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# Heavier Alkaline Earth Metal Borohydride Complexes Stabilized by $\beta$−Diketiminate Ligand

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The reaction of KB[*sec*-Bu]$_3$H with calcium iodide [LCa($\mu$-I)·thf]$_2$] (**1**) and strontium iodide [LSr($\mu$-I)·thf]$_2$ (**2**) yields calcium tri*sec*-butylborohydride LCaB(*sec*-Bu)$_3$H·thf (**3**) and strontium tri*sec*-butylborohydride LSrB(*sec*-Bu)$_3$H·thf (**4**) (L = $CH(CMe2,6\text{-}iPr_2C_6H_3N)_2$), respectively. Compounds **2**, **3**, and **4** were characterized by multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, and single crystal X-ray analysis, whereas **1** was characterized without X-ray structural analysis. Compounds **3** and **4** are monomeric in the solid state with a hydride ligation between the metal and boron centers.

## Introduction

Metal hydrides are important because their complexes are considered as valuable synthons in chemistry[1] and also as potential targets for hydrogen storage. Metal hydrides can act as catalysts in a number of reactions, especially in the case of transition-metal complexes.[2] The main group and the d-block elements form many metal hydrides especially with $\beta$-diketiminate ligands.[3] The unique properties of the $\beta$-diketiminate ligand provide suitable electronic and steric requirements to materialize a number of novel complexes, including hydrides. Works related to $\beta$-diketiminate hydride complexes of Group 2 metals have been preferentially examined. A scorpionate ligand stabilized beryllium hydride was reported in 1992.[4] An attempt to prepare magnesium hydride from magnesium iodide, LMgI·OEt$_2$ with NaBH$_4$ resulted in a hydrogen-bridged magnesium complex, LMg($\mu$-H)$_3$BH·OEt$_2$ by our group.[5] A well-defined heavier alkaline earth metal, calcium hydride [LCaH·thf]$_2$ was reported by Harder and co-workers and showed a startling reactivity.[6] The extension of lanthanide hydride synthetic methods to alkaline earth metals resulted in the successful synthesis of this complex by using PhSiH$_3$ as a hydride transfer agent. Recently Jones and co-workers were successful in isolating [LMgH·thf]$_2$.[7] Moreover, Hill and co-workers reported a magnesium hydride cluster compound with *N*-heterocyclic carbene coordination.[8] Nevertheless, such hydride derivatives are, so far, not reported as stable species for heavy alkaline earth metals, like strontium and barium. So we embarked upon an extension of our successful preparation of well-defined Group 14 hydride complexes to alkaline earth metals by employing alkaline-[R$_3$BH] complexes.[9] The anion [R$_3$BH]$^-$ has found extensive use as a hydride source and as a reducing agent. Moreover, the exploration of heavier alkaline earth metals gained a momentum nowadays that has striking similarity to lanthanides.[10] We

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also assumed that ligation of the alkaline earth metal[11,6b] with $[R_3BH]^-$ is also possible and can stabilize the complex without decomposition or ligand exchange. The latter properties are more pronounced in the heavier alkaline earth metal complexes.[12] Herein, we report the hydrocarbon soluble $\beta$-diketiminate ligand supported alkaline earth metal boron hydride complexes prepared from the corresponding alkaline earth metal iodides and potassium tri*sec*-butylborohydride.

## Results and Discussion

The reaction of LH (L = CH(CMe2,6-*i*$Pr_2C_6H_3N)_2$) and one equiv of $KN(SiMe_3)_2$ with $CaI_2$ or $SrI_2$ at room temperature led to the formation of calcium iodide $[LCa(\mu\text{-I})\cdot thf]_2$ (**1**) and strontium iodide $[LSr(\mu\text{-I})\cdot thf]_2$ (**2**) as colorless compounds in good yields. Compounds **1** and **2** are soluble in organic solvents, like benzene, toluene, and THF. Compounds **1** and **2** have been characterized by mass spectrometry, nuclear magnetic resonance (NMR) spectroscopy ($^1H$, $^{13}C$), X-ray single crystal structure (for **2**), and elemental analysis. The $^1H$ NMR spectra of compounds **1** and **2** show a singlet each [4.80 ppm (**1**), 4.84 ppm (**2**)] for the methine CH protons and a second singlet [1.66 ppm (**1**), 1.69 ppm (**2**)] for the ligand backbone methyl protons, respectively. The molecular ion peak corresponding to the nonsolvated monomer **2** (704.3 (100) $[M^+/2-2THF]$) was observed in the electron impact (EI) mass spectrum, while for **1**, only fragment ions were detected.

