

Supporting Information

Dehydropolymerisation of methylamine borane using a dinuclear 1,3-allenediyl bridged zirconocene complex

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1. Experimental details

General: All manipulations were carried out in an oxygen- and moisture-free argon atmosphere using standard Schlenk and drybox techniques. The solvents were purified with the Grubbs-type column system "Pure Solv MD-5" and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Complexes **1** and **3** were prepared according to literature procedures.^[1] Cp₂ZrCl₂ (MCAT) was used as received. MAB (Boron Specialties), NH₂Me·HCl (Sigma), MeLi (1.6 M solution in Et₂O, Sigma), and D₂ (Linde) were used as received. For stoichiometric conversions of **1** we used a MeLi·BrLi solution 1.5 M in diethyl ether (Sigma) which was transferred to a Schlenk flask and stored under Ar atmosphere in the fridge. Na[HBtEt₃] (2.0 M solution in toluene, Sigma) was transferred to a Schlenk flask and stored under Ar atmosphere in the fridge. GaCl₃ (Sigma, >99.9%) and BH₃·NMe₃ (Sigma) were sublimed prior to use and stored in the glovebox. [(dppp)Rh(nbd)][BF₄] was similarly to a described literature procedure.^[2]

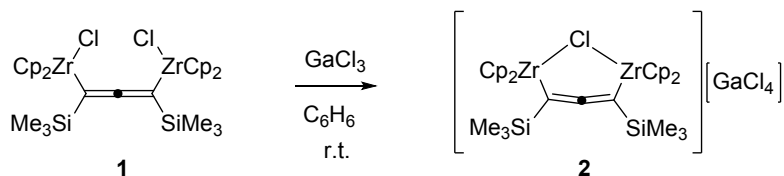
NMR spectra were recorded on Bruker AV300 and AV400 spectrometers. ¹H and ¹³C chemical shifts were referenced to the solvent signal: [D₆]benzene (δ_{H} 7.16, δ_{C} 128.06) and CDCl₃ (δ_{H} 7.26, δ_{C} 77.16)^[3]

Diffraction data for complex **2** and **4** were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods (SHELXS-97)^[4] and refined by full-matrix least-squares procedures on *F*² (SHELXL-2014).^[5] Diamond^[6], XP (Bruker AXS) and Mercury^[7] were used for graphical representations. CCDC 1851926 and 1851927 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

SEC analysis was performed for molar mass determination. All samples were filtered before measurement. The SEC system consists of an isocratic pump series 1200 (Agilent Technologies, US), an autosampler series 1100 (Agilent Technologies, US), an refractive index (RI) detector Dn-2010 (λ =620 nm, Bures, DE), a multi-angle laser light scattering detector (MALLS, Wyatt Technologies, US). For the separation a PL MIXED-C column (300x7.5 mm, 5 μ m PSgel, Agilent Technologies, US) was used. The flow rate was 1.0 mL/min at 25°C.

The calculation of the molar mass from the MALLS detector was performed by taking into account the dn/dc of the samples, which were determined by direct injection into the RI detector of samples with varied concentration.

Synthesis of 2



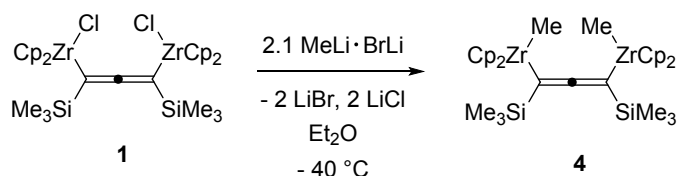
To a colourless stirred solution of GaCl₃ (40 mg, 0.24 mmol) in 10 mL benzene an orange solution of **1** (168 mg, 0.24 mmol) in 7 mL benzene was added dropwise at 0 °C. This leads to immediately precipitation of red **2**. After filtering of the supernatant, washing the precipitate with further benzene (3 x 1 mL) and drying in vacuo reddish **2** was obtained (150 mg, 72%). Due to high reactivity and poor solubility of **2** only unsatisfactorily analytical data could be collected.

Crystals in poor quality due to the fast crystal growth were obtained by slow diffusion of a solution of **1** in benzene into a solution of GaCl₃ in benzene. The structural motif is depicted below.

Attempted solvation experiments of **2** in deuterated DMSO, acetonitrile as well as chloroform only lead to the detection of unidentified decomposition products. Furthermore **2** dissolves nicely in THF but turned to be a good catalyst for its ring opening polymerisation which prevents further analysis.

¹H NMR (300 MHz, C₆D₆, 298 K): δ = 0.25 (br., 18H, Me₃Si), 5.88 (s, 20H, Cp).

Synthesis of 4



Complex **1** (200 mg, 0.29 mmol) was dissolved in diethyl ether (20 mL) and cooled to -78 °C. To this clear orange solution a MeLi·BrLi solution (1.5M, 0.385 mL, 0.57 mmol) was added dropwise and stirred for 5 hours. The resulting reddish solution was stored at -40 °C for 14 hours. This suspension was concentrated to approximately ¼ of the volume and lithium salts were separated by filtration at -40 °C. This clear reddish solution was allowed to cool slowly to -78 °C resulting in the deposition of single crystals of compound **4**.

¹H NMR (25 °C, [D₆]benzene, 300.13 MHz): δ = 5.92 (s, 10H, Cp), 5.90 (s, 10H, Cp), 0.34 (s, 6H, Me), 0.33 (s, 18H, CSi(CH₃)₃). ¹³C{¹H} NMR (25 °C, [D₆]benzene, 100.63 MHz): δ = 111.12 (Cp), 110.79 (Cp), 35.3 (Me), 3.4 (CSi(CH₃)₃) ²⁹Si inept NMR (25 °C, [D₆]benzene, 79.49 MHz): δ = -8.38. MS-Cl⁺ (isobutene): [M⁺-CH₃] 637, [M⁺-2 CH₃] 622 [Cp₂Zr(Me₃SiC₃SiMe₃)⁺] 403.

Single crystals suitable for X-ray diffraction analysis were obtained from a saturated benzene solution.

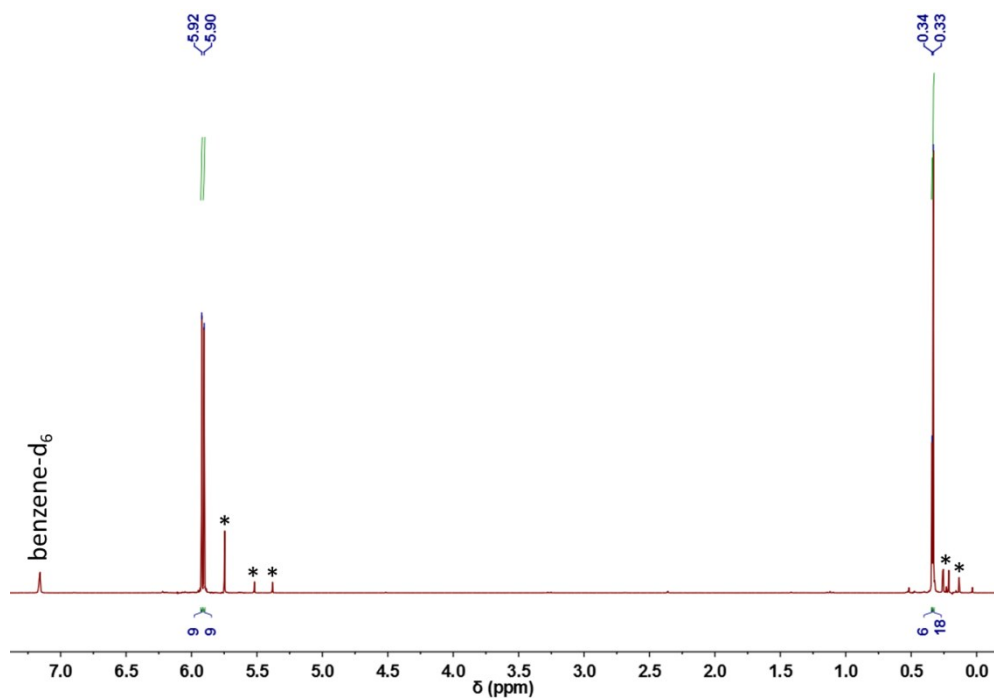


Figure S1. ^1H NMR spectrum of **4** in C_6D_6 , asterisk marks unidentified impurities (25 °C, $[\text{D}_6]$ benzene, 300.13 MHz).

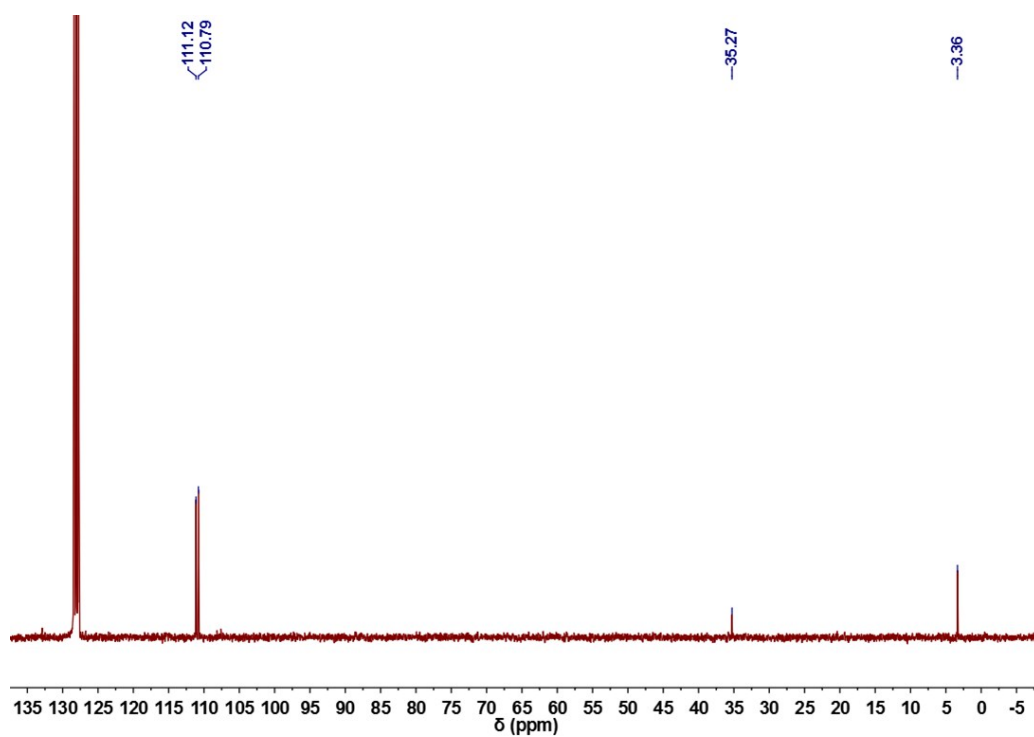


Figure S2. ^{13}C NMR spectrum of **4** in C_6D_6 (25 °C, $[\text{D}_6]$ benzene, 100.63 MHz).

