Supporting Information

Scandium Reduced Arene Complex: Protonation and Reaction with Azobenzene

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Table of Contents

1. General considerations S2

2. Syntheses, spectroscopic data, NMR and IR spectra S2
   2.1. [Sc(N(fBu)(Xy))₂(CH₂SiMe₃)(thf)] (1-CH₂SiMe₃) S2
   2.2. [Sc(N(fBu)(Xy))₂(thf)]₂[BPh₄] (3) S5
   2.3. [Li(thf)]₂[Sc(N(fBu)(Xy))₂(η²-PhNNPh)] (4) S8
   2.4. [Sc(N(fBu)(Xy))₂(μ-η²:η²-PhNNPh)(thf)]₂ (5) S13
   2.5. [Sc(κ²-O₂CN(fBu)(Xy))]₂(thf)]₃ (6) S14
   2.6. [AlH(N(fBu)(Xy))]₂(thf)] (7) S16
   2.7. [Sc(N(fBu)(Xy))]₂(μ-OnBu)]₂ (8) S19

3. Crystal structure determination of 1-CH₂SiMe₃, 3, 4, 5, 6, 7 and 8 S22

4. References S28
1. General considerations

All manipulations were performed under argon atmosphere using standard Schlenk or glovebox techniques. Prior to use, glassware was dried overnight at 150 °C. Solvents were dried, distilled and degassed using standard methods. If not otherwise stated, the reactions were performed at room temperature (21–24 °C) in Schlenk flasks or tubes of suitable size equipped with a PTFE magnetic stir bar. NMR measurements were performed on a Bruker Avance II or Avance III spectrometer operating at 400.3 MHz at 23 °C for 1H nuclei. The frequencies for the heteroatoms were as follows: 7Li (155.57 MHz), 11B (128.38 MHz), 13C (100.67 MHz), 29Si (79.49 MHz) and 45Sc (97.27 MHz). The chemical shifts (δ in ppm) of the 1H and 13C{1H} NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane (TMS). The 7Li{1H}, 11B{1H}, 29Si{1H} and 45Sc{1H} NMR spectra were calibrated against the external references to LiCl, BF3(OEt2), TMS and ScCl3, respectively. If not otherwise stated, the signals in 13C{1H} NMR spectra are sharp singlets. Standard abbreviations indicating multiplicities were used as follows: s (singlet), d (doublet), t (triplet), m (multiplet).

IR spectra were recorded using KBr pellets using an AVATAR 360 FT-IR spectrometer. Elemental analyses were carried out using a CHN-O-Rapid VarioEL Element Analyzer.

The starting materials [ScCl{(N(tBu)(Xy))2(thf)}] (1-Cl) (Xy = 3,5-Me2C6H3) and [Li(thf)3][Sc{(N(tBu)(Xy))2(Anth)}] (2-anth-Li) were prepared according to our previously reported procedures.1 LiCH2SiMe3,2 [NEt3H][BPh4]3 and [Li2(thf)1.4][N2Ph2]4 were prepared according to the literature procedures. Trans-azobenzene, LiAlH4 and 1M solution of NaBEt3H in THF were purchased from Sigma Aldrich. LiAlH4 was further purified by extraction with Et2O before use.

2. Syntheses, spectroscopic data, NMR and IR spectra

2.1. [Sc{(N(tBu)(Xy))2(CH2SiMe3)(thf)}] (1-CH2SiMe3)

A colorless solution of LiCH2SiMe3 (186 mg, 1.98 mmol) in Et2O (5 mL) was dropwise added to a colorless solution of 1-Cl (1.00 g, 1.98 mmol) in Et2O (10 mL) at room temperature. Immediate after addition, the solution turned into a white suspension, which was stirred for 30 minutes. An aliquot 1H NMR shows a selective and complete conversion of the starting materials into the product. The resulting suspension was filtered and the colorless filtrate was evaporated to dryness. The oily residue was extracted with n-pentane (10 mL) and filtered. The filtrate was concentrated to ca. 5 mL and stored at −36 °C for 48 hrs. The resulting colorless crystals were isolated by decantation of the supernatant solution and quickly washing with precooled (−36°C) n-pentane (2 mL), and dried under reduced pressure for 1 hr. to afford 1-CH2SiMe3 as an analytically pure solid. The supernatant solution together with the n-pentane
washing was concentrated to ca. 2 mL and crystallized to obtain another batch of 1-CH$_2$SiMe$_3$.

Combined yield: 841 mg (1.51 mmol, 76%). Anal. calcd. for C$_{32}$H$_{55}$N$_2$O$_n$ScSi (556.83 g/mol): C, 69.02; H, 9.96; N, 5.03%. Found: C, 65.17; H, 9.73; N, 5.17%. Multiple attempts to obtain acceptable carbon value in elemental analysis consistently gave lower values than expected, most likely due to the formation of scandium carbide.

$^1$H NMR (400.3 MHz, benzene-$_d_6$, 296 K): $\delta$ (ppm) = 0.13 (s, 2H, CH$_2$Si(CH$_3$)$_3$), 0.43 (s, 9H, Si(CH$_2$)$_3$), 0.87 (m, 4H, THF), 1.59 (s, 18H, tBu), 2.18 (s, 12H, C$_6$H$_5$(CH$_2$)$_3$), 3.13 (m, 4H, THF), 6.47 (s, 2H, p-C$_6$H$_3$), 6.80 (s, 4H, o-C$_6$H$_3$).