Crystals of **2** suitable for X-ray structural analysis were obtained from a saturated solution of *n*-hexane at room temperature. The structure of **2** crystallizes as a dimer in the space group $P2_1/c$ with one molecule in the asymmetric unit (Figure 1). The structure reveals the presence of two six-membered $C_3N_2Sr$ rings. These six-membered rings are connected to each other by means of two $\mu$-I atoms, which results in the formation of a four-membered $Sr_2I_2$ ring. Unlike its chloride and fluoride counterparts,[13] the coordination geometries around both metal atoms of **2** are the same. Thus, both of the strontium atoms are penta-coordinate and have distorted trigonal bipyramidal geometry with two nitrogen atoms of the $\beta$-diketiminate ligand, two bridging iodine atoms, and one oxygen atom of the THF donor molecule. The binding mode of the metal atoms is different when compared to a similar iodide complex $[Sr(\eta^5\text{-}L^{tBu})(\mu\text{-I})(thf)]_2$ [$L^{tBu}$ = CH(CMe*t*BuN)$_2$].[14] In the latter, each strontium is coordinated to one $\eta^5$-$L^{tBu}$ and one THF molecule in addition to two bridging iodine atoms. Sr1 is 0.75 Å out of the (N1/N2) plane, and Sr2 is located 1.41 Å out of the (N3/N4) ligand plane. The Sr−I bond distances (3.257$_{av}$ Å) are in accordance with those reported (3.282$_{av}$ Å).[14] The Sr−I−Sr bond angles in **2** (96.472(6)°$_{av}$) are more acute than those of Sr−Cl−Sr (101.27°$_{av}$) reported in $[LSr(thf)(\mu\text{-Cl})_2Sr(thf)_2L]$.[13]

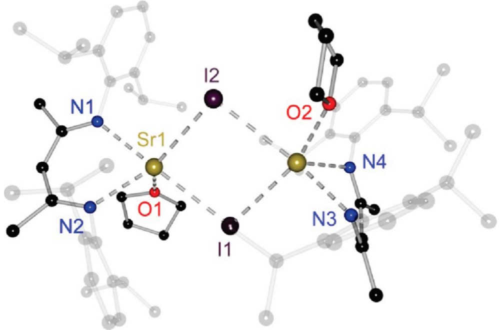

**Figure 1.** Crystal structure of **2**. The substituents on the nitrogen atoms are depicted transparent, while one noncoordinate *n*-hexane molecule and all hydrogen atoms have been omitted for clarity. For selected bond distances (Å) and angles (°) see Table 1.

Unfortunately, we were not able to obtain single crystals of compound **1**.

$KB[sec\text{-}Bu]_3H$ has proven to be a versatile hydride source for the conversion of Group 14 chlorides to the corresponding hydrides.[9a,b] As shown in Scheme 1, potassium tri*sec*-butylborohydride reacts readily with **2**, leading to LSrB($sec$-Bu)$_3$H·thf (**4**) in excellent yield, instead of giving the corresponding hydride complex with two $\mu$-hydrogen (H) bonds bridging the alkaline earth metals. Monodentate ligation of $[HBR_3]^-$ to alkaline earth metal centers is rare, although it contributes to the stability of the hydride complexes. We expected the same type of compound when the $\beta$-diketiminate stabilized calcium iodide **1** was used as a precursor. Indeed, compound **3** (Scheme 1) was formed accordingly.