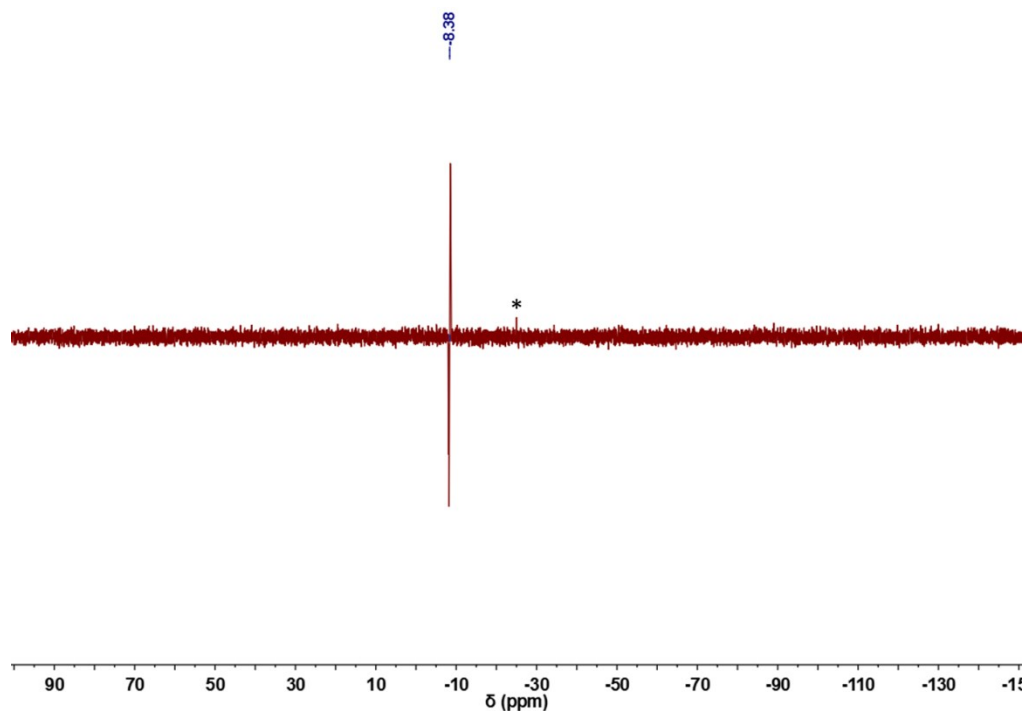


Figure S3. ^{29}Si NMR spectrum of **4** in C_6D_6 , asterisk marks unidentified impurities (25 °C, $[\text{D}_6]$ benzene, 79.49 MHz).

Synthesis of $\text{Li}[\text{MeNH}\cdot\text{BH}_3]$

MAB (360 mg, 8 mmol) was weighed in the glovebox, transferred into a Schlenk flask and dissolved in 20 mL of THF. MeLi (5 mL of a 1.6M solution in Et_2O , 8 mmol) was added dropwise at 0 °C and gas evolution was noticed. The reaction was allowed to warm to room temperature and stirred for 1 h. Volatiles were removed affording $\text{Li}[\text{MeNH}\cdot\text{BH}_3]$ as a white solid (220 mg).

Synthesis of $\text{Et}_3\text{B}\cdot\text{NH}_2\text{Me}$

10 mL of a 1M solution of $\text{Na}[\text{HBEt}_3]$ (10 mmol) in toluene were transferred into a flame dried Schlenk flask and diluted with 40 mL of *n*-hexane. $\text{NH}_2\text{Me}\cdot\text{HCl}$ (15 mmol) was added dropwise into the open Schlenk flask under a flow of argon at 0 °C, during which vigorous bubbling (H_2) was observed. The reaction was allowed to warm to room temperature and stirred for additional 30 min. Filtration and evaporation of the volatiles at room temperature afforded as colourless liquid (780 mg, 60%). **^1H NMR** (300 MHz, C_6D_6 , 298 K): $\delta = 1.49$ (bs, 2H, NH_2), 1.40 (m, 3H, NCH_3), 0.94 (t, $^3J = 7.8$ Hz, 9H, CH_3), 0.32 (q, $^3J = 7.8$ Hz, 6H, CH_2). **^{11}B NMR** (96 MHz, C_6D_6 , 298 K): $\delta = -3.03$ (s). **^{13}C NMR** (100 MHz, C_6D_6 , 298 K): $\delta = 25.8$ (s, N-CH_3), 12.8 (bd, $^1J_{\text{C-B}} = 49$ Hz, B-CH_2), 10.1 (s, CH_3).

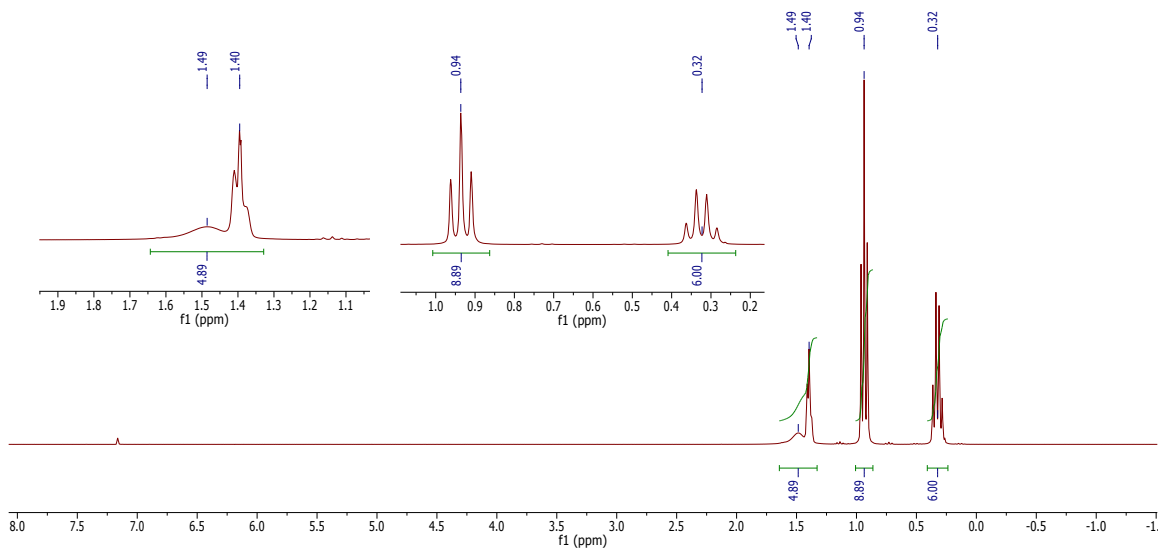


Figure S4. ^1H NMR spectrum of $\text{Et}_3\text{B}\cdot\text{NH}_2\text{Me}$ in C_6D_6 (25 °C, $[\text{D}_6]$ benzene, 300.13 MHz).

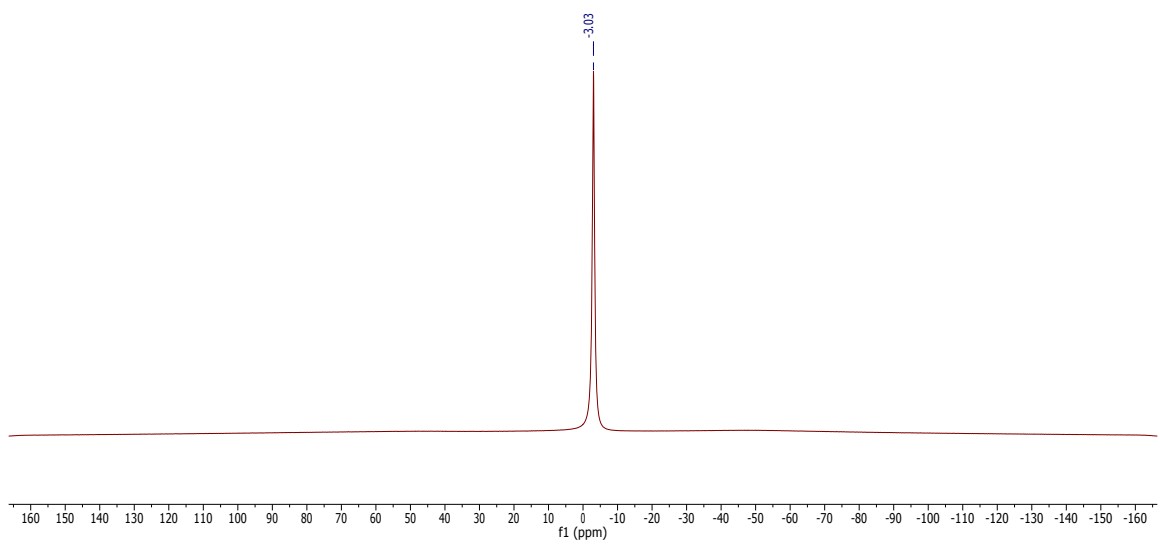


Figure S5. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $\text{Et}_3\text{B}\cdot\text{NH}_2\text{Me}$ in C_6D_6 (25 °C, $[\text{D}_6]$ benzene, 96.32 MHz).

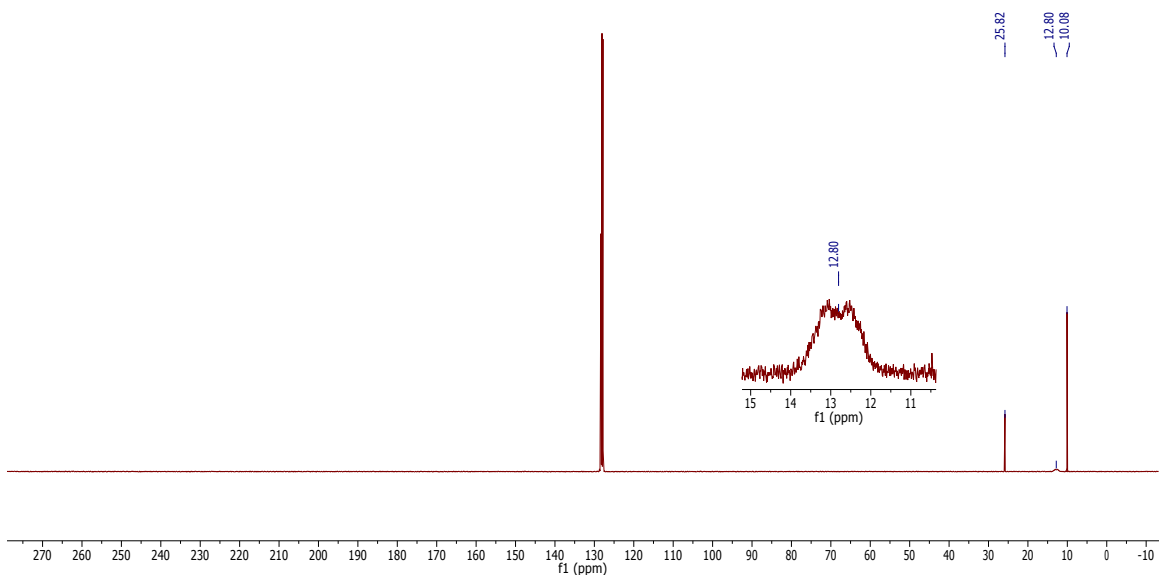


Figure S6. ¹³C NMR spectrum of Et₃B·NH₂Me in C₆D₆ (25 °C, [D₆]benzene, 100.63 MHz).