$^{13}$C($^1$H) NMR (100.67 MHz, benzene-$_d_6$, 296 K): $\delta$ (ppm) = 4.3 (s, 3C, Si(CH$_3$)$_3$), 21.6 (s, 4C, C$_6$H$_5$(CH$_3$)$_2$), 24.8 (s, 2C, THF), 32.4 (s, 6C, C(CH$_3$)$_3$), 37.4 (br s, $\delta_{1/2}$ = 30 Hz, 1C, CH$_2$Si(CH$_3$)$_3$), 55.8 (s, 2C, C(CH$_3$)$_3$), 71.4 (s, 2C, THF), 122.9 (s, 2C, p-C$_6$H$_3$), 123.7 (s, 4C, o-C$_6$H$_3$), 138.7 (s, 4C, m-C$_6$H$_3$), 151.0 (s, 2C, ipso-C$_6$H$_3$).

$^{29}$Si NMR (79.49 MHz, benzene-$_d_6$, 296 K): $\delta$ (ppm) = 2.96 (s).

$^{45}$Sc NMR (97.27 MHz, benzene-$_d_6$, 296 K): $\delta$ (ppm) = 464 (br s, $\delta_{1/2}$ = ~10000 Hz).

Figure S1. $^1$H NMR spectrum of 1-CH$_2$SiMe$_3$ in benzene-$_d_6$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.
**Figure S2.** $^{13}$C($^1$H) NMR spectrum of 1-CH$_2$SiMe$_3$ in benzene-$d_6$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.

**Figure S3.** $^{29}$Si NMR spectrum of 1-CH$_2$SiMe$_3$ in benzene-$d_6$ at 296 K.
Figure S4. $^{45}$Sc NMR spectrum of 1-CH$_2$SiMe$_3$ in benzene-$d_6$ at 296 K; the line broadening (lb) value is set to 50 Hz.

2.2. [Sc(N(tBu)(Xy))$_2$(thf)$_2$][BPh$_4$] (3)

Method A: A colorless THF solution (5 mL) of [NEt$_3$H][BPh$_4$] (52 mg, 0.13 mmol, 1 equiv.) was dropwise added to a pre-cooled (−40°C) solution of 2-anth-Li (100 mg, 0.13 mmol) in THF (5 mL). Upon addition, the color of the solution changed from dark red to light orange. The resulting solution was slowly warmed to r.t. and stirred for 30 mins. An aliquot 1H NMR spectrum of the reaction mixture confirmed a selective and complete conversion of the starting materials into the mono-protonated product [Sc(N(tBu)Xy)$_2$(C$_{14}$H$_{11}$)(thf)]. All the volatiles were removed under reduced pressure and the residue was extracted with n-pentane (10+5 mL) at r.t.. The light orange extract was evaporated to dryness and the solid was dissolved in THF (3 mL). The resulting solution was treated with a solution of [NEt$_3$H][BPh$_4$] (50 mg, 0.12 mmol, 0.95 equiv.) in THF (3 mL) at r.t. and stirred for 1 hr. An aliquot 1H NMR spectrum of the colorless solution confirmed a selective formation of the desired product. All the volatiles were removed and the colorless, sticky residue was washed with Et$_2$O (2 x 3 mL) at r.t.. The resulting solid was dried under reduced pressure for 2 hrs to obtain 3 as a spectroscopically pure, colorless powder. Yield: 87 mg (0.10 mmol, 81%).

Method B: To a colorless solution of 1-CH$_2$SiMe$_3$ (100 mg, 0.18 mmol) in THF (3 mL), a THF solution (2 mL) of [NEt$_3$H][BPh$_4$] (76 mg, 0.18 mmol) was dropwise added and stirred at r.t..
An aliquot $^1$H NMR spectrum of the reaction mixture after 2 hrs confirmed a selective and complete conversion of the starting materials into the product. After completion of the reaction, all the volatiles were removed under reduced pressure and the white residue was washed with Et$_2$O (2 x 2 mL) at r.t. The resulting white powder was dried under reduced pressure for 15 min to obtain compound 3 as a THF bis-solvate. Yield: 136 mg (0.16 mmol, 88%). Anal. calcd. for C$_{56}$H$_{72}$BN$_2$O$_2$Sc (860.97 g/mol): C 78.12; H 8.43; N 3.25%. Found: C 77.55; H 8.29; N 3.30%.

$^1$H NMR (400.3 MHz, THF-$_d_8$, 296 K): δ (ppm) = 1.30 (s, 18H, tBu), 1.78 (m, THF), 2.30 (s, 12H, C$_6$H$_3$(CH$_3$)$_2$), 3.63 (m, THF), 6.67 (s, 4H, o-C$_6$H$_3$), 6.74 (tt, $^3$J$_{H,H}$ = 7.2 Hz, $^4$J$_{H,H}$ = 1.4 Hz, 4H, p-C$_6$H$_5$), 6.82 (s, 2H, p-C$_6$H$_3$), 6.87 (t, $^3$J$_{H,H}$ = 7.4 Hz, 8H, o-C$_6$H$_5$), 7.29 (m, 8H, m-C$_6$H$_5$).

$^{13}$C($^1$H) NMR (100.67 MHz, THF-$_d_8$, 296 K): δ (ppm) = 21.6 (s, 4C, C$_6$H$_3$(CH$_3$)$_2$), 26.4 (s, THF), 32.0 (s, 6C, CH$_3$, tBu), 58.2 (s, 2C, C-N, tBu), 68.3 (s, THF), 121.9 (s, 4C, p-C$_6$H$_5$), 125.7 (q, $^2$J$_{B,C}$ = 2.7 Hz, 8C, o-C$_6$H$_5$), 126.5 (s, 4C, o-C$_6$H$_5$), 127.4 (s, 2C, p-C$_6$H$_5$), 137.2 (q, $^3$J$_{B,C}$ = 1.3 Hz, 8C, m-C$_6$H$_5$), 140.5 (s, 4C, m-C$_6$H$_3$), 148.0 (s, 2C, ipso-C$_6$H$_3$), 165.2 (q, $^1$J$_{B,C}$ = 49.4 Hz, 8C, ipso-C$_6$H$_5$).

$^{11}$B($^1$H) NMR (128.38 MHz, THF-$_d_8$, 296 K): δ (ppm) = −6.5 (s).

