SUPPORTING INFORMATION

Zirconocene amide complex catalysed dehydropolymerisation of phenylsilane: new catalysts and mechanistic insights

Kevin Lindenau, Anke Spannenberg, Fabian Reiß* and Torsten Beweries*

Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany.

Table of contents

1. Experimental Details.................................................................2
2. NMR spectroscopy.....................................................................5
3. Volumetric studies.................................................................32
4. Crystallographic details......................................................33
5. Vibrational spectroscopy....................................................35
6. SEC analysis...........................................................................39
7. Computational details.........................................................45
8. References.............................................................................51
1. Experimental Details

1.1. 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. PhSiH₃, Ph₂SiH₂, Et₂SiH₂ and n-BuSiH₃ were purchased from Sigma-Aldrich. PhSiH₃ and Cp₂Zr(NMe₂)₂ were synthesised according to literature procedures.¹ ²

NMR spectra were recorded on Bruker AV300 and AV400 spectrometers. ¹H and ¹³C chemical shifts were referenced to the solvent signal: benzene-d₆ (δ_H = 7.16 ppm, δ_C = 128.06 ppm), toluene-d₈ (δ_H = 2.08 ppm, δ_C = 20.43 ppm), THF-d₈ (δ_H = 3.58 ppm, δ_C = 25.3 ppm).³

Raman spectra were recorded on a LabRAM HR 800 Raman Horiba spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by different laser sources: 633 nm (17 mW, air-cooled), 784 nm Laser diode (100 mW, air-cooled) or 473 nm Ar+ Laser (20 mW, air-cooled). All measurements were carried out at ambient temperature.

IR spectra were recorded on a Bruker Alpha FT-IR, ATR Spectrometer, spectra are not corrected.

MS analysis was done using a Finnigan MAT 95-XP instrument (Thermo-Electron) in CI⁺/CI⁻ mode (isobutene) and for the air stable compounds in EI mode.

CHN analysis was done using a Leco TruSpec elemental analyser. At this point it should be pointed out that in the case of the bimetallic zirconocene complexes we could not obtain satisfactory elemental analysis in most cases. Despite repeated recrystallisation, repeated measurements with and without oxidiser V₂O₅ and modified furnace temperature, we observed up to 20% less carbon content than calculated/expected. This behaviour might be explained by formation of mixed zircon-silicon-carbides (ceramics) in the furnace and therefore the carbon content dramatically decreases.⁴

Melting points are uncorrected and were determined in sealed capillaries under Ar atmosphere using a Mettler-Toledo MP 70.

Chloride analysis was done using a Radiometer Analytical SAS TitraLab 870 TIM 870. Titration was performed with a turning point titration using a MC6091Ag combination electrode in a range of ± 2000 mV and a resolution of 0.1 mV. The exploration were carried out by oxygen oxidation of Schöniger followed by Mohr titration.⁵ ⁶

X-Ray diffraction data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods (SHELXS-97)⁷ and refined by full-matrix least-squares procedures on F² (SHELXL-2018).⁸ Diamond⁹ was used for graphical representations.

All DFT calculations were carried out with the Gaussian 16 package of molecular orbital programs.
1.2. General procedure of dehydropolymerisation experiments

A mixture of the catalyst (0.01 mmol, 0.2 mol%) and PhSiH₃ (0.23 mL, 6.47 mmol) in a Schlenk tube was stirred (magnetic stirring bar) at the reported temperatures in an open system with pressure compensation. The reaction mixture was stirred for one or more days at room temperature. To obtain an NMR sample, an aliquot of the reaction mixture was added to a dried, argon-filled NMR tube containing C₆D₆. For the GPC sample an aliquot was removed, added to THF and measured immediately.

1.3. Synthesis of 2

```
\( \text{Cp}_2\text{Zr} \equiv \text{Cl} + \text{2 LiNMe}_2 \xrightarrow{\text{Et}_2\text{O}, \text{r.t.}} \text{Cp}_2\text{Zr} \equiv \text{NMe}_2 \)
```

Compound 1b (400 mg, 0.57 mmol) and LiNMe₂ (58.6 mg, 1.15 mmol) were dissolved in 15 mL of Et₂O and the mixture was stirred overnight. The colour of the reaction mixture changed from red to orange and Et₂O was removed in vacuo. The orange solid residue was dissolved in benzene, followed by filtration. After washing with benzene (3x2 mL) the solution was concentrated to obtain orange crystals of 4 (326 mg, 82%). Crystals suitable for X-ray analysis were obtained from a pentane solution.

1H NMR (25 °C, benzene-d₆, 300 MHz): \( \delta \) 6.05 ppm (s, 10H, Cp), 5.99 (s, 10H, Cp), 2.86 (s, 12H, NMe₂), 0.39 (s, \( J_H,^{29}\text{Si} = 6.2 \) Hz, 18H, SiCH₃)₃. 13C NMR (25 °C, benzene-d₆, 100 MHz): \( \delta \) 193.6 (C=C=), 111.6 (Cp), 111.3 (Cp), 85.5 (C=C=C), 51.6 (N(CH₃)₃), 3.2 (Si(CH₃)₃). 29Si-inept NMR (25 °C, benzene- d₆, 79.49 MHz): \( \delta \) -3.78; (SiMe₃). IR (ATR, cm⁻¹): \( \nu \) 3095 (w), 2815 (vw) 2766 (vw) 1760 (s, C=C=C), 1230 (m), 937 (s), 771 (s), 524 (m), 462 (w), 3096 (w), 2962 (w), 2914 (m), 2857 (m), 2808 (m), 2760 (vw), 2771 (vw), 2158 (vw), 2035 (w), 1840 (vw), 1759 (s), 1620 (w), 1558 (w), 1458 (vw), 1434 (vw), 1367 (vw), 1229 (w), 1130 (s), 1069 (w), 943 (m), 845 (w), 802 (w), 674 (w), 625 (w), 544 (w), 534 (w), 352 (w), 292 (w), 264 (w) cm⁻¹. MS-CI⁺ (isobutene): m/z (%): 640 (80) \{[\text{Cp}_2\text{Zr}(\text{Me}_3\text{SiC}_3\text{SiMe}_3\text{NMe}_3)]\}⁺, 403 (7) \{[\text{Cp}_2\text{Zr}(\text{Me}_3\text{SiC}_3\text{SiMe}_3)]\}⁺, 263 (15) \{[\text{Cp}_2\text{ZrNMe}_3]\}⁺, 185 (44) \{[\text{Me}_3\text{SiC}_3\text{SiMe}_3]\}⁺, 109 (100) \{[\text{C}_3\text{SiMe}_3]\}⁺, 73 (15) \{[\text{Si}(\text{CH}_3)_3]\}⁺. Mp: 159 °C (decomp.). CHN analysis: calc (%) for C₃₃H₅₀N₂Si₂Zr₂: C, 55.5; H, 7.1; N, 3.9. Found: C, 48.9; H, 6.4; N, 2.6 (best value of four measurements).

1.4. Synthesis of rac-3

[rac-(ebthi)ZrCl₂] (527 mg 1.24 mmol) and LiNMe₂ (126 mg, 2.47 mmol) were dissolved in 20 mL of Et₂O and the mixture was stirred overnight at room temperature. Et₂O was removed in vacuo. The orange solid residue was dissolved in 20 mL of toluene, followed by filtration. The orange solution was concentrated and stored overnight at -78 °C in toluene to obtain orange crystals of [rac-(ebthi)Zr(NMe₂)₂] (466 mg, 88 %).

