

Electronic Supporting Information

Cationic Strontium Hydride Complexes Supported by an NNNN-Type Macrocycle

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1 General Remarks

All operations were performed under an inert atmosphere of dry argon using standard Schlenk line or glovebox techniques. THF- d_6 , THF, benzene and n-pentane were distilled under argon from sodium/benzophenone ketyl prior to use. Hydrogen (99.999%) and deuterium (99.8%) were purchased from Praxair-Westfalen AG. Commercially available reagents were dried over CaH_2 and distilled, or in case of solids, sublimed before use. ^1H , ^2H , $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ spectra were recorded on a Bruker Avance II 400 or a Bruker Avance III HD 400 spectrometer at 25 °C in J. Young-type NMR tubes. Chemical shifts for ^1H , ^2H and $^{13}\text{C}\{^1\text{H}\}$ spectra were referenced internally using the residual solvent resonance and are reported relative to tetramethylsilane. $^{11}\text{B}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ were referenced externally to $\text{BF}_3(\text{OEt}_2)$ and SiMe_4 . The resonances in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HSQC, HMBC). Elemental analyses were performed on an Elementar vario EL instrument. In several instances, the carbon values were not satisfactory, possibly due to incomplete combustion as the result of carbonate or carbide formation as well as high air- and moisture sensitivity.^[S1] 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane (Me_4TACD),^[S2] $[\text{K}(\text{CH}_2\text{Ph})]$,^[S3] $[\text{NEt}_3\text{H}][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]$,^[S4] $[(\text{Me}_4\text{TACD})\text{Ca}(\text{CH}_2\text{Ph})_2]$,^[S4] $[(\text{Me}_4\text{TACD})\text{Ca}(\text{CH}_2\text{Ph})(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]$ ^[S4] and $[\text{Sr}(\text{CH}_2\text{Ph})_2(\text{thf})]$ ^[S5] were prepared using literature procedures.

2 Synthetic Procedures and Characterizations

2.1 Synthesis of [(Me₄TACD)Sr(CH₂Ph)₂] (**1a**).

To a solution of [SrI₂(thf)] (827 mg, 2.00 mmol) in THF (7.5 mL) was added a solution of K(CH₂Ph) (521 mg, 4 mmol) in THF (5 mL) and the resulting suspension stirred for 2 h at room temperature. After centrifugation and filtration, the volume of the filtrate was reduced by two-thirds under reduced pressure and a solution of Me₄TACD (502 mg, 2.20 mmol) in THF (1 mL) added dropwise. The resulting suspension was stirred for 5 min, centrifuged and the precipitate isolated, washed with n-pentane (3 x 5 mL) and THF (2 x 2 mL) and dried *in vacuo* to give [(Me₄TACD)Sr(thf)(CH₂Ph)₂] as light orange microcrystals (850 mg, 1.70 mmol); yield: 85 %.

Anal. Calc. for C₂₆H₄₂N₄Sr (498.27 g mol⁻¹): C, 62.67; H, 8.50; N, 11.24. Found: C, 61.09; H, 8.33; N, 11.96 %.

Poor solubility in common solvents precluded NMR spectroscopic analysis.

Single crystals grew by layering a solution of Me₄TACD in THF on top of a solution of [Sr(CH₂Ph)₂(thf)] in THF at -40 °C.

2.2 Molecular Structure of [(Me₄TACD)Sr(CH₂Ph)₂(thf)] (**1**).

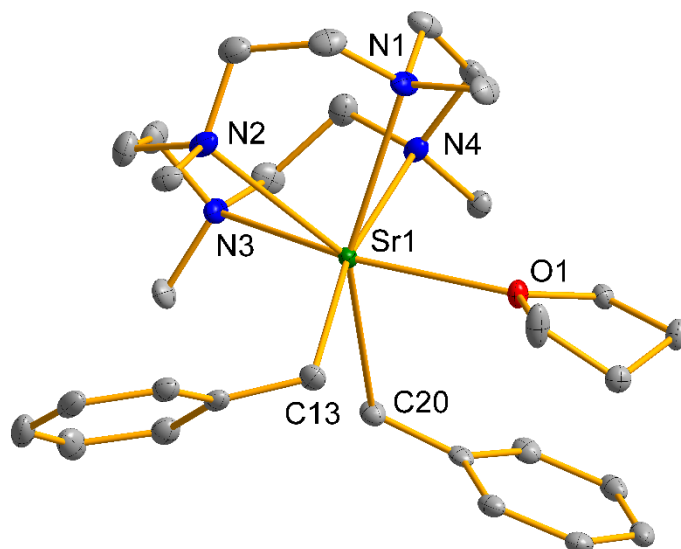


Figure S1: Molecular structure in solid state of **1**. Displacement parameters are shown with 30% probability; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and bond angles [°]: Sr1–N1 2.7868(18), Sr1–N2 2.8264(18), Sr1–N3 2.7982(15), Sr1–N4 2.7560(15), Sr1–O1 2.6662(12), Sr1–C13 2.8025(18), Sr1–C20 2.869(2). C13–Sr1–C20 89.14(6), C13–Sr1–O1 79.08(5), C20–Sr1–O1 84.89(6).

2.3 Synthesis of [(Me₄TACD)Sr(CH₂Ph)(thf)][B(C₆H₃-3,5-Me₂)₄] (**2**).

A solution of [(Me₄TACD)Sr(CH₂Ph)₂] (100 mg, 0.20 mmol) and [NEt₃H][B(C₆H₃-3,5-Me₂)₄] (106 mg, 0.20 mmol) in THF (4 mL) was stirred for 5 min at room temperature, filtered, and the volume of the filtrate reduced by half under reduced pressure. n-Pentane (2 mL) was added dropwise and the resulting suspension stirred for 10 min. The precipitate was isolated, washed with n-pentane (3 x 2 mL) and dried *in vacuo* to give [(Me₄TACD)Sr(CH₂Ph)(thf)][B(C₆H₃-3,5-Me₂)₄] as light orange microcrystals (165 mg, 0.18 mmol); yield: 91%.

Single crystals of THF-free [(Me₄TACD)Sr(CH₂Ph)][B(C₆H₃-3,5-Me₂)₄] (**2a**) grew from the reaction of [(Me₄TACD)Sr(CH₂Ph)₂] with [NEt₃H][B(C₆H₃-3,5-Me₂)₄] in THF upon concentration of the mixture *in vacuo*.

¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ = 1.46 (s, 2H, CH₂Ph), 1.74 – 1.80 (m, 4H, THF), 2.09 (s, 24H, Ar-(CH₃)₂), 1.82 – 2.24 (br. s, 8H, NCH₂), 2.26 (s, 12H, NCH₃), 2.27 – 2.84 (br. s, 8H, NCH₂), 3.59 – 3.63 (m, 4H, THF), 5.80 – 5.86 (m, 1H, *para*-Ph), 6.20 – 6.26 (m, 2H, *ortho*-Ph), 6.33 – 6.37 (m, 4H, *para*-C₆H₃), 6.52 – 6.61 (m, 2H, *meta*-Ph), 6.94 – 6.99 (m, 8H, *ortho*-C₆H₃) ppm.

¹³C{¹H} NMR (101 MHz, THF-*d*₈, 25 °C): δ = 22.4 (s, Ar-(CH₃)₂), 26.4 (s, THF), 45.2 (NCH₃), 46.8 (s, CH₂Ph), 54.2 (br. s, NCH₂), 68.3 (s, THF), 110.0 (s, *para*-Ph), 118.7 (s, *ortho*-Ph), 123.5 (s, *para*-C₆H₃), 129.3 (s, *meta*-Ph), 132.8 (q, ³J_{BC} = 2.7 Hz, *meta*-C₆H₃), 135.5 (*ortho*-C₆H₃), 159.8 (*ipso*-Ph), 165.6 (q, ¹J_{BC} = 49.3 Hz, *ipso*-C₆H₃) ppm.

¹¹B{¹H} NMR (128 MHz, THF-*d*₈, 25 °C): δ = -6.96 ppm.

Anal. Calc. for C₅₅H₇₉BN₄OSr (910.69 g mol⁻¹): C, 72.54; H, 8.74; N, 6.15. Found: C, 69.39; H, 8.34; N, 6.12 %.

2.4 NMR Spectra of $[(\text{Me}_4\text{TACD})\text{Sr}(\text{CH}_2\text{Ph})(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]$ (**2**).

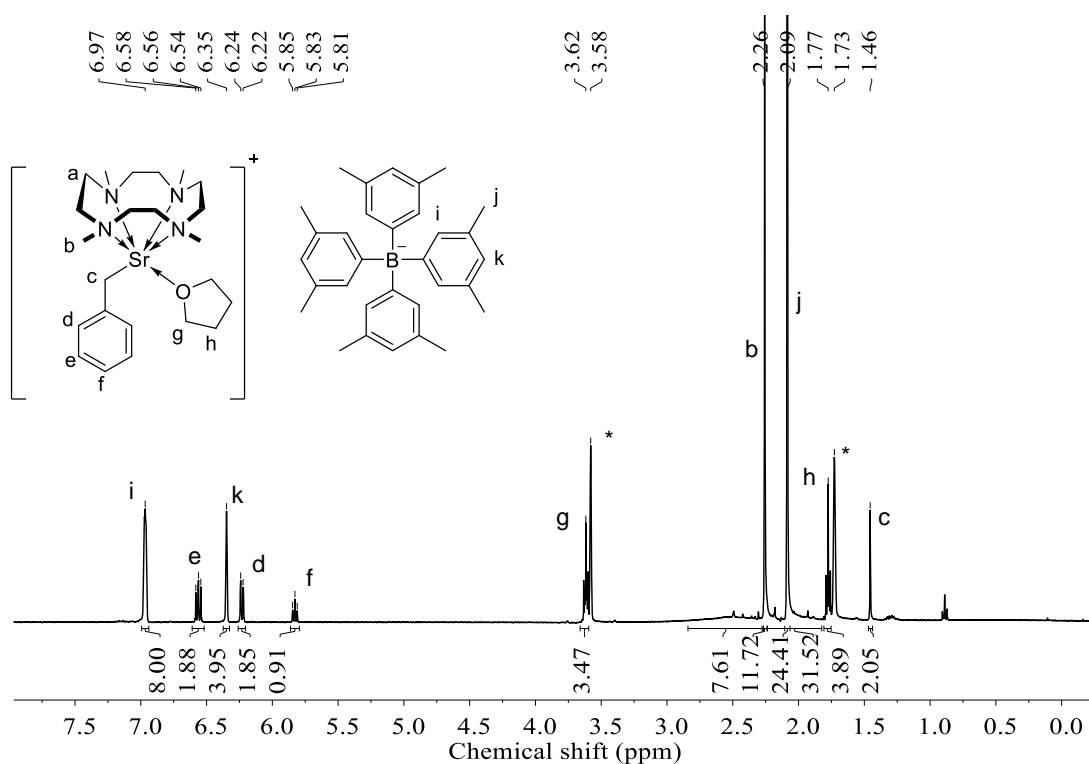


Figure S2: ^1H NMR spectrum (400 MHz, $\text{THF-}d_8$ (*), 25 °C) of $[(\text{Me}_4\text{TACD})\text{Sr}(\text{CH}_2\text{Ph})(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]$. (*) denotes residual proton resonances of $\text{THF-}d_8$.

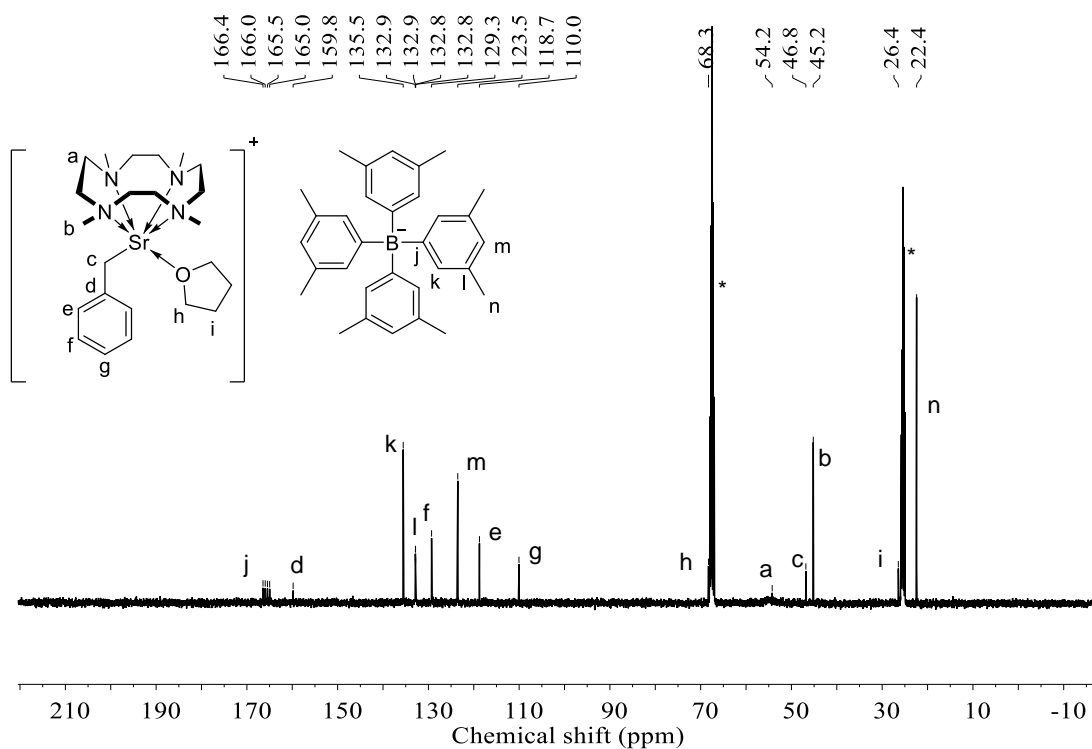


Figure S3: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, $\text{THF-}d_8$, 25 °C) of $[(\text{Me}_4\text{TACD})\text{Sr}(\text{CH}_2\text{Ph})(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]$. (*) denotes carbon resonances of $\text{THF-}d_8$.

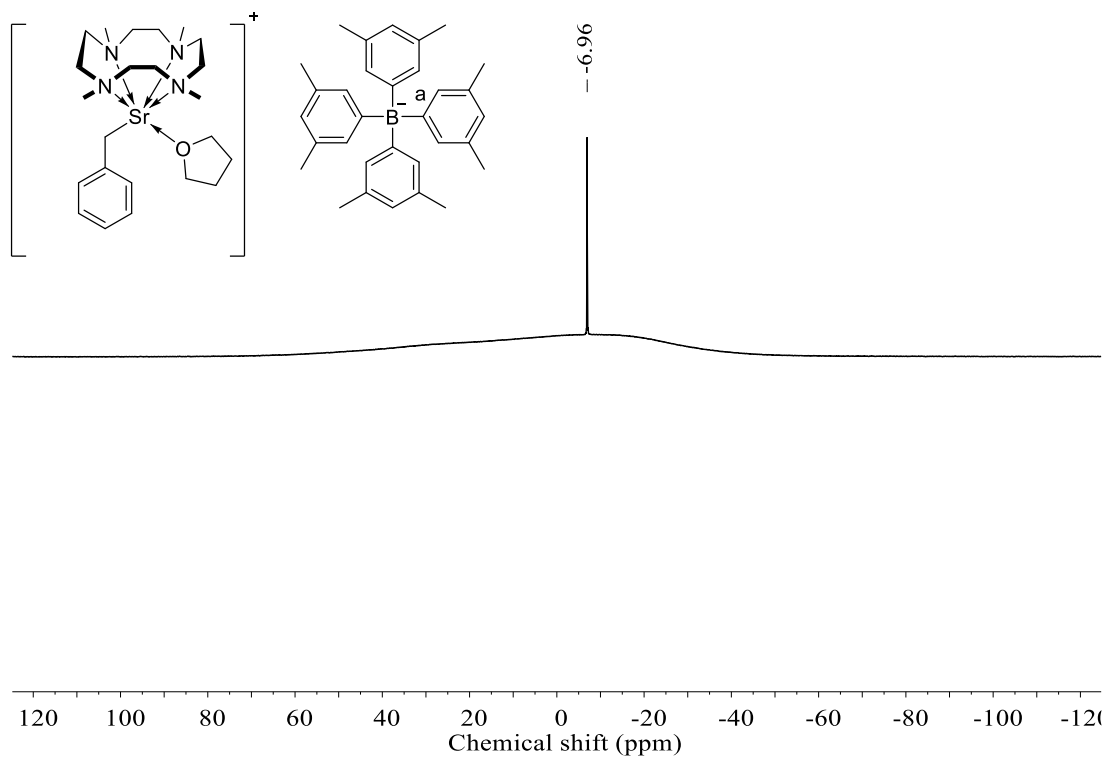


Figure S4: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (128 MHz, $\text{THF-}d_6$, 25 °C) of $[(\text{Me}_4\text{TACD})\text{Sr}(\text{CH}_2\text{Ph})(\text{thf})][\text{B}(\text{C}_6\text{H}_3-3,5-\text{Me}_2)_4]$.