Compounds **3** and **4** are yellow solids soluble in toluene, THF, and benzene. Spectroscopic characterization indicates the formation of both compounds **3** and **4**. The $^1H$ and $^{11}B$ NMR spectra of **3** and **4** show a singlet each [4.76 (**3**) and 4.74 ppm (**4**)] for the methine CH protons of the ligand backbone and a doublet (−4.4 (**3**) and −4.7 ppm (**4**)) for the boron atoms, respectively. The $^{11}B$ nucleus of **3** resonates downfield in the NMR spectrum when compared to those of other calcium borohydride complexes (−12.0 and −13.3 ppm).[6b,11c] The *sec*Bu−methyl groups attached to boron in **3** and **4** are nonequivalent and exhibit three doublets and three triplets. The carbon atoms alpha to boron are asymmetric centers, so that RRR, RRS, RSS, and SSS isomers are possible. The RRR/SSS and RRS/RSS combinations each are pairwise enantiomeric and will give the same NMR spectrum. In the RRR/SSS pair, the three *sec*-Bu groups are equivalent, whereas in the RRS/RSS pair, they are all inequivalent by symmetry. X-ray crystallographic analysis, where the RRS or RSS isomers are observed is also consistent with the NMR spectrum. The resonance corresponding to the (M−$\mu$H−B) hydride appears very broad in the $^1H$ NMR spectrum of both complexes. A $^{11}B$−$^1H$ correlation clearly indicates the presence of this hydride in the complexes. Molecular ions corresponding to **3** and **4** in the EI mass spectra were not observed, and only fragment ions were seen. For the B−H−M unit of **3** and **4,** two absorption bands for **3** (1924 and 1903 cm$^{-1}$) and one weak absorption band at 1932.06 cm$^{-1}$ for **4** are observed in the IR spectrum. The former are comparable to those of the hydrogen-bridged complex $[Ca(HBEt_3)\{1,2,4\text{-}C_5(SiMe_3)_3H_2\}(thf)_2]$ (1935 cm$^{-1}$)[11c] and to the $KB[sec\text{-}Bu]_3H$ (1904 cm$^{-1}$). Therefore, we assume

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**Scheme 1.** Preparation of $\beta$-Diketiminate Supported Calcium and Strontium Borohydride Complexes

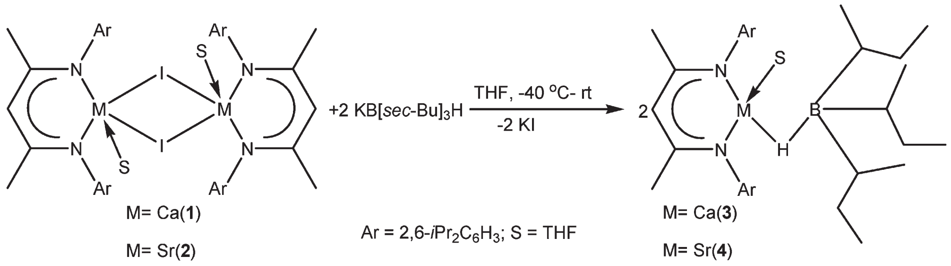

**Table 1.** Selected Bond Distances (Å) and Angles (°) for **2**, **3**, and **4**

| | | | | |
|---|---|---|---|---|
| | | Compound **2** | | |
| bond distances | Sr1−N1 2.5068(15) | Sr1−O1 2.5291(13) | Sr1−I1 3.2404(4) | Sr1−I1 3.2481(4) |
| | Sr2−N3 2.4768(15) | Sr2−O2 2.5118(14) | Sr2−I1 3.2284(4) | Sr2−I2 3.3100(4) |
| | Sr1···Sr2 3.7811(15) | | | |
| bond angles | N1−Sr1−N2 74.69(5) | I1−Sr1−I2 83.892(6) | Sr1−I1−Sr2 97.354(6) | Sr1−I2−Sr2 95.590(6) |
| | N3−Sr2−N4 77.45(5) | I1−Sr2−I2 83.099(6) | | |
| | | Compound **3** | | |
| bond distances | Ca1−N1 2.337(3) | Ca1−N2 2.371(3) | Ca1−O1 2.337(3) | Ca1−B1 2.861(4) |
| | Ca1−H100 2.16(3) | B1−C30 1.643(6) | B−C38 1.655(6) | B−C34 1.673(5) |
| | B1−H100 1.24(3) | | | |
| bond angles | N1−Ca1−N2 78.97(9) | N1−Ca1−B1 130.00(11) | N2−Ca1−B1 143.02(11) | O1−Ca1−N2 96.19(9) |
| | O1−Ca1−B1 102.03(11) | B1−Ca1−H100 23.8(8) | | |
| | | Compound **4** | | |
| bond distances | Sr1−N1 2.486(2) | Sr1−N2 2.509(2) | Sr1−O1 2.501(2) | Sr1−B1 3.003(3) |
| | Sr1−H100 2.325(8) | B1−C34 1.645(4) | B−C38 1.661(5) | B−C42 1.672(4) |
| | B1−H100 1.246(3) | | | |
| bond angles | N1−Sr1−N2 73.00(7) | N1−Sr1−B1 134.97(8) | N2−Sr1−B1 146.01(9) | O1−Sr1−N2 94.28(7) |
| | O1−Sr1−B1 100.31(8) | B1−Sr1−H100 22.8(3) | | |