1H NMR (25 °C, benzene-d₆, 300 MHz): \( \delta \) 6.08 (d, \( J_H,^{31}\text{P} = 2.7 \) Hz, 2H, CH ebthi), 5.31 (d, \( J_H,^{31}\text{P} = 2.8 \) Hz, 2H, CH ebthi), 2.97 (s, 12H, N(CH₃)₃), 2.86-2.77 (m, 2H, CH₂ ebthi), 2.72-2.64 (m, 2H, CH₂ ebthi), 2.64-2.55 (m, 2H, CH₂ ebthi), 2.40-2.24 (m, 3x 6H, CH₃ ebthi), 1.82-1.33 ppm (m, 4x 8H, CH₂ ebthi). 13C NMR (25 °C, benzene-d₆, 100 MHz): \( \delta \) 130.6, 127.4, 116.8 (6x C ebthi), 109.7, 106.0 (4x CH ebthi), 48.5 (4x C N(CH₃)₃), 28.5, 25.7, 24.7, 24.5, 23.2 ppm (10x CH₂ ebthi). IR (ATR, cm⁻¹): \( \nu \) 3075 (w), 2933 (w), 2844 (w), 2805 (m), 2756 (m), 1439 (w), 1418 (w), 1233 (w), 1130 (m), 1055 (w), 938 (s), 771 (s), 524 (m), 462 (w). Raman (632 nm, 20 sec, 15 scans): \( \nu \) 3096 (w), 2962 (w), 2914 (m), 2857 (m), 2808 (m), 2760 (w).
enzene and stirred for 15 minutes.

CHN analysis: MS 1432 (w), 1334 (vw), 1277 (vw), 1238 (m), 944 (m), 681 (w), 535 (w), 314 (m), 148 (m), 91 (m) cm⁻¹. **MS-Cl⁺ (isobutene): m/z (%):** 443 (100) [M]+, 398 (66) [C₂H₄(C₈H₂₀)₂ZrN(CH₃)₂]⁺. **Mp:** 168 °C (decomp.). CHN analysis: calc (%) for C₂₄H₃₅N₂Zr: C, 65.0; H, 8.2; N, 6.3. Found: C, 64.9; H, 8.4; N, 6.3.

1.5. **Synthesis of meso-3**

[meso-(ebthi)ZrCl₂] (436 mg, 1.02 mmol) and LiNMe₂ (105 mg, 2.04 mmol) were dissolved in 15 mL of Et₂O and the mixture was stirred overnight at 60 °C. The colour of the reaction mixture changed from colourless to yellow and Et₂O was removed in vacuo. The yellow residue was dissolved in 15 mL of toluene and filtered off. After addition of 4 eq of LiNMe₂ the yellow solution was stirred over 4 days at 60 °C to obtain [meso-(ebthi)Zr(NMe₂)₂].

³H NMR (25 °C, benzene-d₆, 300 MHz): δ 6.15 (d, 3J_H-H = 2.9 Hz, 2H, CH ebthi), 5.31 (d, 3J_H-H = 2.9 Hz, 2H, CH ebthi), 3.01 (s, 6H, N(CH₃)₂), 2.93 (s, 6H, N(CH₃)₂).

1.6. **Synthesis of rac-4**

[rac-(ebthi)ZrCl₂] (300 mg, 0.70 mmol) and LiNMe₂ (36 mg, 0.70 mmol) were dissolved in 10 mL of Et₂O and the mixture was stirred overnight at room temperature. Subsequently Et₂O was removed in vacuo and dried for 3 h. The orange foam was dissolved in 5 mL of benzene and stirred for 15 minutes. Benzene was filtered off and the orange oil was washed with benzene (3x 1 mL). The orange solution was removed in vacuo and the orange oil was dissolved in 3 mL Et₂O. The Et₂O was removed in vacuo to obtain [rac-(ebthi)Zr(Cl)(NMe₂)] as an orange solid (226 mg, 75 %).

³H NMR (25 °C, benzene-d₆, 300 MHz): δ 6.16 (d, 3J_H-H = 2.9 Hz, 1H, CH ebthi), 6.06 (d, 3J_H-H = 3.0 Hz, 1H, CH ebthi), 5.54 (d, 3J_H-H = 3.0 Hz, 1H, CH ebthi), 5.11 (d, 3J_H-H = 3.0 Hz, 1H, CH ebthi), 3.25-3.15 (m, 2H, CH₂ ebthi), 2.87 (s, 6H, NMe₂), 2.80-2.68 (m, 2H, CH₂ ebthi), 2.57-2.45 (m, 4H, 2 x CH₂ ebthi), 2.44-2.30 (m, 4H, 2 x CH₂ ebthi), 2.27-2.14 (m, 4H, 2 x CH₂ ebthi), 1.54-1.39 ppm (m, 4H, 2 x CH₂ ebthi). **¹³C NMR** (25 °C, benzene-d₆, 100 MHz): δ 133.5, 132.1, 131.0, 123.1, 114.9 (12 x C ebthi), 113.4, 111.1, 109.3, 106.4 (8 x C ebthi), 48.4 (2 x C N(CH₃)₂), 28.8, 28.7, 25.5, 24.8, 24.7, 24.3, 23.3, 22.8 ppm (20 x CH₂ ebthi). **IR (ATR, cm⁻¹):** ν 3065 (m), 2923 (m), 2849 (m), 2811, (m), 2762 (m), 1490 (m), 1435 (m), 1327 (m), 1134 (m), 1059 (w), 940 (s), 802 (s), 783 (s), 690 (s), 530 (m). **Raman** (633 nm, 25 sec, 10 scans): ν 3098 (w), 3082 (vw), 3068 (vw), 3048 (vw), 2929 (m), 2887 (w), 2854 (w), 2767 (w), 1457 (w), 1432 (w), 1334 (vw), 1277 (vw), 1238 (m), 944 (m), 681 (w), 535 (w), 314 (m), 148 (m), 91 (m) cm⁻¹. **MS-Cl⁺ (isobutene): m/z (%):** 434 (100) [M]+, 398 (71) [C₂H₄(C₈H₂₀)₂ZrN(CH₃)₂]⁺. **Mp:** 141 °C (decomp.). CHN analysis: calc (%) for C₂₂H₃₆NClZr: C, 60.7, H, 7.0. Found: C, 60.6, H, 8.8.
1.7. Synthesis of meso-4

[meso-(ebthi)ZrCl₂] (328 mg, 0.77 mmol) and LiNMe₂ (80 mg, 1.58 mmol) were dissolved in 15 mL of Et₂O and the mixture was stirred overnight at room temperature. Et₂O was removed in vacuo. The yellow solid residue was dissolved in 15 mL of benzene, followed by filtration. After washing with benzene (3x3 mL) the solution was removed to obtain [meso-(ebthi)Zr(Cl)(NMe₂)] as a yellow solid (294 mg, 89%). Crystals suitable for X-ray diffraction analysis were obtained from benzene solution.