Preparation of deuterated methylamine boranes H₃B·NMeD₂ and D₃B·NMeH₂

H₃B·NMeD₂ was prepared according to a literature procedure.^[8] D₃B·NMeH₂ was prepared from D₃B·NMe₃ according to a literature procedure.^[9] D₃B·NMe₃ was prepared by deuteration of H₃B·NMe₃ (500 mg, 6.85 mmol) in THF (25 mL) using [(dppp)Rh(nbd)][BF₄] (57 mg, 1.5 mol%) as the catalyst. Deuteration was done at room temperature under 30 bar D₂, followed by transfer of the solution into an oven-dried Schlenk flask and THF removed under a stream of argon at room temperature. The solid was sublimed under static vacuum at room temperature to yield pure H₃B·NMe₃ (220 mg, 44%). Spectroscopic data are in accordance with the literature.^[8]

2. Catalytic tests

General procedure for dehydropolymerisation experiments

Methylamine borane (MAB, 60 mg, 1.33 mmol) and the corresponding Zr catalyst were weighed in the glovebox and transferred to a three-necked reaction vessel. Then, the MAB containing dehydrogenation vessel was connected to the gas burette under Ar atmosphere. The gas burette was initialised and MAB and Zr catalyst were dissolved in 5 mL of toluene. The MeLi solution (0.08M in Et₂O) was transferred to the reaction vessel and data acquisition was started immediately. After completion of the dehydrogenation reaction, a gas sample was taken and analyzed by GC-TCD and an aliquot was analyzed by ¹¹B NMR spectroscopy. The reaction solution was cannula-transferred into an oven dried Schlenk flask under Ar flow and the volume of solution was reduced to half of its volume. The polymer was obtained by precipitation into 50 mL of cold (-78 °C) *n*-hexane, allowed to precipitate for 30 minutes and subsequently filtered. The white solid was dried in vacuum overnight. Isolated yields varied from 55 % to 58 %. Details of the experimental setup were published before.^[10]

Catalyst screening

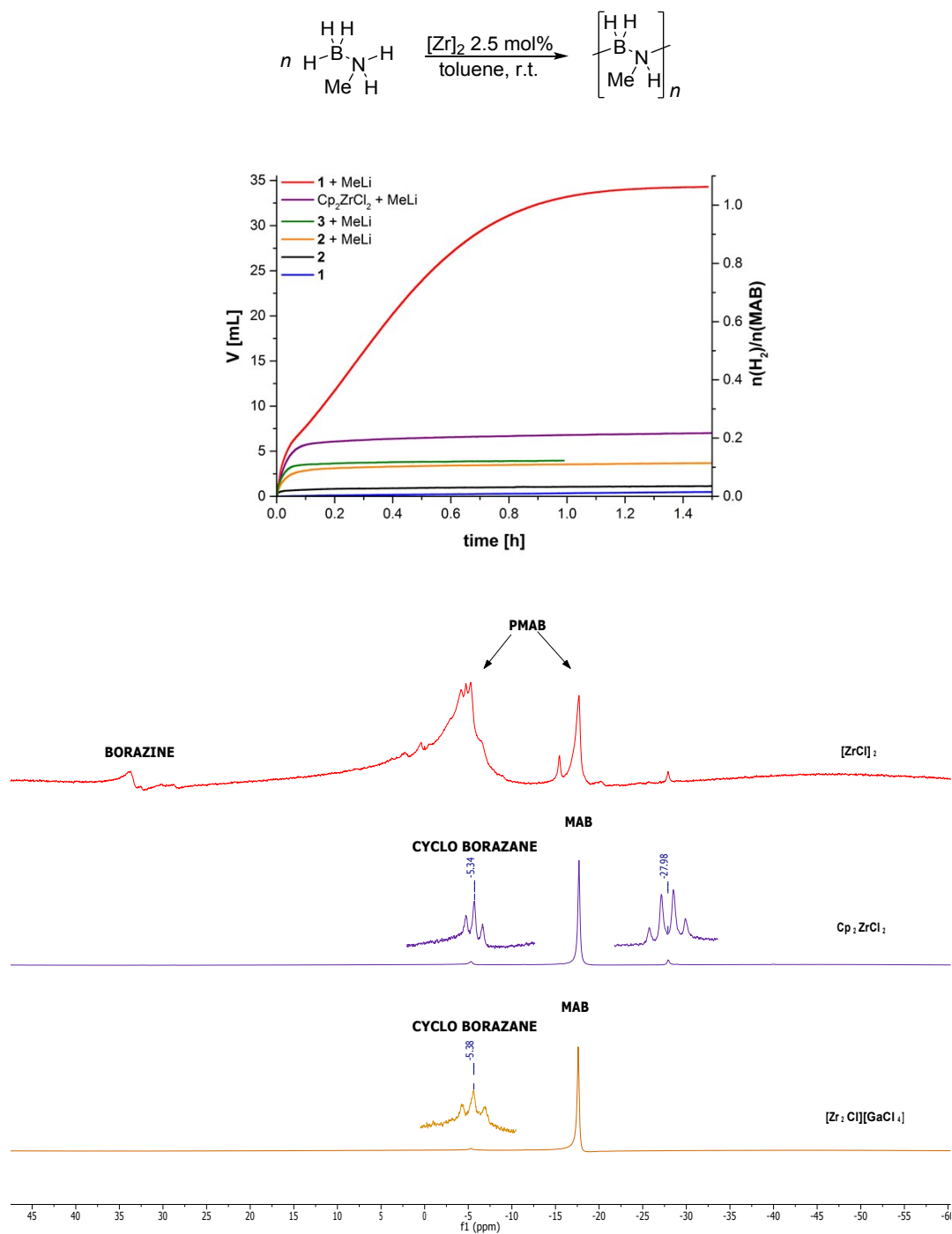


Figure S7. Volumetric curves of MAB dehydrogenative polymerisation with zirconocene complexes (top). $^{11}\text{B}\{^1\text{H}\}$ NMR (25 °C, $[\text{D}_6]$ benzene, 96.32 MHz) spectra of the crude reaction mixture (bottom). Reaction conditions: MAB (1.33 mmol), **1** (2.5 mol%) or Cp_2ZrCl_2 (5 mol%), MeLi (5.5 mol%) in toluene (5 mL) at 25 °C. Note: Formation of cycloborazane ($\delta^{11}\text{B} = -5.2$ ppm) and remaining starting material ($\delta^{11}\text{B} = -18$ ppm) cannot be excluded for the spectra obtained from reactions using **1** due to the overlapping of their signals with those of the polymer.

Variation of catalyst loading

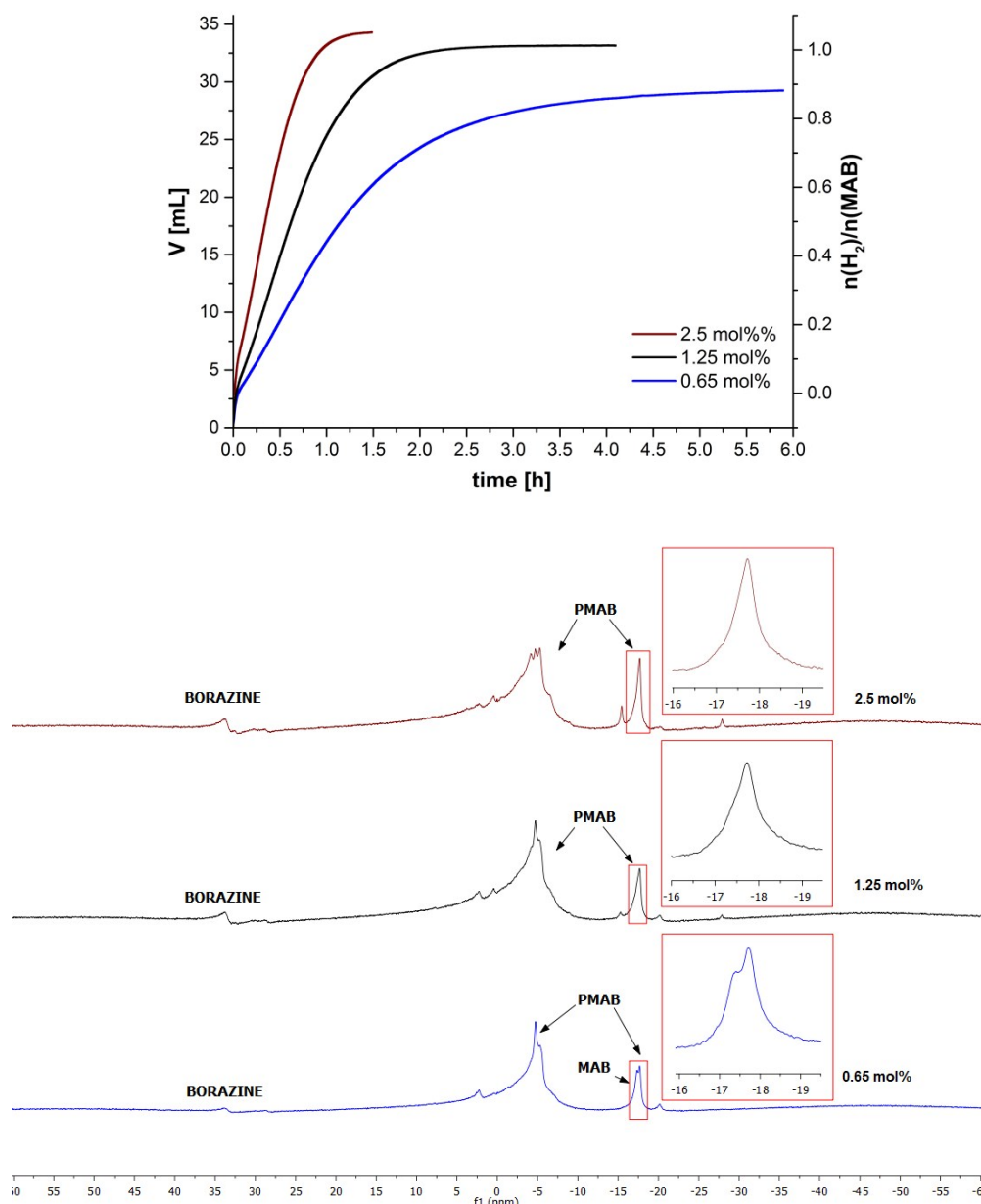
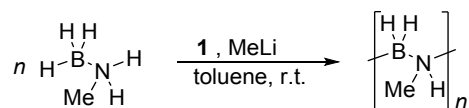


Figure S8. Volumetric curves of MAB dehydropolymerisation with different amount of **1** (top). $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of the crude reaction mixture (bottom, 25 °C, $[\text{D}_6]$ benzene, 96.32 MHz). Reaction conditions: MAB (1.33 mmol), **1** (0.65-2.5 mol%), MeLi (1.4-5.5mol%) in toluene (5 mL) at 25 °C. *Note: Formation of cycloborazine ($\delta^{11}\text{B} = -5.2$ ppm) is not detectable due to its overlapping with the polymer main-chain signal. Remaining starting material ($\delta^{11}\text{B} = -18$ ppm) cannot be excluded due to the overlapping of its signal with those of the polymer end-chain. Residual MAB was present in reactions from which less than one equivalent of hydrogen evolved.*

Dehydropolymerisation of MAB catalyzed by **1** with Li[MeNH·BH₃]

MAB (60 mg, 1.33 mmol) and **1** (11.56 mg, 1.25 mol%) were weighed in the glovebox and transferred to a three-necked reaction vessel. Li[MeNH·BH₃] (1.9 mg, 2.75 mol%) was weighed in the glovebox and transferred to Schlenk flask. Then, the MAB containing dehydrogenation vessel was connected to the gas burette under Ar atmosphere. The gas burette was initialised and MAB was dissolved in 5 mL of toluene. Li[MeNH·BH₃] was dissolved in 0.5 mL of Et₂O and this solution was added to the reaction vessel and data acquisition was started immediately. After completion of the dehydrogenation reaction, a gas sample was taken and analyzed by GC-TCD and an aliquot was analyzed by ¹¹B NMR spectroscopy (Figure S9).