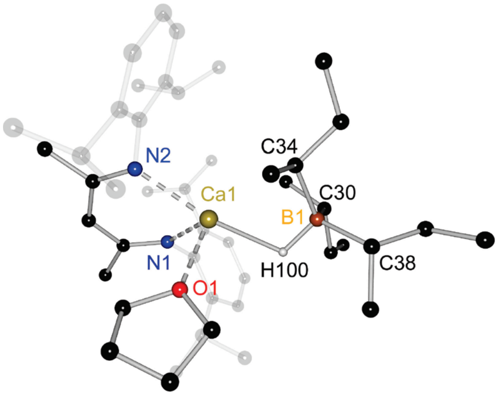

**Figure 2.** Crystal structure of **3**. The substituents on the nitrogen atoms are depicted transparent, and all hydrogen atoms have been omitted for clarity except the hydrogen atom involved in bonding to Ca$^{2+}$. For selected bond distances (Å) and angles (°) see Table 1.

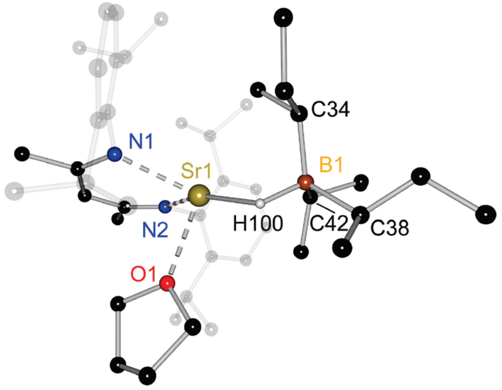

**Figure 3.** Crystal structure of **4**. The substituents on the nitrogen atoms are depicted transparent, and all hydrogen atoms, except the hydrogen atom involved in bonding to Sr$^{2+}$, have been omitted for clarity. For selected bond distances (Å) and angles (°) see Table 1.

that in the solid state for **3** two forms of hydrogen bonds might be present. The one that binds more to the alkaline earth metal and the other more to the boron.

X-ray quality crystals of **3** and **4** were grown from a mixture of toluene and THF. Both isomorphic molecules crystallize in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The boron atoms in **3** and **4** exhibit a distorted tetrahedral coordination environment with bond angles of 104.3(13)−114.9(2)° (Figures 2 and 3). Because of the bulky *sec*-butyl groups, the angles between the hydrogen atom and the carbon atoms are smaller than the ideal tetrahedral angle, whereas the angles between the carbon atoms are larger. As a result of the large metal−boron distance, the metal has only small to no steric influence on the geometry around the boron atom. The metal atoms in **3** and **4** display each a distorted trigonal pyramidal environment with the two nitrogen atoms of the ligand, the boron atom at the base, and the oxygen atom from the THF at the apex. The space at the base of the pyramid is occupied by the bulky substituents of the nitrogen atoms and the boron atom. The hydride bridge seems to have no influence on the geometry in comparison to the bulky *sec*-butyl and *iso*-propyl groups. The bridging $\mu$H was observed in the X-ray structural analysis for **3** as well as for **4**. In both compounds, the borohydride anion coordinates to the $\mathrm{M}^{2+}$ ion through the (M-$\mu$H−B) bond. The B−H···$\mathrm{Ca}^{2+}$(2.16(3) Å) contact compares well to those observed in $[\mathrm{Ca(HBEt_3)\{1,2,4\text{-}(Me_3Si)_3Cp\}(thf)_2}]$ (2.21(4) Å)[11c] and $[\mathrm{LCa(H_2BC_8H_{14})(thf)}]$ (2.25(2) Å).[6a] As expected, the B−H···$\mathrm{Sr}^{2+}$(2.325(8) Å) bond length is longer compared to its lighter counterpart **3** and is shorter to those in the strontium complex, $[\mathrm{(Me_3Si)_2\{Me_2\text{-}(H_3B)P\}C]_2Sr(thf)_5}$ ($2.735_{\mathrm{av}}$ Å).[11a]