¹H NMR (25 °C, benzene-δ₆, 300 MHz): δ 6.06 (d, ³J_H,H = 3.1 Hz, 2H, CH ebthi), 5.38 (d, ³J_H,H = 3.0 Hz, 2H, CH ebthi), 3.12 (m, 2H, CH₂ ebthi), 2.82 (s, 6H, N(CH₃)₂) 2.68-2.60 (m, 2H, CH₂ ebthi), 2.53-2.44 (m, 4H, 2 x CH₂ ebthi), 2.40-2.21 (m, 4H, 2 x CH₂ ebthi), 2.19-1.93 (m, 4H, 2 x CH₂ ebthi), 1.54-1.37 ppm (m, 4H, 2 x CH₂ ebthi). ¹³C NMR (25 °C, benzene-δ₆, 100 MHz): δ 128.8, 127.5, 123.4 (6 x C ebthi), 113.4, 102.4 (4 x CH ebthi), 49.6 (2 x C N(CH₃)₂), 27.6, 24.9, 23.3, 23.0, 22.9 ppm (10 x CH₂ ebthi). IR (ATR, cm⁻¹): ν 3075 (w), 2919 (m), 2851 (m), 2813 (m), 2766 (m), 1437 (m), 1424 (m), 1235 (m), 1134 (m), 1117 (m), 1057 (m), 942 (s), 791 (s), 653 (w), 532 (m). Raman (632 nm, 20 sec, 15 scans): ν 3108 (vw), 3077 (vw), 2932 (m), 2860 (w), 2817 (vw), 2770 (vw), 1471 (w), 1440 (w), 1400 (vw), 1338 (vw), 1295 (vw), 1239 (m), 945 (m), 807 (w), 693 (w), 538 (w), 346 (w), 323 (s), 286 (m), 160 (s), 115 cm⁻¹ (m). MS-CI⁺ (isobutene): m/z (%): 434 (100) [M]⁺, 398 (15) [C₂H₄(C₁₈H₃₀)₂ZrN(CH₃)₂]⁺. Mp: 163 °C (decomp.). CHN analysis: calc (%) for C₂₂H₃₀NClZr: C, 60.7; H, 7.0; N, 3.2. Found: C, 60.4; H, 6.8; N, 2.7 (best value of four measurements).

2. NMR spectroscopy

2.1. NMR spectra of 2

![Figure S1. ¹H NMR spectrum of 2 (25 °C, benzene-δ₆, 300.13 MHz).](image-url)
Figure S2. $^{13}$C NMR spectrum of 2 (25 °C, benzene-$d_6$, 100.63 MHz).

Figure S3. $^{29}$Si INEPT NMR spectrum of 2 (25 °C, benzene-$d_6$, 79.49 MHz).
2.2. NMR spectra of rac-3

Figure S4. $^1$H NMR spectrum of rac-3 (25 °C, benzene-$d_6$, 300.20 MHz).

Figure S5. $^{13}$C NMR spectrum of rac-3 (25 °C, benzene-$d_6$, 75.49 MHz).
2.3. NMR spectra of meso-3

2.3.1. NMR spectrum synthesised from \([\text{meso-(ebthi)Zr(Cl}_2\mu-C_3\text{)(NMe}_2)_2]\)

\[\text{Figure S6. } ^1\text{H NMR spectrum of meso-3 (25 °C, benzene-}d_6, 300.20 \text{ MHz).}\]

2.3.2. NMR spectrum synthesized from \([\text{meso-(ebthi)ZrCl}_2]\)

\[\text{Figure S7. } ^1\text{H NMR spectra (25 °C, benzene-}d_6, 300.20 \text{ MHz) of the reaction of meso-(ebthi)ZrCl}_2\text{ with LiNMe}_2. Conditions: } 60 \text{ °C, diethyl ether, 1.02 mmol meso-(ebthi)ZrCl}_2, 2.04 \text{ mmol LiNMe}_2 \text{ (red: reaction at 60 °C overnight, blue: additional 4 eq LiNMe}_2 \text{ and stirring 24h, green: conversion to rac-3 in toluene/CH}_2\text{Cl}_2 \text{ at room temperature).}\]
Figure S8. $^1$H NMR spectrum of the reaction of [meso-(ebthi)ZrCl$_2$] with LiNMe$_2$. Conditions: 60 °C, benzene, 0.70 mmol [meso-(ebthi)ZrCl$_2$], 2.80 mmol LiNMe$_2$ (25 °C, benzene-$d_6$, 300.20 MHz).

Figure S9. $^1$H NMR spectrum of the reaction of [meso-(ebthi)ZrCl$_2$] with LiNMe$_2$. Conditions: 60 °C, pentane, 0.70 mmol [meso-(ebthi)ZrCl$_2$], 2.80 mmol LiNMe$_2$ (25 °C, benzene-$d_6$, 300.20 MHz).
2.4. NMR spectra of rac-4

Figure S10. $^1$H NMR spectrum of rac-4, asterisk marks silicon grease (25 °C, benzene-$d_6$, 400.13 MHz).

Figure S11. $^{13}$C NMR spectrum of rac-4 (25 °C, benzene-$d_6$, 75.49 MHz).
2.5. NMR spectra of *meso*-4

![NMR spectra](image)

**Figure S12.** $^1$H NMR spectrum of *meso*-4 (25 °C, benzene-d$_6$, 400.13 MHz).

![NMR spectra](image)

**Figure S13.** $^{13}$C NMR spectrum of *meso*-4 (25 °C, benzene-d$_6$, 75.49 MHz).
Figure S14. $^1$H-$^1$H NOESY NMR spectrum of *meso*-4 (25 °C, benzene-$d_6$, 400.13 MHz).

Figure S15. $^1$H-$^{13}$C HMBC NMR spectrum of *meso*-4 (25 °C, benzene-$d_6$, 400.13 MHz, 100.62 MHz).
2.6. NMR spectra of catalytic dehydropolymerisation of PhSiH₃ using 0.1 mol% 2

Figure S16. ¹H NMR spectrum of catalytic dehydropolymerisation of PhSiH₃, asterisk marks silicon grease. Conditions: room temperature, open system with pressure compensation, 6.47 mmol PhSiH₃, 0.1 mol% 2 (25 °C, benzene-d₆, 400.13 MHz).

Figure S17. ²⁹Si DEPT45 NMR spectrum of catalytic dehydropolymerisation of PhSiH₃. Conditions: room temperature, open system with pressure compensation, 6.47 mmol PhSiH₃, 0.1 mol% 2 (25 °C, benzene-d₆, 79.49 MHz).
Figure S18. $^{29}$Si DEPT135 NMR spectrum of catalytic dehydropolymerisation of PhSiH$_3$. Conditions: room temperature, open system with pressure compensation, 6.47 mmol PhSiH$_3$, 0.1 mol% 2 (25 °C, benzene-d$_6$, 79.49 MHz).
2.7. NMR spectra of catalytic dehydropolymerisation of PhSiH₃ using 0.2 mol% of 2

Figure S19. ¹H NMR spectrum of catalytic dehydropolymerisation of PhSiH₃. Asterisks mark decomposition products. Conditions: room temperature, open system with pressure compensation, 6.47 mmol PhSiH₃, 0.2 mol% 2 (25 °C, benzene-d₆, 400.13 MHz).