2.5 Synthesis of [(Me₄TACD)Sr(thf)₂][B(C₆H₃-3,5-Me₂)₄]₂ (**3**).

A solution of [(Me₄TACD)Sr(CH₂Ph)₂] (25 mg, 0.05 mmol) and [NEt₃H][B(C₆H₃-3,5-Me₂)₄] (53 mg, 0.10 mmol) in THF (2 mL) was stirred for 5 min at room temperature, filtered, and the volume of the filtrate reduced by half under reduced pressure. n-Pentane (2 mL) was added dropwise and the resulting suspension stirred for 5 min. The precipitate was isolated, washed with n-pentane (3 x 2 mL) and dried *in vacuo* to give [(Me₄TACD)Sr(thf)₂][B(C₆H₃-3,5-Me₂)₄]₂ as a colorless powder (60 mg, 4.5·10⁻⁶ mol); yield: 91%.

¹H NMR (400 MHz, THF-*d*₆, 25 °C): δ = 1.74 – 1.80 (m, 8H, THF), 2.09 (s, 48H, Ar-(CH₃)₂), 1.85 – 3.05 (br. s, 16H, NCH₂), 2.12 (s, 12H, NCH₃), 3.59 – 3.63 (m, 8H, THF), 6.34 – 6.40 (m, 8H, *para*-C₆H₃), 6.94 – 7.00 (m, 16H, *ortho*-C₆H₃) ppm.

¹³C{¹H} NMR (101 MHz, THF-*d*₆, 25 °C): δ = 22.5 (s, Ar-(CH₃)₂), 26.5 (s, THF), 44.9 (NCH₃), 55.8 (br. s, NCH₂), 68.4 (s, THF), 123.7 (s, *para*-C₆H₃), 133.1 (q, ³J_{BC} = 2.7 Hz, *meta*-C₆H₃), 135.6 (*ortho*-C₆H₃), 165.8 (q, ¹J_{BC} 49.3 Hz, *ipso*-C₆H₃) ppm.

¹¹B{¹H} NMR (128 MHz, THF-*d*₆, 25 °C): δ = -8.83 ppm.

Anal. Calc. for C₈₄H₁₁₆B₂N₄O₂Sr (1332.12 g mol⁻¹): C, 76.25; H, 8.84; N, 4.23. Found: C, 75.76; H, 8.89; N, 4.60%.

2.6 NMR spectra of $[(\text{Me}_4\text{TACD})\text{Sr}(\text{thf})_2][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$ (**3**).

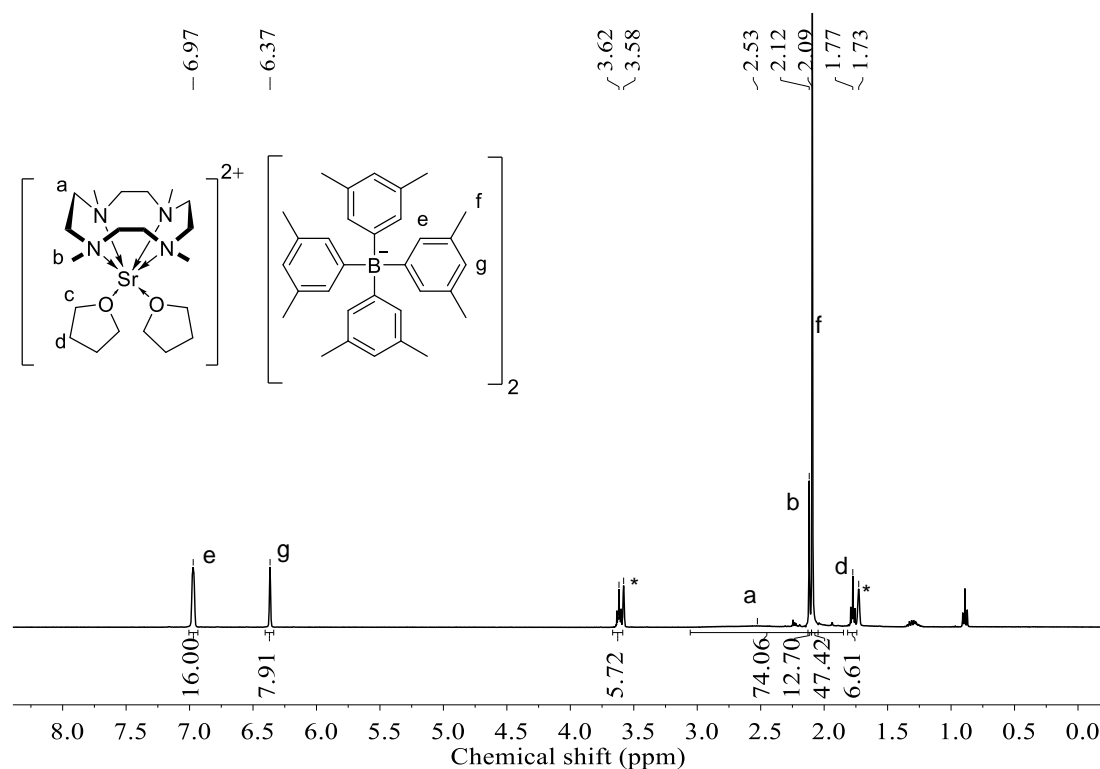


Figure S5: ^1H NMR spectrum (400 MHz, THF-d_8 , 25 °C) of $[(\text{Me}_4\text{TACD})\text{Sr}(\text{thf})_2][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$. (*) denotes residual proton resonances of THF-d_8 .

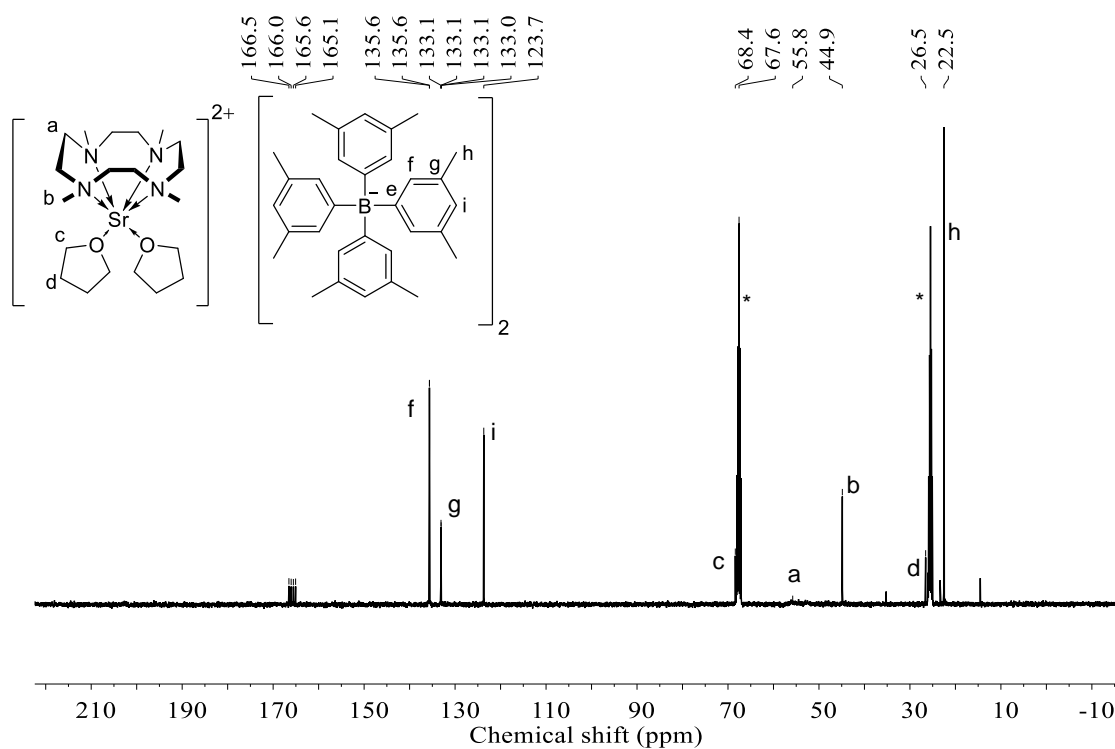


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, THF-d_8 , 25 °C) of $[(\text{Me}_4\text{TACD})\text{Sr}(\text{thf})_2][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$. (*) denotes carbon resonances of THF-d_8 .

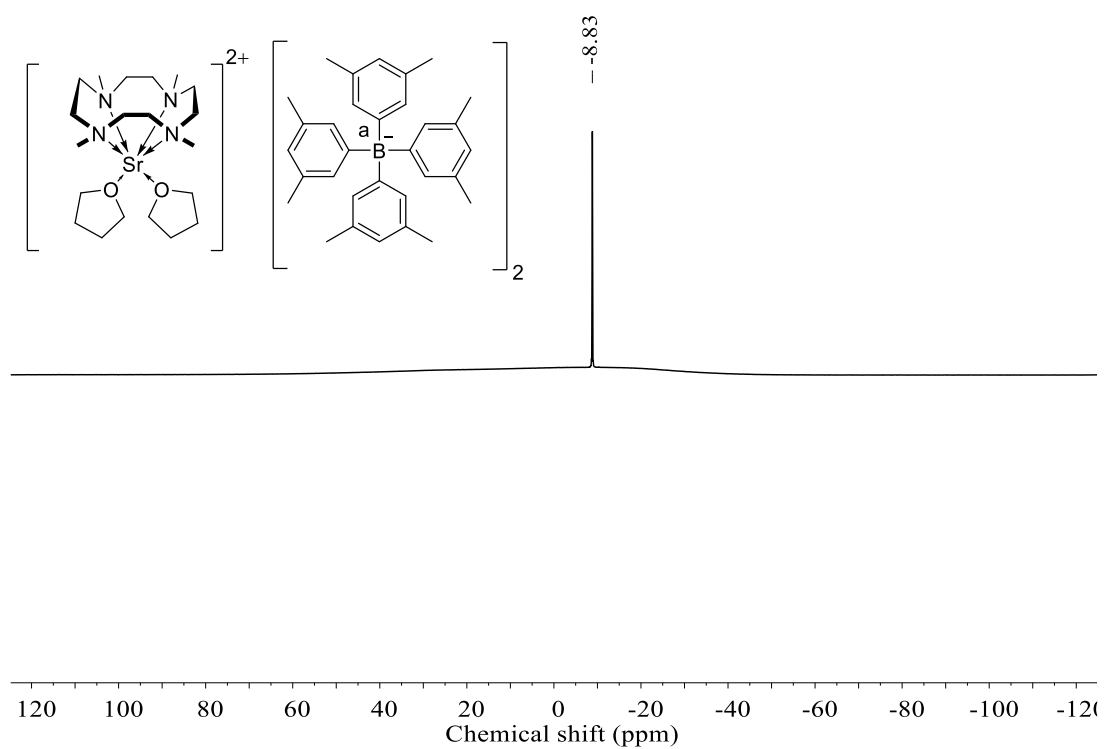


Figure S7: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (128 MHz, $\text{THF-}d_6$, 25 °C) of $[(\text{Me}_4\text{TACD})\text{Sr}(\text{thf})_2][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$.

2.7 Synthesis of [(Me₄TACD)Ca(thf)₂][B(C₆H₃-3,5-Me₂)₄]₂ (**3-Ca**).

A solution of [(Me₄TACD)Ca(CH₂Ph)₂] (45 mg, 0.10 mmol) and [NEt₃H][B(C₆H₃-3,5-Me₂)₄] (106 mg, 0.20 mmol) in THF (2 mL) was stirred for 16 h at room temperature. The resulting clear solution was filtered, the volume of the filtrate reduced by half under reduced pressure, layered with n-pentane (2 mL) and stored at -40 °C. After 24 hours colorless crystals grew that were isolated, washed with n-pentane (3 x 2 mL) and dried *in vacuo* to give [(Me₄TACD)Ca(thf)₂][B(C₆H₃-3,5-Me₂)₄]₂ as colorless crystals (115 mg, 0.09 mmol); yield: 90%.

¹H NMR (400 MHz, THF-*d*₆, 25 °C): δ = 1.74 – 1.80 (m, 8H, THF), 2.09 (s, 12H, NCH₃), 2.10 (s, 48H, Ar-(CH₃)₂), 2.02 – 2.23 (br. s, 8H, NCH₂), 2.29 – 2.58 (br. s, 8H, NCH₂), 3.59 – 3.63 (m, 8H, THF), 6.36 – 6.40 (m, 8H, *para*-C₆H₃), 6.96 – 7.00 (m, 16H, *ortho*-C₆H₃) ppm.

¹³C{¹H} NMR (101 MHz, THF-*d*₆, 25 °C): δ = 22.4 (s, Ar-(CH₃)₂), 26.4 (s, THF), 44.4 (NCH₃), 54.0 (br. s, NCH₂), 68.3 (s, THF), 123.7 (s, *para*-C₆H₃), 133.1 (q, ³J_{BC} = 2.7 Hz, *meta*-C₆H₃), 135.5 (*ortho*-C₆H₃), 165.8 (q, ¹J_{BC} 49.3 Hz, *ipso*-C₆H₃) ppm.

¹¹B{¹H} NMR (128 MHz, THF-*d*₆, 25 °C): δ = -7.00 ppm.

Anal. Calc. for C₈₄H₁₁₆B₂N₄O₂Ca (1275.58 g mol⁻¹): C, 79.10; H, 9.17; N, 4.73. Found: C, 78.40; H, 9.01; N, 4.78%.

2.8 NMR spectra of $[(\text{Me}_4\text{TACD})\text{Ca}(\text{thf})_2][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$ (**3-Ca**).

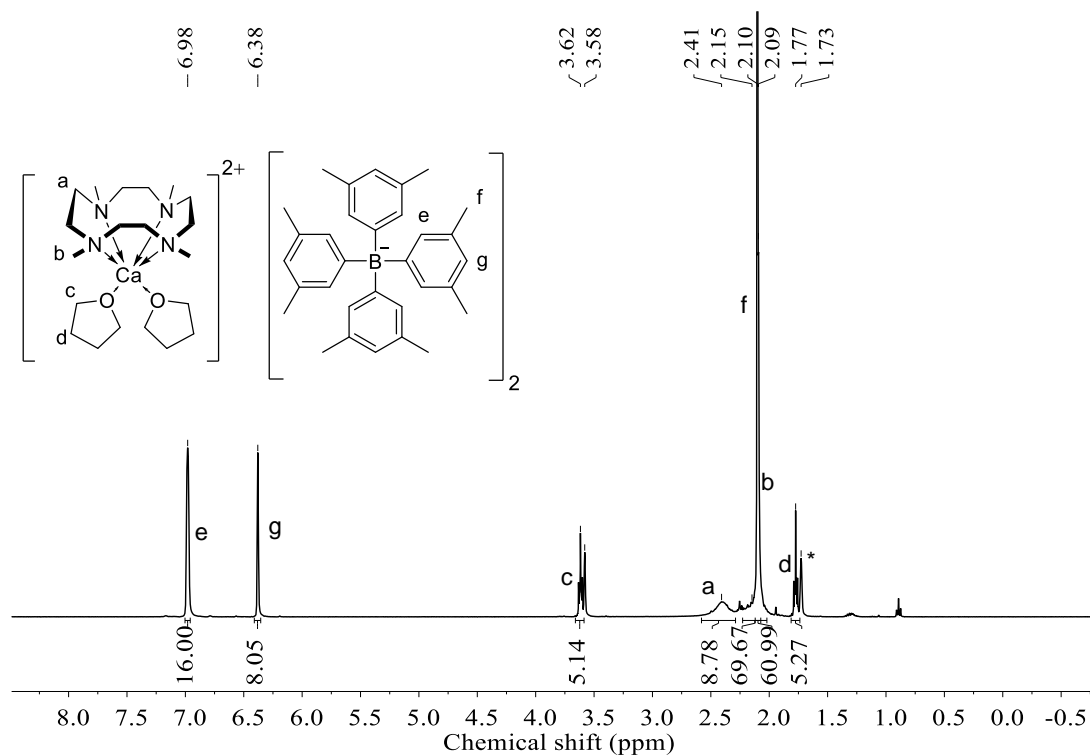


Figure S8: ^1H NMR spectrum (400 MHz, $\text{THF-}d_6$, 25 $^\circ\text{C}$) of $[(\text{Me}_4\text{TACD})\text{Ca}(\text{thf})_2][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$. (*) denotes residual proton resonances of $\text{THF-}d_6$.