$^{45}$Sc NMR (97.27 MHz, THF-$_d_8$, 296 K): δ (ppm) = 312 (br s, $\delta V_{1/2} = ~10000$ Hz).

Figure S5. $^1$H NMR spectrum in THF-$_d_8$ at 296 K of the crude product mixture obtained from the reaction of 2-anth-Li with two equivalents of [NEt$_3$H][BPh$_4$]; the character S denotes the residual proton signal.
of the deuterated solvent; the character # corresponds to the free 9,10-dihydroanthracene and * denotes the signals of a small amount of free anthracene present in the starting material.

Figure S6. $^1$H NMR spectrum of 3 in THF-$d_8$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.

Figure S7. $^{13}$C($^1$H) NMR spectrum of 3 in THF-$d_8$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.
2.3. \([\text{Li(thf)}_2][\text{Sc(}t\text{Bu)(Xy)})_2(\eta^2-\text{PhNNPh})]\) (4)

**Method A:** To a pre-cooled (−36 °C) solution of 2-anth-Li (300 mg, 0.38 mmol) in THF (8 mL), a bright orange solution of azobenzene (68 mg, 0.38 mmol, 1 equiv.) in THF (2 mL) was dropwise added. Upon addition, the color of the solution immediately changed from dark red
to light yellow. An aliquot $^1$H NMR spectrum after 5 min confirmed a complete consumption of the starting materials and formation of the azobenzene complex 4 along with a small amount of unknown impurities. All the volatiles were removed under reduced pressure and the residue was extracted with a 1:1 mixture of Et$_2$O/n-pentane (12 mL) at r.t.. The light-yellow extract was evaporated to dryness and the residue was reextracted with n-pentane (8 + 2 mL). The combined extract was stored at −36 °C for 48 hrs, which resulted in the formation of a microcrystalline solid. The colorless microcrystals were isolated by decantation of the light-yellow supernatant, washed with cold (−36 °C) n-pentane (1 mL), and dried under reduced pressure for 2 hrs. to afford compound 4 as a spectroscopically pure solid. Yield: 128 mg (0.18 mmol, 46%).

**Method B:** [Sc([N(tBu)Xyl])$_2$(thf)$_4$][BPh$_4$] (200 mg, 0.24 mmol) and [Li(thf)$_4$][N$_2$H$_2$] (73 mg, 0.24 mmol) were each dissolved in THF (2 mL) and cooled to −36°C. Two solutions were mixed and stored at −38 °C overnight before being allowed to warm up to r. t.. All the volatiles were removed under reduced pressure and the residue was extracted with n-pentane (ca. 10 mL). The volume of the extract was reduced to ca. 5 mL and stored at −38 °C for crystallization. The microcrystalline solid that precipitate out from the solution was isolated by decantation of the supernatant solution. The isolated solid was washed with cold n-pentane (2 x 1 mL) and dried under reduced pressure to obtain compound 4 as an analytically pure, white solid. Yield: 90 mg (0.12 mmol, 51%). Anal. calcd. for C$_{44}$H$_{62}$LiN$_4$O$_2$Sc (730.88 g/mol): C 72.31; H 8.55; N 7.67%. Found: C 70.85; H 8.59; N 7.80%.

$^1$H NMR (400.3 MHz, THF-$d_8$, 296 K): δ (ppm) = 1.19 (s, 18H, tBu), 1.78 (m, THF), 2.08 (s, 12H, C$_6$H$_3$(CH$_3$)$_2$), 3.62 (m, THF), 5.94 (t, $^3$J$_{H,H}$ = 7.0 Hz, 2H, p-C$_6$H$_5$), 6.1 − 7.0 (very broad signal, 4H, o-C$_6$H$_5$), 6.16 (s, 2H, p-C$_6$H$_5$), 6.49 (s, 4H, o-C$_6$H$_5$), 6.71 (t, $^3$J$_{H,H}$ = 7.6 Hz, 4H, m-C$_6$H$_5$).

$^1$H NMR (400.3 MHz, THF-$d_8$, 253 K): δ (ppm) = 1.20 (s, 18H, tBu), 1.78 (m, THF), 2.08 (s, 12H, C$_6$H$_3$(CH$_3$)$_2$), 3.62 (m, THF), 5.88 (t, $^3$J$_{H,H}$ = 6.9 Hz, 2H, p-C$_6$H$_5$), 6.08 and 6.77 (each d, $^3$J$_{H,H}$ = 8.1 Hz, 2H each, o-C$_6$H$_5$), 6.12 (br s, 2H, p-C$_6$H$_5$; this signal overlaps with one of the o-C$_6$H$_5$ signals), 6.48 (s, 4H, o-C$_6$H$_5$), 6.64 and 6.70 (each t, $^3$J$_{H,H}$ = 7.0 Hz, 2H each, m-C$_6$H$_5$).

$^{13}$C($^1$H) NMR (100.67 MHz, THF-$d_8$, 253 K): δ (ppm) = 22.0 (s, 4C, C$_6$H$_3$(CH$_3$)$_2$), 26.4 (s, THF), 31.9 (s, 6C, CH$_3$, tBu), 54.9 (s, 2C, C-N, tBu), 108.9 (s, 2C, p-C$_6$H$_5$), 111.6 and 116.9 (each s, 2C each, o-C$_6$H$_5$), 119.2 (br s, 2C, p-C$_6$H$_5$), 125.3 (very br, 4C, o-C$_6$H$_5$), 127.0 and 128.5 (each s, 2C each, m-C$_6$H$_5$), 136.2 (s, 4C, m-C$_6$H$_5$), 156.2 (s, 2C, ipso-C$_6$H$_5$), 160.3 (s, 2C, ipso-C$_6$H$_5$).

$^7$Li($^1$H) NMR (155.57 MHz, THF-$d_8$, 253 K): δ (ppm) = −0.5 (s).