Figure S20. ²⁹Si DEPT45 NMR spectrum of catalytic dehydropolymerisation of PhSiH₃. Conditions: room temperature, open system with pressure compensation, 6.47 mmol PhSiH₃, 0.2 mol% 2 (25 °C, benzene-d₆, 79.49 MHz).
Figure S21. $^{29}$Si DEPT135 NMR spectrum of catalytic dehydropolymerisation of PhSiH$_3$. Conditions: room temperature, open system with pressure compensation, 6.47 mmol PhSiH$_3$, 0.2 mol% 2 (25 °C, benzene-$d_6$, 79.49 MHz).

2.8. NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$ using 0.4 mol% 2

Figure S22. $^1$H NMR spectrum of catalytic dehydropolymerisation of PhSiH$_3$, asterisks mark decomposition products. Conditions: room temperature, open system with pressure compensation, 6.47 mmol PhSiH$_3$, 0.4 mol% 2 (25 °C, benzene-$d_6$, 400.13 MHz).
Figure S23. $^{29}$Si DEPT45 NMR spectrum of catalytic dehydropolymerisation of PhSiH$_3$. Conditions: room temperature, open system with pressure compensation, 6.47 mmol PhSiH$_3$, 0.4 mol% 2 (25 °C, benzene-$d_6$, 79.49 MHz).

Figure S24. $^{29}$Si DEPT135 NMR spectrum of catalytic dehydropolymerisation of PhSiH$_3$. Conditions: room temperature, open system with pressure compensation, 6.47 mmol PhSiH$_3$, 0.4 mol% 2 (25 °C, benzene-$d_6$, 79.49 MHz).
2.9. NMR spectra of dehydropolymerisation experiment using 0.4 mol% of 2 with addition of a second portion of PhSiH₃

Figure S25. $^1$H NMR spectrum of catalytic dehydropolymerisation of PhSiH₃, asterisks mark decomposition products. Conditions: room temperature, open system with pressure compensation, 1.85 mmol PhSiH₃, 0.4 mol% 2 (25 °C, benzene-$d_6$, 400.13 MHz).

Figure S26. $^{29}$Si DEPT45 NMR spectrum of catalytic dehydropolymerisation of PhSiH₃. Conditions: room temperature, open system with pressure compensation, 1.85 mmol PhSiH₃, 0.4 mol% 2 (25 °C, benzene-$d_6$, 79.49 MHz).
Figure S27. $^{29}$Si DEPT135 NMR spectrum of catalytic dehydro- polymerisation of PhSiH$_3$. Conditions: room temperature, open system with pressure compensation, 0.4 mol% 2 (25 °C, benzene-$d_6$, 79.49 MHz).
2.10. NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$ using 0.4 mol% of 1

**Figure S28.** $^1$H NMR spectrum of catalytic dehydropolymerisation of PhSiH$_3$, asterisk marks silicon grease. Conditions: room temperature, open system with pressure compensation, 1.85 mmol PhSiH$_3$, 0.4 mol% 1 (25 °C, THF-$d_8$, 400.13 MHz).

**Figure S29.** $^{29}$Si NMR spectrum of catalytic dehydropolymerisation of PhSiH$_3$. Conditions: room temperature, open system with pressure compensation, 1.85 mmol PhSiH$_3$, 0.4 mol% 1 (25 °C, THF-$d_8$, 79.49 MHz).
2.11. NMR spectra of catalytic dehydropolymerisation of PhSiH₃ using 0.8 mol% of 1

Figure S30. $^1$H NMR spectrum of catalytic dehydropolymerisation of PhSiH₃, asterisk marks silicon grease. Conditions: room temperature, open system with pressure compensation, 1.85 mmol PhSiH₃, 0.8 mol% 1 (25 °C, Benzene-$d_6$, 400.13 MHz).

Figure S31. $^{29}$Si DEPT45 NMR spectrum of catalytic dehydropolymerisation of PhSiH₃. Conditions: room temperature, open system with pressure compensation, 1.85 mmol PhSiH₃, 0.8 mol% 1 (25 °C, Benzene-$d_6$, 79.49 MHz).
2.12. NMR spectrum of catalytic dehydropolymerisation of $p$-TolSiH$_3$ using 0.2 mol% of 2

![NMR spectrum of catalytic dehydropolymerisation of $p$-TolSiH$_3$ using 0.2 mol% of 2](image)

Figure S32. $^1$H NMR spectrum of catalytic dehydropolymerisation of $p$-tolSiH$_3$, asterisks mark formation of [1,3-bis-(trimethylsilyl)prop-1-yn]. Conditions: room temperature, open system with pressure compensation, 1.85 mmol PhSiH$_3$, 0.2 mol% 2 (25 °C, benzene-$d_6$, 400.13 MHz).

2.13. NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$ using 0.2 mol% of 2 in a closed system

![NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$ using 0.2 mol% of 2 in a closed system](image)

Figure S33. $^1$H NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$. Conditions: room temperature, 1.85 mmol PhSiH$_3$, 0.2 mol% 2 (green: closed system stored overnight, purple: open system stored in a glove box for 2 days) (25 °C, benzene-$d_6$, 400.13 MHz).
2.14. NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$ using 0.2 mol% of 2 in open system with solvent

**Figure S34.** $^1$H NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$. Conditions: room temperature, 1.85 mmol PhSiH$_3$, 0.2 mol% 2 (green: open NMR tube stored overnight, purple: open system stored in a glove box for two weeks (25 °C, benzene-$_d_6$, 400.13 MHz).

2.15. NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$ using 0.4 mol% of rac-3

**Figure S35.** $^1$H NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$. Asterisk marks silicon grease, hash marks unknown species. Conditions: 1.85 mmol PhSiH$_3$, 0.4 mol% rac-3 (green: open system with pressure compensation, room temperature, purple: open system with pressure compensation, stirred 3 days at 60 °C) (25 °C, benzene-$_d_6$, 300.20 MHz).
2.16. NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$ using 0.8 mol% of rac-3

Figure S36. $^1$H NMR spectra of catalytic dehydropolymerisation of PhSiH$_3$. Asterisk marks silicon grease. Conditions: open system with pressure compensation, 1.85 mmol PhSiH$_3$, 0.8 mol% rac-3, 60 °C, 5 days (25 °C, benzene-$d_6$, 300.20 MHz).

Figure S37. $^{29}$Si DEPT45 NMR spectrum of catalytic dehydropolymerisation of PhSiH$_3$. Conditions: open system with pressure compensation, 1.85 mmol PhSiH$_3$, 0.8 mol% rac-3, 60 °C, 5 days (25 °C, benzene-$d_6$, 79.49 MHz).
2.17. NMR spectrum of catalytic dehydropolymerisation of PhSiH$_3$ using 0.4 mol% of meso-4
2.18. NMR spectrum of catalytic dehydropolymerisation of PhSiH₃ using 0.4 mol% of rac-4

Figure S40. ¹H NMR spectra of catalytic dehydropolymerisation of PhSiH₃. Asterisk marks silicon grease. Conditions: room temperature, open system with pressure compensation, 1.85 mmol PhSiH₃, 0.4 mol% rac-4 (25 °C, benzene-d₆, 300.20 MHz).