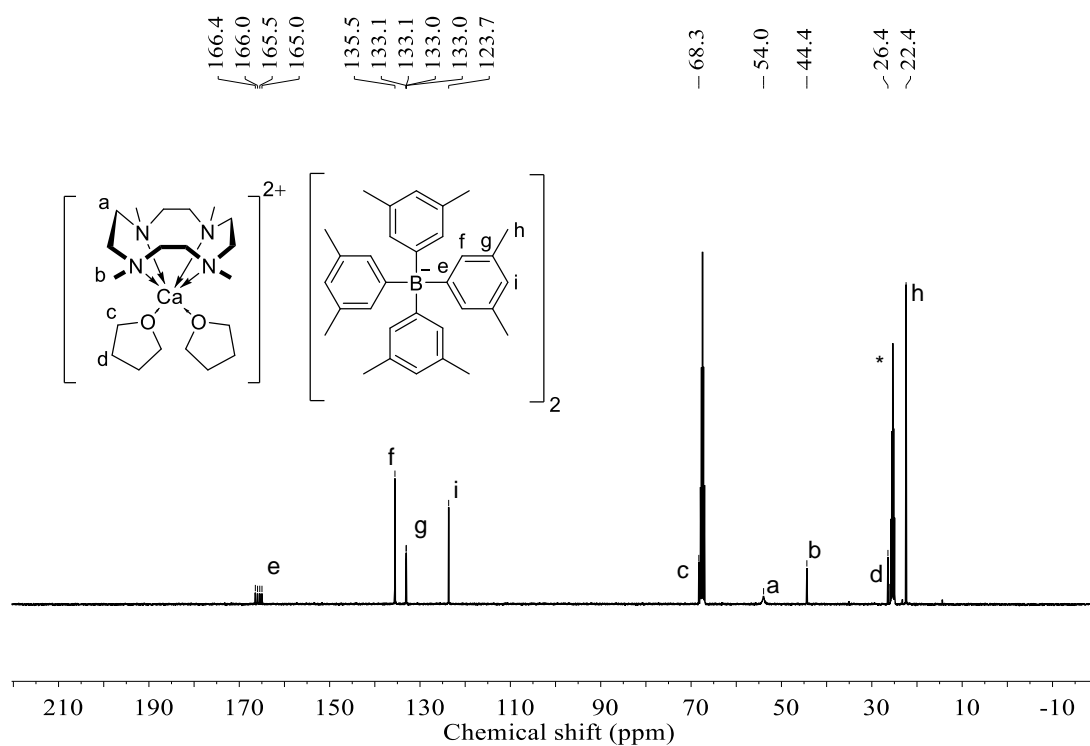


Figure S9: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, $\text{THF-}d_6$, 25 $^\circ\text{C}$) of $[(\text{Me}_4\text{TACD})\text{Ca}(\text{thf})_2][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$. (*) denotes carbon resonances of $\text{THF-}d_6$.

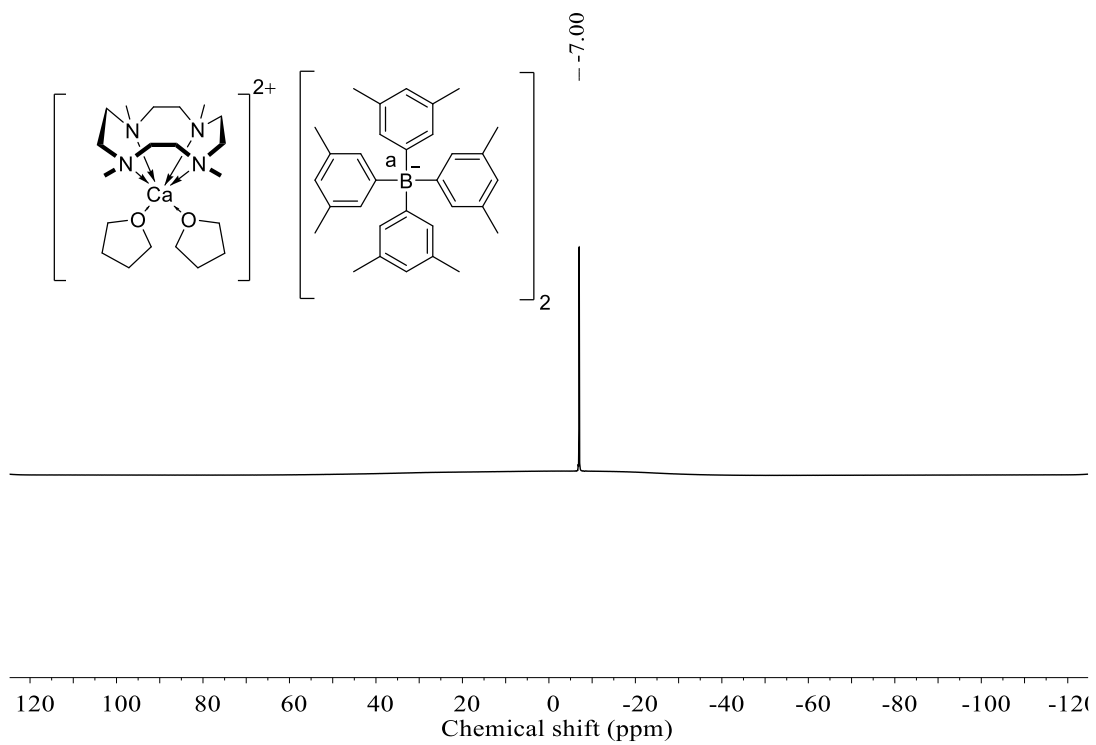


Figure S10: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (128 MHz, $\text{THF-}d_6$, 25 °C) of $[(\text{Me}_4\text{TACD})\text{Ca}(\text{thf})_2][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$.

2.9 Synthesis of $[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-H})_4(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ (**4**).

A suspension of $[(\text{Me}_4\text{TACD})\text{Sr}(\text{CH}_2\text{Ph})_2]$ (50 mg, 0.1 mmol) and $[(\text{Me}_4\text{TACD})\text{Sr}(\text{thf})(\text{CH}_2\text{Ph})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]$ (182 mg, 0.2 mmol) in THF (6 mL) was charged with H_2 (1 bar) by applying three “freeze-pump-thaw” cycles and stirred for 30 min at room temperature. The resulting clear solution was filtered, the volume reduced to half under reduced pressure, layered with n-pentane (3 mL) and stored at -40°C for 16 h. The resulting colorless crystals were isolated, washed with n-pentane (3 x 2 mL) and carefully dried. $[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-H})_4(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ was isolated as colorless crystals (145 mg, 0.08 mmol); yield: 77%.

$[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-D})_4(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ (**4-d₄**) was prepared analogously using D_2 .

^1H NMR (400 MHz, $\text{THF-}d_6$, 25°C): $\delta = 1.74 - 1.80$ (m, 8H, THF), 1.96 – 2.35 (br. s, 16H, NCH_2), 2.09 (s, 48H, $\text{Ar-}(\text{CH}_3)_2$), 2.30 (br. s, 12H, NCH_3), 2.35 – 2.77 (br. s, 32H, NCH_2), 2.51 (s, 24H, NCH_3), 3.59 – 3.63 (m, 8H, THF), 5.99 (s, 4H, Sr-H), 6.32 – 6.36 (m, 8H, *para*- C_6H_3), 6.95 – 6.99 (m, 16H, *ortho*- C_6H_3) ppm.

^2H NMR (61 MHz, $\text{THF-}d_6$, 25°C): $\delta = 6.08$ ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{THF-}d_6$, 25°C): $\delta = 22.6$ (s, $\text{Ar-}(\text{CH}_3)_2$), 26.6 (s, THF), 44.2 (NCH_3), 45.7 (NCH_3), 54.7 (br. s, NCH_2), 68.4 (s, THF), 123.6 (s, *para*- C_6H_3), 132.9 (q, $^3J_{\text{BC}} = 2.7$ Hz, *meta*- C_6H_3), 135.7 (*ortho*- C_6H_3), 165.8 (q, $^1J_{\text{BC}} = 49.3$ Hz, *ipso*- C_6H_3) ppm.

$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, $\text{THF-}d_6$, 25°C): $\delta = -6.95$ ppm.

Anal. Calc. for $\text{C}_{104}\text{H}_{168}\text{B}_2\text{N}_{12}\text{OSr}_3$ (1887.05 g mol $^{-1}$): C, 66.20; H, 8.97; N, 8.91. Found: C, 63.59; H, 8.62; N, 8.28 %.

2.10 NMR Spectra of $[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-H})_4(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ (**4**).

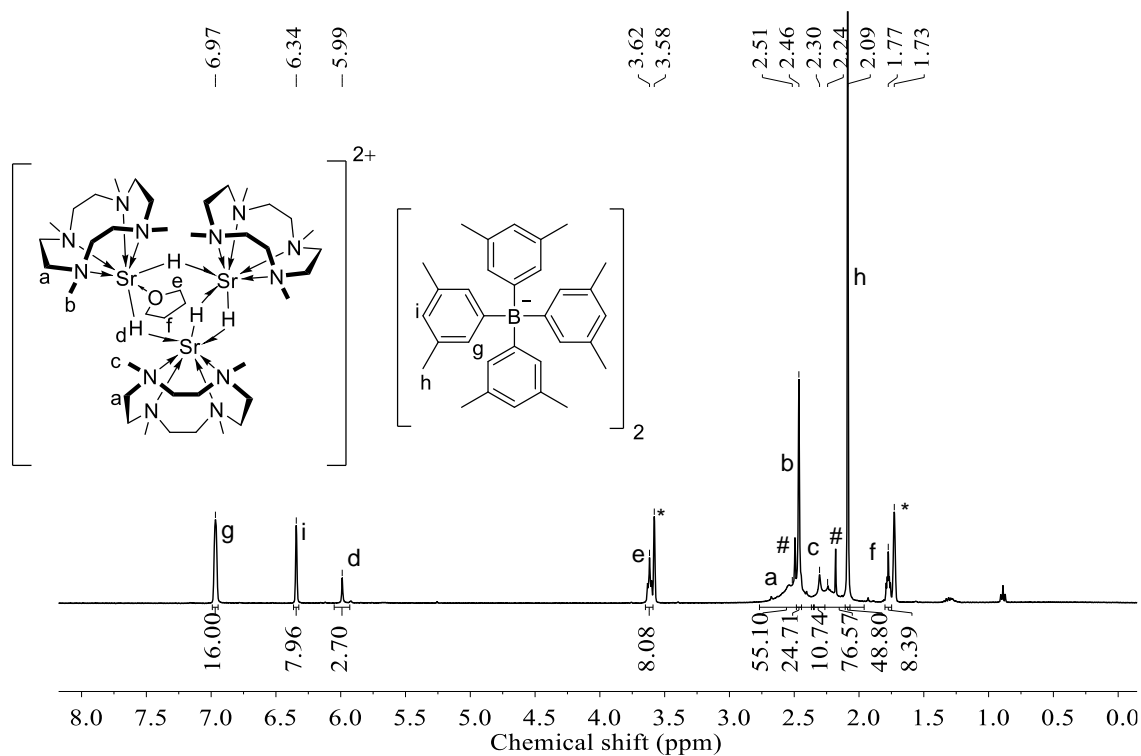


Figure S11: ^1H NMR spectrum (400 MHz, $\text{THF-}d_8$, 25 °C) of $[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-H})_4(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$. (*) denotes residual proton resonances of $\text{THF-}d_8$; #denotes resonances due to free Me_4TACD .

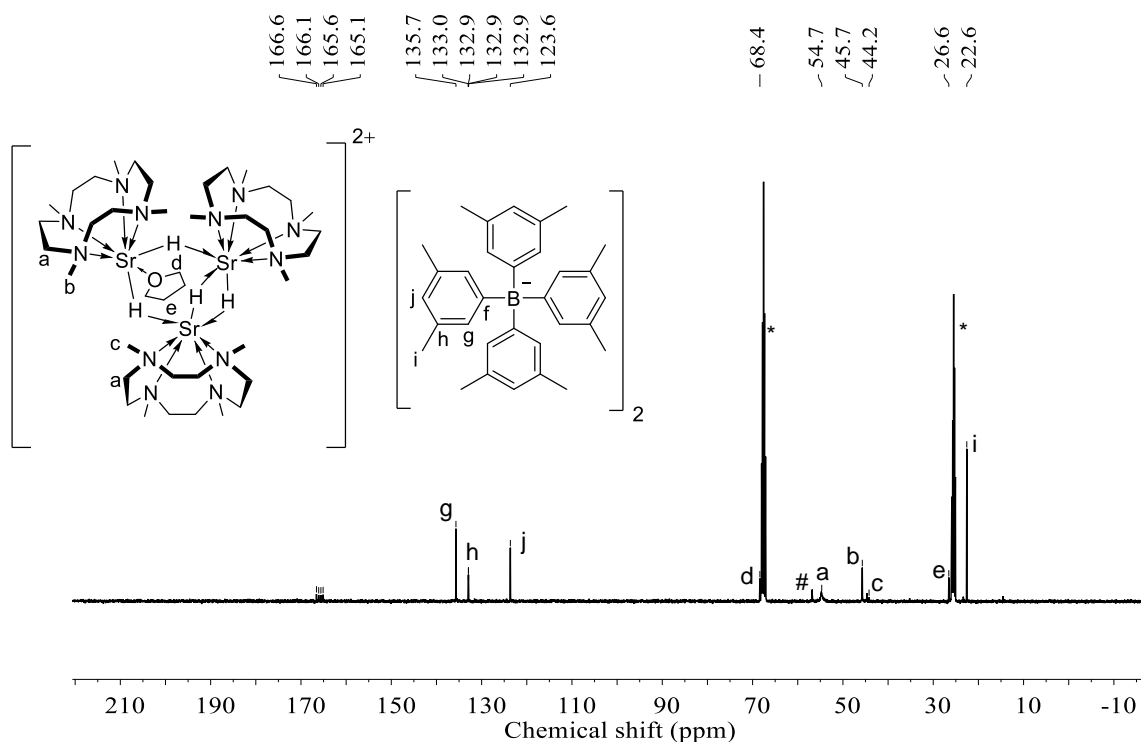


Figure S5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, $\text{THF-}d_8$, 25 °C) of $[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-H})_4(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$. (*) denotes carbon resonances of $\text{THF-}d_8$. #denotes resonances due to free Me_4TACD .

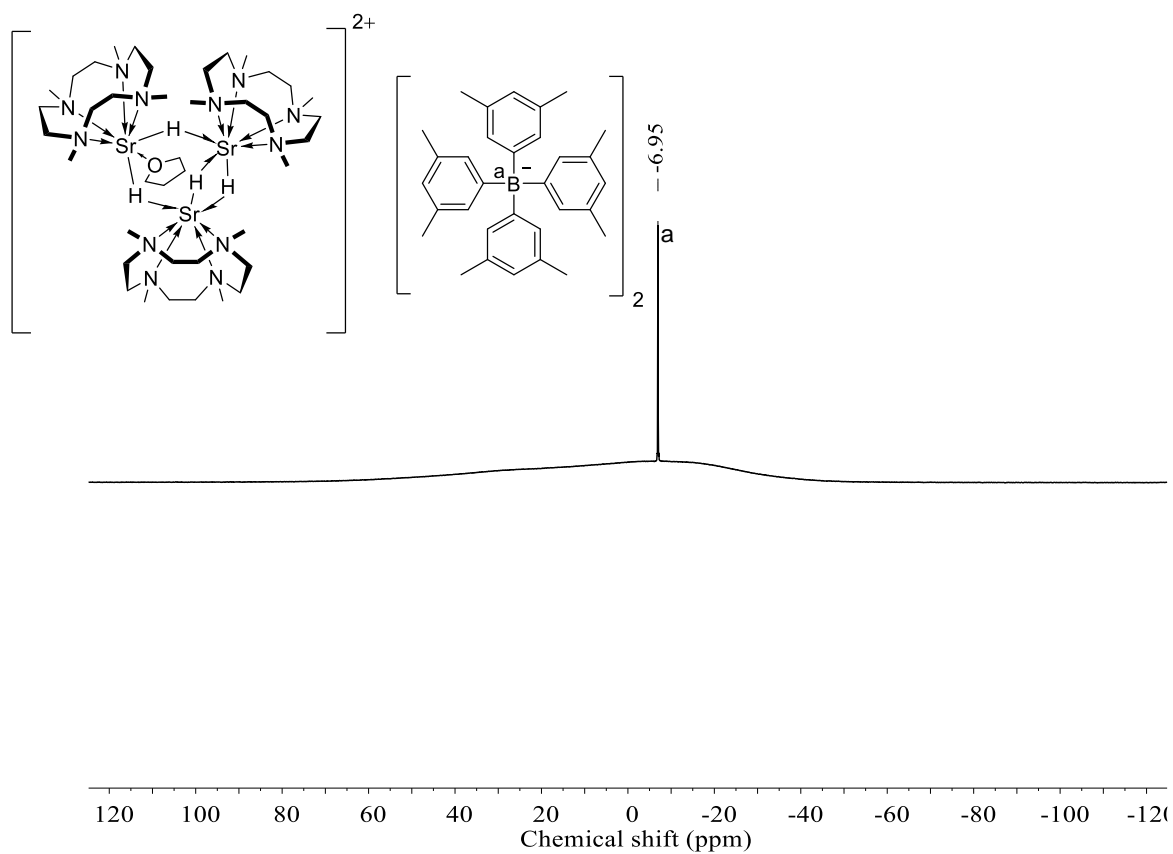


Figure S6: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (128 MHz, $\text{THF-}d_6$, 25 °C) of $[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-H})_4(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$.

