

Supporting Information

Trinuclear Scandium Methyldyne Complexes Stabilized by Pentamethylcyclopentadienyl Ligands

Peng Deng,^{[a][b]} Xianghui Shi,^[a] Xun Gong^{[a][b]} and Jianhua Cheng^{*[a][b]}

[a] State Key Laboratory of Polymer Physics and Chemistry

Changchun Institute of Applied Chemistry

Chinese Academy of Sciences

No. 5625, Renmin Street, Changchun 130022 (China)

E-mail: jhcheng@ciac.ac.cn

[b] University of Science and Technology of China

Hefei, Anhui 230029 (China)

Contents	Page
1. Experimental section	S3
2. Selected NMR spectra	S7
3. X-Ray crystallographic studies	S16
4. Tables of crystal data and structure refinement	S18
5. ORTEP drawing of complexes	S26
6. References	S32

Experimental Procedures

General remarks

All reactions were carried out under a dry and oxygen-free nitrogen atmosphere using Schlenk techniques and a Vigor glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4 Å) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by O₂ (GE) / H₂O (Xentaur) to ensure both were always below 0.1 ppm. Toluene, hexane and Et₂O were purified by use of a Vigor VSPS-5 solvent purification system, and dried over fresh Na chips in the glovebox. THF, isooctane and C₆D₆ were distilled from Na/K alloy/benzophenone, degassed by the freeze-pump-thaw method (three times), and dried over fresh Na chips in the glovebox. ScCl₃(THF)₃^[1] and LiCH₂^tBu^[2] were synthesized according to the published procedures with some modifications. Other reagents were purchased and used without purification.

Samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 or AV500 spectrometer. The elemental analyses were performed on Elementar Vario EL cube (WO₃ was used as pro-oxidant) at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC).

Synthesis of [(Cp^{*})ScMe₂]₂ (**1**)

Following the same procedure as [(Cp')ScMe₂]₂,^[3] [(Cp^{*})ScMe₂]₂ (**1**) was isolated as white solid in 55% yield. Single crystals of **1**, suitable for X-ray analysis, were grown from benzene solution at room temperature. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = -0.02 (s, 12H, Sc-Me₂), 1.96 (s, 30H, C₅Me₅). ¹³C {¹H} NMR (125 MHz, C₆D₆, 25 °C): δ = 11.63 (s, C₅Me₅), 121.42 (s, C₅Me₅). (* The carbon signal of Sc-Me could not be located.) Anal. Calcd. for (**1**) C₂₄H₄₂Sc₂ (420.49): C, 68.55; H, 10.06. Found: C, 68.77; H, 10.45.

In C₆D₆, complex **1** is stable at room temperature, but decomposed quickly above 60 °C. Solid of complex **1** can be stored at -30 °C for a week.

Synthesis of [(Cp^{*})Sc(μ₂-CH₂)₄] (**2**)

A benzene solution of [(Cp^{*})ScMe₂]₂ (**1**) (210 mg, 0.50 mmol) was heated to 90 °C for 2 h, then the volatiles were removed under vacuum and the residue was washed by cold hexane (3 x 1 mL) to give [(Cp^{*})Sc(μ₂-CH₂)₄] (**2**) (165 mg, 0.212 mmol, 85% yield) as yellow-brown solid. Single crystals of **2**, suitable for X-ray analysis, were obtained from the benzene/THF solution at room temperature. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 1.71 (s, 8H, Sc-CH₂), 2.13

(s, 60H, C_5Me_5). ^{13}C { 1H } NMR (125 MHz, C_6D_6 , 25 °C): δ = 12.11 (s, C_5Me_5), 119.64 (s, C_5Me_5). (* The carbon signal of Sc-CH₂ could not be located). Anal. Calcd. for (**2**) $C_{44}H_{68}Sc_4$ (776.82): C, 68.03; H, 8.82. Found: C, 68.41; H, 8.99.

In C_6D_6 , complex **2** is stable at 60 °C, but decomposed quickly above 100 °C. Solid of complex **2** can be stored at -30 °C for a week.

Synthesis of $[(Cp^*)Sc(\mu_2-Br)]_3(\mu_3-CH)$ (**3**)

t BuBr (590 mg, 4.30 mmol) in toluene (5 mL) was added dropwise to a solution (20 mL) of $[(Cp^*)ScMe_2]_2$ (**1**) (905 mg, 2.15 mmol) in toluene. The solution was stirred at elevated temperature for 2 h and heated to 90 °C for 20 h to afford a dark brown suspension. After removal of all the volatiles under vacuum, the residue was washed by hexane (3 x 3 mL) to give $[(Cp^*)Sc(\mu_2-Br)]_3(\mu_3-CH)$ (**3**) (996 mg, 1.26 mmol, 88% yield) as yellow brown solid. Single crystals of **3**, suitable for X-ray analysis, were grown from a toluene solution at room temperature. 1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 2.11 (s, 45H, C_5Me_5), 12.15 (s, 1H, Sc-CH). ^{13}C { 1H } NMR (125 MHz, C_6D_6 , 25 °C): δ = 12.34 (s, C_5Me_5), 123.26 (s, C_5Me_5). (* The carbon signal of Sc-CH could not be located.) Anal. Calcd. for (**3**) $C_{31}H_{46}Br_3Sc_3$ (793.29): C, 46.93; H, 5.84. Found: C, 47.42; H, 5.99.

In C_6D_6 , complex **3** is stable at 60 °C, but decomposed quickly above 100 °C. Solid of complex **3** can be stored at room temperature.

Synthesis of $[(Cp^*)Sc(\mu_2-Me)]_3(\mu_3-CH)$ (**4**)

Solid LiMe (43.6 mg, 1.98 mmol) was added to a suspension of $[(Cp^*)Sc(\mu_2-Br)]_3(\mu_3-CH)$ (**3**) (500 mg, 0.63 mmol) in toluene (15 mL), the mixture was stirred at room temperature for 4 h. After removal of toluene under vacuum, the residue was extracted with hexane (3 x 10 mL). The filtrate was concentrated under vacuum and stored at -30 °C to give $[(Cp^*)Sc(\mu_2-Me)]_3(\mu_3-CH)$ (**4**) (347 mg, 0.58 mmol, 92%) as red-orange crystals, which were suitable for X-ray analysis. 1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 0.04 (s, 9H, Sc-Me), 2.07 (s, 45H, C_5Me_5), 12.24 (s, 1H, Sc-CH). ^{13}C { 1H } NMR (125 MHz, C_6D_6 , 25 °C): δ = 11.76 (s, C_5Me_5), 30.24 (s, Sc-CH), 119.55 (s, C_5Me_5), 325.66 (s, Sc-CH). Anal. Calcd. for (**4**) $C_{34}H_{55}Sc_3$ (598.66): C, 68.20; H, 9.26. Found: C, 68.61; H, 9.54.

In C_6D_6 , complex **4** is stable at room temperature, but decomposed quickly above 60 °C. Solid of complex **4** can be stored at -30 °C for a week.

Synthesis of $[(Cp^*)Sc]_3(\mu_2-CH_2^tBu)(\mu_2-Br)_2(\mu_3-CH)$ (**5**)

A toluene solution of LiCH_2^tBu (29.5 mg, 0.38 mmol) was added dropwise to a suspension of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-Br})]_3(\mu_3\text{-CH})$ (**3**) (300 mg, 0.38 mmol) in toluene (15 mL). The mixture was stirred at 60 °C for 8 h. After filtration, the filtrate was concentrated to 2 mL under vacuum and stored at -30 °C to give $[(\text{Cp}^*)\text{Sc}]_3(\mu_3\text{-CH})(\mu_2\text{-Br})_2(\mu_2\text{-CH}_2^t\text{Bu})$ (**5**) (165 mg, 0.21 mmol, 55%) as yellow-brown crystals, which were suitable for X-ray analysis. ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 0.56 (s, 2H, $\text{CH}_2\text{C}(\text{CH}_3)_3$), 1.20 (s, 9H, $\text{CH}_2\text{C}(\text{CH}_3)_3$), 2.11 (s, 30H, C_5Me_5), 2.16 (s, 15H, C_5Me_5), 12.45 (s, 1H, Sc-CH). ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 25 °C): δ = 12.41 (s, C_5Me_5), 12.68 (s, C_5Me_5), 34.64 (s, $\text{CH}_2\text{C}(\text{CH}_3)_3$), 35.03 (s, $\text{CH}_2\text{C}(\text{CH}_3)_3$), 121.00 (s, C_5Me_5), 122.63 (s, C_5Me_5), 337.90 (s, Sc-CH). Anal. Calcd. for (**5**) $\text{C}_{36}\text{H}_{57}\text{Br}_2\text{Sc}_3$ (784.51): C, 55.11; H, 7.32. Found: C, 55.56; H, 7.62.

In C_6D_6 , complex **5** is stable at room temperature, but decomposed quickly above 60 °C. Solid of complex **5** can be stored at -30 °C for a week.

Synthesis of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})]_3(\mu_3\text{-CH})$ (**6**)

Solid LiOMe (95.7 mg, 2.52 mmol) was added dropwise to a suspension of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-Br})]_3(\mu_3\text{-CH})$ (**3**) (500 mg, 0.63 mmol) in toluene/ Et_2O (15 mL/15 mL), then the mixture was stirred at room temperature for 4 days to afford a yellow suspension. This suspension was concentrated under vacuum until all diethyl ether was removed, then filtered. After removal of all the volatiles under vacuum, the residue was washed with cold hexane (3 x 2 mL) to give $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})]_3(\mu_3\text{-CH})$ (**6**) (338 mg, 0.52 mmol, 83%) as light-yellow solid. Single crystals of **6**, suitable for X-ray analysis, were grown from a toluene solution by slow evaporation at room temperature. ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 2.12 (s, 45H, C_5Me_5), 3.56 (s, 9H, Sc-OMe), 11.00 (s, 1H, Sc-CH). ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 25 °C): δ = 11.14 (s, C_5Me_5), 52.24 (s, Sc-OMe), 117.47 (s, C_5Me_5). (* The carbon signal of Sc-CH could not be located.) Anal. Calcd. for (**6**) $\text{C}_{34}\text{H}_{55}\text{O}_3\text{Sc}_3$ (646.66): C, 63.15; H, 8.57. Found: C, 63.63; H, 8.93.

In C_6D_6 , complex **6** is stable at 60 °C, but decomposed quickly above 100 °C. Solid of complex **6** can be stored at room temperature.

Synthesis of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})]_3(\eta^2:\eta^3:\eta^1\text{-CHCN}^t\text{Bu})$ (**7**)

$^t\text{BuN}\equiv\text{C}$ (25.8 mg, 0.31 mmol) in toluene (1 mL) was added to a solution of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})]_3(\mu_3\text{-CH})$ (**5**) (100 mg, 0.155 mmol) then stirred for 30 h at room temperature. The volatiles were removed under vacuum and the residue was extracted with hexane (3 x 1 mL). This solution was stored at -30 °C to give $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})]_3(\eta^2:\eta^3:\eta^1\text{-CHCN}^t\text{Bu})$ (**7**) (75.7 mg, 0.104 mmol, 67%) as yellow crystals. Single crystals of **7**, suitable for X-ray analysis, were grown from a benzene solution by slow evaporation at room temperature. ^1H NMR (400 MHz,

C₆D₆, 25 °C): δ = 1.44 (s, 9H, C(CH₃)₃), 2.06 (s, 45H, C₅Me₅), 3.59 (s, 9H, Sc-OMe), 7.38 (s, 1H, CHCN^tBu). ¹³C {¹H} NMR (100 MHz, C₆D₆, 25 °C): δ = 11.87 (s, C₅Me₅), 29.72 (s, C(CH₃)₃), 31.41 (s, C(CH₃)₃), 55.80 (s, Sc-OMe), 60.09 (s, Sc-OMe), 118.02 (s, C₅Me₅), 169.98 (s, CHCN^tBu), 217.93 (s, CHCN^tBu). Anal. Calcd. for (7) C₃₉H₆₄NO₃Sc₃ (729.79): C, 64.18; H, 8.84, N, 1.92. Found: C, 64.53; H, 9.12, N, 1.63.