Figure S41. ²⁹Si DEPT45 NMR spectrum of catalytic dehydropolymerisation of PhSiH₃. Conditions: room temperature, open system with pressure compensation, 1.85 mmol PhSiH₃, 0.4 mol% rac-4 (25 °C, benzene-d₆, 79.49 MHz).
2.19. NMR spectrum of stoichiometric reaction of 2 with 4 eq PhSiH$_3$

![NMR spectrum of stoichiometric reaction](image)

Figure S42. $^1$H NMR spectrum of stoichiometric reaction, asterisk marks unknown species. Conditions: room temperature, 0.02 mmol PhSiH$_3$, 0.006 mmol 2 (25 °C, benzene-$d_6$, 400.13 MHz).

2.20. NMR spectra of the catalytic reaction of PhSiH$_3$ with LiNMe$_2$

![NMR spectrum of catalytic reaction](image)

Figure S43. $^1$H NMR spectrum of the catalytic reaction stirred overnight, asterisk marks silicon grease. Conditions: room temperature, 1.39 mmol PhSiH$_3$, 0.06 mmol LiNMe$_2$ (25 °C, benzene-$d_6$, 400.13 MHz).
Figure S44. $^{29}$Si NMR spectrum of the catalytic reaction. Conditions: room temperature, 1.39 mmol PhSiH$_3$, 0.06 mmol LiNMe$_2$ (25 °C, benzene-$d_6$, 79.49 MHz).

Figure S45. $^1$H NMR spectra of the catalytic reaction, asterisk marks silicon grease. Conditions: room temperature, 1.39 mmol PhSiH$_3$, 0.06 mmol LiNMe$_2$ (25 °C, benzene-$d_6$, 400.13 MHz).
2.21. NMR spectra of the reaction of PhSiH₃ with tetramethylethylenediamine (TMEDA)

Figure S46. $^1$H NMR spectrum of the reaction. Conditions: room temperature, 1.85 mmol PhSiH₃, 0.37 mmol tetramethylethylenediamine (25 °C, benzene-$d_6$, 400.13 MHz).

Figure S47. $^{29}$Si NMR spectrum of the reaction. Conditions: room temperature, 1.85 mmol PhSiH₃, 0.37 mmol tetramethylethylenediamine (25 °C, benzene-$d_6$, 79.49 MHz).
2.22. NMR spectrum of catalytic reaction of Ph₂SiH₂ using 2

Figure S49. $^1$H NMR spectrum of dehydrocoupling experiment using Ph₂SiH₂, asterisk marks silicon grease. Conditions: 40 °C, open system with pressure compensation, benzene, 5.0 mol% 2 (25 °C, benzene-$d_6$, 400.13 MHz).

Figure S48. $^1$H NMR spectra of the reaction. Conditions: room temperature, 1.85 mmol PhSiH₃, 0.37 mmol tetramethylethylenediamine (25 °C, benzene-$d_6$, 400.13 MHz).
2.23. NMR spectrum of catalytic reaction of Et$_2$SiH$_2$ using 2

Figure S50. $^1$H NMR spectrum of dehydrocoupling experiment using Et$_2$SiH$_2$, asterisks mark decomposition products. Conditions: 40 °C, open system with pressure compensation, benzene, 5.0 mol% 2 (25 °C, benzene-$d_6$, 300.20 MHz).

2.24. NMR spectrum of catalytic reaction of $n$-BuSiH$_3$ using 2

Figure S51. $^1$H NMR spectrum of dehydrocoupling experiment using $n$-BuSiH$_3$, asterisk marks decomposition products. Conditions: 40 °C, open system with pressure compensation, benzene, 5.0 mol% 2 (25 °C, benzene-$d_6$, 300.20 MHz).
3. Volumetric studies

3.1. Dehydropolymerisation of PhSiH$_3$ using different concentrations of 1

![Graph showing volumetric curves for dehydropolymerisation of PhSiH$_3$ with different concentrations of 1.](image1)

*Figure S52.* Volumetric curves of dehydropolymerisation of PhSiH$_3$ with 1. Conditions: room temperature, 1.85 mmol PhSiH$_3$.

3.2. Dehydropolymerisation of PhSiH$_3$ using rac-4

![Graph showing volumetric curve for dehydropolymerisation of PhSiH$_3$ with rac-4.](image2)

*Figure S53.* Volumetric curve of dehydropolymerisation of PhSiH$_3$ with rac-4. Conditions: room temperature, 1.85 mmol PhSiH$_3$. 


4. Crystallographic details

Table S 1. Crystallographic details of rac-3 and meso-4

|                  | rac-3                      | meso-4                     |
|------------------|----------------------------|----------------------------|
| Chem. Formula    | C_{24}H_{36}N_2Zr          | C_{22}H_{30}ClN_2Zr        |
| Form. Wght [g mol\(^{-1}\)] | 443.77                     | 435.14                     |
| Colour           | yellow                     | yellow                     |
| Cryst. system    | orthorhombic               | orthorhombic               |
| Space group      | Pbca                       | P2_1_2_1                   |
| a [Å]            | 9.8199(3)                  | 11.0777(3)                 |
| b [Å]            | 13.2654(4)                 | 12.1942(4)                 |
| c [Å]            | 32.3207(9)                 | 44.1788(14)                |
| α [°]            | 90                         | 90                         |
| β [°]            | 90                         | 90                         |
| γ [°]            | 90                         | 90                         |
| V [Å\(^3\)]     | 4210.3(2)                  | 5967.8(3)                  |
| Z                | 8                          | 12                         |
| ρ_{calc} [g cm\(^{-3}\)] | 1.400                      | 1.453                      |
| μ [mm\(^{-1}\)] | 0.533                      | 0.692                      |
| T [K]            | 150(2)                     | 200(2)                     |
| radiation type  | Mo Kα                      | Mo Kα                      |
| reflections      | 36367                      | 113014                     |
| measured         |                            |                            |
| independent      | 5484                        | 15672                      |
| reflections      |                            |                            |
| observed         | 4575                        | 15088                      |
| reflections with \( I > 2\sigma(I) \) |                            |                            |
| \( R_{int.} \)   | 0.0309                     | 0.0314                     |
| F(000)           | 1872                       | 2712                       |
| \( R_1 (I > 2\sigma(I)) \) | 0.0276                     | 0.0283                     |
| wR_2 (all data)  | 0.0707                     | 0.0661                     |
| GOF on \( F^2 \) | 1.049                      | 1.095                      |
| Parameters       | 248                        | 720                        |
| CCDC number      | 2181386                    | 2181387                    |
Figure S54. Molecular structure of *meso*-4. Illustrated was the asymmetric unit with three isomers and disorders. The lower occupied parts of the disorder are shown with unfilled bonds. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.
5. Vibrational spectroscopy

In the following chapter the experimental infrared and Raman spectra are reported. Furthermore, selected significant bands were assigned to molecule-specific vibrations. The assignment of the vibrations was done with the help of the uncorrected calculated vibration spectra at the B3LYP/GD3BJ/def2svp level of the theory (further details see in Chapter 7).