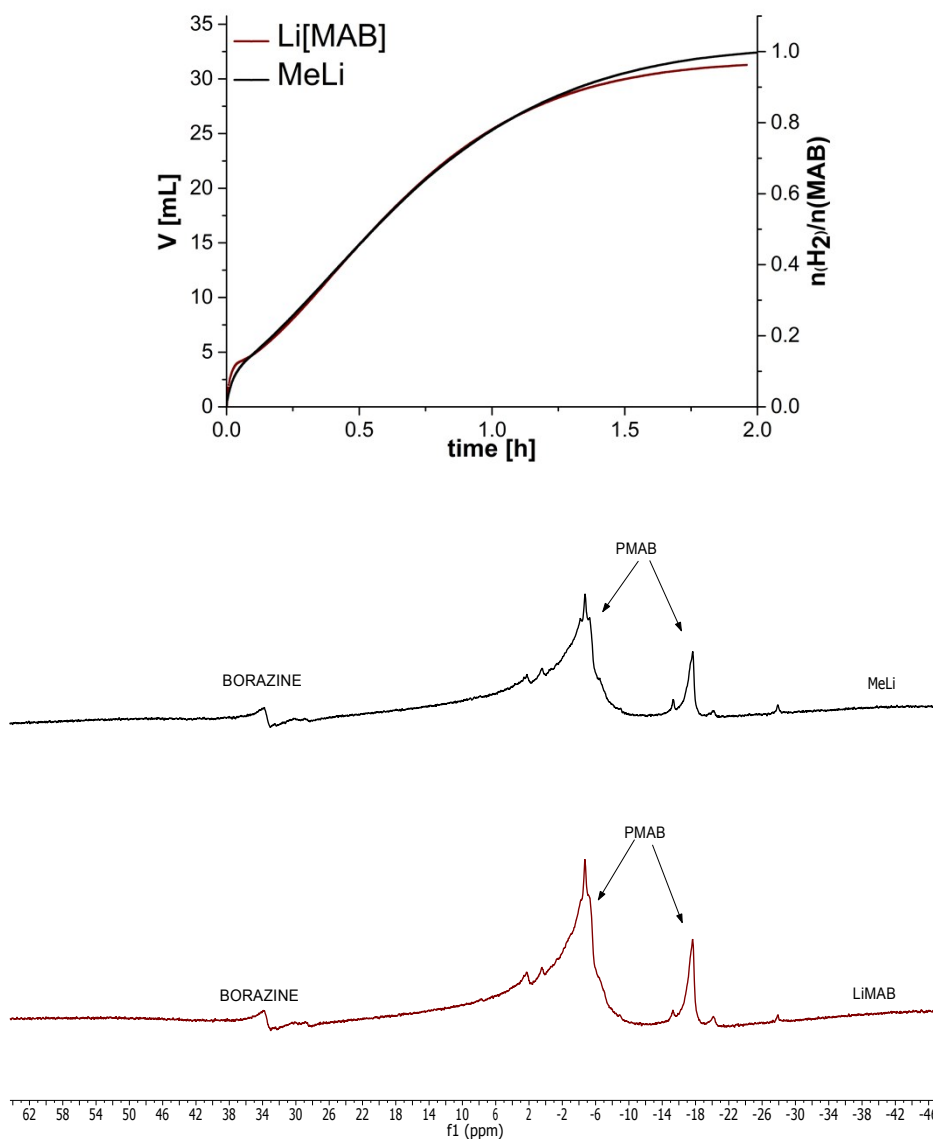


Figure S9. Comparison of the volumetric curve (top) and ¹¹B{¹H} NMR spectra of catalytic dehydropolymerisation of MAB with MeLi or Li[MAB] (bottom, 25 °C, [D₆]benzene, 96.32 MHz). Reaction conditions: MAB (1.33 mmol), **1** (1.25 mol%), MeLi or Li[MeNH·BH₃] (2.75 mol%) in toluene (5 mL) at 25 °C.

Reaction with *n*-BuLi

MAB (60 mg, 1.33 mmol) and **1** (11.56 mg, 1.25 mol%) were weighed in the glovebox and transferred to a three-necked reaction vessel. Then, the MAB containing dehydrogenation vessel was connected to the gas burette under Ar atmosphere. The gas burette was initialised and MAB and **1** catalyst were dissolved in 5 mL of toluene. Then 0.46 mL of a *n*-BuLi solution (0.08 M in hexane, 2.75 mol%) were added to the reaction vessel and data acquisition was started immediately. After completion of the dehydrogenation reaction, a gas sample was taken and analyzed by GC-TCD, which show only H₂ produced, and an aliquot was analyzed by ¹¹B NMR spectroscopy. The reaction solution was cannula-transferred into an oven dried Schlenk flask under Ar flow and the volume of solution was reduced to half of its volume. The polymer was obtained by precipitation into 50 mL of cold (-78 °C) *n*-hexane, allowed to precipitate for 30 minutes and subsequently filtered. The waxy yellowish solid was dried in vacuum overnight affording 32% isolated yield.

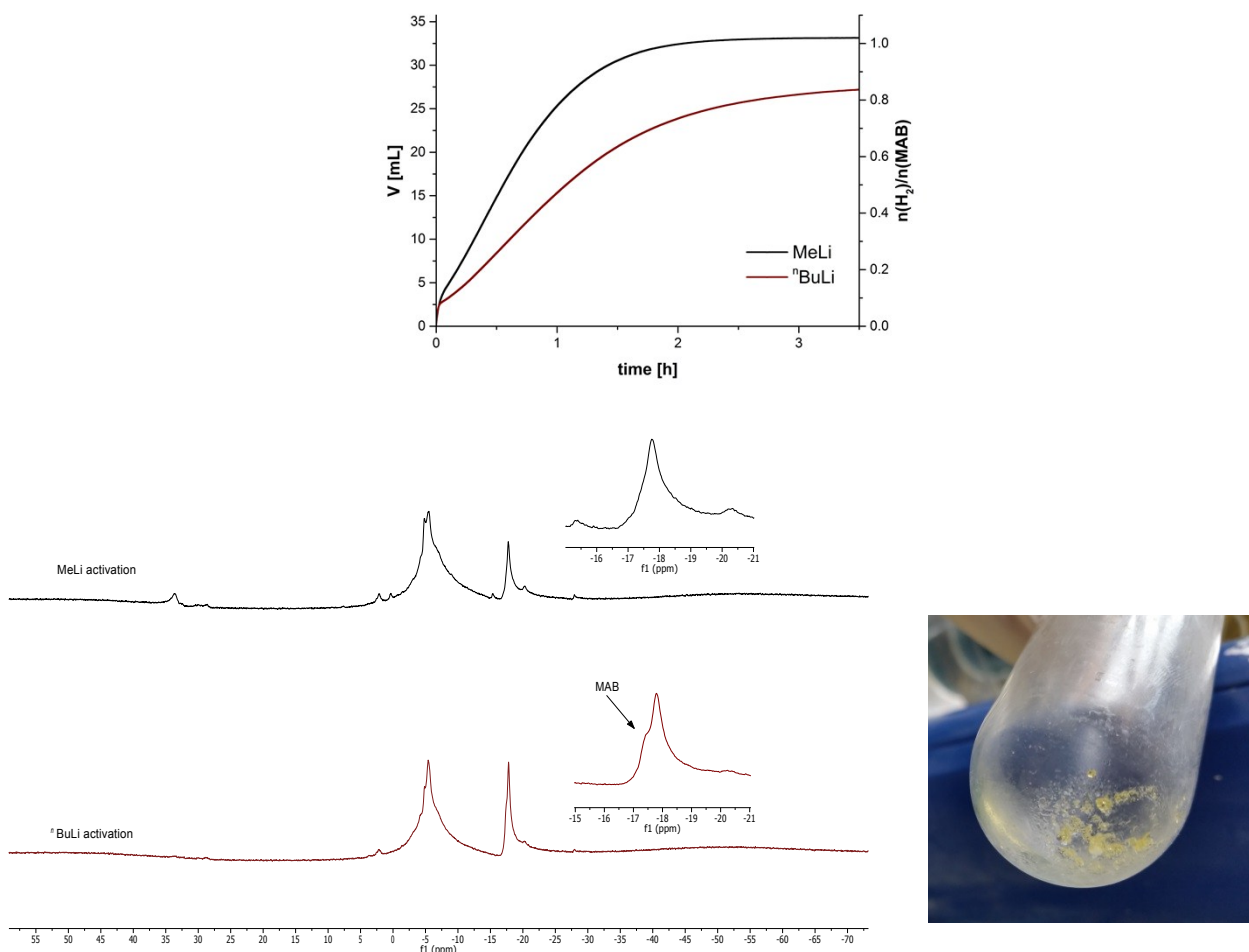


Figure S10. Comparison of the volumetric curve (top) and ¹¹B{¹H} NMR spectra of catalytic dehydropolymerisation of MAB with activation using MeLi and *n*-BuLi (bottom left, 25 °C, [D₆]benzene, 96.32 MHz). Isolated waxy material from the reaction with *n*-BuLi (bottom right). Reaction conditions: MAB (1.33 mmol), **1** (1.25 mol%), MeLi or *n*-BuLi (2.75 mol%) in toluene (5 mL) at 25 °C.

Poisoning experiment

MAB (60 mg, 1.33 mmol) and **1** (11.56 mg, 1.25 mol%) were weighed in the glovebox and transferred to a three-necked reaction vessel. Then, the MAB containing dehydrogenation vessel was connected to the gas burette under Ar atmosphere. The gas burette was initialised and MAB and **1** catalyst were dissolved in 5 mL of toluene. Then 0.46 mL of a MeLi solution (0.08M in Et₂O, 2.75 mol%) were added to the reaction vessel and data acquisition was started immediately. After a conversion of approximately 30%, 50 equivalents of mercury (1 mL, 13.5 g, 66.65 mmol) were transferred into the reaction solution via syringe and hydrogen gas evolutions was found to continue (Figure S11).

