098 x 0.118 x 0.140	0.329 x 0.189 x 0.155	0.212 x 0.273 x 0.291	0.186 x 0.056 x 0.053
cryst. system	triclinic	triclinic	monoclinic	orthorhombic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	13.275(3)	12.099(4)	18.0198(13)	11.1027(12)
<i>b</i> [Å]	13.327(3)	12.786(4)	23.3262(17)	17.3897(19)
<i>c</i> [Å]	17.445(5)	15.286(4)	24.3189(17)	20.542(2)
α [°]	85.470(6)	90.005(5)	90	90
β [°]	86.305(5)	109.607(4)	108.3360(10)	90
γ [°]	83.301(5)	103.636(4)	90	90
<i>V</i> [Å ³]	3050.8(14)	2156.8(11)	9703.1(12)	3966.1(7)
<i>Z</i>	2	2	4	4
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.138	1.175	0.905	1.127
μ [mm ⁻¹]	0.104	0.107	0.091	0.122
F (000)	1114	832	2832	1472
θ range [°]	1.173/25.184	1.419/24.712	1.746/23.852	2.085/27.166
unique reflns	9558	7361	14946	8754
observed reflns	48977	49371	157365	95948
[^a]R ₁ /[^b]wR ₂ (<i>I</i> > 2 σ) [^a]	0.1806/0.3484	0.0737/0.1292	0.0981/0.2943	0.0525/0.1223
[^a]R ₁ /[^b]wR ₂ (all data)	0.2128/0.3571	0.1093/0.1438	0.1276/0.3271	0.0756/0.1350
GOF [^c]	2.154	1.084	1.022	1.019

[^a]R₁ = $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $F_o > 4\sigma(F_o)$, [^b]wR₂ = $\{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, [^c]GOF = $[\Sigma w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$

*connectivity only.

Table S4. Crystallographic Data for Compounds **9** and **10**

	9	10
formula	C ₄₉ H ₇₂ Al ₂ MgN ₆ ·2.5(C ₆ D ₆)	C ₄₅ H ₅₉ AlMgN ₆ ·2(C ₇ H ₈)
CCDC	2386229	2386226
M [g mol ⁻¹]	1033.75	919.54
color	colorless/plate	colorless/block
crystal dimensions [mm]	0.488 x 0.102 x 0.065	0.273 x 0.103 x 0.089
cryst. system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ /c	<i>P</i> $\bar{1}$
<i>a</i> [Å]	21.4977(15)	12.9915(16)
<i>b</i> [Å]	18.5064(13)	13.6495(17)
<i>c</i> [Å]	15.4454(11)	15.6799(19)
α [°]	90	88.421(3)
β [°]	97.1020(10)	83.625(3)
γ [°]	90	78.741(3)
<i>V</i> [Å ³]	6097.7(7)	2710.1(6)
<i>Z</i>	4	2
<i>T</i> [K]	100(2)	100(2)
wavelength [Å]	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.126	1.127
μ [mm ⁻¹]	0.100	0.091
<i>F</i> (000)	2204	992
θ range [°]	1.457/27.463	1.307/25.081
unique reflns	13915	9624
observed reflns	85399	59387
^[a] <i>R</i> ₁ / ^[b] <i>wR</i> ₂ (<i>I</i> > 2 σ) ^[a]	0.0471/0.1032	0.0423/0.1017
^[a] <i>R</i> ₁ / ^[b] <i>wR</i> ₂ (all data)	0.0859/0.1232	0.0636/0.1148
GOF ^[c]	1.015	1.020

$$^{\text{[a]}}R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|, F_o > 4\sigma(F_o), ^{\text{[b]}}wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}, ^{\text{[c]}}GOF = [\Sigma w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$$

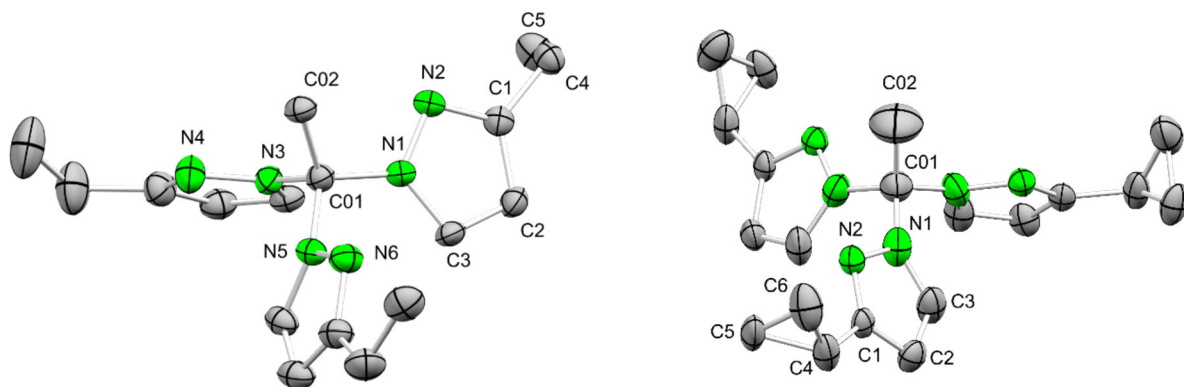


Figure S1. Crystal structures of **3a** (left) and **3b** (right), thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

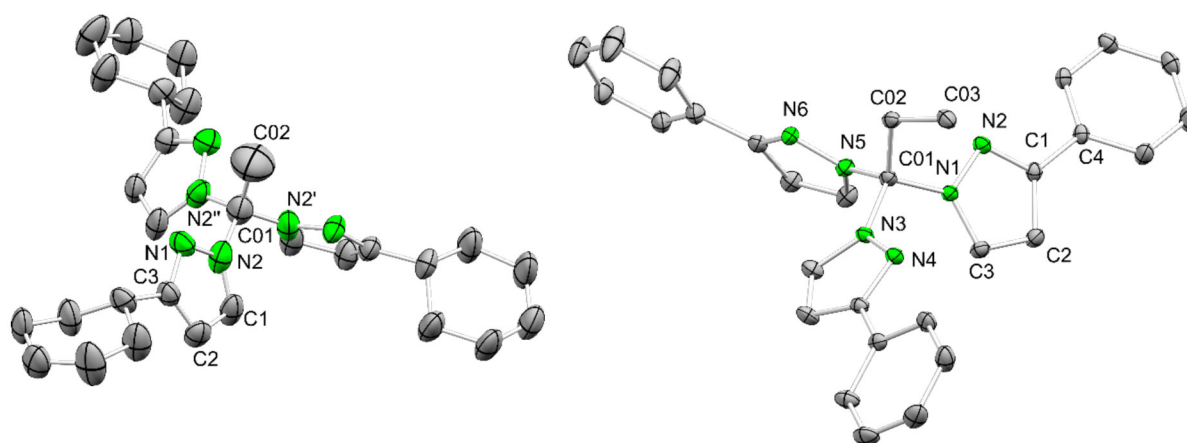


Figure S2. Connectivity structure of **3c** (left) and crystal structure **3e** (right), thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

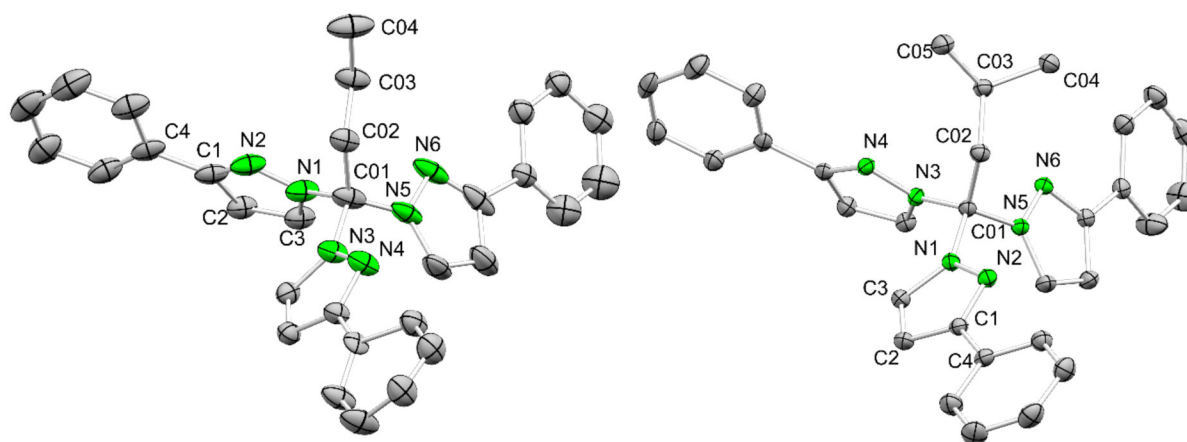


Figure S3. Crystal structures of **3f** (left) and **3g** (right), thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

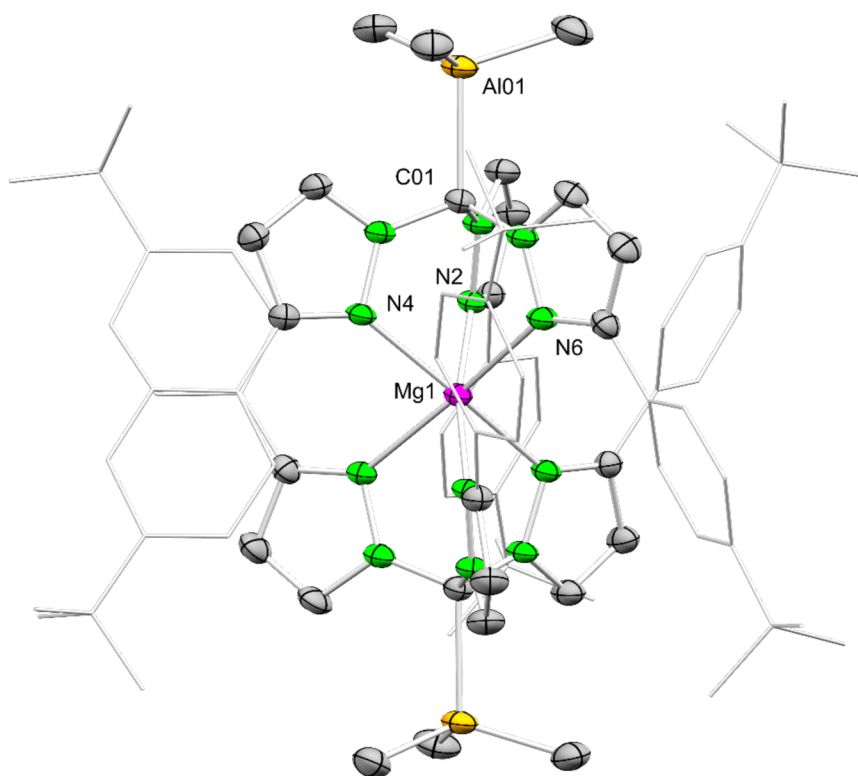


Figure S4. Crystal structures of **4**. Thermal ellipsoids set at 50% probability. Hydrogen atoms and one lattice toluene are omitted and *p*-*t*BuPh moieties are set as wireframe for clarity. Selected interatomic distances [Å]: Mg1–N2 2.221(3), Mg1–N4 2.2214(3), Mg1–N6 2.222(2), Al01–C01 2.209(4).

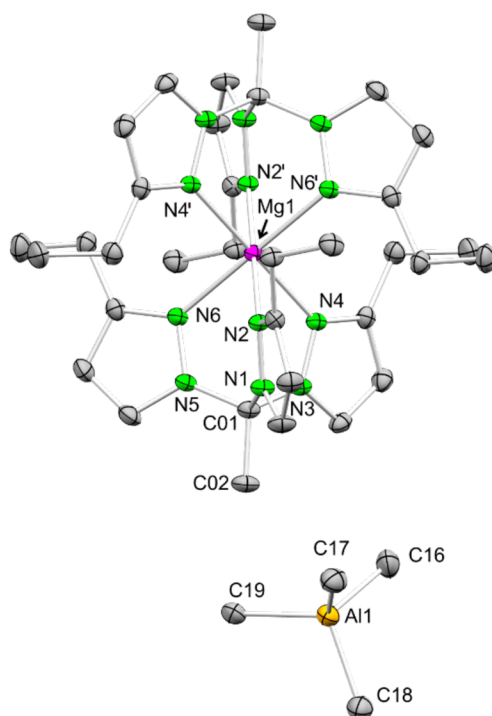


Figure S5. Crystal structure of **5a**, thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Mg1–N2 2.1666(10), Mg1–N4 2.1676(10), Mg1–N6 2.1458(10).

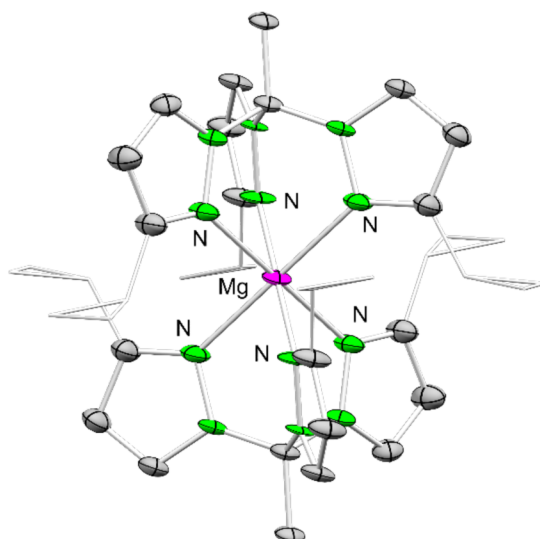


Figure S6. Connectivity of **5b**, hydrogen atoms are omitted for clarity. Thermal ellipsoids set at 50%. $[\text{AlMe}_4]^-$ and C_6D_6 are omitted for clarity.

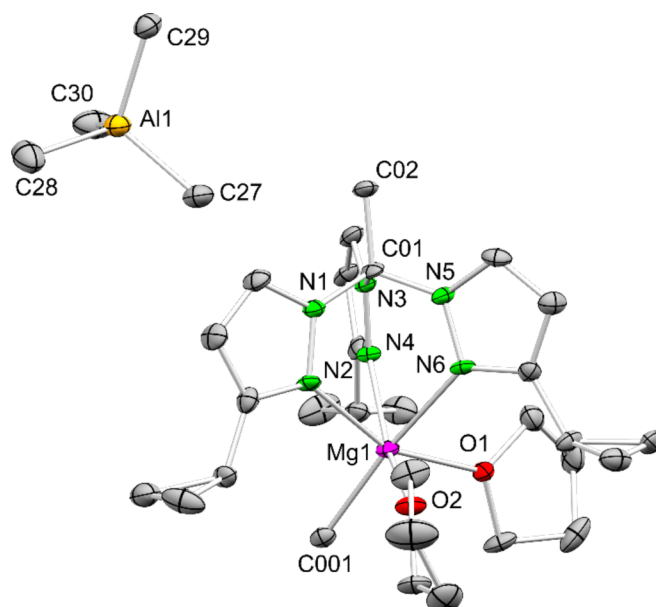


Figure S7. Crystal structure of **6**, thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected interatomic distances [$\text{\AA}$]: Mg1–N2 2.234(4), Mg1–N4 2.230(4), Mg1–N6 2.233(3), Mg1–C001 2.182(4), Mg1–O1 2.184(4), Mg1–O2 2.186(4).

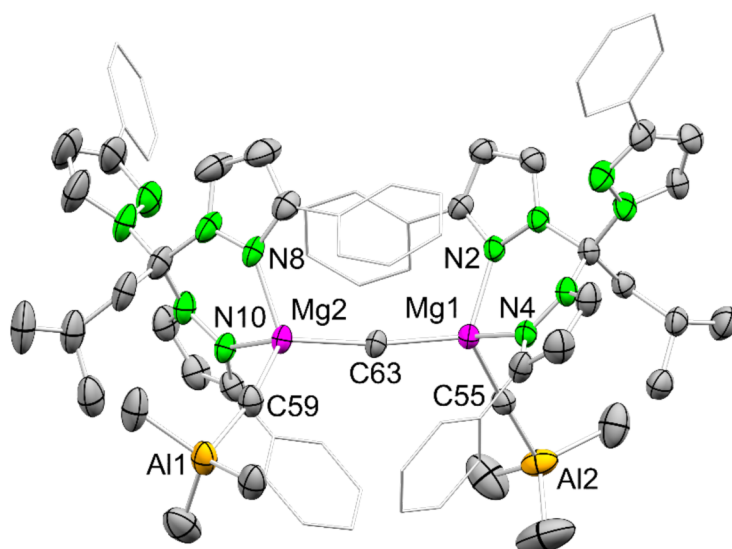


Figure S8. Connectivity of **7**, thermal ellipsoids set at 50% probability. Hydrogen atoms and the counter ion $[\text{AlMe}_4]^-$ are omitted for clarity. Phenyl moieties are set as wireframe.

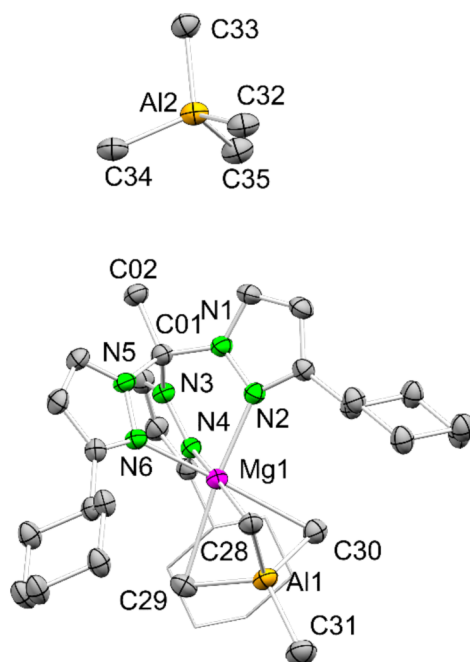


Figure S9. Crystal structures of **8**, thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Mg1–N2 2.123(3), Mg1–N4 2.128(3), Mg1–N6 2.143(3), Mg1–C28 2.545(4), Mg1–C29 2.633(4), Mg1–C30 2.442(4), Mg1–C28–Al1 66.84(13), Mg1–C29–Al1 65.13(12), Mg1–C30–Al1 68.74(13).

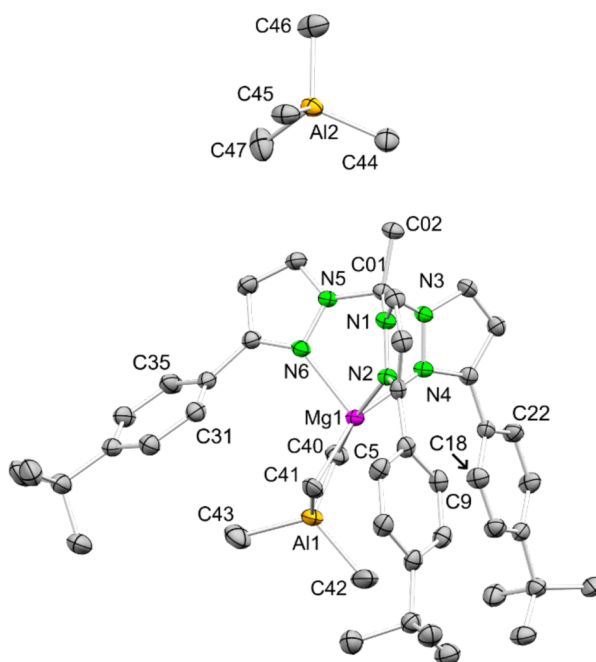


Figure S10. Crystal structures of **9**, thermal ellipsoids set at 50% probability. Hydrogen atoms and 2.5 lattice solvent C_6D_6 are omitted for clarity. Selected interatomic distances [$\text{\AA}$] and angles [$^\circ$]: Mg1–N2 2.1933(15), Mg1–N4 2.1882(15), Mg1–N6 2.1387(15), Mg1–C40 2.346(2), Mg1–C41 2.284(2); Mg1–C40–Al1 77.85(7), Mg1–C41–Al1 78.65(7).

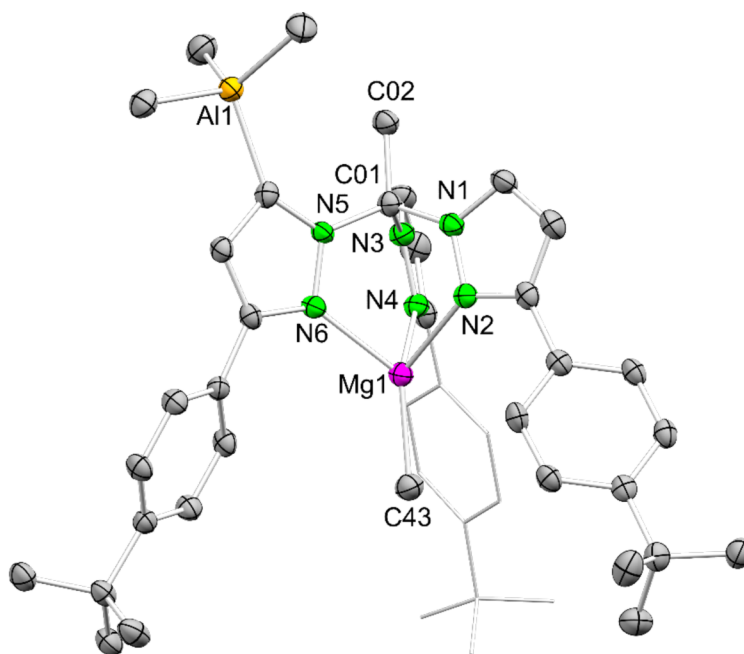
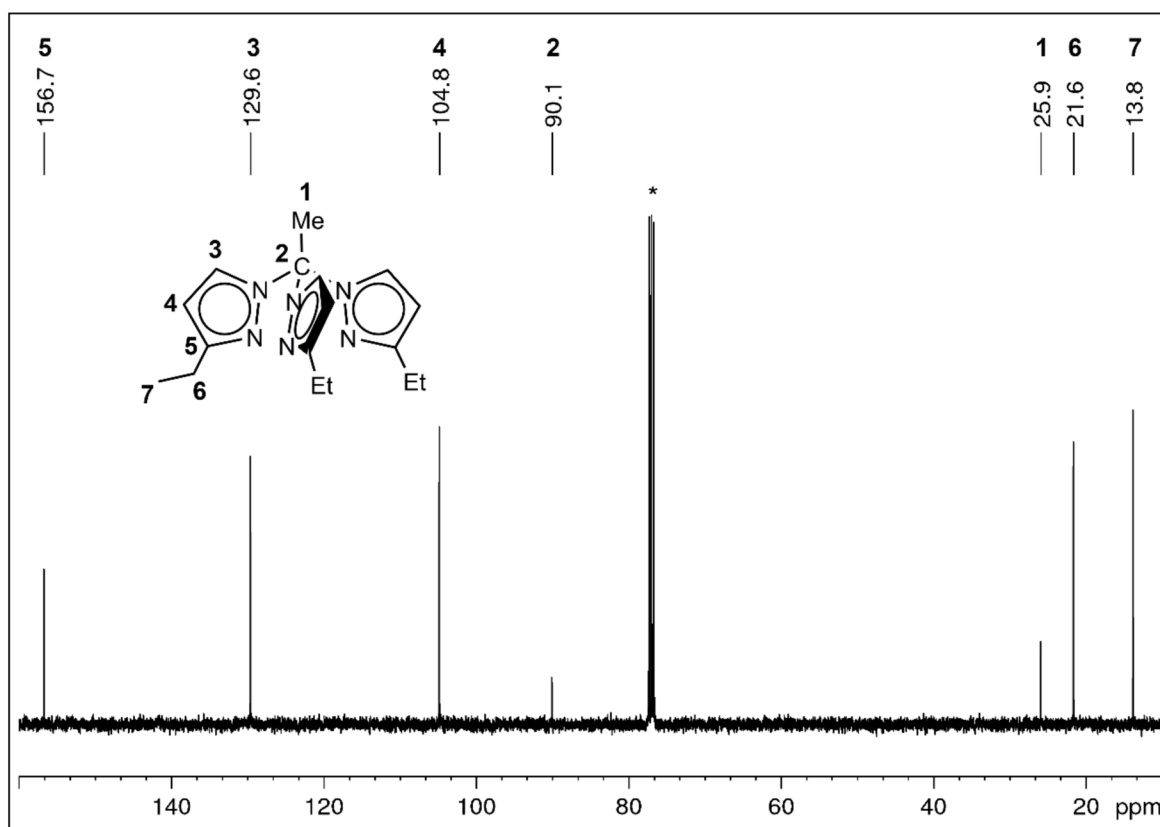
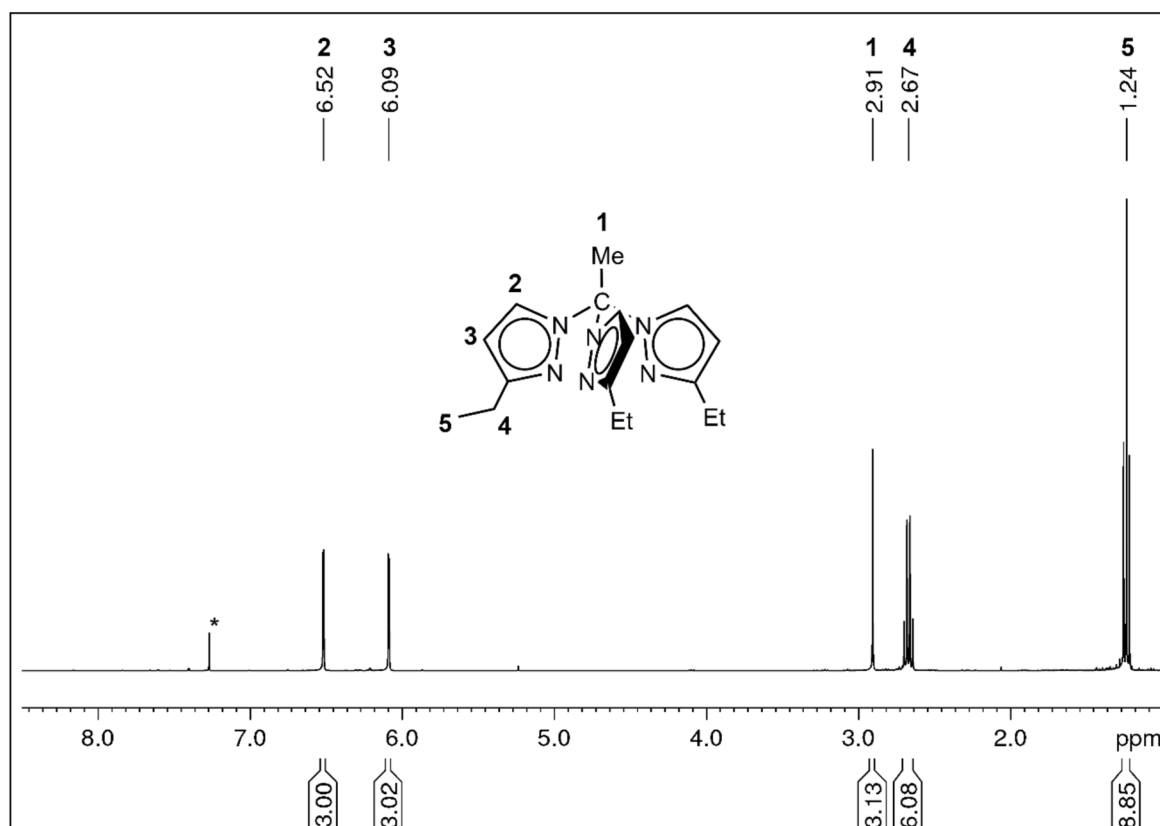


Figure S11. Crystal structures of **10**, thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected interatomic distances [$\text{\AA}$]: Mg1–N2 2.1398(16), Mg1–N4 2.1231(16), Mg1–N6 2.0965(16), Mg1–C43 2.090 (2).



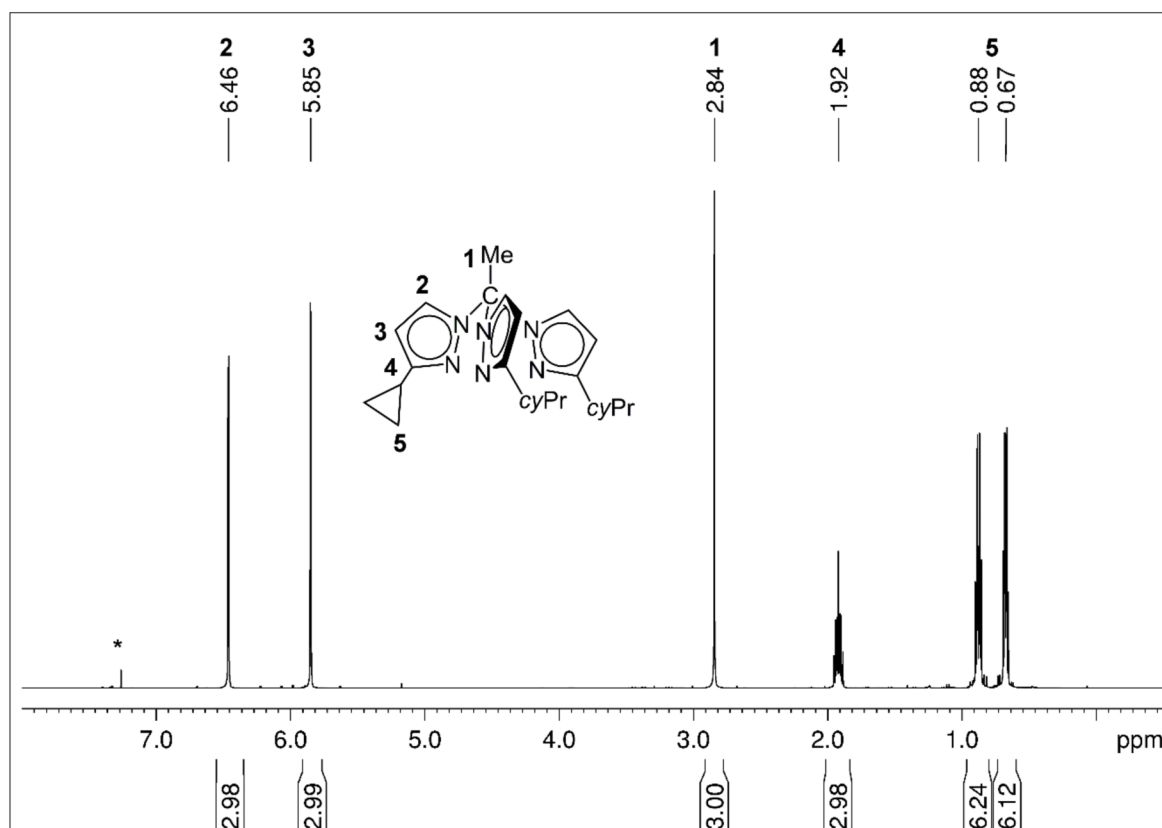


Figure S14. ¹H NMR spectrum (400 MHz) of **3b** in CDCl₃ (*) at 26 °C.

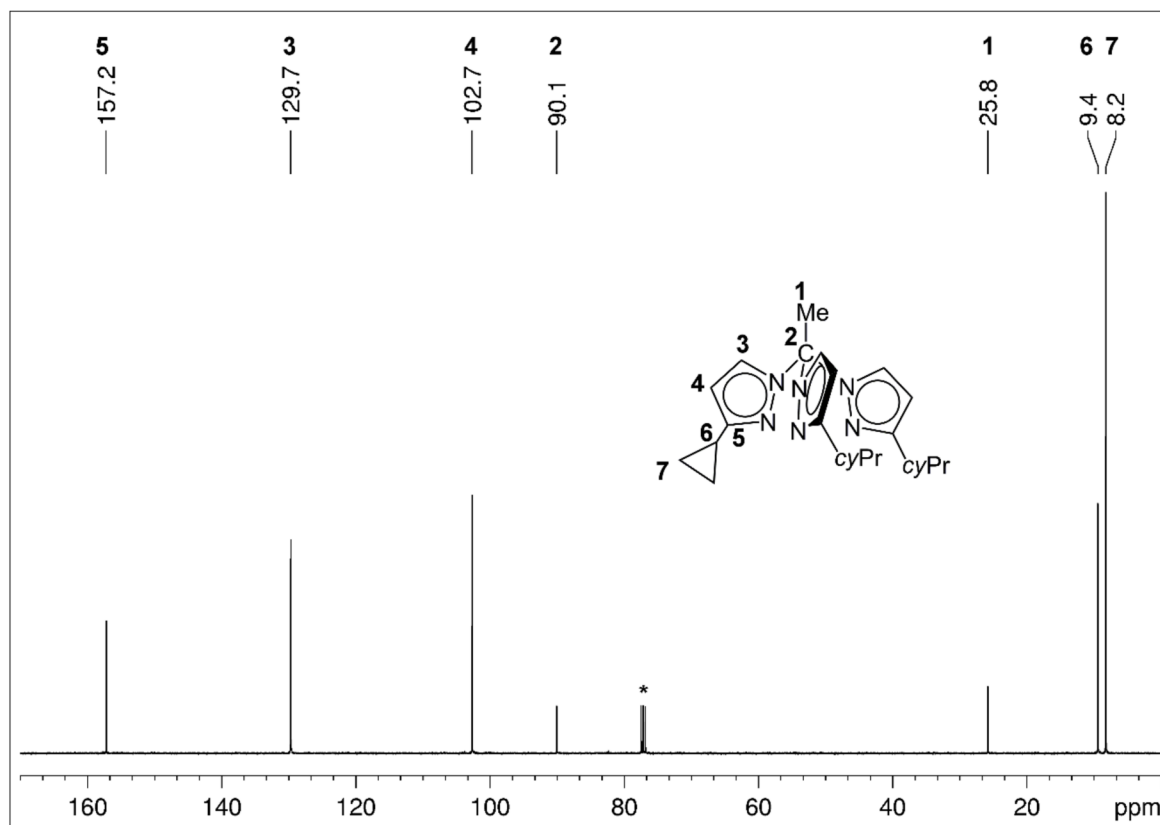


Figure S15. ¹³C{¹H} NMR spectrum (101 MHz) of **3b** in CDCl₃ (*) at 26 °C.

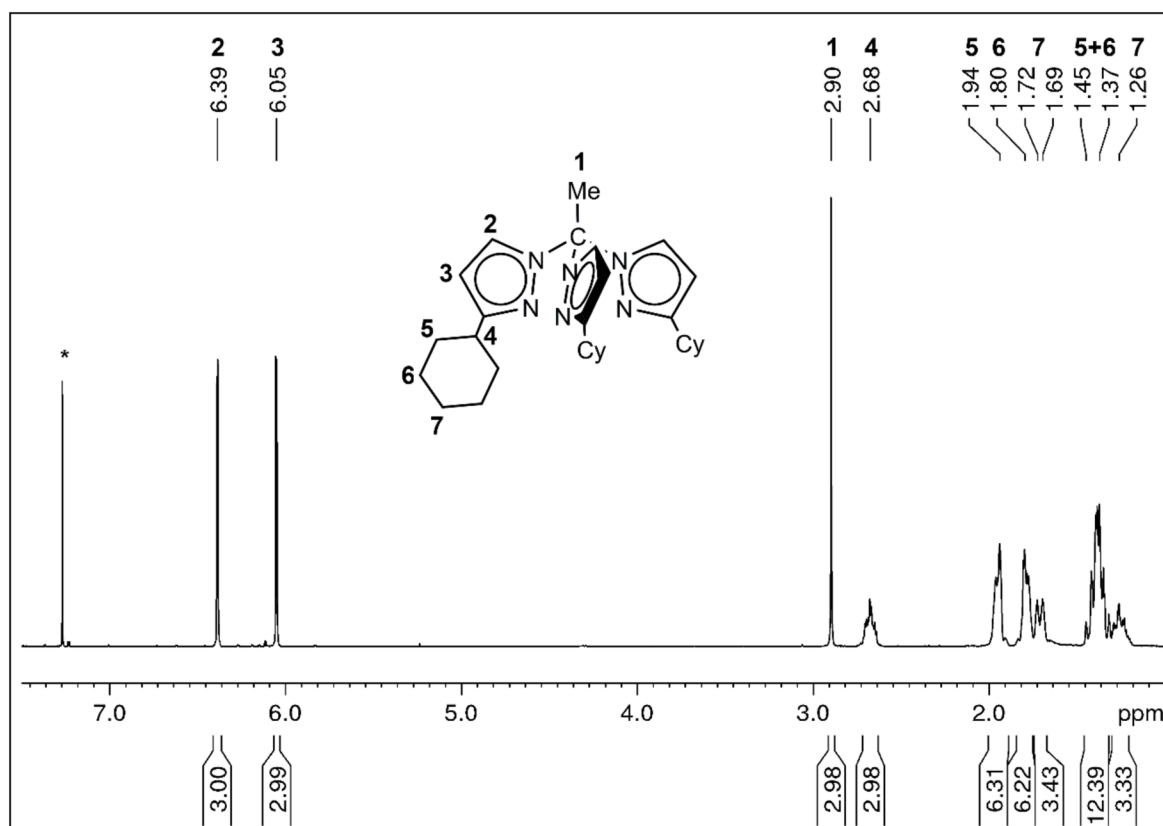


Figure S16. ¹H NMR spectrum (400 MHz) of **3c** in CDCl₃ (*) at 26 °C.

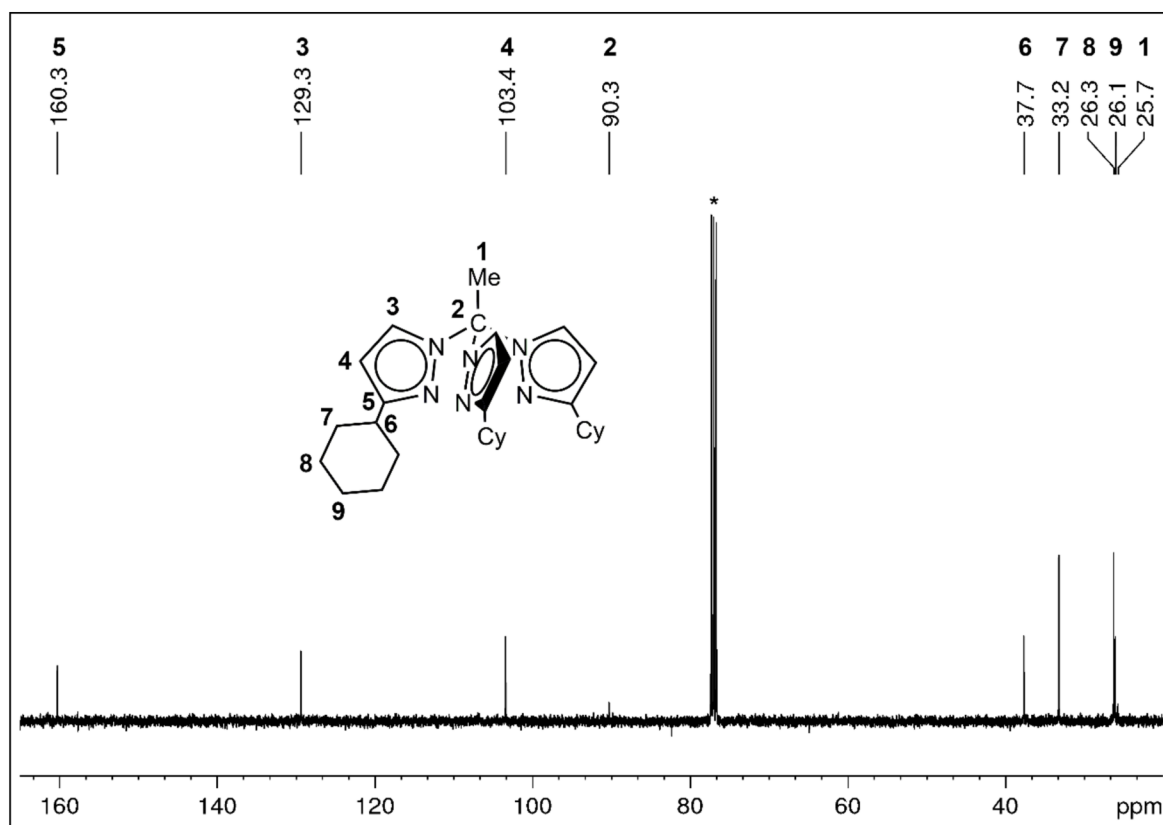


Figure S17. ¹³C{¹H} NMR spectrum (101 MHz) of **3c** in CDCl₃ (*) at 26 °C.

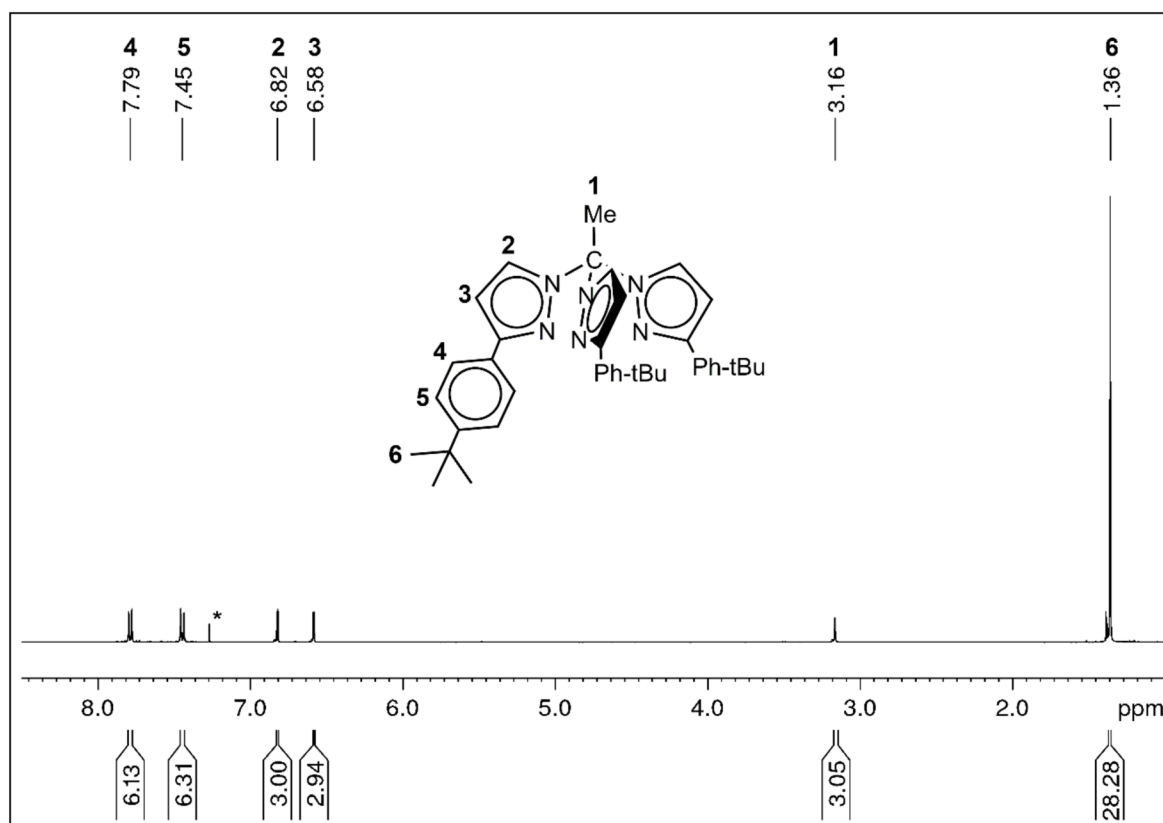


Figure S18. ¹H NMR spectrum (400 MHz) of **3d** in CDCl₃ (*) at 26 °C.

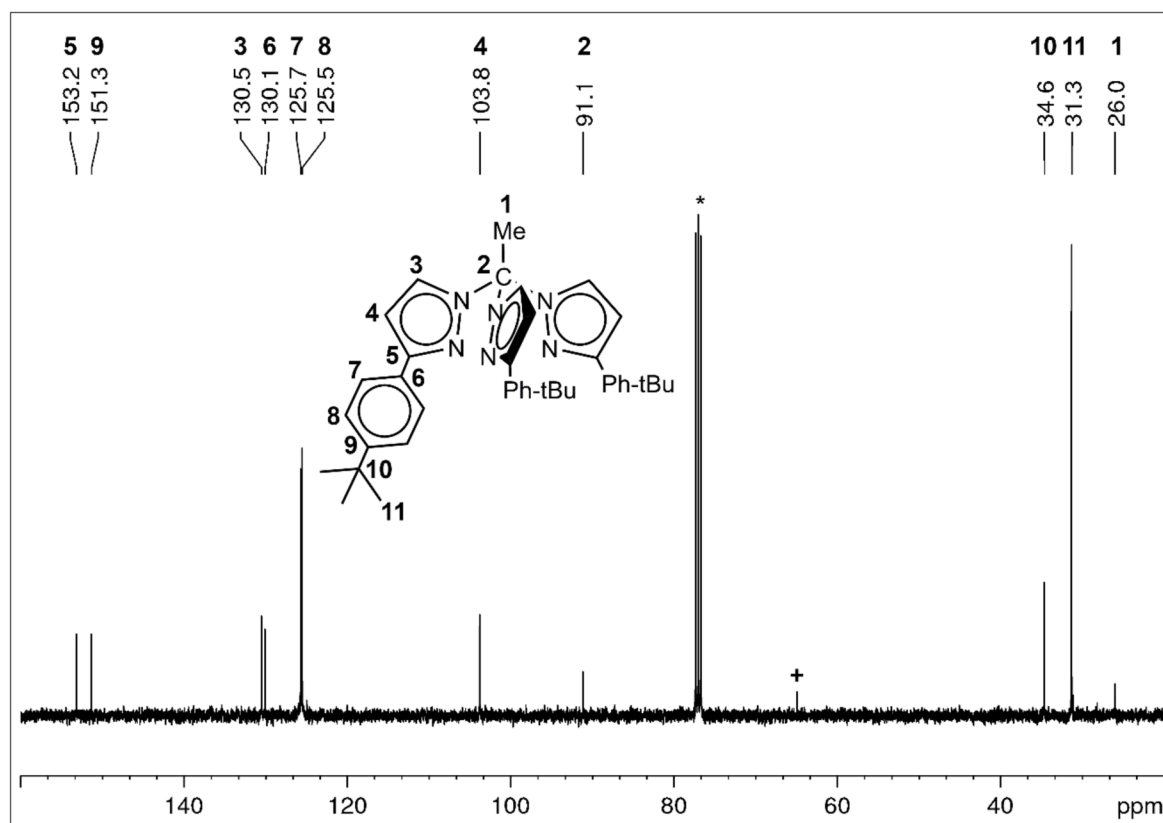


Figure S19. ¹³C{¹H} NMR spectrum (101 MHz) of **3d** in CDCl₃ (*) at 26 °C (+ impurities).