Table S 2. Assignment of selected infrared vibrations values are reported in wavenumbers [cm$^{-1}$].

| complex | exp. | calc. $\delta$ H$_3$CNCH$_3$ | exp. | calc. $\delta$ CH (ebthi) | exp. | calc. $\nu$ H$_3$CNCH$_3$ | exp. | calc. CH$_3$ wagging (N(CH$_3$)$_2$) $^a$ |
|---------|------|-----------------------------|------|-----------------------------|------|-----------------------------|------|-------------------------------------|
| rac-3   | 524 (m) | 531 | 771 (s) | 806 | 938 (s) | 992 | 1130 (m) | 1197 |
| rac-4   | 530 (m) | 539 | 783 (s) | 820 | 940 (s) | 981 | 1134 (m) | 1198 |
| meso-4  | 532 (m) | 537 | 791 (s) | 809 | 942 (s) | 982 | 1134 (m) | 1199 |

[a] highly coupled with strong H$_3$CNCH$_3$ $\nu$ as vibration.

Table S 3. Assignment of selected infrared vibrations values are reported in wavenumbers [cm$^{-1}$].

| complex | exp. | calc. CH$_3$ wagging (N(CH$_3$)$_2$) $^b$ | exp. | calc. $\delta$ CH$_2$ (ebthi) | exp. | calc. $\nu$ CH$_3$ (N(CH$_3$)$_2$) | exp. | calc. $\nu$ CH (ebthi) |
|---------|------|----------------------------------------|------|-----------------------------|------|---------------------------------------|------|-----------------------|
| rac-3   | 1233 (w) | 1273-1278 | 1418 (w)-1439 (w) | 1461-1477 | 2756 (m) | 2906 | 3065 (m) | 3240 |
| rac-4   | 1237 (m) | 1280 | 1435 (m) | 1454-1477 | 2762 (m) | 2923 | 3065 (m) | 3221 |
| meso-4  | 1235 (m) | 1280 | 1424 (m)-1437 (m) | 1455-1473 | 2766 (m) | 2930 | 3075 (w) | 3241 |

[b] highly coupled with strong H$_3$CNCH$_3$ $\nu$ vibration.
Figure S55. IR spectrum of rac-3.

Figure S56. Raman spectrum of rac-3.
Figure S57. IR spectrum of \textit{meso-4}.

Figure S58. Raman spectrum of \textit{meso-4}.
Figure S59. IR spectrum of rac-4.

Figure S60. RAMAN spectrum of rac-4.
6. SEC analysis

6.1. SEC analysis of polymer from dehydropolymerisation of PhSiH₃ using 1

Figure S61. Size-exclusion chromatogram of isolated polymer from dehydropolymerisation of PhSiH₃. Conditions: room temperature, 1.85 mmol PhSiH₃, 0.4 mol% 1.

Figure S62. Size-exclusion chromatogram of isolated polymer from dehydropolymerisation of PhSiH₃. Conditions: room temperature, 1.85 mmol PhSiH₃, 0.8 mol% 1.
6.2. SEC analysis of polymer from dehydropolymerisation of PhSiH$_3$ using 2

Figure S63. Size-exclusion chromatogram of isolated polymer from dehydropolymerisation of PhSiH$_3$. Conditions: room temperature, 6.47 mmol PhSiH$_3$, 0.1 mol% 2.

Figure S64. Size-exclusion chromatogram of isolated polymer from dehydropolymerisation of PhSiH$_3$. Conditions: room temperature, 6.47 mmol PhSiH$_3$, 0.2 mol% 2.
Figure S 65. Size-exclusion chromatogram of isolated polymer from dehydropolymerisation of PhSiH₃. Conditions: room temperature, 6.47 mmol PhSiH₃, 0.4 mol% 2.

6.3. SEC analysis of isolated polymer from dehydropolymerisation experiments of PhSiH₃ using 2, with addition of a second portion of PhSiH₃

Figure S 66. Size-exclusion chromatogram of isolated polymer from catalytic dehydropolymerisation of PhSiH₃. Conditions: room temperature, 1.85 mmol PhSiH₃, 0.4 mol% 2.
6.4. SEC analysis of isolated polymer from variable-time dehydropolymerisation experiments

Figure S67. Size-exclusion chromatogram of isolated polymer from an experiment stopped after 60 minutes. Conditions: room temperature, 1.85 mmol PhSiH₃, 0.2 mol% 2.

Figure S68. Size-exclusion chromatogram of isolated polymer from an experiment stopped after 90 minutes. Conditions: room temperature, 1.85 mmol PhSiH₃, 0.2 mol% 2.
Figure S69. Size-exclusion chromatogram of isolated polymer from an experiment at full conversion. Conditions: room temperature, 1.85 mmol PhSiH₃, 0.2 mol% 2.

6.5. SEC analysis of isolated polymer from dehydropolymerisation of PhSiH₃ using rac-3

Figure S70. Size-exclusion chromatogram of isolated polymer from dehydropolymerisation of PhSiH₃. Conditions: 60 °C, 1.85 mmol PhSiH₃, 0.8 mol% rac-3.
6.6. SEC analysis of isolated polymer from the dehydropolymerisation of PhSiH\textsubscript{3} using rac-4

![Graph showing SEC analysis](image)

**Figure S71.** Size-exclusion chromatogram of isolated polymer from dehydropolymerisation of PhSiH\textsubscript{3}. Conditions: room temperature, 1.85 mmol PhSiH\textsubscript{3}, 0.4 mol\% *rac-4*.
7. Computational details

In this chapter, we give the summary of a detailed analysis of the steric demand of the ebthi amide and halide complexes. For this analysis, we used the Web Tool SambVca 2.0. Since not all complexes could be analysed by SC-XRD, all structures were optimised using Gaussian 16. We optimised the real-size molecules using the hybrid density functional method B3LYP, in combination with the basis set def2svpp, and the empirical dispersion correction GD3BJ (notation: B3LYP/GD3BJ/def2svpp). Vibrational frequencies were computed, to include zero-point vibrational energies in thermodynamic parameters and to characterise all structures as minima on the potential energy surface. To be able to generate a coordinate system/axis system that is as uniform as possible during the subsequent buried volume analysis, a "dummy" hydrogen atom was inserted into the optimised structures with the aid of GaussView. This dummy atom was placed exactly in the middle between the hetero atoms N and Cl in each of the seven complexes studied and was deleted again during the analysis. Generation of the respective coordinate system with the help of this dummy atom is documented for each molecule. For the calculation of thermodynamic relative energies of the different isomers we furthermore performed single point calculations on triple-ζ basis (def2tzvp) to obtain more accurate values.

In addition to the electronic supporting information, we provide a multi-structure xyz-file including all calculated molecules.

Please note that all computations were carried out for single, isolated molecules in the gas phase (ideal gas approximation). There may well be significant differences between gas phase and condensed phase.