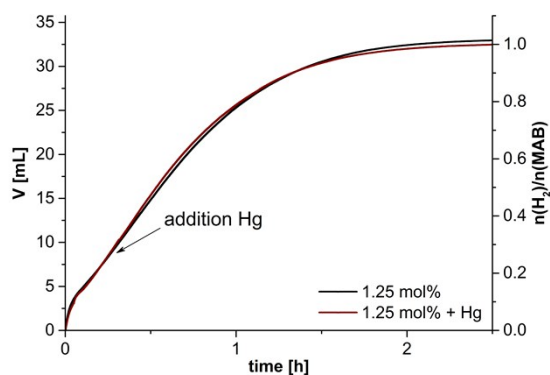


Figure S11. Comparison of the volumetric curve of catalytic dehydropolymerisation of MAB with and without addition of mercury. Reaction conditions: MAB (1.33 mmol), **1** (1.25 mol%), MeLi (2.75 mol%), Hg (10 equiv.) in toluene (5 mL) at 25 °C.

Trapping the aminoborane [MeNH=BH₂] in the presence of cyclohexene

MAB (60 mg, 1.33 mmol) and **1** (11.56 mg, 1.25 mol%) were weighed in the glovebox and transferred to a three-necked reaction vessel. Then, the MAB containing dehydrogenation vessel was connected to the gas burette under Ar atmosphere. The gas burette was initialised and MAB and **1** were dissolved in 4 mL of toluene. A solution of cyclohexene (109.3 mg, 1.33 mmol) in toluene (1 mL) was added to the reaction vessel, followed by 0.46 mL of a MeLi solution (0.08 M in Et₂O, 2.75 mol%) and data acquisition was started immediately. After completion of the dehydrogenation reaction an aliquot was analyzed by ¹¹B NMR spectroscopy. The ¹¹B NMR spectrum did not show signals for MeNH=BCy₂ (Figure S12, highlighted area indicates the expected region for the hydroboration product) and the addition of cyclohexene does not affect catalyst activity and product distribution.

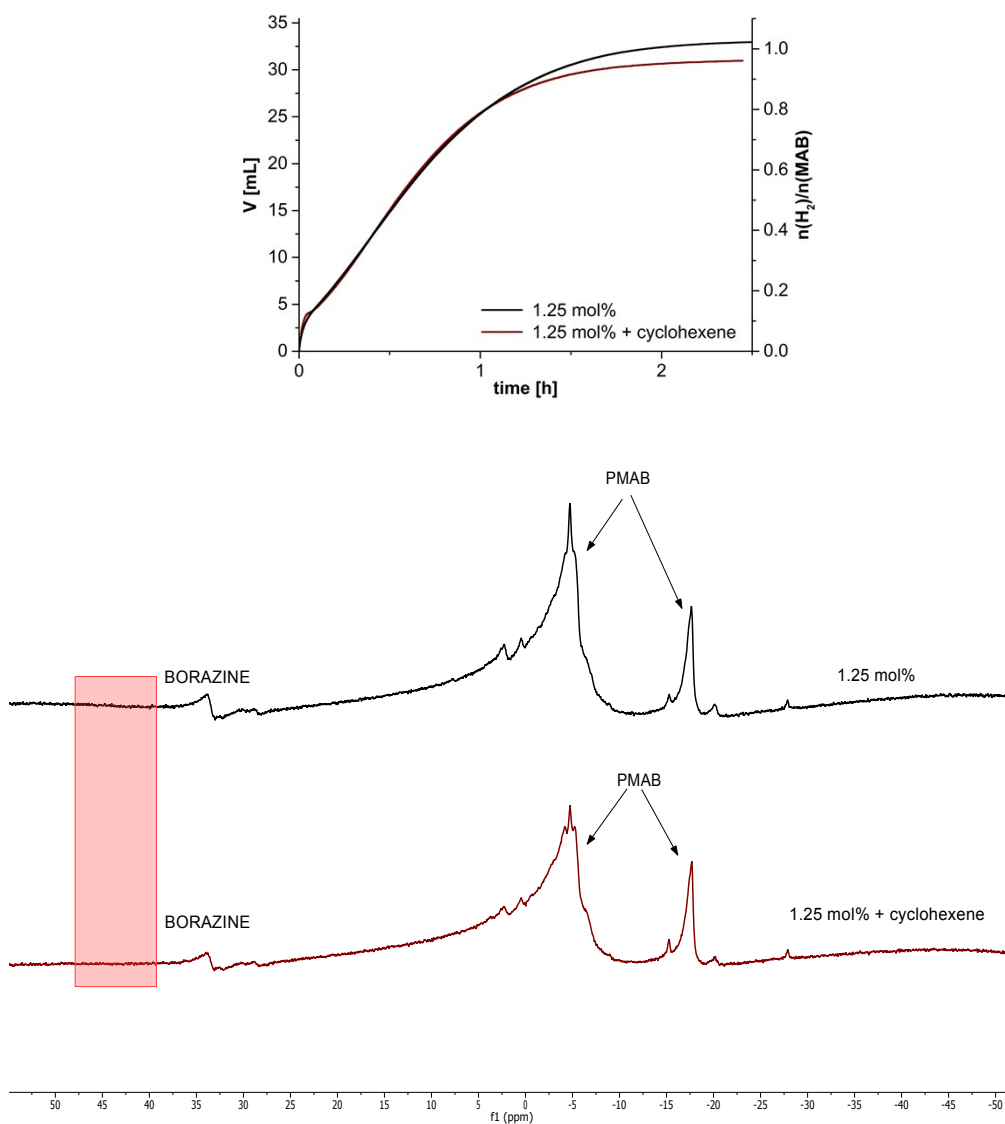


Figure S12. Comparison of the volumetric curve (top) and ¹¹B{¹H} NMR spectra of catalytic dehydropolymerisation of MAB with and without cyclohexene (bottom, 25 °C, [D₆]benzene, 96.32 MHz). Reaction conditions: MAB (1.33 mmol), **1** 1.25 mol%, MeLi (2.75 mol%), cyclohexene (1.33 mmol) in toluene (5 mL) at 25 °C.

KIE experiments

$\text{H}_3\text{B}\cdot\text{NMeD}_2$ or $\text{D}_3\text{B}\cdot\text{NMeH}_2$ (63 mg, 1.33 mmol) and **1** (11.56 mg, 1.25 mol%) were weighed in the glovebox and transferred to a three-necked reaction vessel. Then, the amine borane containing dehydrogenation vessel was connected to the gas burette under Ar atmosphere. The gas burette was initialised and $\text{H}_3\text{B}\cdot\text{NMeD}_2$ or $\text{D}_3\text{B}\cdot\text{NMeH}_2$ and precatalyst **1** were dissolved in 5 mL of toluene. Then 0.46 mL of a MeLi solution (0.08M in Et_2O , 2.75 mol%) were added to the reaction vessel and data acquisition was started immediately (Figure S13).

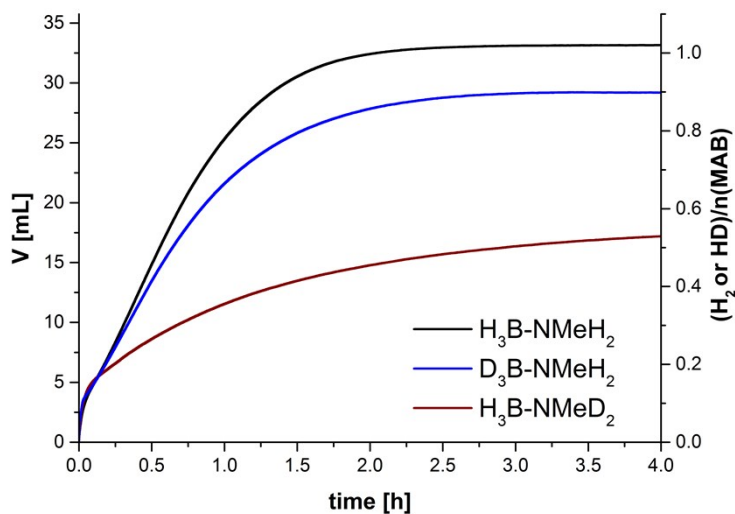


Figure S13. Comparison of the volumetric curve of catalytic dehydropolymerisation of MAB, $\text{H}_3\text{B}\cdot\text{NMeD}_2$ and $\text{D}_3\text{B}\cdot\text{NMeH}_2$.