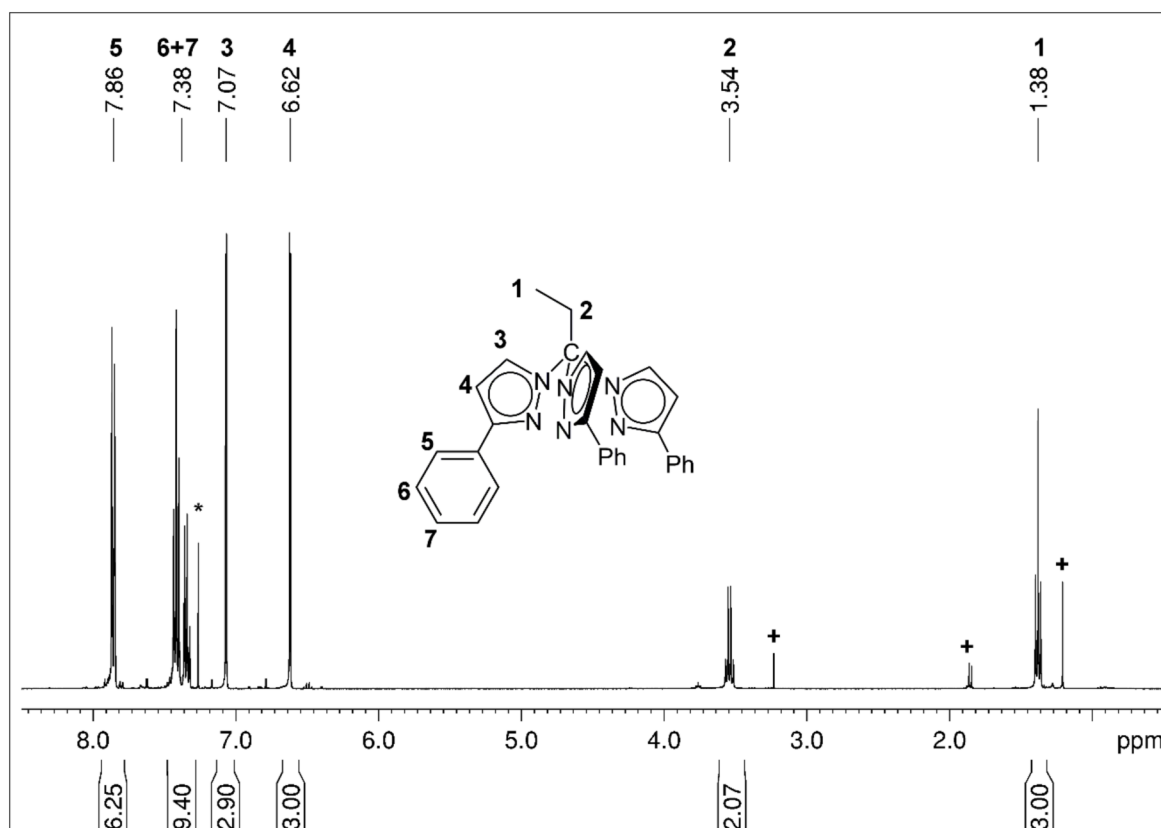


Figure S20. ^1H NMR spectrum (400 MHz) of **3e** in CDCl_3 (*) at 26 °C (+ impurities).

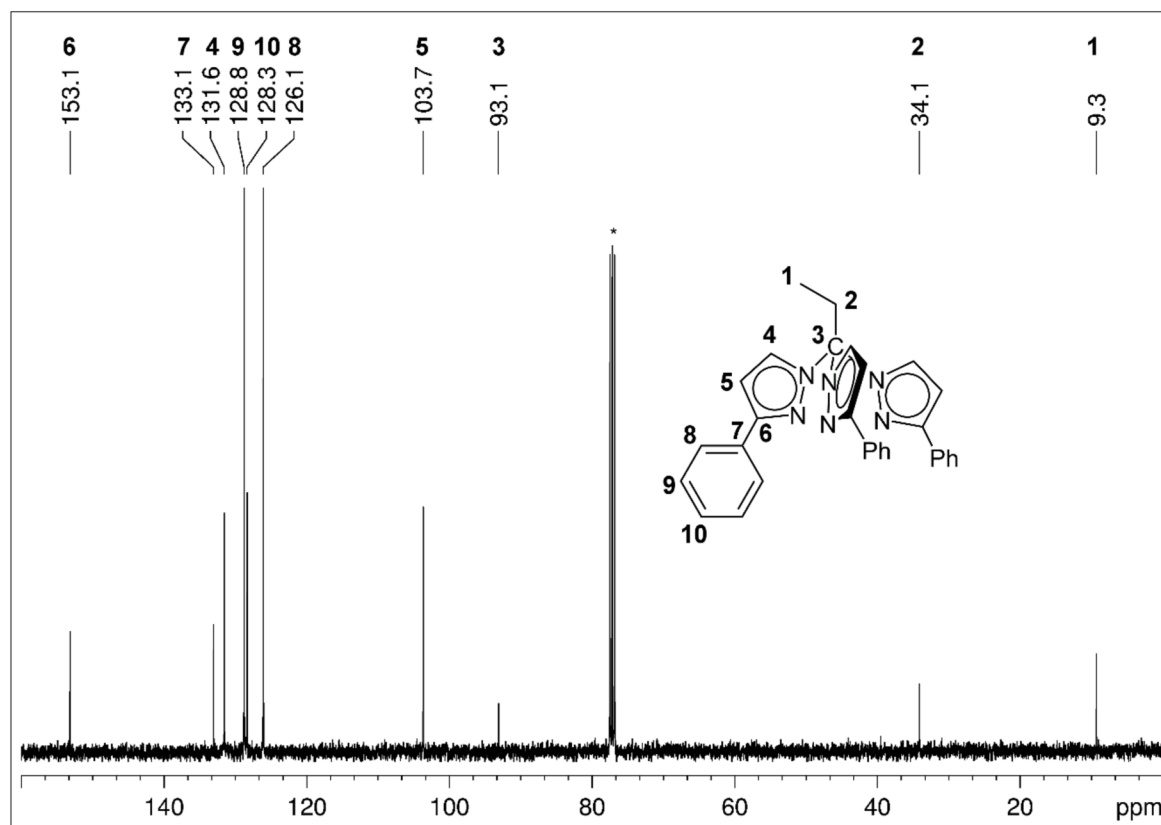


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of **3e** in CDCl_3 (*) at 26 °C.

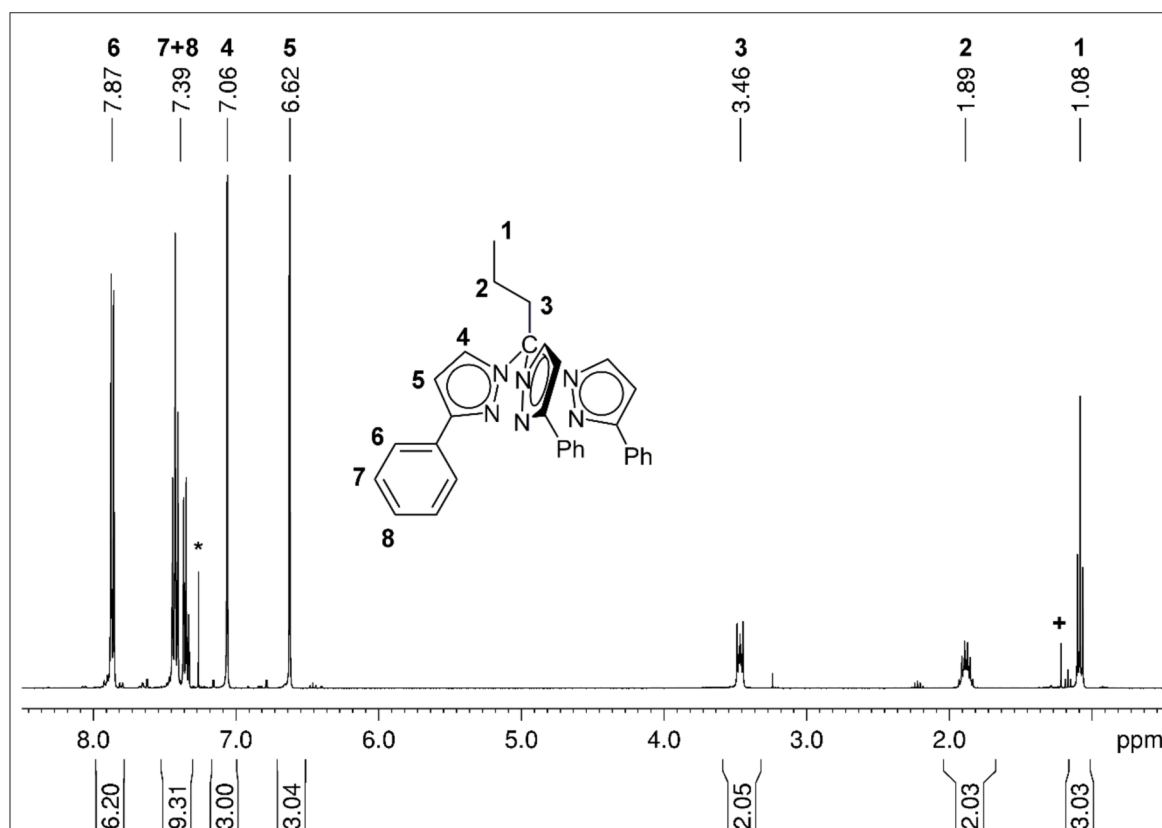


Figure S22. ^1H NMR spectrum (400 MHz) of **3f** in CDCl_3 (*) at 26 °C (+ mtbe).

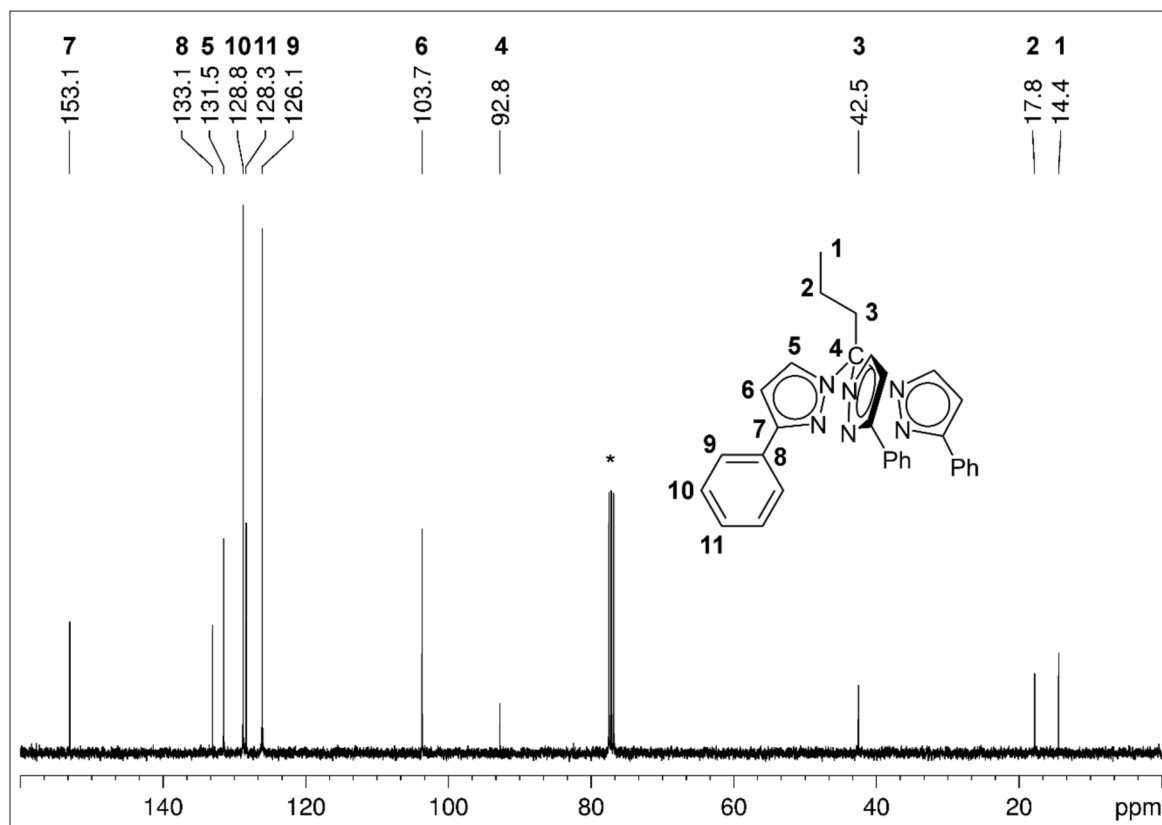
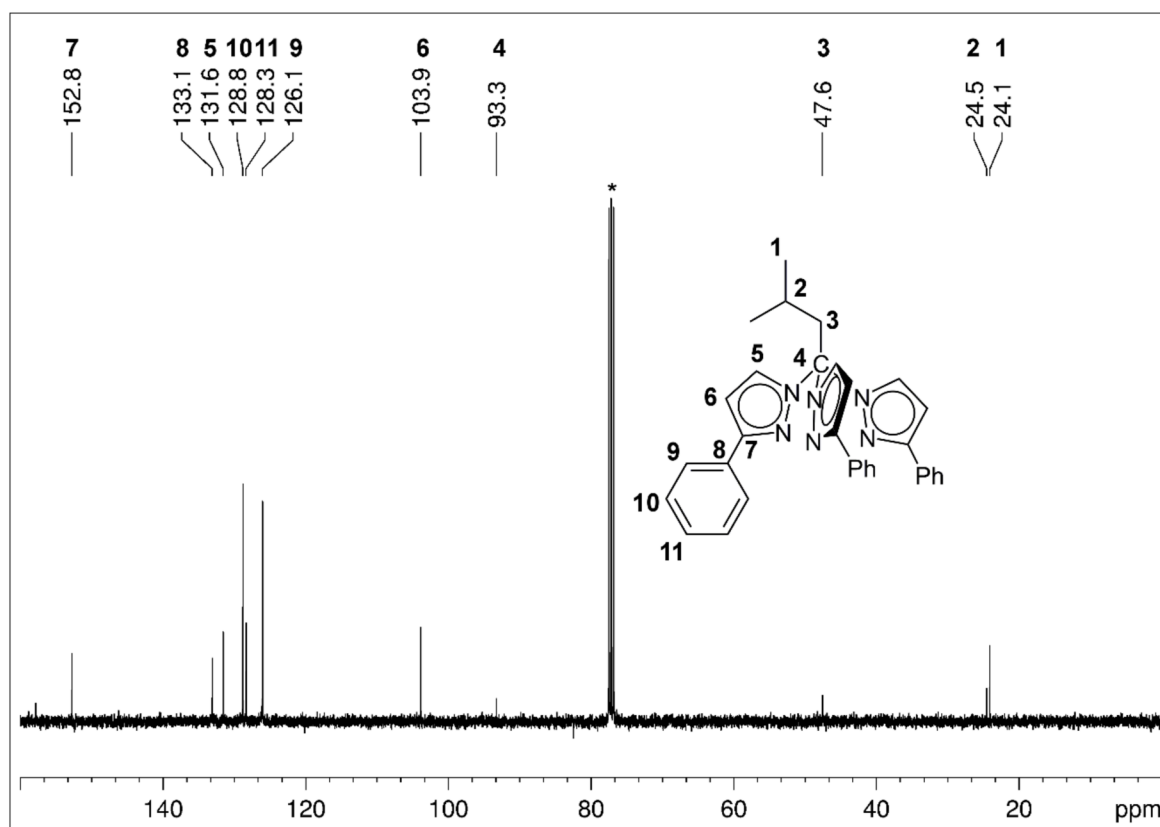
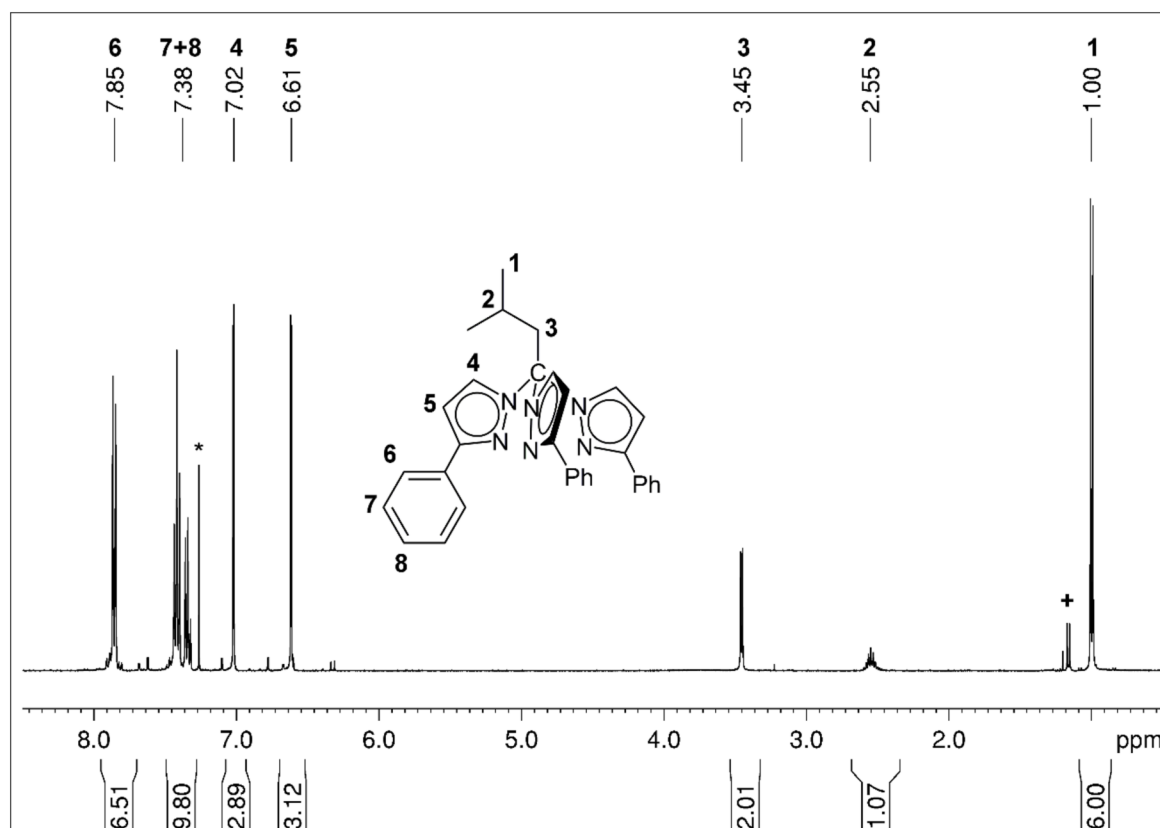


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of **3f** in CDCl_3 (*) at 26 °C.



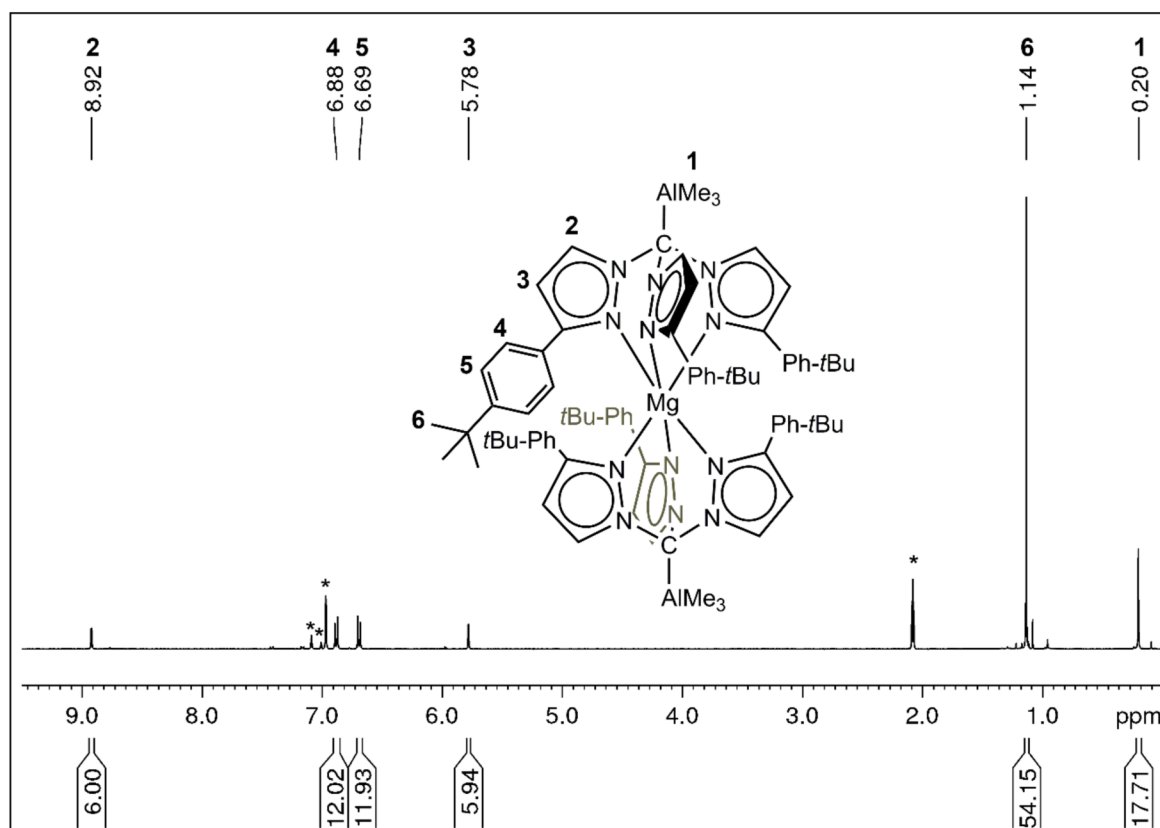


Figure S26. ¹H NMR spectrum (400 MHz) of **4** in [D₈]toluene (*) at 26 °C.

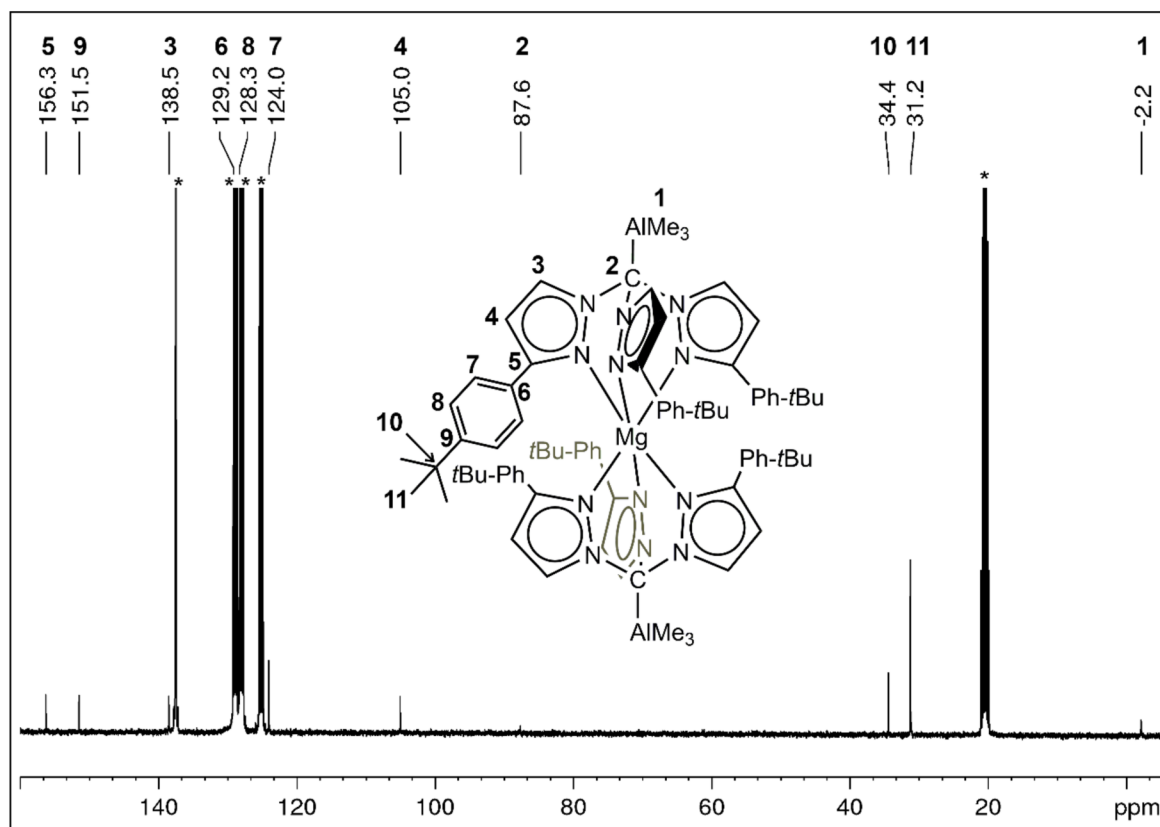


Figure S27. ¹³C{¹H} NMR spectrum (101 MHz) of **4** in [D₈]toluene (*) at 26 °C.

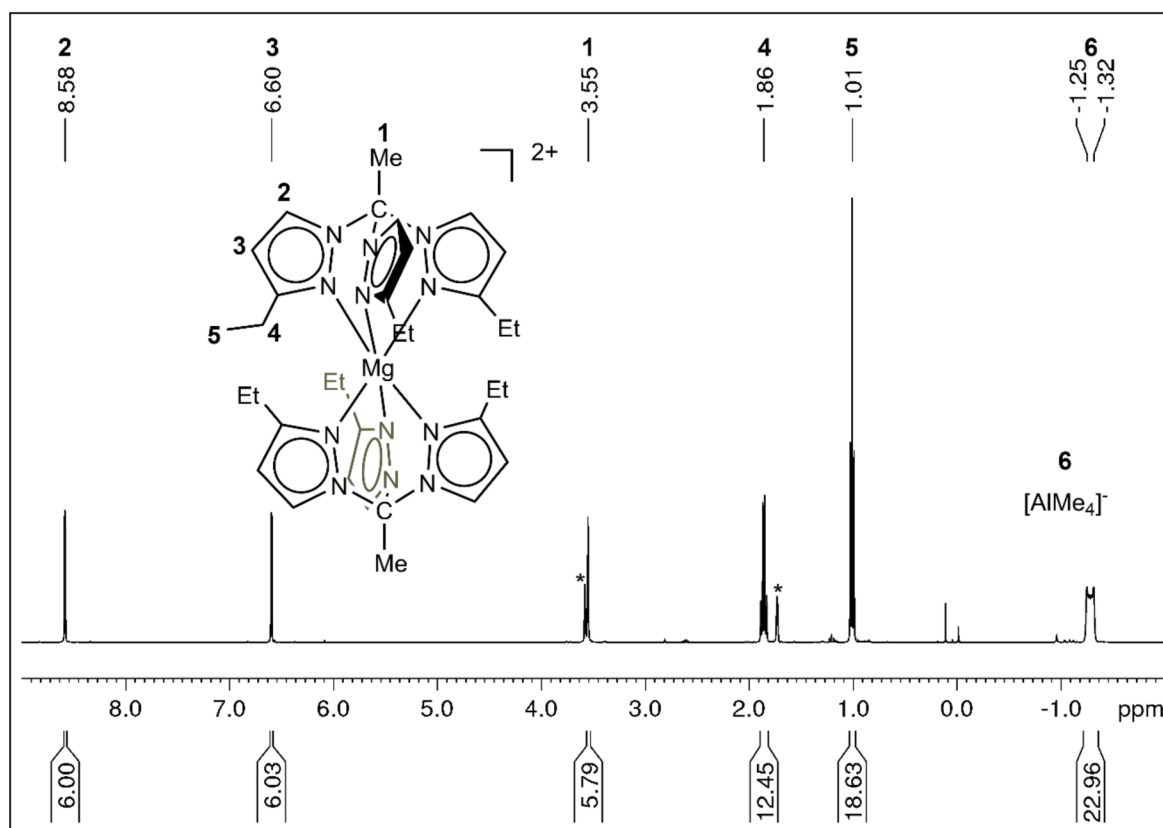


Figure S28. ¹H NMR spectrum (400 MHz) of **5a** in [D₈]thf (*) at 26 °C.

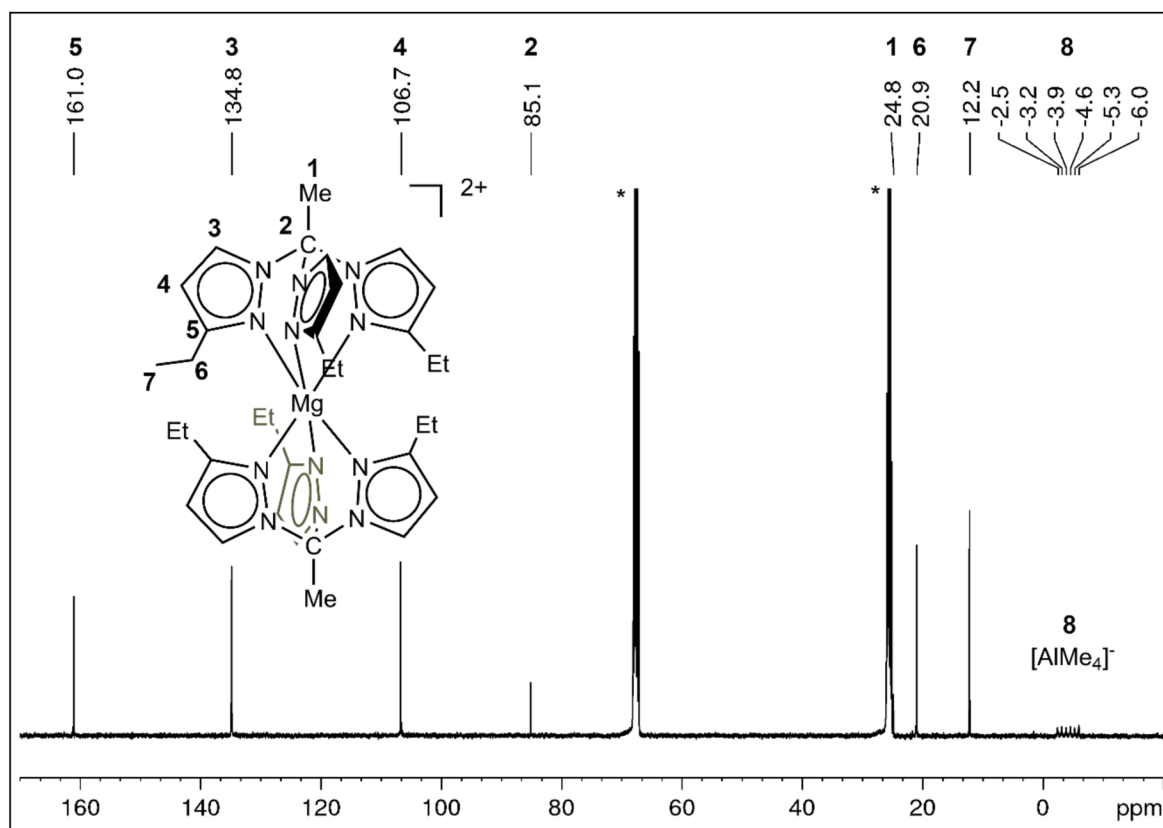


Figure S29. ¹³C{¹H} NMR spectrum (101 MHz) of **5a** in [D₈]thf (*) at 26 °C.

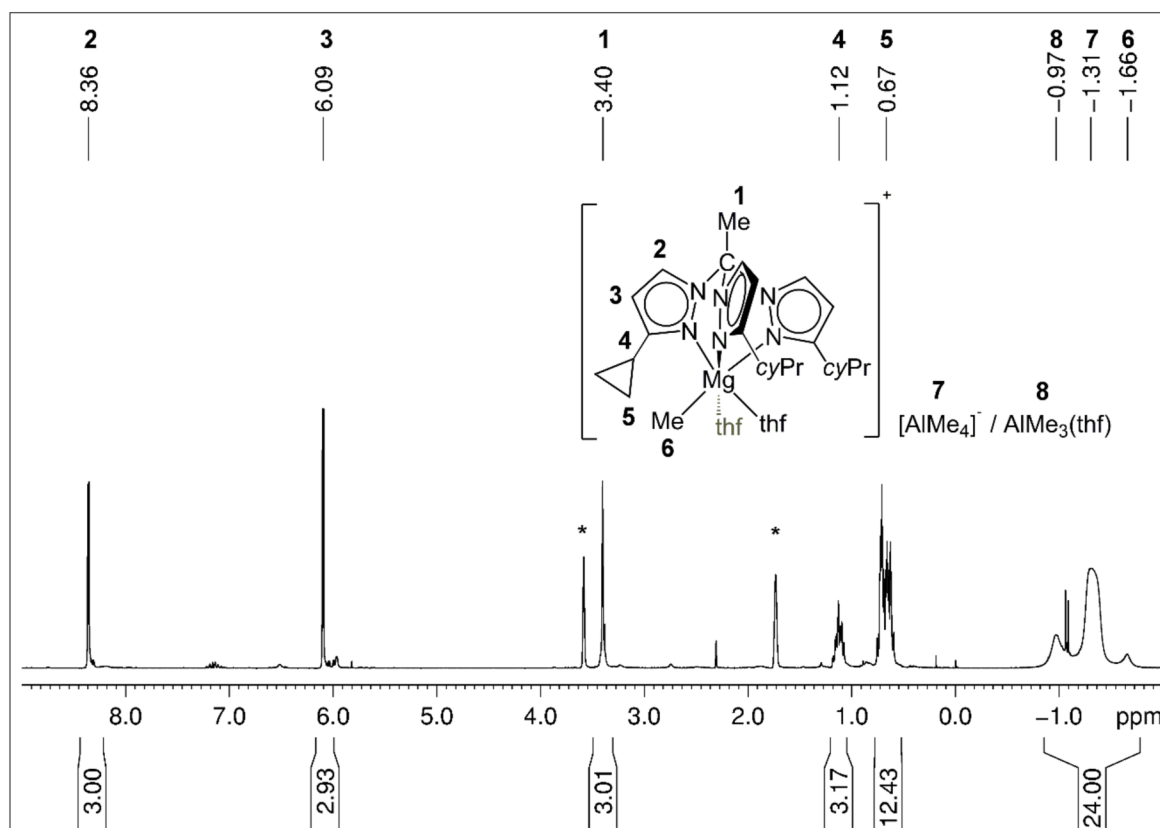


Figure S30. ¹H NMR spectrum (400 MHz) of **6** in [D₈]thf (*) at 26 °C.

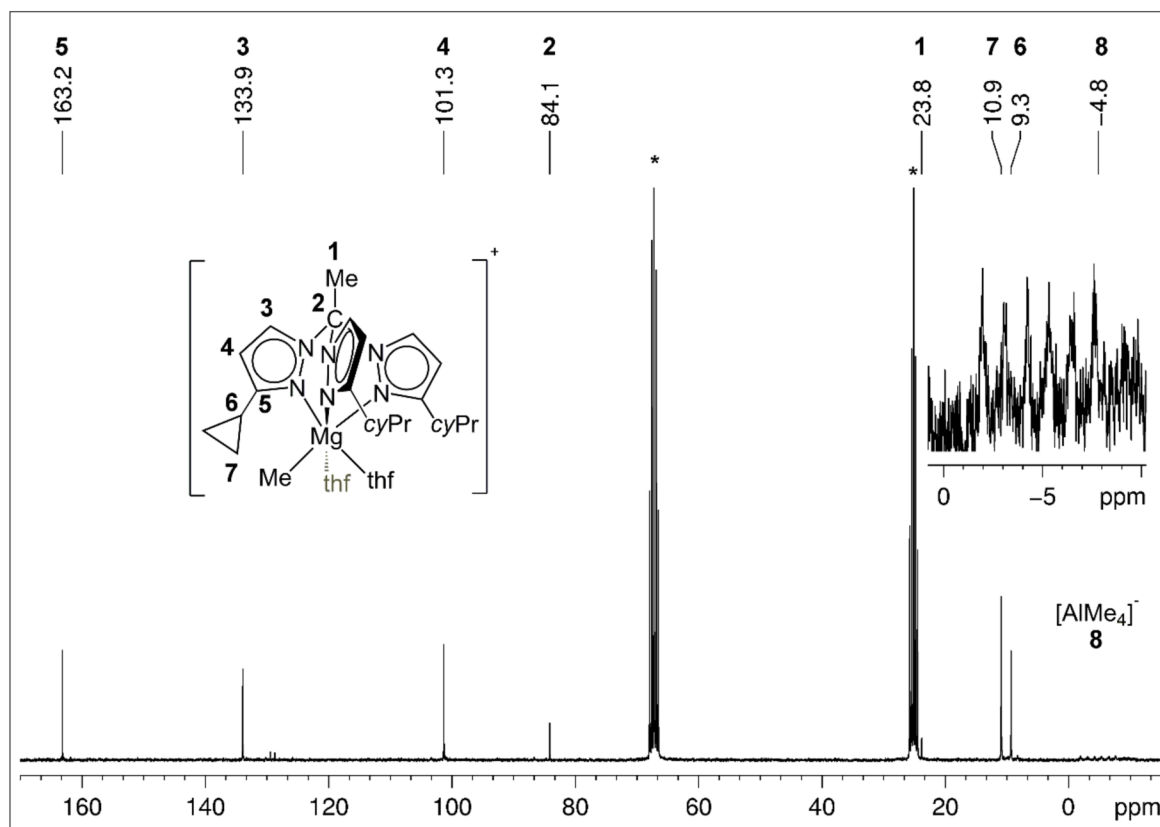


Figure S31. ¹³C{¹H} NMR spectrum (101 MHz) of **6** in [D₈]thf (*) at 26 °C.

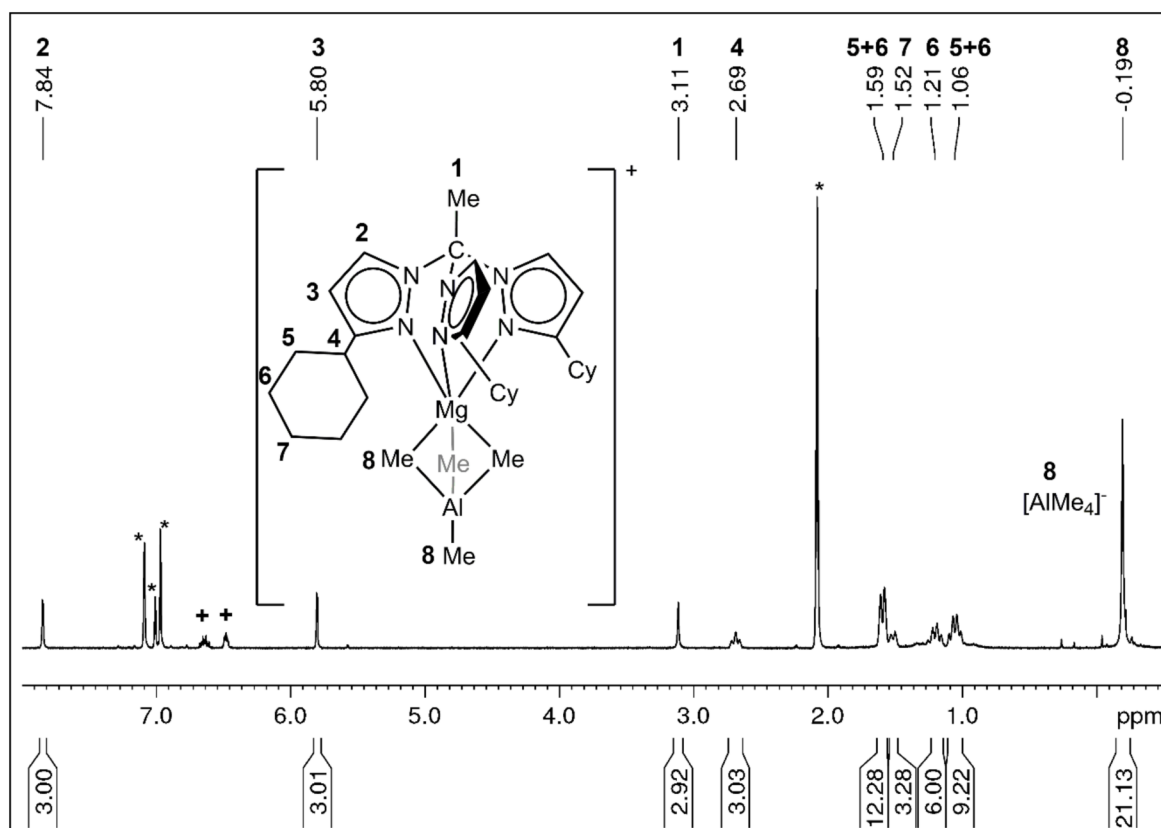


Figure S32. ¹H NMR spectrum (400 MHz) of **8** in [D₈]toluene (*) at 26 °C (+ 1,2DFB).

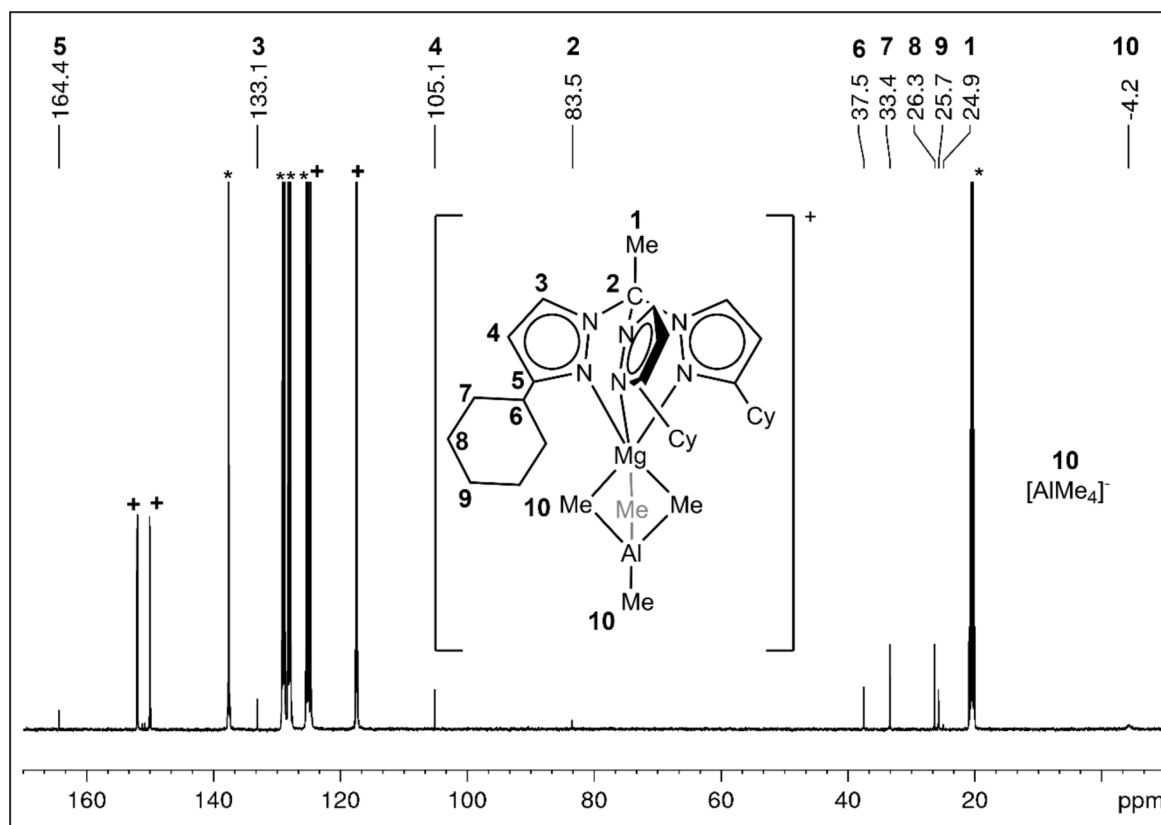


Figure S33. ¹³C{¹H} NMR spectrum (101 MHz) of **8** in [D₈]toluene(*)/1,2DFB(+) at 26 °C.