7.1. Thermodynamic considerations of the isomerism between rac-3 and meso-3 as well as two different isomers of meso-4

| Investigated isomerism                  | Δ_rxH [kJ/mol] | Δ_rxG [kJ/mol] | Δ_rxH [kcal/mol] | Δ_rxG [kcal/mol] |
|----------------------------------------|----------------|----------------|------------------|------------------|
| rac- vs. meso-(ebthi)Zr(NMe_2)_2        | -18.5          | -14.8          | -4.4             | -3.5             |
| meso-(ebthi)ZrClNMe_2 iso1 vs. iso2     | -33.8          | -32.9          | -8.1             | -7.9             |
### 7.2. Summary of calculated thermodynamic data

| File-Name               | Nimag | HF          | ZPE [kcal/mol] | Th. Corr. H | Th. Corr. G | Htot [a.u.] | Gtot [a.u.] | Method          | Basisset         | Calc            |
|-------------------------|-------|-------------|----------------|-------------|-------------|-------------|-------------|-----------------|-----------------|-----------------|
| HCl                     | 0     | -460.6619105 | 4.06516        | 0.009783    | -0.011433   | -460.652128 | -460.673343 | B3LYP/GD3BJ     | def2svpp opt/freq |
| HNMe2                   | 0     | -135.0547443 | 57.67045       | 0.097218    | 0.066479    | -134.957526 | -134.988265 | B3LYP/GD3BJ     | def2svpp opt/freq |
| racEBTHiZrCl2           | 0     | -1743.554177 | 247.764        | 0.416944    | 0.346303    | -1743.137233 | -1743.207874 | B3LYP/GD3BJ     | def2svpp opt/freq |
| mesoEBTHiZrCl2          | 0     | -1743.554184 | 247.78158      | 0.417015    | 0.346224    | -1743.13717 | -1743.20796  | B3LYP/GD3BJ     | def2svpp opt/freq |
| racEBTHiZrClNMe2        | 0     | -1417.896568 | 298.22807      | 0.500396    | 0.424444    | -1417.396172 | -1417.472124 | B3LYP/GD3BJ     | def2svpp opt/freq |
| mesoEBTHiZrClNMe2 iso1  | 0     | -1417.898098 | 298.00044      | 0.500233    | 0.423697    | -1417.397865 | -1417.474401 | B3LYP/GD3BJ     | def2svpp opt/freq |
| mesoEBTHiZrClNMe2 iso2  | 0     | -1417.884589 | 298.09164      | 0.500415    | 0.423562    | -1417.384174 | -1417.461027 | B3LYP/GD3BJ     | def2svpp opt/freq |
| racEBTHiZrNMe2_2_opt_freq_svp | 0 | -1092.233684 | 348.58168      | 0.58361     | 0.502551    | -1091.650074 | -1091.731132 | B3LYP/GD3BJ     | def2svpp opt/freq |
| mesoEBTHiZrNMe2_2_opt_freq_svp | 0 | -1092.225566 | 348.19766      | 0.583331    | 0.500858    | -1091.642235 | -1091.742708 | B3LYP/GD3BJ     | def2svpp opt/freq |
| HCl                     |       | -460.835443  |                |             |             | -460.82566  | -460.846876 | B3LYP/GD3BJ     | def2tvp sp       |
| HNMe2                   | -     | -135.2293904 |                |             |             | -135.132172 | -135.1629114 | B3LYP/GD3BJ     | def2tvp sp       |
| racEBTHiZrCl2           | -     | -1744.764653 |                |             |             | -1744.347709 | -1744.41835  | B3LYP/GD3BJ     | def2tvp sp       |
| mesoEBTHiZrCl2          | -     | -1744.764219 |                |             |             | -1744.347204 | -1744.417995 | B3LYP/GD3BJ     | def2tvp sp       |
| racEBTHiZrClNMe2        | -     | -1419.112688 |                |             |             | -1418.612292 | -1418.688244 | B3LYP/GD3BJ     | def2tvp sp       |
| mesoEBTHiZrClNMe2 iso1  | -     | -1419.114194 |                |             |             | -1418.613961 | -1418.690497 | B3LYP/GD3BJ     | def2tvp sp       |
| mesoEBTHiZrClNMe2 iso2  | -     | -1419.101511 |                |             |             | -1418.601096 | -1418.677949 | B3LYP/GD3BJ     | def2tvp sp       |
| racEBTHiZrNMe2_2        | -     | -1093.456256 |                |             |             | -1092.872646 | -1092.953705 | B3LYP/GD3BJ     | def2tvp sp       |
| mesoEBTHiZrNMe2_2       | -     | -1093.448942 |                |             |             | -1092.865611 | -1092.948084 | B3LYP/GD3BJ     | def2tvp sp       |
7.3. Buried Volume Analysis of *rac*-{ebthi}ZrCl$_2$

**Axis-System**

**Buried Volume Analysis**

| Settings: | \(\%V_{\text{free}}\) | \(\%V_{\text{bur}}\) | \(\%V_{\text{tot}}\) |
| --- | --- | --- | --- |
| Coordinating Atoms: Cl1, Dummy, Cl2 | 55.2 | 44.8 | 100.0 |
| Z-axis defined by Zr atom z-negative | | | |
| XZ-Plane defined by Cl1, Zr1, Dummy | | | |
| Atomic radii scaled by 1.17 | | | |
| Sphere radius 5.5 | | | |
| Distance of coord. Point from centre 0.0 | | | |
| Mesh spacings for int. 0.05 | | | |
| H’s includes | | | |

| Quadrant | \(V_{\text{free}}\) | \(V_{\text{bur}}\) | \(V_{\text{total}}\) | \(\%V_{\text{free}}\) | \(\%V_{\text{bur}}\) |
| --- | --- | --- | --- | --- | --- |
| SW | 110.8 | 63.4 | 174.2 | 63.6 | 36.4 |
| NW | 81.4 | 92.8 | 174.2 | 46.7 | 53.3 |
| NE | 110.8 | 63.4 | 174.2 | 63.6 | 36.4 |
| SE | 81.4 | 92.8 | 174.2 | 46.7 | 53.3 |

7.4. Buried Volume Analysis of *meso*-{ebthi}ZrCl$_2$

**Axis-System**

**Buried Volume Analysis**

| Settings: | \(\%V_{\text{free}}\) | \(\%V_{\text{bur}}\) | \(\%V_{\text{tot}}\) |
| --- | --- | --- | --- |
| Coordinating Atoms: Cl1, Dummy, Cl2 | 53.7 | 46.3 | 100.0 |
| Z-axis defined by Zr atom z-negative | | | |
| XZ-Plane defined by Cl1, Zr1, Dummy | | | |
| Atomic radii scaled by 1.17 | | | |
| Sphere radius 5.5 | | | |
| Distance of coord. Point from centre 0.0 | | | |
| Mesh spacings for int. 0.05 | | | |
| H’s includes | | | |

| Quadrant | \(V_{\text{free}}\) | \(V_{\text{bur}}\) | \(V_{\text{total}}\) | \(\%V_{\text{free}}\) | \(\%V_{\text{bur}}\) |
| --- | --- | --- | --- | --- | --- |
| SW | 73.0 | 101.2 | 174.2 | 41.9 | 58.1 |
| NW | 77.5 | 96.7 | 174.2 | 44.5 | 55.5 |
| NE | 113.1 | 61.1 | 174.2 | 64.9 | 35.1 |
| SE | 110.4 | 63.8 | 174.2 | 63.4 | 36.6 |
### 7.5. Buried Volume Analysis of *rac*-3

| Settings: | %V<sub>free</sub> | %V<sub>bur</sub> | %V<sub>tot</sub> |
|-----------|-----------------|-----------------|-----------------|
| Coordinating Atoms: N1, Dummy, N2 | 45.0 | 55.0 | 100.0 |
| Z-axis defined by Zr atom z-negative | | | |
| XZ-Plane defined by N1, Dummy, N2 | | | |
| Atomic radii scaled by 1.17 | | | |
| Sphere radius 5.5 | | | |
| Distance of coord. Point from centre 0.0 | | | |
| Mesh spacings for int. 0.05 | | | |
| H’s includes | | | |
| | | | |

| Quadrant | V<sub>free</sub> | V<sub>bur</sub> | V<sub>total</sub> | %V<sub>free</sub> | %V<sub>bur</sub> |
|-----------|-----------------|-----------------|-----------------|----------------|----------------|
| SW        | 92.2            | 82.1            | 174.2           | 52.9           | 47.1           |
| NW        | 64.5            | 109.7           | 174.2           | 37.1           | 62.9           |
| NE        | 92.1            | 82.1            | 174.2           | 52.9           | 47.1           |
| SE        | 64.5            | 109.7           | 174.2           | 37.1           | 62.9           |