In C₆D₆, complex 7 is stable at 60 °C, but decomposed quickly above 100 °C. Solid of complex 7 can be stored at room temperature.

Synthesis of [(Cp^{*})Sc(μ₂-OMe)]₃(η²:η²:η³-CHC(Ph)N) (8)

PhC≡N (31.9 mg, 0.310 mmol) in toluene (1 mL) was added to a solution of [(Cp^{*})Sc(μ₂-OMe)]₃(μ₃-CH) (5) (100 mg, 0.155 mmol) then stirred for 48 h at room temperature to afford an orange solution. The volatiles were removed under vacuum and the residue was extracted with hexane (3 x 1 mL). The solution was stored at -30 °C to give [(Cp^{*})Sc(μ₂-OMe)]₃(η²:η²:η³-CHC(Ph)N) (8) (84.8 mg, 0.113 mmol, 73%) as pale-yellow crystals. Single crystals of 8, suitable for X-ray analysis, were grown from a benzene/isooctane solution by slow evaporation at room temperature. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 1.92 (s, 30H, C₅Me₅), 2.19 (s, 15H, C₅Me₅), 3.44 (s, 3H, Sc-OMe), 3.73 (s, 6H, Sc-OMe), 7.22 (t, 1H, Ph), 7.35 (t, 2H, Ph), 7.85 (s, 1H, CH), 8.12 (d, 2H, Ph). ¹³C {¹H} NMR (125 MHz, C₆D₆, 25 °C): δ = 11.17 (s, C₅Me₅), 54.81 (s, Sc-OMe), 117.78 (s, C₅Me₅), 127.14 (s, Ph), 127.73 (s, Ph), 128.59 (s, Ph), 137.78 (s, Ph), 158.33 (s, CHC(Ph)N), 175.53 (s, CHC(Ph)N). Anal. Calcd. for (8) C₄₁H₆₀NO₃Sc₃ (749.33): C, 65.68; H, 8.07, N, 1.87. Found: C, 65.91; H, 8.45, N, 2.13.

In C₆D₆, complex 8 is stable at 60 °C, but decomposed quickly above 100 °C. Solid of complex 8 can be stored at room temperature.

2. Selected NMR Spectra

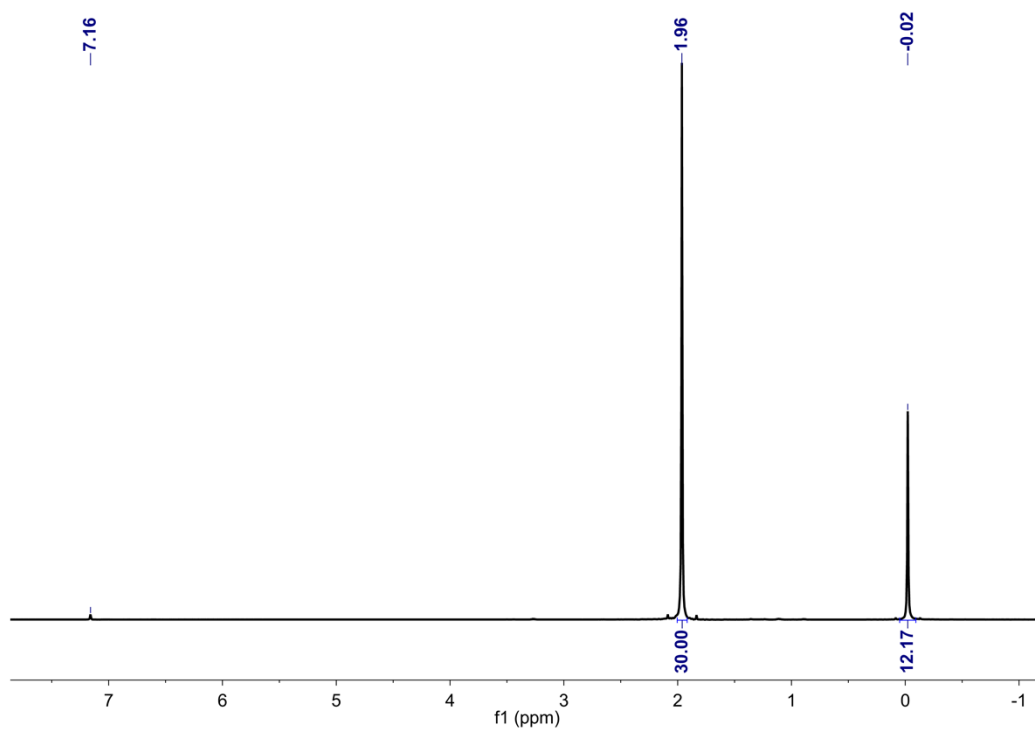


Figure S1. ^1H NMR spectrum (500 MHz) of $[(\text{Cp}^*)\text{ScMe}_2]_2$ (**1**) in C_6D_6 at 25 °C.

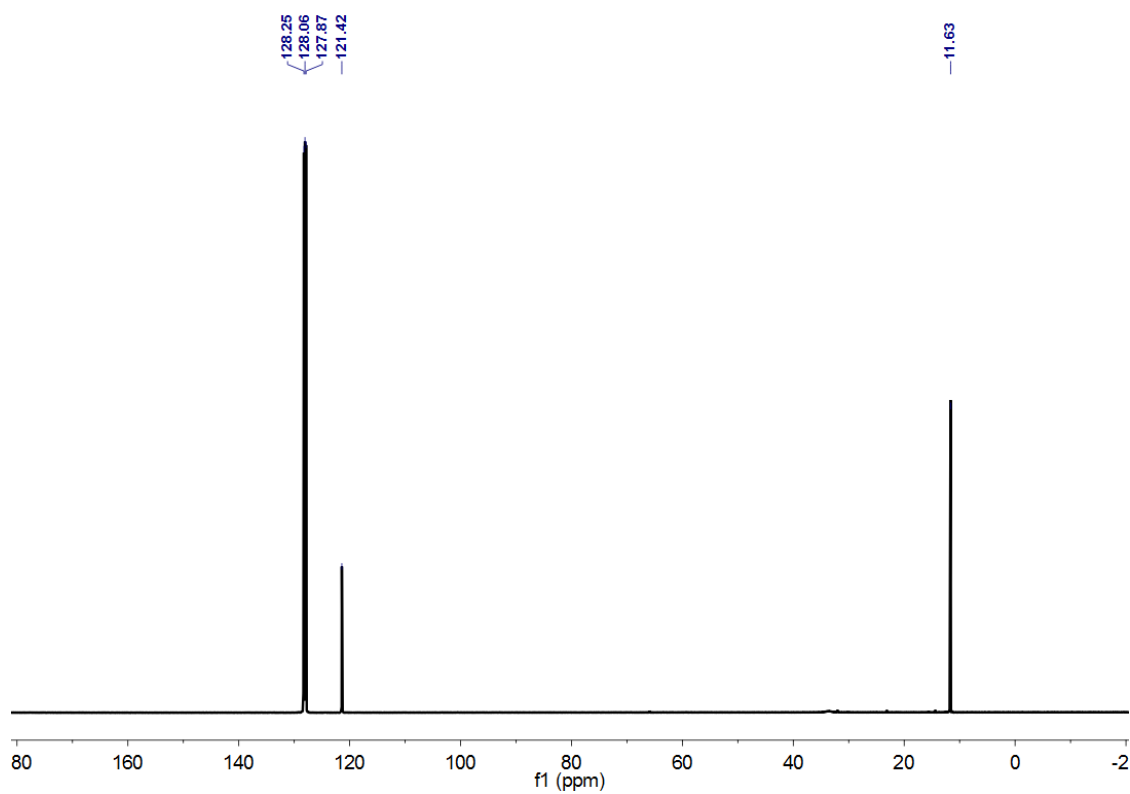


Figure S2. ^{13}C $\{^1\text{H}\}$ NMR spectrum (125 MHz) of $[(\text{Cp}^*)\text{ScMe}_2]_2$ (**1**) in C_6D_6 at 25 °C.

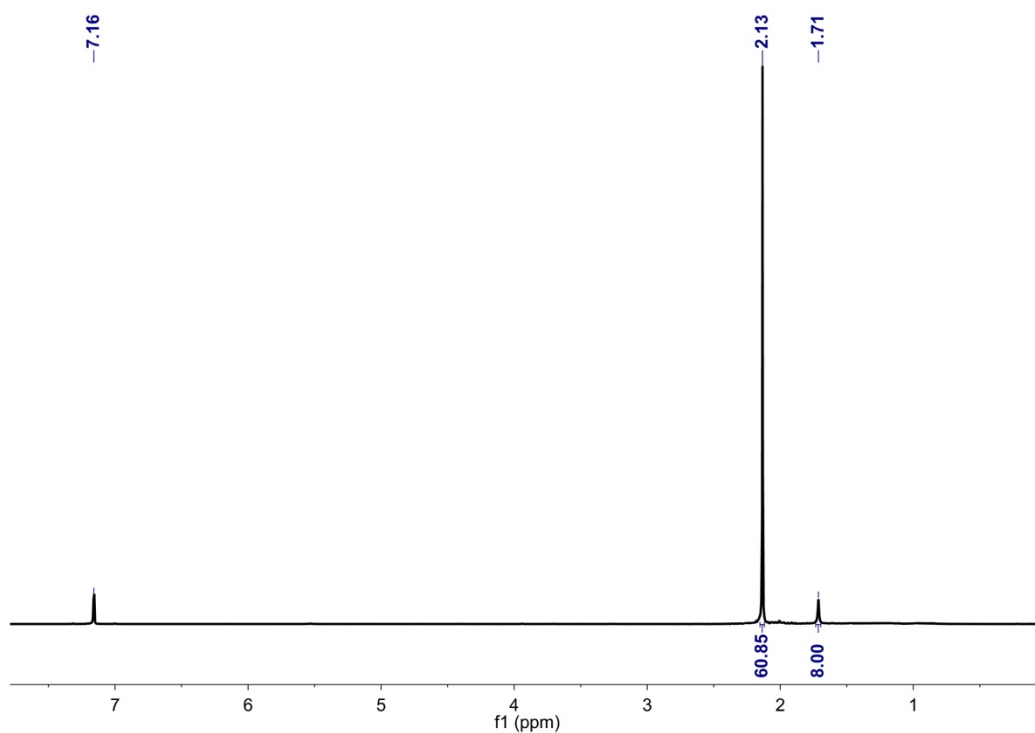


Figure S3. ^1H NMR spectrum (500 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-CH}_2)]_4$ (**2**) in C_6D_6 at $25\text{ }^\circ\text{C}$.