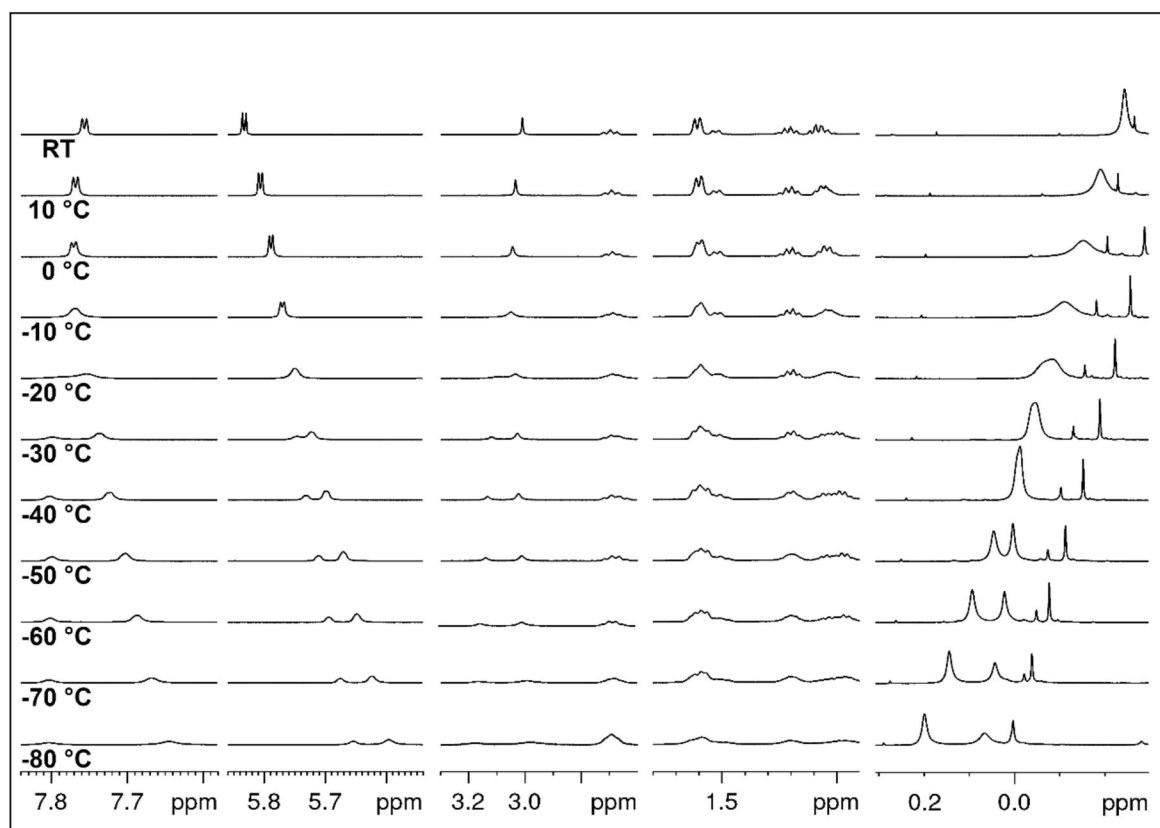


Figure S34. VT ^1H NMR spectrum (500 MHz) of **8** in $[\text{D}_8]\text{toluene}/1,2\text{DFB}$.

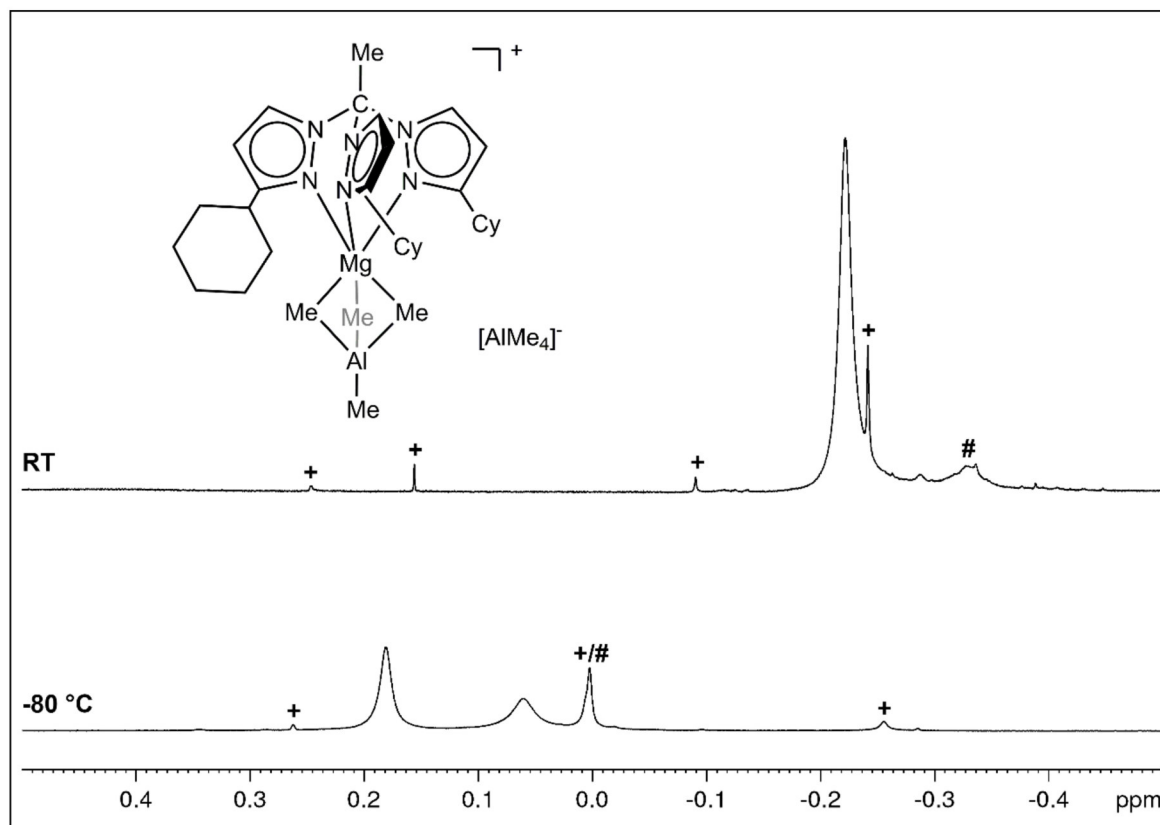


Figure S35. VT ^1H NMR spectrum (500 MHz) of **8** in $[\text{D}_8]\text{toluene}/1,2\text{DFB}$.

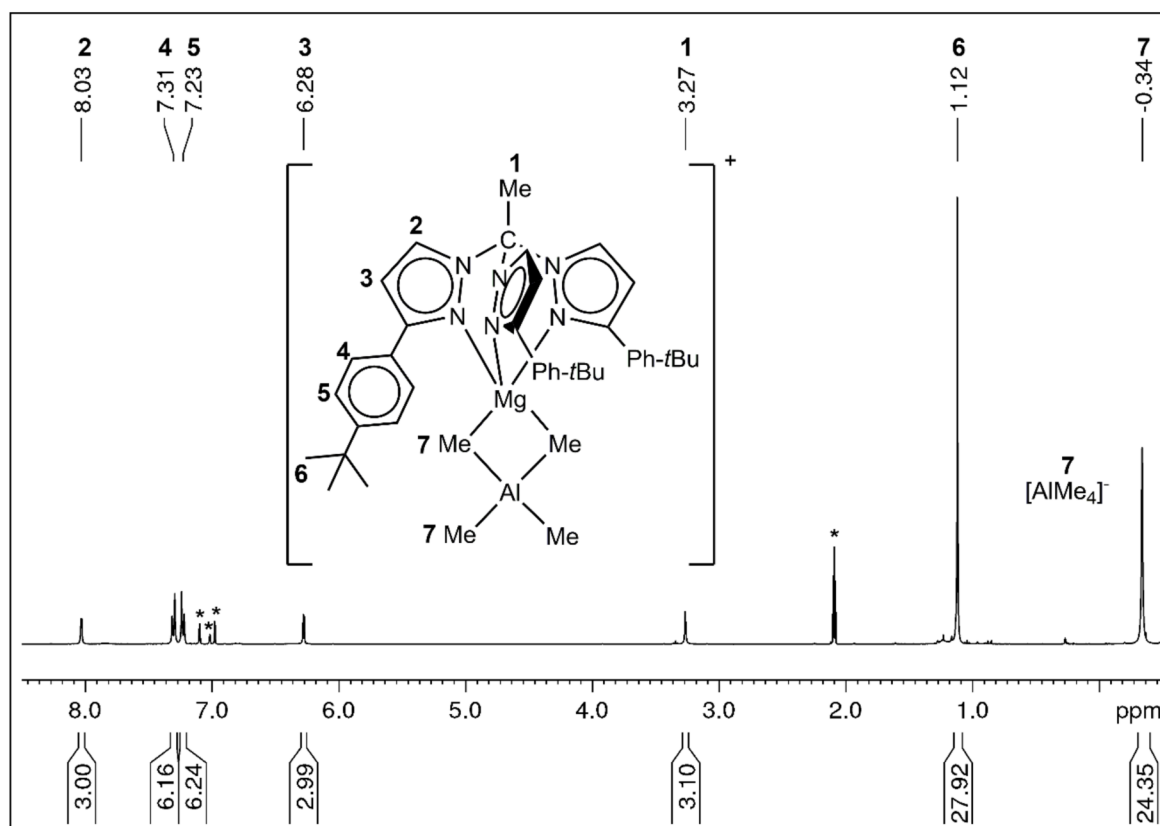


Figure S36. ¹H NMR spectrum (400 MHz) of 9 in [D₈]toluene (*) at 26 °C.

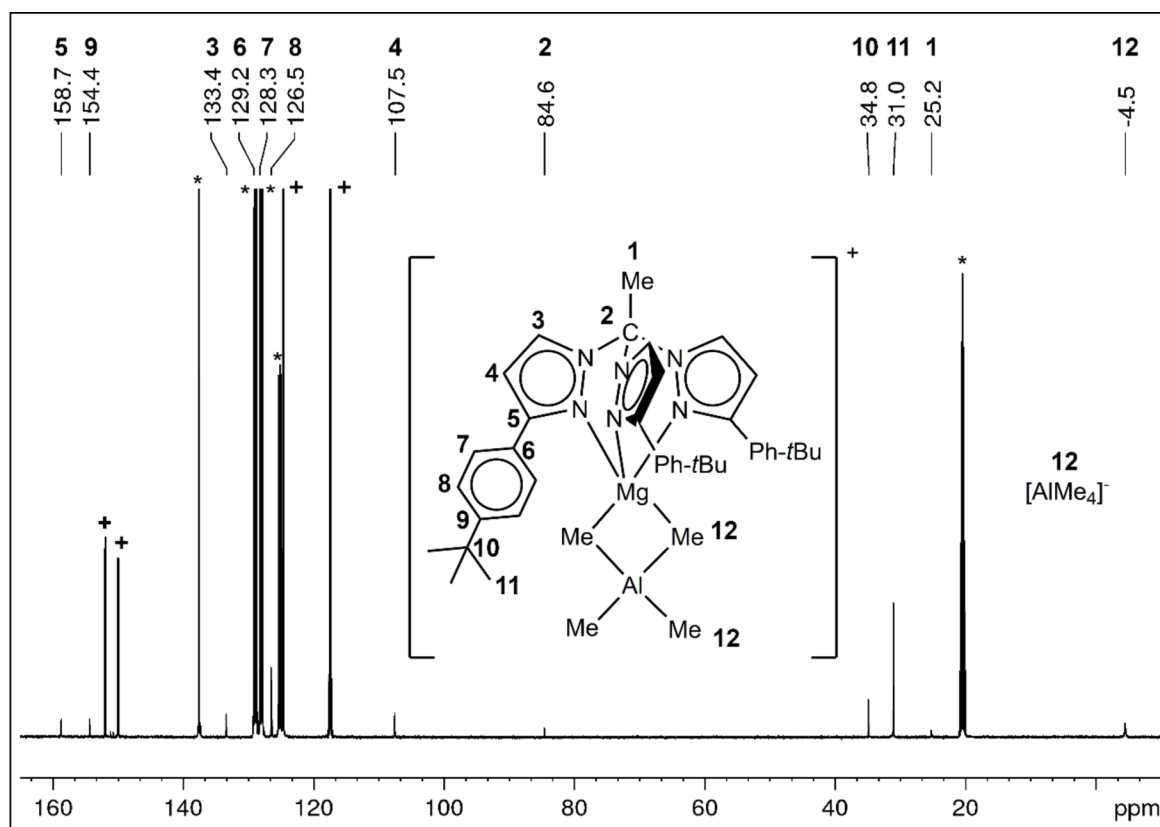


Figure S37. ¹³C{¹H} NMR spectrum (101 MHz) of 9 in [D₈]toluene(*)/1,2DFB(+) at 26 °C.

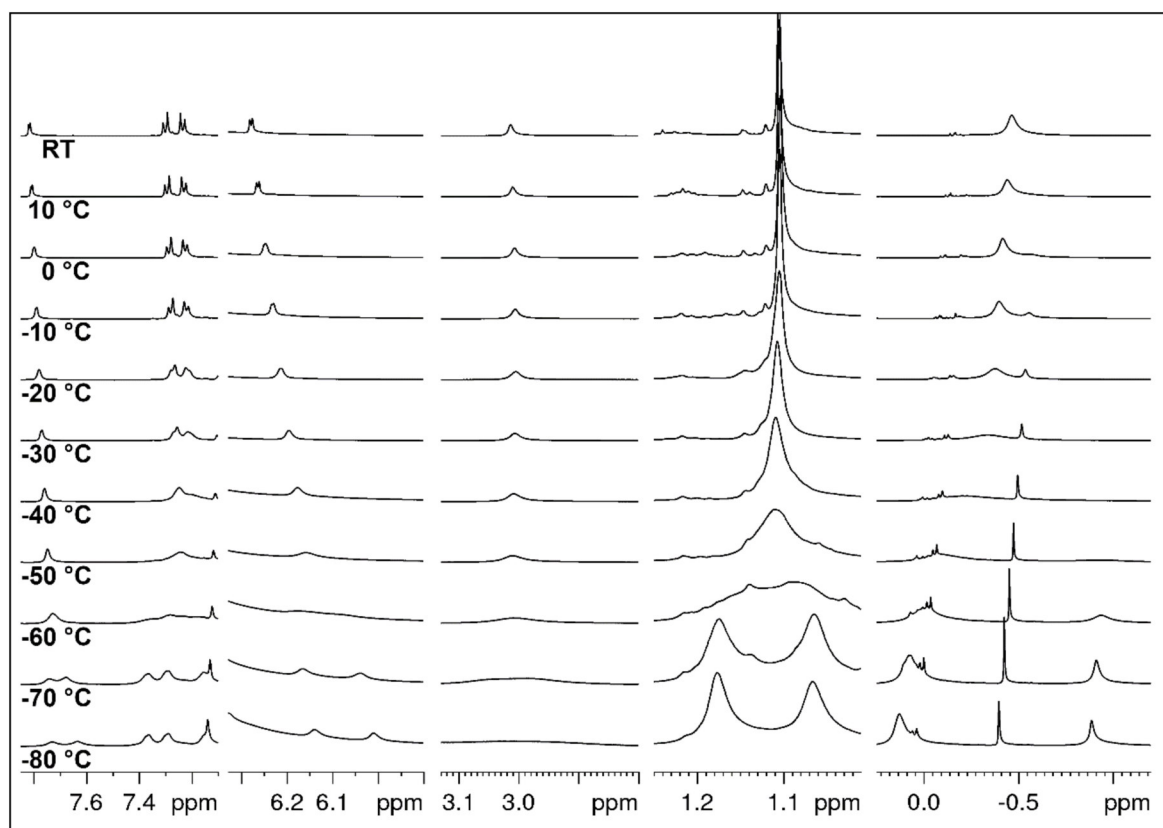


Figure S38. VT ¹H NMR spectrum (500 MHz) of **9** in [D₈]toluene/1,2DFB.

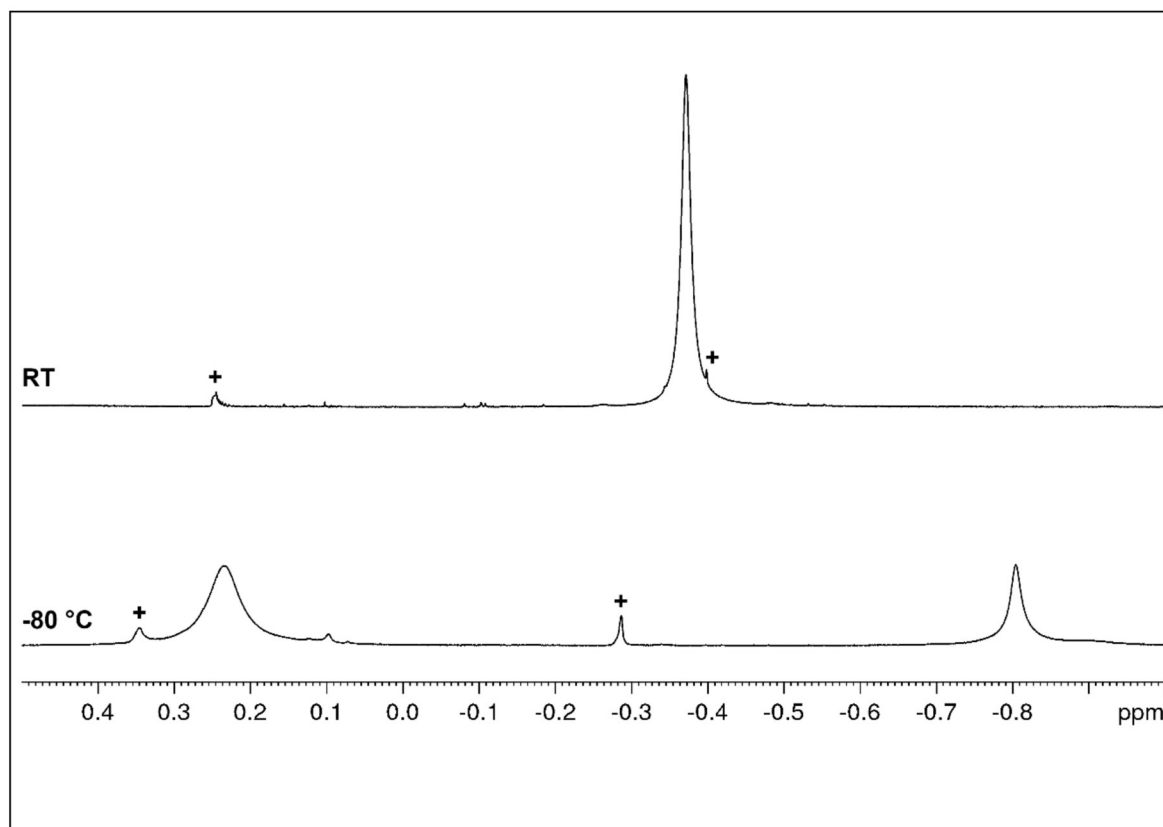


Figure S39. VT ¹H NMR spectrum (500 MHz) of **9** in [D₈]toluene/1,2DFB (+ impurities).

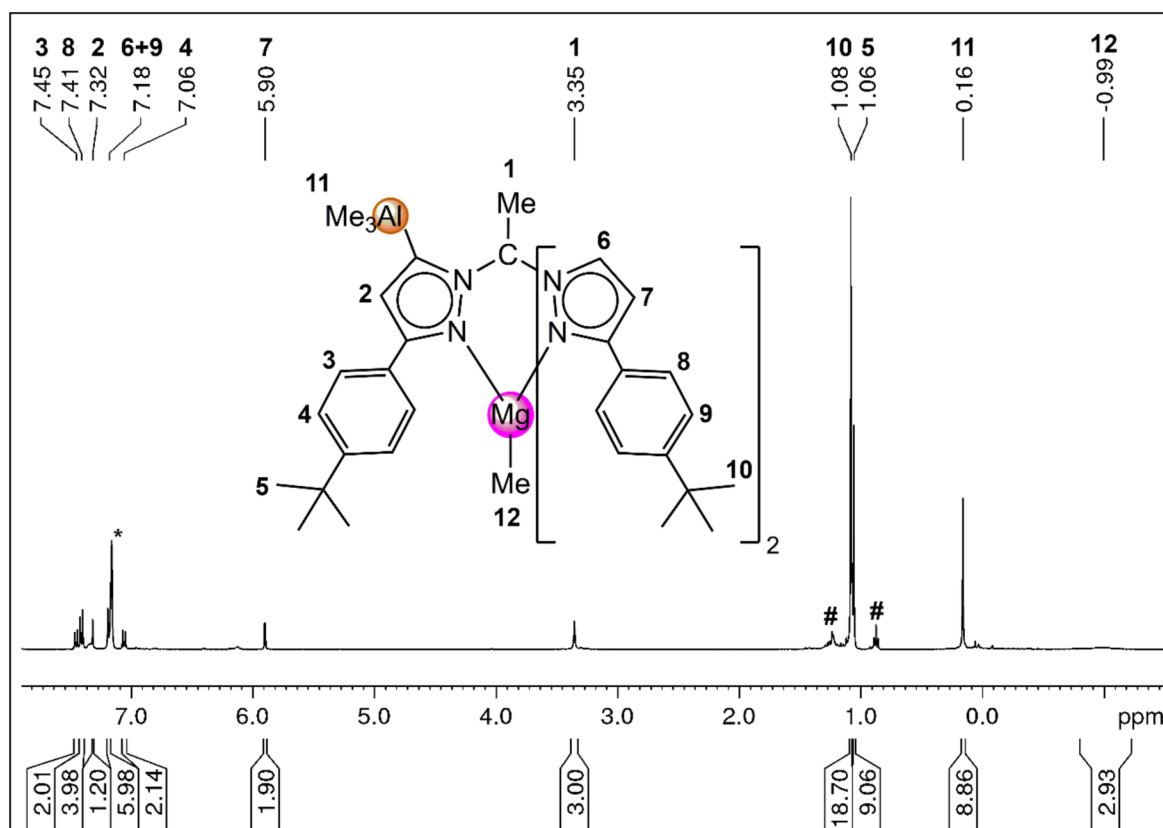


Figure S40. ¹H NMR spectrum (400 MHz) of **10** in [D₆]benzene (*) at 26 °C (# impurities).

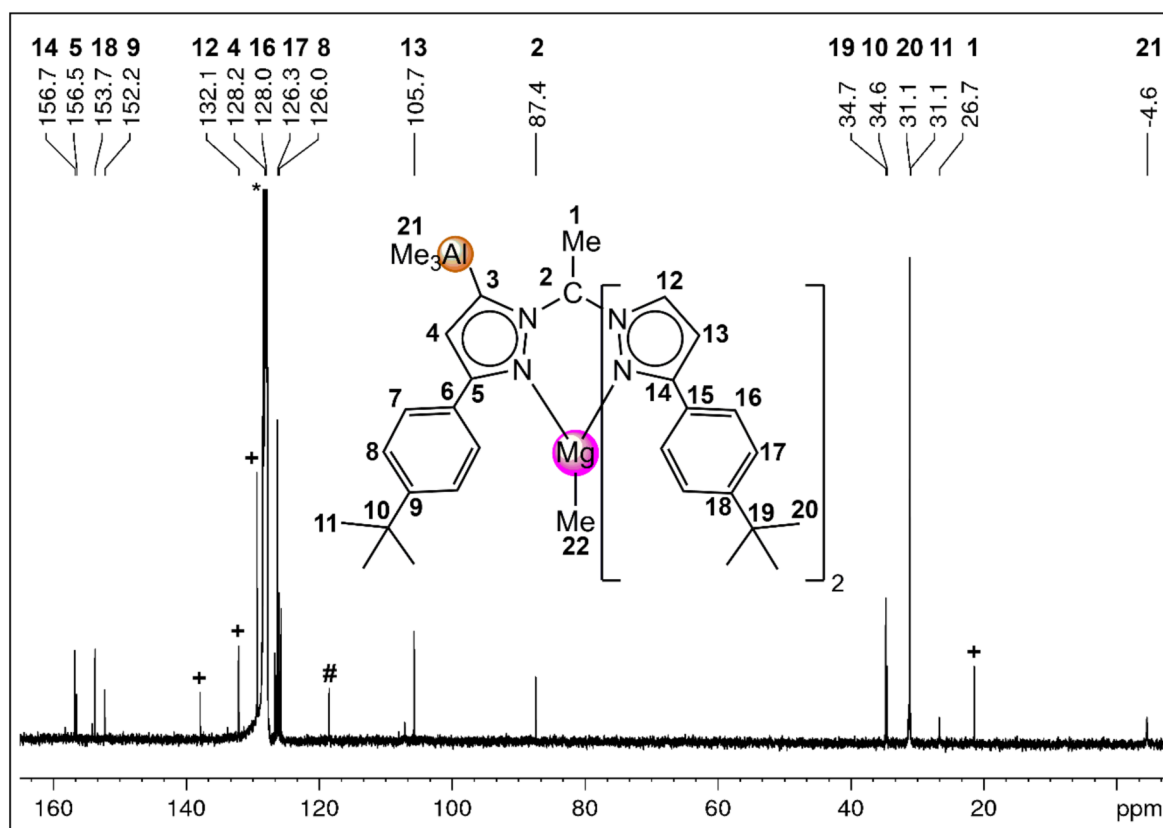


Figure S41. ¹³C{¹H} NMR spectrum (101 MHz) of **10** in [D₆]benzene(*) at 26 °C (+ toluene/# impurities).

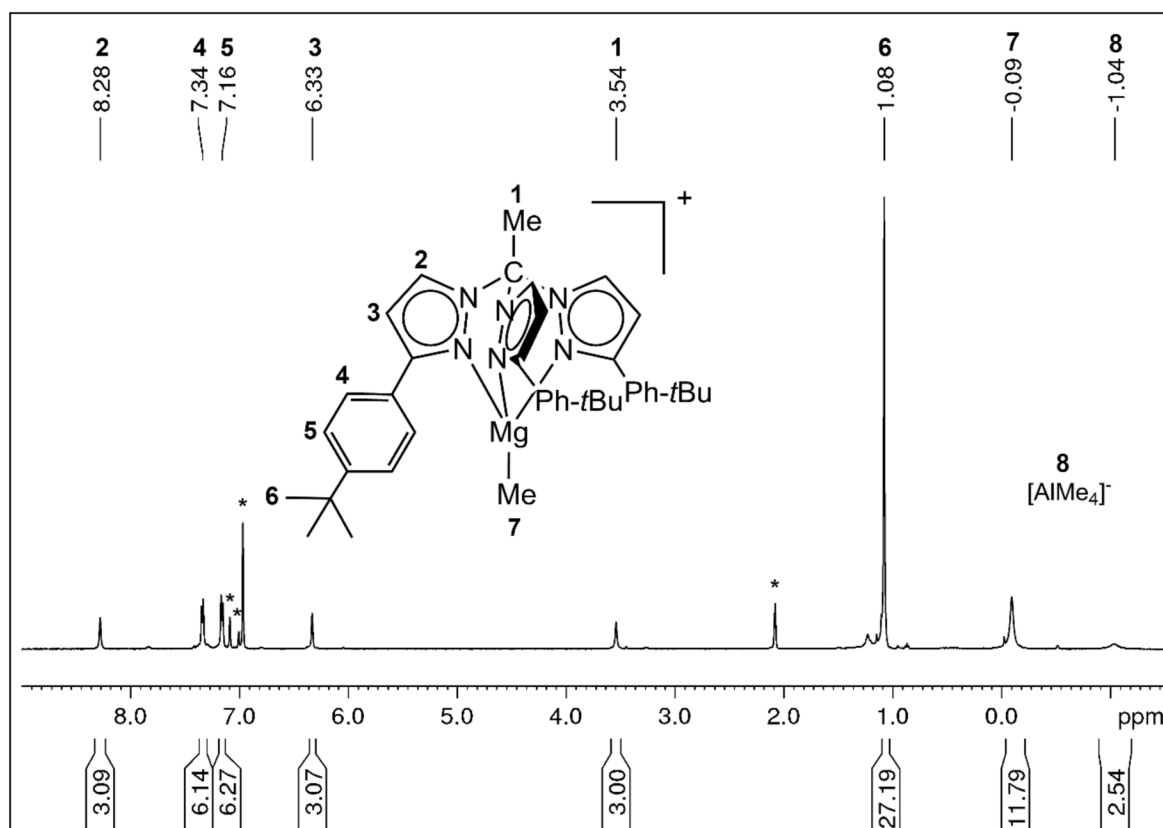


Figure S42. ^1H NMR spectrum (400 MHz) of **11** in $[\text{D}_8]\text{toluene}$ (*) at 26 °C.

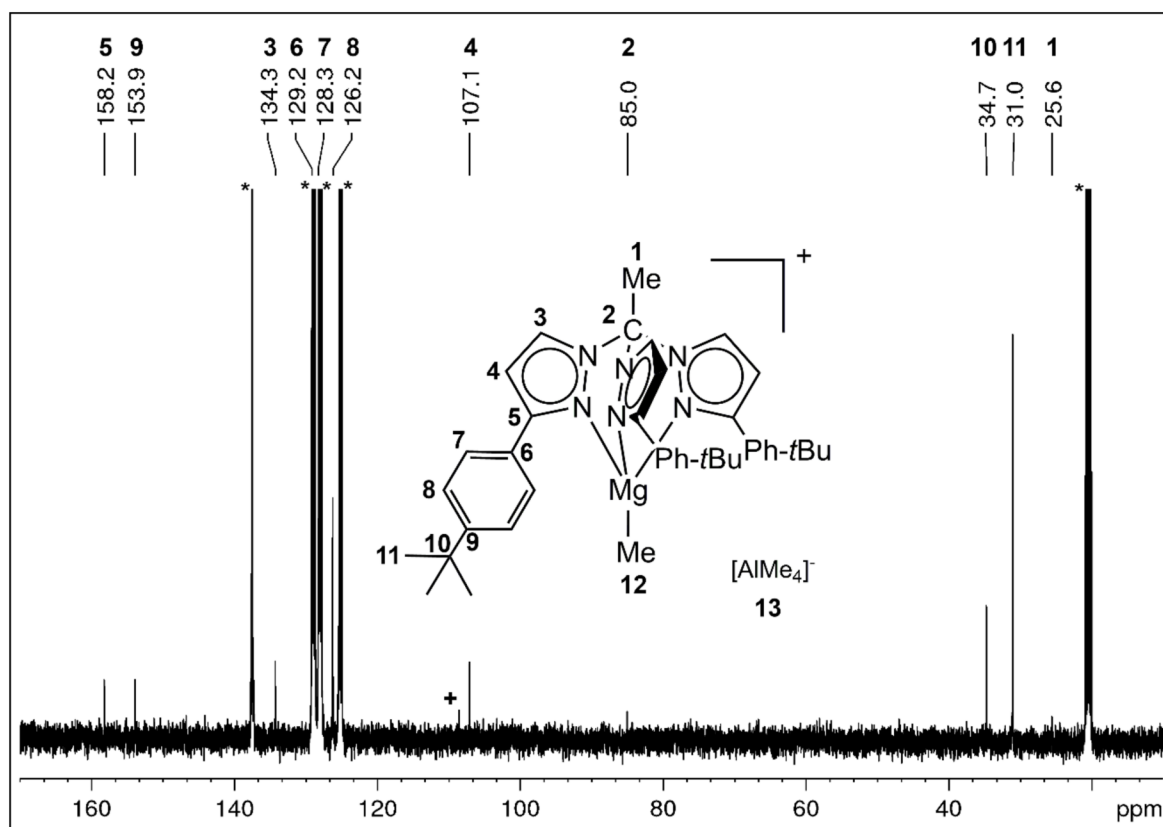
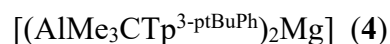


Figure S43. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of **11** in $[\text{D}_8]\text{toluene}$ (*) at 26 °C (+ impurities).

Cone-Angle Calculation

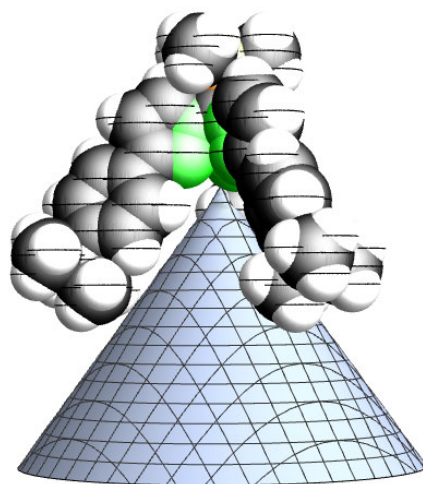
For the calculation of the mathematically exact cone angles .xyz files were generated from the final .cif files with Mercury. The Mathematica package was downloaded free of charge from <http://www.ccqc.uga.edu/references/software.php>. The adopted van der Waals radii were $r = 1.20, 1.70, 1.55, 1.52, 1.84, 1.73 \text{ \AA}$ for H, C, N O, Al and Mg in this order.



Ligand atoms forming cone = {31, 55, 90}

Cone angle (deg) = 288.022

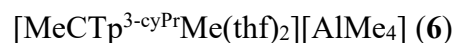
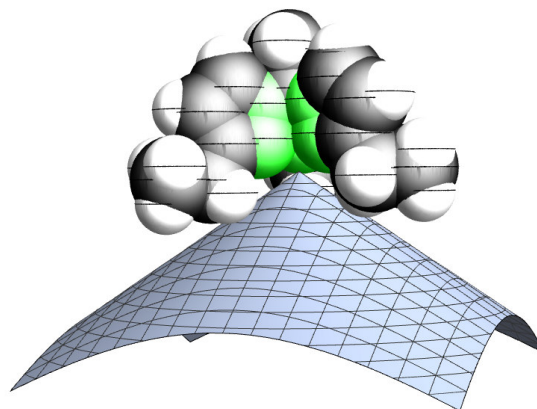
Cone axis = $\{-0.00734705, 0.157434, -0.987502\}$



Ligand atoms forming cone = {15, 26, 38}

Cone angle (deg) = 247.949

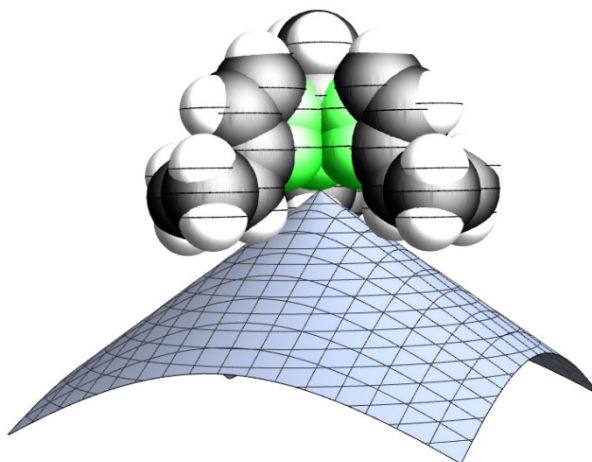
Cone axis = $\{0.395488, -0.110808, 0.911762\}$



Ligand atoms forming cone = {13, 26, 39}

Cone angle (deg) = 250.799

Cone axis = $\{0.15295, -0.986949, -0.0503766\}$

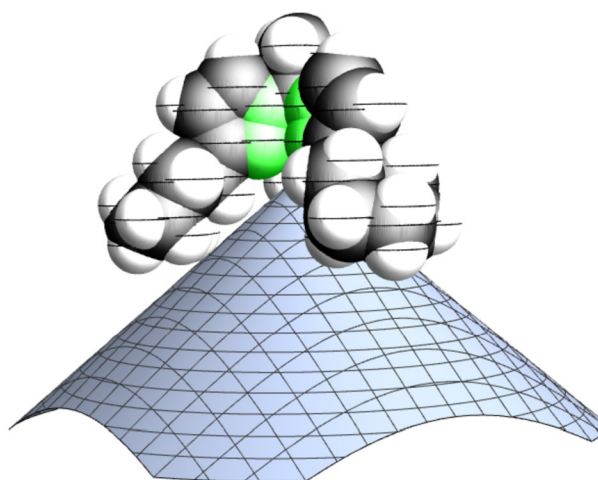


$[(\text{MeCTp}^{3\text{-Cy}})\text{Mg}(\text{AlMe}_4)]$ (**8**)

Ligand atoms forming cone = {20, 41, 58}

Cone angle (deg) = 260.64

Cone axis = {0.259263, -0.0918334, 0.961431}



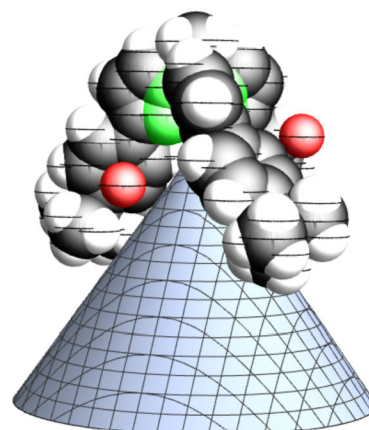
Because of the ample distance between two of the *p*-*t*BuPh substituents in complex **9** it was necessary to place two dummy germanium atoms between those substituents; otherwise the program would not find an appropriate cone.

$[(\text{MeCTp}^{3\text{-ptBuPh}})\text{Mg}(\text{AlMe}_4)][\text{AlMe}_4]_1$ (**9**)

Ligand atoms forming cone = {34, 78, 90}

Cone angle (deg) = 289.6

Cone axis = {0.862318, 0.272602, -0.426728}

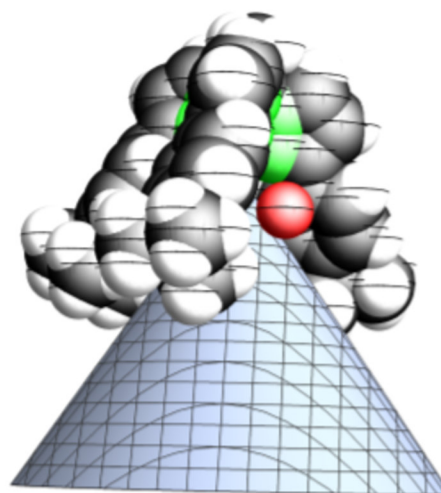


$[(\text{MeCTp}^{3\text{-ptBuPh}})\text{Mg}(\text{AlMe}_4)][\text{AlMe}_4]_2$ (**9**)

Ligand atoms forming cone = {34, 78, 87}

Cone angle (deg) = 291.336

Cone axis = {0.870764, 0.248934, -0.42403}

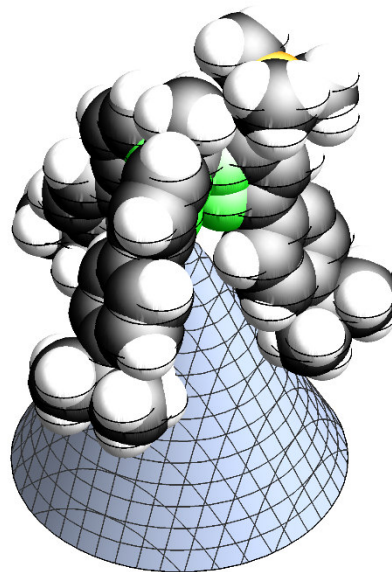


[MeC(pz3-p-tBuPh)2(pz3-p-tBuPh,5-AlMe3)]MgMe_10

Ligand atoms forming cone = {19, 54, 76}

Cone angle (deg) = 299.101

Cone axis = {0.282265, -0.854919, -0.435247}



Raw Data Files for Cone Angle Calculations

ComplexDataBase1.txt

(X1) [(AlMe3CTp-3-ptBuPh)2Mg]_4

1	Mg	16.549421	25.589250	9.767125
2	N	17.881427	25.590274	7.051083
3	N	18.153696	25.094866	8.318465
4	N	15.532675	25.128985	6.947942
5	N	15.163848	24.792571	8.235640
6	N	16.320824	27.362073	7.307372
7	N	16.364155	27.519362	8.679458
8	C	19.429747	24.676908	8.273146
9	C	19.987934	24.934165	7.004201
10	H	20.877416	24.756746	6.719782
11	C	18.986882	25.492352	6.271276
12	H	19.052050	25.766669	5.363324
13	C	20.152046	24.009540	9.379565
14	C	19.525963	23.338078	10.410974
15	H	18.581207	23.238451	10.389096
16	C	20.233932	22.805822	11.478325
17	H	19.765137	22.354769	12.170619
18	C	21.614045	22.918756	11.554900
19	C	22.261965	23.532898	10.482860
20	H	23.211156	23.583053	10.484423
21	C	21.555361	24.078461	9.407695
22	H	22.023815	24.497442	8.695085
23	C	22.416865	22.459514	12.773837
24	C	22.917732	23.709293	13.531766
25	H	23.456812	23.429517	14.300634
26	H	22.150055	24.231314	13.842751
27	H	23.463636	24.258609	12.931674
28	C	21.549560	21.689448	13.777116
29	H	22.081817	21.464263	14.567862
30	H	21.222018	20.863769	13.359864
31	H	20.785295	22.245588	14.044344
32	C	23.572817	21.580267	12.378464
33	H	24.060719	21.300492	13.181712
34	H	24.176723	22.081817	11.789311
35	H	23.238451	20.788707	11.906516
36	C	14.113666	23.964162	8.101244
37	C	13.821266	23.764566	6.730721
38	H	13.135815	23.221391	6.360352
39	C	14.737702	24.517231	6.057180
40	H	14.800822	24.596387	5.113285
41	C	13.359294	23.352750	9.206101
42	C	13.314940	23.904113	10.484423
43	H	13.719250	24.749923	10.643822
44	C	12.687150	23.234698	11.534584
45	H	12.685444	23.627408	12.400342
46	C	12.064478	22.007779	11.347055

47	C	12.052878	21.500088	10.045293
48	H	11.603872	20.679526	9.873391
49	C	12.680326	22.161655	8.987318
50	H	12.641090	21.795217	8.112183
51	C	11.469784	21.170498	12.489418
52	C	11.743760	21.791805	13.842751
53	H	11.358215	21.228842	14.544421
54	H	11.341156	22.682311	13.880257
55	H	12.712739	21.863455	13.977147
56	C	12.112245	19.758313	12.442536
57	H	11.753996	19.212409	13.172335
58	H	13.084637	19.840198	12.539426
59	H	11.904119	19.335237	11.583029
60	C	9.978784	21.020716	12.283136
61	H	9.590851	20.539638	13.042628
62	H	9.812624	20.519167	11.458010
63	H	9.566968	21.907810	12.215939
64	C	16.161829	28.832261	8.898242
65	C	15.974175	29.508500	7.680867
66	H	15.807333	30.437560	7.560536
67	C	16.079944	28.562038	6.711968
68	H	15.998399	28.711139	5.777450
69	C	16.135899	29.501676	10.231259
70	C	15.352526	30.625556	10.381282
71	H	14.855413	30.956169	9.640543
72	C	15.281559	31.288147	11.614284
73	H	14.753056	32.075272	11.692421
74	C	15.979634	30.807751	12.736331
75	C	16.792348	29.690695	12.537863
76	H	17.301745	29.362811	13.267663
77	C	16.881058	29.049599	11.326740
78	H	17.451868	28.294887	11.231412
79	C	15.859876	31.459424	14.117793
80	C	17.240331	31.942208	14.586615
81	H	17.144798	32.440345	15.424244
82	H	17.632699	32.522231	13.902135
83	H	17.823766	31.167706	14.733513
84	C	14.889532	32.604116	14.167801
85	H	14.838353	32.948718	15.083566
86	H	14.002438	32.293633	13.884945
87	H	15.193191	33.317203	13.566146
88	C	15.350138	30.393205	15.136700
89	H	15.309195	30.792397	16.032150
90	H	15.964280	29.628940	15.146076
91	H	14.456220	30.089546	14.872597
92	C	16.588999	26.101035	6.615078
93	C	17.021628	24.624023	3.642747
94	H	17.700937	24.726039	2.944202
95	H	16.209937	24.238138	3.253625
96	H	17.359747	24.030012	4.344417
97	C	18.024385	27.789243	4.083440

98	H	17.670230	28.489365	3.494287
99	H	18.792745	27.360026	3.652123
100	H	18.304844	28.189118	4.932007
101	C	14.775233	27.071721	3.984987
102	H	14.387982	26.507051	3.281754
103	H	14.828117	27.998051	3.669314
104	H	14.210564	27.029072	4.785110
105	Al	16.601282	26.418683	4.428961
0				