### 7.6. Buried Volume Analysis of *meso*-3

| Settings: | %V<sub>free</sub> | %V<sub>bur</sub> | %V<sub>tot</sub> |
|-----------|-----------------|-----------------|-----------------|
| Coordinating Atoms: N1, Dummy, N2 | 45.1 | 54.9 | 100.0 |
| Z-axis defined by Zr atom z-negative | | | |
| XZ-Plane defined by N1, Dummy, Zr | | | |
| Dummy deleted | | | |
| Atomic radii scaled by 1.17 | | | |
| Sphere radius 5.5 | | | |
| Distance of coord. Point from centre 0.0 | | | |
| Mesh spacings for int. 0.05 | | | |
| H’s includes | | | |
| | | | |

| Quadrant | V<sub>free</sub> | V<sub>bur</sub> | V<sub>total</sub> | %V<sub>free</sub> | %V<sub>bur</sub> |
|-----------|-----------------|-----------------|-----------------|----------------|----------------|
| SW        | 64.5            | 109.7           | 174.2           | 37.0           | 63.0           |
| NW        | 62.6            | 111.6           | 174.2           | 35.9           | 64.1           |
| NE        | 95.5            | 78.7            | 174.2           | 54.8           | 45.2           |
| SE        | 91.6            | 82.6            | 174.2           | 52.6           | 47.4           |
7.7. Buried Volume Analysis of $N_{in} Cl_{out}$ isomer of meso-4

**Axis-System**

- Coordinating Atoms: N1, Dummy, Cl1
- Z-axis defined by Zr atom z-negative
- XZ-Plane defined by N1, Dummy, Cl1
- Atomic radii scaled by 1.17
- Sphere radius 5.5
- Distance of coord. Point from centre 0.0
- Mesh spacings for int. 0.05
- H’s includes

**Buried Volume Analysis**

| Quadrant | $V_{free}$ | $V_{bur}$ | $V_{total}$ | %$V_{free}$ | %$V_{bur}$ |
|----------|------------|-----------|-------------|-------------|------------|
| SW       | 71.1       | 103.1     | 174.2       | 39.2        | 60.7       |
| NW       | 68.5       | 105.7     | 174.2       | 41.9        | 58.1       |
| NE       | 107.6      | 66.6      | 174.2       | 61.8        | 38.2       |
| SE       | 107.2      | 67.0      | 174.2       | 61.6        | 38.4       |

7.8. Buried Volume Analysis of $N_{out} Cl_{in}$ isomer of meso-4

**Axis-System**

- Coordinating Atoms: N1, Dummy, Cl1
- Z-axis defined by Zr atom z-negative
- XZ-Plane defined by Cl1, Dummy, N1
- Atomic radii scaled by 1.17
- Sphere radius 5.5
- Distance of coord. Point from centre 0.0
- Mesh spacings for int. 0.05
- H’s includes

**Buried Volume Analysis**

| Quadrant | $V_{free}$ | $V_{bur}$ | $V_{total}$ | %$V_{free}$ | %$V_{bur}$ |
|----------|------------|-----------|-------------|-------------|------------|
| SW       | 68.3       | 105.9     | 174.2       | 39.2        | 60.8       |
| NW       | 73.0       | 101.2     | 174.2       | 41.9        | 58.1       |
| NE       | 100.0      | 74.2      | 174.2       | 57.4        | 42.6       |
| SE       | 96.1       | 78.1      | 174.2       | 55.2        | 44.8       |
7.9. Buried Volume Analysis of *rac*-4

**Axis-System**

![Diagram of axis system](image)

**Buried Volume Analysis**

| Quadrant | \( V_{\text{free}} \) | \( V_{\text{bur}} \) | \( V_{\text{total}} \) | \( \%V_{\text{free}} \) | \( \%V_{\text{bur}} \) |
|----------|----------------|----------------|----------------|----------------|----------------|
| SW       | 96.8           | 77.4           | 174.2          | 55.6           | 44.4           |
| NW       | 71.7           | 102.5          | 174.2          | 41.2           | 58.8           |
| NE       | 106.7          | 67.4           | 174.2          | 61.3           | 38.7           |
| SE       | 73.6           | 100.6          | 174.2          | 42.3           | 57.7           |

**Settings:**
- Coordinating Atoms: N1, Dummy, Cl1
- Z-axis defined by Zr atom z-negative
- XZ-Plane defined by N1, Dummy, Cl1
- Atomic radii scaled by 1.17
- Sphere radius 5.5
- Distance of coord. Point from centre 0.0
- Mesh spacings for int. 0.05
- H’s includes...
8. References

[1] K. A. Erickson, M. P. Cibuzar, N. T. Mucha, R. Waterman, *Dalton Trans.* **2018**, *47*, 2138-2142.
[2] C. Chen, H. Wang, Y. Sun, J. Cui, J. Xie, Y. Shi, S. Yu, X. Hong, Z. Lu, *iScience* **2020**, *23*, 100985.
[3] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176-2179.
[4] Chen, S.; Wang, J.; Wang, H., Synthesis, characterization and pyrolysis of a high zirconium content zirconocene–polycarbosilane precursor without Zr–O bond. *Materials & Design* **2016**, *90*, 84-90.
[5] W. Schöniger, *Microchim. Acta*, 1955, **43**, 123-129.
[6] F. Mohr, Lehrbuch der chemisch-analytischen Titrirmethode: *Abtheilungen 1 und 2*, Vieweg, Braunschweig, 1856.
[7] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst.*, 2008, **A64**, 112-122.
[8] Sheldrick, G. M. *SHELXT* - Integrated space-group and crystal-structure determination. *Acta Cryst.*, 2015, **C71**, 3-8.
[9] Diamond - Crystal and Molecular Structure Visualization, Crystal Impact - Dr. H. Putz & Dr. K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany, [http://www.crystalimpact.com/diamond](http://www.crystalimpact.com/diamond).
[10] L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, *Organometallics* **2016**, *35*, 2286-2293.
[11] *Gaussian 16, Revision C.01*, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016
[12] a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100; b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824.
[13] a) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200–1211; b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789; c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200–206; d) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[14] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
[15] a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., *J. Chem. Phys.* **2010**, *132*, 154104; b) Grimme, S.; Ehrlich, S.; Goerigk, L., *J. Comput. Chem.* **2011**, *32*, 1456–1465.