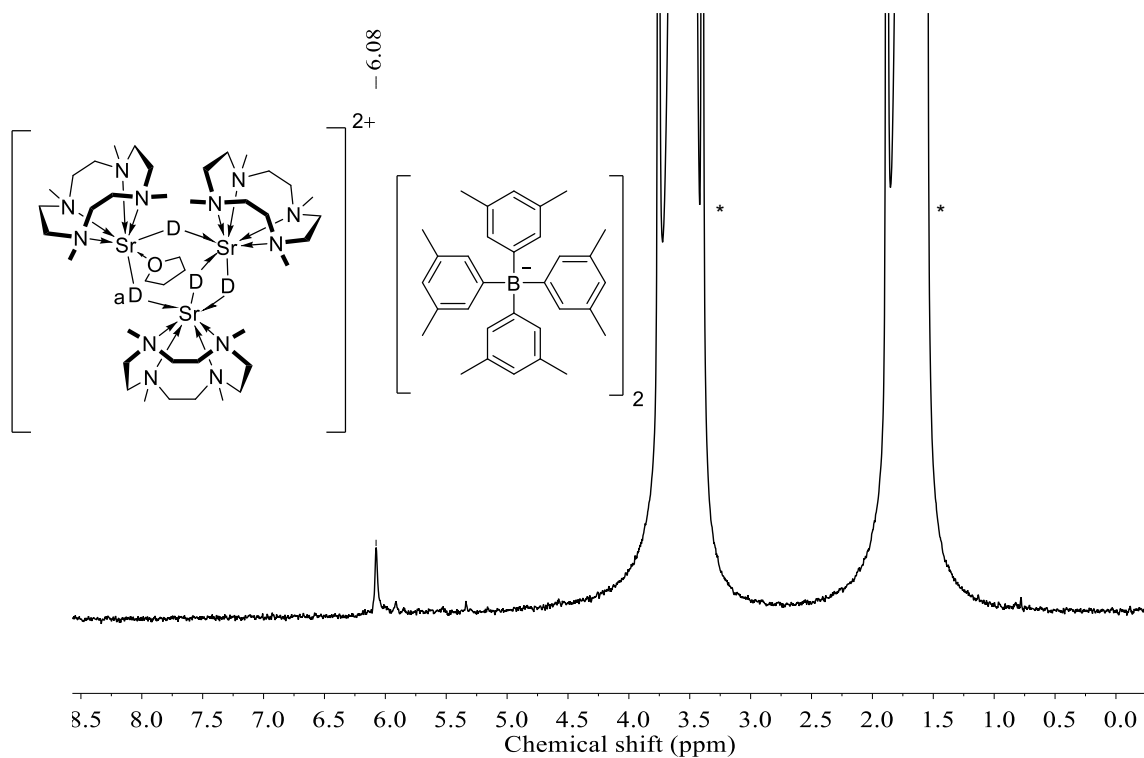


Figure S14: ^2H NMR spectrum (61 MHz, $\text{THF-}d_6$, 25 °C) of $[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-D})_4(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$. (*) denotes resonances of $\text{THF-}d_6$.

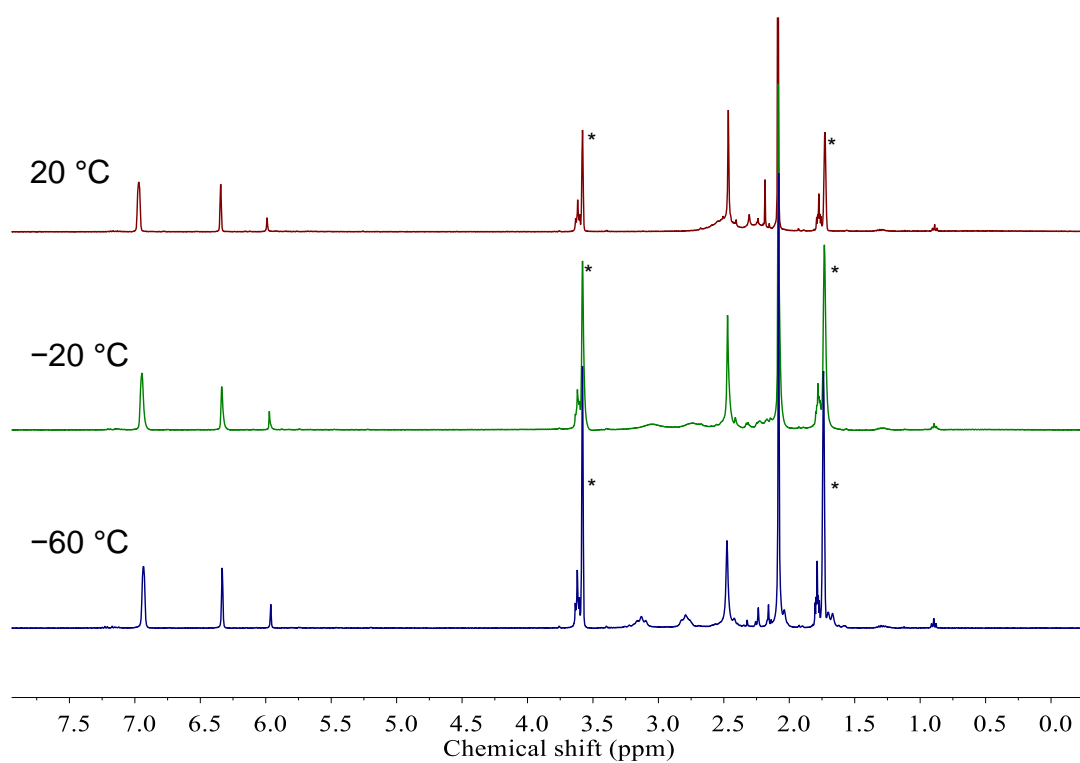


Figure S7: Variable-temperature ¹H NMR spectra of [(Me₄TACD)₃Sr₃(μ-H)₄(thf)][B(C₆H₃-3,5-Me₂)₄]₂. (*) denotes resonances of THF-*d*₈.

2.11 Molecular Structure of $[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-H})_4(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ (**4**).

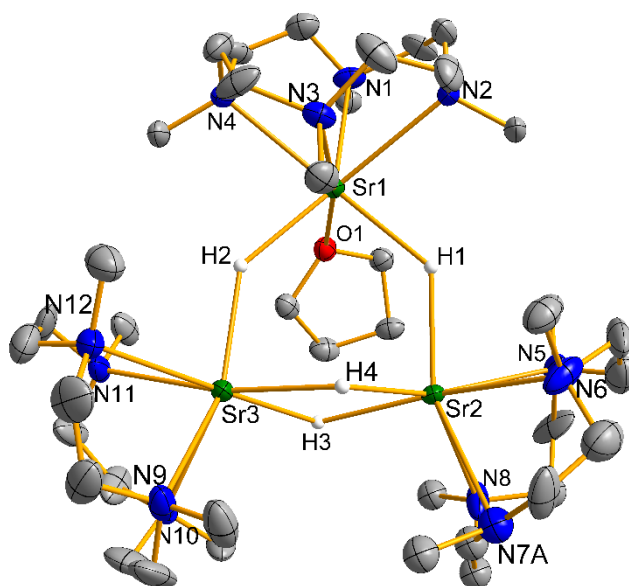


Figure S16: Molecular structure of one of the crystallographically independent molecular cations in the solid state of **4**. Displacement parameters are shown with 30% probability; hydrogen atoms except the hydrides are omitted for clarity. Disordered atoms are only shown with one split position. Selected interatomic distances [\AA]: Sr1 \cdots Sr2 4.4248(6), Sr1 \cdots Sr3 4.5701(6), Sr2 \cdots Sr3 3.9555(6), Sr1–N1 2.851(5), Sr1–N2 2.832(4), Sr1–N3 2.692(5), Sr1–N4 2.773(4), Sr2–N5 2.865(5), Sr2–N6 2.768(6), Sr2–N7A 3.03(2), Sr2–N7B 2.724(9), Sr2–N8 2.819(5), Sr3–N9 2.810(5), Sr3–N10 2.798(5), Sr3–N11 2.825(5), Sr3–N12 2.820(5), Sr1–O1 2.600(4), Sr1–H1 2.427(17), Sr1–H2 2.435(17), Sr2–H1 2.435(17), Sr2–H3 2.438(18), Sr2–H4 2.448(18), Sr3–H2 2.433(16), Sr3–H3 2.435(17), Sr3–H4 2.458(18).

2.12 Synthesis of $[(\text{Me}_4\text{TACD})_2\text{CaSr}(\mu\text{-H})_2(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ (**5**).

A suspension of $[(\text{Me}_4\text{TACD})\text{Sr}(\text{CH}_2\text{Ph})(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]$ (182 mg, 0.20 mmol) and $[(\text{Me}_4\text{TACD})\text{Ca}(\text{thf})(\text{CH}_2\text{Ph})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]$ (172 mg, 0.20 mmol) in THF (4 mL) was charged with H_2 (1 bar) by applying three “freeze-pump-thaw” cycles and stirred for 20 min at room temperature until a clear solution was obtained. Stirring was turned off and colorless crystals precipitated from the reaction mixture within 16 h. The crystals were isolated and washed with n-pentane (3 x 2 mL). $[(\text{Me}_4\text{TACD})_2\text{CaSr}(\mu\text{-H})_2(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ was isolated as colorless crystals (260 mg, 0.17 mmol); yield: 85%.

$[(\text{Me}_4\text{TACD})_2\text{CaSr}(\mu\text{-D})_2(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ (**5-d₂**) was prepared analogously using D_2 .

5 dissociates in solution to give several undefined strontium hydride species as well as $[(\text{Me}_4\text{TACD})_2\text{Ca}_2(\mu\text{-H})_2][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ and $[(\text{Me}_4\text{TACD})\text{Ca}_2(\mu\text{-H})_3][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]$ in addition to **5**. The NMR spectroscopic data assigned to **5** are given below.

^1H NMR (400 MHz, $\text{THF-}d_8$, 25 °C): δ = 1.74 – 1.80 (m, 8H, THF), 2.14 – 2.31 (br. s, 16H, NCH_2), 2.09 (s, 48H, $\text{Ar}(\text{CH}_3)_2$), 2.29 (s, 12H, NCH_3), 2.35 (s, 12H, NCH_3), 2.41 – 2.62 (br. s, 16H, NCH_2), 3.59 – 3.63 (m, 8H, THF), 5.10 (s, 2H, CaSr-H), 6.34 – 6.38 (m, 8H, *para*- C_6H_3), 6.95 – 6.99 (m, 16H, *ortho*- C_6H_3) ppm.

^2H NMR (61 MHz, $\text{THF-}d_8$, 25 °C): δ = 5.18 ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{THF-}d_8$, 25 °C): δ = 22.5 (s, $\text{Ar}(\text{CH}_3)_2$), 26.6 (s, THF), 44.6 (NCH_3), 44.6 (NCH_3), 53.9 (br. s, NCH_2), 54.4 (br. s, NCH_2), 68.4 (s, THF), 123.7 (s, *para*- C_6H_3), 133.0 (q, $^3J_{\text{BC}} = 2.7$ Hz, *meta*- C_6H_3), 135.7 (*ortho*- C_6H_3), 165.8 (q, $^1J_{\text{BC}} = 49.3$ Hz, *ipso*- C_6H_3) ppm.

$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, $\text{THF-}d_8$, 25 °C): δ = -6.96 ppm.

Anal. Calc. for $\text{C}_{92}\text{H}_{138}\text{B}_2\text{CaN}_8\text{OSr}$ (1521.49 g mol⁻¹): C, 72.63; H, 9.14; N, 7.36. Found: C, 71.09; H, 9.09; N, 7.04 %.

2.13 NMR spectra of $[(\text{Me}_4\text{TACD})_2\text{CaSr}(\mu\text{-H})_2(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ (**5**)

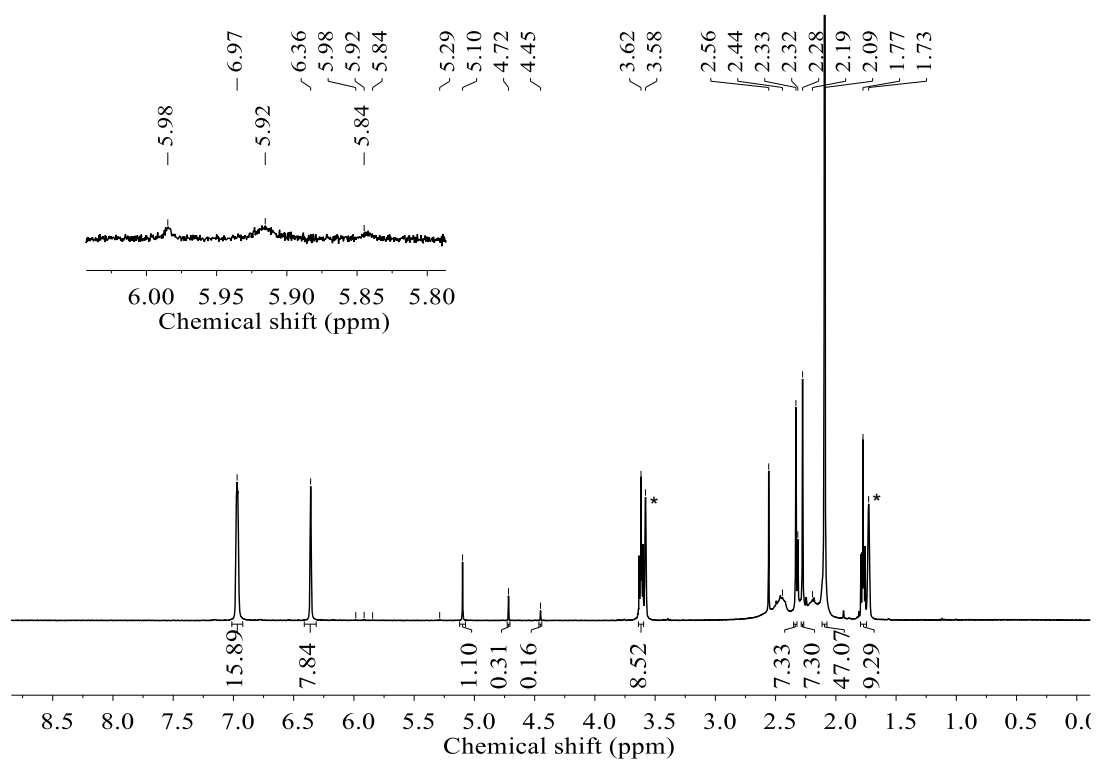


Figure S8: ^1H NMR spectrum (400 MHz, $\text{THF-}d_8$, 25 °C) of $[(\text{Me}_4\text{TACD})_2\text{CaSr}(\mu\text{-H})_2(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$. (*) denotes residual proton resonances of $\text{THF-}d_8$.

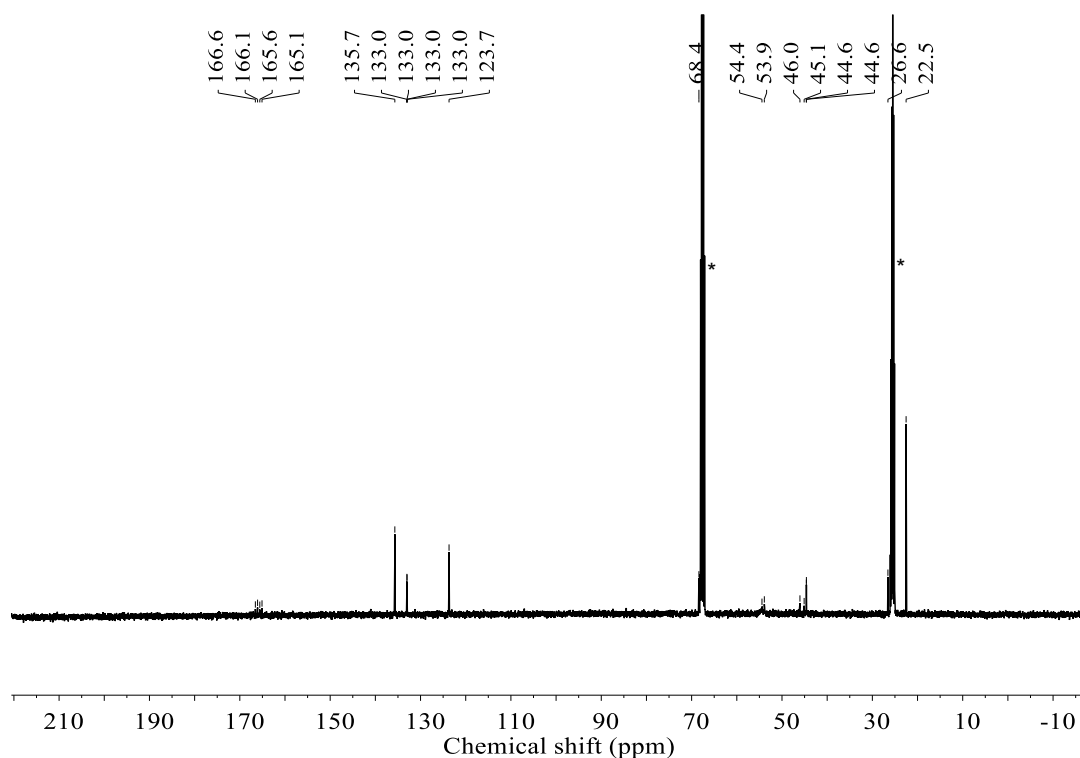


Figure S9: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, $\text{THF-}d_8$, 25 °C) of $[(\text{Me}_4\text{TACD})_2\text{CaSr}(\mu\text{-H})_2(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$. (*) denotes carbon resonances of $\text{THF-}d_8$.

