

Supporting Information

**Reaction of a Bulky Amine Borane with Lanthanide Trialkyls.
Formation of Alkyl Lanthanide Imide Complexes**

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General Information

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon by using modified Schlenk line and glovebox techniques. Elemental analyses were carried out on an Elementar Vario EL analyzer. The ^1H , ^{11}B and ^{13}C NMR spectroscopic data were recorded on a Bruker AV400 spectrometer. Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrophotometer. The solvents (THF, toluene and *n*-hexane) were freshly distilled from sodium and degassed prior to use. Chemical shifts were referenced to residual solvent peaks (^1H and ^{13}C NMR) or external $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (^{11}B NMR). YCl_3 , SmCl_3 and $\text{BH}_3 \cdot \text{THF}$ were purchased from Alfa-Aesar and J&K Scientific. $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$, $\text{Sm}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$, and ArNH_2 ($\text{Ar} = 2,6\text{-}(3,5\text{-Me}_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$) were prepared according to the procedures described in literature.^{S1}

Synthesis of $\text{ArNH}_2 \cdot \text{BH}_3$ (1): To a solution of ArNH_2 (3.3 mmol, 1.0 g) in THF (20 mL) was slowly added $\text{BH}_3 \cdot \text{THF}$ (4 mmol, 1M in THF) at 0 °C. The mixture was warmed to room temperature and stirred for 3 h, after then the solution was concentrated to 5 mL to give colorless crystals of **1** at -40 °C overnight (0.9 g, 86%). Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{BN}$ (315.26): C, 83.82; H, 8.31; N, 4.44; Found: C, 83.71; H, 8.14; N, 4.41. ^1H NMR (400 MHz, CDCl_3 , 23 °C): δ 7.30–7.09 (m, 9H, Ar-*H*), 5.48 (s, 2H, *NH*₂), 2.37 (s, 12H, Ar-*Me*₂). ^{13}C NMR (101 MHz, CDCl_3 , 23 °C): δ 138.9, 137.5, 135.4, 130.3, 130.2, 127.1, 126.9, 126.3 (Ar-*C*), 21.5 (Ar-*Me*₂). ^{11}B NMR (128 MHz, CDCl_3 , 23 °C): δ -16.1. IR (KBr, cm^{-1}): $\tilde{\nu}$ (B-H) 2404.5, 2327.7, 2270.9.

Synthesis of $[\text{Y}(\text{CH}_2\text{SiMe}_3)(\mu_2\text{-NArBH}_3)]_2$ (2): A solution of **1** (0.50 g, 1.6 mmol) in toluene (40 mL) was slowly added to a stirred solution of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (0.79 g, 1.6 mmol) in toluene (20 mL) at -78 °C. The mixture was stirred overnight at -60 °C and then warmed to room temperature. The color of the mixture changed to pale yellow gradually. Then the solution was concentrated to 5 mL to give pale

yellow crystals of **2** at $-40\text{ }^{\circ}\text{C}$ for overnight (0.47 g, 60%). M.p.: $130\text{ }^{\circ}\text{C}$ (dec.). Anal. Calcd for $\text{C}_{52}\text{H}_{70}\text{B}_2\text{N}_2\text{Si}_2\text{Y}_2$ (978.73): C, 63.81; H, 7.21; N, 2.86; Found: C, 63.56; H, 6.98; N, 2.47. ^1H NMR (400 MHz, C_6D_6 , $23\text{ }^{\circ}\text{C}$): δ 7.54 (s, 2H, Ar-*H*), 7.46 (s, 2H, Ar-*H*), 7.42 (s, 2H, Ar-*H*), 6.96 (s, 2H, Ar-*H*), 6.83 (s, 2H, Ar-*H*), 6.77 (s, 4H, Ar-*H*), 6.56 (s, 2H, Ar-*H*), 6.41 (s, 2H, Ar-*H*), 2.32 (s, 6H, Ar-*Me*₂), 2.16 (s, 6H, Ar-*Me*₂), 2.01 (s, 6H, Ar-*Me*₂), 1.87 (s, 6H, Ar-*Me*₂), 0.29 (s, 18H, Si-*Me*₃), -0.44 (d, 2H, $^2J_{\text{HH}} = 10.5$ Hz, $^2J_{\text{YH}} = 4.0$ Hz, Y-*CH*₂), -1.25 (d, 2H, $^2J_{\text{HH}} = 10.5$ Hz, $^2J_{\text{YH}} = 3.2$ Hz, Y-*CH*₂). ^{13}C NMR (101 MHz, C_6D_6 , $23\text{ }^{\circ}\text{C}$): δ 156.2, 147.3, 145.8, 143.7, 143.6, 138.6, 138.4, 138.3, 136.8, 136.0, 132.8, 132.3, 131.3, 130.5, 129.9, 127.0, 123.9, 119.2 (Ar-*C*), 39.2 (d, $^1J_{\text{YC}} = 40.4$ Hz, Y-*CH*₂), 22.3, 22.2, 21.9, 21.6 (Ar-*Me*₂), 4.7 (Si-*Me*₃). ^{11}B NMR (128 MHz, C_6D_6 , $23\text{ }^{\circ}\text{C}$): δ -17.3 . IR (KBr, cm^{-1}): $\tilde{\nu}$ (B-*H*) 2364.8, 2270.3, 2161.6.