$^{45}$Sc NMR (97.27 MHz, THF-$d_8$, 253K): δ (ppm) = 349 (br s, $\delta^{45}$Sc = ~35000 Hz).
**Figure S10.** $^1$H NMR spectrum in THF-$d_8$ at 296 K of the crude product mixture obtained from the reaction of 2-anth-Li with trans-azobenzene; the character S denotes the residual proton signal of the deuterated solvent; the character * denotes the signals of small amount of side products as well as decomposition product of 4.

**Figure S11.** $^1$H NMR spectrum of 4 in THF-$d_8$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent; the character * denotes the signals of a small amount of n-pentane.
**Figure S12.** $^1$H NMR spectrum of 4 in THF-$d_8$ at 253 K; the character S denotes the residual proton signal of the deuterated solvent; the character * denotes the signals of a small amount of $n$-pentane.

**Figure S13.** $^{13}$C($^1$H) NMR spectrum of 4 in THF-$d_8$ at 253 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent; the character * denotes the signals of a small amount of $n$-pentane.
Figure S14. $^7$Li($^1$H) NMR spectrum of 4 in THF-d$_8$ at 253 K.

Figure S15. $^{45}$Sc NMR spectrum of 4 in THF-d$_8$ at 253 K; the line broadening (lb) value is set to 100 Hz.
2.4. \([\text{Sc} (\text{N(tBu)(Xy)}) (\mu-\eta^2::\eta^2-\text{PhNNPh})(\text{thf})]_2\) (5)

A light-yellow solution of 4 (50 mg, 0.08 mmol) in THF-\(d_8\) (0.4 mL) was heated to 70 °C for 8 hrs in an NMR tube equipped with a J-Young valve. Upon heating, a microcrystalline solid started to form and the color of the solution turned lighter. A \(^1\text{H}\) NMR spectrum of the suspension showed the formation of compound 5 along with [\text{LiN((tBu)Xy)}]_2] and a small amount of unknown impurities. The suspension was cooled to +5°C for 18 hrs for further crystallization. The resulting precipitate was collected by decantation of the supernatant solution, washed with pre-cooled (-36°C) THF (0.2 mL), and dried under reduced pressure for 1 hr to obtain 5 as an analytically pure, white solid. Yield: 23 mg (0.024 mmol, 62%). Anal. calcd. for C_{56}H_{72}N_6O_2Sc_2 (951.12 g/mol): C 70.72; H 7.63; N 8.84%. Found: C 66.93; H 7.42; N 8.85%. Multiple attempts to obtain acceptable carbon value in elemental analysis consistently gave lower values, most likely due to the formation of scandium carbide.

\(^1\text{H}\) NMR (400.3 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 1.31 (s, 18H, tBu), 2.08 (s, 12H, C\(_6\)H\(_3\)(CH\(_3\))\(_2\)), 6.30 – 6.55 (br s, 8H, o-C\(_6\)H\(_5\)), 6.47 (t, \(^3\)J\(_{H,H}\) = 7.2 Hz, 4H, p-C\(_6\)H\(_5\)), 6.55 (s, 2H, p-C\(_6\)H\(_5\)), 6.71 (s, 4H, o-C\(_6\)H\(_5\)), 6.90 (t, \(^3\)J\(_{H,H}\) = 7.6 Hz, 8H, m-C\(_6\)H\(_5\)).

\(^{13}\text{C}([\text{\text{^1}}}\text{H})\) NMR (100.67 MHz, THF-\(d_8\), 296 K): \(\delta\) (ppm) = 21.7 (s, 4C, C\(_6\)H\(_3\)(CH\(_3\))\(_2\)), 32.6 (s, 6C, CH\(_3\), tBu), 56.5 (s, 2C, C-N, tBu), 117.3 (s, 4C, p-C\(_6\)H\(_5\)), 118.1 (br s, 8C, o-C\(_6\)H\(_5\)), 125.6 (s, 2C, p-C\(_6\)H\(_5\)), 128.7 (s, 8C, m-C\(_6\)H\(_5\)), 129.4 (s, 4C, o-C\(_6\)H\(_5\)), 138.1 (s, 4C, m-C\(_6\)H\(_5\)), 151.2 (s, 2C, ipso-C\(_6\)H\(_5\)), 153.5 (s, 4C, ipso-C\(_6\)H\(_5\)).

*Figure S16.* \(^1\text{H}\) NMR spectrum of 5 in THF-\(d_8\) at 296 K; the character S denotes the residual proton signal of the deuterated solvent.
Figure S17. $^{13}$C($^1$H) NMR spectrum of 5 in THF-$d_8$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.

2.5. $[\text{Sc}(\kappa^2-\text{O}_2\text{CN}(t\text{Bu})(\text{Xy}))_2(\text{thf})_3][\text{BPh}_4]$ (6)

A Schlenck tube with a colorless solution of 3 (200 mg, 0.23 mmol) in THF (3 mL) was degassed and then treated with CO$_2$ gas at r.t.. An aliquot $^1$H NMR spectrum of the reaction mixture after 30 mins confirmed a selective formation of the CO$_2$ complex 6. After completion of the reaction, all the volatiles were removed under reduced pressure and the residue was washed with $n$-pentane (5 mL). The resulting white solid was dried under reduced pressure for 30 mins to obtain 6 as an analytically pure solid as a THF bis-solvate. Yield: 204 mg (0.21 mmol, 92%). Anal. calcd. for C$_{58}$H$_{72}$BN$_2$O$_6$Sc (948.97 g/mol): C 73.41; H 7.65; N 2.95%. Found: C 70.77; H 7.88; N 2.87%. Multiple attempts to obtain acceptable carbon value in elemental analysis consistently gave low values, most likely due to the formation of scandium carbide.