(X2) [(MeCTp3-Et)2Mg][AlMe4]2_5a

1	Mg	4.137628	6.038048	0.000000
2	N	4.086232	5.393307	2.977860
3	N	3.268001	5.398417	1.878453
4	N	5.864076	6.882195	2.380492
5	N	5.296724	7.387616	1.238442
6	N	6.021866	4.548128	1.847149
7	N	5.680649	4.641693	0.523066
8	C	2.024768	5.274417	2.363836
9	C	2.046068	5.228883	3.765648
10	H	1.298454	5.162812	4.348249
11	C	3.364102	5.297939	4.122391
12	H	3.709871	5.281894	5.007397
13	C	0.834088	5.135950	1.461583
14	H	0.540432	4.190979	1.462410
15	H	1.104938	5.365203	0.537477
16	C	-0.345004	6.017990	1.862506
17	H	-0.114697	6.958786	1.715202
18	H	-0.551263	5.876803	2.810238
19	H	-1.126979	5.784173	1.319477
20	C	5.769926	8.634976	1.123623
21	C	6.630968	8.927930	2.195860
22	H	7.093378	9.743032	2.350724
23	C	6.667941	7.801400	2.972071
24	H	7.163649	7.684399	3.774153
25	C	5.409066	9.497735	-0.050558
26	H	4.657112	9.076058	-0.536296
27	H	6.181727	9.533512	-0.667417
28	C	5.014042	10.918345	0.322250
29	H	4.788814	11.418217	-0.490226
30	H	5.762741	11.356709	0.778456
31	H	4.236894	10.895462	0.917846
32	C	6.276276	3.604640	-0.080917
33	C	6.995524	2.846615	0.855475
34	H	7.505253	2.062946	0.686317
35	C	6.812616	3.465928	2.060250
36	H	7.173176	3.190041	2.894108
37	C	6.123972	3.339423	-1.548997
38	H	6.245302	4.187686	-2.044776
39	H	5.204931	3.015574	-1.724652

40	C	7.122919	2.310706	-2.071118
41	H	6.999633	2.196255	-3.037041
42	H	6.976144	1.453669	-1.618338
43	H	8.034685	2.622096	-1.893573
44	C	5.543912	5.524520	2.833981
45	C	6.209874	5.255059	4.170586
46	H	5.965057	4.358357	4.482914
47	H	5.912154	5.921387	4.824300
48	H	7.182721	5.310561	4.068289
0				

(X3) [MeCTp-3-cyPrMe(thf)2][AlMe4]_6

1	Mg	4.708899	6.565086	10.130630
2	C	5.211565	3.259387	9.986026
3	C	4.239381	5.191196	7.171404
4	C	5.451727	1.752426	9.911428
5	H	5.662178	1.410151	10.805164
6	H	6.202559	1.570028	9.307475
7	H	4.645905	1.308410	9.572870
8	C	4.245122	3.922925	6.566017
9	H	4.017725	3.722824	5.665108
10	C	4.638475	3.041366	7.517135
11	H	4.737554	2.102636	7.409542
12	C	3.894021	6.502473	6.594708
13	H	3.992083	7.286766	7.207268
14	C	2.773956	6.590544	5.594814
15	H	2.315335	5.750256	5.340896
16	H	2.189548	7.389254	5.626375
17	C	4.140269	6.774541	5.150098
18	H	4.421158	7.688749	4.896180
19	H	4.547854	6.050993	4.610701
20	C	2.642720	4.728038	11.918389
21	C	2.386700	3.388364	12.235428
22	H	1.701702	3.053368	12.802082
23	C	3.323822	2.665218	11.562616
24	H	3.410958	1.719754	11.561181
25	C	1.933570	5.927128	12.390362
26	H	2.159294	6.777393	11.914085
27	C	1.607551	6.067961	13.845013
28	H	1.867119	5.327137	14.448966
29	H	1.662742	6.971338	14.245258
30	C	0.528296	5.812334	12.868073
31	H	-0.090504	6.555928	12.661495
32	H	0.113572	4.912970	12.865203
33	C	7.707010	5.537010	11.059083
34	C	8.446649	4.349842	11.179586
35	H	9.345055	4.262176	11.473673
36	C	7.616065	3.360850	10.792253
37	H	7.828534	2.436765	10.759258
38	C	8.119874	6.919418	11.351734

39	H	7.413214	7.616025	11.228362
40	C	9.124883	7.191543	12.453483
41	H	9.005428	8.011886	12.994315
42	H	9.487009	6.415331	12.949843
43	C	9.521564	7.350286	11.026088
44	H	10.132931	6.674294	10.640189
45	H	9.651349	8.270850	10.684660
46	N	4.864680	3.754221	8.651878
47	N	4.608084	5.091011	8.453908
48	N	4.104948	3.544228	10.898411
49	N	3.695526	4.834705	11.104989
50	N	6.424793	3.915478	10.457999
51	N	6.466683	5.278033	10.621540
0				

(X4) [(MeCTp-3-Cy)Mg(AlMe4)]_8

1	Mg	5.119677	6.696426	4.109222
2	C	4.109109	3.923116	5.437878
3	C	4.195710	3.314477	6.695870
4	H	3.807116	2.486727	6.953467
5	C	4.944032	4.138749	7.475850
6	H	5.171638	3.997892	8.387299
7	C	3.397426	3.432727	4.219121
8	H	3.625032	4.048322	3.463381
9	C	3.844865	2.018944	3.822866
10	H	4.821903	2.013727	3.662639
11	H	3.652788	1.391176	4.564432
12	C	3.123190	1.558117	2.567750
13	H	3.407419	0.634724	2.350005
14	H	3.378552	2.142411	1.811804
15	C	1.606561	1.587680	2.738249
16	H	1.170225	1.333790	1.885756
17	H	1.334545	0.935566	3.430514
18	C	1.162453	2.982334	3.144980
19	H	0.184305	2.982334	3.296991
20	H	1.354529	3.613580	2.407522
21	C	1.865254	3.460550	4.406259
22	H	1.613222	2.877995	5.166313
23	H	1.574363	4.383943	4.617842
24	C	8.349230	6.839369	4.466036
25	C	9.235226	6.938490	5.547778
26	H	10.174514	7.074130	5.503202
27	C	8.483573	6.802851	6.674917
28	H	8.805551	6.811545	7.567673
29	C	8.682311	6.867193	3.007965
30	H	7.828514	6.844586	2.487636
31	C	9.516124	5.642958	2.626089
32	H	10.341055	5.625568	3.173739
33	H	9.000959	4.820425	2.822471
34	C	9.891395	5.663825	1.143368

35	H	10.469846	4.886506	0.940824
36	H	9.069796	5.585572	0.595718
37	C	10.621953	6.943707	0.777309
38	H	11.491295	6.973270	1.248954
39	H	10.800707	6.954141	-0.197203
40	C	9.803684	8.164464	1.150352
41	H	8.974312	8.185332	0.610097
42	H	10.321070	8.983519	0.949040
43	C	9.440626	8.145335	2.639647
44	H	10.268887	8.202721	3.179902
45	H	8.881050	8.933089	2.853284
46	C	3.839314	8.986997	6.016341
47	C	3.778249	9.242626	7.392655
48	H	3.280848	9.927780	7.822394
49	C	4.573202	8.312277	7.992071
50	H	4.723089	8.213155	8.925499
51	C	3.165380	9.750405	4.924945
52	H	3.491799	9.400872	4.046774
53	C	1.634317	9.592159	4.975272
54	H	1.396720	8.637464	4.870508
55	H	1.299016	9.898217	5.856524
56	C	0.977038	10.400780	3.876275
57	H	-0.006662	10.313831	3.948172
58	H	1.251274	10.040813	2.995024
59	C	1.360081	11.875426	3.962552
60	H	0.959273	12.365816	3.200444
61	H	1.003684	12.263216	4.800665
62	C	2.864497	12.033672	3.931739
63	H	3.207570	11.738048	3.050487
64	H	3.095433	12.990106	4.042666
65	C	3.530659	11.228529	5.022519
66	H	3.250871	11.578062	5.905825
67	H	4.513248	11.329390	4.952676
68	C	6.016553	6.416799	7.129307
69	C	6.462882	6.262031	8.577312
70	H	7.104618	5.524708	8.644074
71	H	5.684582	6.069005	9.141190
72	H	6.887005	7.091520	8.878252
73	N	5.307091	5.198825	6.711071
74	N	4.785264	5.081096	5.445068
75	N	7.188998	6.651039	6.288112
76	N	7.091294	6.679036	4.908305
77	N	5.112793	7.554433	7.005644
78	N	4.656472	7.960657	5.776000
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(X5) [(MeCTp3-ptBuPh)Mg(AlMe4)][AlMe4]_9_1

1	Mg	15.170285	9.647016	5.566269
2	C	17.782064	10.312506	3.873413
3	C	18.987124	10.647287	3.014954

4	H	19.142422	9.923132	2.374136
5	H	19.776038	10.754069	3.586494
6	H	18.820017	11.481371	2.528938
7	C	16.903935	12.219406	6.737244
8	C	17.875075	13.082914	6.211991
9	H	18.176958	13.902008	6.585968
10	C	18.295548	12.504219	5.052665
11	H	18.967369	12.839740	4.469323
12	C	16.167986	12.287139	8.014741
13	C	15.525768	13.457854	8.415693
14	H	15.633941	14.257331	7.913277
15	C	14.726145	13.453598	9.552029
16	H	14.288059	14.255480	9.812280
17	C	14.549982	12.298798	10.322359
18	C	15.269298	11.168057	9.961717
19	H	15.218967	10.387642	10.501990
20	C	16.063006	11.163060	8.821089
21	H	16.542921	10.376538	8.589193
22	C	13.541417	12.301944	11.477547
23	C	13.906972	13.407517	12.474102
24	H	13.983120	14.262882	12.000960
25	H	14.763180	13.193213	12.900649
26	H	13.209062	13.474510	13.158141
27	C	13.511260	10.971889	12.226879
28	H	13.260239	10.254396	11.608592
29	H	12.856100	11.020561	12.954293
30	H	14.398602	10.787381	12.600242
31	C	12.136312	12.556777	10.903095
32	H	12.124488	13.420841	10.440682
33	H	11.481473	12.567696	11.633115
34	H	11.907060	11.844096	10.270554
35	C	17.609693	7.426618	5.922926
36	C	18.883271	7.218421	5.378975
37	H	19.475572	6.499448	5.566729
38	C	19.099848	8.256075	4.527565
39	H	19.882225	8.405607	4.011049
40	C	16.965164	6.598642	6.951514
41	C	16.152907	7.140694	7.944237
42	H	16.001699	8.078044	7.963856
43	C	15.564142	6.335111	8.901402
44	H	15.019056	6.730778	9.570115
45	C	15.752964	4.956754	8.906000
46	C	16.591163	4.428952	7.929370
47	H	16.755739	3.494008	7.916342
48	C	17.190357	5.231944	6.976497
49	H	17.765996	4.841274	6.330008
50	C	15.024779	4.077145	9.917575
51	C	14.498885	10.260133	2.483111
52	C	15.240279	10.070072	1.303399
53	H	14.896795	9.973099	0.423022
54	C	16.545484	10.054527	1.678908

55	H	17.293034	9.943489	1.102004
56	C	13.051433	10.497755	2.572926
57	C	12.532823	11.516348	3.360422
58	H	13.107912	11.993998	3.945143
59	C	11.188352	11.846132	3.305245
60	H	10.856665	12.539937	3.862378
61	C	10.312191	11.181197	2.450464
62	C	10.835428	10.148540	1.687951
63	H	10.258032	9.662191	1.109667
64	C	12.179106	9.806541	1.746040
65	H	12.504455	9.090344	1.213890
66	C	8.833713	11.584266	2.402798
67	C	8.695215	13.100125	2.223779
68	H	9.149205	13.374575	1.399346
69	H	9.101663	13.557789	2.988745
70	H	7.746283	13.337562	2.168756
71	C	8.098452	10.905822	1.250522
72	H	8.529509	11.144554	0.403097
73	H	7.165670	11.203775	1.238413
74	H	8.129543	9.934236	1.370225
75	C	8.175661	11.156768	3.719378
76	H	7.231329	11.420299	3.713707
77	H	8.633425	11.592409	4.469323
78	H	8.241825	10.184072	3.816397
79	N	17.580778	11.359043	4.881617
80	N	16.701954	11.176385	5.920321
81	N	17.992713	9.035565	4.553468
82	N	17.045359	8.529600	5.414073
83	N	16.591177	10.224601	3.018632
84	N	15.324792	10.321760	3.542812
85	C	13.957213	3.221964	9.016814
86	H	13.360540	3.840078	8.543212
87	H	13.426365	2.642714	9.602301
88	H	14.442338	2.674175	8.366953
89	C	14.167907	4.830170	10.897424
90	H	13.486962	5.337246	10.410028
91	H	14.726986	5.446434	11.413940
92	H	13.733275	4.195401	11.504369
93	C	15.945066	3.120179	10.523448
94	H	16.387620	2.602000	9.818410
95	H	15.446465	2.513169	11.108935
96	H	16.617129	3.601345	11.047627
97	Ge	14.045359	5.529600	5.414073
98	Ge	14.045359	14.52960	5.414073
0				

(X6) [(MeCTp3-ptBuPh)Mg(AlMe4)][AlMe4]_9_2

1	Mg	15.170285	9.647016	5.566269
2	C	17.782064	10.312506	3.873413
3	C	18.987124	10.647287	3.014954

4	H	19.142422	9.923132	2.374136
5	H	19.776038	10.754069	3.586494
6	H	18.820017	11.481371	2.528938
7	C	16.903935	12.219406	6.737244
8	C	17.875075	13.082914	6.211991
9	H	18.176958	13.902008	6.585968
10	C	18.295548	12.504219	5.052665
11	H	18.967369	12.839740	4.469323
12	C	16.167986	12.287139	8.014741
13	C	15.525768	13.457854	8.415693
14	H	15.633941	14.257331	7.913277
15	C	14.726145	13.453598	9.552029
16	H	14.288059	14.255480	9.812280
17	C	14.549982	12.298798	10.322359
18	C	15.269298	11.168057	9.961717
19	H	15.218967	10.387642	10.501990
20	C	16.063006	11.163060	8.821089
21	H	16.542921	10.376538	8.589193
22	C	13.541417	12.301944	11.477547
23	C	13.906972	13.407517	12.474102
24	H	13.983120	14.262882	12.000960
25	H	14.763180	13.193213	12.900649
26	H	13.209062	13.474510	13.158141
27	C	13.511260	10.971889	12.226879
28	H	13.260239	10.254396	11.608592
29	H	12.856100	11.020561	12.954293
30	H	14.398602	10.787381	12.600242
31	C	12.136312	12.556777	10.903095
32	H	12.124488	13.420841	10.440682
33	H	11.481473	12.567696	11.633115
34	H	11.907060	11.844096	10.270554
35	C	17.609693	7.426618	5.922926
36	C	18.883271	7.218421	5.378975
37	H	19.475572	6.499448	5.566729
38	C	19.099848	8.256075	4.527565
39	H	19.882225	8.405607	4.011049
40	C	16.965164	6.598642	6.951514
41	C	16.152907	7.140694	7.944237
42	H	16.001699	8.078044	7.963856
43	C	15.564142	6.335111	8.901402
44	H	15.019056	6.730778	9.570115
45	C	15.752964	4.956754	8.906000
46	C	16.591163	4.428952	7.929370
47	H	16.755739	3.494008	7.916342
48	C	17.190357	5.231944	6.976497
49	H	17.765996	4.841274	6.330008
50	C	15.024779	4.077145	9.917575
51	C	14.498885	10.260133	2.483111
52	C	15.240279	10.070072	1.303399
53	H	14.896795	9.973099	0.423022
54	C	16.545484	10.054527	1.678908

55	H	17.293034	9.943489	1.102004
56	C	13.051433	10.497755	2.572926
57	C	12.532823	11.516348	3.360422
58	H	13.107912	11.993998	3.945143
59	C	11.188352	11.846132	3.305245
60	H	10.856665	12.539937	3.862378
61	C	10.312191	11.181197	2.450464
62	C	10.835428	10.148540	1.687951
63	H	10.258032	9.662191	1.109667
64	C	12.179106	9.806541	1.746040
65	H	12.504455	9.090344	1.213890
66	C	8.833713	11.584266	2.402798
67	C	8.695215	13.100125	2.223779
68	H	9.149205	13.374575	1.399346
69	H	9.101663	13.557789	2.988745
70	H	7.746283	13.337562	2.168756
71	C	8.098452	10.905822	1.250522
72	H	8.529509	11.144554	0.403097
73	H	7.165670	11.203775	1.238413
74	H	8.129543	9.934236	1.370225
75	C	8.175661	11.156768	3.719378
76	H	7.231329	11.420299	3.713707
77	H	8.633425	11.592409	4.469323
78	H	8.241825	10.184072	3.816397
79	N	17.580778	11.359043	4.881617
80	N	16.701954	11.176385	5.920321
81	N	17.992713	9.035565	4.553468
82	N	17.045359	8.529600	5.414073
83	N	16.591177	10.224601	3.018632
84	N	15.324792	10.321760	3.542812
85	C	13.543348	4.158573	9.674491
86	H	13.343218	3.841929	8.768518
87	H	13.246659	5.087409	9.767831
88	H	13.073769	3.599495	10.327263
89	C	15.483384	2.619766	9.870522
90	H	15.287250	2.242976	8.987692
91	H	15.007865	2.106028	10.557167
92	H	16.448453	2.576091	10.037585
93	C	15.324651	4.604762	11.356771
94	H	16.285723	4.545172	11.533490
95	H	14.837392	4.062155	12.011689
96	H	15.036793	5.538966	11.429267
97	Ge	14.045359	5.529600	5.414073
98	Ge	14.045359	14.52960	5.414073

0

(X7) [MeC(pz3-p-tBuPh)2(pz3-p-tBuPh,5-AlMe3)]MgMe_10

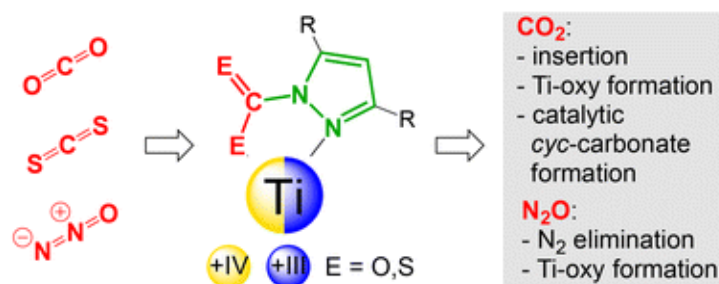
1	Mg	9.921594	8.286851	3.133050
2	C	8.417664	5.660597	4.305021
3	C	8.382184	4.288323	3.995550
4	H	7.791439	3.635323	4.352237

5	C	9.371052	4.090964	3.078822
6	H	9.599875	3.263743	2.670868
7	C	7.567657	6.396576	5.255252
8	C	8.088728	7.372256	6.107156
9	H	9.009313	7.600056	6.055421
10	C	7.276022	8.007094	7.023416
11	H	7.652494	8.672203	7.587197
12	C	5.914725	7.703973	7.149324
13	C	5.408377	6.742751	6.275293
14	H	4.485902	6.522657	6.317210
15	C	6.210098	6.101426	5.348904
16	H	5.830854	5.451754	4.769852
17	C	5.056161	8.428448	8.189778
18	C	4.932609	9.907281	7.788837
19	H	5.823607	10.315855	7.767956
20	H	4.373384	10.377476	8.441127
21	H	4.522626	9.971945	6.901560
22	C	5.718747	8.333469	9.577570
23	H	5.811097	7.391227	9.831100
24	H	5.161466	8.796617	10.237807
25	H	6.603970	8.752285	9.545937
26	C	3.647985	7.841400	8.294806
27	H	3.183297	7.951100	7.439162
28	H	3.151443	8.308562	8.998986
29	H	3.707591	6.887977	8.514365
30	C	9.375715	8.117982	-0.052358
31	C	9.804578	7.298279	-1.100603
32	H	9.659020	7.436189	-2.028862
33	C	10.475375	6.260948	-0.521240
34	H	10.886985	5.533590	-0.973916
35	C	8.622568	9.383676	-0.123726
36	C	7.622311	9.696517	0.785210
37	H	7.391630	9.071692	1.463212
38	C	6.954163	10.911489	0.716179
39	H	6.271081	11.103115	1.347900
40	C	7.266347	11.859664	-0.262879
41	C	8.247067	11.516575	-1.193008
42	H	8.464046	12.129121	-1.887060
43	C	8.910606	10.307064	-1.128496
44	H	9.573005	10.101677	-1.777981
45	C	6.541507	13.215055	-0.289058
46	C	7.241154	14.218992	-1.211708
47	H	7.216311	13.888002	-2.133266
48	H	8.173589	14.327658	-0.928727
49	H	6.781938	15.082604	-1.162466
50	C	5.103275	12.988941	-0.779289
51	H	4.621887	13.842600	-0.782250
52	H	4.649209	12.360291	-0.180759
53	H	5.121634	12.620281	-1.687602
54	C	6.504473	13.819286	1.123821
55	H	6.075281	14.699939	1.090786

56	H	7.418869	13.913701	1.463212
57	H	5.994936	13.229837	1.718767
58	C	13.033777	7.896159	3.677508
59	C	13.959437	6.858621	3.556430
60	H	14.835337	6.861638	3.923714
61	C	13.406559	5.822987	2.818591
62	C	13.229096	9.217318	4.301593
63	C	14.083085	9.345482	5.398301
64	H	14.479687	8.568918	5.776492
65	C	14.360884	10.590262	5.943538
66	H	14.934502	10.648096	6.698985
67	C	13.818501	11.757590	5.410299
68	C	12.961925	11.618629	4.321383
69	H	12.567397	12.394511	3.940855
70	C	12.671090	10.375199	3.778016
71	H	12.080719	10.315435	3.035502
72	C	14.181398	13.126704	6.017244
73	C	13.619855	14.288651	5.191051
74	H	13.959977	14.231853	4.274324
75	H	13.900333	15.139385	5.591058
76	H	12.641426	14.238650	5.179676
77	C	15.710660	13.280231	6.058382
78	H	16.064349	13.270577	5.145394
79	H	16.099315	12.538863	6.568091
80	H	15.942207	14.130076	6.488619
81	C	13.618418	13.196600	7.441187
82	H	12.646584	13.068737	7.415788
83	H	13.822427	14.072569	7.830286
84	H	14.025449	12.492536	7.987671
85	C	15.108049	4.341268	0.387229
86	H	14.529338	3.731529	-0.118428
87	H	16.045593	4.085857	0.255556
88	H	14.972436	5.258762	0.070122
89	C	13.913540	2.467293	2.903829
90	H	13.456317	2.042396	2.148849
91	H	13.276472	2.604234	3.635434
92	H	14.643813	1.890829	3.210028
93	C	16.275303	4.637599	3.420550
94	H	16.964830	3.964643	3.242751
95	H	16.039471	4.622044	4.370936
96	H	16.616778	5.525188	3.183537
97	C	11.036966	5.601911	1.876152
98	C	11.538290	4.320346	1.246924
99	H	10.810803	3.894717	0.747968
100	H	11.851675	3.711867	1.949391
101	H	12.278709	4.523230	0.637331
102	N	9.970508	5.285718	2.853652
103	N	9.380580	6.270687	3.603334
104	N	10.445146	6.460343	0.821985
105	N	9.769407	7.609831	1.126626
106	N	12.137397	6.296436	2.545116

107	N	11.885647	7.556082	3.069316
108	Al	14.655052	4.233154	2.327582
0				

Reactivity of titanium pyrazolates towards CO₂, CS₂ and N₂O



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The tetravalent titanium pyrazolate Ti(pz^{Me₂})₄ inserts two molecules of carbon dioxide instantly at ambient temperature and 1 bar heteroallene, forming the complex Ti(CO₂·pz^{Me₂})₂(pz^{Me₂})₂ (pz^{Me₂} = 3,5-dimethylpyrazolato). CO₂ insertion is reversible as proven by thermogravimetric analysis (TGA). Solid Ti(CO₂·pz^{Me₂})₂(pz^{Me₂})₂ exhibits an exceptionally high stability at ambient atmosphere but converts in solution over time *via* deoxygenation into the oxo-bridged species [Ti(CO₂·pz^{Me₂})₂(pz^{Me₂})₂](μ-O) and [Ti(μ-O)₂(μ-pz^{Me₂})₄](Ti{CO₂·pz^{Me₂}}(pz^{Me₂}))₂]. Treatment of Ti(pz^{Me₂})₄ with CS₂ results in a mono-insertion to Ti(CS₂·pz^{Me₂})(pz^{Me₂})₃, which is reversible at 110 °C. Applying similar conditions, trivalent Ti(pz^{tBu₂})₃ inserts also two molecules of CO₂ to afford Ti(CO₂·pz^{tBu₂})₂(pz^{tBu₂}) displaying complete de-insertion at 70 °C. At elevated temperatures compound Ti(CO₂·pz^{tBu₂})₂(pz^{tBu₂}) does neither display redox activity nor engages in a deoxygenation reaction. While tetravalent Ti(pz^{Me₂})₄ does not react with N₂O under ambient conditions, trivalent Ti(pz^{tBu₂})₃ converts into oxo-bridged [Ti(pz^{tBu₂})₃](μ-O) *via* initial N₂O insertion and subsequent fast release of N₂.

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Introduction

The rapidly rising greenhouse gas emissions and concomitant record-high concentrations in the Earth's atmosphere are the primary cause for the anthropogenic global climate change, with carbon dioxide (CO₂) having the greatest impact, followed by methane (CH₄) and nitrous oxide (N₂O).^{1–13} Although the concentration of N₂O (337.69 ppb, 2024) is relatively low when compared to CO₂ (427 ppm, 2024; 50% increase since start of industrialization), its global warming potential is 300 times stronger, contributing 6% to the anthropogenic greenhouse effect.^{1,12,13} The activation of these small, mostly inert molecules leading to their capture, conversion, storage, and ultimately climate change mitigation, has become a major focus of research in the past decades. For the development of efficient capture materials, a fundamental understanding of the activation of such small molecules by metal centres is crucial. In particular, amine-functionalized and M–N(ligand) components/materials feature efficient systems for CO₂ capture and valorization.^{14,15}

Titanium is attractive as a sustainable metal, not only because it is affordable and non-toxic, but also because of its high abundance in the Earth's crust. Already in the 1970s, CO₂ insertion into the Ti–N bond of tetravalent Ti(NMe₂)₄ under formation of carbamate complex Ti(CO₂·NMe₂)₄ was reported. However, such carbamate complexes were structurally elucidated only three decades later.^{16–18} Similar examples exist for trivalent titanium complexes.^{19–21} In addition, a twofold addition of CO₂ across the Ti=N double bond of the tetravalent imide complex (C₅Me₅)Ti(=NAr)(L) (Ar = 2,6-C₆H₃Me₂; L = (NiPr₂)₂CR; R = Me, Ph) was achieved resulting in (C₅Me₅)Ti({CO₂})₂·NAr(L).^{22,23} For sterically less demanding imido ligands, the mono-inserted congener (C₅Me₅)Ti(CO₂·NtBu)(L) (L = (NR¹)₂CR²; R¹ = SiMe₃, *i*Pr; R² = Ph, Me) was shown to rapidly deoxygenate CO₂ under formation of the oxo-bridged dimer [(C₅Me₅)Ti(L)(μ-O)]₂ and elimination of the corresponding isocyanate (Scheme 1A).

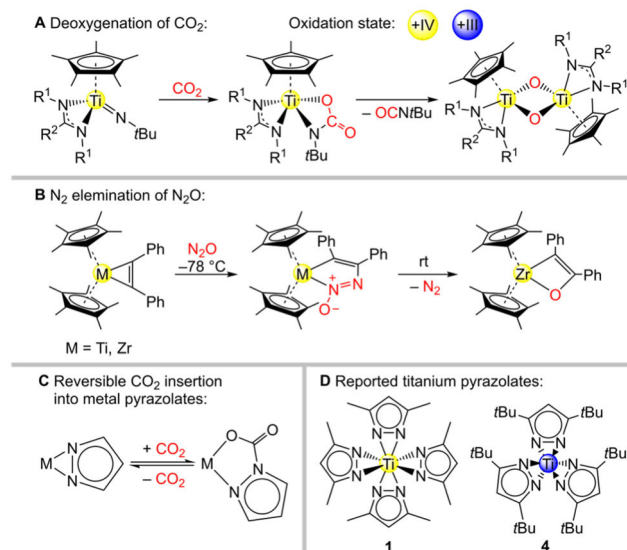
Light-induced deoxygenation of CO₂ is feasible on a TiO₂ surface in the presence of H₂O under formation of CH₄, CH₃OH, H₂ and O₂,^{24,25} whereas CO₂ deoxygenation reactions were also observed for divalent and trivalent titanium compounds.^{26,27}

The activation of N₂O with trivalent titanocene complex (Cp₂TiCl)₂ has been reported, proceeding *via* slow oxidation of the titanium centre under formation of oxo-bridged species [Cp₂TiCl]₂O and elimination of N₂.^{28–31} Only a few examples of N₂O-inserted compounds prior to N₂ elimination have been reported,^{28,30} including azoxymetallacylopentene complex (C₅Me₅)₂Ti(N{O})NCPPhCPh obtained from (C₅Me₅)₂Ti(PhCCPh) (Scheme 1B).²⁸

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†Electronic supplementary information (ESI) available: Supporting figures, detailed crystallographic data, spectroscopic data (NMR, IR), analytical details. CCDC 2423931–2423936. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5dt00957j>



Scheme 1 A: addition of CO₂ across a Ti=N bond and subsequent deoxygenation;²² B: N₂O insertion into titanium/zirconium complexes and subsequent N₂ elimination;²⁸ C: reversible CO₂ insertion into metal pyrazolates;^{32–34} D: literature-known tetra- and trivalent homoleptic titanium pyrazolate complexes.^{35,36}

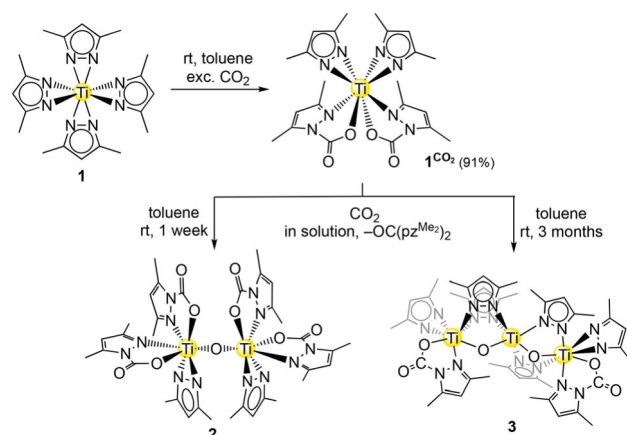
Recently, we found that homoleptic metal pyrazolates [M(pz^{R,R'})_x] insert CO₂ readily and reversibly, forming the corresponding carbamate complexes (see Scheme 1C).³² Structurally characterized examples comprise redox-active Ce(CO₂·pz^{Me₂})₄, the tetranuclear cluster [Ce(CO₂·pz^{Me₂})₃]₄, and the light metal derivatives Mg(CO₂·pz^{tBu₂})₂(thf)₂, Al(CO₂·pz^{tBu₂})₂(pz^{tBu₂})₂ and [Sc(μ-CO₂·pz^{tBu₂})(pz^{tBu₂})₂]₂.^{33,34} Using unsubstituted [Mg(pz)₂]_n, exceptionally high reversible CO₂ capacities of up to 35.7 wt% have been achieved, highlighting its potential as an efficient CO₂ capture material. Spurred by these findings, we envisaged the reactivity of pyrazolate complexes of the light metal titanium toward both carbon dioxide, CS₂ and N₂O. Homoleptic complexes, tetravalent Ti(pz^{Me₂})₄ (**1**) and trivalent Ti(pz^{tBu₂})₃ (**4**), previously reported by Winter and Mösch-Zanetti, respectively, were chosen as discrete precursors (see Scheme 1D).^{35,36}

Results and discussion

CO₂ activation with tetravalent Ti(pz^{Me₂})₄

Exposure of tetravalent Ti(pz^{Me₂})₄ (**1**) to a 1 bar CO₂ atmosphere in benzene or toluene gave the twofold inserted carbamate complex Ti(CO₂·pz^{Me₂})₂(pz^{Me₂})₂ (**1**^{CO₂}) (Scheme 2). The insertion reaction occurred instantly, as monitored by an immediate colour change of the solution from yellow to orange. The CO₂ uptake of complex **1**^{CO₂} equals a mass fraction of 17.0 wt% CO₂ or 3.8 mmol CO₂ per gram.

A single crystal X-ray diffraction (SCXRD) analysis of **1**^{CO₂} revealed two distinct molecules in the unit cell with slightly varying metrical parameters. The four ligands of **1**^{CO₂} arrange in a distorted square planar geometry, with the *cis*-positioned



Scheme 2 Reaction of Ti(pz^{Me₂})₄ (**1**) with an excess of CO₂ and subsequent deoxygenation in solution affording oxo-bridged species.

carbamato ligands coordinated in the κ²(N,O) mode (Fig. 1). The pyrazolato ligands are tilted out of the plane spanned by the titanium centre and the two coordinating nitrogen atoms, by 26.6° and 18.9°, respectively. The inserted CO₂ exhibits localized C–O single (1.275(3)–1.277(3) Å) and double bonds (1.205(3)–1.207(3) Å) and OCO angles ranging from 128.5(2) to 129.0(3)°. The loss of aromaticity of the pyrazole ring of the carbamate ligand is indicated by distinct C–C and C–N double/single bonds. Additional CO₂ insertion into **1**^{CO₂} is most likely impeded by the coordinative saturation of the small titanium centre, and would cause unfavourable tilting and hence significant steric interference of newly formed carbamate ligands. Fourfold inserted Ce(CO₂·pz^{Me₂})₄ clearly supports the size-determining influence of the metal centre for CO₂ insertion (effective ionic radii for 6-coordination: Ti⁴⁺ 0.605, Ce⁴⁺ 0.87 Å).³⁷ Although an electronic effect caused by saturation of the titanium centre with two oxygen atoms might play a role as well, this is opposed by the comparatively higher oxophilicity of titanium (θ = 1.0) versus cerium (θ = 0.9).³⁸

Formation of the twofold inserted complex **1**^{CO₂} was confirmed by solution NMR spectroscopy. The ¹H NMR spectrum

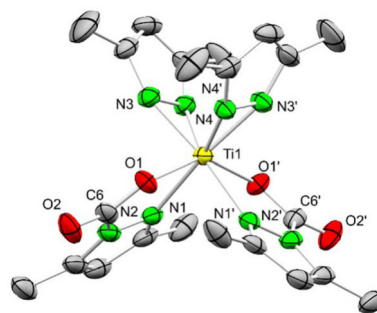


Fig. 1 Crystal structure of Ti(CO₂·pz^{Me₂})₂(pz^{Me₂})₂ (**1**^{CO₂}). Ellipsoids are set at the 50% probability level. Hydrogen, lattice toluene and a second molecule of **1**^{CO₂} are omitted for clarity. See ESI† for selected interatomic distances and angles.

shows three methyl group signals at $\delta = 2.62$, 2.21 and 2.17 ppm with an integral of 6, 6 and 12 protons, respectively. The two signals at lower field can be assigned to the distinct methyl groups of the two carbamate ligands, caused by CO₂ insertion. The third signal is attributed to the magnetically equal methyl groups of the two unchanged pyrazolato ligands. Further, two signals for the ring protons at $\delta = 5.72$ and 5.00 ppm were detected. The ¹³C NMR spectrum is consistent with the ¹H NMR spectrum and a signal for the inserted CO₂ could be resolved at $\delta = 150.5$ ppm *via* experiments with labelled ¹³CO₂ (see Fig. S4†). A diffuse reflectance infrared Fourier transform (DRIFT) measurement revealed a strong band at $\tilde{\nu} = 1740$ cm⁻¹ assigned to the C=O stretching vibration. The CO₂ uptake was corroborated by a thermogravimetric analysis (TGA) showing a CO₂ releasing step of 17.5% between 90–150 °C which is in good agreement with the aforementioned calculated uptake of 17.0 wt%. When solid **1** is exposed to an atmosphere of 1 bar CO₂ a colour change of the powder from yellow to orange was observed. The orange product was identified as **1**^{CO₂} by ¹H NMR spectroscopy. This can be further interpreted as a fully reversible CO₂ insertion process in the solid state of compound **1**. Application of higher CO₂ pressure of up to 10 bar did not lead to any additional insertion of CO₂ but only the formation of **1**^{CO₂}. The combination of the small titanium(IV) centre and the steric bulk of the pyrazolato ligand seem to suppress further insertion reactions.

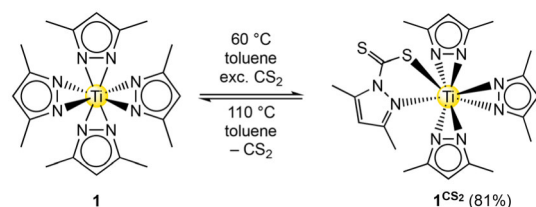
Strikingly, different to our previous studies on magnesium, aluminium and rare-earth-metal pyrazolates, solid **1**^{CO₂} remained stable under ambient atmosphere. After one month only small amounts of the hydrolysis product HOOCpz^{Me₂} were observed in the ¹H NMR spectrum and the solid kept its orange colour (Fig. S6†). In stark contrast, decomposition of **1**^{CO₂} readily occurred in solution, both under an argon or CO₂ atmosphere (Fig. S7†). Overnight a new signal set appeared in the ¹H NMR spectrum which accumulated over time and after one week only a minor amount of **1**^{CO₂} was left. The observed decomposition is reproducible at ambient temperature. The obtained solution provided access to crystals suitable for a SCXRD analysis, which revealed the formation of the oxo-bridged bimetallic complex [Ti(CO₂·pz^{Me₂})₂(pz^{Me₂})₂(μ-O)] (**2**) (Scheme 2 and Fig. S35†). Each titanium centre of **2** is coordinated by two terminal carbamate and one terminal pyrazolato ligand. However, NMR experiments showed the presence of more than one species ruling out a clear signal assignment to **2**. Further, after three months morphologically different crystals formed in the same solution and could be identified by a SCXRD measurement as the oxo-bridged trimetallic complex [Ti(μ-O)₂(μ-pz^{Me₂})₄(Ti{CO₂·pz^{Me₂}}{pz^{Me₂}})₂] (**3**, Scheme 2 and Fig. S36†). The central titanium of **3** is bridged by one oxo and two pyrazolato ligands in the μ-N,N mode to each of the outer titanium atoms. The coordination sphere of the outer titanium centres is completed by one terminal pyrazolato ligand in the κ²(N,N) mode and one carbamate ligand in the κ²(N,O) mode. The Ti–O(oxo) interatomic distances of **2** and **3** range from 1.790(2) to 1.8199(12) Å with one exception

for the inner titanium centre of **3** which is slightly elongated (1.8465(12) Å). The latter is comparable with the reported bis-oxo [(C₅Me₅)Ti((NSiMe₃)₂CPh)(μ-O)]₂ (1.8429(13)–1.8604(12) Å) and mono-oxo [(C₅H₄Me)₂TiCl]₂O (1.837(2) Å).^{23,39} Similarly, the Ti–O(carbamate) interatomic distances of oxo-bridged **2** and **3** are slightly shorter (1.9930(18)–2.0286(19) Å) than in oxo-free **1**^{CO₂} (2.0445(18)–2.0484(16) Å), with again one exception detected for **3** (2.0437(13) Å).

Decomposition of **1**^{CO₂} was not observed when the solution is kept at 0 °C. Deoxygenation of inserted CO₂ or hydrolysis and a subsequent dissociation of pyrazole/carbamic acid are likely decomposition pathways of **1**^{CO₂} (Fig. S42†), which would result in oxo complexes like **2** and **3**. Note that single-crystalline **1**^{CO₂} was obtained after three years at –40 °C, while the corresponding ¹H NMR spectrum revealed that it remained stable during this time span. This makes a hydrolysis pathway highly unlikely. However, reactions of titanium compounds with CO₂ involving a deoxygenation process and subsequent formation of oxo bridges have been reported previously.²² Unfortunately, conclusive organic co-products of a putative deoxygenation reaction involving **1**^{CO₂} could not be identified by ¹³C NMR spectroscopy, even when labelled ¹³CO₂ was used. The formation of CO was not observed. Mass spectrometry experiments revealed a [M + H]⁺-fragment of 219.16 g mol⁻¹ which fits well to the urea derivative OC(pz^{Me₂})₂ (219.12 g mol⁻¹). This is in good agreement with the displacement of two pz^{Me₂}-moieties upon the formation of **2**. Experiments in amber glass NMR tubes showed the same decomposition pattern, excluding a light-induced mechanism. The elongation of the titanium-oxo chain indicates that this decomposition pathway might ultimately lead to the formation of titania, TiO₂. However, it has remained unclear whether trimetallic **3** is formed *via* bimetallic **2**.

CS₂ activation with tetravalent Ti(pz^{Me₂})₄

To examine the feasibility of a sulfido-bridged compound similar to complexes **2** or **3**,⁴⁰ **1** was reacted with an excess of CS₂. ¹H NMR monitoring at ambient temperature indicated a rather slow conversion which was not complete even after several weeks. Therefore, the reaction was conducted at 60 °C affording full conversion to the mono-inserted complex Ti(CS₂·pz^{Me₂})(pz^{Me₂})₃ (**1**^{CS₂}) after five days (Scheme 3). The thio-carbamate ligand coordinates to the metal centre in the κ²(N,S) mode similar to the carbamate ligand in complex **1**^{CO₂} (Fig. 2). The C–S interatomic distances of the inserted CS₂ moiety reveal



Scheme 3 Reaction of Ti(pz^{Me₂})₄ (**1**) with an excess of CS₂.



localized double and single bonds of 1.6543(19) Å and 1.7019(19) Å, respectively, forming an angle of 121.64(12)°.

Accordingly, the degree of electron delocalization is comparatively larger in **1**^{CS₂} ($\Delta_{\text{C-S}}$ 0.0476 Å) than in **1**^{CO₂} ($\Delta_{\text{C-O}}$ 0.068–0.072 Å). An additional insertion of CS₂ seems disfavoured for steric reasons considering the larger size of the sulphur atoms. Moreover, the HSAB mismatch according to Pearson, the low thiophilicity of titanium ($S = 0.0$),³⁸ and changed electrophilicity of the heteroallene will counteract a second insertion.

At ambient temperature, the ¹H NMR spectrum of **1**^{CS₂} shows the thiocarbamato ligand as sharp signals, with the aromatic backbone proton resonating at $\delta = 5.05$ ppm and distinct methyl groups at $\delta = 2.38$ and 2.36 ppm. In the aromatic region two broad signals appeared at $\delta = 5.75$ and 5.61 ppm in a 2 : 1 integral ratio, while the remaining methyl groups gave one broad signal. The integral ratios of the aromatic protons indicate that the pyrazolato ligands positioned *trans* and *cis* to the thiocarbamato ligand are magnetically unequal. Correspondingly, a variable temperature (VT) ¹H NMR experiment at –60 °C revealed a sharpening of the broadened resonances resulting in three distinct signals sets with an integral ratio of 1 : 1 : 2, assigned to the thiocarbamato ligand, the *trans*- and the two *cis*-positioned pyrazolato ligands (Fig. S12†). The ¹³C signal of the inserted CS₂ is resolved at $\delta = 209.2$ ppm being consistent with the literature.⁴¹ In the DRIFT spectrum of **1**^{CS₂} vibrations characteristic of C–S double and single bonds are detected in the fingerprint region at $\tilde{\nu} = 1071$ and 895 cm^{–1}, respectively.^{42,43} A TGA experiment revealed a CS₂ releasing step of 14.8% between 110–180 °C, which is close to the theoretical value of 15.1%.

Any decomposition of **1**^{CS₂} could not be observed at ambient temperature, while heating to 110 °C led to de-insertion of CS₂ under full recovery of **1**. Again, this is most likely caused by the soft Lewis base character of sulphur, which also disfavours the formation of sulphido bridges. Crucially, complex **1** features a hard titanium(IV) centre featuring a significantly higher oxophilicity ($\theta = 1.0$) than thiophilicity ($S = 0.0$).³⁸

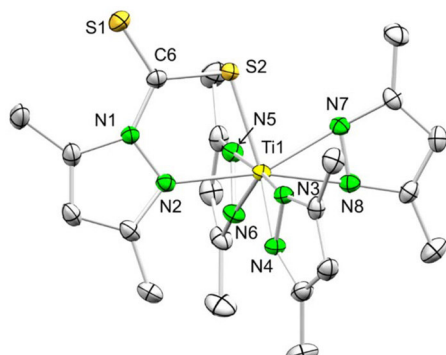
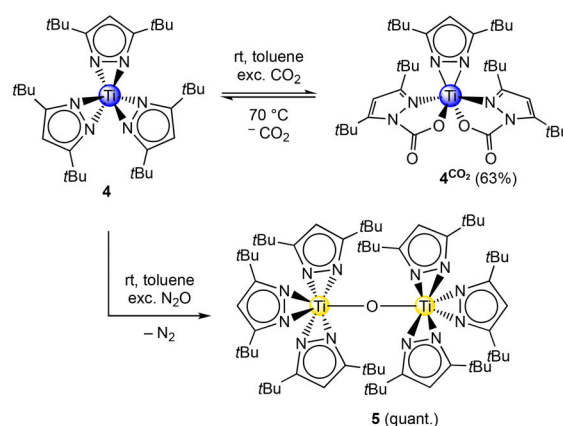


Fig. 2 Crystal structure of $\text{Ti}(\text{CS}_2 \cdot \text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_3$ (**1**^{CS₂}). Ellipsoids are set at the 50% probability level. Hydrogen atoms and one toluene lattice are omitted for clarity. See ESI† for selected interatomic distances and angles.