3. Polymer characterisation

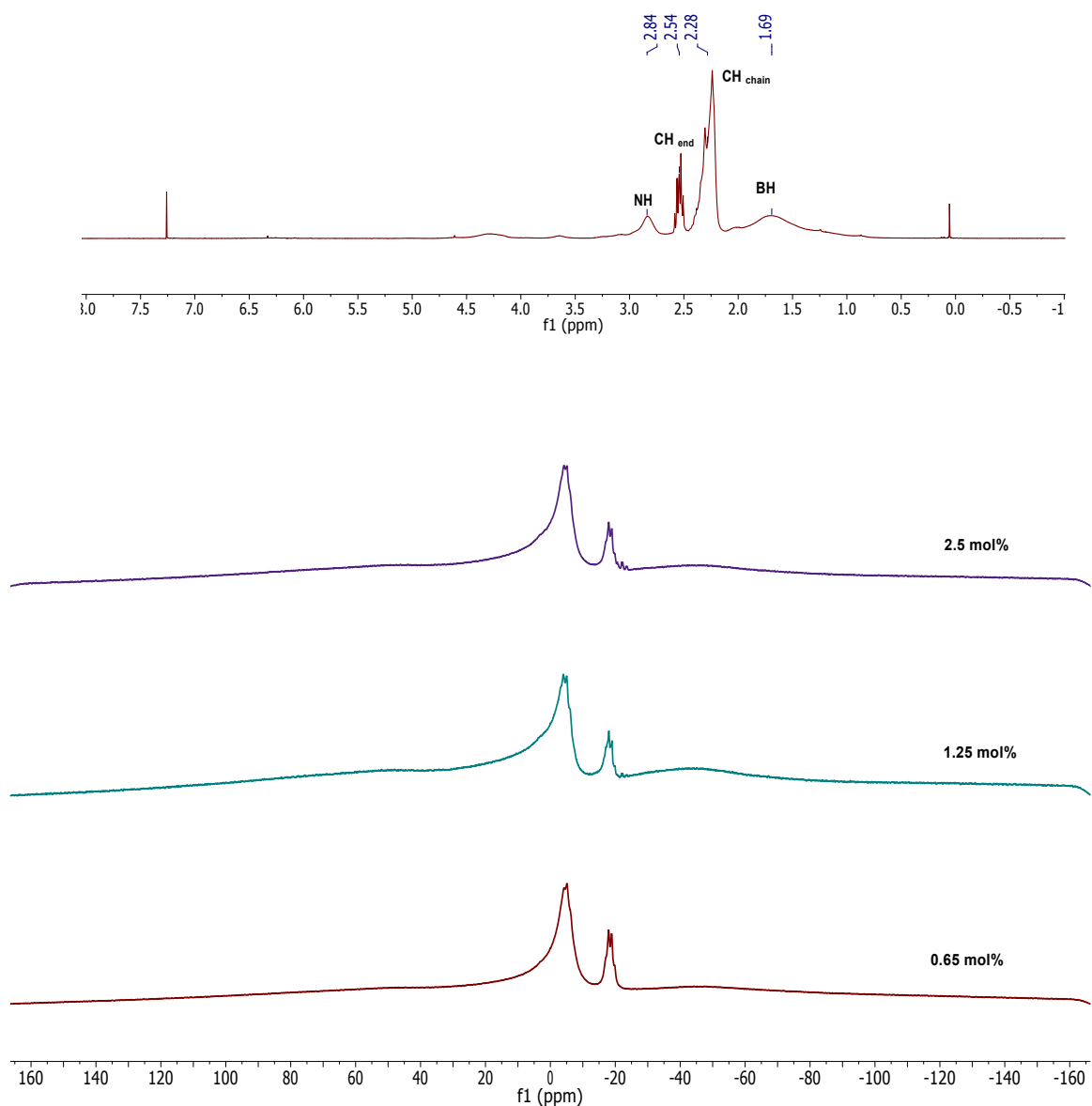


Figure S14. ^1H NMR spectrum (25 °C, CDCl_3 , 300.13 MHz) of a representative sample of isolated PMAB (top) and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra (25 °C, CDCl_3 , 96.32 MHz) of isolated PMABs at different catalyst loadings (bottom). Note: Remaining cycloborazane ($\delta^{11}\text{B} = -5.2$ ppm) and starting material ($\delta^{11}\text{B} = -18$ ppm) cannot be excluded due to the overlapping of their signals with those of the polymer.

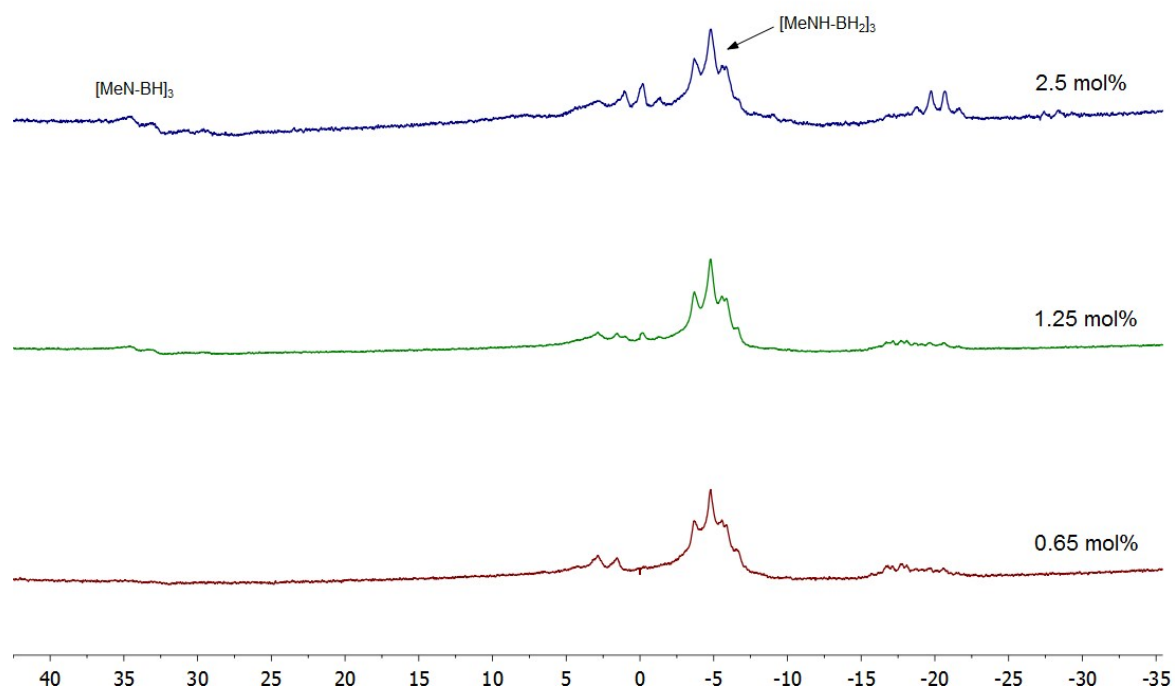
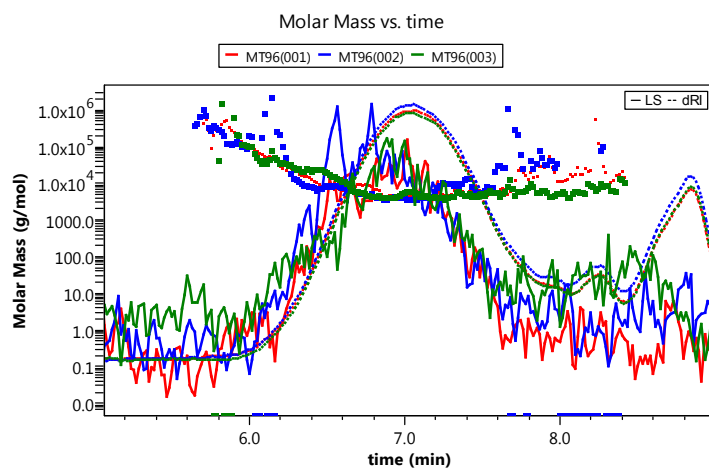


Figure S15. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra (25 °C, CDCl_3 , 96.3 MHz) of the *n*-hexane phase after precipitation of the polymer at different catalyst loadings.

SEC analysis

2.5 mol% catalyst loading

a) $c = 1.96 \text{ mg/mL}$



b) $c = 4.35 \text{ mg/mL}$

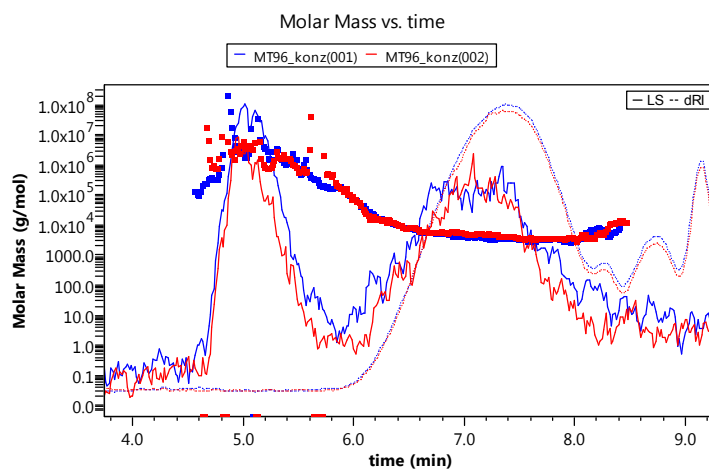


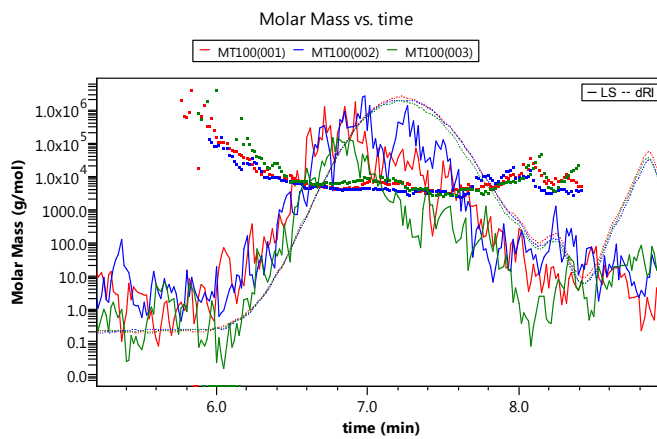
Figure S16. Chromatogram at a) low and b) higher concentration, duplicate injections, molar mass, MALLS and RI signal vs. elution time (2.5 mol% catalyst loading)

Table S1. Average molar mass and molar mass dispersities measured by SEC-MALLS at two different concentrations (2.5 mol% catalyst loading).

Measure- ment	M_n (g·mol ⁻¹)	M_w (g·mol ⁻¹)	\bar{D} (M_w/M_n)	M_n (g·mol ⁻¹)	M_w (g·mol ⁻¹)	\bar{D} (M_w/M_n)
c = 1.96 mg/mL			c = 4.35mg/mL			
1	6020±2400	8770±3490	1,46	3920±370	5530±503	1,41
2	5600±2300	7810±3210	1,39	4530±580	6110±780	1,35
3	5.500±2130	7560±2930	1,38			
Average	5710±2280	8050±3210	1,41	4220±470	5820±650	1,38

1.25 mol% catalyst loading

a) $c = 2.01 \text{ mg/mL}$



b) $c = 4.18 \text{ mg/mL}$

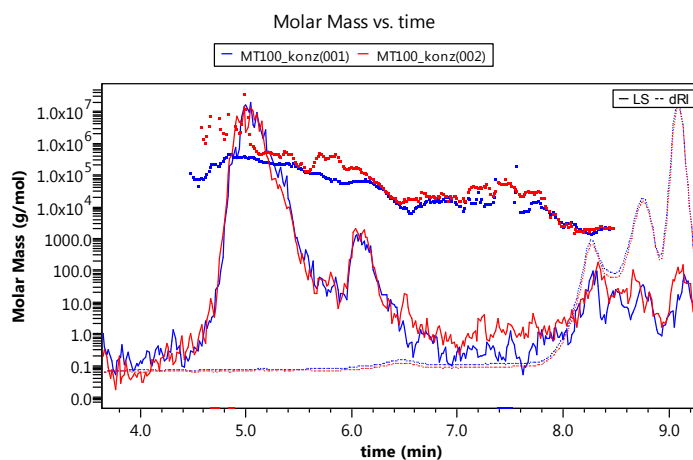


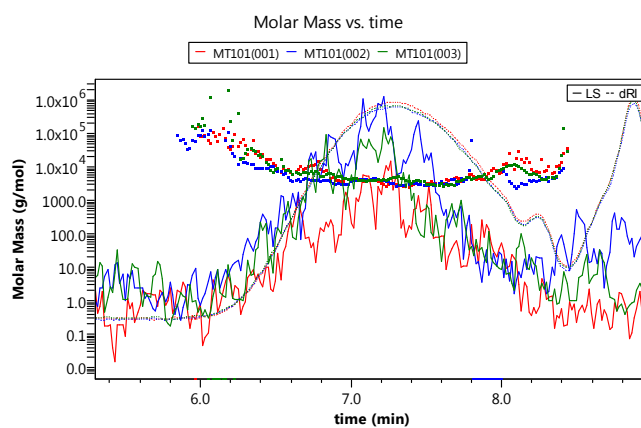
Figure S17. Chromatogram at a) low and b) higher concentration, duplicate, molar mass, LS and RI signal vs. elution time.