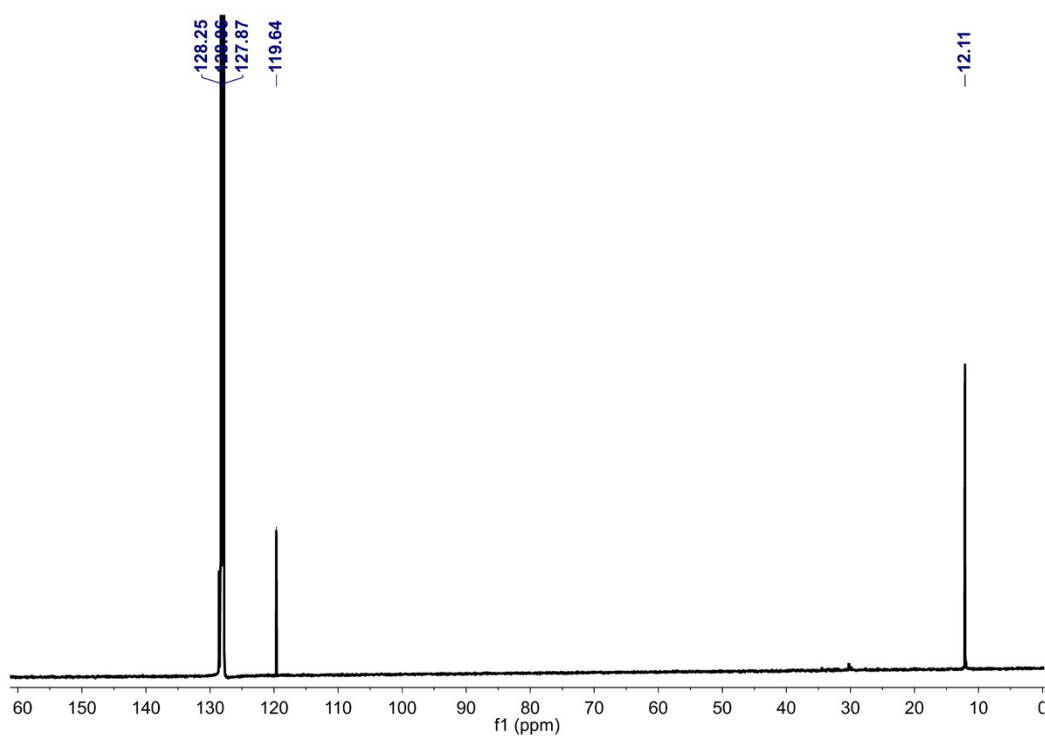


Figure S4. ^{13}C $\{^1\text{H}\}$ NMR spectrum (125 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-CH}_2)]_4$ (**2**) in C_6D_6 at $25\text{ }^\circ\text{C}$.

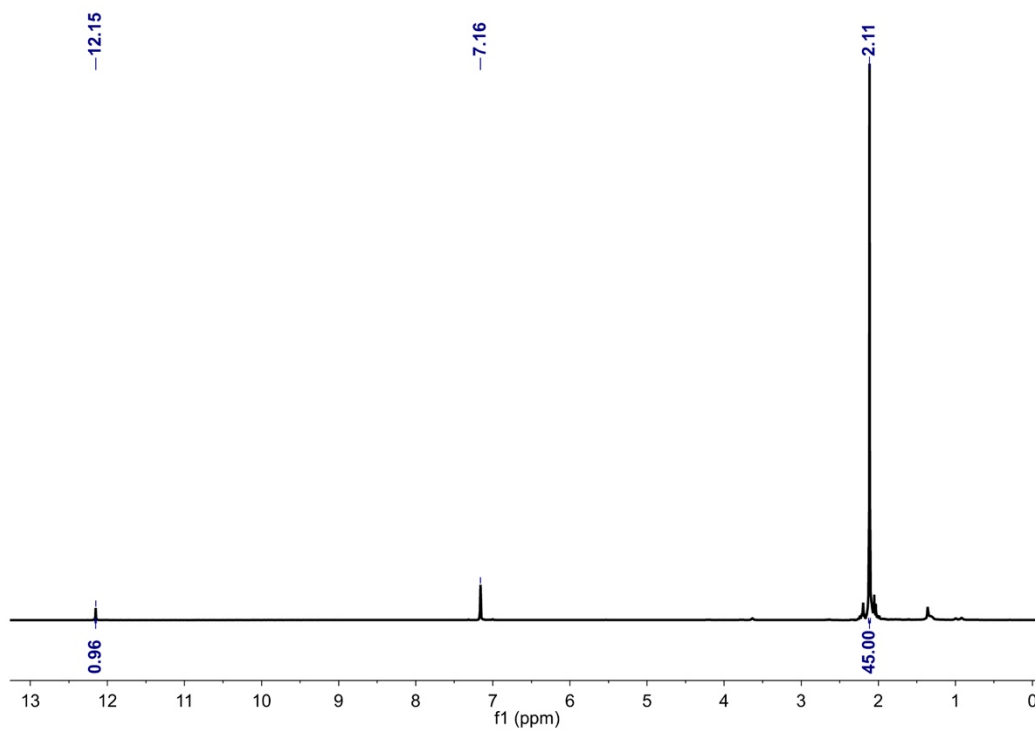


Figure S5. ^1H NMR spectrum (500 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-Br})_3(\mu_3\text{-CH})]$ (**3**) in C_6D_6 at $25\text{ }^\circ\text{C}$.

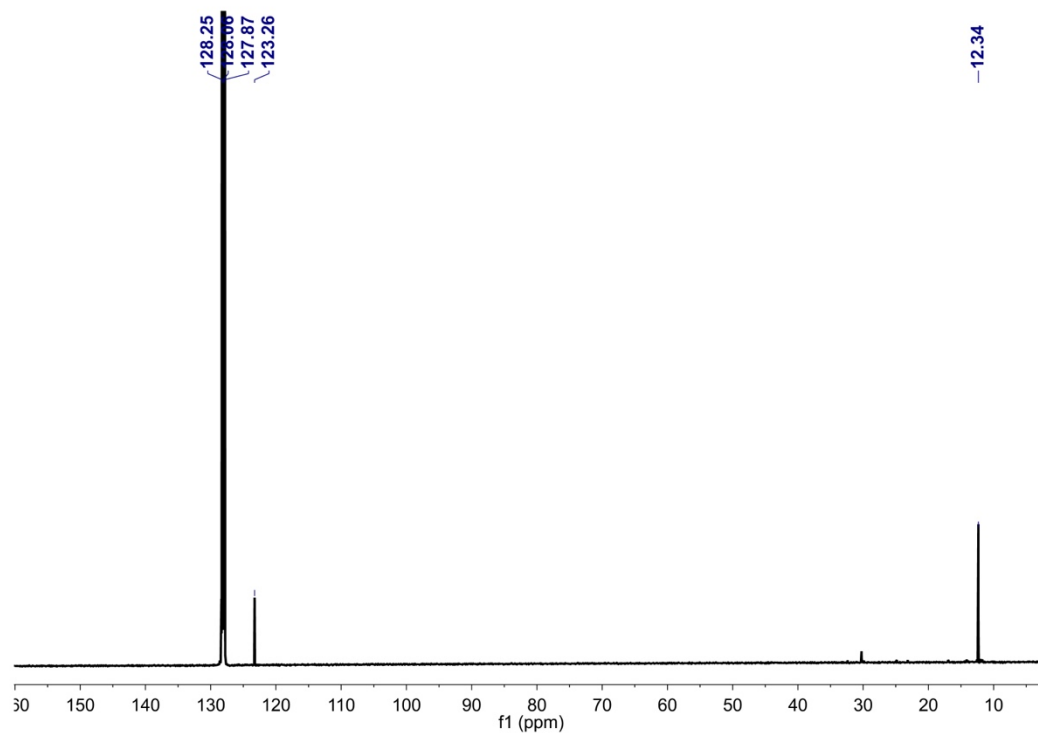


Figure S6. ^{13}C $\{^1\text{H}\}$ NMR spectrum (125 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-Br})_3(\mu_3\text{-CH})]$ (**3**) in C_6D_6 at $25\text{ }^\circ\text{C}$.

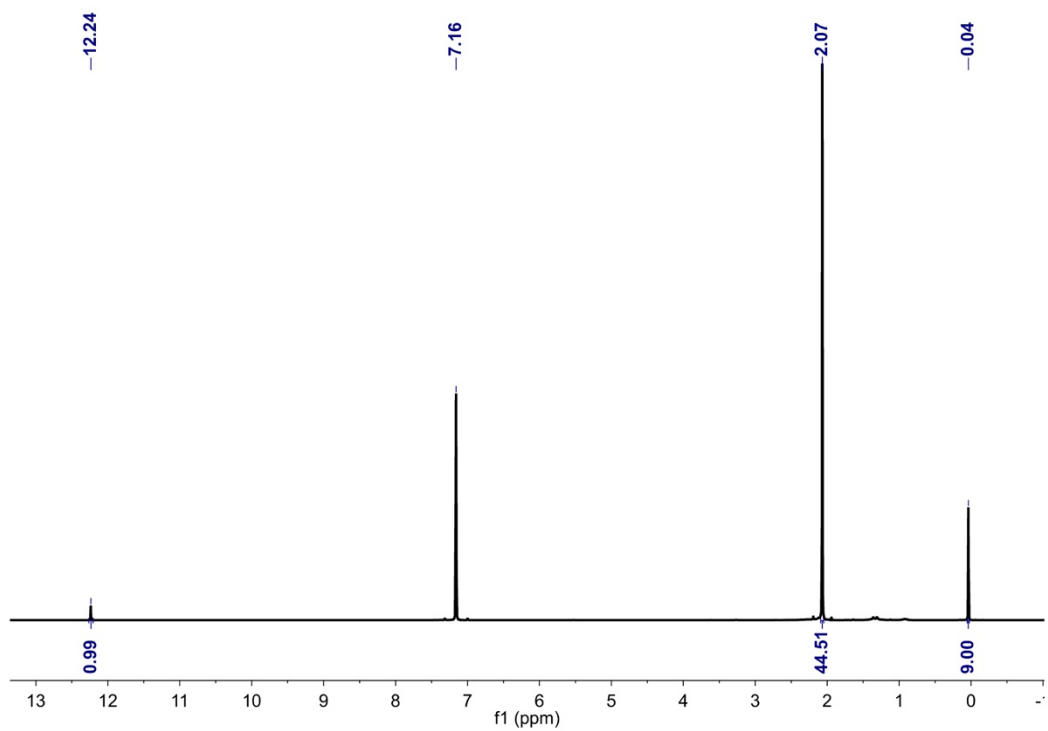


Figure S7. ^1H NMR spectrum (500 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-Me})]_3(\mu_3\text{-CH})$ (**4**) in C_6D_6 at 25°C .