A reaction was carried out on a NMR scale to check whether the bridging hydride can be released from compound **4**. $\mathrm{LSrB}(\mathit{sec}\text{-}\mathrm{Bu})_3\mathrm{H\cdot thf}$ converts LGeCl → LGeH at room temperature, and the chemical shift of the product was in agreement with the reported value.[3c] Moreover, **3** and **4** on heating yield mainly homoleptic calcium, $\mathrm{L_2Ca}$, and strontium, $\mathrm{L_2Sr}$, compounds.[15]

## Experimental Section

**General Procedures.** All manipulations were performed in a dry and oxygen-free atmosphere ($\mathrm{N_2}$ or Ar) using Schlenk-line and glovebox techniques. Solvents were purified with the M-Braun solvent drying system. $\mathrm{CaI_2}$, $\mathrm{SrI_2}$, $\mathrm{KN(SiMe_3)_2}$ (95%), and $\mathrm{KB}[\mathit{sec}\text{-}\mathrm{Bu}]_3\mathrm{H}$ (1 M solution in THF) were purchased from Aldrich and used as such. $^1$H (500.13 MHz) and $^{13}$C (125.77 MHz) NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer. Chemical shifts are reported in ppm with reference to $\mathrm{SiMe_4}$ (external). IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer in the range of 4000−350 $\mathrm{cm^{-1}}$ as nujol mulls. Mass spectra were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV) by EI-MS method. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

**Synthesis of 1.** LH (3.349 g, 8.00 mmol) and $\mathrm{KN(SiMe_3)_2}$ (1.676 g, 8.40 mmol) were dissolved in THF (60 mL) and stirred for 5 h at room temperature. The clear solution was added to a suspension of $\mathrm{CaI_2}$ (2.351 g, 8 mmol) in THF (60 mL) at room temperature and stirred for another 12 h. The solvent was removed from the solution in vacuum, and the residue was extracted with toluene (90 mL). Removal of the solvent from the filtrate in vacuum gave compound **1** as off-white solid. Yield (3.82 g, 2.91 mmol, 72.8%); mp 360−368 °C (decomp). $^1$H NMR (500.13 MHz, $\mathrm{C_6D_6}$): $\delta$ 7.17−7.10 (m, 12 H, *m*-, *p*-Ar−H), 4.80 (s, 2 H, $\gamma$-C*H*), 3.65 (m, 8 H, $\mathrm{O{-}C}H_2\mathrm{{-}CH_2}$), 3.22 (sept, 8H, C*H*$\mathrm{(CH_3)_2}$), 1.66 (s, 12 H, C$H_3$), 1.36 (d, 24 H, $\mathrm{CH(C}H_3)_2$), 1.32 (m, 8H, $\mathrm{O{-}CH_2{-}C}H_2$), and 1.23 (d, 24 H, $\mathrm{CH(C}H_3)_2$) ppm. $^{13}$C{$^1$H} NMR (125.77 MHz, $\mathrm{C_6D_6}$): $\delta$ 165.9, 147.1, 141.8, 124.59, 123.8, 94.8, 69.5, 28.5, 25.6, 25.3, 24.8, and 24.5 ppm. MS (70 eV): *m*/*z* (%): 704.3 (100) [$\mathrm{L^+}$−Me]. Anal. calcd for $\mathrm{C_{66}H_{98}Ca_2I_2N_4O_2}$ (1313.47): C, 60.35; H, 7.52; N, 4.27. Found: C, 60.08; H, 7.92; N, 4.31.