$^1$H NMR (400.3 MHz, THF-$d_8$, 296 K): δ (ppm) = 1.38 (s, 18H, tBu), 2.25 (s, 12H, C$_6$H$_3$(CH$_3$)$_2$), 6.66 (s, 4H, o-C$_6$H$_5$), 6.71 (tt, $^3$J$_{HH}$ = 7.2 Hz, $^4$J$_{HH}$ = 1.3 Hz, 4H, p-C$_6$H$_5$), 6.86 (t, $^3$J$_{HH}$ = 7.3 Hz, 8H, o-C$_6$H$_5$), 6.92 (s, 2H, p-C$_6$H$_5$), 7.29 (m, 8H, m-C$_6$H$_5$).

$^{13}$C($^1$H) NMR (100.67 MHz, THF-$d_8$, 296 K): δ (ppm) = 21.2 (s, 4C, C$_6$H$_3$(CH$_3$)$_2$), 26.4 (s, 6C, THF), 30.1 (s, 6C, CH$_3$, C(CH$_3$)$_3$), 57.8 (s, 2C, C(CH$_3$)$_3$), 121.8 (s, 4C, p-C$_6$H$_5$), 125.7 (q, $^2$J$_{B,C}$ = 2.8 Hz, 8C, o-C$_6$H$_5$), 127.9 (s, 4C, o-C$_6$H$_5$), 130.0 (s, 2C, p-C$_6$H$_5$), 137.2 (q, $^3$J$_{B,C}$ = 1.3 Hz, 8C, m-C$_6$H$_5$), 139.0 (s, 4C, m-C$_6$H$_5$), 140.9 (s, 2C, ipso-C$_6$H$_5$), 165.3 (q, $^1$J$_{B,C}$ = 49.4 Hz, 8C, ipso-C$_6$H$_5$) 170.6 (s, 2C, CO$_2$).
$^{11}$B(\textsuperscript{1}H) NMR (128.38 MHz, THF-$d_8$, 296 K): $\delta$ (ppm) = $-6.5$ (s).

$^{45}$Sc NMR (97.27 MHz, THF-$d_8$, 296K): $\delta$ (ppm) = 67 (br s, $\alpha_{1/2} = \sim$1100 Hz).

Figure S18. \textsuperscript{1}H NMR spectrum of 6 in THF-$d_8$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.

Figure S19. $^{13}$C(\textsuperscript{1}H) NMR spectrum of 6 in THF-$d_8$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.

S15
Figure S20. $^{11}$B NMR spectrum of 6 in THF-\(d_8\) at 296 K.

Figure S21. $^{45}$Sc NMR spectrum of 6 in THF-\(d_8\) at 296 K; the line broadening (lb) value is set to 20 Hz.

2.6. \([\text{AlH}(\text{N(tBu)(Xy)})_2(\text{thf})]\) (7)

To a pre-cooled (\(-38^\circ\text{C}\)) solution of \([\text{Sc}(\text{N(tBu)(Xy)})_2(\text{thf})_4][\text{BPh}_4]\) (200 mg, 0.24 mmol) in THF (3 mL), a solution of LiAlH$_4$ (2.44 mL, \(c = 0.1 \text{ ML}^{-1}\), 1 equiv.) was added dropwise. After addition, the resulting colorless solution was slowly brought to r.t. and stirred for 2 hrs. An
aliquot $^1$H NMR spectrum after 2 hrs shows complete reaction and formation of the aluminum hydride 7 along with a small amount of unknown impurities. All the volatiles were removed under reduced pressure and the oily residue was extracted with $n$-pentane (10 mL). The colorless extract was concentrated to ca. 2 mL and stored at –38°C for crystallization. After 48 hrs, a microcrystalline solid was isolated by decantation of the supernatant solution and washing with pre-cooled (–38°C) $n$-pentane (0.5 mL). After drying at r.t. for 4 hrs, compound 7 was isolated as an analytically pure, colorless solid. Yield: 61 mg (0.13 mmol, 55%). Anal. calcd. for C$_{28}$H$_{45}$AlN$_2$O (452.65 g/mol): C 74.30; H 10.02; N 6.15%. Found: C 73.79; H 9.72; N 6.13%.

$^1$H NMR (400.3 MHz, benzene-$d_6$, 296 K): δ (ppm) = 0.87 (m, 4H, THF), 1.47 (s, 18H, tBu), 2.26 (s, 12H, C$_6$H$_{12}$(CH$_3$)$_2$), 3.47 (m, 4H, THF), 4.66 (br s, $\delta_{1/2} = \sim$125 Hz, 1H, AlH), 6.67 (s, 2H, p-C$_6$H$_3$), 6.71 (s, 4H, o-C$_6$H$_3$).

$^{13}$C($^1$H) NMR (100.67 MHz, benzene-$d_6$, 296 K): δ (ppm) = 21.6 (s, 4C, C$_6$H$_3$(CH$_3$)$_2$), 24.5 (s, 2C, THF), 32.6 (s, 6C, C(CH$_3$)$_3$), 54.1 (s, 2C, C(CH$_3$)$_3$), 70.4 (s, 2C, THF), 124.2 (s, 2C, p-C$_6$H$_3$), 130.8 (s, 4C, o-C$_6$H$_3$), 135.6 (s, 4C, m-C$_6$H$_3$), 152.3 (s, 2C, ipso-C$_6$H$_3$).

IR (KBr pellet, 298 K): ν (cm$^{-1}$) = 2962 (vs), 2910 (m), 2856 (m), 1773 (s, ν(Al-H)), 1594 (vs), 1455 (m), 1382 (w), 1354 (m), 1302 (s), 1197 (s), 1161 (vs), 1031 (m), 1013 (m), 986 (m), 869 (m), 839 (m), 730 (s), 710 (vs), 699 (s), 681 (vs), 536 (w).

**Figure S22.** $^1$H NMR spectrum of 7 in benzene-$d_6$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.
Figure S23. $^{13}$C($^1$H) NMR spectrum of 7 in benzene-$d_6$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.