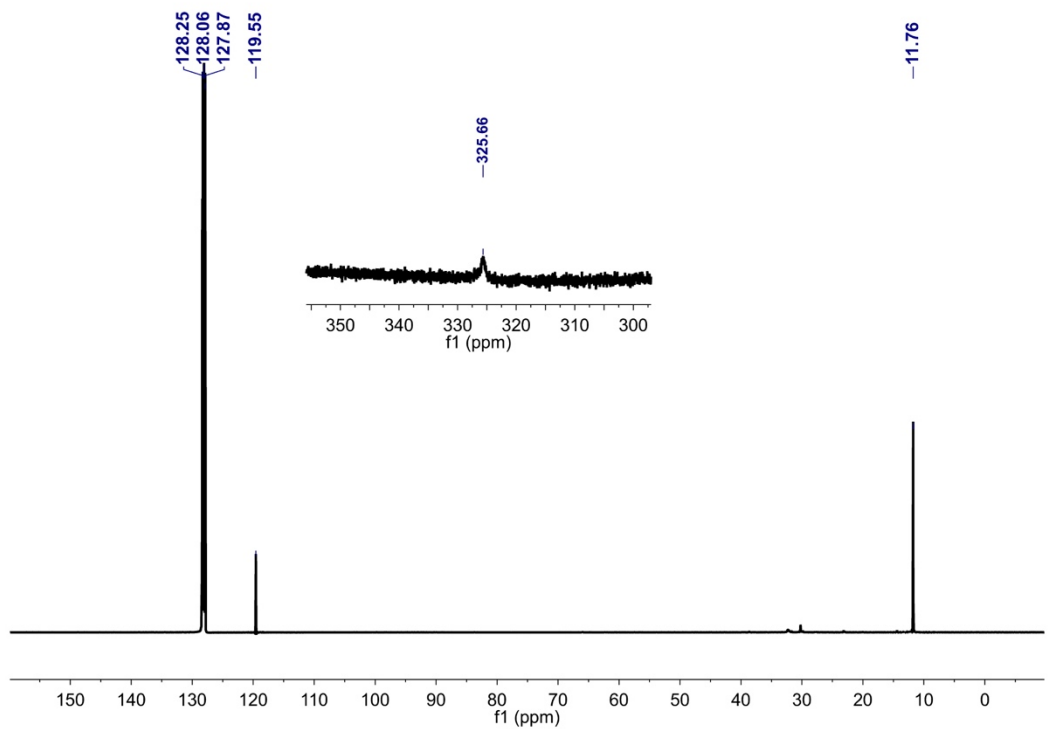


Figure S8. ^{13}C $\{^1\text{H}\}$ NMR spectrum (125 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-Me})]_3(\mu_3\text{-CH})$ (**4**) in C_6D_6 at 25°C .

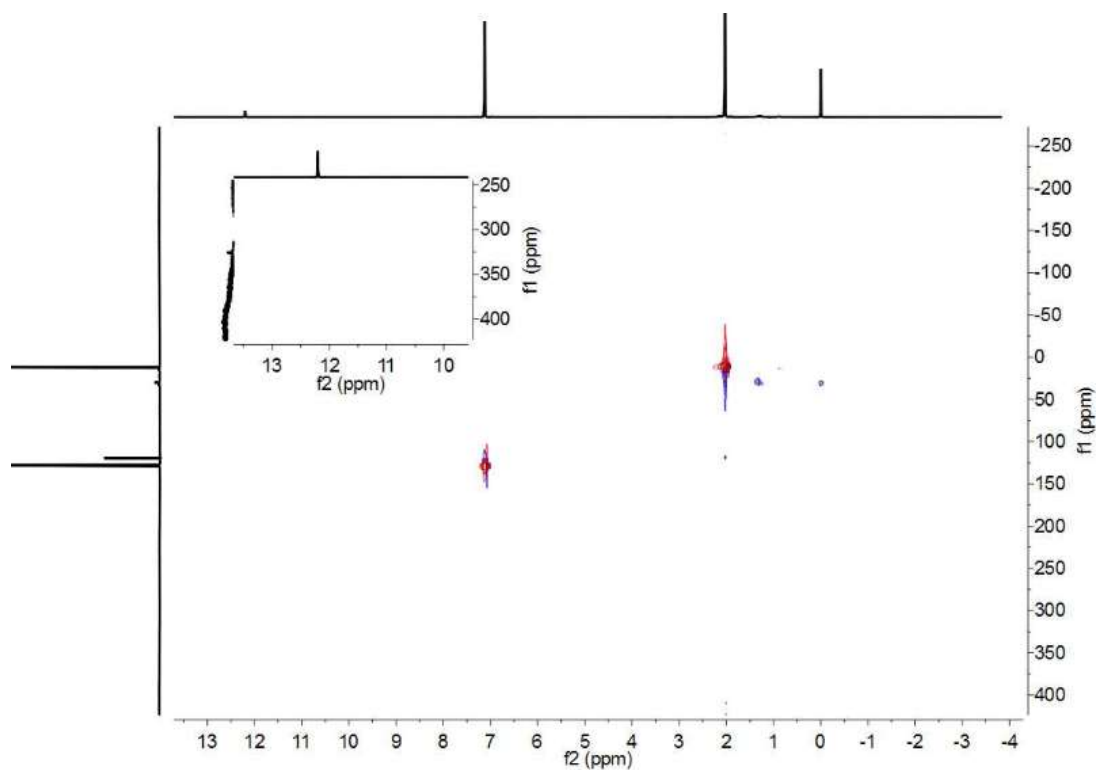


Figure S9. ^1H - ^{13}C HSQC NMR spectrum (500 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-Me})_3(\mu_3\text{-CH})]$ (**4**) in C_6D_6 at 25 °C.

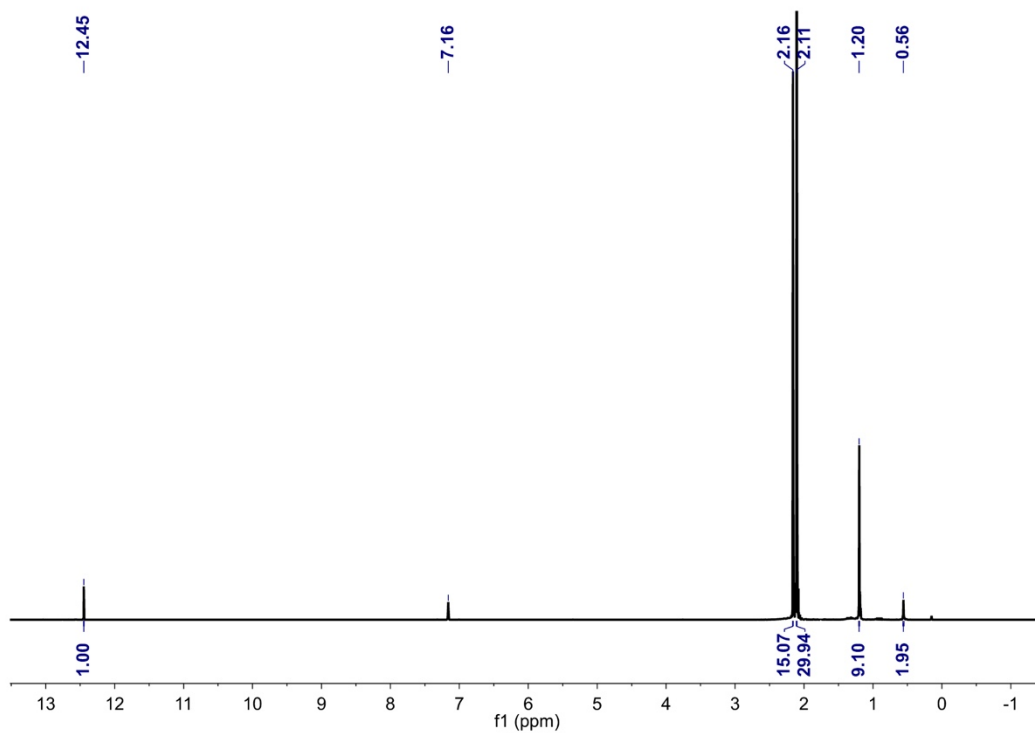


Figure S10. ^1H NMR spectrum (500 MHz) of $[(\text{Cp}^*)\text{Sc}]_3(\mu_3\text{-CH})(\mu_2\text{-Br})_2(\mu_2\text{-CH}_2^t\text{Bu})$ (**5**) in C_6D_6 at 25 °C.

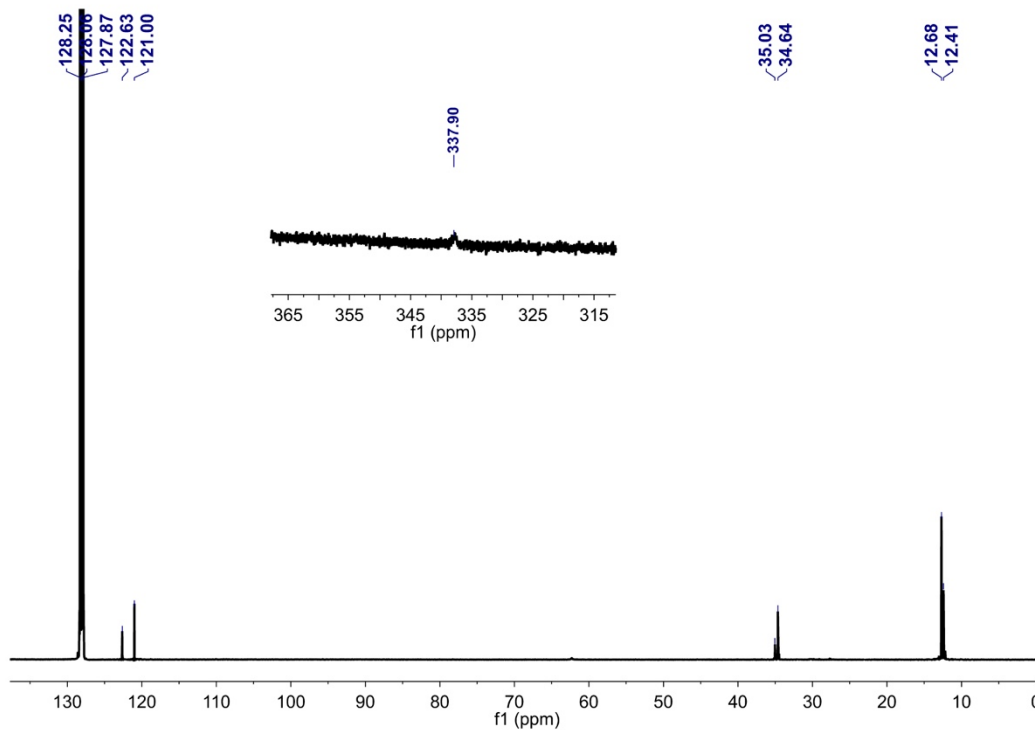


Figure S11. ^{13}C $\{^1\text{H}\}$ NMR spectrum (125 MHz) of $[(\text{Cp}^*)\text{Sc}]_3(\mu_3\text{-CH})(\mu_2\text{-Br})_2(\mu_2\text{-CH}_2^t\text{Bu})$ (**5**) in C_6D_6 at 25 °C.

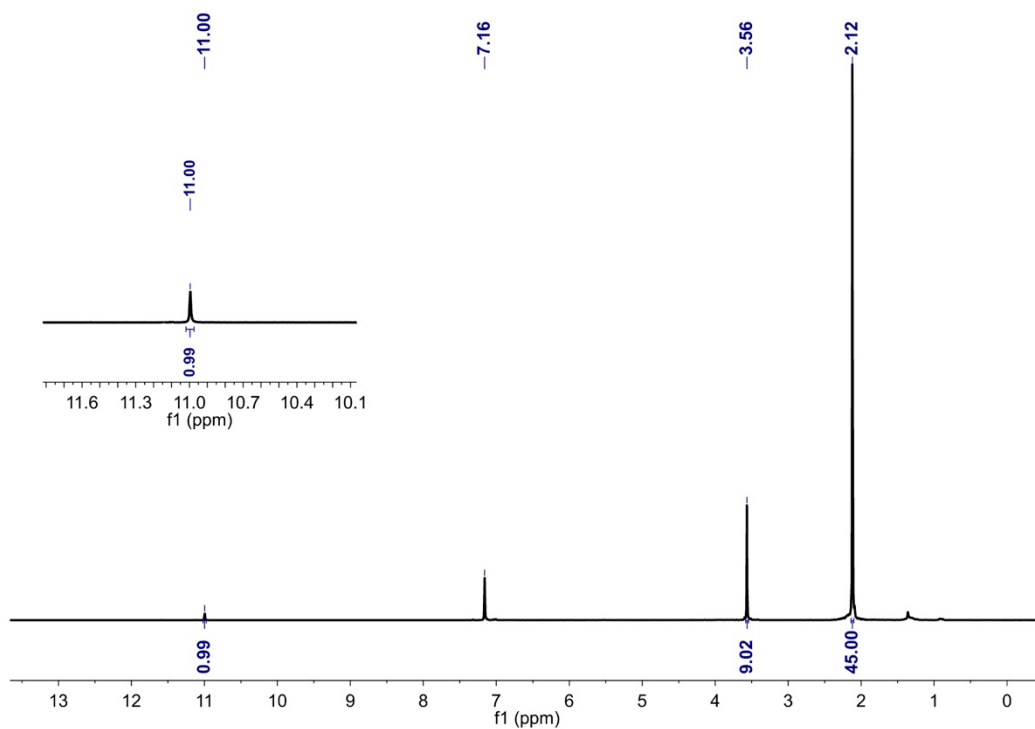


Figure S12. ^1H NMR spectrum (500 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})]_3(\mu_3\text{-CH})$ (**6**) in C_6D_6 at 25°C .