**Synthesis of 2.** Compound **2** was prepared by the same method as compound **1** with LH (3.349 g, 8.00 mmol), $\mathrm{KN(SiMe_3)_2}$ (1.676 g, 8.40 mmol), and $\mathrm{SrI_2}$ (2.731 g, 8.00 mmol). The solid upon crystallization from a saturated solution of *n*-hexane at −5 °C gave analytically pure sample of **2.** Yield (4.247 g, 3.02 mmol, 75.4%); mp 188−190 °C. $^1$H NMR (500.13 MHz, $\mathrm{C_6D_6}$): $\delta$ 7.20−7.15 (m, 12 H, *m*-, *p*-Ar−H), 4.84 (s, 2 H, $\gamma$-C*H*), 3.56 (m, 8 H, $\mathrm{O{-}C}H_2\mathrm{{-}CH_2}$), 3.29 (sept, 8 H, C*H*$\mathrm{(CH_3)_2}$), 1.69 (s, 12 H, C$H_3$), 1.36 (d, 24 H, $\mathrm{CH(C}H_3)_2$), 1.25 (d, 24 H, $\mathrm{CH(C}H_3)_2$), and 1.19 (m, 8 H, $\mathrm{O{-}CH_2{-}C}H_2$) ppm. $^{13}$C{$^1$H}NMR (125.77 MHz, $\mathrm{C_6D_6}$): $\delta$ 164.6, 146.6, 141.6, 124.4, 124.0, 94.0, 69.5, 28.4, 26.2, 25.0, 24.7, and 24.6 ppm. MS (70 eV): *m*/*z* (%): 704.3 (100) [$\mathrm{M^+}$/2−2THF]. Anal. calcd for $\mathrm{C_{66}H_{98}I_2N_4O_2Sr_2}$ (1408.56): C, 56.28; H, 7.01; N, 3.98. Found: C, 56.48; H, 7.29; N, 3.66.

**Synthesis of 3.** A solution of compound **1** (1.31 g, 1 mmol) in THF (25 mL) was cooled to −40 °C, and 2 equiv of potassium tri*sec*-butylborohydride (1 M solution in THF) (2.00 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 2 h. From the solution all volatiles were removed in vacuum, and the residue was extracted with toluene (30 mL). All volatiles were again removed, and single crystals of **3** were obtained from a solution of toluene−THF mixture (1:0.25) (8 mL) stored at −32 °C in a freezer. Yield (1.09 g, 1.53 mmol, 76.8%); mp 175−177 °C. $^1$H NMR (500.13 MHz, $\mathrm{C_6D_6}$): $\delta$ 7.14 (m, 6 H, *m*-, *p*-Ar−H), 4.76 (s, 1 H, $\gamma$-C*H*), 3.84 (m, 4 H, $\mathrm{O{-}C}H_2\mathrm{{-}CH_2}$), 3.10 (br, sept, 4H, C*H*$\mathrm{(CH_3)_2}$), 1.72−1.06, 1.66−1.34, 1.67−0.73 (m, 6 H, $\mathrm{B{-}CH(C}H_2\mathrm{{-}CH_3)(CH_3))}$, 1.62 (s, 6 H, C$H_3$), 1.34 (m, (4 H, $\mathrm{O{-}CH_2{-}C}H_2$), 1.33 (d, 12 H, $\mathrm{CH(C}H_3)_2$), 1.17 (d, 12 H, $\mathrm{CH(C}H_3)_2$), 1.08 (t, 3 H, $\mathrm{B{-}CH(CH_2{-}C}H_3\mathrm{)(CH_3))}$, 1.05 (d, 3 H, $\mathrm{B{-}CH(CH_2{-}CH_3)(C}H_3))$, 0.92 (t, 3 H, $\mathrm{B{-}CH(CH_2{-}C}H_3\mathrm{)(CH_3))}$, 0.83 (t, 3 H, $\mathrm{B{-}CH(CH_2{-}C}H_3\mathrm{)(CH_3))}$, 0.76 (d, 3H, $\mathrm{B{-}CH(CH_2{-}CH_3)(C}H_3))$, 0.73 (d, 3 H, $\mathrm{B\text{-}CH(CH_2{-}CH_3)(C}H_3))$, 0.41 (m, 1 H, $\mathrm{B{-}C}H\mathrm{(CH_2{-}CH_3)(CH_3))}$, 0.07 (m br, 2 H, $\mathrm{B{-}C}H\mathrm{(CH_2{-}CH_3)(CH_3))}$, and −0.05 (br, H, Ca−H−B) ppm. $^{13}$C{$^1$H}NMR(125.77 MHz, $\mathrm{C_6D_6}$): $\delta$ 166.6, 146.6, 141.6, 125.2, 124.3, 94.6, 70.3, 31.1, 30.1, 29.7, 28.6, 25.2, 25.1, 25.0, 25.0, 24.9, 24.7, 20.5, 20.2, 19.9, 15.4, 14.9, and 14.7 ppm (B−C is not visible). $^{11}$B NMR (128.38 MHz, $\mathrm{C_7D_8}$): $\delta$ −4.4 ppm (d, $^1J_{\mathrm{BH}} = 50$ Hz B, BR). IR (Nujol, $\mathrm{cm^{-1}}$): $\tilde{\nu}$ 2649, 2601, 1924, 1903, 1771, 1696, 1625, 1540, 1514, 1458, 1377, 1313, 1262, 1225, 1167, 1098, 1054, 1018, 926, 871, 834, 788, 759, 747, 694, 668, 622, and 597. MS (70 eV): *m*/*z* (%): 403.3 (100) [$\mathrm{L^+}$−Me]. Anal. calcd for $\mathrm{C_{45}H_{77}BCaN_2O}$ (712.99): C, 75.80; H, 10.89; N, 3.93 Found: C, 73.41; H, 10.86; N, 4.01. (The low value for carbon probably due to the high air sensitivity of the compound, partial loss of coordinate THF molecule, and/or metal carbide formation, see also ref [11c]).