CO₂ and N₂O activation with trivalent $\text{Ti}(\eta^2\text{-pz}^{\text{tBu}_2})_3$

Exposure of trivalent $\text{Ti}(\text{pz}^{\text{tBu}_2})_3$ (**4**) to a 1 bar CO₂ atmosphere in toluene gave an immediate colour change of the solution from blue over green and yellow to finally red. An SCXRD analysis revealed the formation of the twofold-inserted titanium (III) complex $\text{Ti}(\text{CO}_2 \cdot \text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (**4**^{CO₂}) (Scheme 4). The CO₂ uptake of complex **4**^{CO₂} amounts to a mass fraction of 13.1 wt% CO₂ or 3.0 mmol CO₂ per gram.

Complex **4**^{CO₂} is isostructural to the aluminium complex $\text{Al}(\text{CO}_2 \cdot \text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ reported recently (Fig. 3).³⁴ Accordingly, two carbamato ligands in the $\kappa^2(\text{N,O})$ mode and one pyrazolato in the $\kappa^2(\text{N,N})$ mode adopt a propeller-like geometry with both stereoisomers (Λ, Δ) present in the unit cell. Another CO₂ insertion into the third pyrazolato ligand is impeded by the bulky *t*Bu moieties, which prevent the pyrazolato ligand from the necessary tilting (*cf.*, effective ionic radii for 6-coordination: Ti^{3+} 0.670, Al^{3+} 0.535 Å).³⁷ The unit cell holds three distinct molecules of **4**^{CO₂} and six lattice toluene, which form a superstructure with alternating layers of complex **4**^{CO₂} and toluene (Fig. S39†).



Scheme 4 Reactions of $\text{Ti}(\text{pz}^{\text{tBu}_2})_3$ (**4**) with an excess of CO₂ and N₂O.

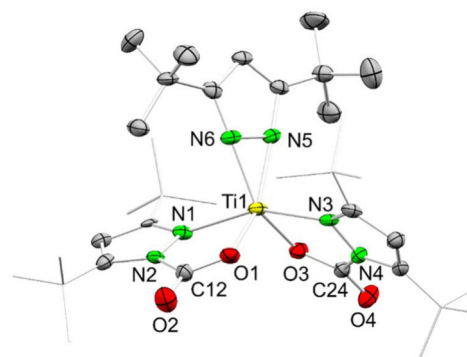


Fig. 3 Connectivity of $\text{Ti}(\text{CO}_2 \cdot \text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (**4**^{CO₂}). Ellipsoids are set at the 50% probability level and *t*Bu moieties are displayed in wireframe projection for clarity. Hydrogen atoms, two additional molecules of **4**^{CO₂} and six lattice toluene are omitted for clarity.



The DRIFT spectrum of 4^{CO_2} shows two characteristic bands for C=O stretching vibration at $\tilde{\nu} = 1765$ and 1753 cm^{-1} similar to the aluminium congener. Due to the paramagnetic character of 4^{CO_2} the signals in the ^1H NMR spectrum are significantly broadened and only two signals are resolved. One very broad signal between $\delta = 7\text{--}3\text{ ppm}$ can most likely be assigned to aromatic protons in the pyrazolato/carbamato backbones while the other broadened signal at $\delta = 1.55\text{ ppm}$ can be ascribed to *t*Bu moieties. Despite the broadened signals, the CO_2 insertion reaction can be easily monitored by ^1H NMR spectroscopy (Fig. S16†). At the start of the reaction signals for **4** and 4^{CO_2} in addition to another signal at $\delta = 1.67\text{ ppm}$ could be observed. The additional signal likely arises from a mono-inserted product, which was also found for the aluminium congener. The EPR spectrum of 4^{CO_2} is shown in Fig. S41.†

After one hour the conversion of **4** to 4^{CO_2} is complete, which is also indicated by the red colour of the solution. A VT ^1H NMR study revealed a complete CO_2 release already at $70\text{ }^\circ\text{C}$ suggesting that the overall CO_2 insertion process into **4** is reversible (Fig. S18†). This is again also indicated by the colour of the solution which turns blue after the experiment and again red after several hours at ambient temperature. Shining UV light on compound 4^{CO_2} led to oxidation of the titanium centre, however, the formation of a significant amount of oxalate was not observed by ^{13}C NMR spectroscopy. A TGA experiment revealed an initial toluene solvent release of 13.9% between $77\text{--}110\text{ }^\circ\text{C}$, which is in line with the high lattice toluene content in the crystalline material. Subsequently, a CO_2 releasing step of 12.1% between $110\text{--}150\text{ }^\circ\text{C}$ was observed. Both releasing steps fit to a toluene/ 4^{CO_2} ratio of 1 : 1 (toluene: 12.0%; CO_2 : 11.5%). Interestingly, different to tetravalent 1^{CO_2} no deoxygenation reaction was observed for 4^{CO_2} over time in solution, however, a fast decomposition of neat 4^{CO_2} occurred at ambient atmosphere to unidentified products.

Treatment of tetravalent **1** with an excess of N_2O led to no visible reaction as suggested by ^1H NMR spectroscopy and the unchanged yellow colour of the solution. In contrast, exposure of trivalent **4** to N_2O resulted in an immediate colour change from blue to green and after 10 minutes to yellow. A ^1H NMR spectrum revealed the presence of a paramagnetic (not **4**) and a diamagnetic species. Overnight, orange crystals formed in a toluene solution and a SCXRD measurement revealed the formation of the oxo-bridged species $[\text{Ti}(\text{pz}^{\text{tBu}_2})_3]_2(\mu\text{-O})$ (**5**) (Scheme 4). Both titanium centres of **5** underwent N_2O -promoted $+III \rightarrow +IV$ oxidation under elimination of N_2 . The ^1H NMR spectrum of the supernatant solution revealed a full conversion of **4** to **5**, while the signals of the new paramagnetic species disappeared completely. The latter paramagnetic species is most likely the elusive N_2O insertion complex in which the titanium centre is still in the formal oxidation state $+III$. So far, attempts to isolate this paramagnetic species were not successful.

The connectivity structure of **5** indicates a highly symmetrical structure with only one symmetrically independent pyrazo-

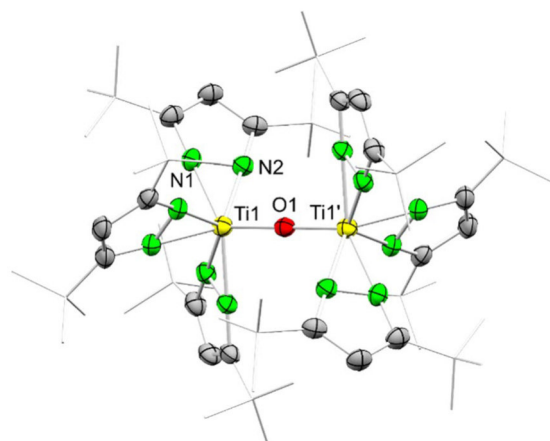


Fig. 4 Connectivity of $[\text{Ti}(\text{pz}^{\text{tBu}_2})_3]_2(\mu\text{-O})$ (**5**). Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted and *t*Bu moieties are displayed in the wireframe projection for clarity.

lato ligand, the titanium centre and bridging oxygen in the asymmetric unit (Fig. 4).

Each titanium centre is coordinated by three terminal pyrazolato ligands in the $\kappa^2(\text{N},\text{N})$ mode adopting a propeller-like geometry. NMR studies corroborate the highly symmetric character of **5** showing only one signal set for all six pyrazolato ligands. The ^1H NMR spectrum displays a sharp signal at $\delta = 6.36\text{ ppm}$ with an integral of six protons assignable to the aromatic ring protons and a slightly broadened signal at $\delta = 1.01\text{ ppm}$ with an integral of 108 protons for the *t*Bu moieties. Similarly, the ^{13}C NMR spectrum revealed one signal set, however, the quaternary carbon ring atom could only be resolved in a $^1\text{H}\text{--}^{13}\text{C}$ HMBC NMR experiment at $\delta = 157.5\text{ ppm}$.

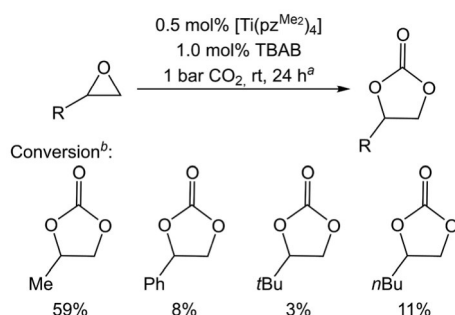
The core structure of **5** is reminiscent of **2** except the inserted CO_2 . Therefore, we wondered about whether **5** can be transformed into putative $\{\text{Ti}(\text{CO}_2\text{-pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})\}_2(\mu\text{-O})$ or $\{\text{Ti}(\text{CO}_2\text{-pz}^{\text{tBu}_2})(\text{pz}^{\text{tBu}_2})_2\}_2(\mu\text{-O})$ when exposed to an excess of CO_2 . Due to the insolubility of **5** in non-donating solvents these experiments were conducted in THF, which however did not result in any CO_2 insertion at ambient conditions as indicated by ^1H NMR experiments. This behaviour can be ascribed to the enhanced steric bulk of the *t*Bu moieties blocking the titanium centres, in addition to the low solubility of **5** in THF. Attempts to synthesize the sterically less demanding $\text{Ti}(\text{pz}^{\text{Me}_2})_3$ as a precursor in order to access putative $[\text{Ti}(\text{pz}^{\text{Me}_2})_3]_2(\mu\text{-O})$ were not successful.

Catalytic formation of cyclic carbonates

Titanium complexes are widely used in the copolymerization of CO_2 and epoxides.^{44–48} Since metal pyrazolates effectively promote the catalytic cycloaddition of CO_2 and epoxides, a similar behaviour of the titanium derivatives could be anticipated.^{32–34} For better comparability, the conditions of the catalytic transformations were adapted to our previous studies (Scheme 5).

Tetravalent $\text{Ti}(\text{pz}^{\text{Me}_2})_4$ (**1**) exhibits moderate catalytic activity for the conversion of propylene oxide (59%), ranging between





Scheme 5 Catalytic conversion of CO₂ and epoxide into cyclic carbonates by applying titanium pyrazolate **1** as catalyst. ^aReaction conditions: 1 bar CO₂, 0.5 mol% catalyst (**1** and **2**), 1 mol% tetra-*n*-butylammonium bromide (TBAB) as cocatalyst at ambient temperature for 24 h in neat epoxide; ^bConversion determined by comparison of the integral protons at the α -position of the epoxide and the corresponding cyclic carbonate (exception: 2-*tert*-butyloxirane/3,3-dimethyl-1,2-butene carbonate where the integral of the *t*Bu moieties was used).

magnesium (42–59%) and rare-earth-metal pyrazolates (84–99%) and close to Al(pz^{*t*Bu})₃ (65%).^{32–34} This is in line with the carboxophilicity criterion (as derived from the CO₂-release temperature),³³ and reflects both the enhanced oxophilicity and Lewis acidity of titanium(IV).⁴¹ As expected, the conversion of sterically more demanding epoxides was considerably lower, being lowest for 2-*tert*-butyloxirane (3%) and highest for epoxy hexane (11%). Trivalent Ti(pz^{*t*Bu})₃ (**4**) showed a significantly lower conversion of 27% for propylene oxide compared to tetravalent **1**. This can be ascribed to side reactions, as indicated by an immediate colour change upon the addition of epoxide. Trivalent titanium compounds are known to catalytically convert epoxides to alcohols under ring opening and oxidation of the titanium center.⁴⁹ Examples of titanium-based catalysts in this cycloaddition reaction are rather rare.^{50–55} The highest catalytic activity was observed for the tetrazole containing (C₅Me₅)TiCl₂(O,*N*-L) (L = 5-(2-hydroxyphenolate)-1*H*-tetrazole) featuring a maximum TOF of 422 for propylene oxide at 75 °C and 22 bar CO₂.⁵² Recently, the Ti₃₁ cluster (C₂H₈N)₈[Ti₃₁O₅₂(O^{*i*Pr})₄(PhCO₂)₂₄] was reported to reach a quantitative conversion for propylene oxide when a catalyst load of 0.83 mol% is used at 80 °C and 1 bar CO₂ over five days, according to a photocatalytic mechanism.⁵⁵

Conclusions

Tetravalent Ti(pz^{Me})₄ undergoes a twofold CO₂ insertion to Ti(CO₂·pz^{Me})₂(pz^{Me})₂ when exposed to an excess of CO₂ as proven by SCXRD, NMR and DRIFT experiments. A thermogravimetric analysis showed an exhaustive CO₂ release between 90–150 °C pointing to the reversibility of the CO₂ insertion. In solid form, Ti(CO₂·pz^{Me})₂(pz^{Me})₂ showed an exceptionally high stability, when compared to derivatives of other light metals. Even after a month at ambient atmosphere only minor hydrolysis products were observed. Strikingly, in solution under a 1 bar CO₂ atmosphere Ti(CO₂·pz^{Me})₂(pz^{Me})₂ con-

verted into oxo-bridged species [Ti(CO₂·pz^{Me})₂(pz^{Me})₂](μ-O) and [Ti(μ-O)₂(μ-pz^{Me})₄](Ti{CO₂·pz^{Me}}{pz^{Me}})₂], *en route* to titania. This transformation reflects the highly polarizing nature of titanium(IV) and is accelerated at elevated temperatures. Heteroallene CS₂ undergoes a fully reversible mono-insertion into Ti(pz^{Me})₄ *via* formation of Ti(CS₂·pz^{Me})(pz^{Me})₃. The thiocarbamate complex does not engage in the formation of sulfido-bridged species, even under thermal treatment. Trivalent Ti(pz^{*t*Bu})₃ also undergoes a twofold CO₂ insertion and the obtained bis(carbamato) complex Ti(CO₂·pz^{*t*Bu})₂(pz^{*t*Bu})₂ is stable in solution against oxidation and deoxygenation. Ti(CO₂·pz^{*t*Bu})₂(pz^{*t*Bu})₂ de-inserts CO₂ exhaustively already at 70 °C without a decomposition side reaction. Distinct reactivity of tetravalent Ti(pz^{Me})₄ and trivalent Ti(pz^{*t*Bu})₃ is also found when treated with nitrous oxide. The tetravalent pyrazolate displayed inert behaviour toward N₂O, whereas Ti(pz^{*t*Bu})₃ gets oxidized to afford the oxo-bridged complex [Ti(pz^{*t*Bu})₃]₂(μ-O) *via* fast release of N₂.

Conflicts of interest

There are no conflicts of interest.

Data availability

The data that support the findings of this study are available in the ESI† of this article.

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Supporting Information

Reactivity of titanium pyrazolates towards CO₂, CS₂ and N₂O

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Experimental Section

General Considerations. All manipulations were performed under rigorous exclusion of air and moisture under argon atmosphere (< 0.1 ppm O_2 , < 0.1 ppm of H_2O) in a MB200B glovebox (MBraun) or according to standard Schlenk techniques and in oven-dried glassware. Solvents (THF, Et_2O *n*-pentane, *n*-hexane and toluene) were purified by using SPS Grubbs-type columns (MBraun SPS-800, solvent purification system) and stored inside a glovebox. THF was dried further over molecular sieves. $[D_8]$ toluene, C_6D_6 and $[D_8]$ THF were obtained from Sigma Aldrich and dried over Na/K alloy and filtered prior to use. 3,5-Dimethyl pyrazole (99%), hydrazine hydrate, styrene oxide ($>97\%$, degassed prior to use), tetrakis(dimethylamido)titanium (99.999%), 2,2,6,6-tetramethylheptane-3,5-dione and titanium tetrachloride (99.9%) were purchased from Sigma Aldrich and used as received. Carbon disulfide (99.9%), propylene oxide (99.5%) and pyrazole (98%) were purchased from Acros Organics and the former was degassed prior to use. 2-*tert*-Butyloxirane was purchased from abcr and degassed prior to use. 1,2-Epoxyhexane (97%) was purchased from Thermo Fischer Scientific and degassed prior to use. 3,5-Di-*tert*-butylpyrazole¹, $TiCl_3(thf)_3$ ² and $Ti(pz^{tBu_2})_3$ ³ (**2**) were synthesized according to literature known synthesis routes. Argon and CO_2 were supplied by Westfalen AG. Solution 1H and ^{13}C spectra were recorded in a J. Young valve NMR tube on a Bruker AVII+400 spectrometer (1H : 400.11 MHz; ^{13}C : 100.61 MHz) or a Bruker AVII+500 spectrometer (1H : 500.13 MHz; ^{13}C : 125.76 MHz) at 299 K. The chemical shifts listed in the experimental section are referenced to solvent residual resonances in parts per million in relation to tetramethylsilane. Solid-state NMR spectra were obtained at ambient temperature on a Bruker AVIIIHD-300WB spectrometer (1H : 300.13 MHz, ^{13}C : 75.47 MHz) equipped with MAS (magic angle spinning) hardware using a ZrO_2 rotor with an outside diameter of 4 mm. IR spectra were recorded on a Bruker Invenio R spectrometer (Bruker). The samples were mixed with KBr powder and measured in a DRIFT cell with KBr windows. DRIFT data were converted by using the Kubelka-Munk refinement. EPR spectra were measured on a continuous wave X-band Bruker ESP 300E instrument using 5 mm O.D. Wilmad quartz (CFQ) EPR tubes. Spectra are referenced to the Bruker strong pitched standard $g_{iso} = 2.0088$. Elementary analyses were performed on an Elementar vario MICRO cube in CHNS mode. Mass spectrometry experiments were conducted on an AmaZon SL (Bruker). Single crystals were grown from saturated solutions of toluene by standard techniques. Suitable single crystals from **1**^{CO₂}, **2**, **3**, **1**^{CS₂}, **4**^{CO₂} and **5** for X-ray structure studies were selected in a glovebox and coated with Parabar 10312 (Hampton research). Crystallographic data were measured on a Bruker APEX II DUO instrument equipped with μS micro focus sealed tube and QUAZAR optics for MoK_{α} radiation ($\lambda = 0.71073$ Å). The data collection strategy was determined using COSMO⁴ employing ω - and φ scans. Raw data were processed using APEX⁵ and SAINT,⁶ corrections for absorption effects were applied using SADABS.⁷ The structures were solved by direct methods and refined against all data by full-matrix least-squares methods on F2 using SHELXTL⁸ and ShelXle.⁹ For **1**^{CO₂} and **2**, disorder models were calculated using DSR¹⁰, a program included in ShelXle, for refining disorder. For **1**^{CO₂}, embedded solvent molecules, which are seriously disordered, were treated by using PLATON/Squeeze.¹¹ All graphics were produced employing Mercury 2022.2.¹²

Ti(pz^{Me₂})₄ (1**).** To a solution of $Ti(NMe_2)_4$ (237 mg, 1.06 mmol) in 10 mL toluene a solution of Hpz^{Me_2} (407 mg, 4.22 mmol) in 3 mL toluene was added dropwise and the resulting dark red solution was stirred overnight at ambient temperature. The solvent was removed under reduced pressure and **1** was obtained as yellow crystals (443 mg, 1.03 mmol, 98%). The analytical data was consistent with the literature.¹³ DRIFTS: $\tilde{\nu} = 3110$ (w), 2981 (w), 2954 (m), 2922 (m), 2859 (w), 1582 (vw), 1548 (vw), 1520 (s), 1462 (vs), 1440 (vs), 1415 (vs), 1366 (s), 1390 (w), 1174 (vw), 1139 (s), 1063 (w), 1015 (vs), 964 (m), 787 (vs), 729 (m), 663 (vw), 639 (w), 586 (w), 553 (vw), 478 (m), 437 (vs) cm^{-1} .

Ti(CO₂·pz^{Me₂})₂(pz^{Me₂})₂ (1**^{CO₂}).** In a 25 mL Schlenk tube a solution of $Ti(pz^{Me_2})_4$ (201 mg, 469 μ mol) in 5 mL toluene was stirred under 1 bar CO_2 for 3 h at 0 °C. The solution was transferred to the glovebox and

stored at $-40\text{ }^{\circ}\text{C}$. A yellow amorphous precipitate was formed and over time of three years orange crystals suitable for a SCXRD analysis were formed. The supernatant solution was removed and the residue was dried for 30 min at reduced pressure and **1^{CO2}** was obtained as orange powder (224 mg, 435 μmol , 93%). ^1H NMR (500.1 MHz, C_6D_6 , $26\text{ }^{\circ}\text{C}$): δ = 5.72 (s, 2 H, 4-*H*(pz)), 5.00 (s, 2 H, 4-*H*($\text{CO}_2\cdot\text{pz}$)), 2.62 (s, 6 H, 5- $\text{CH}_3(\text{CO}_2\cdot\text{pz})$), 2.21 (s, 3-6 H, $\text{CH}_3(\text{CO}_2\cdot\text{pz})$), 2.17 (s, 12 H, 3/5- $\text{CH}_3(\text{pz})$) ppm. $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$: $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6 , $26\text{ }^{\circ}\text{C}$): δ = 150.5 (CO_2), 150.3 (5- $\text{C}(\text{CO}_2\cdot\text{pz})$), 144.7 (3/5- $\text{C}(\text{pz})$), 141.8 (3- $\text{C}(\text{CO}_2\cdot\text{pz})$), 141.8 (3- $\text{C}(\text{CO}_2\cdot\text{pz})$), 116.2 (4- $\text{C}(\text{pz})$), 110.2 (4- $\text{C}(\text{CO}_2\cdot\text{pz})$), 110.2 (4- $\text{C}(\text{CO}_2\cdot\text{pz})$), 13.3 (5- $\text{CH}_3(\text{CO}_2\cdot\text{pz})$), 12.3 (3- $\text{CH}_3(\text{CO}_2\cdot\text{pz})$), 11.9 (3/5- $\text{CH}_3(\text{pz})$) ppm. DRIFTS: $\tilde{\nu}$ = 3131 (vw), 3104 (vw), 2978 (vw), 2929 (vw), 2867 (vw), 1740 (vs), 1690 (vw), 1559 (vw), 1521 (vw), 1459 (m), 1440 (w), 1413 (w), 1386 (w), 1348 (m), 1287 (s), 1230 (w), 1138 (w), 1048 (s), 1024 (m), 987 (w), 848 (s), 804 (s), 778 (s), 728 (w), 630 (vw), 583 (vw), 478 (m), 441 (s), 406 (m) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{22}\text{H}_{28}\text{N}_8\text{O}_4\text{Ti}$ (516.39 g mol^{-1}): C 51.17, H 5.47, N 21.70; found C 51.63, H 5.28, N 21.83. After 1 week at ambient temperature a few crystals of **2** suitable for a SCXRD analysis were formed. Fragments of the side product urea derivative $\text{OC}(\text{N-pz}^{\text{Me}_2})_2$ were analyzed by mass spectrometry. LRMS(ESI): m/z calcd. for $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$ 219.12; found 219.16. After 3 months at ambient temperature a few crystals of **3** suitable for a SCXRD analysis were formed.

$\text{Ti}(\text{CS}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_3$ (1^{CS2}**)**. In a pressure tube, an excess of CS_2 (504 mg, 6.62 mmol) was added to a solution of $\text{Ti}(\text{pz}^{\text{Me}_2})_4$ (100 mg, 233 μmol) in 10 mL toluene. The mixture was heated to $60\text{ }^{\circ}\text{C}$ and stirred for 5 d. The solution was concentrated and stored at $-40\text{ }^{\circ}\text{C}$. Overnight yellow crystals were obtained suitable for a SCXRD measurement. The supernatant solution was removed and **1^{CS2}** was obtained as yellow powder after evaporation of the solvent (94.9 mg, 188 μmol , 81%). ^1H NMR (500.1 MHz, C_6D_6 , $-60\text{ }^{\circ}\text{C}$): δ = 5.76 (s, 2 H, 4-*H*(*cis*-pz)), 5.52 (s, 1 H, 4-*H*(*trans*-pz)), 4.78 (4-*H*($\text{CS}_2\cdot\text{pz}$)), 2.41 (s, 3 H, 5- $\text{CH}_3(\text{CS}_2\cdot\text{pz})$), 2.39 (s, 6 H, 3/5 $\text{CH}_3(\text{cis-pz})$), 2.27 (s, 3 H, 3- $\text{CH}_3(\text{CS}_2\cdot\text{pz})$), 2.06 (s, 6 H, 3/5- $\text{CH}_3(\text{trans-pz})$), 1.97 (s, 6 H, 3/5- $\text{CH}_3(\text{cis-pz})$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6 , $26\text{ }^{\circ}\text{C}$): δ = 209.2 (CS_2), 150.6 (5- $\text{C}(\text{CS}_2\cdot\text{pz})$), 145.5 (3/5- $\text{C}(\text{cis-pz})$), 145.0 (3- $\text{C}(\text{CS}_2\cdot\text{pz})$), 144.0 (3/5- $\text{C}(\text{trans-pz})$), 114.2 (4- $\text{C}(\text{trans-pz})$), 113.8 (4- $\text{C}(\text{cis-pz})$), 113.2 (4- $\text{C}(\text{CS}_2\cdot\text{pz})$), 17.9 (3- $\text{CH}_3(\text{CS}_2\cdot\text{pz})$), 15.7 (5- $\text{CH}_3(\text{CS}_2\cdot\text{pz})$), 12.9 (3/5- $\text{CH}_3(\text{cis-pz})$), 12.5 (3/5- $\text{CH}_3(\text{trans-pz})$) ppm. DRIFTS: $\tilde{\nu}$ = 3105 (w), 2972 (w), 2954 (w), 2621 (m), 2861 (w), 1579 (s), 1520 (s), 1477 (m), 1462 (s), 1439 (vs), 1414 (s), 1373 (s), 1323 (vs), 1313 (s), 1247 (vs), 1168 (w), 1131 (vs), 1071 (vs), 1033 (vs), 1015 (s), 985 (s), 895 (s), 814 (m), 795 (m), 749 (m), 729 (m), 665 (vw), 635 (vw), 586 (w), 548 (vw), 523 (vw), 480 (m), 438 (vs), 408 (vs) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{21}\text{H}_{28}\text{N}_8\text{S}_2\text{Ti}$ (504.50 g mol^{-1}): C 50.00, H 5.59, N 22.21, S 12.71; found C 49.79, H 5.65, N 22.05, S 12.42.

$\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})_3$ (4^{CO2}**)**. In a 25 mL Schlenk tube, a solution of $\text{Ti}(\text{pz}^{\text{tBu}_2})_3$ (100 mg, 233 μmol) in 5 mL toluene was stirred under 1 bar CO_2 for 3 h at ambient temperature. The color of the blue solution turned green, then yellow and finally red. The solution was transferred to the glovebox and stored at $-40\text{ }^{\circ}\text{C}$. A red amorphous precipitate formed and overnight also colorless crystals suitable for a SCXRD measurement. The supernatant solution was removed and the residue was dried for 30 min at reduced pressure yielding **4^{CO2}** as a light red powder (99.1 mg, 147 μmol , 63%). ^1H NMR (500.1 MHz, C_6D_6 , $26\text{ }^{\circ}\text{C}$): δ = 5.30 (4-*H*(pz)), 1.55(*tBu*) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6 , $26\text{ }^{\circ}\text{C}$): δ = 170.7 (pz), 30.9 (*tBu*) ppm. DRIFTS: $\tilde{\nu}$ = 2962 (s), 2911 (w), 2871 (w), 1765 (s), 1753 (vs), 1545 (vw), 1513 (vw), 1482 (vw), 1462 (w), 1435 (w), 1393 (vw), 1363 (w), 1324 (m), 1259 (s), 1239 (s), 1179 (w), 1138 (vw), 1062 (m), 1016 (w), 976 (vw), 857 (w), 825 (w), 818 (m), 780 (w), 525 (vw), 498 (w), 437 (w), 404 (w) cm^{-1} . Elemental analysis calcd. (%) for $\text{C}_{35}\text{H}_{57}\text{N}_6\text{O}_4\text{Ti}$ (673.75 g mol^{-1}): C 62.40, H 8.53, N 12.47; found C 63.16, H 8.35, N 12.71. The carbon value is outside analytical purity, but no better elemental analysis could be obtained to date, due to the high content of solvent molecules in the lattice.

$[\text{Ti}(\text{pz}^{\text{tBu}_2})_3]_2(\mu\text{-O})$ (5**)**. In a 25 mL Schlenk tube, a solution of $\text{Ti}(\text{pz}^{\text{tBu}_2})_3$ (100 mg, 233 μmol) in 5 mL toluene was stirred under 1 bar N_2O for 30 min at ambient temperature. The color of the blue solution turned green, then yellow and finally orange. Orange crystals suitable for a SCXRD measurement formed overnight under ambient temperature. The supernatant solution was removed and the residue was dried at reduced pressure yielding **5** as an orange powder (100 mg, 84.5 μmol , 99%). ^1H NMR (400.11 MHz, THF-d_8 , $26\text{ }^{\circ}\text{C}$): δ = 6.36 (4-*H*), 1.01 ($\text{C}(\text{CH}_3)_3$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, THF-d_8 , 26

°C): δ = 157.5 (3/5-C), 109.5 (4-C), 32.3 (C(CH₃)₃), 31.1 (C(CH₃)₃) ppm. The signal at 157.5 ppm was only resolved in an ¹H-¹³C-HMBC experiment. DRIFTS: $\tilde{\nu}$ = 3118 (vw), 2961 (vs), 2929 (m), 2903 (m), 2867 (w), 1520 (m), 1501 (m), 1484 (w), 1461 (w), 1427 (m), 1388 (vw), 1363 (s), 1288 (vw), 1253 (m), 1229 (m), 1206 (w), 1020 (vw), 999 (w), 801 (s), 744 (vs), 708 (m), 627 (vw), 564 (vw), 531 (w), 482 (s) cm⁻¹. Elemental analysis calcd. (%) for C₆₆H₁₁₄N₁₂OTi₂ (1186.82 g mol⁻¹): C 66.76, H 9.68, N 14.15; found C 67.14, H 9.20, N 14.17.

General procedure of the catalytic conversion of epoxides and CO₂ to cyclic carbonates.

Representative example: A Schlenk tube was charged with Ti(pz^{Me₂})₄ (10.5 mg, 24.5 μ mol) and TBAB (15.8 mg, 49.0 μ mol) dissolved in propylene oxide (343 μ L, 4.90 mmol). The atmosphere was exchanged with 1 bar CO₂ and the reaction mixture was stirred for 24 h. The conversion was determined *via* ¹H NMR spectroscopy by dissolving the reaction mixture in CDCl₃.

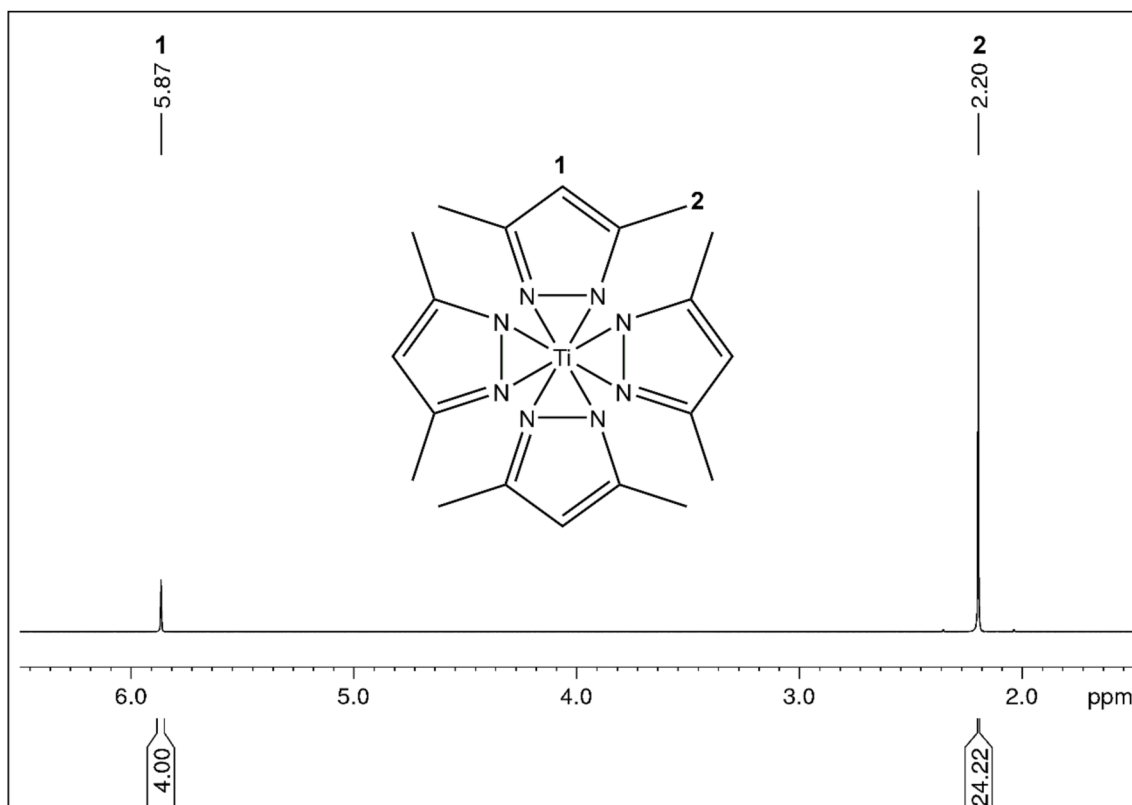


Figure S1. ^1H NMR spectrum (400.11 MHz, C_6D_6) of $\text{Ti}(\text{pz}^{\text{Me}_2})_4$ (1) at 26 °C.

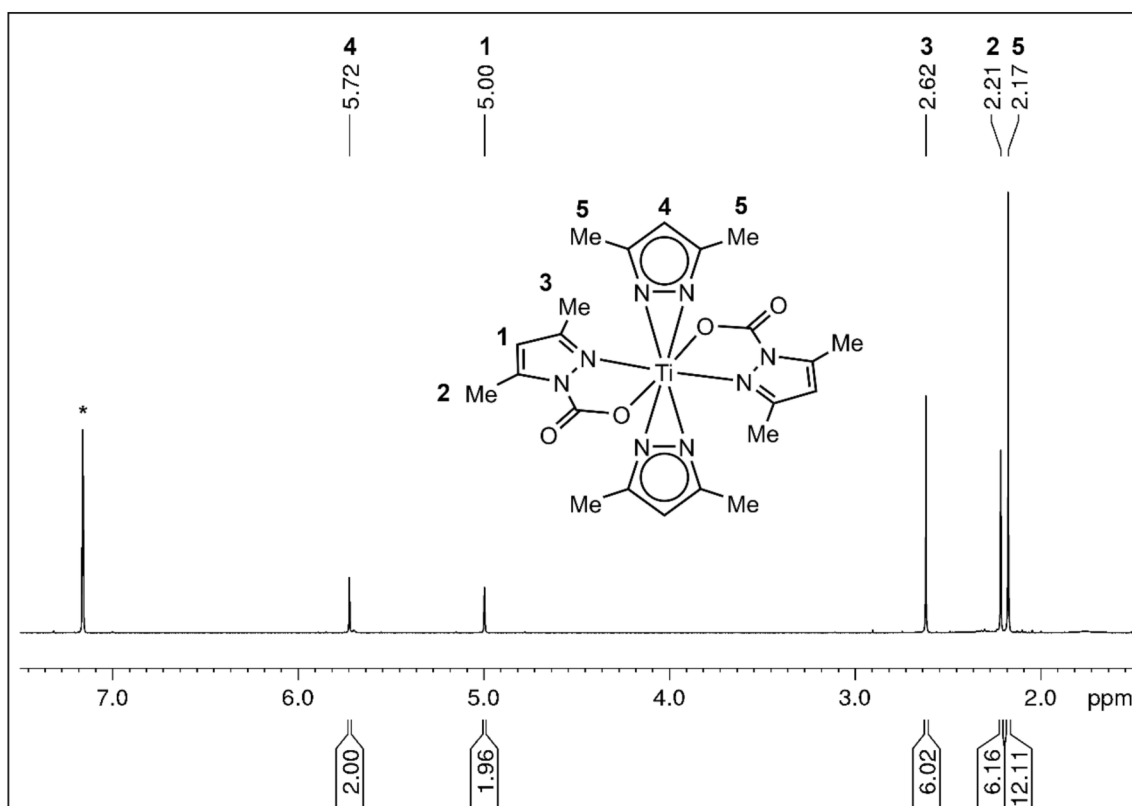


Figure S2. ^1H NMR spectrum (500.13 MHz, C_6D_6) of $\text{Ti}(\text{CO}_2\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ (1 $^{\text{CO}_2}$) at 26 °C.

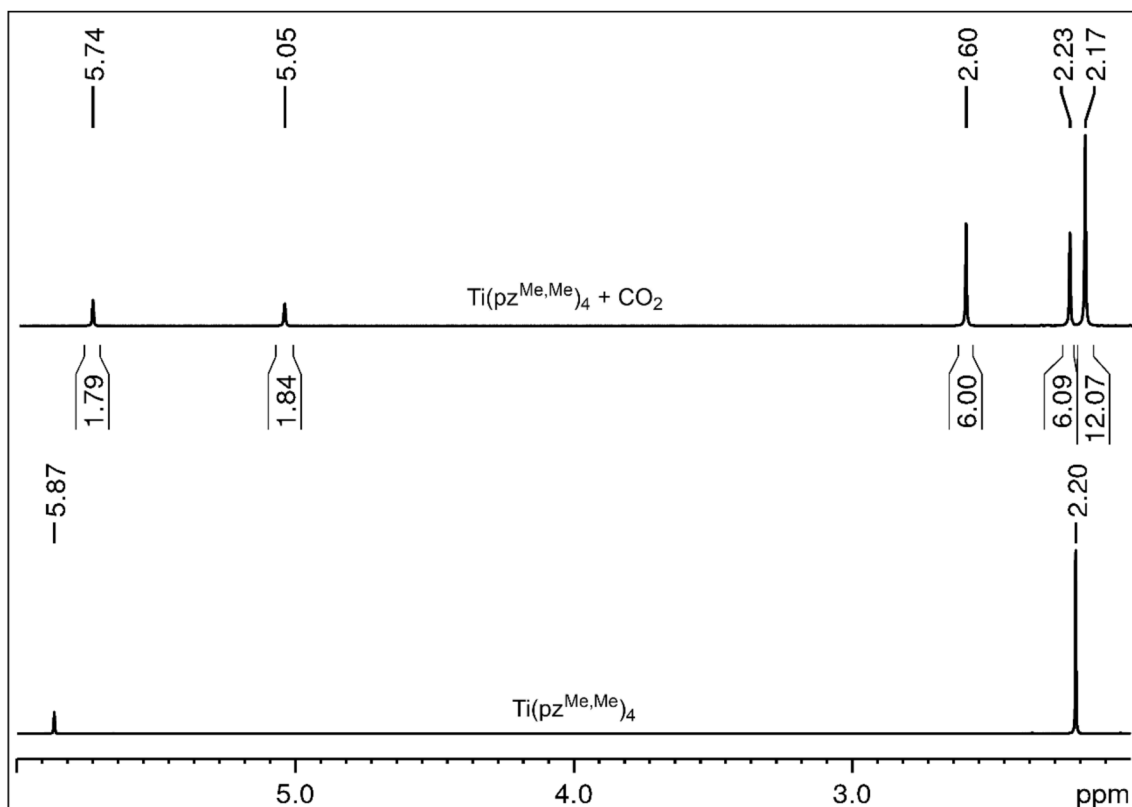


Figure S3. Comparison of ^1H NMR spectra (400.11 MHz, C_6D_6) of $\text{Ti}(\text{pz}^{\text{Me}_2})_4$ (**1**, bottom) and $\text{Ti}(\text{CO}_2 \cdot \text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ (**1**^{CO₂}, top) at 26 °C.

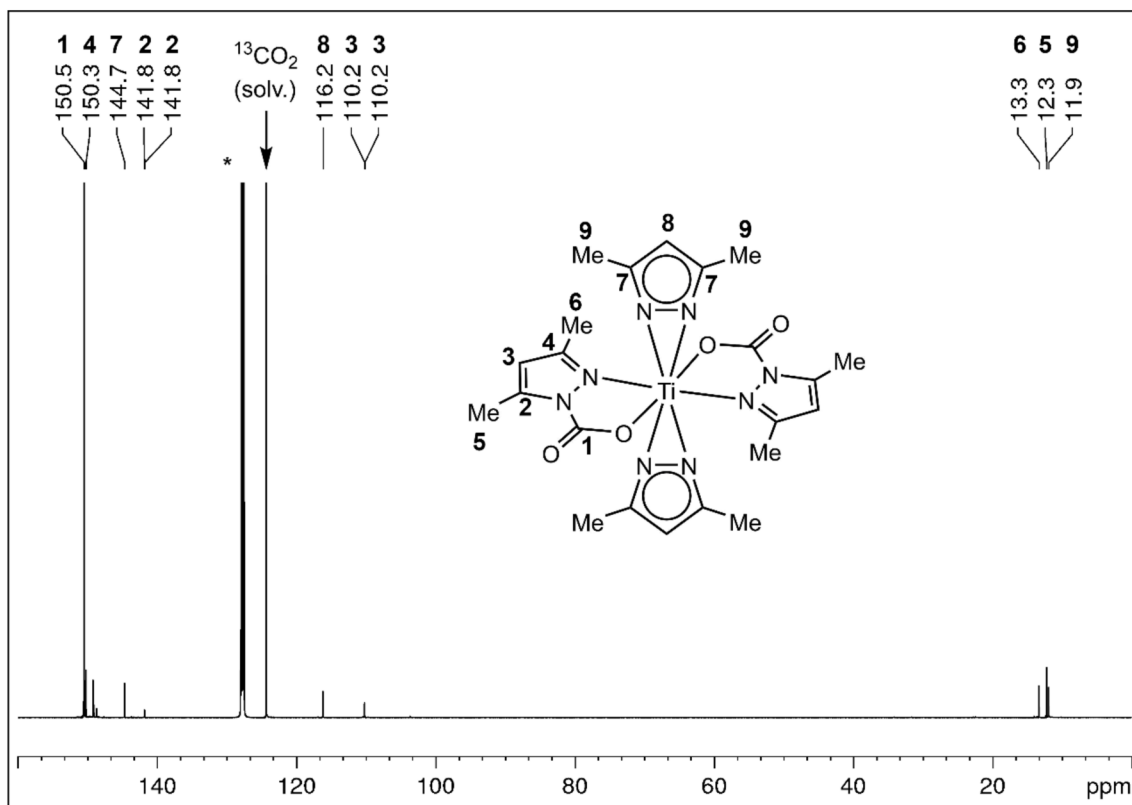


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.76 MHz, C_6D_6) of $\text{Ti}(^{13}\text{CO}_2 \cdot \text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ (**1**^{13CO₂}) at 10 °C.

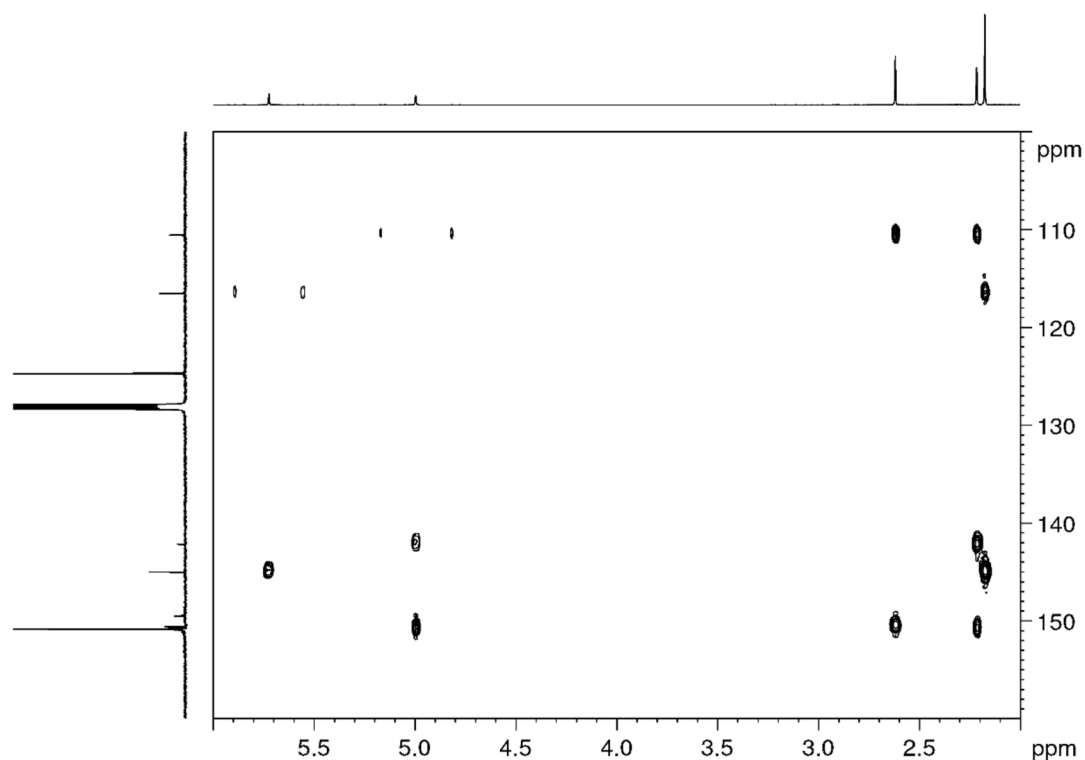


Figure S5. ^1H - ^{13}C HMBC NMR spectrum (^1H : 500.13 MHz, ^{13}C : 125.76 MHz, C_6D_6) of $\text{Ti}(^{13}\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ ($\mathbf{1}^{13\text{CO}_2}$) at 26 °C.