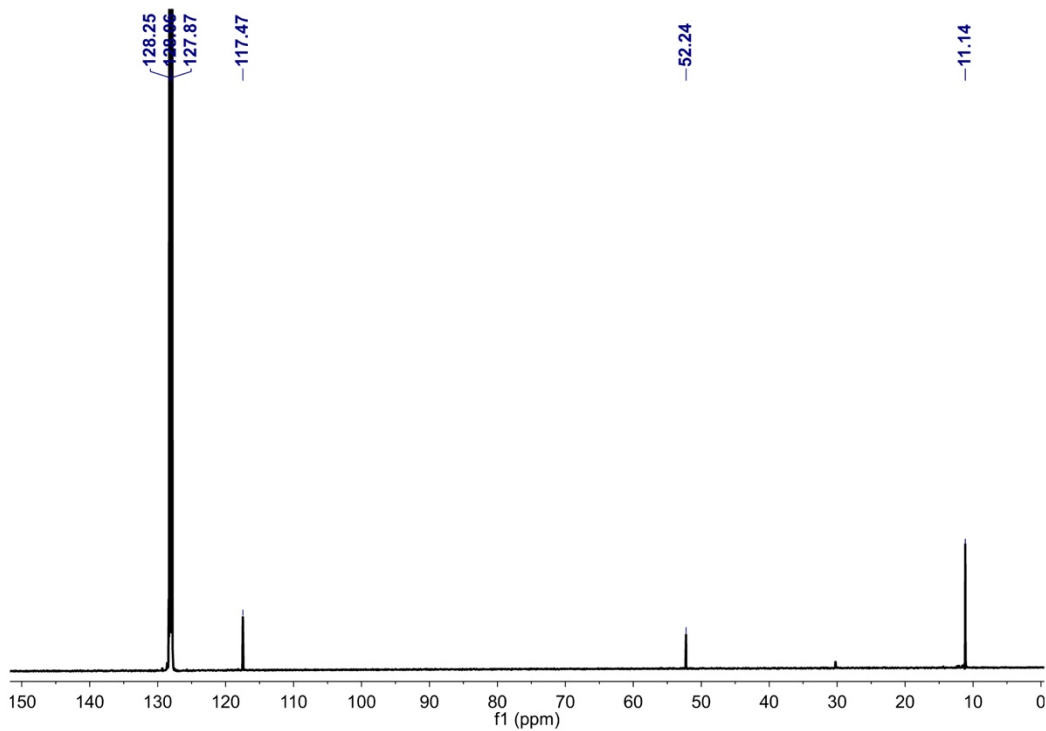


Figure S13. ^{13}C $\{^1\text{H}\}$ NMR spectrum (125 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})]_3(\mu_3\text{-CH})$ (**6**) in C_6D_6 at 25°C .

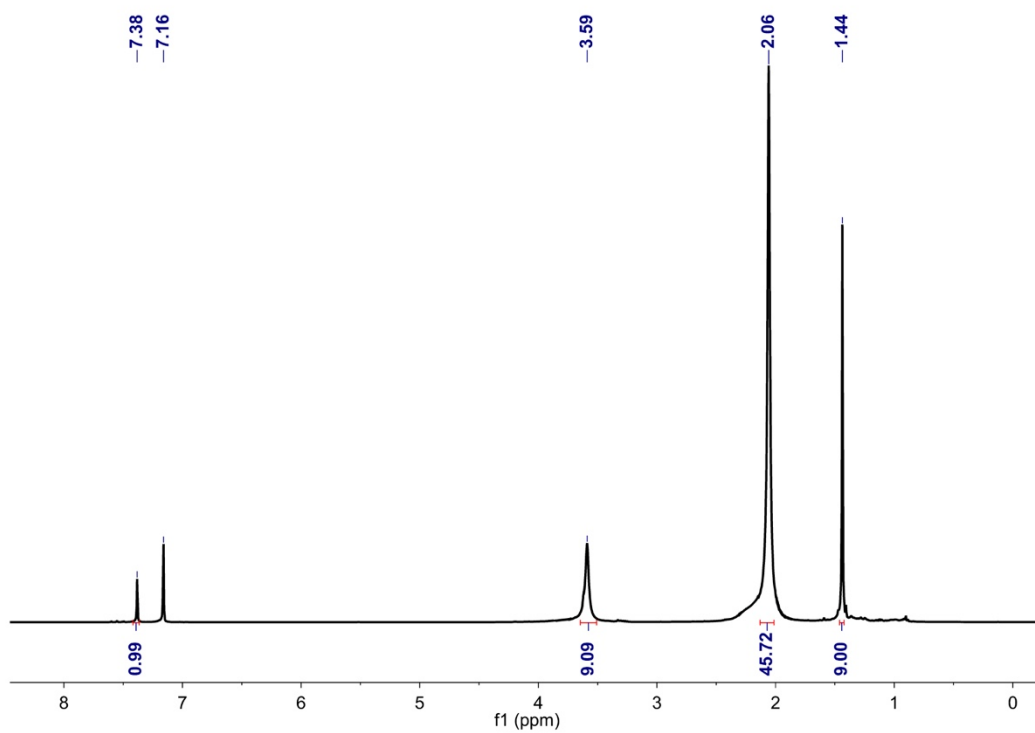


Figure S14. ^1H NMR spectrum (400 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})_3(\eta^2:\eta^3:\eta^1\text{-CHCN}^t\text{Bu})]$ (**7**) in C_6D_6 at 25 °C.

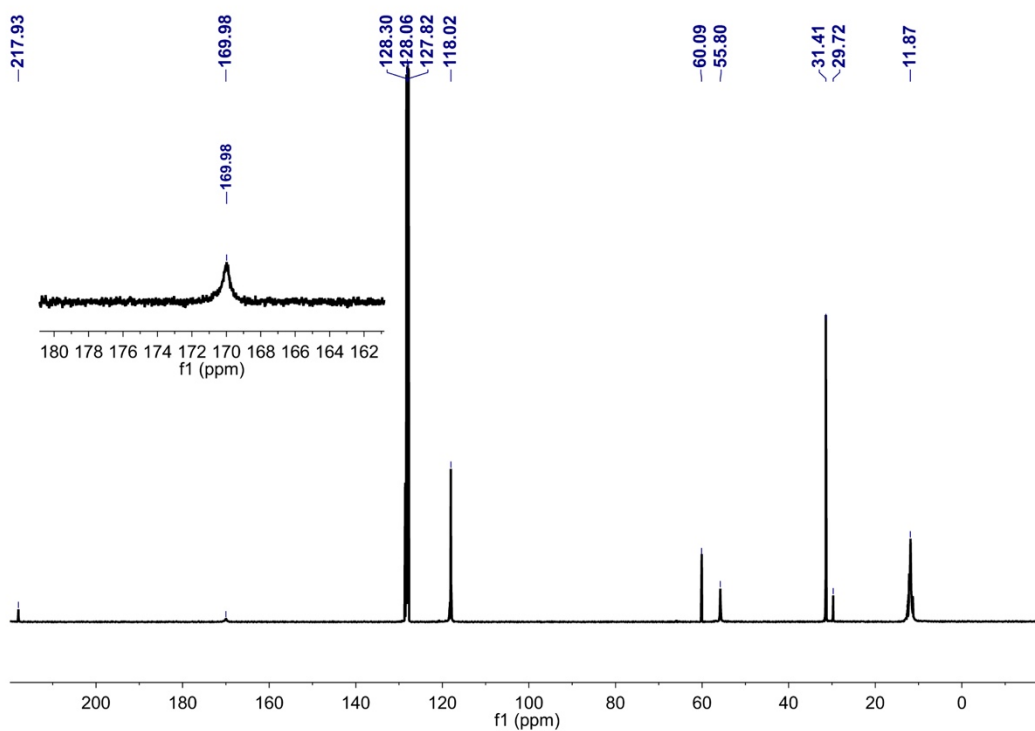


Figure S15. ^{13}C $\{^1\text{H}\}$ NMR spectrum (100 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})_3(\eta^2:\eta^3:\eta^1\text{-CH-C=N}^t\text{Bu})]$ (**7**) in C_6D_6 at 25 °C.

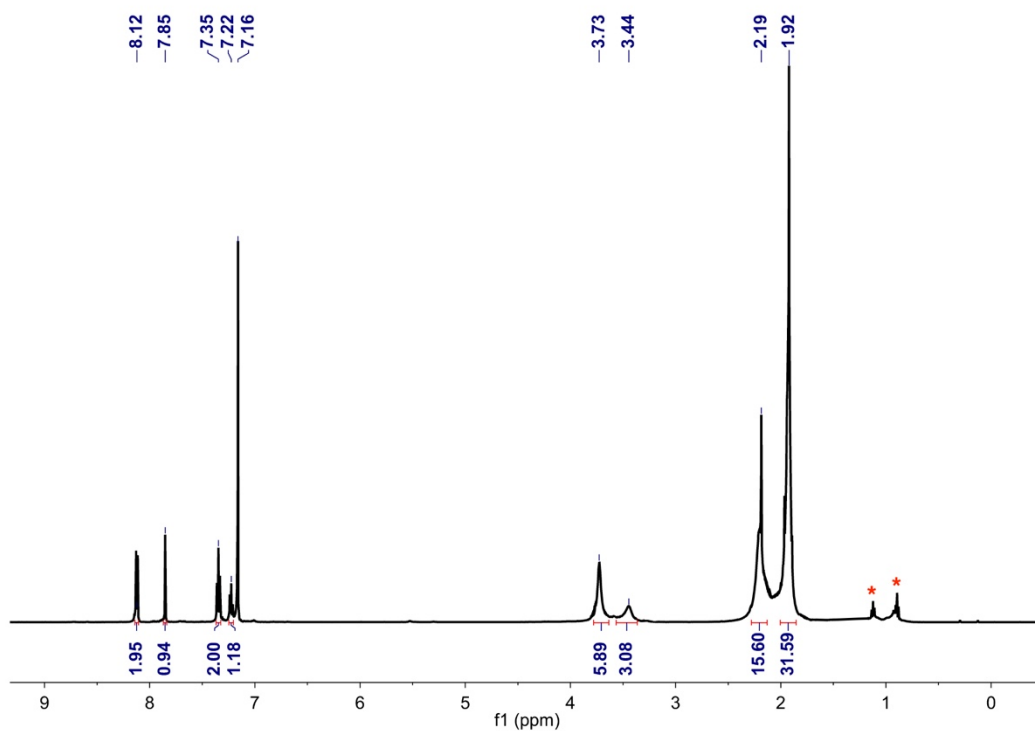


Figure S16. ^1H NMR spectrum (500 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})]_3(\eta^2:\eta^2:\eta^3\text{-CH-C(Ph)N})$ (**8**) in C_6D_6 at 25 °C (*: residual hexane).