**Synthesis of 4.** Compound **4** was prepared by the same method as described for compound **3** with $[\mathrm{LSr}(\mu\text{-}\mathrm{I})\cdot\mathrm{thf}]_2$ (1.409 g, 1.00 mmol) and potassium tri*sec*-butylborohydride (1 M solution in THF) (2.00 mmol). Analytically pure compound **4** was obtained when a solution of **4** in toluene−THF (1:0.25) (8 mL) was stored at −5 °C in a freezer. Yield of **4** (1.15 g, 1.51 mmol, 75.7%); mp 195 °C. $^1$H NMR (500.13 MHz, $\mathrm{C_7D_8}$): $\delta$ 7.11−7.06 (m, 6 H, *m*-, *p*-Ar−H), 4.74 (s, 1 H, $\gamma$-C*H*), 3.80 (m, 4 H, $\mathrm{O{-}C}H_2\mathrm{{-}CH_2}$), 3.09 (br sept, 4 H, C*H*$\mathrm{(CH_3)_2}$), 1.69−1.53 (m, 3 H, $\mathrm{B{-}CH(C}H_2\mathrm{{-}CH_3)(CH_3)}$, 1.65 (s, 6 H, C$H_3$), 1.40 (m, 4 H, $\mathrm{O{-}CH_2{-}C}H_2$), 1.29 (br d, 12 H, $\mathrm{CH(C}H_3)_2$), 1.23 (m, 1 H, $\mathrm{B{-}CH(C}H_2\mathrm{{-}CH_3)(CH_3)}$, 1.18 (d, 12 H, $\mathrm{CH(C}H_3)_2$), 1.02 (t, 3 H, $\mathrm{B{-}CH(CH_2{-}C}H_3\mathrm{)(CH_3))}$, 1.02 (m, 1 H, $\mathrm{B{-}CH(C}H_2\mathrm{{-}CH_3)(CH_3)}$, 0.93 (d, 3 H, $\mathrm{B{-}CH(CH_2{-}CH_3)(C}H_3))$, 0.92 (t, 3 H, $\mathrm{B{-}CH(CH_2{-}C}H_3\mathrm{)(CH_3))}$, 0.89 (d, 3 H, $\mathrm{B{-}CH(CH_2{-}CH_3)(C}H_3))$, 0.82 (t, 3 H, $\mathrm{B{-}CH(CH_2{-}C}H_3\mathrm{)(CH_3))}$, 0.68 (d, 3 H, $\mathrm{B{-}CH(CH_2{-}CH_3)(C}H_3))$, 0.62 (d, 3 H, $\mathrm{B{-}CH(CH_2{-}CH_3)(C}H_3))$, 0.58 (m, 1 H, $\mathrm{B{-}CH(C}H_2\mathrm{{-}CH_3)(CH_3)}$, 0.24−0.16, and 0.09 to −0.08 (m, 3 H, $\mathrm{B{-}C}H\mathrm{(CH_2{-}CH_3)(CH_3))}$ ppm. $^{13}$C{$^1$H} NMR(125.77 MHz, $\mathrm{C_7D_8}$): $\delta$ 165.4, 145.9, 141.5, 125.0, 124.4, 94.2, 69.8, 31.0, 30.8, 30.4, 28.5, 25.2, 25.0, 24.8, 24.7, 20.5, 20.3, 19.9, 15.41, 15.22, and 15.11 ppm. $^{11}$B NMR (128.38 MHz, $\mathrm{C_7D_8}$): $\delta$ −4.7 ppm (d, $^1J_{\mathrm{BH}} = 55$ Hz, B, BR). IR (Nujol, $\mathrm{cm^{-1}}$): $\tilde{\nu}$ 2377.21, 2346.89, 1932.06, 1624.06, 1551.52, 1511.58, 1404.65, 1311.02, 1261.36, 1222.12, 1164.31, 1097.60, 1054.10, 1020.09, 925.73, 868.55, 785.96, 757.73, 741.99, 722.78, 664.57, and 619.22. MS (70 eV): *m*/*z* (%): 403.3 (100) [$\mathrm{L^+}$−Me]. Anal. calcd for $\mathrm{C_{45}H_{77}BN_2OSr}$ (760.54): C, 71.07; H, 10.20; N, 3.68 Found: C, 70.42; H, 9.90; N, 3.70.