Figure S24. Solid state IR spectrum of 7 collected on KBr pellet at room temperature.
2.7. [Sc\{N(tBu)(Xy)\}$_2$(µ-OnBu)$_2$] (8)

To a pre-cooled (−36 °C) solution of [Sc\{N(tBu)(Xy)\}$_2$(thf)$_{1.4}$][BPh$_4$] (200 mg, 0.24 mmol) in THF (5 mL), a solution of [NaBEt$_3$H] (2.44 mL, c = 0.1 ML$^{-1}$, 1 equiv.) was added dropwise. After addition, the resulting colorless solution was slowly brought to r.t. and stirred for 6 hrs. Monitoring the reaction by $^1$H NMR spectroscopy revealed a selective formation of compound 8 through an unknown intermediate. After completion of the reaction, all the volatiles were removed under reduced pressure and the oily residue was extracted with n-pentane (5 mL). The colorless extract was concentrated to ~2 mL and stored at −36 °C for crystallization. After 48 hrs, a crystalline solid was isolated by decantation of the supernatant solution and washing with pre-cooled (−36 °C) n-pentane (0.5 mL). The crystals were finally dried for 3 hrs under reduced pressure to obtain compound 8 as an analytically pure, colorless solid. Yield: 67 mg (0.07 mmol, 58%). Anal. calcd. for C$_{56}$H$_{90}$N$_4$O$_2$Sc$_2$ (941.25 g/mol): C 71.46; H 9.64; N 5.95%. Found: C 70.93; H 9.86; N 5.99%.

$^1$H NMR (400.3 MHz, benzene-$d_6$, 296 K): δ (ppm) = 0.95 (t, $^3$J$_{H,H} = 7.2$ Hz, 6H, O(CH$_2$)$_3$CH$_3$), 1.08 (m, $^3$J$_{H,H} = 7.5$ Hz, 4H, O(CH$_2$)$_2$CH$_2$CH$_3$), 1.32 (s, 36H, tBu), 1.62 (m, 4H, OCH$_2$CH$_2$CH$_2$CH$_3$), 2.31 (s, 24H, C$_6$H$_5$O(C$_6$H$_5$)$_2$), 3.50 (m, 4H, OCH$_2$(CH$_2$)$_2$CH$_3$), 6.71 (s, 4H, p-C$_6$H$_5$), 6.99 (s, 8H, o-C$_6$H$_5$).

$^{13}$C($^1$H) NMR (100.67 MHz, benzene-$d_6$, 296 K): δ (ppm) = 14.2 (s, 2C, O(CH$_2$)$_3$CH$_3$), 19.2 (s, 2C, O(CH$_2$)$_2$CH$_2$CH$_3$), 21.6 (s, 8C, C$_6$H$_5$(CH$_3$)$_2$), 31.6 (s, 12C, C(CH$_3$)$_3$), 37.5 (s, 2C, OCH$_2$CH$_2$CH$_2$CH$_3$), 56.0 (s, 4C, C(CH$_3$)$_3$), 69.0 (s, 2C, OCH$_2$(CH$_2$)$_2$CH$_3$), 125.5 (s, 4C, p-C$_6$H$_5$), 128.7 (s, 8C, o-C$_6$H$_5$), 138.2 (s, 8C, m-C$_6$H$_5$), 150.1 (s, 4C, ipso-C$_6$H$_5$).

$^{45}$Sc NMR (97.27 MHz, benzene-$d_6$, 296 K): δ (ppm) = 347 (br s, $\Delta^1/2 = ~35000$ Hz).
Figure S25. $^1$H NMR spectrum of 8 in benzene-$d_6$ at 296 K; the character S denotes the residual proton signal of the deuterated solvent.

Figure S26. $^{13}$C($^1$H) NMR spectrum of 8 in benzene-$d_6$ at 296 K; the character S denotes the $^{13}$C NMR signal of the deuterated solvent.
Figure S27. $^{45}$Sc NMR spectrum of 8 in benzene-$d_6$ at 296 K; the line broadening (lb) value is set to 50 Hz.
3. Crystal structure determination of 1-CH$_2$SiMe$_3$, 3, 4, 5, 6, 7 and 8

X-ray diffraction data were collected on an Eulerian 4-circle diffractometer STOE STADIVARI in $\omega$-scan mode at 100 K with Mo-K$\alpha$ radiation (1-CH$_2$SiMe$_3$, 3, 4 and 5) or with Cu-K$\alpha$ radiation (6, 7 and 8). Using the program system Olex2,$^5$ the structures were solved by direct methods with the program SHELXT.$^6$ In the structure of 3, the position of carbon atom C31 which is part of a coordinated thf molecule is disordered. The disorder was resolved with split positions. Compound 5 was found in space group $P2_1/n$ with crystallographic inversion of the molecule. Compound 6 co-crystallized with non-coordinated thf molecules in the packing. Two of these molecules could be reliably refined, but the squeeze routine was also employed to take account of an additional molecule of thf which could not be reliably refined. The solvent region adds up to a volume of 153 $\text{Å}^3$ and contains 40.6 electrons. A well-ordered molecule of thf would require 104 $\text{Å}^3$ $^7$, but disordered molecules are usually less close-packed. One thf molecule should contribute 40 electrons. Both criteria suggest an acceptable match. This compound shows disorder of the atoms C37, C65 and C70 which belong to CH$_2$ groups of thf molecules. This disorder could be modelled with split positions. Compound 7 is found in space group $P\overline{1}$ with two crystallographically independent molecules. Compound 8 is found in space group $P\overline{1}$ with crystallographic inversion symmetry of the molecule. All refinements were carried out against $F^2$ using SHELXL with anisotropic displacement parameters for the non-hydrogen atoms.$^8$