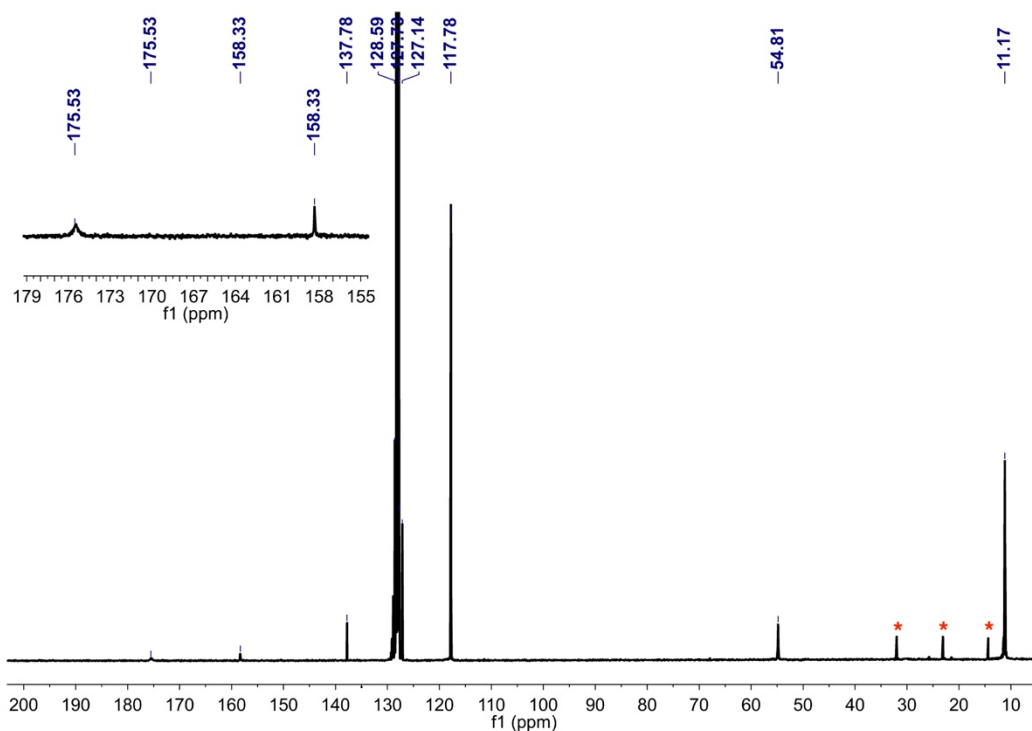


Figure S17. ^{13}C $\{^1\text{H}\}$ NMR spectrum (125 MHz) of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})]_3(\eta^2:\eta^2:\eta^3\text{-CH-C(Ph)N})$ (**8**) in C_6D_6 at 25 °C (*: residual hexane).

3. X-Ray Crystallographic Studies

Single crystals suitable for X-Ray analysis were obtained as described in the preparation. The crystals were manipulated in the glovebox under a microscope in the glovebox, Data collection was performed at -80 °C on a Bruker D8 Venture diffractometer with a CCD area detector, using graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). The determination of the crystal class and unit cell parameters was carried out by the SMART program packages^[4]. The raw frame data were processed using SAINT^[5] and absorption corrections using SADABS^[6] to yield the reflection data file. The structures were solved by using SHELXS-2018^[7] or SUPERFLIP^[8] in the WinGX program package^[9]. Refinements were performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method using SHELXL-2018 program^[7].

Refinement of **2**: The hydrogen atoms of the bridged $[\text{CH}_2]^{2-}$ groups were located by difference Fourier syntheses, and refined. Two of the four Cp^* ligands were highly disordered. C5~C10 and C5'~C10' disordered over two sites with occupancies 0.437:0.563. C15~C20 and C15'~C20' disordered over two sites with occupancies 0.307:0.693.

Refinement of **3**: The hydrogen atom of the $[\text{CH}]^{3-}$ unit was located by difference Fourier syntheses, and refined.

Refinement of **4**: The hydrogen atom of the $[\text{CH}]^{3-}$ unit was located by difference Fourier syntheses, and refined.

Refinement of **5**: The hydrogen atoms of the $[\text{CH}]^{3-}$ and $[\text{CH}_2]^{2-}$ groups were located by difference Fourier syntheses, and refined. One of the three Cp^* ligands were highly disordered. C10~C15 and C10'~C15' disordered over two sites with occupancies 0.546:0.454.

Refinement of **6**: The hydrogen atom of the $[\text{CH}]^{3-}$ unit was located by difference Fourier syntheses, and refined.

Refinement of **7**: There are two independent molecules with similar metrical parameters in the unit cell. The hydrogen atoms of the $[\text{CH}]^{3-}$ units were located by difference Fourier syntheses, and refined.

Refinement of **8**: The SQUEEZE^[10] routine of the program PLATON^[11] was implemented to remove the contributions of two disordered isoctanes to the observed structure factors. There are two independent molecules with similar metrical parameters in the unit cell. The hydrogen atoms of the $[\text{CH}]^{3-}$ units were located by difference Fourier syntheses, and refined. One of the two $[\text{CHC}(\text{Ph})\text{N}]^{3-}$ units was highly disordered. N2, C50~C57 and N2', C50'~C57' disordered over two sites with occupancies 0.585:0.415.

Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystal data and analysis results are listed in Table **S1-8**.

CCDC 2034368 (1), 2034369 (2), 2034370 (3), 2034371 (4), 2034372 (5), 2034373 (6), 2034374 (7), 2068269 (8) contain the supplementary crystallographic X-Ray data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for complex 1.

CCDC number	2034368
Empirical formula	C ₂₄ H ₄₂ Sc ₂
Formula weight	420.49
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
a	11.302(3) Å
b	13.079(4) Å
c	17.093(5) Å
α	90 °
β	103.306(5) °
γ	90 °
Volume	2458.8(13)Å ³
Z, Calculated density	4, 1.136 Mg/m ³
Absorption coefficient	0.557 mm ⁻¹
F(000)	912
Crystal size	0.300 x 0.280 x 0.250 mm
Theta range for data collection	1.971 to 25.000 °
Limiting indices	-13<=h<=12, -15<=k<=15, -20<=l<=18
Reflections collected / unique	12813 / 4305 [R(int) = 0.0827]
Completeness to theta	(25.00 °) 99.3 %
Absorption correction	Empirical
Max. and min. transmission	0.870 and 0.846
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4305 / 6 / 259
Goodness-of-fit on F ²	0.968
Final R indices [I>2sigma(I)]	R1 = 0.0629, wR2 = 0.1451
R indices (all data)	R1 = 0.1300, wR2 = 0.1768
Largest diff. peak and hole	0.543 and -0.370 e. Å ⁻³

Table S2. Crystal data and structure refinement for complex **2**.

CCDC number	2034369
Empirical formula	C ₄₄ H ₆₈ Sc ₄
Formula weight	776.82
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	11.331(3) Å
b	11.495(3) Å
c	18.812(5) Å
α	82.373(5) °
β	81.188(5) °
γ	65.634(4) °
Volume	2199.1(10) Å ³
Z, Calculated density	2, 1.173 Mg/m ³
Absorption coefficient	0.617 mm ⁻¹
F(000)	832
Crystal size	0.220 x 0.180 x 0.150 mm
Theta range for data collection	1.951 to 24.997 °
Limiting indices	-13<=h<=9, -13<=k<=13, -21<=l<=22
Reflections collected / unique	11446 / 7597 [R(int) = 0.0628]
Completeness to theta	(24.997 °) 98.0 %
Absorption correction	Empirical
Max. and min. transmission	0.912 and 0.875
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7597 / 58 / 417
Goodness-of-fit on F ²	0.979
Final R indices [I>2sigma(I)]	R1 = 0.0855, wR2 = 0.1898
R indices (all data)	R1 = 0.1836, wR2 = 0.2414
Largest diff. peak and hole	0.533 and -0.497 e. Å ⁻³

Table S3. Crystal data and structure refinement for complex **3**.

CCDC number	2034370
Empirical formula	C ₃₁ H ₄₆ Br ₃ Sc ₃
Formula weight	793.29
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, R3
a	19.234(5) Å
b	19.234(5) Å
c	8.042(5) Å
α	90 °
β	90 °
γ	120 °
Volume	2577(2) Å ³
Z, Calculated density	3, 1.534 Mg/m ³
Absorption coefficient	4.083 mm ⁻¹
F(000)	1200
Crystal size	0.150 x 0.120 x 0.080 mm
Theta range for data collection	3.522 to 24.996 °
Limiting indices	-22 ≤ h ≤ 20, -19 ≤ k ≤ 22, -9 ≤ l ≤ 9
Reflections collected / unique	3948 / 1741 [R(int) = 0.0502]
Completeness to theta	(24.996 °) 97.2 %
Absorption correction	Empirical
Max. and min. transmission	0.721 and 0.561
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1741 / 1 / 116
Goodness-of-fit on F ²	0.943
Final R indices [I > 2σ(I)]	R1 = 0.0353, wR2 = 0.0747
R indices (all data)	R1 = 0.0405, wR2 = 0.0759
Largest diff. peak and hole	0.540 and -0.305 e. Å ⁻³

Table S4. Crystal data and structure refinement for complex **4**.

CCDC number	2034371
Empirical formula	C ₃₄ H ₅₅ Sc ₃
Formula weight	598.66
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, R-3
a	19.1878(9) Å
b	19.1878(9) Å
c	15.6298(14) Å
α	90 °
β	90 °
γ	120 °
Volume	4983.5(6) Å ³
Z, Calculated density	6, 1.197 Mg/m ³
Absorption coefficient	0.615 mm ⁻¹
F(000)	1932
Crystal size	0.170 x 0.130 x 0.110 mm
Theta range for data collection	2.123 to 24.983 °
Limiting indices	-22<=h<=22, -22<=k<=22, -18<=l<=18
Reflections collected / unique	52107 / 1941 [R(int) = 0.0660]
Completeness to theta	(24.983 °) 99.5 %
Absorption correction	Empirical
Max. and min. transmission	0.935 and 0.909
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1941 / 0 / 126
Goodness-of-fit on F ²	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.1118
R indices (all data)	R1 = 0.0470, wR2 = 0.1176
Largest diff. peak and hole	0.471 and -0.422 e. Å ⁻³

Table S5. Crystal data and structure refinement for complex **5**.

CCDC number	2034372
Empirical formula	C ₃₆ H ₅₇ Br ₂ Sc ₃
Formula weight	784.51
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	11.1532(7) Å
b	11.2183(7) Å
c	16.7650(9) Å
α	98.580(2) °
β	97.778(2) °
γ	110.900(2) °
Volume	1896.9(2) Å ³
Z, Calculated density	2, 1.374 Mg/m ³
Absorption coefficient	2.650 mm ⁻¹
F(000)	812
Crystal size	0.150 x 0.130 x 0.120 mm
Theta range for data collection	1.989 to 24.999 °
Limiting indices	-13<=h<=13, -13<=k<=13, -19<=l<=19
Reflections collected / unique	80629 / 6653 [R(int) = 0.0837]
Completeness to theta	(24.999 °) 99.5 %
Absorption correction	Empirical
Max. and min. transmission	0.728 and 0.679
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6653 / 1 / 365
Goodness-of-fit on F ²	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0485, wR2 = 0.1274
R indices (all data)	R1 = 0.0581, wR2 = 0.1353
Largest diff. peak and hole	0.931 and -0.851 e. Å ⁻³

Table S6. Crystal data and structure refinement for complex **6**.