**Crystallographic Details for Compounds 2, 3, and 4.** The data for **2**, **3**, and **4** were collected from shock-cooled crystals at 100 K. The data for **2** were collected on a Bruker TXS-Mo

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**Table 2.** Crystallographic and Structure Refinement Data

| param | $\mathbf{2} \cdot 0.5C_6H_{14}$ | **3** | **4** |
|---|---|---|---|
| empirical formula | $C_{69}H_{105}I_2N_4O_2Sr_2$ | $C_{45}H_{77}BCaN_2O$ | $C_{45}H_{77}BN_2OSr$ |
| Fw | 1451.61 | 712.98 | 760.52 |
| $T$(K) | 100.0(5) | 100.0(5) | 100.0(5) |
| cryst system | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$ (Å) | 21.500(6) | 20.749(5) | 20.721(4) |
| $b$ (Å) | 15.4867(18) | 13.176(3) | 13.395(2) |
| $c$ (Å) | 23.025(3) | 16.106(4) | 16.093(3) |
| $\beta$ (°) | 112.0880(10) | 99.155(5) | 100.014(3) |
| $V$ (Å$^3$) | 7014.1(14) | 4350(1) | 4398.7(13) |
| $Z$ | 4 | 4 | 4 |
| $\rho_{calcd}$ (Mg/m$^3$) | 1.357 | 1.089 | 1.148 |
| $F$(000) | 2980 | 1576 | 1648 |
| $\mu$ (Mo K$\alpha$) | 2.413 | 0.178 | 1.259 |
| $\theta$ range for data collcn (°) | 1.62−26.77 | 0.99−25.51 | 1.82−25.11 |
| no. of reflcns collcd/unique | 137550/15123 | 31406/7992 | 66750/7808 |
| obsd reflcns[ $I > 2\sigma(I)$] | ($R_{int}$ = 0.0286) | ($R_{int}$ = 0.1110) | ($R_{int}$ = 0.0654) |
| data/restraints/params | 15 123/16/733 | 7992/0/471 | 7808/21/471 |
| Gof on $F^2$ | 1.061 | 1.001 | 1.077 |
| $R1$, $wR2$[ $I > 2\sigma(I)$] | 0.0224, 0.0528 | 0.0645, 0.1480 | 0.0426, 0.1022 |
| $R1$, $wR2$ (all data) | 0.0283, 0.0545 | 0.1346, 0.1797 | 0.0624, 0.1087 |
| largest diff peak/hole (e Å$^3$) | 0.698 and −0.439 | 0.381 and −0.602 | 0.659 and −0.488 |

rotating anode instrument. For the data collections of **3** and **4** an Incoatec microfocus source was employed.[16] Both diffractometers were equipped with a low-temperature device[17] and used monochromated Mo K$\alpha$ radiation, $\lambda$ = 0.71073 Å. Both machines used mirror optics as radiation monochromator. The data of **2**, **3**, and **4** were integrated with SAINT,[18] and an empirical absorption correction (SADABS) was applied.[19] All structures were solved by direct methods (SHELXS-97)[20] and refined by full-matrix least-squares methods against $F^2$ (SHELXL-97).[21] All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their $U_{iso}$ values constrained to 1.5 times the $U_{eq}$ of their pivot atoms for terminal sp$^3$ carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths and isotropic displacement parameter restraints.[22] Crystal data and experimental details for the X-ray measurements are listed in Table 2. The crystals of compound **3** for X-ray structural analysis were not of good quality.

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**Supporting Information Available:** X-ray data for **2**, **3**, and **4** (CIf ). This material is available free of charge via the Internet at http://pubs.acs.org.

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