The hydrogen atoms were included in calculated positions and were treated as riding during the refinement. Only the Al/H-hydrogen atoms H1 and H2 in 7 and all hydrogen atoms in 8 were refined in their position. Refinement results are given in Table S1. Graphical representations were performed with the program DIAMOND.$^9$ CCDC 2091773 – 2091779 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table S1: Crystallographic data of 1-CH$_2$SiMe$_3$, 3, 4, 5, 6, 7 and 8.

|                  | 1-CH$_2$SiMe$_3$ | 3                     | 4                     | 5                     |
|------------------|-----------------|-----------------------|-----------------------|-----------------------|
| formula          | C$_{32}$H$_{55}$N$_2$OScSi | C$_{32}$H$_{52}$N$_2$O$_2$Sc, C$_{24}$H$_{30}$B | C$_{44}$H$_{64}$LiN$_2$O$_2$Sc | C$_{56}$H$_{72}$N$_2$O$_2$Sc$_2$ |
| $F_w$/g mol$^{-1}$ | 556.83          | 860.92                | 732.89                | 951.11                |
| cryst. color, habit | colorless plate | colorless plate        | colorless block       | colorless plate       |
| crystal size / mm | 0.29 $\times$ 0.17 $\times$ 0.05 | 0.31 $\times$ 0.22 $\times$ 0.08 | 0.4 $\times$ 0.4 $\times$ 0.3 | 0.90 $\times$ 0.40 $\times$ 0.14 |
| crystal system    | monoclinic      | monoclinic            | triclinic             | monoclinic            |
| space group       | $P2_1/c$        | $P2_1/c$              | $P1$                  | $P2_1/n$              |
| $a$/Å             | 9.3858(8)       | 14.0537(4)            | 11.8032(15)           | 13.7136(8)            |
| $b$/Å             | 20.564(2)       | 13.4440(3)            | 13.4101(15)           | 13.2859(9)            |
| $c$/Å             | 17.5807(13)     | 26.1368(8)            | 13.8972(17)           | 14.1276(8)            |
| $\alpha$/°        | 95.189(6)       | 91.602(3)             | 94.634(10)            | 95.187(10)            |
| $\beta$/°         |                  |                       |                      |                      |
| $\gamma$/°        |                  |                       |                      |                      |
| V/Å$^3$           | 3379.3(5)       | 4936.3(2)             | 2073.7(4)             | 2561.6(3)             |
| Z                 | 4               | 4                     | 2                     | 2                     |
| $d_{calc}$/Mg m$^{-3}$ | 1.094          | 1.158                 | 1.174                 | 1.233                 |
| $\mu$(MoKα)/mm$^{-1}$ | 0.277          | 0.191                 | 0.217                 | 0.312                 |
| $F(000)$          | 1216            | 1856                  | 792                   | 1016                  |
| $\theta$ range /° | 2.297, 25.681   | 2.174, 26.369         | 2.196, 26.371         | 2.501, 26.371         |
| index ranges      | -11≤h≤11; -25≤k≤21; -21≤l≤20 | -14≤h≤17; -21≤k≤32; -17≤l≤17 | -14≤h≤14; -12≤k≤16; -17≤l≤17 | -17≤k≤16 |
| refln.           | 12863           | 24259                 | 15655                 | 11969                 |
| independ. reflns (Rint) | 6280 (0.0987) | 9856 (0.0439)         | 8179 (0.0492)         | 5093 (0.0521)         |
| observed reflns  | 2631            | 6352                  | 5197                  | 3007                  |
| data/ restr./ param. | 6280 / 0 / 347 | 9856 / 0 / 579         | 8179 / 0 / 481         | 5093 / 0 / 303         |
| $R_1$, wR2 [$I$ > 2$\sigma$(I)] | 0.0560, 0.0952 | 0.0455, 0.1040         | 0.0840, 0.2259         | 0.0431, 0.0819         |
| $R_1$, wR2 (all data) | 0.1845, 0.1118 | 0.0818, 0.1142         | 0.1207, 0.2598         | 0.0923, 0.0905         |
| GooF on $F^2$    | 0.834           | 0.929                 | 1.014                 | 0.882                 |
| largest diff. peak, hole/ e Å$^3$ | 0.385, -0.296 | 0.462, -0.622         | 0.852, -1.060          | 0.368, -0.353          |
| CCDC number      | 2091773         | 2091774               | 2091775               | 2091776               |
Table S2: Crystallographic data of 1-CH$_2$SiMe$_3$, 3, 4, 5, 6, 7 and 8 (continued)