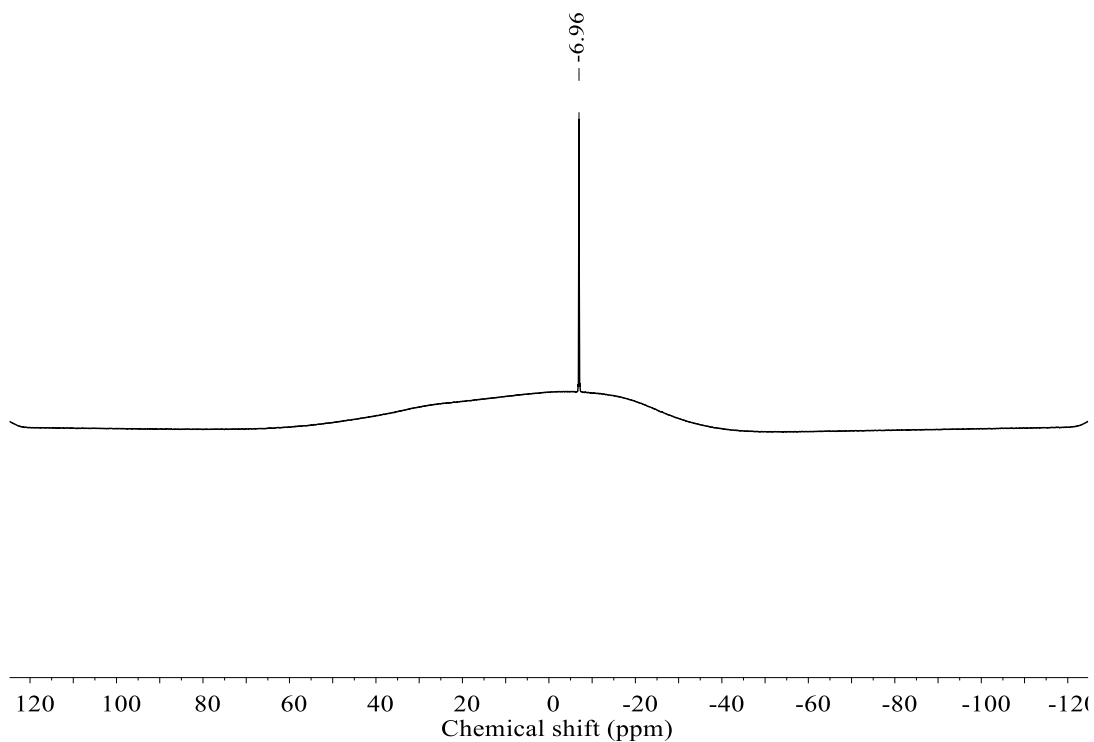


Figure S10: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (128 MHz, $\text{THF-}d_8$, 25 °C) of $[(\text{Me}_4\text{TACD})_2\text{CaSr}(\mu\text{-H})_2(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$.

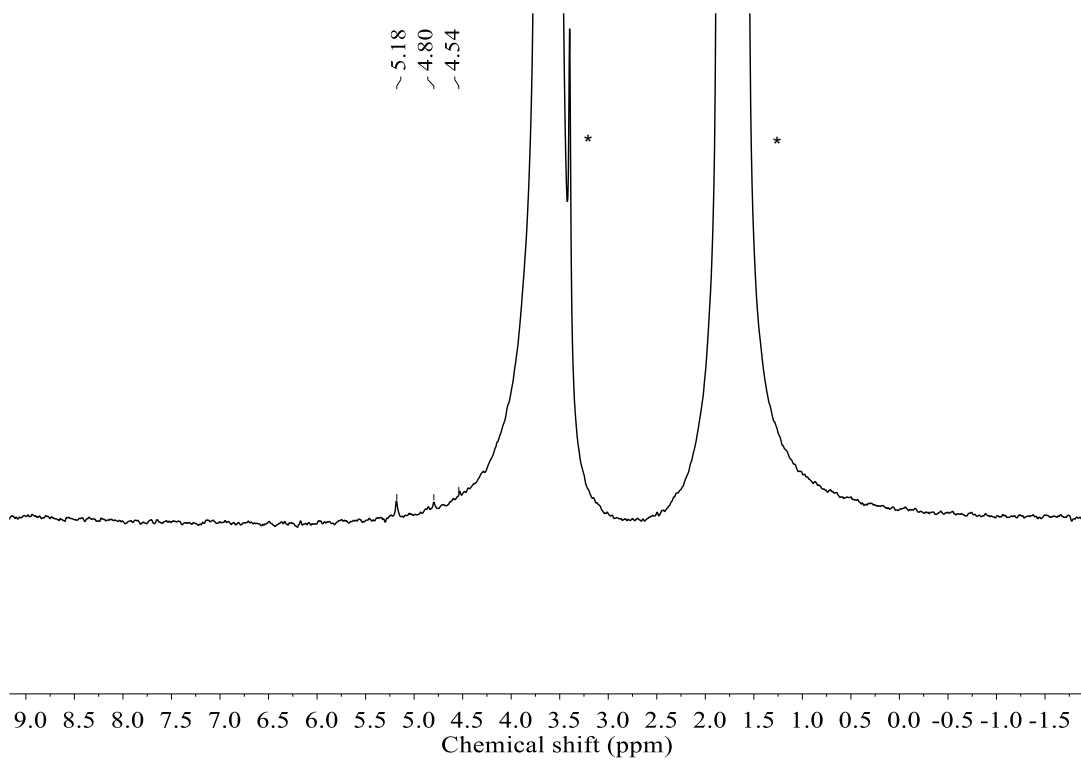


Figure S11: ^2H NMR spectrum (61 MHz, $\text{THF-}d_8$, 25 °C) of $[(\text{Me}_4\text{TACD})_2\text{CaSr}(\mu\text{-D})_2(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$. (*) denotes resonances of $\text{THF-}d_8$.

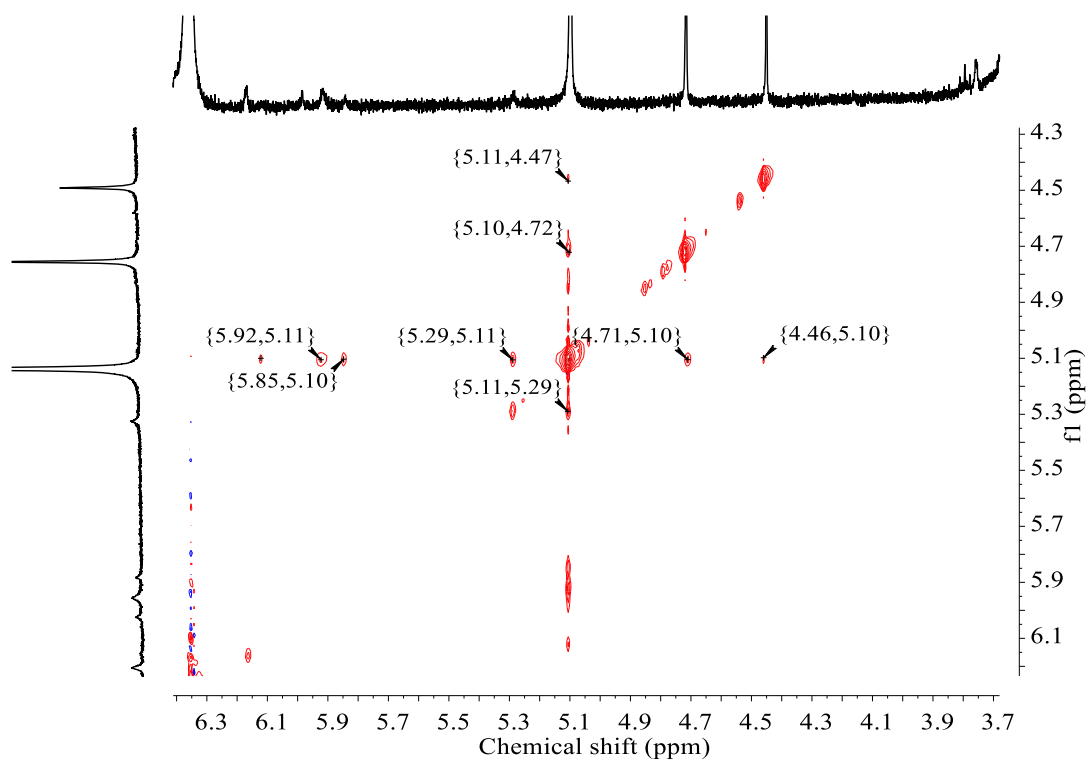


Figure S12: Cutout of the hydride region of the ^1H - ^1H EXSY NMR spectrum (400 MHz, $\text{THF-}d_6$, 25 $^\circ\text{C}$) of $[(\text{Me}_4\text{TACD})_2\text{CaSr}(\mu\text{-H})_2(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$.

2.14 Molecular Structure of $[(\text{Me}_4\text{TACD})_2\text{CaSr}(\mu\text{-H})_2(\text{thf})][\text{B}(\text{C}_6\text{H}_3\text{-3,5-Me}_2)_4]_2$ (**5**).

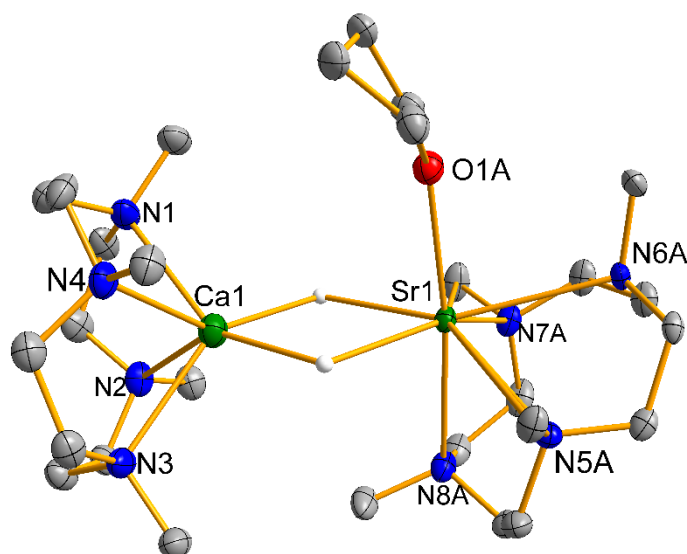


Figure S13: Molecular structure of the molecular dication of **5** in the solid state. Displacement parameters are shown with 30% probability; hydrogen atoms except of the hydride ligands are omitted for clarity. Disordered atoms are only shown with one split position. The atoms of the coordinated and disordered thf ligand are only shown with one split position. Selected interatomic distances [Å]: Ca1... Sr1/Ca2 3.7095(5), Ca1–N1 2.545(2), Ca1–N2 2.590(2), Ca1–N3 2.545(2), Ca1–N4 2.548(2), Sr1/Ca2–O1A 2.491(9), Sr1/Ca2–N5A 2.666(4), Sr1/Ca2–N6A 2.823(6), Sr1/Ca2–N7A 2.666(3), Sr1/Ca2–N8A 2.704(3), Ca1–H1 2.22(3), Ca1–H2 2.24(3), Sr1/Ca2–H1 2.40(3), Sr1/Ca2–H2 2.42(3).

3 Reactivity Studies

3.1 Reaction of **1a** with H₂ (1 bar).

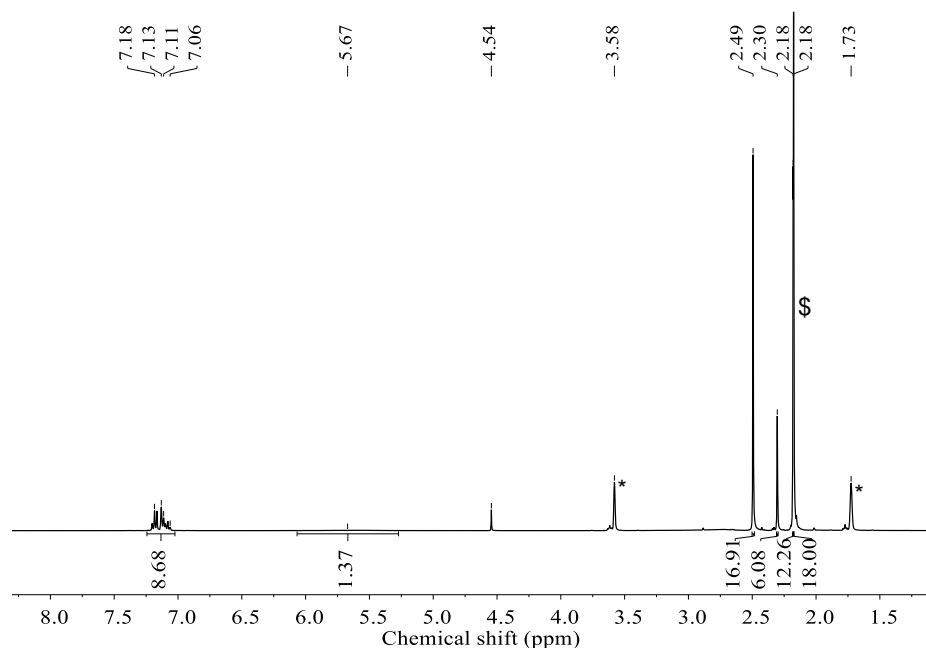


Figure S14: *In-situ* NMR spectrum of the reaction of **1a** with H₂ (1 bar) after 30 min in THF-*d*₈ (*) with hexamethylbenzene (\$) as internal standard.

3.2 Variation of stoichiometry in strontium hydride synthesis.

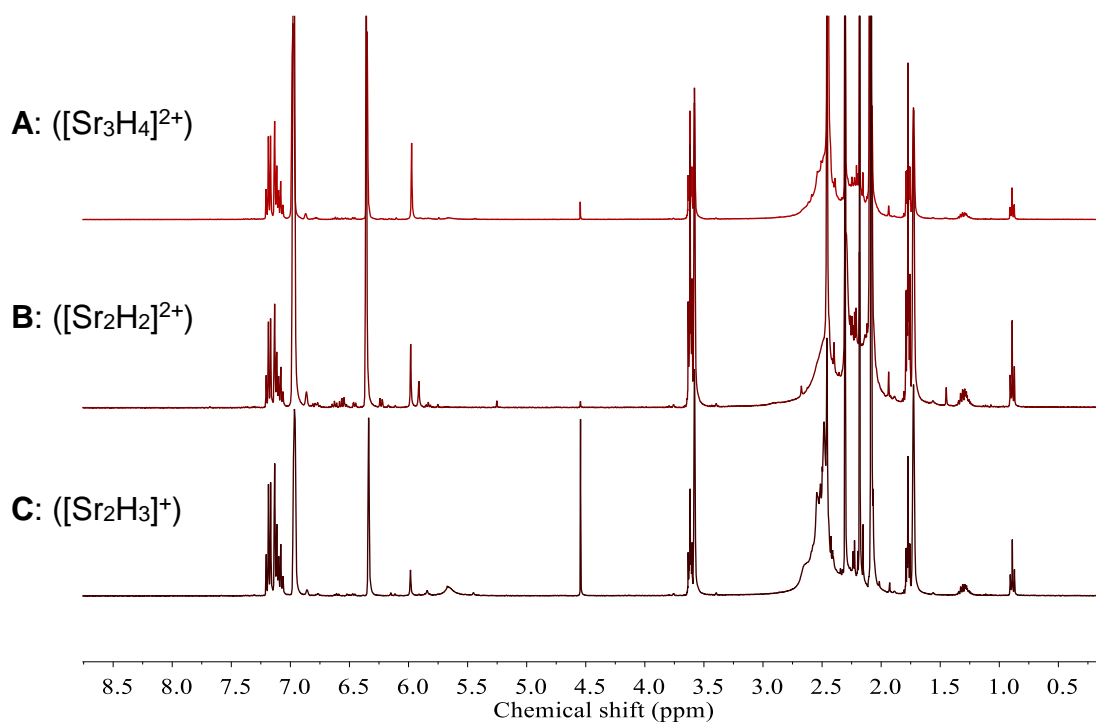


Figure S15: *In-situ* NMR spectra after addition of H₂ (1 bar) to a mixture of **1a** and **2** in varied stoichiometry in THF-*d*₈. The formula in parenthesis corresponds to the expected hydride species for each case. **A:** **1a** in the presence of two equivalents of **2**. **B:** Pure **2**. **C:** **1a** in the presence of one equivalent of **2**. Hydride species **4** is formed in all three cases, but **B** and **C** show several additional hydride peaks.