CCDC number	2034373
Empirical formula	C ₃₄ H ₅₅ O ₃ Sc ₃
Formula weight	646.66
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	8.4677(5) Å
b	11.4252(6) Å
c	18.6662(9) Å
α	90.449(2) °
β	90.296(2) °
γ	100.656(2) °
Volume	1774.63(16) Å ³
Z, Calculated density	2, 1.210 Mg/m ³
Absorption coefficient	0.586 mm ⁻¹
F(000)	692
Crystal size	0.150 x 0.130 x 0.120 mm
Theta range for data collection	2.182 to 25.000 °
Limiting indices	-10<=h<=10, -13<=k<=13, -22<=l<=22
Reflections collected / unique	61814 / 6187 [R(int) = 0.1025]
Completeness to theta	(25.00 °) 99.0 %
Absorption correction	Empirical
Max. and min. transmission	0.932 and 0.916
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6187 / 0 / 365
Goodness-of-fit on F ²	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0581, wR2 = 0.1595
R indices (all data)	R1 = 0.0692, wR2 = 0.1733
Largest diff. peak and hole	0.613 and -0.655 e. Å ⁻³

Table S7. Crystal data and structure refinement for complex 7.

CCDC number	20134374
Empirical formula	C ₇₈ H ₁₂₈ N ₂ O ₆ Sc ₆
Formula weight	1459.58
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	12.1700(6) Å
b	19.2637(9) Å
c	19.9851(10) Å
α	63.681(2) °
β	77.428(2) °
γ	76.109(2) °
Volume	4043.3(3) Å ³
Z, Calculated density	2, 1.199 Mg/m ³
Absorption coefficient	0.523 mm ⁻¹
F(000)	1568
Crystal size	0.140 x 0.130 x 0.090 mm
Theta range for data collection	1.941 to 24.999 °
Limiting indices	-14<=h<=14, -22<=k<=22, -23<=l<=23
Reflections collected / unique	111818 / 14160 [R(int) = 0.0604]
Completeness to theta	(24.999 °) 99.5 %
Absorption correction	Empirical
Max. and min. transmission	0.954 and 0.929
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	14160 / 0 / 840
Goodness-of-fit on F ²	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1038
R indices (all data)	R1 = 0.0569, wR2 = 0.1135
Largest diff. peak and hole	0.426 and -0.363 e. Å ⁻³

Table S8. Crystal data and structure refinement for complex **8**.

CCDC number	2068269
Empirical formula	C ₈₂ H ₁₂₀ N ₂ O ₆ Sc ₆
Formula weight	1499.55
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	16.9260(15) Å
b	17.5138(18) Å
c	18.0380(17) Å
α	67.491(3) °
β	87.569(3) °
γ	79.633(3) °
Volume	4857.1(8) Å ³
Z, Calculated density	2, 1.025 Mg/m ³
Absorption coefficient	0.437 mm ⁻¹
F(000)	1600
Crystal size	0.150 x 0.110 x 0.070 mm
Theta range for data collection	1.920 to 25.000 °
Limiting indices	-20 ≤ h ≤ 20, -20 ≤ k ≤ 20, -21 ≤ l ≤ 21
Reflections collected / unique	133745 / 17000 [R(int) = 0.1107]
Completeness to theta	(25.00 °) 99.4 %
Absorption correction	Empirical
Max. and min. transmission	0.970 and 0.944
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17000 / 12 / 894
Goodness-of-fit on F ²	1.029
Final R indices [I > 2σ(I)]	R1 = 0.0662, wR2 = 0.1653
R indices (all data)	R1 = 0.1119, wR2 = 0.1974
Largest diff. peak and hole	1.367 and -0.626 e. Å ⁻³

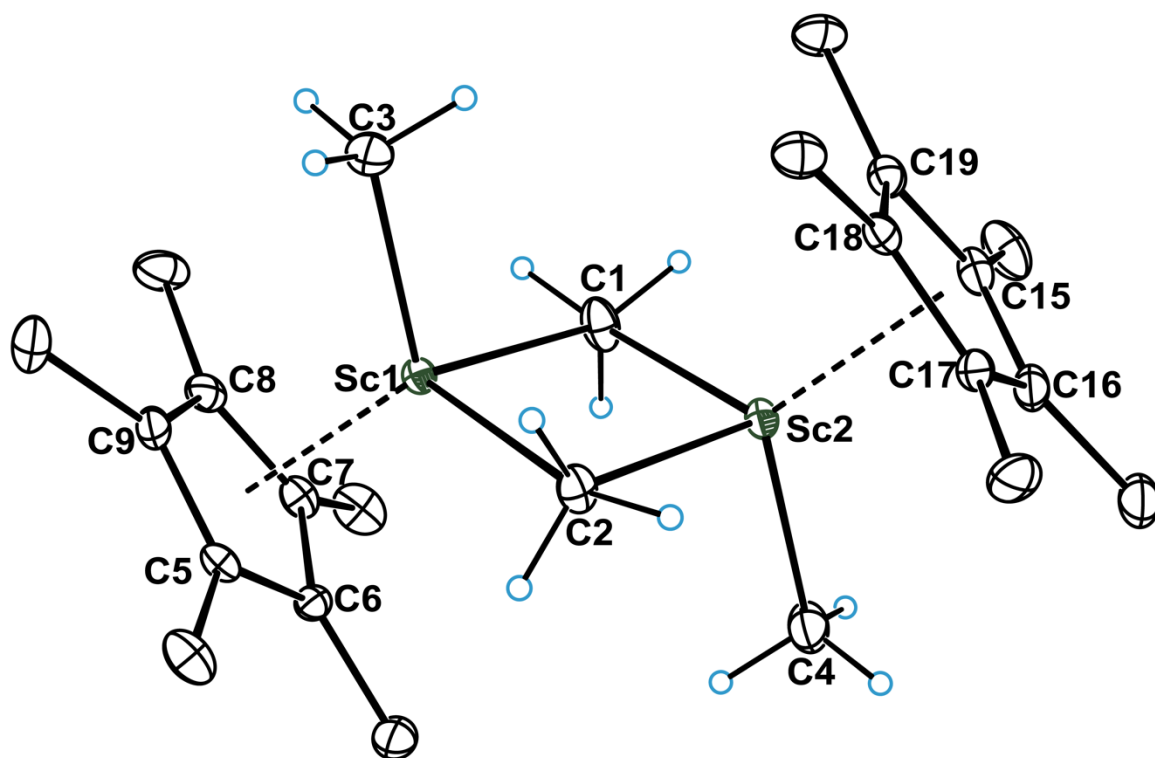


Figure S18. ORTEP plot (20% probability) of $[(Cp^*)ScMe_2]_2$ (**1**). All the hydrogen atoms in Cp^* rings are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sc1–C1 2.342(5), Sc1–C2 2.332(5), Sc1–C3 2.206(5), Sc2–C1 2.333(5), Sc2–C2 2.355(5), Sc2–C4 2.213(5), Sc1–C1–Sc2 84.87(17), Sc1–C2–Sc2 84.59(15).

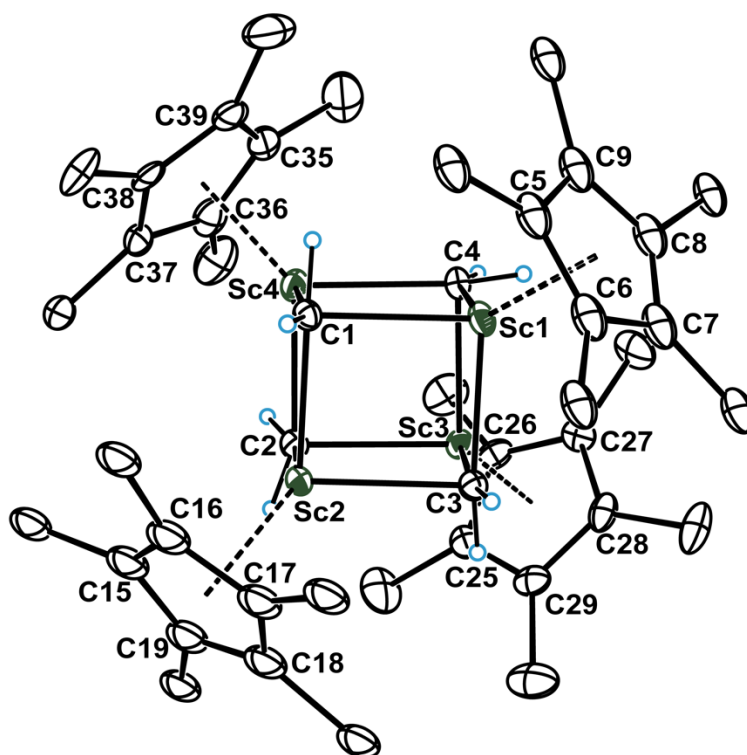


Figure S19. ORTEP plot (20% probability) of $[(\text{Cp}^*)\text{Sc}(\mu_3\text{-CH}_2)]_4$ (**2**). All the hydrogen atoms in Cp^* rings are omitted for clarity. Selected interatomic distances [Å]: Sc1–C1 2.293(7), Sc1–C3 2.230(7), Sc1–C4 2.246(8), Sc2–C1 2.230(7), Sc2–C2 2.210(8), Sc2–C3 2.303(7), Sc3–C2 2.301(7), Sc3–C3 2.217(8), Sc3–C4 2.255(7), Sc4–C1 2.217(8), Sc4–C2 2.250(8), Sc4–C4 2.265(7), Sc1---Sc2 3.214(2), Sc1---Sc3 3.080(2), Sc1---Sc4 3.184(2), Sc2---Sc3 3.199(2), Sc2---Sc4 3.091(2), Sc3---Sc4 3.227(2).

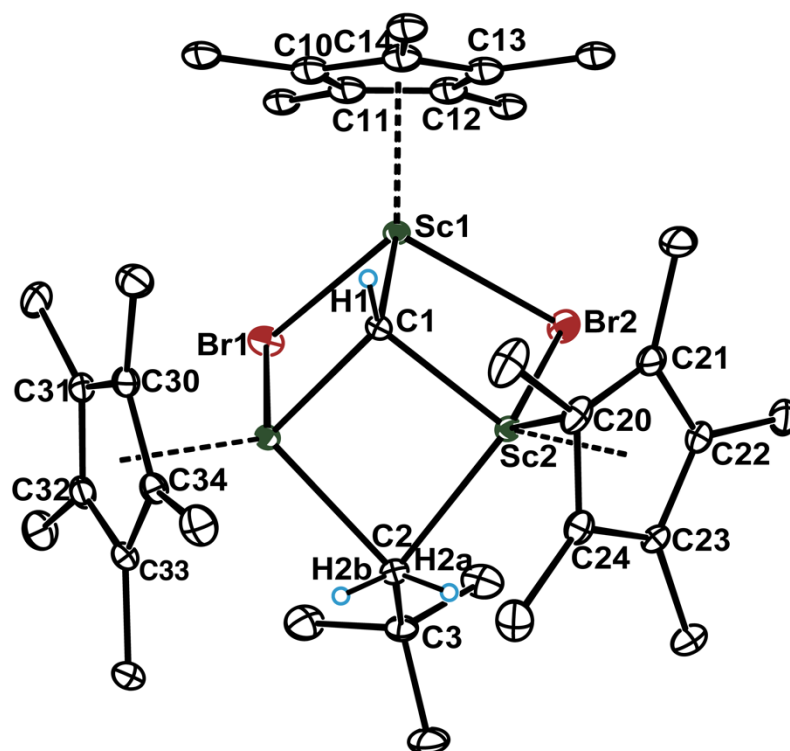


Figure S20. ORTEP drawing of $[(\text{Cp}^*)\text{Sc}]_3(\mu_3\text{-CH})(\mu_2\text{-Br})_2(\mu_2\text{-CH}_2^t\text{Bu})$ (**5**) with thermal ellipsoids drawn at the 20% probability level. All the hydrogen atoms in Cp^* ligands and *tert*-butyl group are omitted for clarity. Selected interatomic distances [\AA]: Sc1–C1 2.143(4), Sc1–Br1 2.642(1), Sc1–Br2 2.652(1), Sc1---Sc2 3.293(1), Sc1---Sc3 3.334(1), Sc2–C1 2.111(4), Sc2–C2 2.440(4), Sc2–Br2 2.687(1), Sc2---Sc3 3.133(1), Sc3–C1 2.125(4), Sc3–C2 2.403(4), Sc3–Br1 2.698(1).