|   | 6                          | 7                          | 8                          |
|---|----------------------------|----------------------------|----------------------------|
| formula | C$_{38}$H$_{60}$N$_2$O$_7$Sc, C$_{24}$H$_{20}$B, 2(C$_4$H$_8$O) | C$_{28}$H$_{45}$AlN$_2$O | C$_{56}$H$_{90}$N$_4$O$_2$Sc$_2$ |
| $Fw$/g·mol$^{-1}$ | 1165.25 | 452.64 | 941.23 |
| cryst. color, habit | colorless block | colorless block | colorless block |
| crystal size / mm | 0.22 x 0.17 x 0.15 | 0.23 x 0.16 x 0.11 | 0.27 x 0.26 x 0.25 |
| crystal system | triclinic | triclinic | triclinic |
| space group | P1 | P1 | P1 |
| $a$/Å | 11.6938(18) | 9.3789(3) | 9.38148(14) |
| $b$/Å | 13.7735(2) | 16.5712(4) | 13.08023(19) |
| $c$/Å | 23.0361(3) | 18.3875(5) | 13.1426(2) |
| $α$/° | 100.9680(12) | 105.513(2) | 118.8656(11) |
| $β$/° | 96.3122(12) | 91.092(2) | 100.0931(13) |
| $γ$/° | 109.8447(12) | 94.215(2) | 94.8808(12) |
| $V$/Å$^3$ | 3364.46(9) | 2743.99(14) | 1363.32(4) |
| $Z$ | 2 | 4 | 1 |
| $d_{calc}$/Mg·m$^{-3}$ | 1.150 | 1.096 | 1.146 |
| $μ$(CuKα)/mm$^{-1}$ | 1.366 | 0.790 | 2.449 |
| $F$(000) | 1256 | 992 | 512 |
| $θ$ range / ° | 1.989, 67.679 | 3.194, 71.737 | 3.921, 72.026 |
| index ranges | -11≤$h$≤14; -14≤$k$≤16; -27≤$l$≤28 | -11≤$h$≤8; -16≤$k$≤20; -22≤$l$≤15 | -11≤$h$≤9; -14≤$k$≤14; -11≤$l$≤16 |
| refln. | 41147 | 33477 | 24966 |
| independ. reflns ($R$(int)) | 12597 (0.0239) | 10275 (0.0278) | 5211 (0.0142) |
| observed reflns | 10727 | 8239 | 5045 |
| data/ restr./ param. | 12597 / 0/ 786 | 10275 / 0/ 605 | 5211 / 0/ 425 |
| $R_1$, $wR_2$ ($>2σ(I)$) | 0.0443, 0.1155 | 0.0450, 0.0622 | 0.0300, 0.0823 |
| $R_1$, $wR_2$ (all data) | 0.0549, 0.1267 | 0.1092, 0.1233 | 0.0310, 0.0832 |
| GooF on $F^2$ | 1.023 | 1.055 | 1.024 |
| largest diff. peak, hole/ eÅ$^3$ | 0.499, -0.343 | 0.387, -0.278 | 0.267, -0.388 |
| CCDC number | 2091777 | 2091778 | 2091779 |
Figure S28. Molecular structure of $1$-$\text{CH}_2\text{SiMe}_3$ in the solid state with displacement parameters at 30\% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 \(2.080(3)\), Sc1-N2 \(2.064(3)\), Sc1-O1 \(2.190(2)\), Sc1-C25 \(2.238(3)\); N1-Sc1-N2 \(115.89(10)\), N1-Sc1-C25 \(102.98(12)\), N2-Sc1-C25 \(105.56(12)\), O1-Sc1-N1 \(133.57(11)\), O1-Sc1-N2 \(98.85(11)\), O1-Sc1-C25 \(95.66(9)\).

Figure S29. Molecular structure of 3 in the solid state with displacement parameters at 30\% probability level. H atoms and [BPh$_4$] anion are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 \(1.9913(16)\), Sc1-N2 \(2.0327(18)\), Sc1-O1 \(2.1478(14)\), Sc1-O2 \(2.1357(14)\); N1-Sc1-N2 \(118.46(7)\), N1-Sc1-O1 \(122.76(6)\), N2-Sc1-O1 \(113.87(6)\), N1-Sc1-O2 \(103.24(6)\), N2-Sc1-O2 \(101.96(7)\), O1-Sc1-O2 \(86.69(6)\).
**Figure S30.** Molecular structure of 4 in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.150(3), Sc1-N2 2.038(3), Sc1-N3 2.206(3), Sc1-N4 2.055(3), Sc1-O1 2.207(3), N1-N2 1.469(4), Li1-N1 1.961(7), Li1-N3 2.126(8), Li1-O2 1.912(6); N1-Sc1-N2 40.96(10), N3-Sc1-N4 131.26(11), N1-Sc1-N3 89.85(11), N1-Sc1-N4 110.39(12), N2-Sc1-N3 107.27(11), N2-Sc1-N4 117.09(12), N3-Sc1-O1 93.83(11), N4-Sc1-O1 96.02(11), N1-Li1-N3 97.6(3).

**Figure S31.** Molecular structure of 5 in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.0781(18), Sc1-N1' 2.3191(19), Sc1-N2 2.5155(19), Sc1-N2' 2.083(2), Sc1-N3 2.042(2), Sc1-O1 2.1953(16), N1-N2 1.457(2); N1-Sc1-N2 35.39(6), N1-Sc1-N3 110.86(7), N2-Sc1-N3 137.05(7), O1-Sc1-N1 127.97(7), O1-Sc1-N2 96.49(6), O1-Sc1-N3 93.97(7), Sc1-N1-Sc1' 86.98(6), Sc1-N2-Sc1' 81.90(6).
Figure S32. Molecular structure of 6 in the solid state with displacement parameters at 30% probability level. H atoms and [BPh₄] anion are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-O1 2.1407(13), Sc1-O2 2.1407(13), Sc1-O3 2.1468(12), Sc1-O4 2.1572(12), Sc1-O5 2.1622(14), Sc1-O6 2.1958(14), Sc1-O7 2.1952(12), C1-N1 1.354(2), C2-N2 1.353(2); O1-Sc1-O2 61.2(5), O3-Sc1-O4 61.27(4), O5-Sc1-O6 175.62(5), O5-Sc1-O7 91.53(5), O1-Sc1-O4 115.19(5), O2-Sc1-O6 91.64(5), O3-Sc1-O6 87.84(5).

Figure S33. Molecular structure of 7 in the solid state with displacement parameters at 30% probability level. H atoms (except Al bonded H) are omitted for clarity. Selected interatomic distances (Å) and angles (°): Al1-N1 1.8437(15), Al1-N2 1.8223(15), Al1-O1 1.9083(13), Al1-H1 1.52(2); N1-Al1-N2 117.26(7), N1-Al1-O1 105.12(6), N2-Al1-O1 101.78(6).
Figure S34. Molecular structure of 8 in the solid state with displacement parameters at 30% probability level. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sc1-N1 2.0788(11), Sc1-N2 2.0220(10), Sc1-O1 2.0869(9), Sc1'-O1 2.0695(9); N1-Sc1-N2 111.49(4), N1-Sc1-O1 121.11(4), N2-Sc1-O1 107.27(4), N1-Sc1-O1' 111.82(4), N2-Sc1-O1' 124.55(4).

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