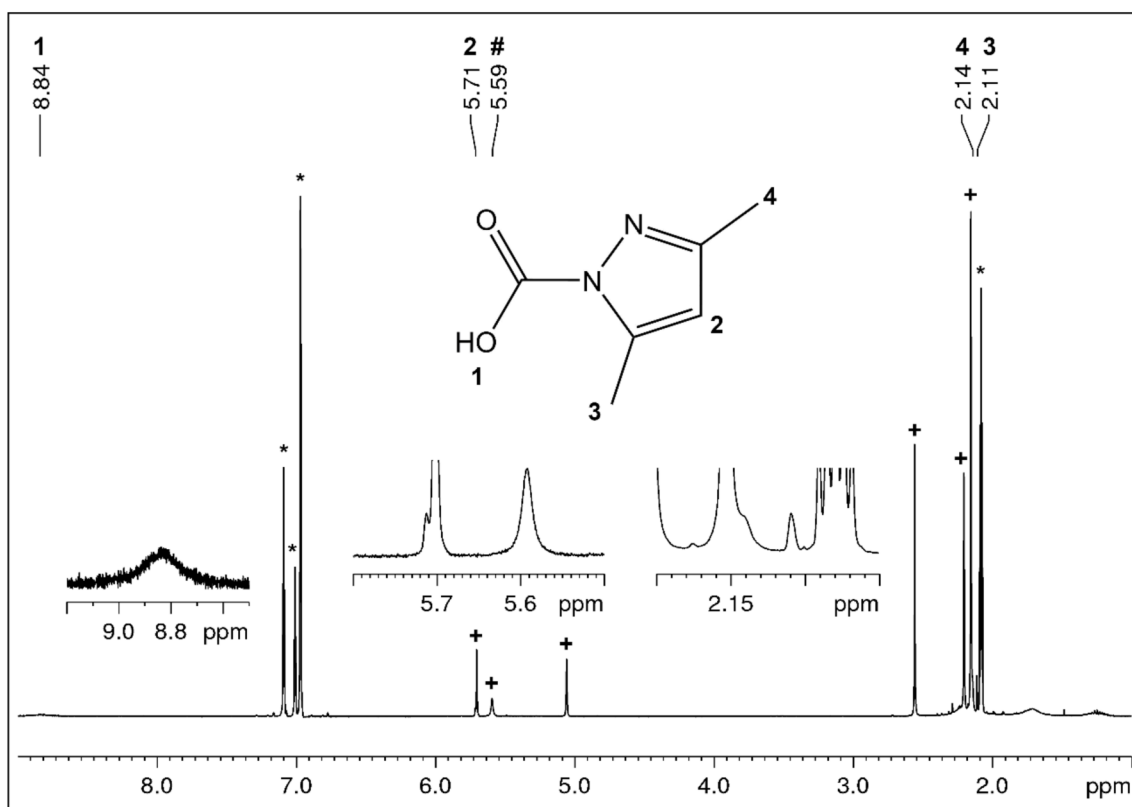


Figure S6. ^1H NMR spectrum (400.11 MHz, C_6D_6) of $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ (+, $\mathbf{1}^{\text{CO}_2}$) at 26 °C after being stored for one month at ambient atmosphere and the formation of small amounts of carbamic acid $\text{HO}_2\text{Cpz}^{\text{Me}_2}$ (# most likely mono-insertion product).

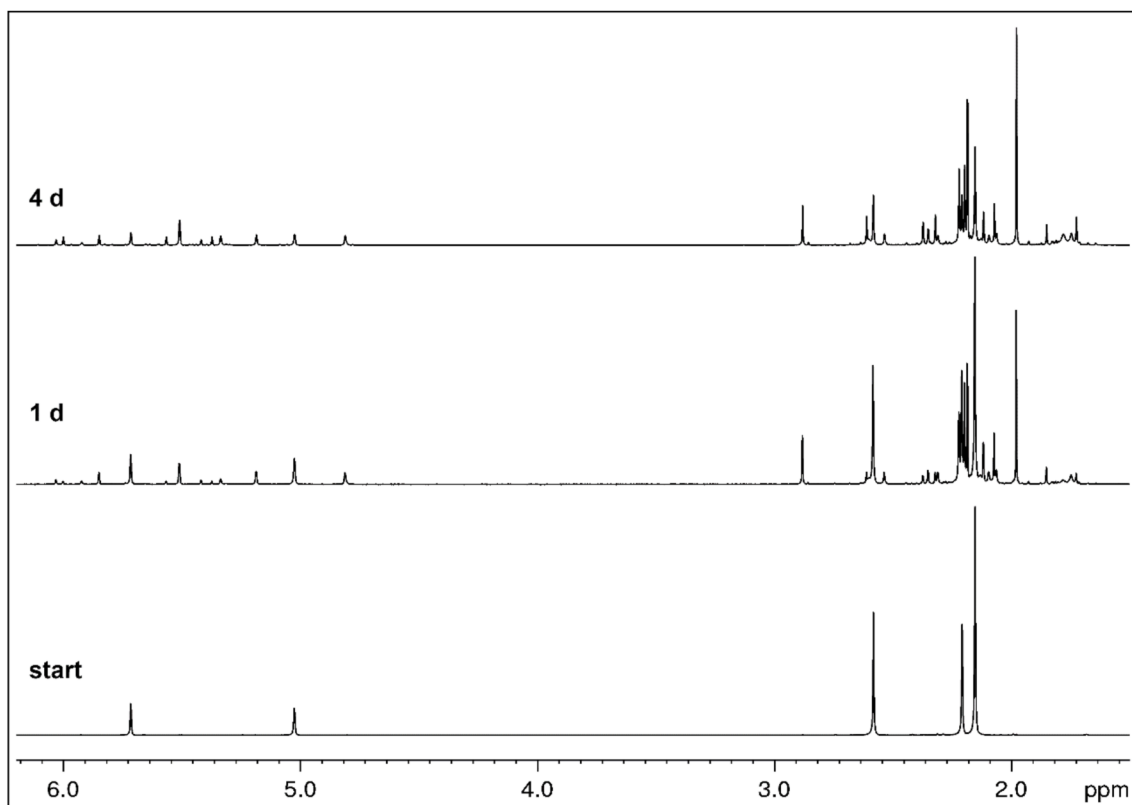


Figure S7. Comparison of ^1H NMR spectra (400.11 MHz, C_6D_6) of the decomposition of $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ ($\mathbf{1}^{\text{CO}_2}$) over time at 26 °C.

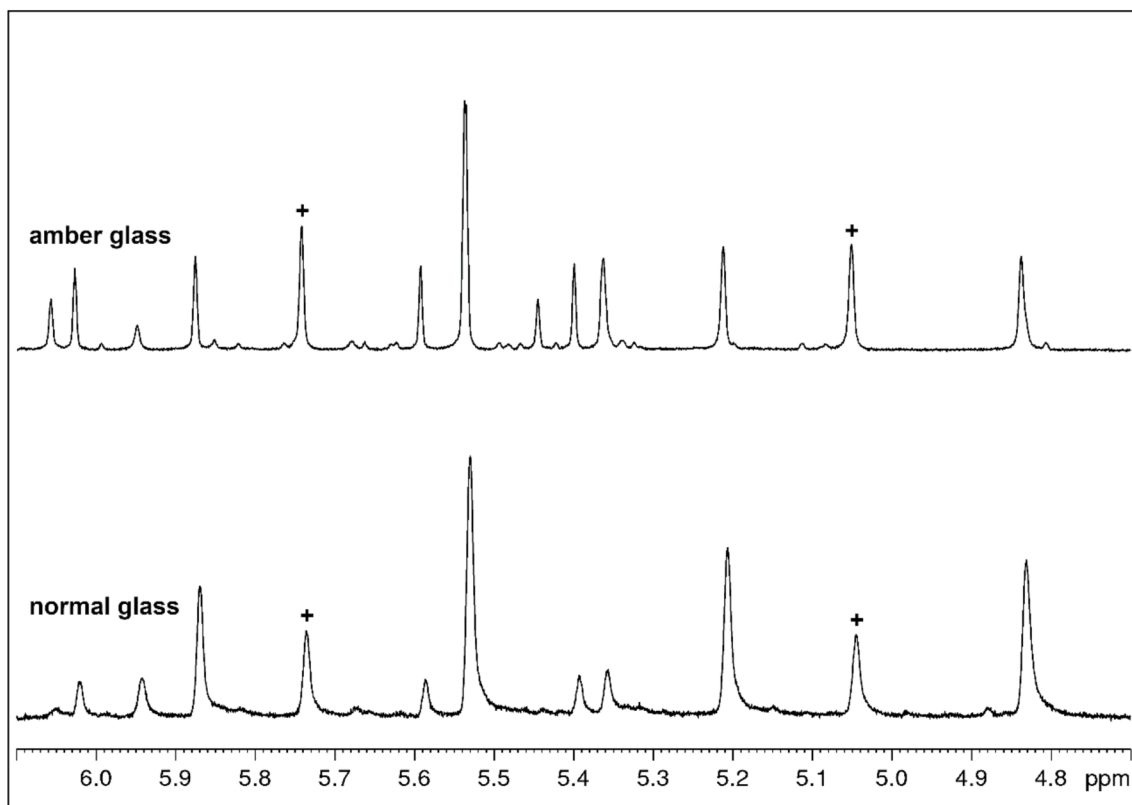


Figure S8. Monitoring of the decomposition of $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ ($\mathbf{1}^{\text{CO}_2}$) after one week *via* ^1H NMR spectra (400.11 MHz, C_6D_6) in a normal NMR tube (bottom) and an amber glass NMR tube (top) (+ $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ ($\mathbf{1}^{\text{CO}_2}$)) at 26 °C.

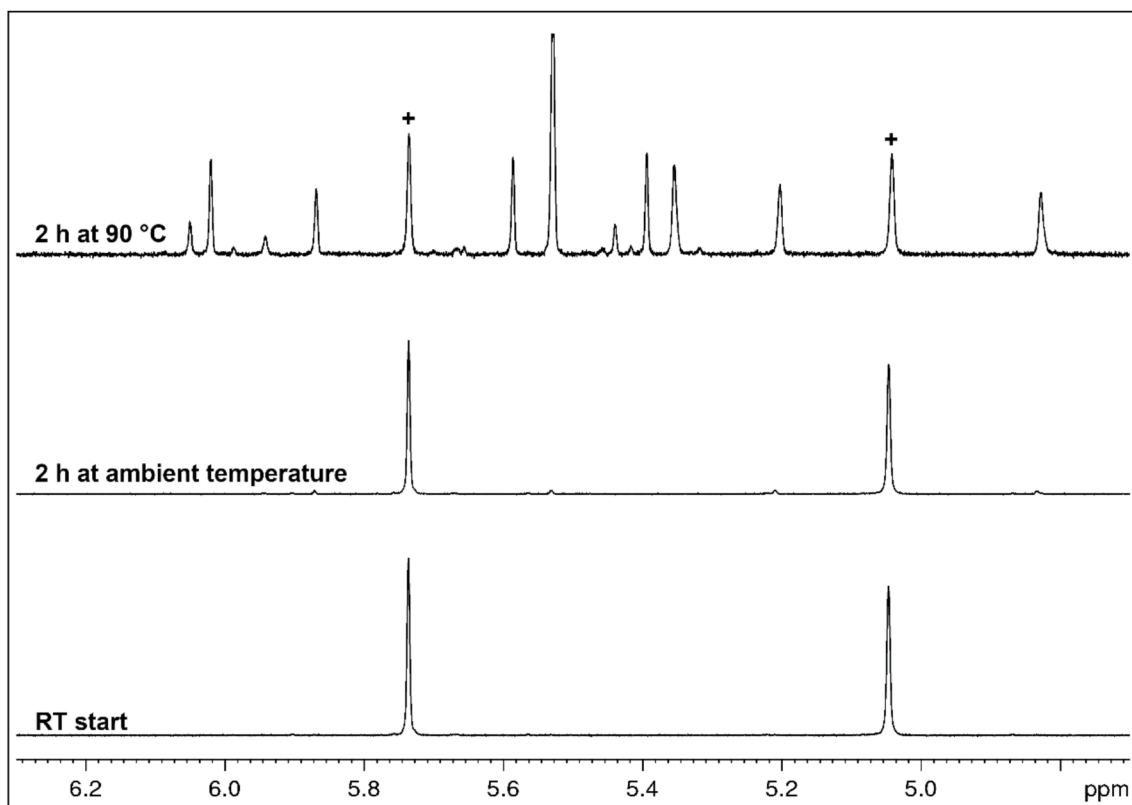


Figure S9. Acceleration of the decomposition of $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ (+ $\mathbf{1}^{\text{CO}_2}$) at elevated temperature. ^1H NMR spectra (500.13 MHz, $[\text{D}_8]$ toluene, 26 °C).

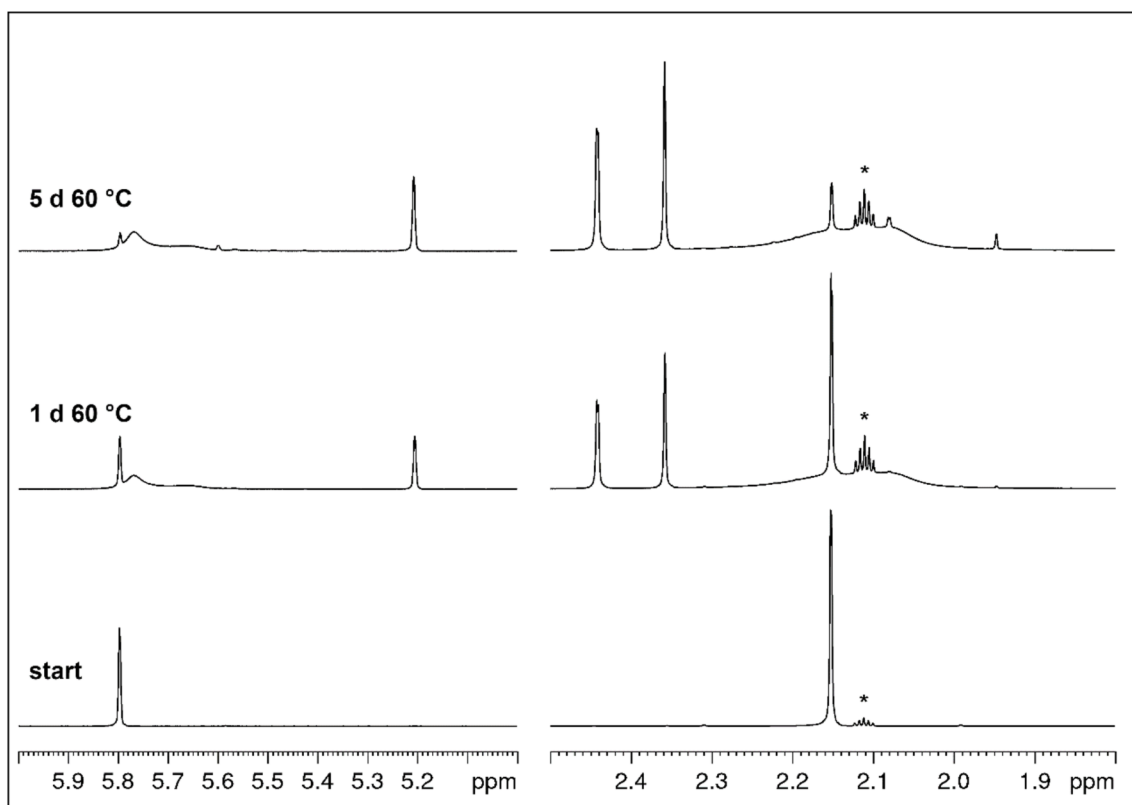


Figure S10. Monitoring of the reaction of $\text{Ti}(\text{pz}^{\text{Me}_2})_4$ ($\mathbf{1}$) with CS_2 via ^1H NMR spectra (400.11 MHz, $[\text{D}_8]$ toluene) at 26 °C.

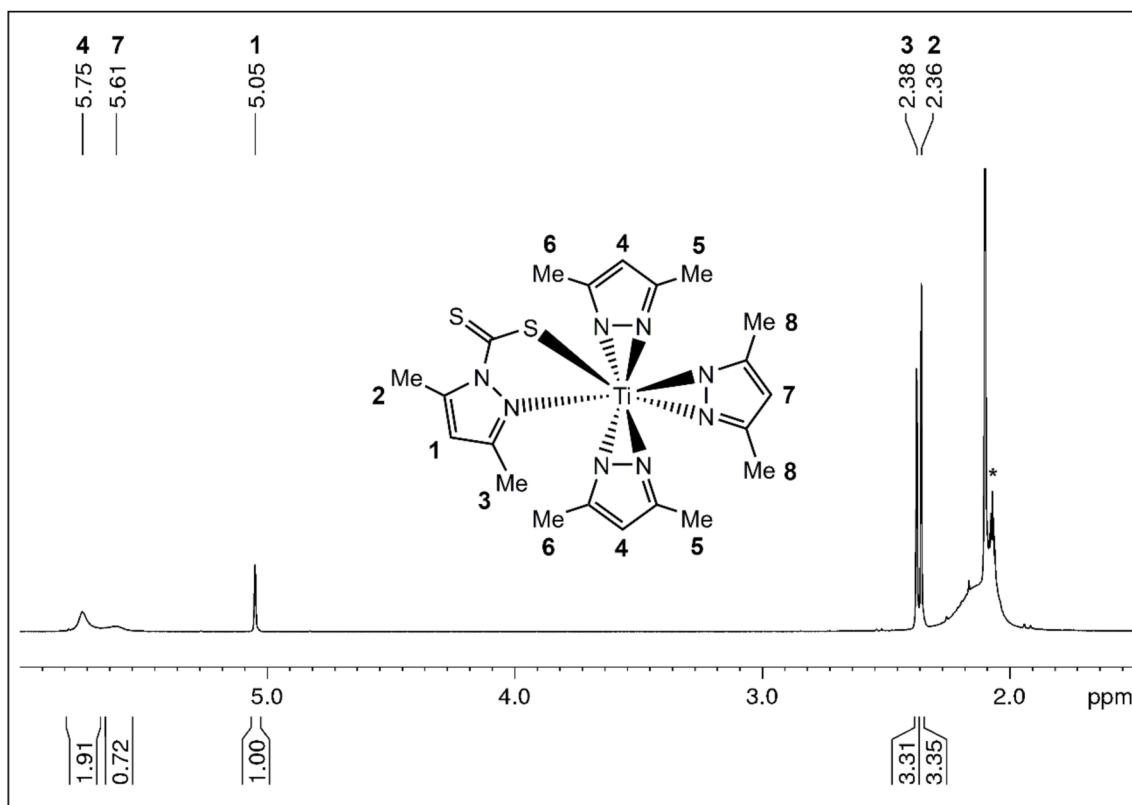


Figure S11. ¹H NMR spectrum (400.11 MHz, [D₈]toluene) of Ti(CS₂·pz^{Me2})(pz^{Me2})₃ (**1**^{CS2}) at 26 °C.

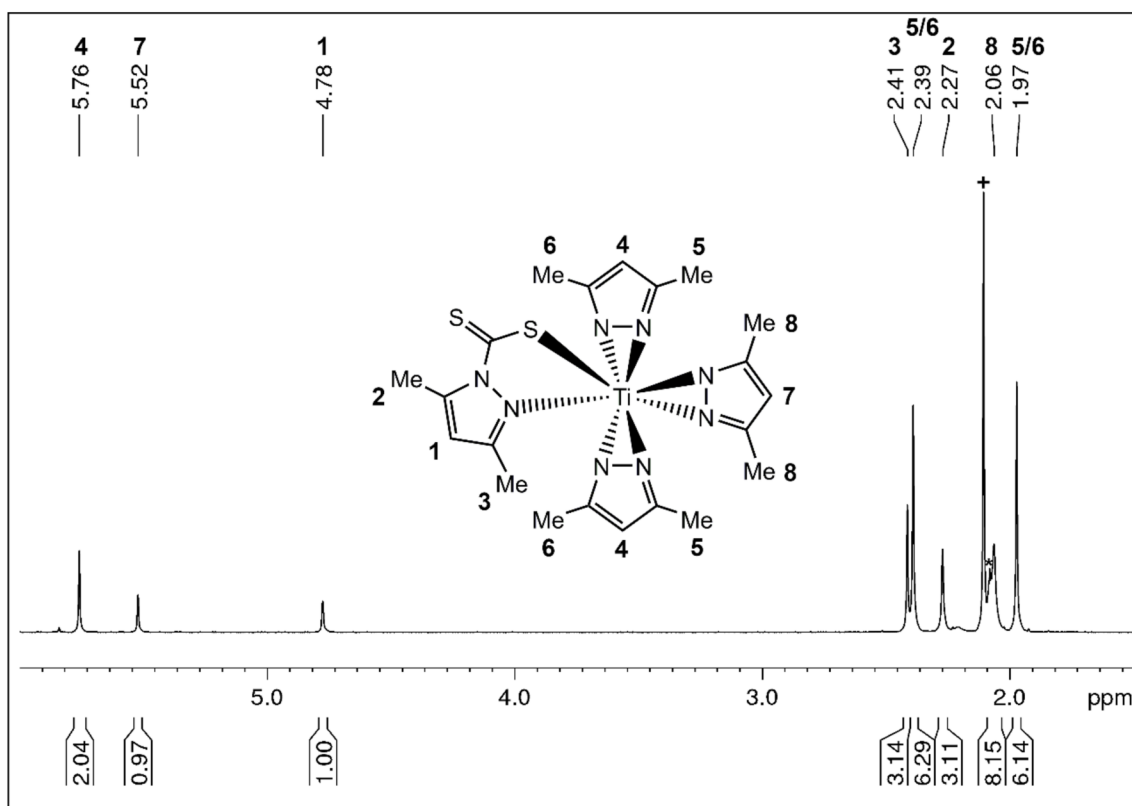


Figure S12. ¹H NMR spectrum (500.13 MHz, [D₈]toluene) of Ti(CS₂·pz^{Me2})(pz^{Me2})₃ (**1**^{CS2}) (+ toluene) at -60 °C.

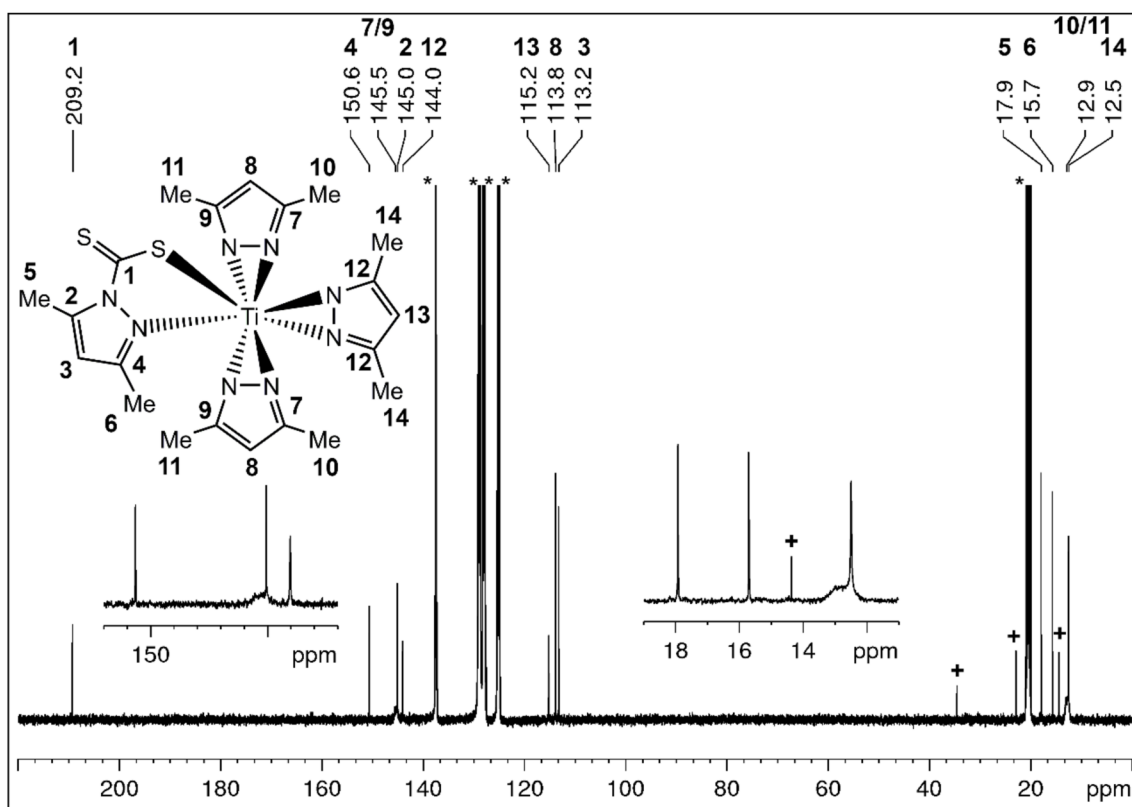


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.76 MHz, $[\text{D}_8]\text{toluene}$) of $\text{Ti}(\text{CS}_2 \cdot \text{pz}^{\text{Me}_2})(\text{pz}^{\text{Me}_2})_3$ (**1^{CS2}**) (+ *n*-hexane) at 0 °C.

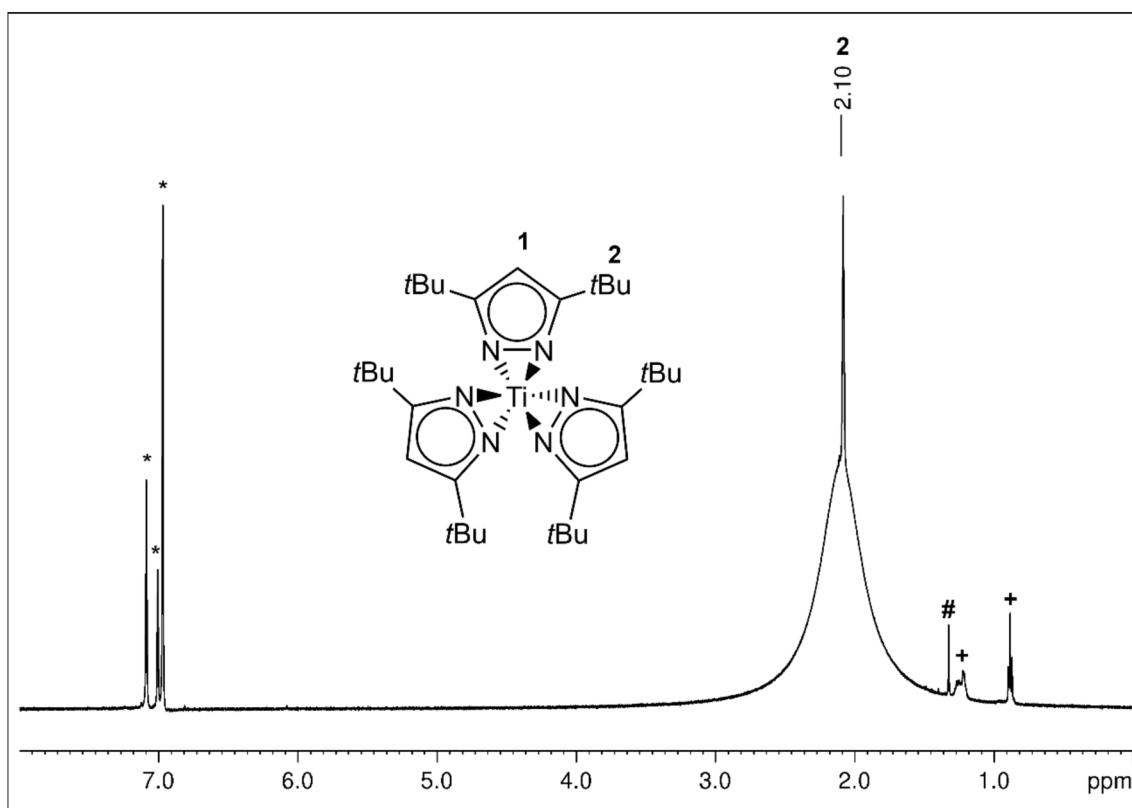


Figure S14. ^1H NMR spectrum (400.11 MHz, $[\text{D}_8]\text{toluene}$) of $\text{Ti}(\text{pz}^{\text{tBu}_2})_3$ (**4**) at 26 °C (+ *n*-hexane, # grease).

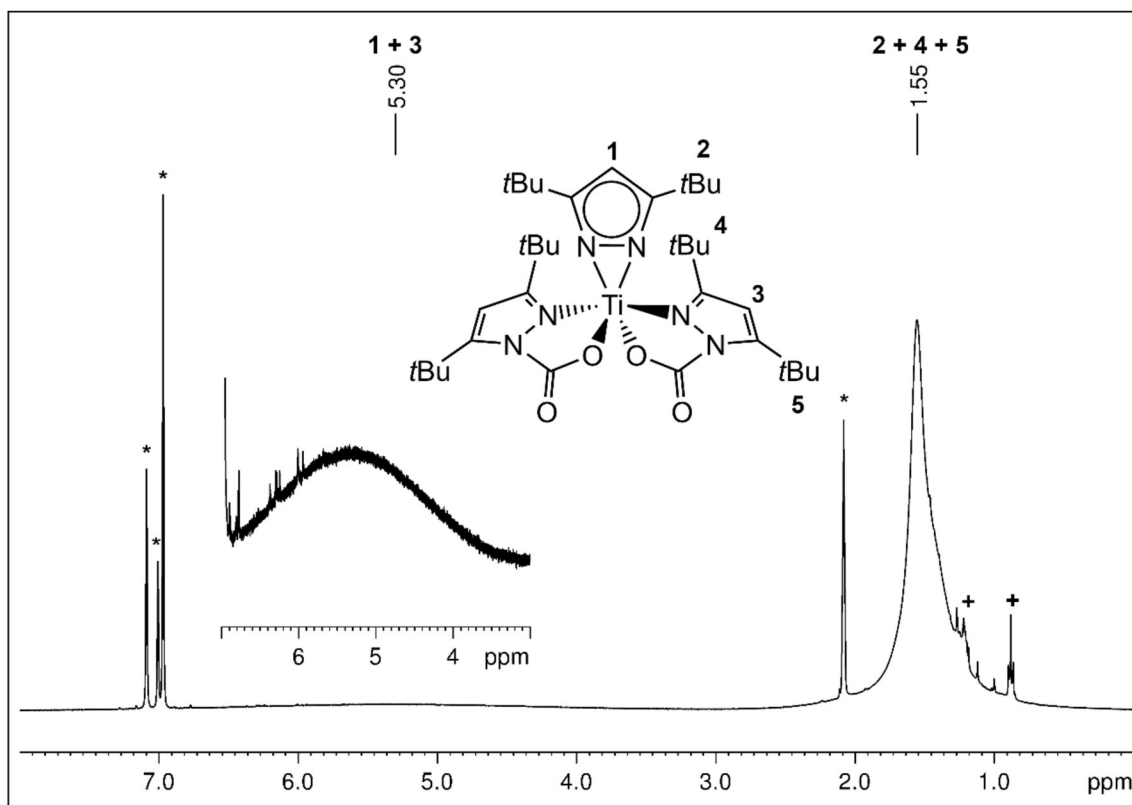


Figure S15. ^1H NMR spectrum (500.13 MHz, $[\text{D}_8]\text{toluene}$) of $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (4^{CO_2}) at 26 °C (+ *n*-hexane).

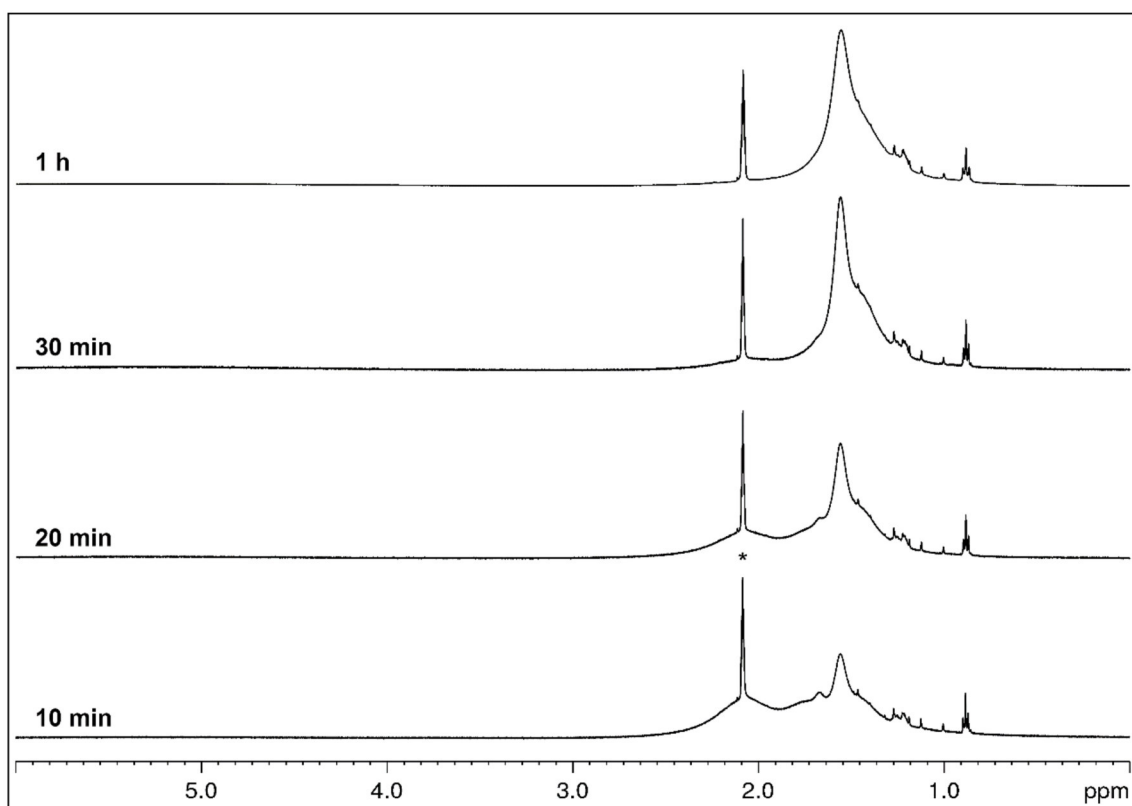


Figure S16. Monitoring of the conversion of $\text{Ti}(\text{pz}^{\text{tBu}_2})_3$ (4) to $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})_2$ (4^{CO_2}) via ^1H NMR spectra (400.11 MHz, $[\text{D}_8]\text{toluene}$) at 26 °C.

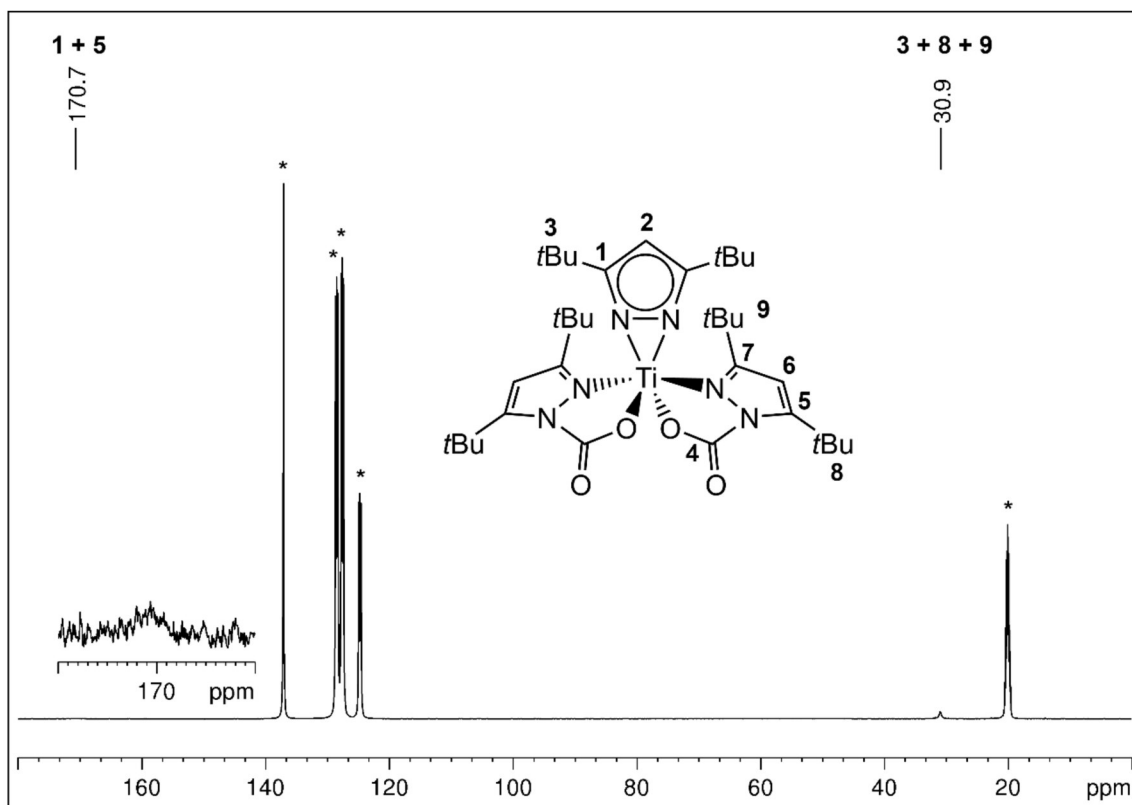


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.76 MHz, $[\text{D}_8]$ toluene) of $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{tBu}2})_2(\text{pz}^{\text{tBu}2})_2$ ($4^{\text{CO}2}$) at 26 °C.

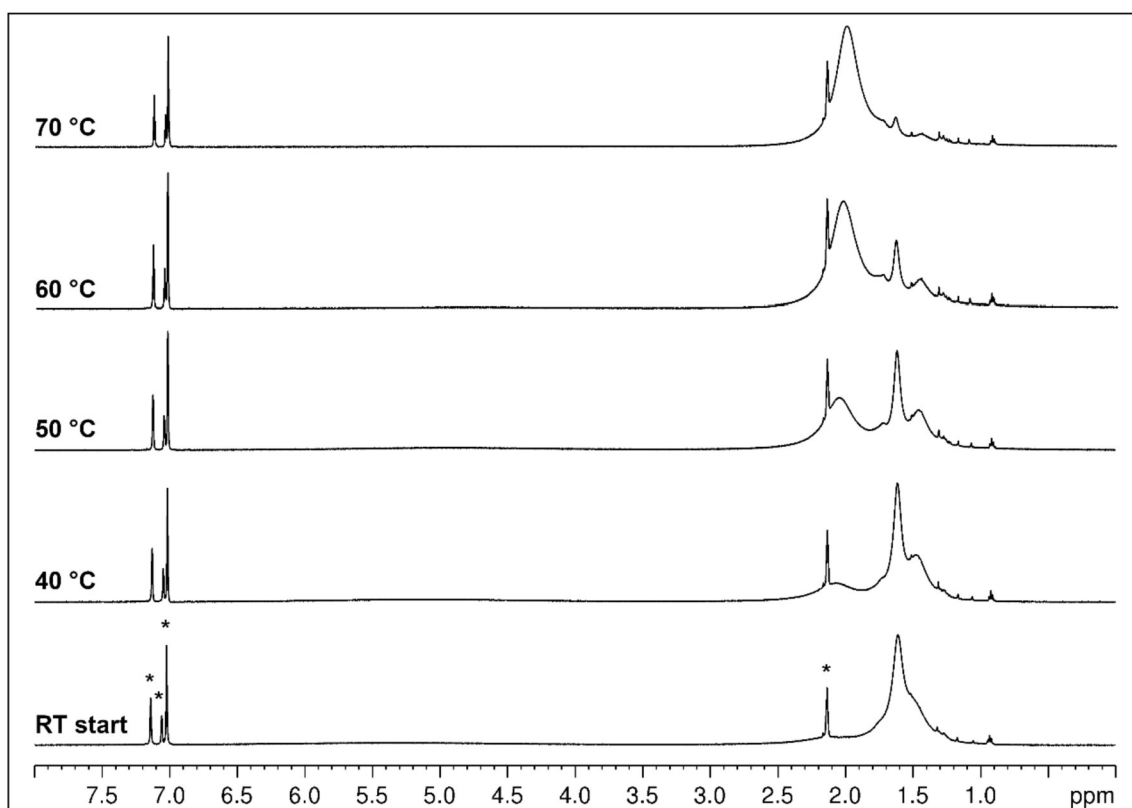


Figure S18. VT ^1H NMR spectra (500.13 MHz, $[\text{D}_8]$ toluene) of $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{tBu}2})_2(\text{pz}^{\text{tBu}2})_2$ ($4^{\text{CO}2}$) in the range of 26 °C and 70 °C showing the formation of $\text{Ti}(\text{pz}^{\text{tBu}2})_3$ (**4**).

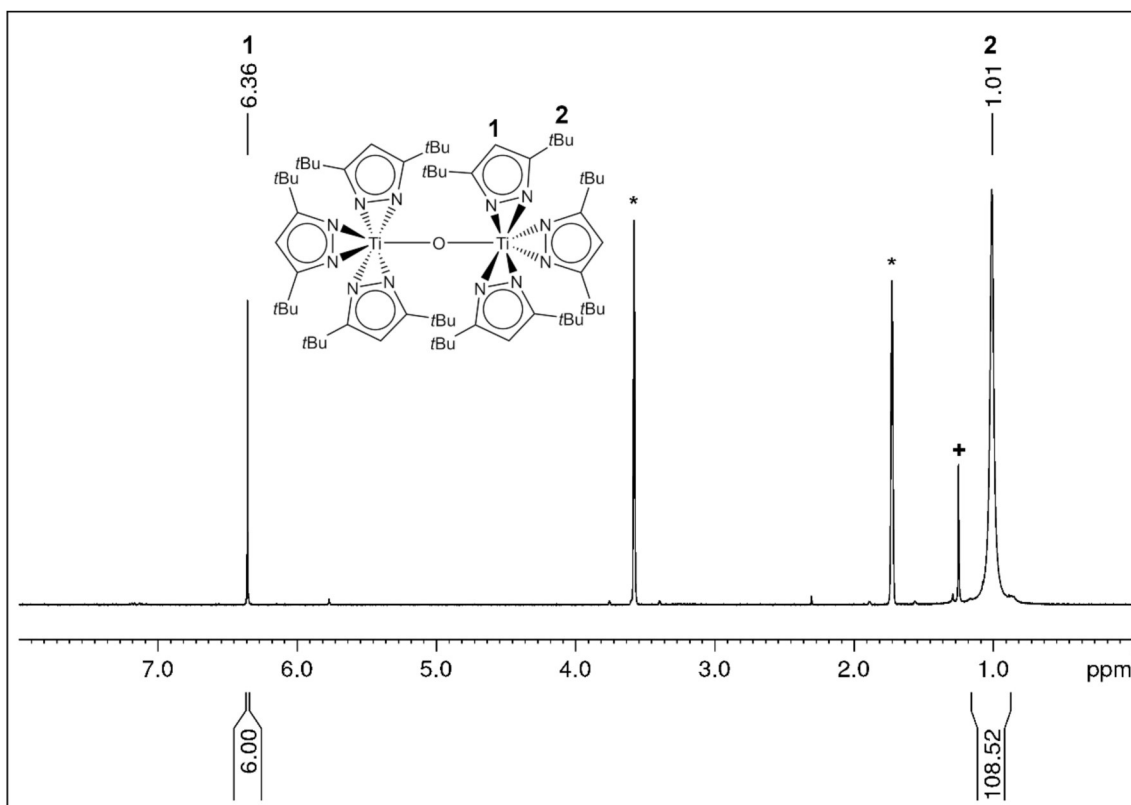


Figure S19. ^1H NMR spectrum (400.11 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Ti}(\text{pz}^{\text{tBu}_2})_3]_2(\mu\text{-O})$ (5) at 26 °C (+ H grease).