Table S2. Average molar mass and molar mass dispersities measured by SEC-MALLS at two different concentrations (1.25 mol% catalyst loading).

Measure- ment	M_n ($\text{g}\cdot\text{mol}^{-1}$)	M_w ($\text{g}\cdot\text{mol}^{-1}$)	\mathfrak{D} (M_w/M_n)	M_n ($\text{g}\cdot\text{mol}^{-1}$)	M_w ($\text{g}\cdot\text{mol}^{-1}$)	\mathfrak{D} (M_w/M_n)
c = 2.01 mg/mL			c = 4.18 mg/mL			
1	5140±1800	6370±2240	1,24	2410±380	14600±2310	6,07
2	4105±1510	5,15±1,88	1,24	2440±390	16000±2530	6,57
3	5100±1560	6710±2050	1,32			
Average	4790±1630	6080±2070	1,27	2430±380	15300±2420	6,32

0.65 mol% catalyst loading

a) $c = 1.99 \text{ mg/mL}$



b) $c = 4.27 \text{ mg/mL}$

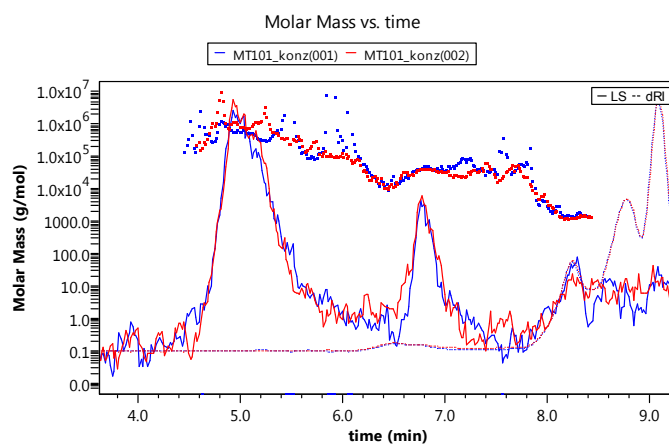


Figure S18. Chromatogram at a) low and b) higher concentration, duplicate, molar mass, LS and RI signal vs. elution time.

Table S3. Average molar mass and molar mass dispersities measured by SEC-MALLS at two different concentrations (0.65 mol% catalyst loading).

Measure- ment	M_n (g·mol ⁻¹)	M_w (g·mol ⁻¹)	\mathcal{D} (M_w/M_n)	M_n (g·mol ⁻¹)	M_w (g·mol ⁻¹)	\mathcal{D} (M_w/M_n)
c = 1.99 mg/mL			c = 4.27 mg/mL			
1	4450±2130	5890±3040	1,32	2040±420	15900±3310	7,78
2	3690±1440	4300±2000	1,16	1810±380	13400±2790	7,38
3	4650±1760	5740±2540	1,23			
Average	4270±1770	5310±2520	1,24	1930±400	14600±3040	7,58

4. Stoichiometric test

In situ reaction of **1**, MAB and MeLi·BrLi

Complex **1** (17 mg, 0.02 mmol) and MAB (3 mg, 0.05 mmol) were transferred into a J-Young NMR tube and dissolved in C₆D₆ (0.7 mL). To this solution a solution of MeLi·BrLi (0.05 mmol, 0.03 mL) was added slowly at 0 °C. The colour of the reaction mixture gradually changed from orange to red within 15 minutes, then to brown within two hours and finally to petrol (> 15 h).

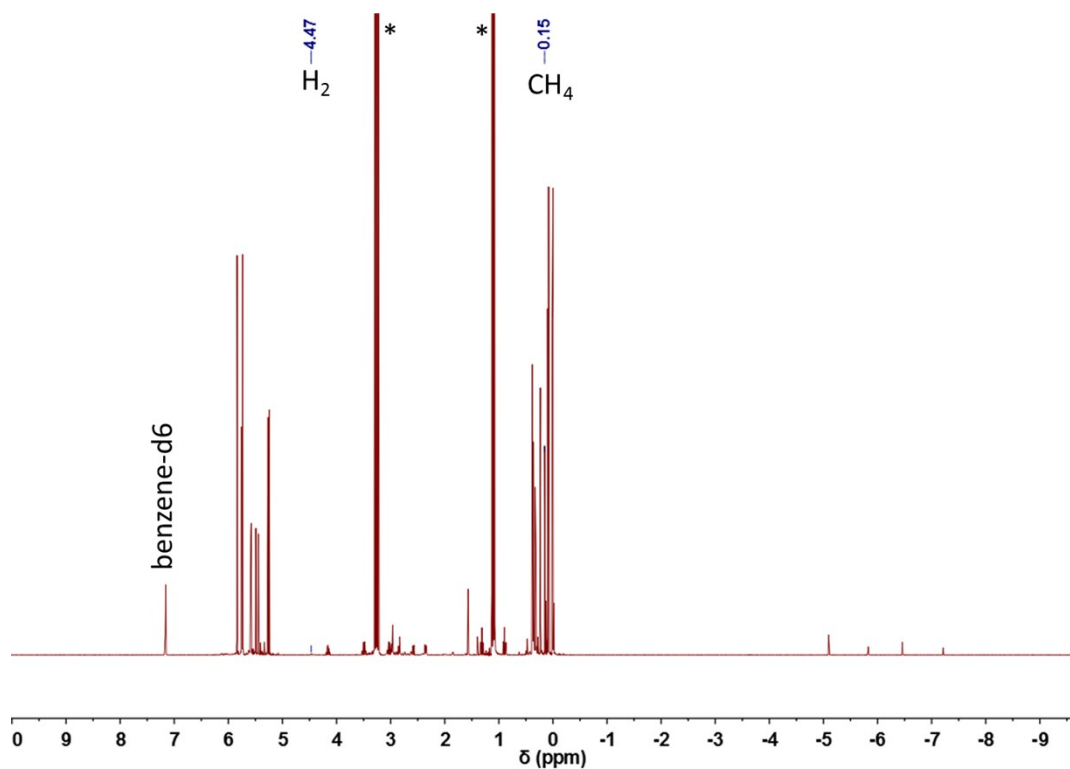


Figure S19. ¹H NMR spectrum (25 °C, [D₆]benzene, 300.13 MHz) of the above *in situ* experiment showing the formation of H₂^[11] and CH₄^[10] in addition to a series of new unidentified zirconocene species. The four resonances found at higher field support the formation of Zr hydride species which were postulated as catalytically active intermediates. Asterisk marks diethyl ether of the MeLi·BrLi solution.

Reaction of complex 1 and Li[MeNH·BH₃]:

1 (23 mg, 0.033 mmol) and Li[MeNH·BH₃] (3.4 mg, 0.033 mmol) were transferred into a J-Young NMR tube and C₆D₆ (0.7 mL) was added. The reaction was monitored by ¹H and ¹¹B NMR spectroscopy. The colour of the reaction mixture gradually changed from orange to red within 15 minutes, then to brown within two hours and finally to petrol (> 15h).

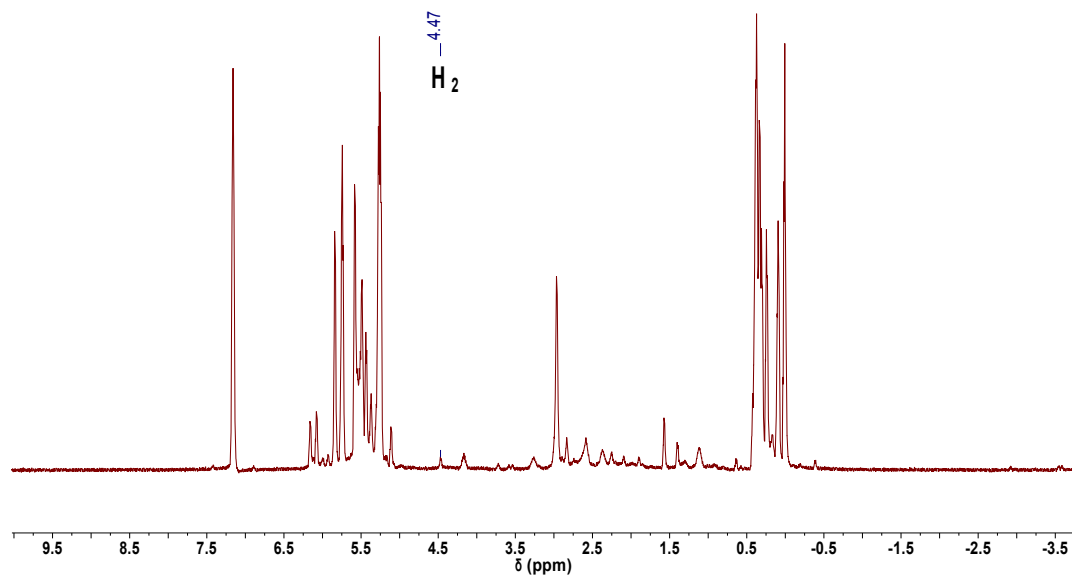


Figure S20. ¹H NMR spectrum (25 °C, [D₆]benzene, 300.13 MHz) of the above *in situ* experiment showing the formation of H₂ in addition to a series on new unidentified zirconocene species.

5. Crystallographic details

Table S4. Crystallographic details of **2** and **4**.

	2	4
Chem. Formula	C ₂₉ H ₃₈ Cl ₅ GaSi ₂ Zr ₂ ·C ₆ H ₆	C ₃₁ H ₄₄ Si ₂ Zr ₂
Form. Wght [g mol ⁻¹]	950.29	655.28
Color	orange	yellow
Cryst. system	monoclinic	orthorhombic
Space group	<i>P2₁/c</i>	<i>P2₁2₁2₁</i>
a [Å]	9.8303(2)	10.9699(3)
b [Å]	21.7110(4)	17.2760(4)
c [Å]	19.0242(3)	32.6586(9)
α [°]	90	90
β [°]	94.3510(8)	90
γ [°]	90	90
V [Å ³]	4048.55(13)	6189.3(3)
Z	4	8
ρ _{calc.} [g cm ⁻³]	1.559	1.406
μ [mm ⁻¹]	8.705	0.768
T [K]	150(2)	150(2)
radiation type	CuK\α	MoK\α
reflections measured	35215	89921
independent reflections	7146	14925
observed reflections with I > 2σ(I)	6289	13905
R _{int.}	0.0417	0.0365
F(000)	1912	2704
R ₁ (I > 2σ(I))	0.0681	0.0252
wR ₂ (all data)	0.2005	0.0545
GOF on F ²	1.039	1.033
Parameters	401	647
CCDC number	1851926	1851927

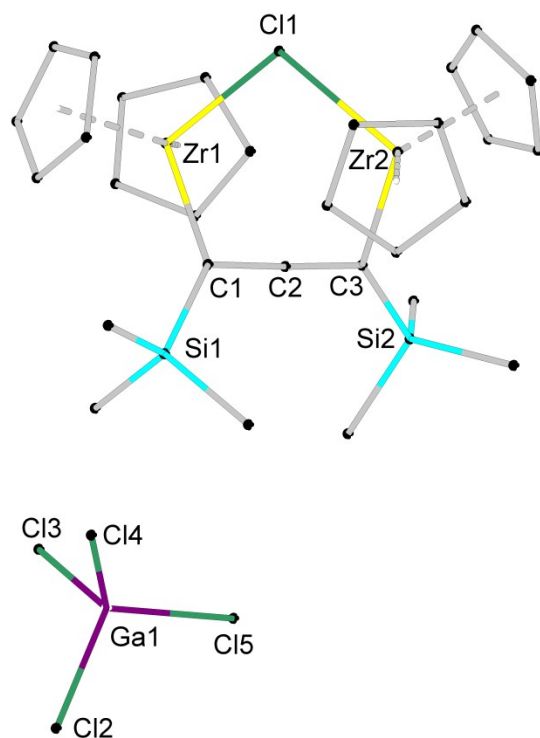


Figure S21. Structural motif of **2**, H atoms and benzene solvent molecule are omitted for clarity. Due to the very fast crystallisation of this compound only crystals of poor quality were obtained resulting in a R_1 ($I > 2\sigma(I)$) value of only 0.0681 and wR_2 (all data) of 0.2005. Furthermore high residual electron density was observed (largest diff. peak: $5.22 \text{ e}\cdot\text{\AA}^{-3}$ 1.14 \AA from Si1 and deepest hole: $-0.67 \text{ e}\cdot\text{\AA}^{-3}$ 0.74 \AA from Zr1) Therefore no further details are reported and we only use the structural motif to confirm the formation of complex **2**.