3.3 Reaction of **4** with **3**.

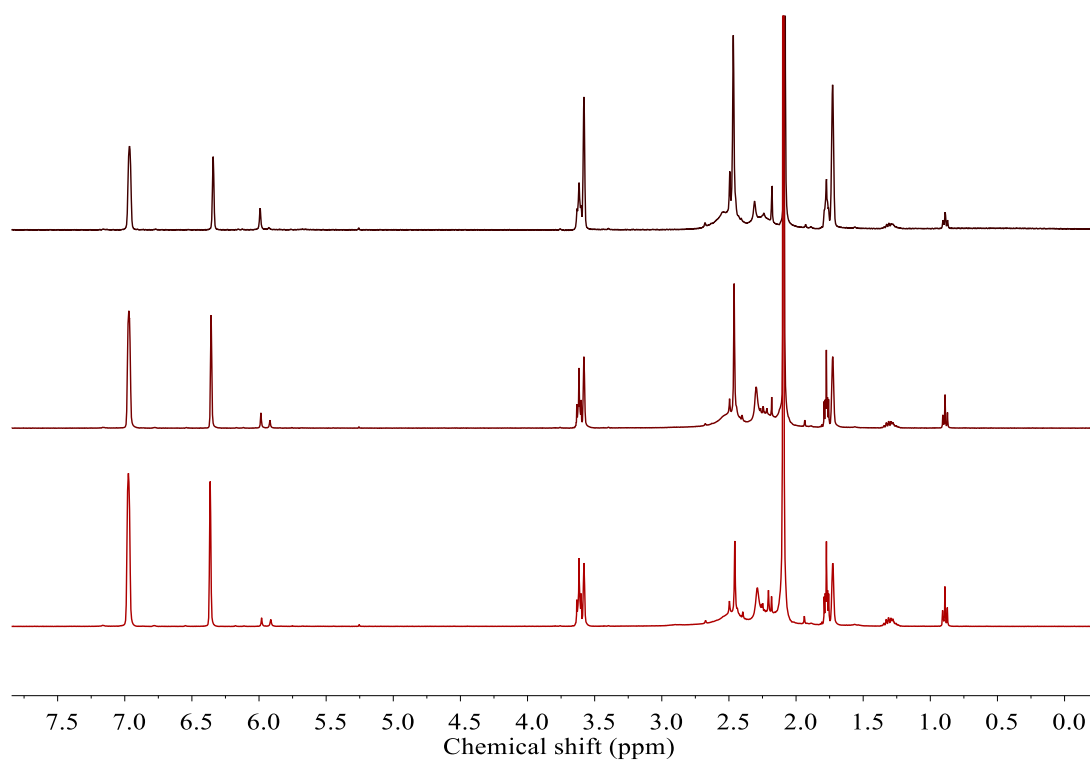


Figure S16: ¹H NMR spectra of the reaction of strontium hydride **4** with strontium bis(borate) **3** in THF-*d*₈. Top: Pure **4**. Middle: After addition of one equivalent of **3**. Bottom: After addition of two equivalents of **3**. Upon addition of **3**, a second major hydride species at $\delta = 5.92$ ppm is observed.

3.4 Reaction of **4** with [NEt₃H][B(C₆H₃-3,5-Me₂)₄].

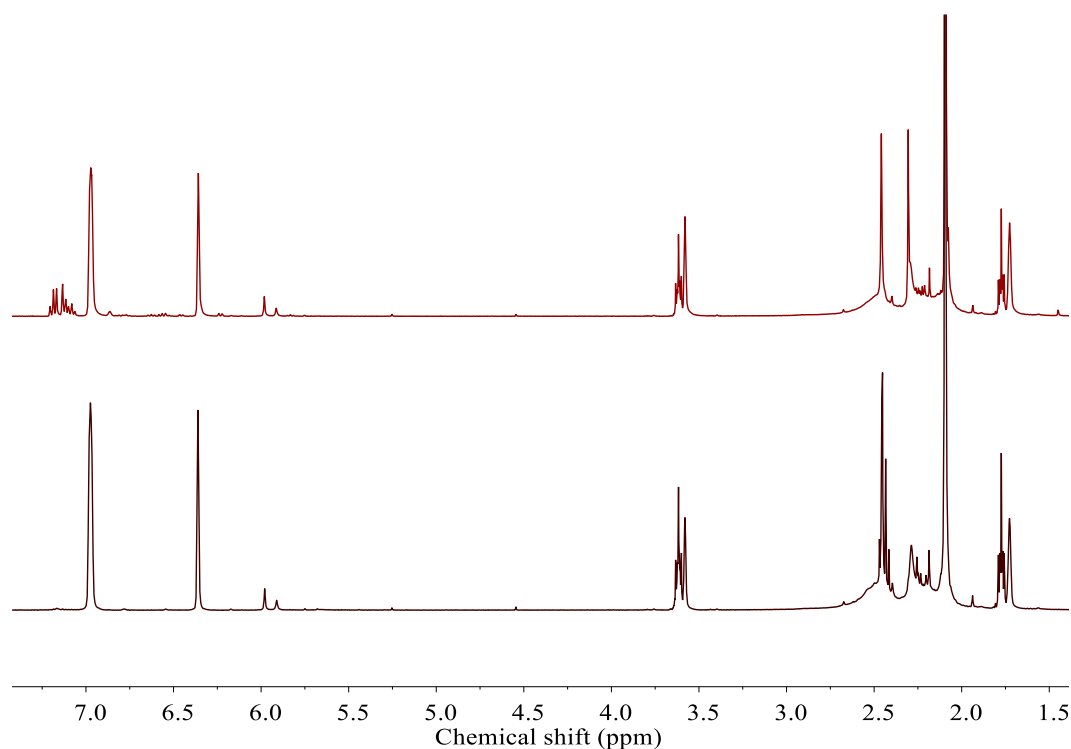


Figure S17: Comparison of the *in-situ* NMR spectra of the reactions of **2** with H₂ (1 bar) (top) and of **4** with one equivalent of [NEt₃H][B(C₆H₃-3,5-Me₂)₄] (bottom) in THF-*d*₈. The same equilibrium mixture is obtained in both cases.

3.5 Reaction of **4** with D₂.

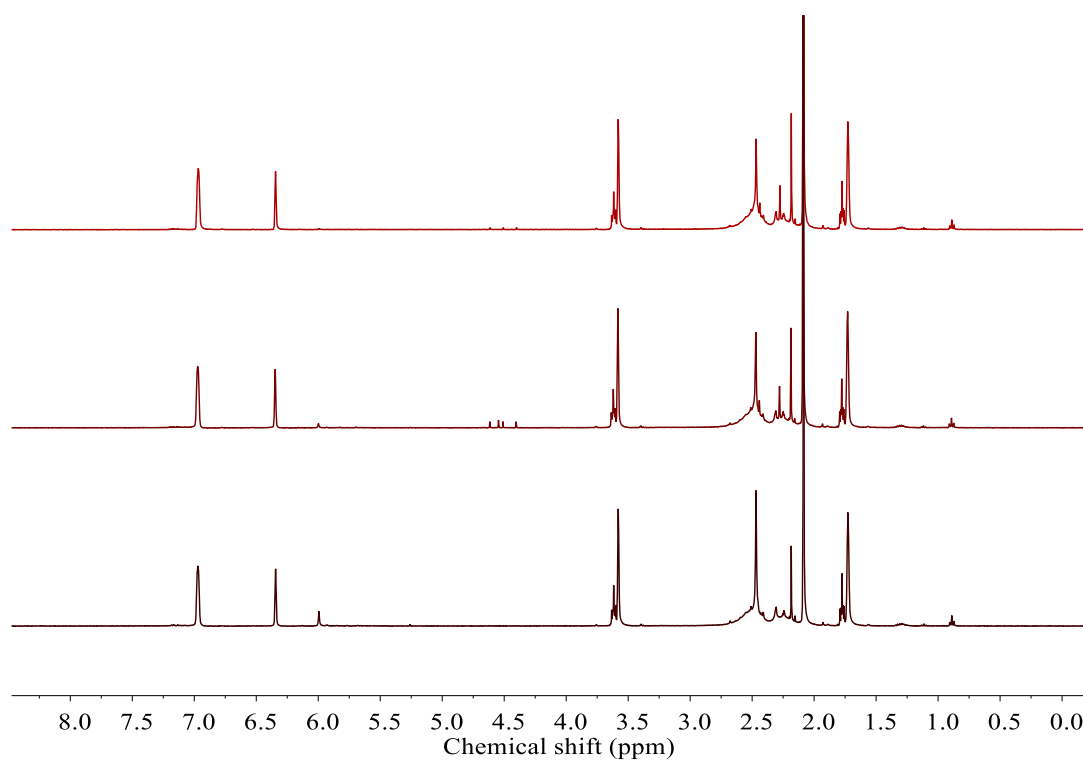


Figure S27: NMR spectra of the reaction of **4** with D₂ (1 bar) in THF-*d*₈. Bottom: Before addition of D₂. Middle: 5 min after addition of D₂. Top: 30 min after addition of D₂.

3.6 Comparison of ¹H NMR spectrum of hydrogenolysis reaction mixtures of **2** + **2-Ca** and **1a** + **3-Ca** with that of isolated **5**

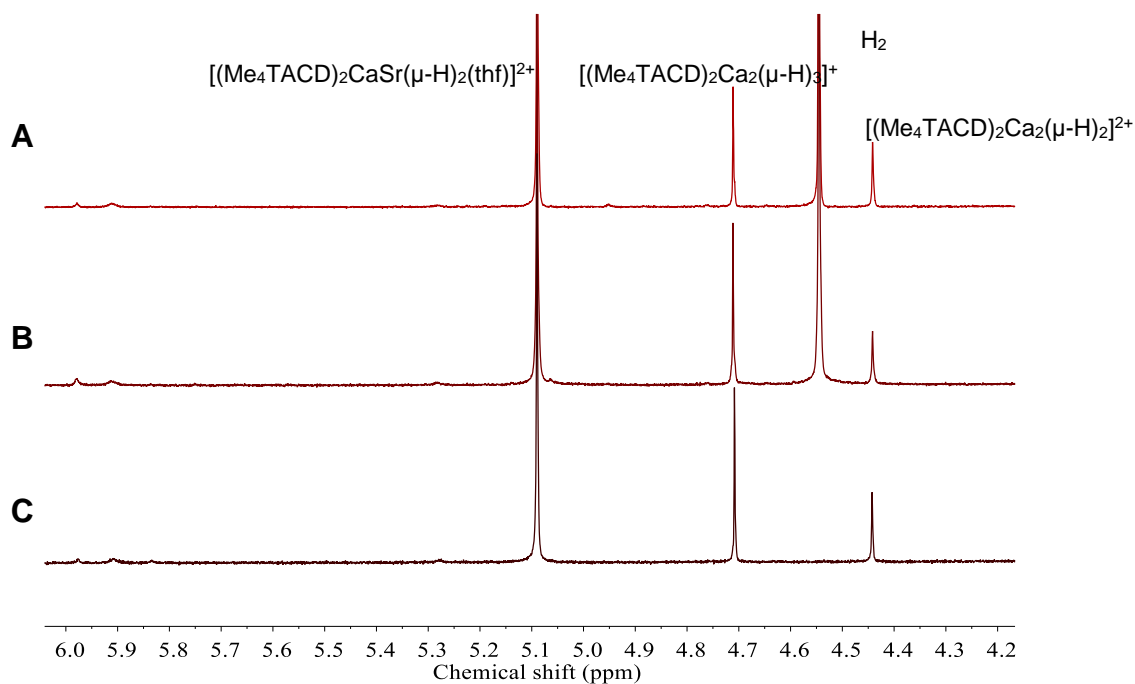


Figure S18: Cut-out of the hydride region of the *in-situ* ¹H NMR spectra of the hydrogenolysis of **2** in presence of **2-Ca** (A), **1a** in the presence of **3-Ca** (B) and isolated **5** (C) in THF-*d*₈. The same equilibrium mixture is obtained in all three cases.

3.7 Reaction of **5** with **3-Ca**.

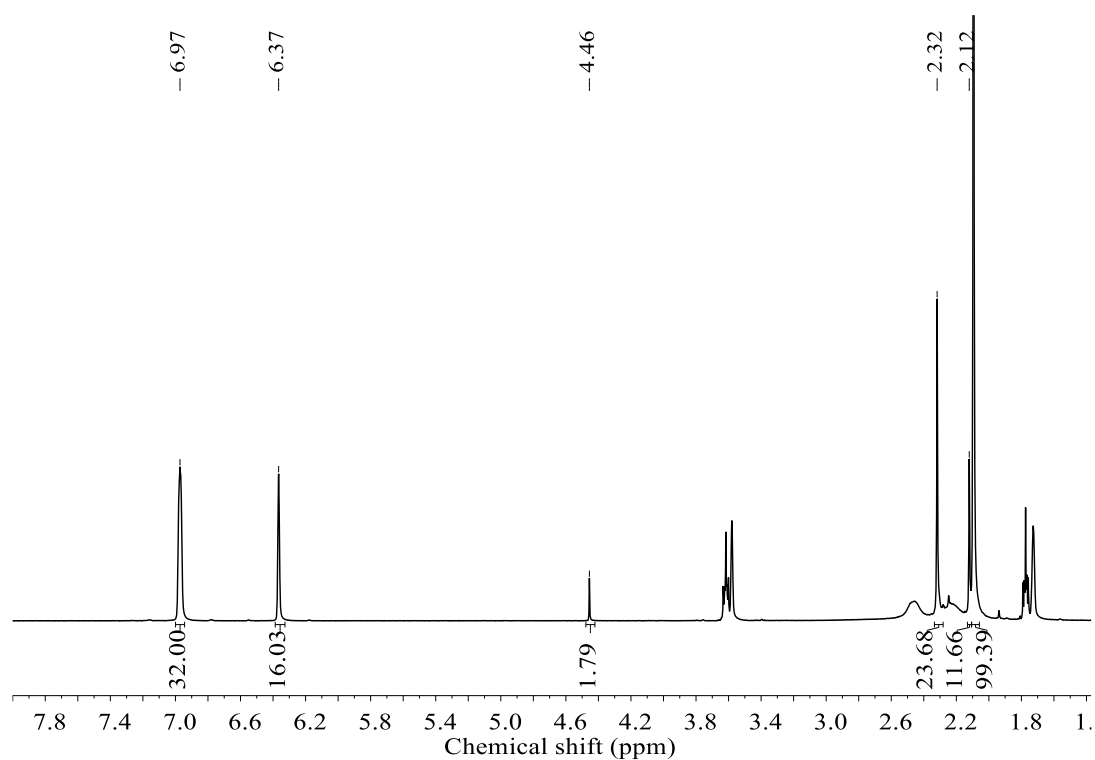


Figure S19: *In-situ* ^1H NMR spectrum of the reaction of **5** with **3-Ca** in $\text{THF-}d_8$. Clean formation of $[(\text{Me}_4\text{TACD})_2\text{Ca}_2(\mu\text{-H})_2][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$ and **3** is observed.