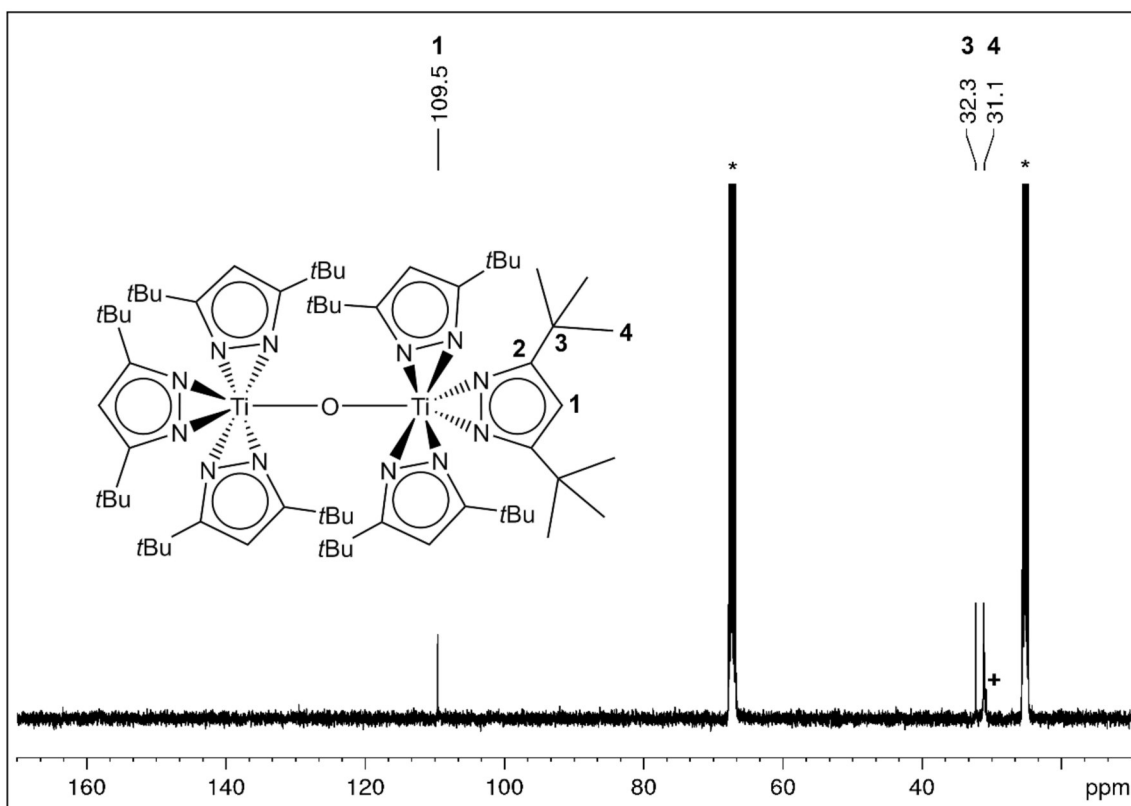


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.61 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Ti}(\text{pz}^{\text{tBu}_2})_3]_2(\mu\text{-O})$ (5) at 26 °C (+ H grease).

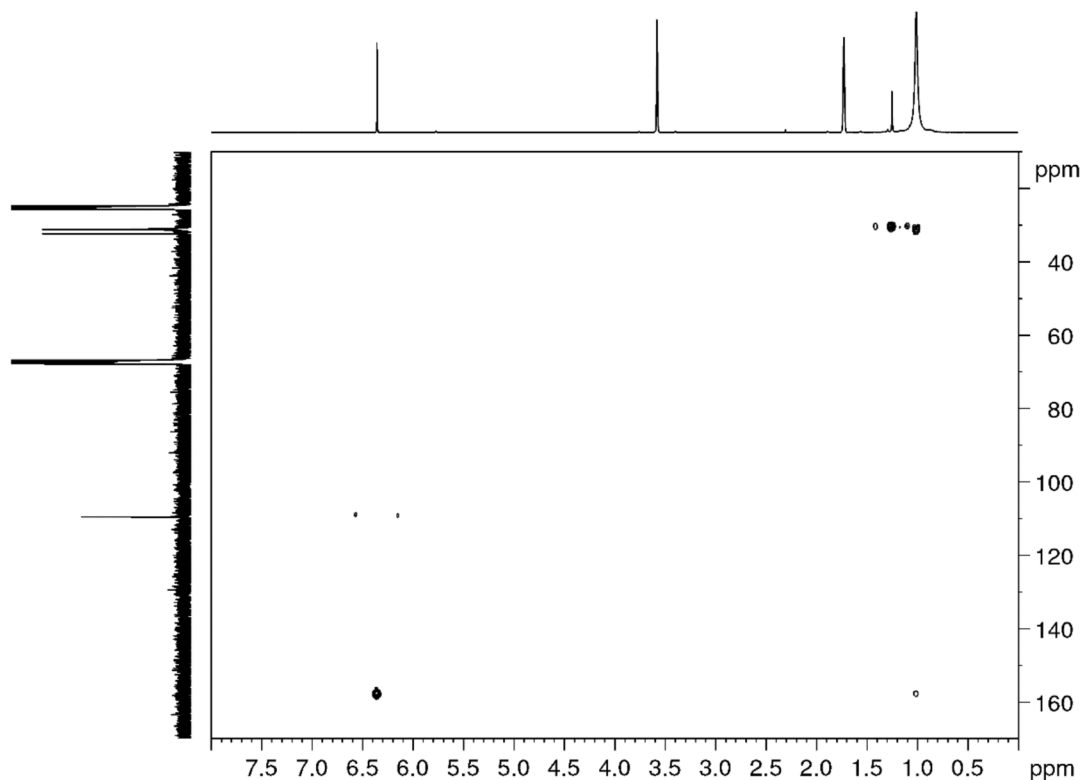


Figure S21. ^1H - ^{13}C HMBC NMR spectrum (^1H : 400.11 MHz, ^{13}C : 100.61 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Ti}(\text{pz}^{\text{tBu}2})_3](\mu\text{-O})$ (**5**) at 26 °C (+ H grease).

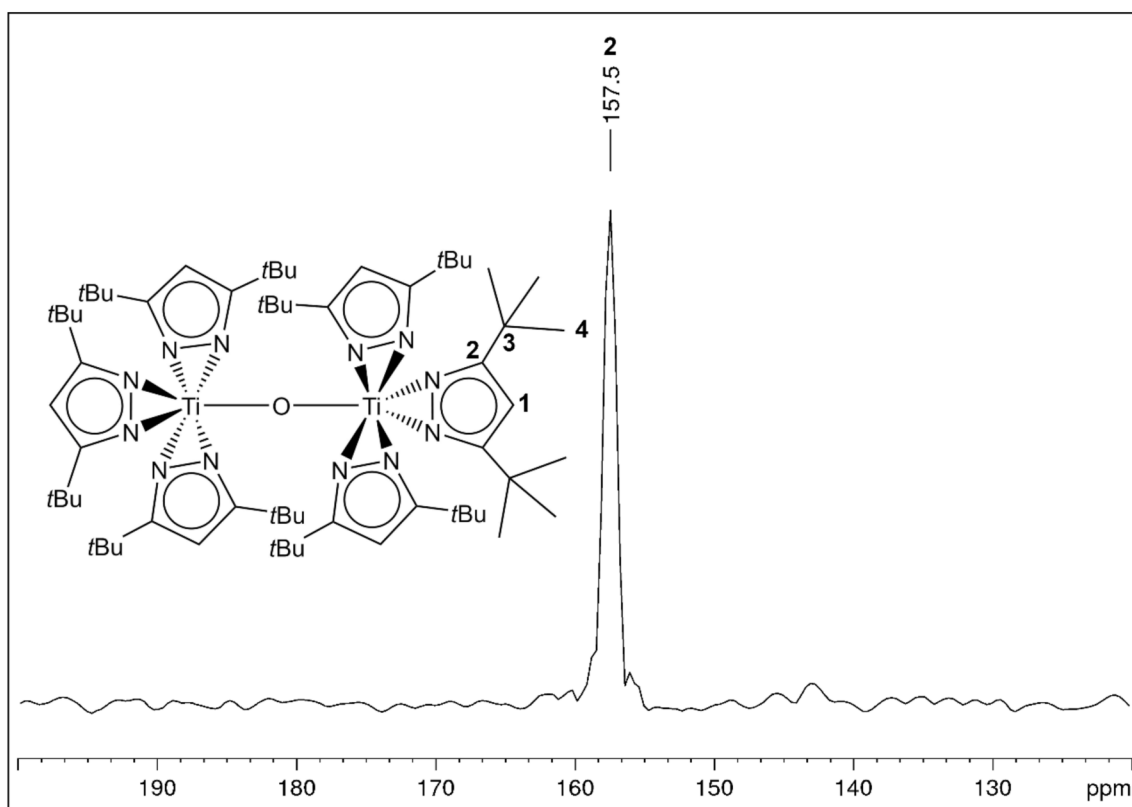


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR projection calculated from ^1H - ^{13}C HMBC NMR spectrum (^1H : 400.11 MHz, ^{13}C : 100.61 MHz, $[\text{D}_8]\text{toluene}$) of $[\text{Ti}(\text{pz}^{\text{tBu}2})_3](\mu\text{-O})$ (**5**) at 26 °C.

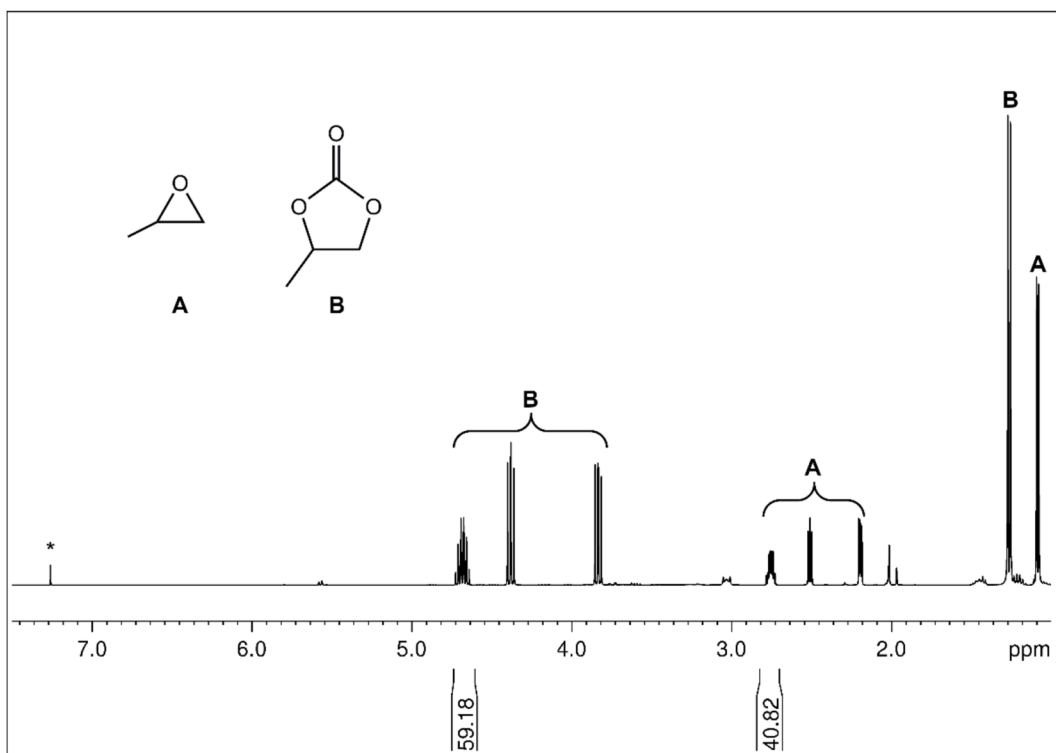


Figure S23. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Ti}(\text{pz}^{\text{Me}_2})_4$ (**1**) as catalyst at 26 °C.

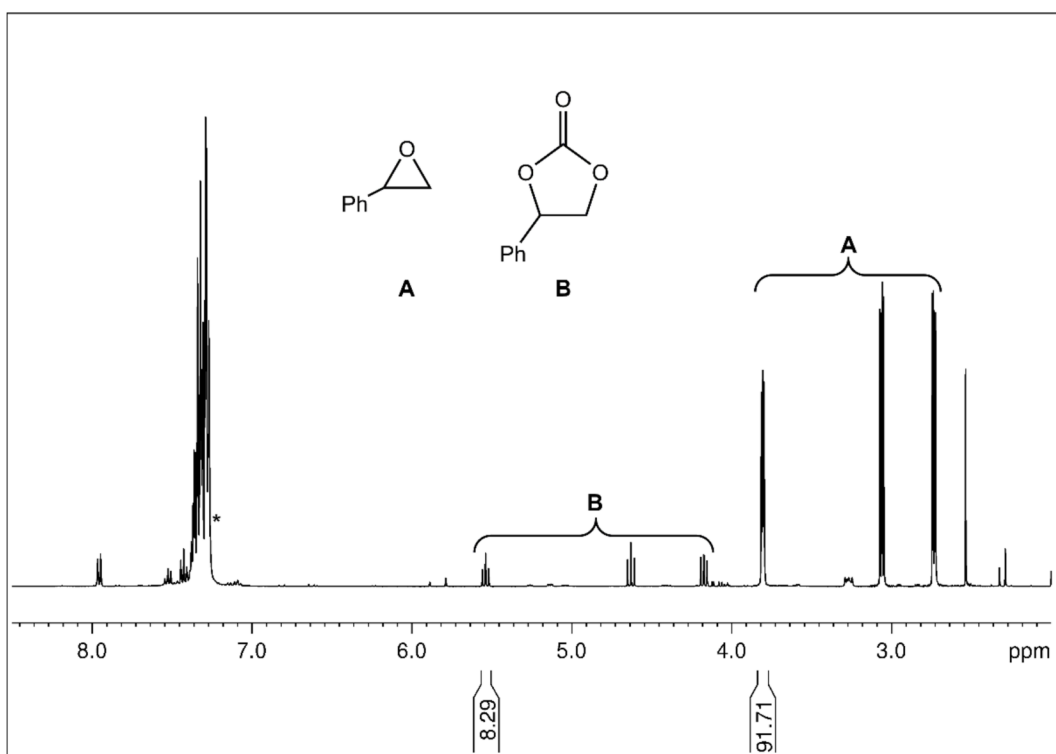


Figure S24. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of styrene oxide and CO_2 to styrene carbonate by using 0.5 mol% of $\text{Ti}(\text{pz}^{\text{Me}_2})_4$ (**1**) as catalyst at 26 °C.

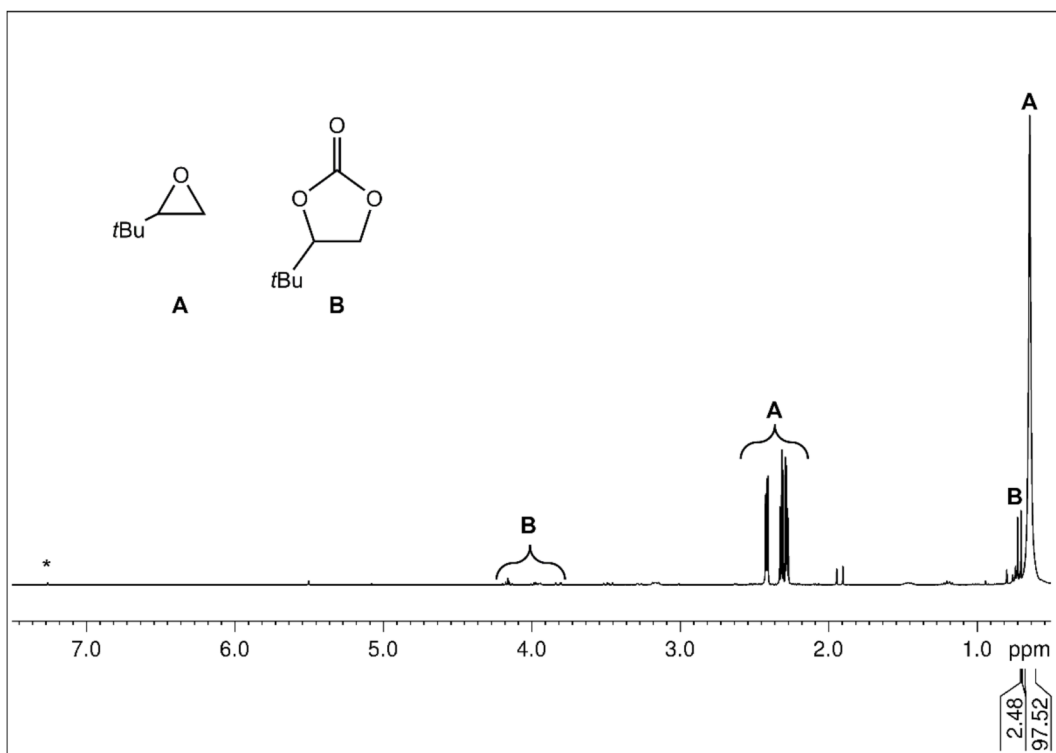


Figure S25. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 2-*tert*-butyloxirane and CO₂ to 3,3-dimethyl-1,2-butene carbonate by using 0.5 mol% of Ti(pz^{Me₂})₄ (**1**) as catalyst at 26 °C.

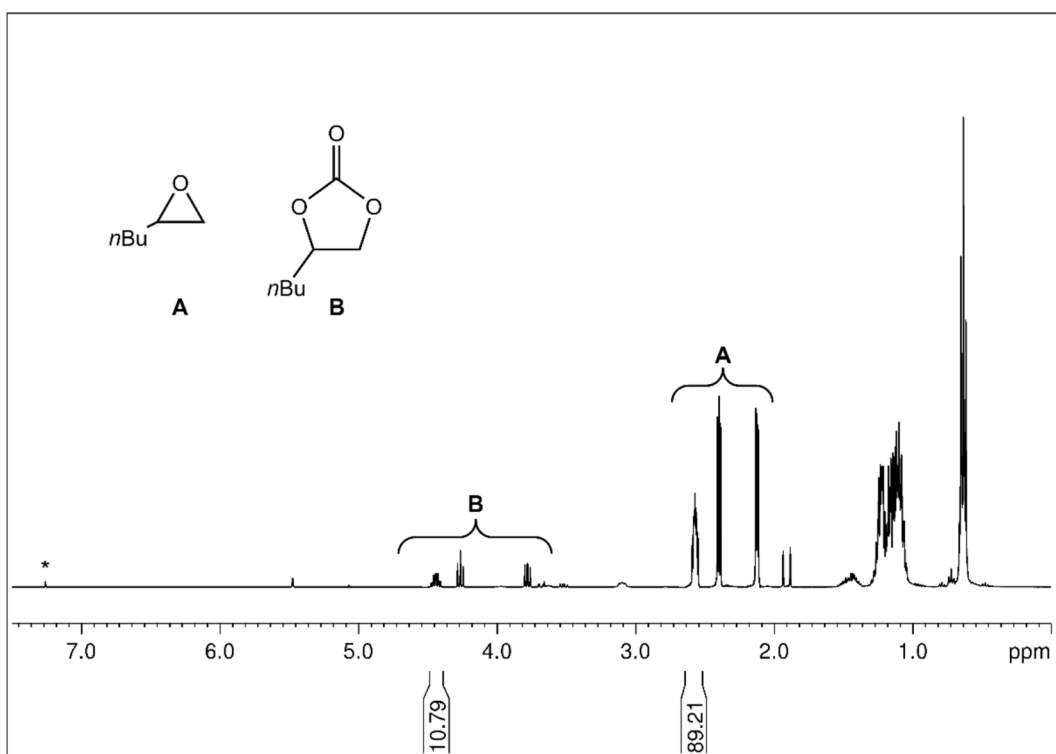


Figure S26. ¹H NMR spectrum (26 °C, 400.11 MHz, chloroform-*d*) of the reaction mixture of the catalytic conversion of 1,2-epoxyhexane and CO₂ to 1,2-*n*-hexylene carbonate by using 0.5 mol% of Ti(pz^{Me₂})₄ (**1**) as catalyst at 26 °C.

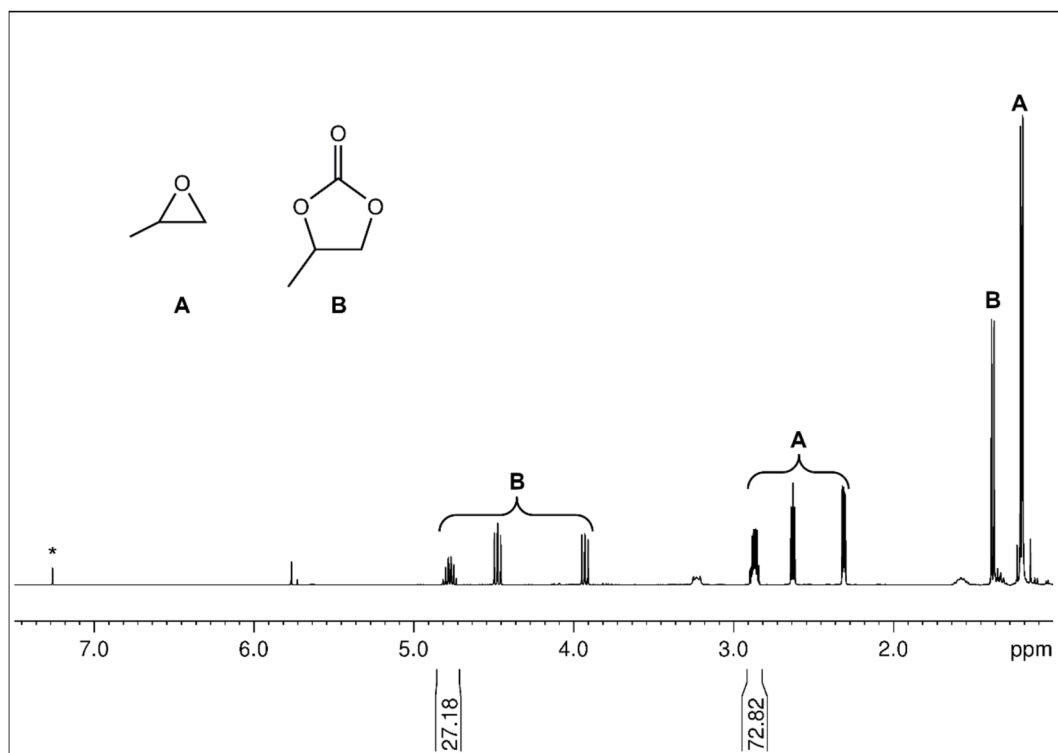


Figure S27. ^1H NMR spectrum (26 °C, 400.11 MHz, chloroform- d) of the reaction mixture of the catalytic conversion of propylene oxide and CO_2 to propylene carbonate by using 0.5 mol% of $\text{Ti}(\text{pz}^{\text{tBu}_2})_3$ (**4**) as catalyst at 26 °C.

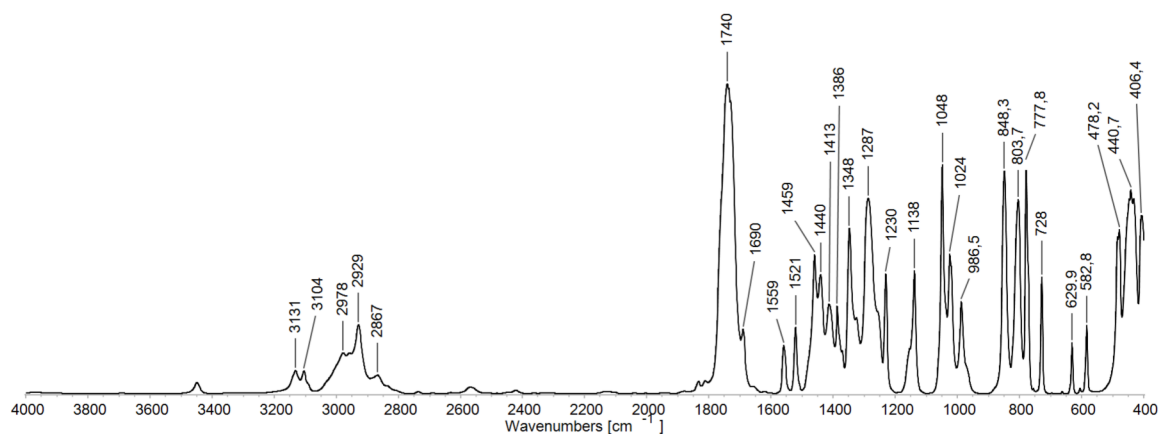


Figure S28. DRIFT spectrum of $\text{Ti}(\text{CO}_2 \cdot \text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ (1^{CO_2}) at 25 °C.

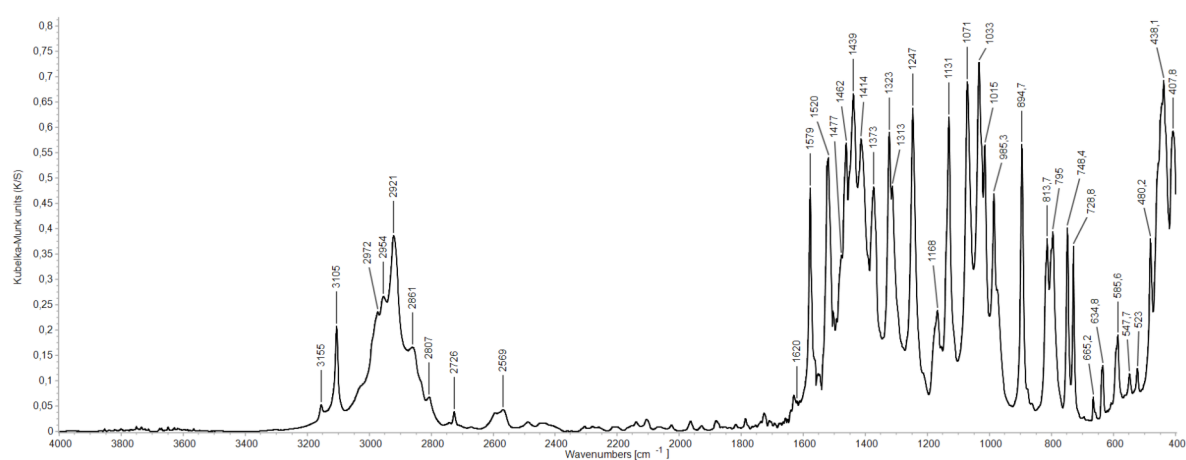


Figure S29. DRIFT spectrum of $\text{Ti}(\text{CS}_2 \cdot \text{pz}^{\text{Me}_2})(\text{pz}^{\text{Me}_2})_3$ (1^{CS_2}) at 25 °C.

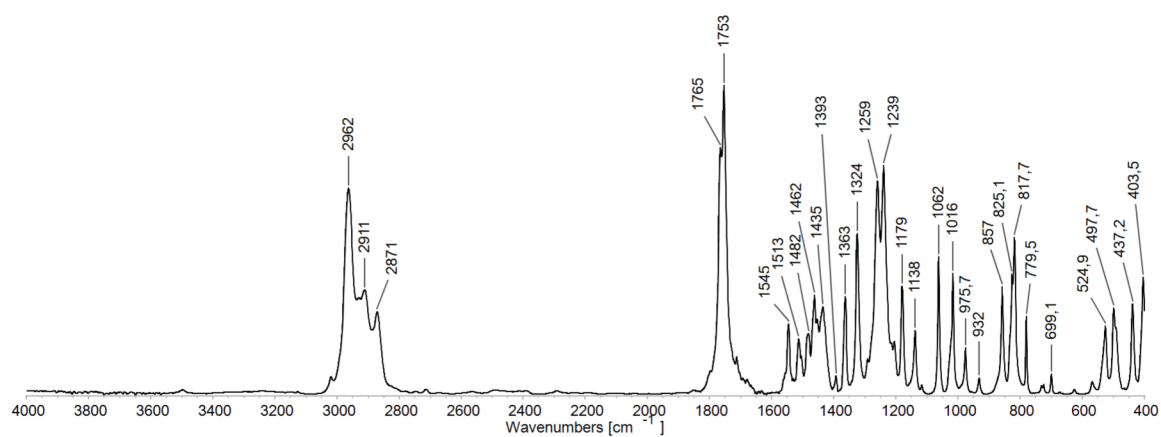


Figure S30. DRIFT spectrum of $\text{Ti}(\text{CO}_2 \cdot \text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (4^{CO_2}) at 25 °C.

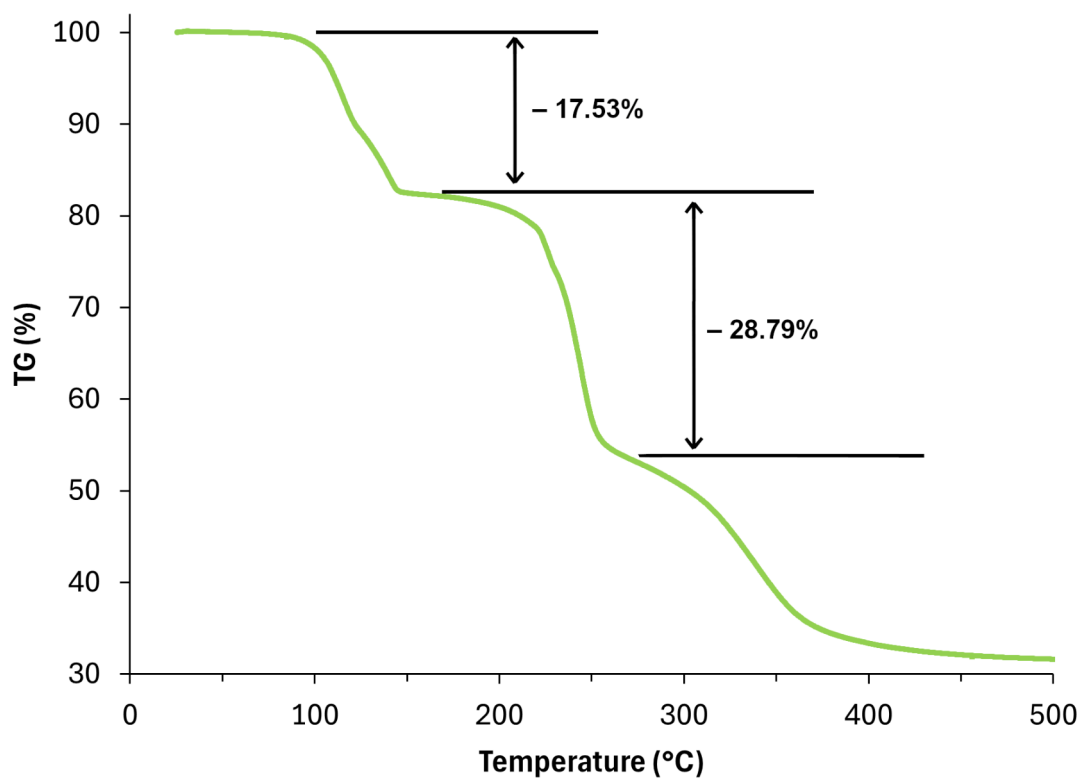


Figure S31. TGA of $\text{Ti}(\text{CO}_2 \cdot \text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ (**1^{CO2}**). The sample was heated from 27 °C to 1000 °C with a heating ratio of 2 Kmin⁻¹ under constant Ar flow.

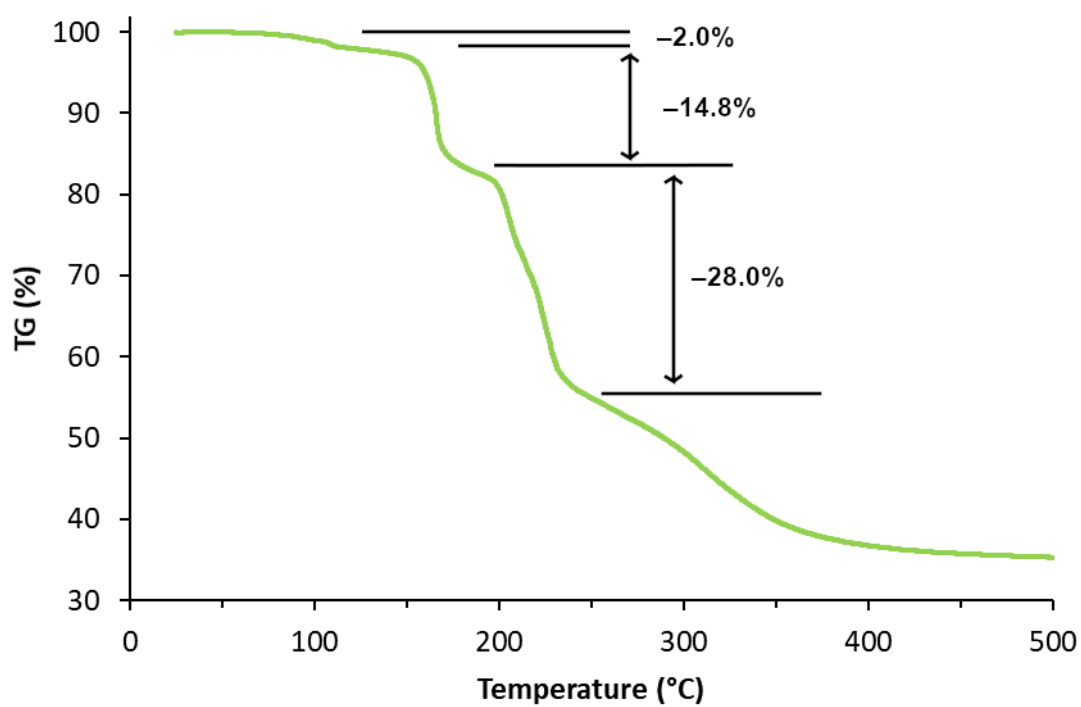


Figure S32. TGA of $\text{Ti}(\text{CS}_2 \cdot \text{pz}^{\text{Me}_2})(\text{pz}^{\text{Me}_2})_3$ (**1^{CS2}**). The sample was heated from 27 °C to 1000 °C with a heating ratio of 2 Kmin⁻¹ under constant Ar flow.

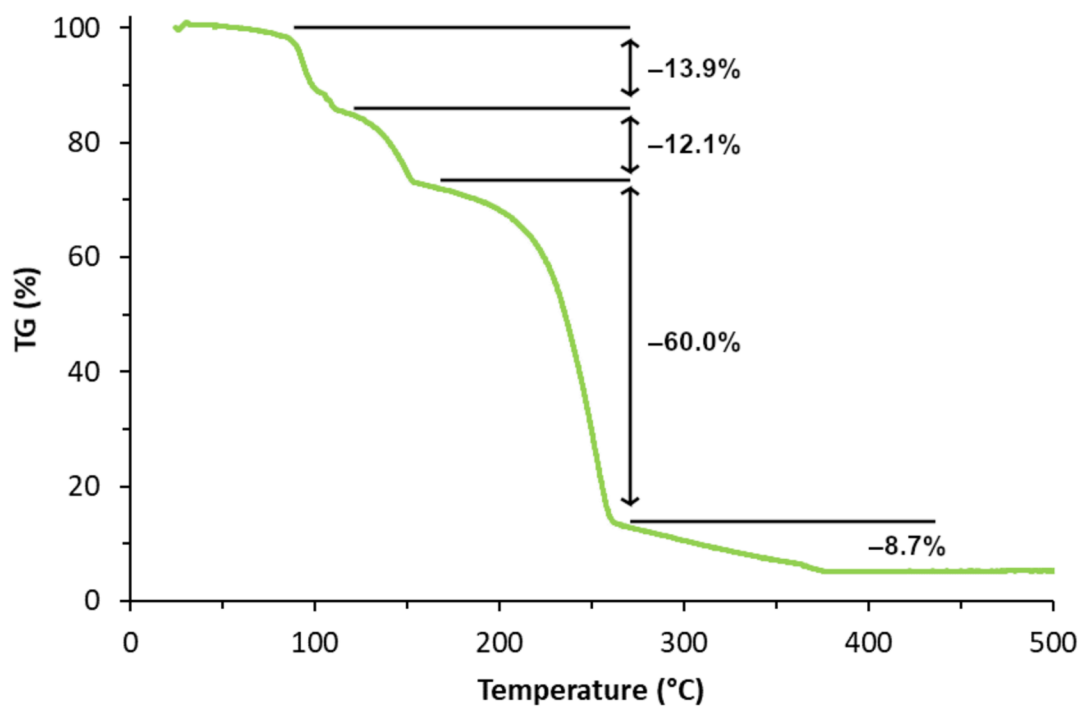


Figure S33. TGA of $\text{Ti}(\text{CO}_2 \cdot \text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})$ (4^{CO_2}). The sample was heated from 27 °C to 1000 °C with a heating ratio of 2 Kmin⁻¹ under constant Ar flow.

Table S1. Crystallographic data for complexes **1^{CO2}**, **2**, **3** and **1^{CS2}**

	1^{CO2}	2	3	1^{CS2}
CCDC	2423933	2423932	2423934	2423931
formula	C ₂₂ H ₂₈ N ₈ O ₄ Ti · 0.5 C ₇ H ₈	C ₃₄ H ₄₂ N ₁₂ O ₉ Ti ₂ · C ₇ H ₈	C ₄₂ H ₅₆ N ₁₆ O ₆ Ti ₃ · 0.5 C ₇ H ₈	C ₂₁ H ₂₈ N ₈ S ₂ Ti · C ₇ H ₈
M [g mol ⁻¹]	562.49	950.73	1070.79	596.67
color/shape	orange/plate	yellow/plate	orange/block	yellow/plate
Crystal dimensions [mm]	0.210 x 0.103 x 0.069	0.183 x 0.151 x 0.053	0.172 x 0.163 x 0.140	0.264 x 0.150 x 0.112
cryst. system	orthorhombic	monoclinic	triclinic	orthorhombic
space group	<i>Pccn</i>	<i>P2₁/n</i>	<i>P</i> $\bar{1}$	<i>Pbca</i>
a [Å]	13.996(4)	12.0147(16)	10.2731(3)	14.9266(7)
b [Å]	15.781(5)	12.7078(17)	13.7173(4)	16.7993(8)
c [Å]	27.295(8)	29.572(4)	18.2960(6)	24.6971(13)
α [°]	90	90	82.3550(10)	90
β [°]	90	92.721(3)	81.5940(10)	90
γ [°]	90	90	85.9250(10)	90
V [Å ³]	6029(3)	4510.0(11)	2524.38(13)	6193.0(5)
Z	8	4	2	8
T [K]	100(2)	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.239	1.400	1.409	1.280
μ [mm ⁻¹]	0.326	0.421	0.527	0.442
F(000)	2360	1984	1118	2512
ϑ range [°]	1.945/28.776	1.379/27.143	1.764/28.744	2.003/26.398
unique reflns	7839	9977	13079	6339
observed reflns	93953	64412	100585	40857
R ₁ ^[a] /wR ₂ ($I > 2\sigma$) ^[b]	0.0606/0.1559	0.0502/0.1115	0.0413/0.1032	0.0381/0.0932
R ₁ ^[a] /wR ₂ (all data) ^[b]	0.0756/0.1641	0.0931/0.1316	0.0554/0.1126	0.0497/0.1015
GOF ^[c]	1.106	1.017	1.047	1.053

^[a]R₁ = $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $F_o > 4\sigma(F_o)$, ^[b]wR₂ = $\{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, ^[c]GOF = $[\Sigma w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$.

Table S2. Crystallographic data for complexes **4^{CO2*}** and **5***

	4^{CO2*}	5*
CCDC	2423936	2423935
formula	C ₃₅ H ₅₇ N ₆ O ₄ Ti · 2 C ₇ H ₈	C ₆₆ H ₁₁₄ N ₁₂ OTi ₂
M [g mol ⁻¹]	858.03	1187.46
color/shape	colorless/column	yellow/block
Crystal dimensions [mm]	0.434 x 0.179 x 0.143	0.212 x 0.199 x 0.168
cryst. system	orthorhombic	cubic
space group	<i>Pbca</i>	<i>Pa$\bar{3}$</i>
a [Å]	28.975(4)	19.2439(11)
b [Å]	23.619(3)	19.2439(11)
c [Å]	43.439(6)	19.2439(11)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
V [Å ³]	29728(7)	7126.6(12)
Z	24	4
T [K]	100(2)	100(2)
wavelength [Å]	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.150	1.107
μ [mm ⁻¹]	0.219	0.270
F(000)	11112	2584
θ range [°]	1.455/24.462	1.833/28.740
unique reflns	24573	3094
observed reflns	199425	138932
R ₁ ^[a] /wR ₂ ($I > 2\sigma$) ^[b]	0.0844/0.1760	0.0923/0.2387
R ₁ ^[a] /wR ₂ (all data) ^[b]	0.1548/0.2094	0.1061/0.2466
GOF ^[c]	1.039	1.133

^[a]R₁ = $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $F_o > 4\sigma(F_o)$, ^[b]wR₂ = $\{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, ^[c]GOF = $[\Sigma w(F_o^2 - F_c^2)^2 / (n_o - n_p)]^{1/2}$

* Connectivity structure only.

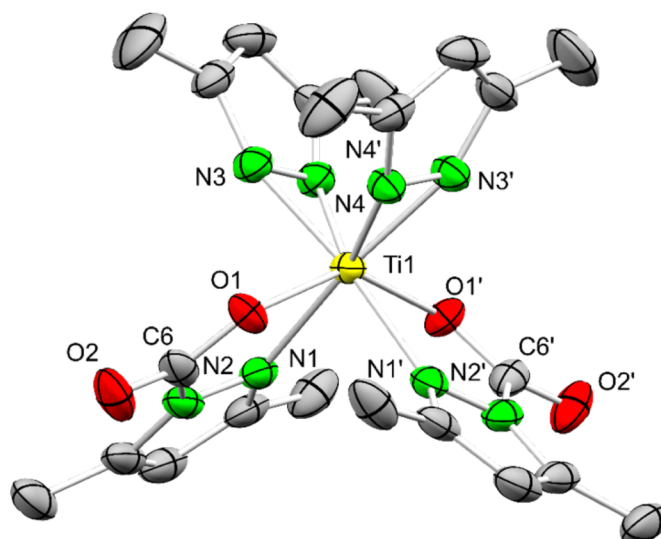


Figure S34. Crystal structure of $[\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2]$ ($\mathbf{1}^{\text{CO}_2}$), thermal ellipsoids set at 50% probability. Hydrogen atoms, one lattice solvent toluene and a second unit of $\mathbf{1}^{\text{CO}_2}$ are omitted for clarity. Selected interatomic distances [$\text{\AA}$]: Ti1–O1 2.0445(18), Ti1–N1 2.211(2), Ti1–N3 2.045(2), Ti1–N4 2.016(2), C6–O1 1.275(3), C6–O2 1.207(3). Selected angles [$^\circ$]: O1–Ti1–O1' 141.77(11), O1–C6–O2 129.0(3), O1–Ti1–N1 72.82(8), O1'–Ti1–N1 80.61(8). $^{-x+1/2, -y+3/2, z}$

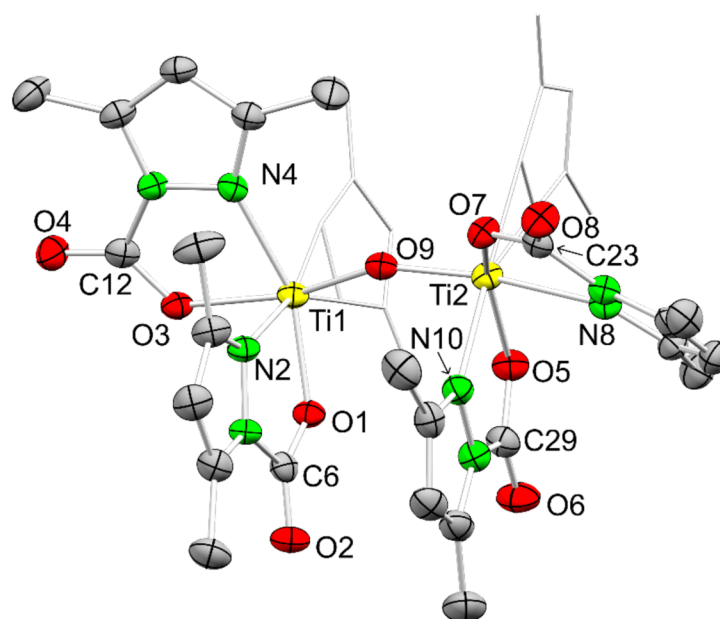


Figure S35. Crystal structure of $[\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})]_2(\mu\text{-O})$ ($\mathbf{2}$), thermal ellipsoids set at 50% probability. Hydrogen atoms and one lattice solvent toluene are omitted for clarity. Selected interatomic distances [$\text{\AA}$]: Ti1–O1 1.9930(18), Ti1–O3 2.0286(19), Ti1–O9 1.8164(19), Ti1–N2 2.244(2), Ti–N4 2.164(2), Ti2–O5 1.995(2), Ti2–O7 2.0140(19), Ti2–O9 1.790(2), Ti2–N8 2.214(2), Ti2–N10 2.222(2), O1–C6 1.290(3), O2–C6 1.208(3), O3–C12 1.280(3), O4–C12 1.209(3), O5–C29 1.297(3), O6–C29 1.203(3), O7–C23 1.275(3), O8–C23 1.215(3). Selected angles [$^\circ$]: O1–Ti1–N2 73.13(8), O3–Ti1–N4 74.09(8), O5–Ti2–N10 73.97(9), O7–Ti2–N8 73.79(8), O1–C6–O2 127.6(3), O3–C12–O4 129.4(3), O5–C29–O6 128.1(3), O7–C23–O8 129.2(3), Ti1–O9–Ti2 148.94(11).