Synthesis of [Sm(CH₂SiMe₃)(μ_2 -NArBH₃)]₂ (3**):** A solution of **1** (0.50 g, 1.6 mmol) in toluene (50 mL) was slowly added to a stirred solution of $\text{Sm}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ prepared in situ (0.89 g, 1.6 mmol) in hexane (20 mL) at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred overnight at $-60\text{ }^{\circ}\text{C}$ and then warmed to room temperature. Then the solution was concentrated to 5 mL to give dark brown crystals of **3** at $-40\text{ }^{\circ}\text{C}$ for overnight (0.57 g, 65%). M.p.: $150\text{ }^{\circ}\text{C}$ (dec.). Anal. Calcd for $\text{C}_{52}\text{H}_{70}\text{B}_2\text{N}_2\text{Si}_2\text{Sm}_2$ (1101.64): C, 56.69; H, 6.40; N, 2.54; Found: C, 56.33; H, 6.23; N, 2.38. ^1H NMR (400 MHz, C_6D_6 , $23\text{ }^{\circ}\text{C}$): δ 8.80 (s, 2H, Ar-*H*), 6.02 (s, 2H, Ar-*H*), 5.94 (s, 2H, Ar-*H*), 5.88 (s, 2H, Ar-*H*), 5.45 (s, 2H, Ar-*H*), 5.28 (s, 2H, Ar-*H*), 4.87 (s, 2H, Ar-*H*), 4.57 (s, 2H, Ar-*H*), 4.05 (s, 6H, Ar-*Me*₂), 3.98 (s, 2H, Ar-*H*), 3.91 (s, 6H, Ar-*Me*₂), 1.53 (s, 9H, Si-*Me*₃), 1.36 (s, 4H, Sm-*CH*₂), 1.25 (s, 6H, Ar-*Me*₂), 0.01 (s, 9H, Si-*Me*₃), -0.63 (s, 6H, Ar-*Me*₂). ^{13}C NMR (101 MHz, C_6D_6 , $23\text{ }^{\circ}\text{C}$): δ 170.3, 142.4, 140.2, 137.8, 136.9, 136.3, 136.1, 130.8, 129.6, 129.3, 125.9, 125.7, 125.3, 120.4, 119.0, 118.0, 116.7, 114.7 (Ar-*C*), 30.2 (Sm-*CH*₂), 23.9, 23.7, 20.9, 19.3 (Ar-*Me*₂), 2.3, 0.0 (Si-*Me*₃). ^{11}B NMR (128 MHz, C_6D_6 , $23\text{ }^{\circ}\text{C}$): δ -30.7 . IR (KBr, cm^{-1}): $\tilde{\nu}$ (B-*H*) 2390.5, 2268.9, 2159.5.

X-ray Structural Determinations. Crystals for X-ray analysis of were **2** and **3** obtained from toluene at $-40\text{ }^{\circ}\text{C}$. All intensity data of **2** and **3** were collected with a Rigaku Saturn 724 CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 113(2) K. The structures were resolved by direct methods and refined by full-matrix least-squares on F^2 .^{S2} Hydrogen atoms were considered in calculated positions. All non-hydrogen atoms were refined anisotropically. The ORTEP-3 program was utilized to draw the molecules.^{S3}

References

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- [S2] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.
- [S3] L. J. Farrugia, *J. Appl. Crystallogr.* 1997, **30**, 837.