3.8 Reaction of **5** with two equivalents of **3**.

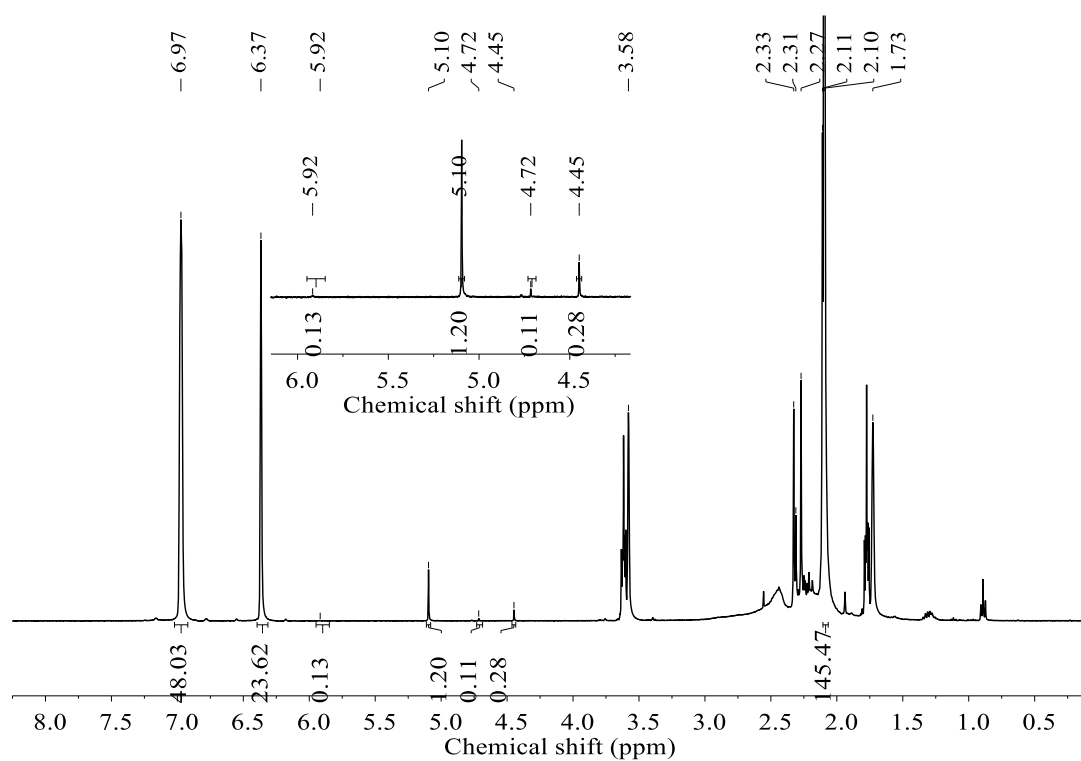
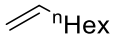
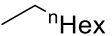
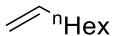
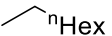
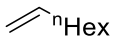
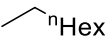
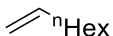
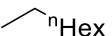
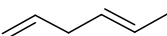
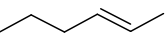
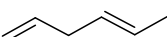
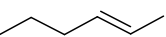
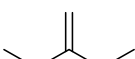
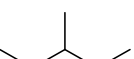
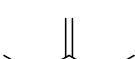
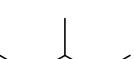




Figure S20: *In-situ* ^1H NMR spectrum of the reaction of **5** with two equivalents of **3** in $\text{THF-}d_8$. The main hydride resonance belongs to **5** and resonances of $[(\text{Me}_4\text{TACD})_2\text{Ca}_2(\mu\text{-H})_2][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]_2$ and $[(\text{Me}_4\text{TACD})_2\text{Ca}_2(\mu\text{-H})_3][\text{B}(\text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2)_4]$ are still observed.

3.9 Catalysis

For catalytic experiments, a stock solution with a total volume of 1 mL containing the substrate (1.00 mmol) and the internal standard 1,4-(SiMe₃)C₆H₄ (55 mg, 0.25 mmol) in THF-*d*₈ was prepared. For each experiment, the catalyst was dissolved in 0.5 mL of THF-*d*₈ and 0.1 mL of the stock solution were added. The mixture was charged with H₂ (1 bar) by applying three “freeze-pump-thaw” cycles and heated to 60 °C for the time indicated in Table S1. Reaction progress was monitored by ¹H NMR spectroscopic analysis.

Table S1: Catalytic hydrogenation of 1-octene with molecular alkaline earth metal hydrides.

Entry	Substrate	Catalyst (mol%) ^[a]	t [h]	Product	% Conv.
1		4 (3.3)	12		93 ^[b]
2		2 (10)	12		91
3		5 (5)	24		95
4 ^[c]		$[(\text{Me}_4\text{TACD})_2\text{Ca}_2(\mu\text{-H})_2]^{2+}$ (5)	24		95 ^[b]
5		4 (3.3)	12		99
6		5 (5)	24		99
7		4 (3.3)	95		20
8		5 (5)	95		0
9 ^[c,d]		$[(\text{Me}_4\text{TACD})_2\text{Ca}_2(\mu\text{-H})_2]^{2+}$ (5)	24		0

[a] equivalent to 10 mol% monomeric AE hydride, [b] 5 % 2-octene, [c] Data taken from [S4], [d] 80 °C.

4 Crystal Structure Determinations

X-ray diffraction data were collected at 100 K on an Eulerian 4-circle diffractometer STOE STADIVARI in ω -scan mode with Cu-K α radiation. The structures were solved by direct methods using SHELXT.^[S6] All refinements were carried out against F^2 with ShelXL^[S7] as implemented in the program system Olex2.^[S8] In the crystal structure of **1**, the CH₂ units of the Me₄TACD ligand C1 – C8 are disordered as well as atom C29 of the coordinated THF ring ligand is disordered. The disorder could be resolved with split positions. Restraints were used in the refinement of the anisotropic displacement parameters of the disordered atoms. All hydrogen atoms in **1** were refined in their position. Diffraction data received from a crystal of dimension 0.15 x 0.25 x 0.43 were obtained for **2a** leading to unit cell parameters $a = 12.4069(3) \text{ \AA}$, $b = 13.016(9) \text{ \AA}$, $c = 19.7043(4) \text{ \AA}$, $\alpha = 76.2476(16)^\circ$, $\beta = 86.8441(17)^\circ$, $\gamma = 86.8028(16)^\circ$, $V = 3086.01(12)^\circ$. Structure solution and refinement in the tentative triclinic space group $P\bar{1}$ showed the molecular connectivity of the molecular cation C₁₉H₃₅N₄Sr, the molecular anion C₃₂H₃₆B as well as three thf molecules C₅H₁₀O. Due to unsatisfactory refinement data, we do not further discuss this structure. Compound **4** was found with two crystallographically independent molecular cations and four corresponding independent molecular anions, as well as five non-coordinated THF molecules. Both crystallographically independent molecular cations have very similar geometrical parameters. In the refinement, the solvent molecules were "squeezed out" with the BYPASS algorithm^[S9] as implemented in PLATON.^[S10] The solvent region adds up to a total volume of 1571 \AA^3 per unit cell and contains 417 electrons. 10 well-ordered THF would require 1040 \AA^3 ;^[S11] but disordered molecules are usually less close-packed. These ten THF molecules should contribute 400 electrons. Both criteria suggest an acceptable match. Due to disorder, the Me₄TACD ligands were partly refined with split positions (involving atoms N7, C17, C18, C19, C23 and C24). The solution and initial refinement showed residual electron densities close to the bridging sites. The reaction conditions and the resulting geometry of these secondary sites suggest the presence of trace amounts of iodine. A structure featuring iodide ligands bridging Sr cations has been described by Fromm et al.^[S12] To deconvolute site occupancy and isotropic displacement parameter, we defined a common displacement parameter for all hydride ligands and the iodide minority sites, and we constrained the sum of the occupancies for mutually exclusive iodide and hydride sites to unity. The trace amount of iodine suggested by the new structure model refined to 4% for the site associated with the highest and 3% for that with the second local density maximum. All non-hydrogen atoms were refined with anisotropic displacement parameters. The disordered atom positions of one coordinated THF ligand in the structure of **4** were refined with isotropic displacement parameters because attempted refinement with anisotropic parameters did not give physically meaningful values. The refinement of the

disordered groups in the structure of this molecule included distance restraints (using the commands SADI and DFIX as implied in ShelXL). In addition, a general RIGU command was employed. All hydrogen atom positions in **4** were included in calculated positions except for the hydride atoms H1 – H4 as well as H5 – H8 within the molecular cation fragment $[\text{Sr}_3\text{H}_4]^{2+}$. Compound **5** is found with two co-crystallized, non-coordinated THF molecules. One of these is located around a center of inversion, leading to disorder around Wyckoff position 2c (involving atoms O4 and C101 – 104). We have refined the occupancies of the metal atoms. Our final refinement gave occupancy factors of 0.743(2) (Sr1) and 0.257(2) (Ca2) with both atoms constrained at the same position and with the same anisotropic displacement parameters. We are aware that the resulting composition does not necessarily apply to the bulk average of the crystals. In addition, the atoms of the ring ligand Me₄TACD (N5 – N8, C13 – C24) and of the coordinated thf ligand O1 and C13 – C16 were refined with split positions. The non-hydrogen atoms on split positions N5 – N8 and C13 – C24 were refined with isotropic displacement parameters. However, the final refinement of the second metal atom position was carried out with 100% multiplicity for calcium, as the refinement of the occupation factor led to a value close to 1. All hydrogen atoms were included in calculated positions and treated as riding throughout the refinement, except of the hydride atoms H1 and H2 which were refined in their position. The position of the hydride atom H4 in one of these clusters was located in a Difference Fourier synthesis and fixed in its position. Refinement results are given in Table S2. Graphical representations were performed with the program DIAMOND.^[S13] CCDC-2078067 (**1**), CCDC-2078068 (**2a**), CCDC-2078069(**4**) and CCDC-2078070 (**5**) 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 S2: Crystallographic data of **1**, **4** and **5**.

	1	4	5
Formula	C ₃₀ H ₅₀ N ₄ OSr	2(C ₄₀ H _{95.97} I _{0.03} N ₁₂ OSr ₃), 4(C ₃₂ H ₃₆ B), 5(C ₄ H ₈ O)	2(C ₂₈ H ₆₆ Ca _{1.23} N ₈ OSr _{0.77}), 4(C ₃₂ H ₃₆ B), 5(C ₄ H ₈ O)
<i>F</i> _w /g·mol ⁻¹	570.36	4134.28	3378.87
cryst. color, habit	yellow rod	colorless block	colorless rod
crystal size / mm	0.06 x 0.15 x 0.30	0.08 x 0.10 x 0.15	0.06 x 0.21 x 0.43
crystal system	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	8.8102(18)	17.2794(2)	22.3924(3)
<i>b</i> / Å	9.0828(18)	24.7939(4)	12.75071(15)
<i>c</i> / Å	19.687(4)	28.3335(5)	35.5684(4)
α / °	88.58(3)	109.8730(12)	
β / °	87.44(3)	90.2679(12)	101.7303(9)
γ / °	70.78(3)	90.7112(12)	
<i>V</i> / Å ³	1486.0(6)	11414.5(3)	9943.4(2)
<i>Z</i>	2	2	2
<i>d</i> _{calc} /Mg·m ⁻³	1.275	1.206	1.129
μ (CuK α)/mm ⁻¹	2.722	2.285	1.593
<i>F</i> (000)	608	4439	3669
θ range / °	2.25, 71.28	2.56, 72.04	4.31, 71.82
index ranges	-9 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 9, -23 ≤ <i>l</i> ≤ 24	-21 ≤ <i>h</i> ≤ 21, -30 ≤ <i>k</i> ≤ 30, -34 ≤ <i>l</i> ≤ 25	-27 ≤ <i>h</i> ≤ 27, -15 ≤ <i>k</i> ≤ 15, -42 ≤ <i>l</i> ≤ 24
refln.	16035	100682	65203
independ. reflns (<i>R</i> _{int})	5489 (0.0265)	42045 (0.0311)	18680 (0.0581)
observed reflns	5064	31137	11925
data/ restr./ param.	5489/ 176 / 339	42045/ 2321/ 2268	18680/ 1060/ 1181
<i>R</i> ₁ , <i>wR</i> ₂ [$>$ 2 σ (<i>I</i>)]	0.0210, 0.0553	0.0670, 0.1616	0.0431, 0.0936
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0238, , 0.0561	0.0932, 0.1788	0.0744, 0.1006
GooF on <i>F</i> ²	1.048	1.014	0.857
largest diff. peak, hole/ e·Å ³	0.473, -0.337	2.028, -1.039	0.465, -0.345
CCDC number	2078067	2078069	2078070

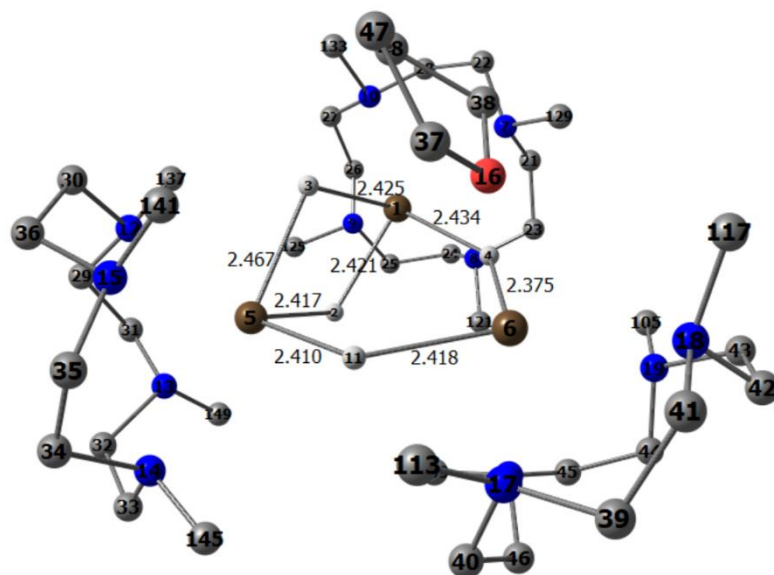
5 Computational Details

The calculations were conducted using a DFT focused methodology – using the Becke’s 3-parameter^[S14] hybrid functional combined with the non-local correlation functions designed by Perdew-Yang (B3PW91).^[S15] In addition to this Grimme’s D3 version of dispersion with Becke-Johnson damping^[S16] was included using the keyword GD3BJ. All calculations were computed using the Gaussian09 software.^[S17] The strontium atom was treated with a small-core Stuttgart Dresden relativistic effective core potential (SDDALL) in combination with a double quality basis set – SDDALL^[S18] Carbon, hydrogen, nitrogen, and boron atoms were described using a double ζ 6-31G** basis set including d and p polarization respectively.^[S19] Geometry optimizations of the various structures were computed without symmetry constraints. The density has been analyzed using the Natural Bonding Orbital (NBO) analysis.^[S20]

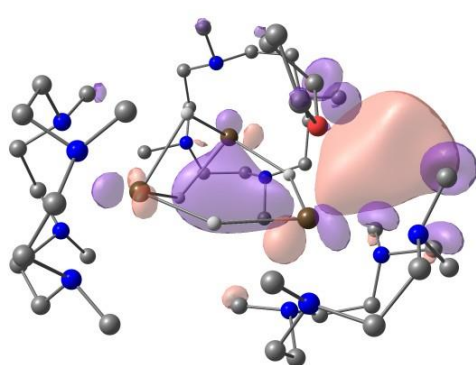
5.1 NBO Information for $[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-H})_4(\text{thf})]^{2+}$ (**4**)

Complex	Natural Charges		NBO			WBI		
			Bond	Occupancy	Center (contribution)			Hybridization (contribution%)
$[(\text{Me}_4\text{TACD})_3\text{Sr}_3\text{H}_4(\text{THF})]^{2+}$	Sr ₁ Sr ₅ Sr ₆	0.79 0.79 0.99	Sr ₁ -H ₂	1.72	Sr ₁ (15%) ; H ₂ (86%)	Sr ₁ (s17 p35 d48) ; H ₂ (s100)	Sr ₁ -H ₂ Sr ₁ -H ₃ Sr ₁ -H ₄ Sr ₁ -H ₁₁	0.34 0.34 0.33 0.04
			Sr ₁ -H ₃	1.71	Sr ₁ (14%) ; H ₃ (86%)	Sr ₁ (s18 p37 d45) ; H ₃ (s100)	Sr ₅ -H ₂ Sr ₅ -H ₃ Sr ₅ -H ₄ Sr ₅ -H ₁₁	0.34 0.33 0.34 0.33
			Sr ₁ -H ₄	1.74	Sr ₁ (13%) ; H ₄ (87%)	Sr ₁ (s20 p36 d44) ; H ₄ (s100)	Sr ₆ -H ₂ Sr ₆ -H ₃ Sr ₆ -H ₄ Sr ₆ -H ₁₁	0.05 0.33 0.05 0.33
			Sr ₅ -H ₁₁	1.74	Sr ₁ (13%) ; H ₁₁ (87%)	Sr ₁ (s18 p36 d46) ; H ₁₁ (s100)		
				Second Order				
			Donor	Acceptor		Total Energy (kcal.mol⁻¹)		
					LP* Sr ₁	578.81	Sr ₆ -H ₂ Sr ₆ -H ₃ Sr ₆ -H ₄ Sr ₆ -H ₁₁	0.03 0.05 0.28 0.29
					LP* Sr ₅	944.88		
					LP* Sr ₆	231.56		
			H ₂ H ₃ H ₄ H ₁₁		LP* Sr ₁	397.83	Sr ₁ - Sr ₅ Sr ₁ - Sr ₆	0.22 0.11 0.12
					LP* Sr ₅	935.55		
					LP* Sr ₆	169.07		
					LP* Sr ₁	261.52	Sr ₅ - Sr ₆	2.32 2.32
					LP* Sr ₅	220.15		
					LP* Sr ₆	372.77	Sr ₁ Sr ₅ Sr ₆	1.94 0.78 0.78
				LP* Sr ₁	73.77			
				LP* Sr ₅	415.19			
				LP* Sr ₆	671.89	H ₂ H ₃ H ₄ H ₁₁	0.73 0.74	