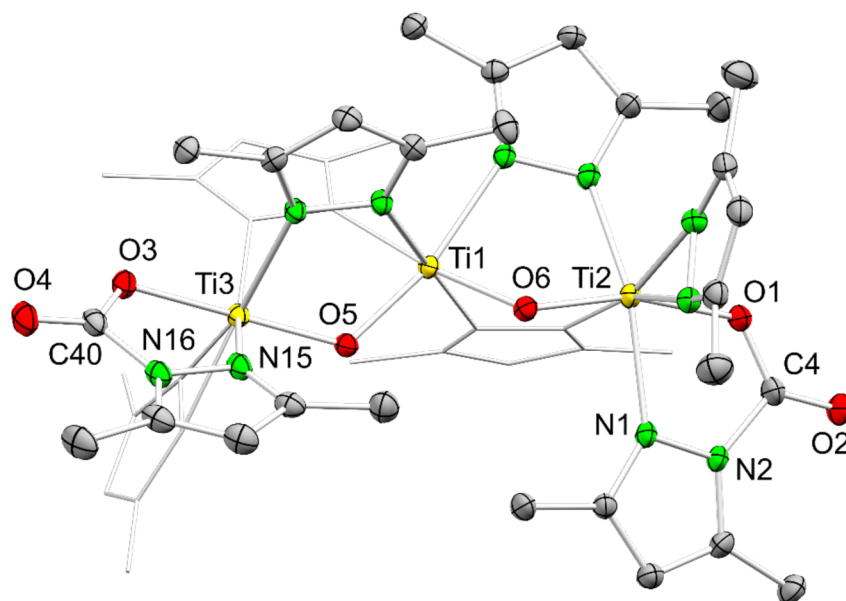


Figure S36. Crystal structure of $[\text{Ti}(\mu\text{-O})_2(\mu\text{-pz}^{\text{Me}_2})_4(\text{Ti}\{\text{CO}_2\cdot\text{pz}^{\text{Me}_2}\}\{\text{pz}^{\text{Me}_2}\})_2]$ (**3**), thermal ellipsoids set at 50% probability. Hydrogen atoms and one lattice solvent toluene are omitted for clarity. Selected interatomic distances [Å]: Ti1–O5 1.8465(12), Ti1–O6 1.8199(12), Ti2–O1 2.0126(13), Ti2–N1 2.2030(16), Ti2–O6 1.8075(12), Ti3–O3 2.0437(13), Ti3–O5 1.7935(12), Ti3–N15 2.1877(15). Selected angles [°]: O1–C4–O2 129.38(18), O3–C40–O4 129.64(19), O1–Ti2–N1 73.78(5), O3–Ti3–N15 73.32(6), Ti1–O6–Ti2 123.94(7), Ti1–O5–Ti3 122.70(7), O5–Ti1–O6 104.58(6).

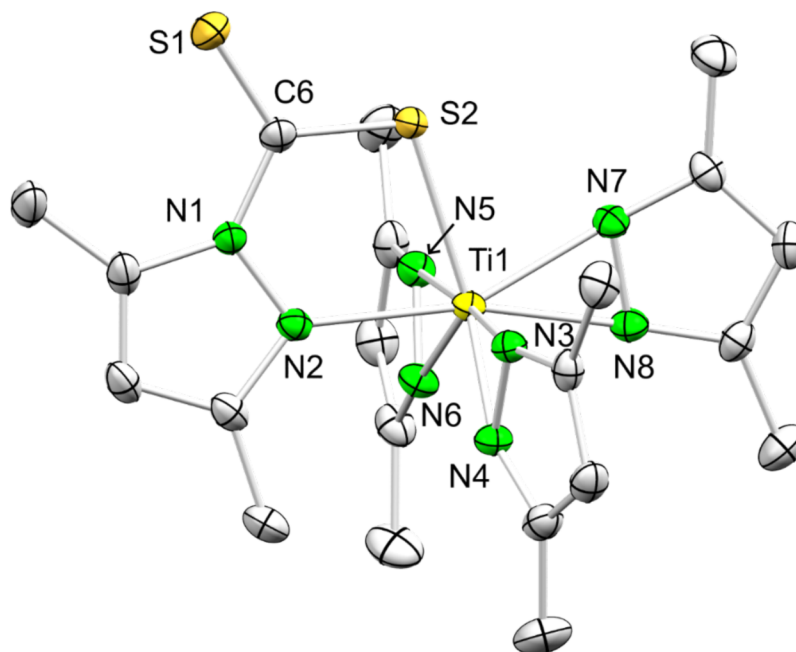


Figure S37. Crystal structure of $[\text{Ti}(\text{CS}_2\cdot\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2]$ (**1^{CS2}**), thermal ellipsoids set at 50% probability. Hydrogen atoms and one lattice solvent toluene are omitted for clarity. Selected interatomic distances [Å]: Ti1–S2 2.4617(5), S1–C6 1.6543(19), S2–C6 1.7019(19). Selected angles [°]: S1–C6–S2 121.64(12), S2–Ti1–N2 74.75(4).

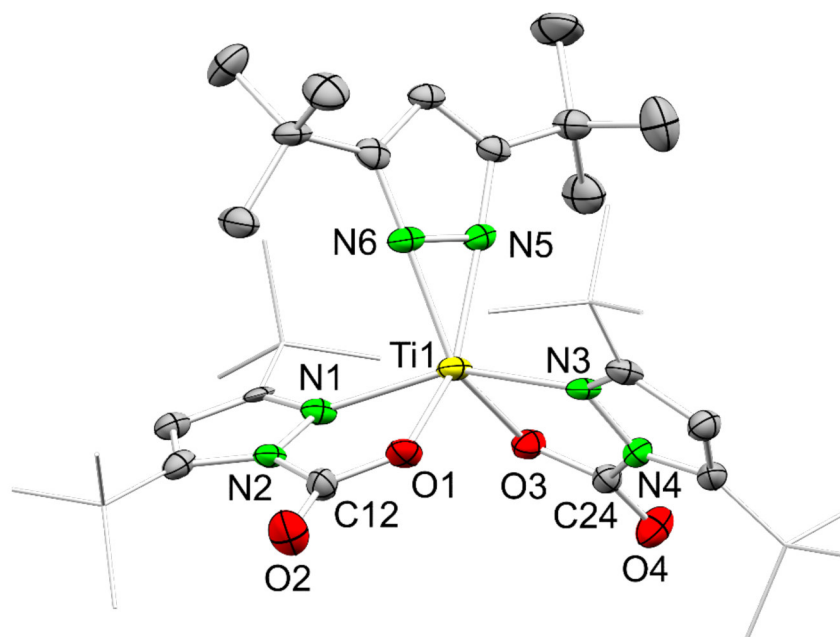


Figure S38. Connectivity of $[\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})]$ (4^{CO_2}), thermal ellipsoids set at 50% probability. Hydrogen atoms, six lattice solvent toluene and two molecules of 4^{CO_2} are omitted for clarity.

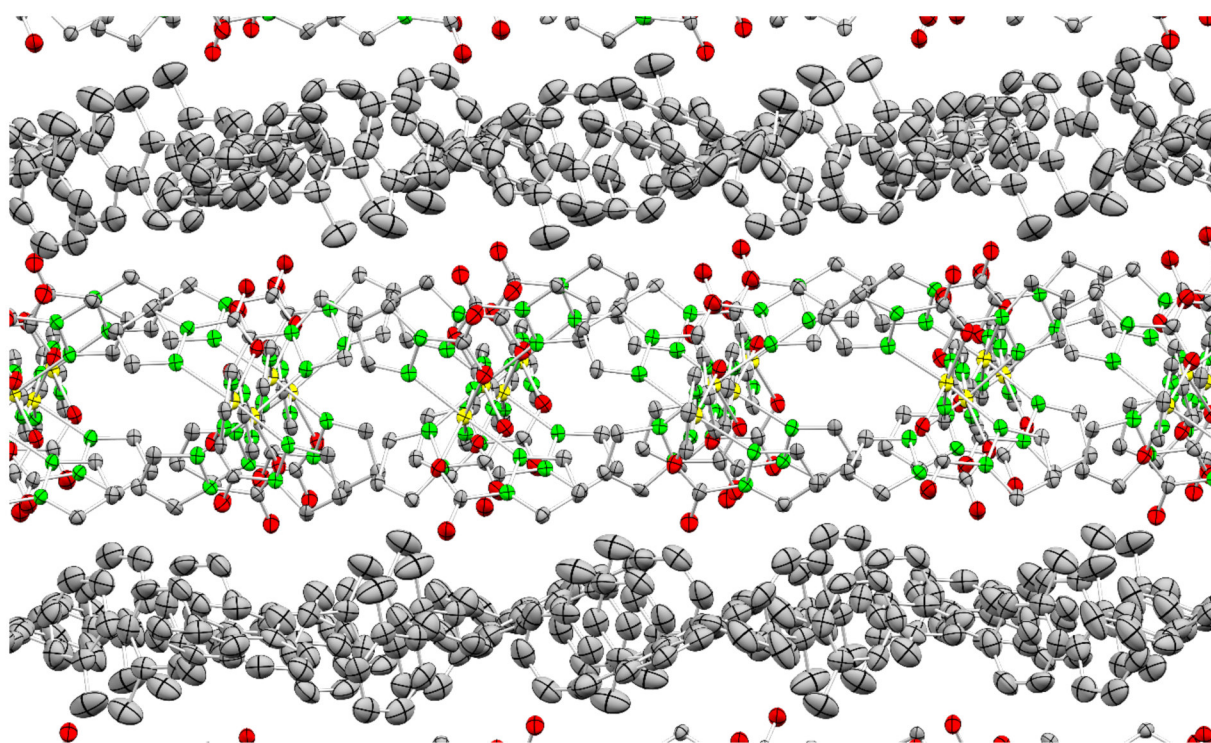


Figure S39. Layer arrangement of $[\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{tBu}_2})_2(\text{pz}^{\text{tBu}_2})]$ (4^{CO_2}) and lattice toluene. Thermal ellipsoids set at 50% probability. Hydrogen atoms and *t*Bu moieties are omitted for clarity.

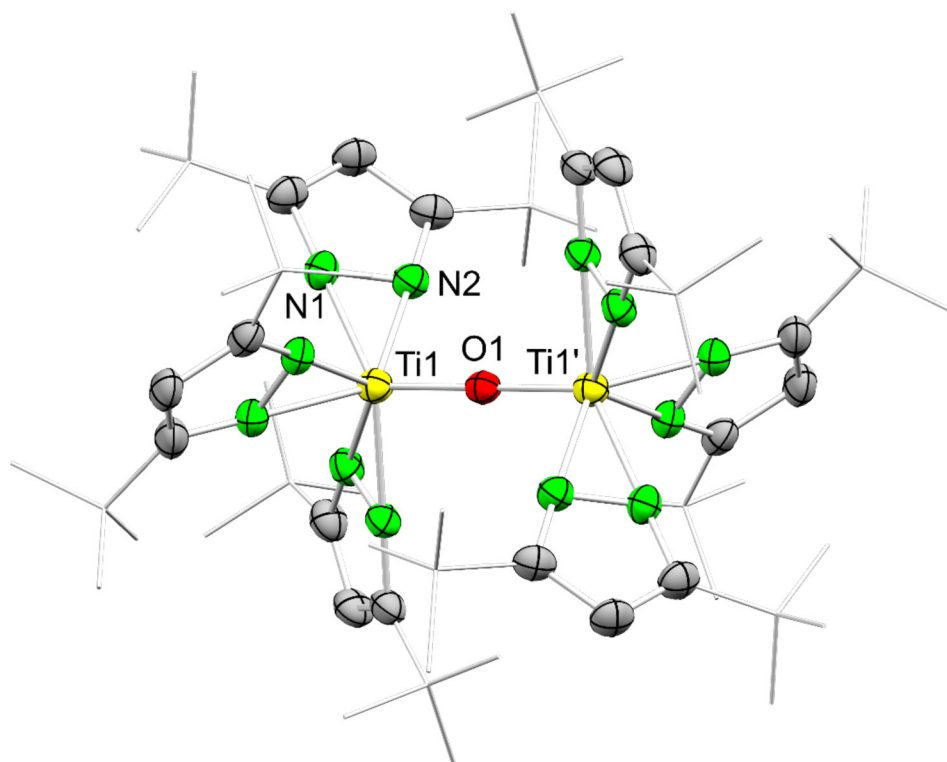


Figure S40. Connectivity of $\text{O}[\text{Ti}(\text{pz}^{\text{tBu}_2})_3]_2$ (**5**), thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted and *t*Bu moieties are set as wireframe for clarity.

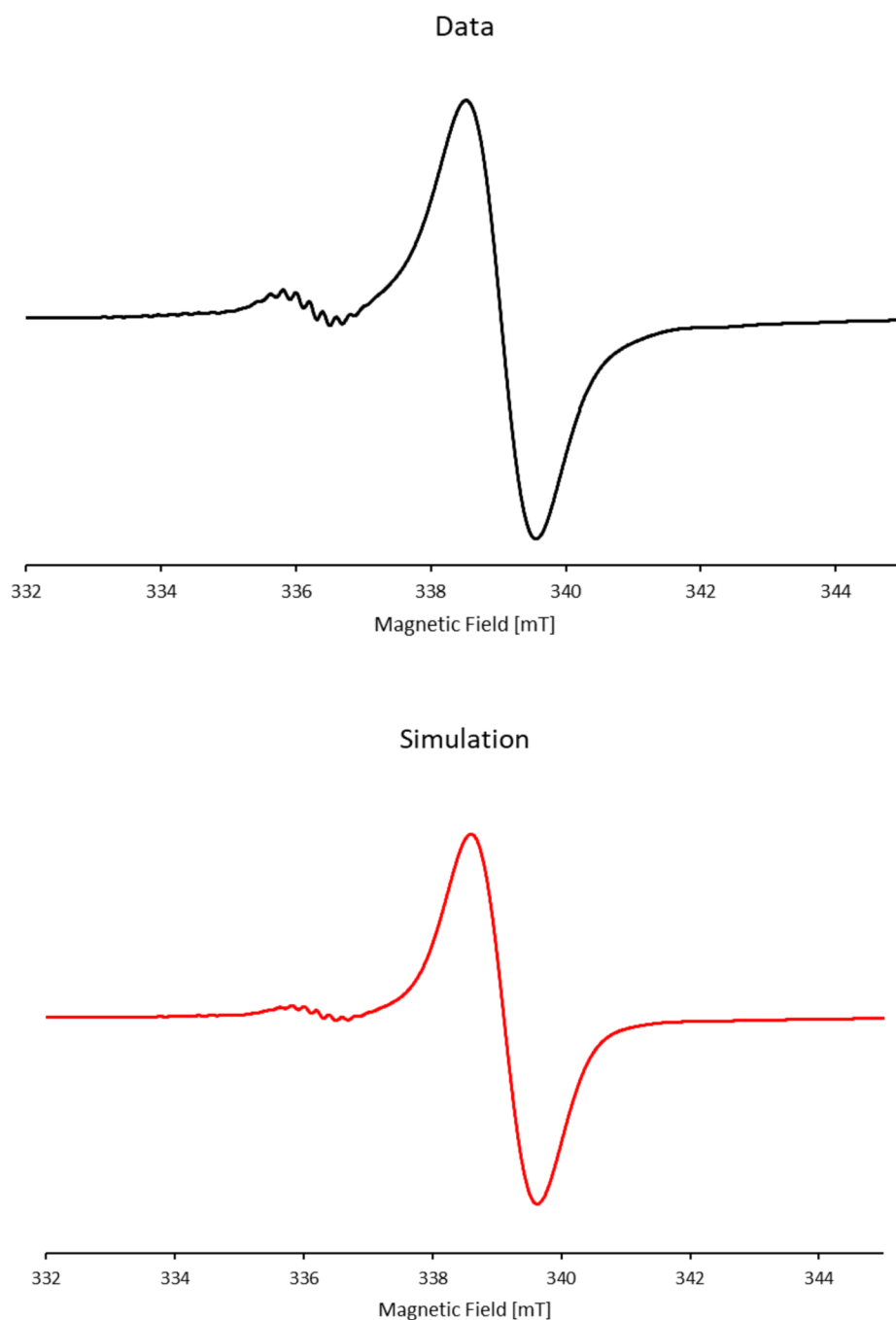


Figure S41. X-Band ($\nu = 9.2808$ GHz) cw-EPR spectrum of $\text{Ti}(\text{CO}_2\cdot\text{pz}^{\text{tBu2}})_2(\text{pz}^{\text{tBu2}})$ (**4^{CO2}**) in toluene at 298 K. Parameters for simulation: $S = 1/2$; $g_{\parallel} = 1.975$, $g_{\perp} = 1.956$; (2*) $A_{\perp}, H = 5$ MHz, (1*) $A_{\perp}, H = 5$ MHz; due to the unresolved hyperfine coupling in the $g_{\parallel}$ direction, an HStrain (x, y, z)^[a] of 4 MHz, 20 MHz, and 20 MHz was employed. A second signal at $g_{\text{iso}} = 1.955$ overlaps; parameters for simulation: $S = 1/2$; $g = 1.955$; Gaussian Line (lwpp)^[b] with 1 mT.

[a] HStrain: anisotropic residual line width (FWHM), in MHz, describing broadening due to unresolved hyperfine couplings or other transition-independent effects. [b] lwpp: Line width for isotropic broadening.

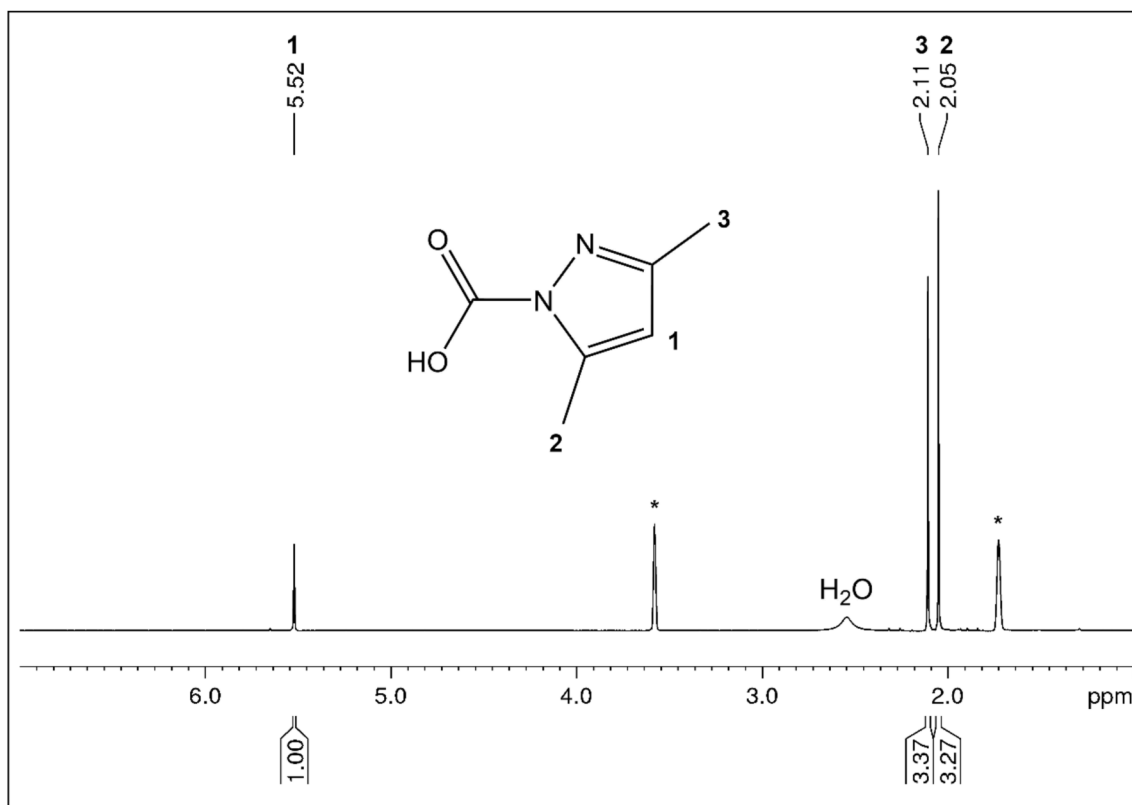


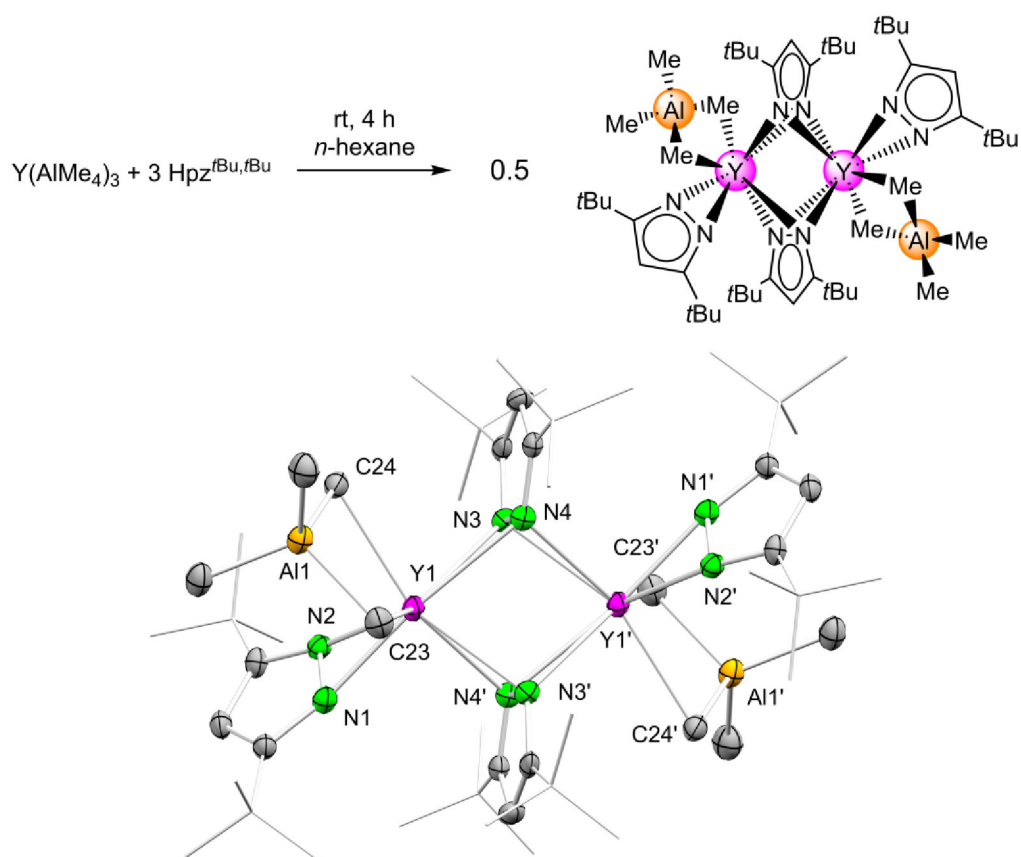
Figure S42. ^1H NMR spectrum (400.11 MHz, $[\text{D}_8]\text{THF}$) of the carbamic acid $\text{HOOCpz}^{\text{Me}_2}$ at 26 °C. It was isolated from the reaction of $\text{Ti}(\text{CO}_2\text{pz}^{\text{Me}_2})_2(\text{pz}^{\text{Me}_2})_2$ ($\mathbf{1}^{\text{CO}_2}$) with a 2 M H_2O solution in THF. The protonolysis reaction produced also a white amorphous precipitate.¹⁴

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F

Appendix

Structurally characterized compounds not included in publication or unpublished results of this thesis



$[\text{Y}(\mu\text{-pz}^{t\text{Bu}_2})(\text{pz}^{t\text{Bu}_2})(\text{AlMe}_4)]_2$ FK265

$R_1[I > 2\sigma]$ 5.08%; $wR_2(\text{all data})$ 12.47%

$a = 13.730(2) \text{ \AA}$; $\alpha = 89.538(2)^\circ$

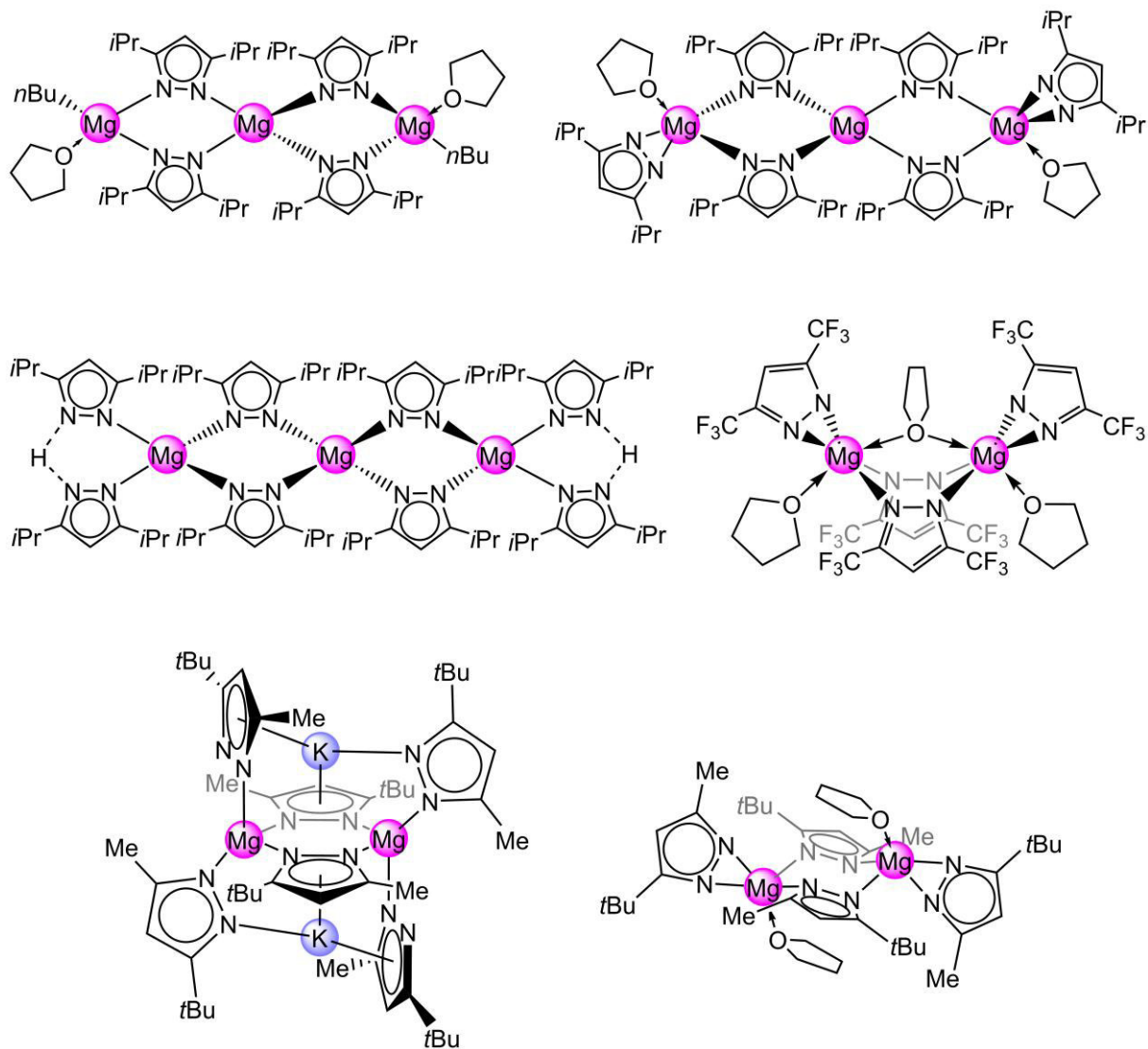
$b = 14.304(2) \text{ \AA}$; $\beta = 83.008(3)^\circ$

$c = 17.987(3) \text{ \AA}$; $\gamma = 67.121(2)^\circ$

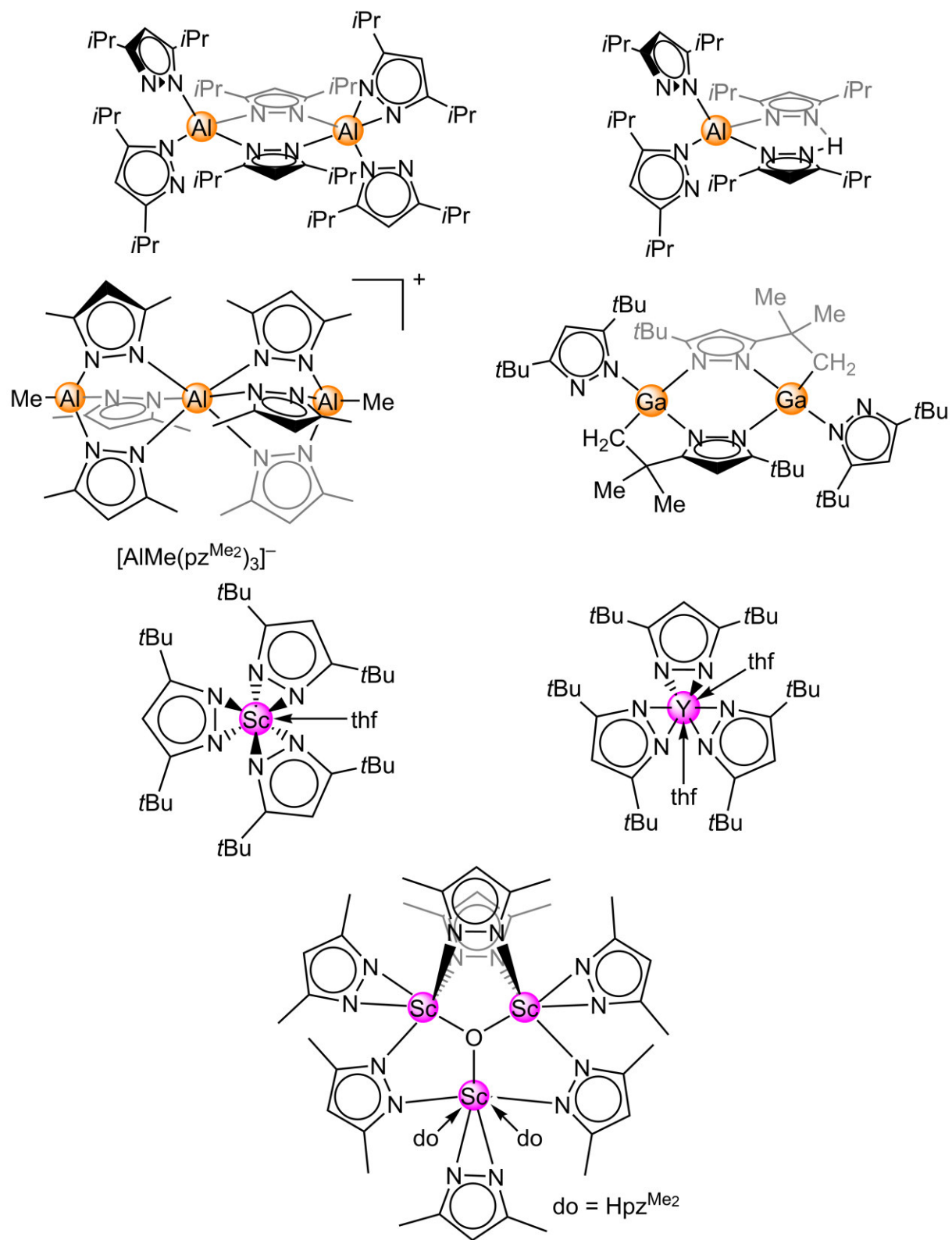
Structurally characterized complexes

On the following pages all compounds structurally characterized *via* SC-XRD are listed as *ChemDraw* sketches.

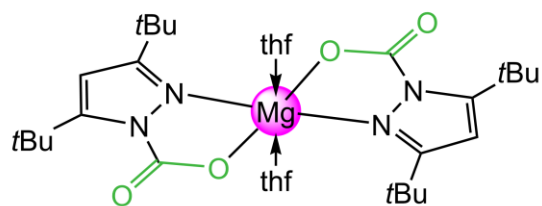
Magnesium Pyrazolates (Paper I)



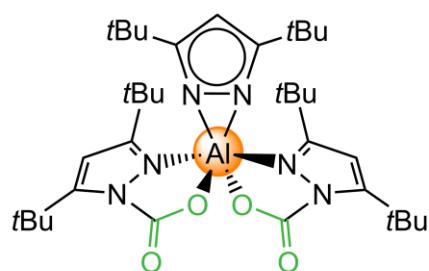
Group III and XIII metal pyrazolates (Paper II)



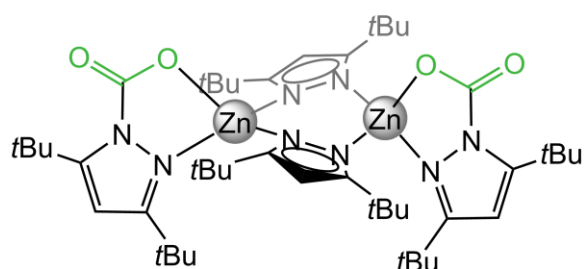
CO₂, CS₂ and N₂O Insertion into Titanium Pyrazolates (Paper I, II and Unpublished Results)



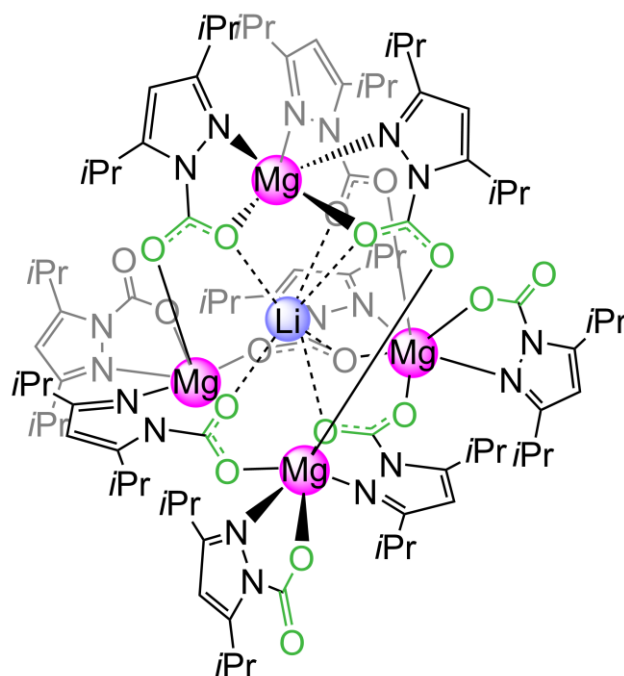
Paper I



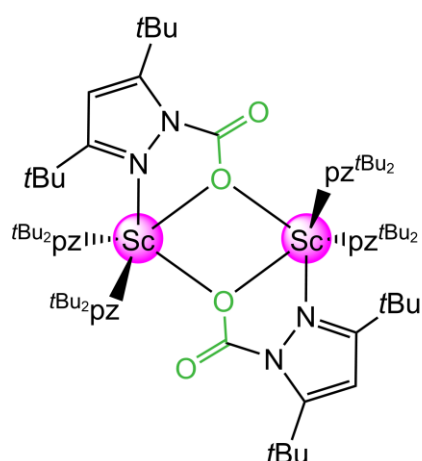
Paper II



Unpublished (PP12)

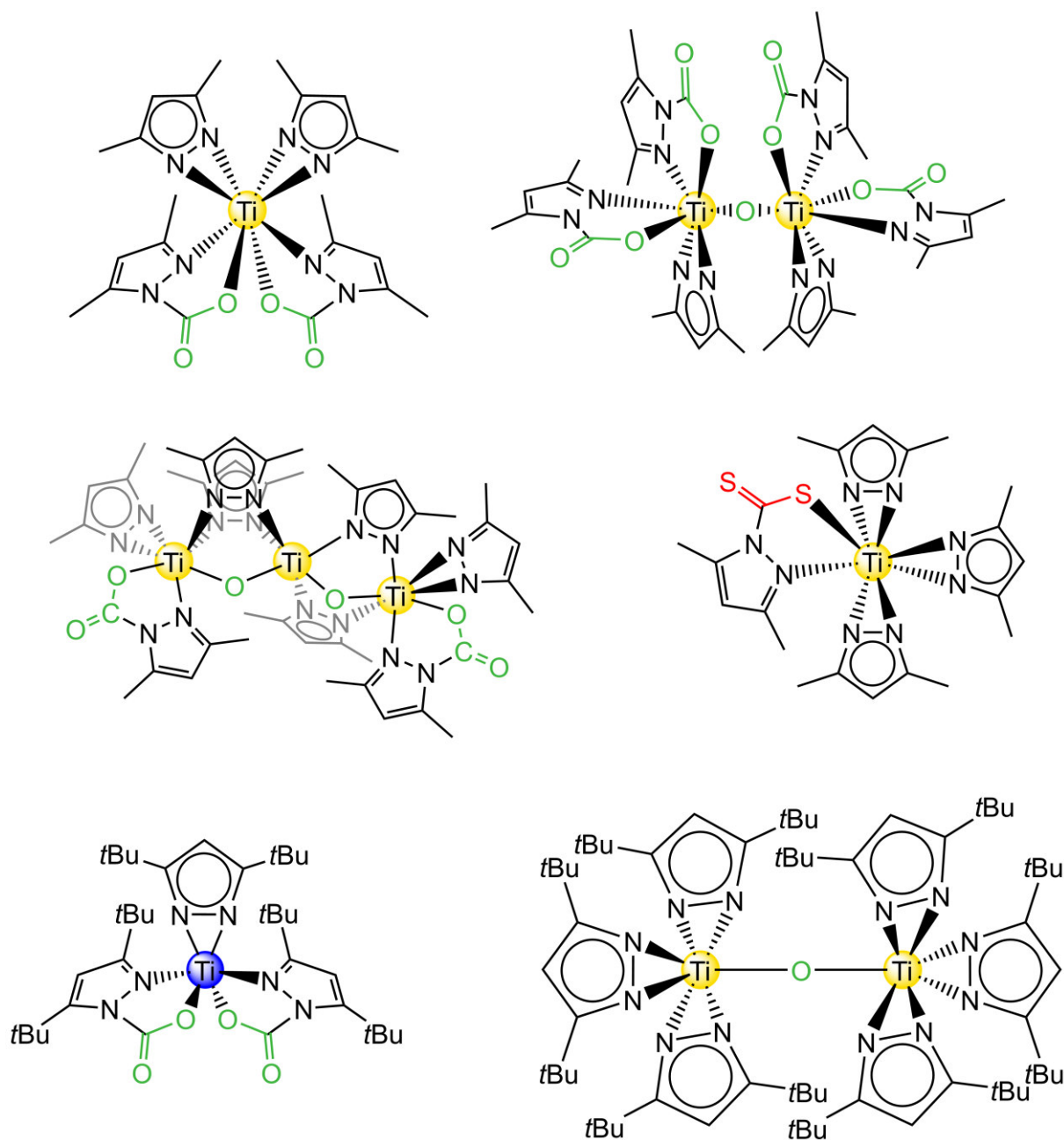


Paper I

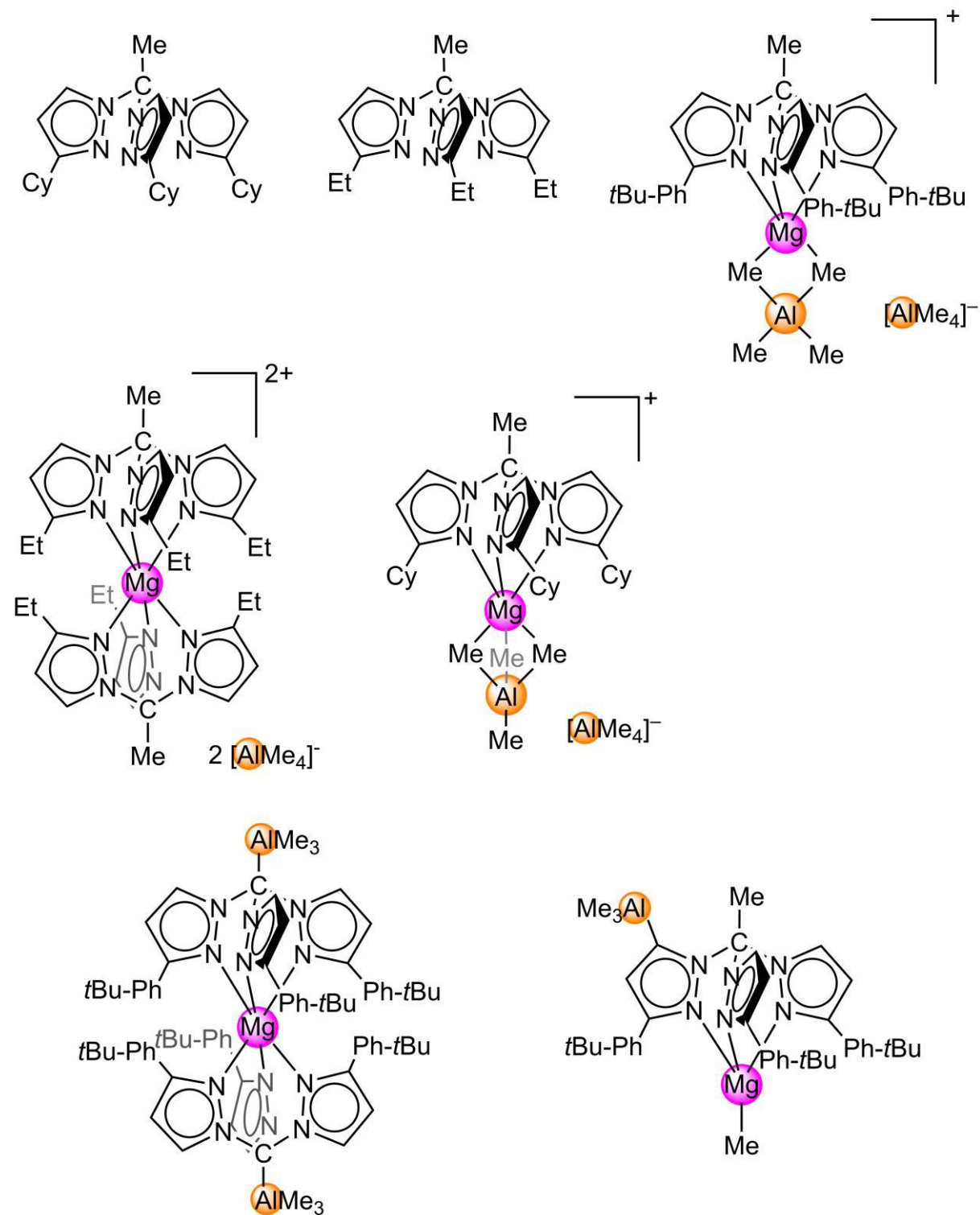


Paper II

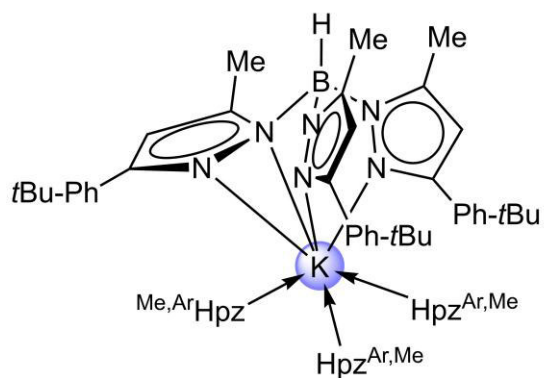
CO₂, CS₂ and N₂O Insertion into Titanium Pyrazolates (Paper IV)



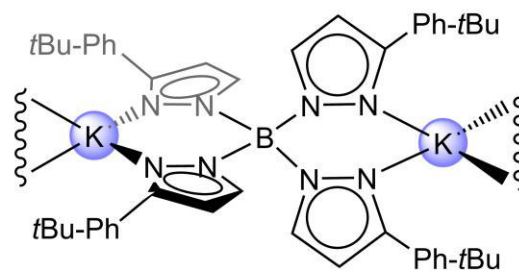
MeCTp Ligands and Magnesium CTp Complexes (Paper III)



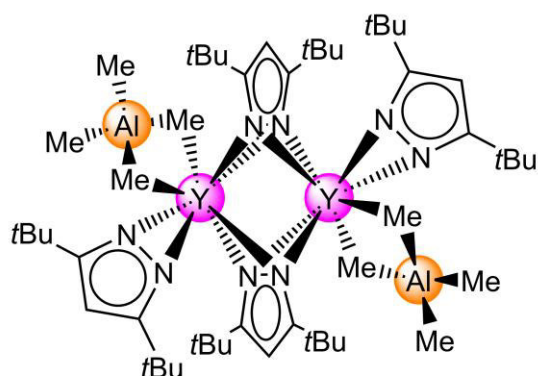
Unpublished Crystal Structures or from Publication with minor Contribution



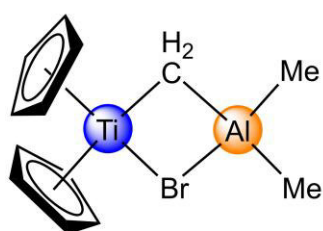
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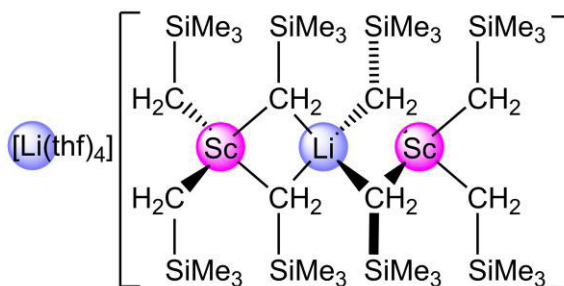
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Unpublished (FK265)



Paper V



Paper VI