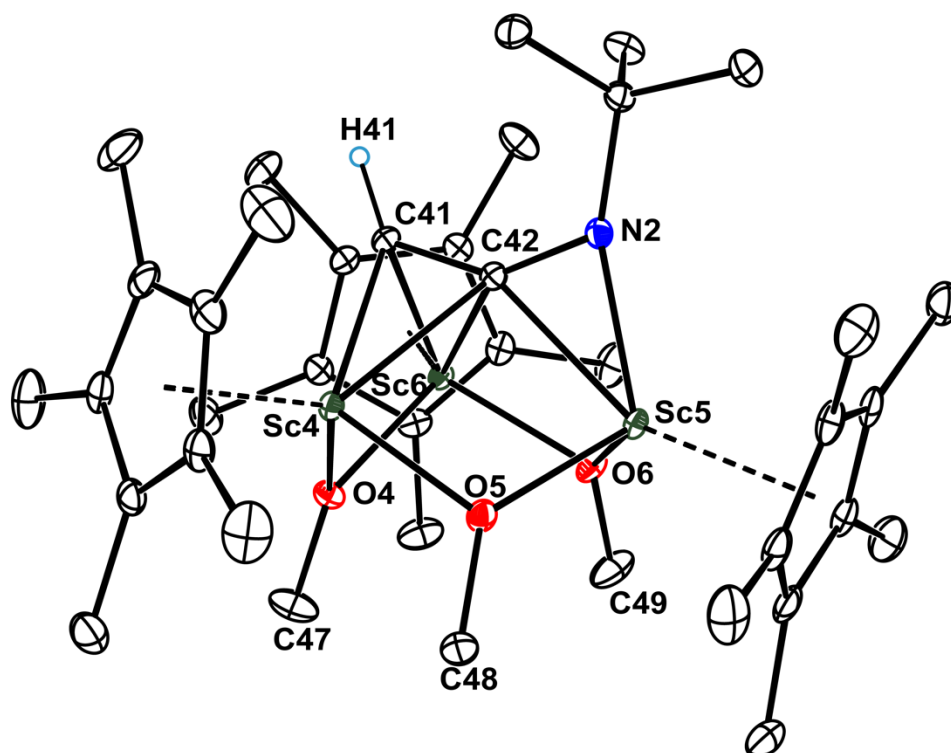


Figure S21. ORTEP drawing of $[(\text{Cp}^*)\text{Sc}(\mu_2\text{-OMe})]_3(\eta^2:\eta^3:\eta^1\text{-CHCN}^t\text{Bu})$ (**7**) with thermal ellipsoids drawn at the 20% probability level (the other molecular in unit cell). All the hydrogen atoms, except H1, are omitted for clarity. Selected interatomic distances [\AA] and bond angles [deg]: C41–C42 1.375(4), N2–C42 1.353(3), Sc4–C41 2.271(3), Sc4–C42 2.355(2), Sc4---Sc5 3.3048(7), Sc4---Sc6 3.0037(7), Sc5–N2 2.102(2), Sc5–C42 2.281(3), Sc5---Sc6 3.3636(6), Sc6–C41 2.251(3), Sc6–C42 2.429(2), C41–C42–N2 143.0(2).

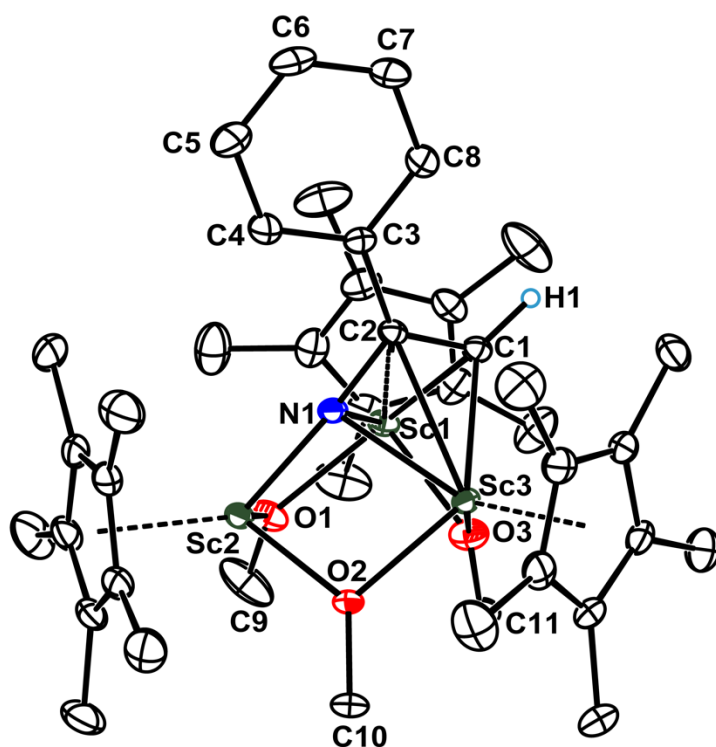


Figure S22. ORTEP drawing of $[(Cp^*)Sc(\mu_2-OMe)]_3(\eta^2:\eta^2:\eta^3-CHC(Ph)N)$ (**8-A**) with thermal ellipsoids drawn at the 20% probability level. All the hydrogen atoms, except H1, are omitted for clarity. Selected interatomic distances [Å] and bond angles [deg]: C1–C2 1.369(6), N1–C2 1.385(5), Sc1–N1 2.262(4), Sc1–C1 2.322(4), Sc1–C2 2.556(4), Sc1---Sc2 3.2123(12), Sc1---Sc3 2.9623(11), Sc2–N1 1.979(3), Sc2---Sc3 3.2102(11), Sc3–N1 2.277(3), Sc3–C1 2.321(4), Sc3–C2 2.580(4), C1–C2–N1 112.2(3).

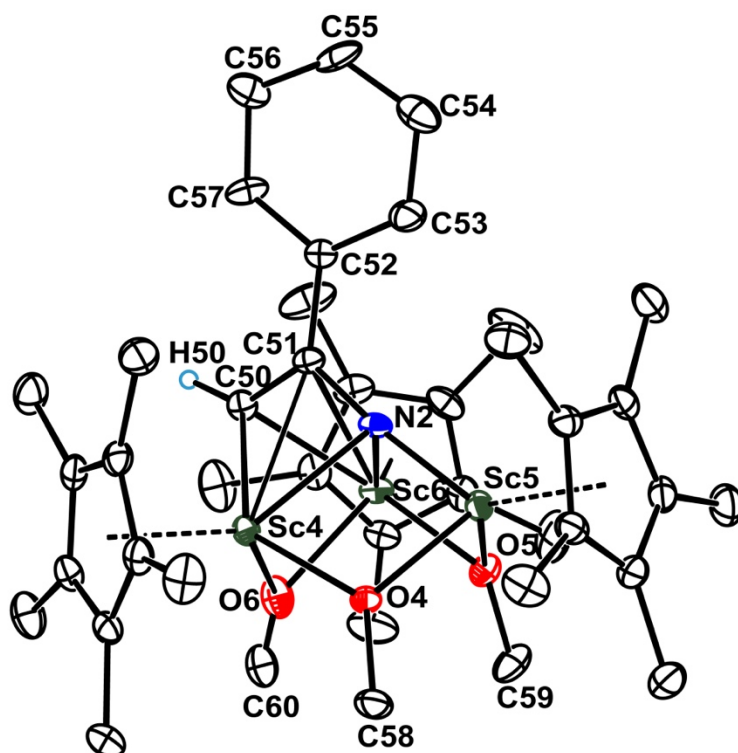


Figure S23. ORTEP drawing of $[(Cp^*)Sc(\mu_2-OMe)_3(\eta^2:\eta^2:\eta^3-CHC(Ph)N)1(\mathbf{8-B})]$ with thermal ellipsoids drawn at the 20% probability level (the other molecular in unit cell). All the hydrogen atoms, except H1, are omitted for clarity. Selected interatomic distances [\AA] and bond angles [deg]: C50–C51 1.365(10), N2–C51 1.386(11), Sc4–N2 2.318(6), Sc4–C50 2.397(7), Sc4–C51 2.653(7), Sc4---Sc5 3.207(2), Sc4---Sc6 3.086(2), Sc5–N2 1.921(8), Sc5---Sc6 3.083(2), Sc6–N2 2.236(7), Sc6–C50 2.394(8), Sc6–C51 2.578(7), C50–C51–N2 111.4(7).

8. References

- [1] Manzer, L. E.; Deaton, J.; Sharp, P.; Schrock, R. R. Tetrahydrofuran complexes of selected early transition metals. In *Inorganic Syntheses*; Fackler, J. P., Ed.; John Wiley & Sons, Inc., **1982**; pp 135-140.
- [2] Schrock, R. R.; Fellman, J. D. Multiple metal-carbon bonds. 8. Preparation, characterization, and mechanism of formation of the tantalum and niobium neopentylidene complexes, $M(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$, *J. Am. Chem. Soc.* **1978**, *100*, 3359-3370.
- [3] Robert, D.; Spaniol, T. P.; Okuda, J. Neutral and monocationic half-sandwich methyl rare-earth metal complexes: Synthesis, structure, and 1,3-butadiene polymerization catalysis. *Eur. J. Inorg. Chem.* **2008**, 2801-2809.
- [4] SMART Software Users Guide, Version 4.21; Bruker AXS, Inc.: Madison, WI, **1997**.
- [5] SAINT, Version 6.45; Bruker AXS, Inc.: Madison, WI **2003**.
- [6] Sheldrick, G. M. SADABS, Version 2.10; Bruker AXS, Inc.: Madison, WI **2003**.
- [7] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.
- [8] a) Palatinus, L.; Chapuis, G.; SUPERFLIP - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J. Appl. Cryst.* **2007**, *40*, 786–790; b) Palatinus, L.; Prathapa, S. J.; van Smaalen, S. EDMA: a computer program for topological analysis of discrete electron densities. *J. Appl. Cryst.* **2012**, *45*, 575–580.
- [9] Farrugia, L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **2012**, *45*, 849–854.
- [10] Sluis, P. Van der.; Spek, A. L. Bypass - an effective method for the refinement of crystal structures containing disordered solvent regions. *Acta Cryst.* **1990**, *A46*, 194–201.
- [11] Spek, A. L. Structure validation in chemical crystallography. *Acta Cryst.* **2009**, *D65*, 148–155.