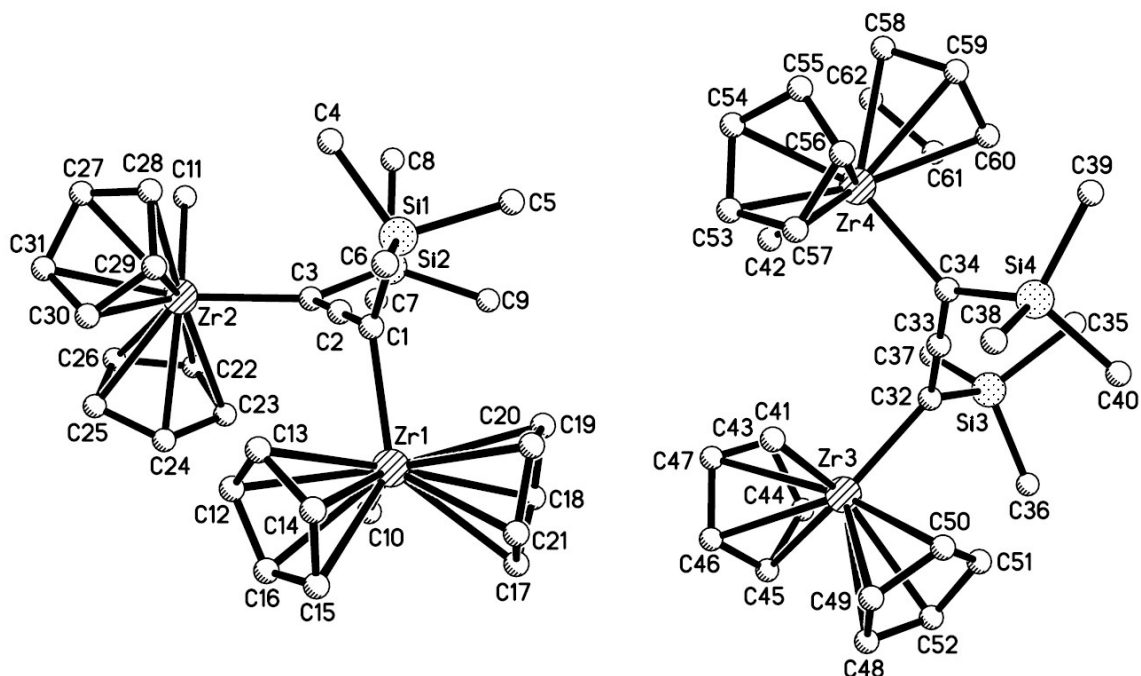


Figure S22. Numbering Scheme of **4**. Hydrogen atoms are omitted for clarity.

Table S5. Selected bond lengths (Å), angles (°) of **4**.

C1–C2/ C32–C33	1.310(4)/ 1.310(4)	C1–C2–C3/ C32–C33–C34	178.6(3)/ 179.2(3)
C2–C3/ C33–C34	1.312(4)/ 1.312(4)	C2–C1–Zr1/ C33–C32–Zr3	109.4(2)/ 108.0(2)
C1–Zr1/ C32–Zr3	2.280(3)/ 2.286(3)	Si1–C1–Zr1/ Si3–C32–Zr3	130.80(16)/ 132.45(15)
C10–Zr1/ C41–Zr3	2.273(3)/ 2.260(3)	C10–Zr1–C1/ C41–Zr3–C32	104.46(13)/ 104.75(11)
C3–Zr2/ C34–Zr4	2.286(3)/ 2.271(3)	C2–C3–Si2/ C33–C34–Si4	110.8(2)/ 119.7(2)
C11–Zr2/ C42–Zr4	2.266(3)/ 2.283(3)	C2–C3–Zr2/ C33–C34–Zr4	125.2(2)/ 110.0(2)
C1–Si1/ C32–Si3	1.852(3)/ 1.849(3)	Si2–C3–Zr2/ Si4–C34–Zr4	123.34(15)/ 129.99(16)
C3–Si2/ C34–Si4	1.869(3)/ 1.848(3)	C11–Zr2–C3/ C34–Zr4–C42	99.28(12)/ 105.34(12)

Axial Chirality of compounds **1**, **2** and **4**.

Due to the allendiyl bridge in the examined complexes the molecules show an axial chirality. Compound **4** crystallized in the space group $P2_12_12_1$ (Flack parameter $x = -0.07(1)$) with both enantiomers in the asymmetric unit. **2** crystallized in the centrosymmetric space group $P2_1/c$, therefore **2** is racemic too. The recently published starting material **1** (space group Cc) was also obtained as racemic mixture in the solid state. To demonstrate these enantiomers we show the capped stick representations of complexes **1**, **2** and **4**. For clarity H atoms, solvent molecules as well as the $[GaCl_4]$ anion in the case of **2** were omitted.

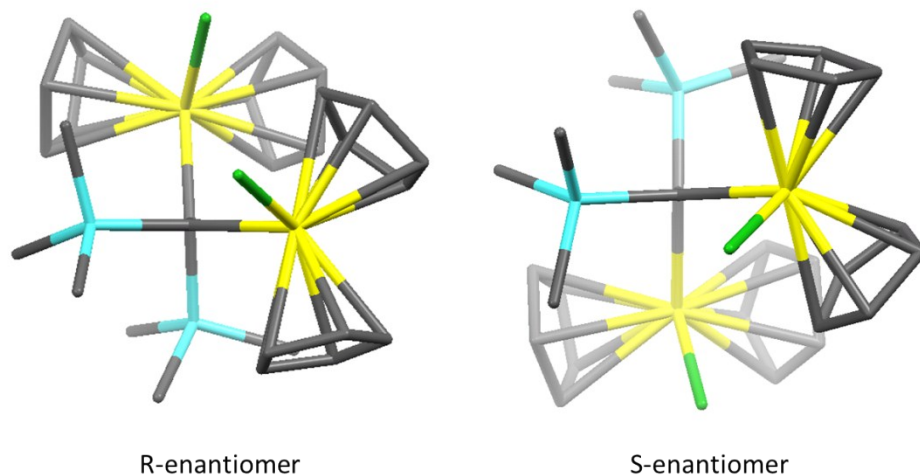


Figure S23. Representation of the R/S-isomers of **1**.

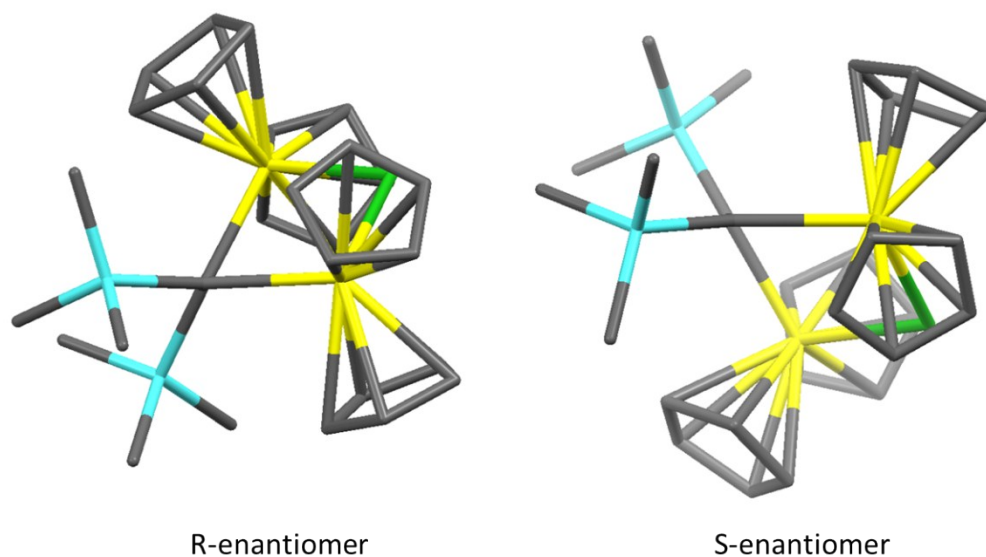
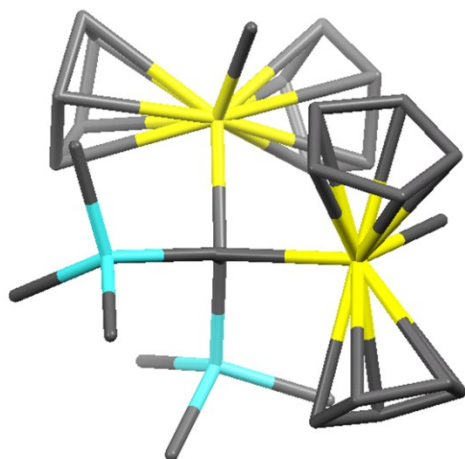
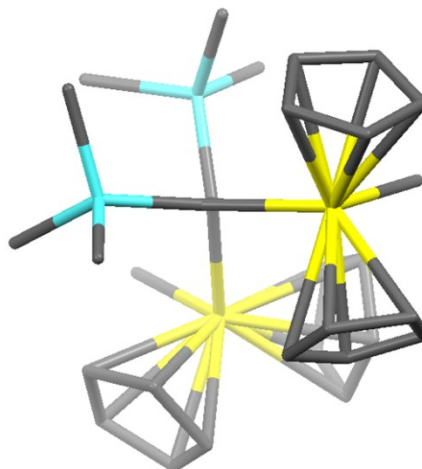


Figure S24. Representation of the R/S-isomers of **2**.



R-enantiomer



S-enantiomer

Figure S25. Representation of the R/S-isomers of **4**.

6. References

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