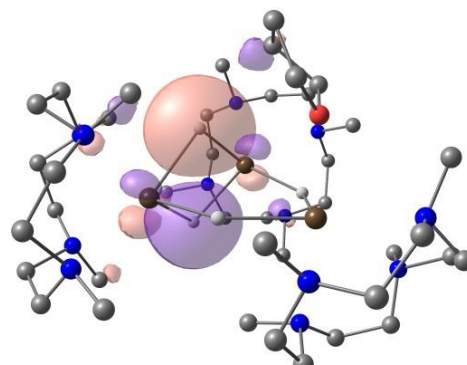
5.2 Orbitals and bond length for $[(\text{Me}_4\text{TACD})_3\text{Sr}_3(\mu\text{-H})_4(\text{thf})]^{2+}$ (4)



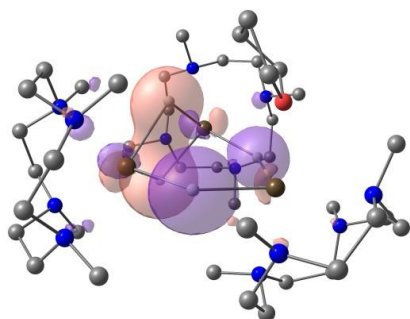
Bond length and atom numbers



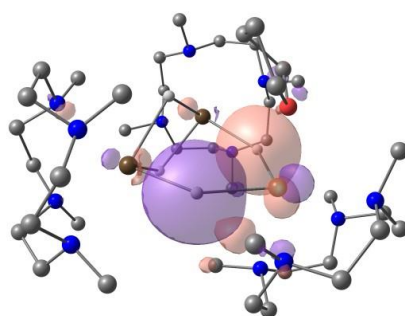
LUMO (229)



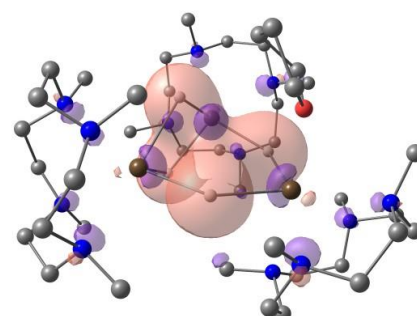
HOMO (228)



HOMO-1 (227)



HOMO-2 (226)

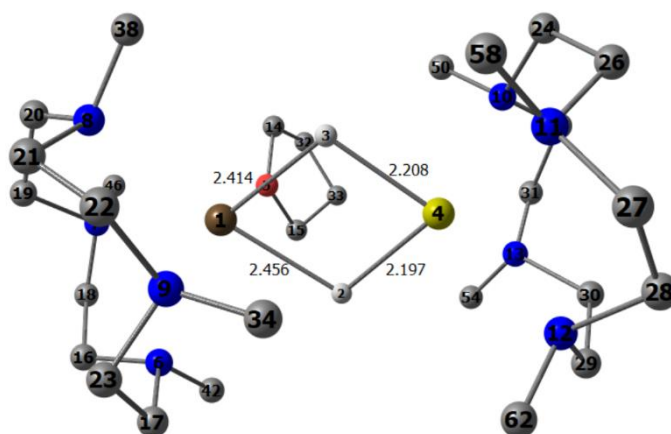


HOMO-3 (225)

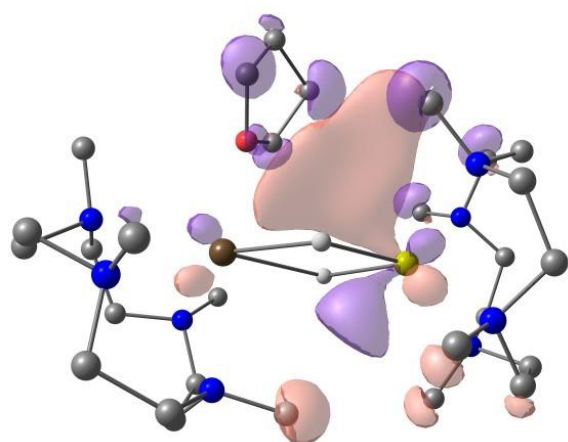
5.3 NBO Information for 5

Complex	Natural Charges		NBO			WBI		
			Bond	Occupancy	Center (contribution)			Hybridization (contribution%)
[(Me ₄ TACD) ₂ CaSrH ₂ (THF)] ²⁺	Sr	0.93	Sr-H ₂	1.77	Sr (14%) ; H ₂ (86%)	Sr (s17 p35 d48) ; H ₂ (s100)	Sr-H ₂	0.37
			Sr-H ₃	1.78	Sr (14%) ; H ₃ (86%)	Sr (s18 p35 d47) ; H ₃ (s100)	Sr-H ₃	0.38
	Ca	1.23	Second Order			Ca-H ₂	0.31	
			Donor	Acceptor	Total Energy (kcal.mol ⁻¹)	Ca-H ₃	0.30	
	H ₂ H ₃	-0.53 -0.53	Sr-H ₂	LP* Sr LP* Ca	80.99 189.5	Ca-Sr	0.17	
			Sr-H ₃	LP* Ca	200.66	Sr	2.02	
			LP* Sr	LP* Ca	48.88	Ca	1.48	
					H ₂	0.73		
					H ₃	0.72		

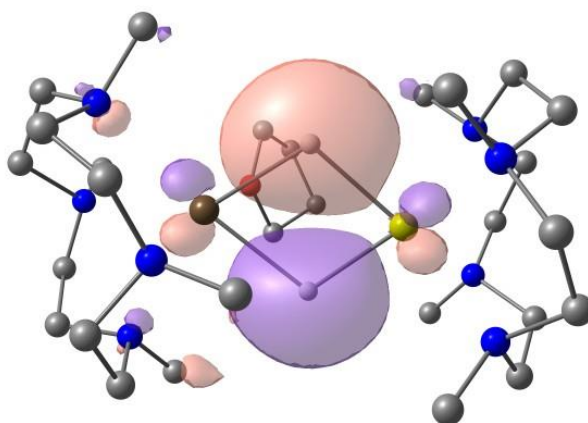
5.4 Orbitals and bond length for [(Me₄TACD)₂CaSrH₂(THF)]²⁺ (5)



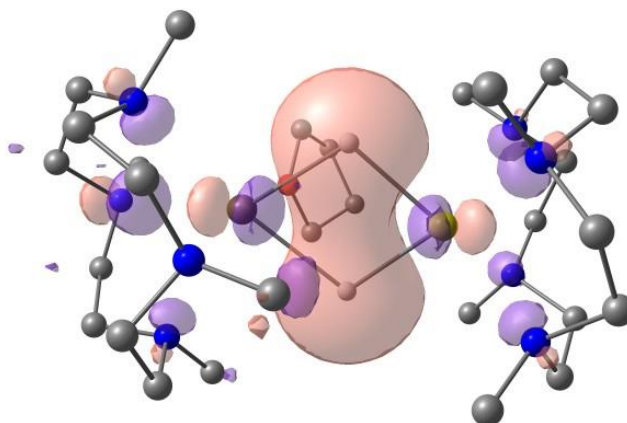
Bond length and atom numbers



LUMO (164)



HOMO (163)



HOMO-1 (162)

Cartesian coordinates of optimized structures

$[(\text{Me}_4\text{TACD})_3\text{Sr}_3\text{H}_4(\text{THF})]^{2+}$ (**4**)

152

Sr	-1.710140	16.569870	6.241224
H	0.201865	17.765583	5.361597
H	-0.585593	14.969747	4.807875
H	-0.376968	15.811086	8.130794
Sr	1.551866	16.080128	4.275531
Sr	1.708635	14.741385	8.512849
N	-3.712702	15.816330	8.121113
N	-2.241134	18.532106	8.012023
N	-2.887137	18.865921	5.080605
N	-4.249032	16.141939	5.180121
H	2.490185	15.061025	6.247250
N	0.336180	15.830949	1.790095
N	2.160398	18.173179	2.532815
N	4.309108	16.309430	3.480955
N	2.453474	13.964699	2.809600
O	0.767035	12.472899	7.741452
N	4.375956	14.121384	8.564844
N	2.468938	13.040669	10.658424
N	1.352363	15.820056	11.139748
N	3.218950	16.934303	9.009829

C	-4.066528	17.044162	8.849246
C	-4.886270	15.259691	7.433017
C	-2.866140	17.916242	9.189038
C	-3.053103	19.624533	7.468839
C	-2.695701	19.970683	6.032583
C	-4.307739	18.615588	4.807644
C	-4.555840	17.226337	4.233632
C	-5.299692	16.049934	6.203416
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C	0.527443	14.456392	1.308589
C	1.116830	18.182545	1.497212
C	3.491979	18.082694	1.921529
C	4.567216	17.632817	2.895427
C	4.567158	15.246973	2.498222
C	3.919365	13.919615	2.859980
C	1.960165	13.960564	1.428455
C	1.351257	11.416544	6.951816
C	-0.656226	12.500303	7.521138
C	4.785805	13.489480	9.823906
C	5.072284	15.393576	8.324453
C	3.777793	12.460674	10.317676
C	2.556908	13.776133	11.927783
C	1.408936	14.745506	12.141648
C	2.419265	16.804808	11.373143
C	2.701222	17.682511	10.164135
C	4.620457	16.540281	9.217943
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C	-0.831951	11.969482	6.112724
H	-4.598516	16.795745	9.782962
H	-4.773913	17.616272	8.245049
H	-3.174761	18.681601	9.921074
H	-2.103157	17.300486	9.670368
H	-2.950961	20.534254	8.083999
H	-4.106470	19.339618	7.527361
H	-1.641448	20.256887	5.976485
H	-3.276362	20.857816	5.728135
H	-4.713966	19.365937	4.109491
H	-4.870040	18.736084	5.736474
H	-3.927991	17.078347	3.349431
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H	2.169633	11.857073	6.377566
H	1.763884	10.654579	7.623155
H	6.163551	15.272702	8.432659
H	4.880573	15.656227	7.282669
H	4.750693	16.264255	10.267155
H	5.291532	17.398381	9.046784
H	1.780187	18.179026	9.845304
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H	3.329993	16.271032	11.653837
H	0.457601	14.206553	12.098572

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H	2.592010	13.076754	12.779295
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H	4.916785	14.269093	10.578065
H	5.768583	13.001313	9.718739
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H	5.652028	15.092887	2.371895
H	4.194972	15.577531	1.525854
H	5.543436	17.658503	2.382564
H	4.639773	18.348985	3.719716
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H	3.791193	19.052562	1.490377
H	0.192310	18.530568	1.967117
H	1.353618	18.913281	0.705556
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H	0.202745	14.351870	0.259572
H	2.618722	14.589270	0.824151
H	2.020841	12.949597	0.991642
C	0.048734	16.478010	11.240727
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H	-0.130025	16.879402	12.251593
C	3.082603	17.748003	7.797059
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H	3.466908	17.189627	6.942289
H	2.025590	17.944476	7.591846
C	4.637572	13.221803	7.437275
H	5.717010	13.078329	7.269006
H	4.194980	12.241503	7.624926
H	4.164429	13.642857	6.544913
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H	0.502763	12.374225	11.043295
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H	-0.896865	19.740135	9.156039
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H	-0.416400	19.431149	7.461340
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H	-2.489058	20.219999	3.478086
C	-3.185706	14.821458	9.057574
H	-3.890955	14.613490	9.878750
H	-2.996708	13.886871	8.524984
H	-2.230677	15.162844	9.460042
C	-4.134249	14.870531	4.459199
H	-3.889943	14.060993	5.150907
H	-5.065237	14.605675	3.933321
H	-3.321709	14.929326	3.732131
C	-1.093881	16.063796	1.989101
H	-1.670769	15.915608	1.061347
H	-1.444730	15.389792	2.774288
H	-1.255416	17.083926	2.337929
C	1.890959	12.850381	3.571313
H	0.800447	12.893218	3.551557

H	2.219774	11.871940	3.184595
H	2.197902	12.952180	4.615843
C	5.181050	16.125918	4.640066
H	4.972162	15.169450	5.119473
H	6.248419	16.164382	4.366721
H	4.986219	16.914505	5.371225
C	2.057954	19.391387	3.344250
H	1.119840	19.376888	3.904182
H	2.865737	19.422053	4.079568
H	2.121496	20.302688	2.728637

$[(\text{Me}_4\text{TACD})_2\text{CaSrH}_2(\text{THF})]^{2+}$ (**5**)

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Sr	14.882511	9.409872	6.966817
H	15.730411	8.087230	8.853940
H	13.601215	9.905328	8.951526
Ca	14.517461	8.719404	10.572897
O	16.658639	11.118773	7.665528
N	15.978039	7.400165	5.551004
N	15.682561	10.198824	4.427524
N	12.807123	10.258110	5.428400
N	13.095987	7.438727	6.511068
N	14.325015	10.707491	12.112976
N	12.241778	8.520620	11.729629
N	14.427161	6.487156	11.813400
N	16.484196	8.680190	12.208434
C	16.518815	12.530362	7.953687
C	17.948965	10.650473	8.111544
C	16.139091	7.747462	4.130781
C	15.120852	6.213870	5.711706
C	16.608982	9.177064	3.907791
C	14.484770	10.300461	3.576187
C	13.317359	10.996694	4.259744
C	12.000429	9.104136	4.996648
C	11.827851	8.045061	6.074494
C	13.638690	6.506720	5.510821
C	12.909140	10.802480	12.515524
C	15.205178	10.534297	13.281154
C	12.301444	9.453254	12.871525
C	12.046819	7.135534	12.196644
C	13.312374	6.522947	12.778387
C	15.717648	6.318742	12.509886
C	16.212265	7.596272	13.169884
C	16.570540	9.977177	12.903873
C	17.846082	12.967189	8.567631
C	18.389858	11.662580	9.153761
C	12.896406	6.754642	7.787713
H	12.146840	5.949982	7.717301
H	13.840402	6.334001	8.135513
H	12.562560	7.489145	8.527142
C	12.004554	11.151877	6.273849
H	11.123167	11.540740	5.741668
H	11.679025	10.629382	7.175205
H	12.614490	12.000850	6.595964
C	17.285828	7.150105	6.171793
H	17.148764	7.001156	7.246608
H	17.787806	6.273109	5.735903
H	17.940844	8.014154	6.032317

C	16.379189	11.490067	4.460888
H	15.708799	12.274912	4.817813
H	17.225145	11.433164	5.148711
H	16.746366	11.784278	3.466041
C	14.701733	11.903227	11.349196
H	15.752224	11.844822	11.053799
H	14.099143	11.945151	10.438293
H	14.560872	12.825749	11.931693
C	17.736012	8.414256	11.486448
H	18.592256	8.323137	12.171238
H	17.649357	7.500348	10.897078
H	17.931692	9.229172	10.787478
C	11.142276	8.901141	10.830945
H	11.329232	9.885510	10.400618
H	11.084223	8.191016	10.003001
H	10.173452	8.906392	11.352308
C	14.245905	5.381519	10.863442
H	15.024033	5.431485	10.097147
H	14.295966	4.401458	11.360211
H	13.274779	5.460129	10.370885
H	11.365312	8.496480	6.957441
H	11.125027	7.278728	5.709226
H	12.475056	8.659817	4.118577
H	11.002284	9.433695	4.666082
H	13.626160	11.988706	4.602999
H	12.519579	11.166557	3.519277
H	14.184062	9.292203	3.282542
H	14.717964	10.833371	2.640380
H	15.183105	7.590977	3.625217
H	16.853591	7.065332	3.642782
H	17.573591	9.330061	4.402059
H	16.792526	9.323296	2.830959
H	15.287490	5.828006	6.721491
H	15.422035	5.411987	5.018700
H	13.084967	5.553877	5.523514
H	13.479091	6.934868	4.518408
H	16.448195	5.975278	11.772415
H	15.651042	5.525855	13.270670
H	17.115734	7.365034	13.755875
H	15.467831	7.952053	13.887221
H	17.195542	9.906846	13.807457
H	17.080619	10.676014	12.234605
H	15.341724	11.487398	13.815405
H	14.712671	9.860168	13.986441
H	13.083655	5.510943	13.146877
H	13.632302	7.096943	13.651431
H	11.241484	7.074985	12.945048
H	11.711684	6.544721	11.339116
H	11.294936	9.615378	13.287829
H	12.887961	8.986967	13.667471
H	12.787878	11.486566	13.369408
H	12.360189	11.246710	11.681119
H	15.678838	12.646054	8.645974
H	16.284929	13.057655	7.024638
H	17.913917	11.446564	10.117307
H	19.471457	11.673757	9.303204
H	18.522641	13.342929	7.794200
H	17.718670	13.756711	9.311194
H	18.641569	10.631601	7.259639
H	17.810258	9.632537	8.488673

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