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Samarium-Mediated Tandem Reactions of *o*-Carborane. Synthesis and Molecular Structure of $[\{\eta^5:\eta^1:\eta^6\text{-}Me_2Si(C_9H_5CH_2CH_2G)(C_2B_{10}H_{10})Sm\}_2(\mu\text{-}Cl)][Li(THF)_4]$ ($G = NMe_2$ and OMe)

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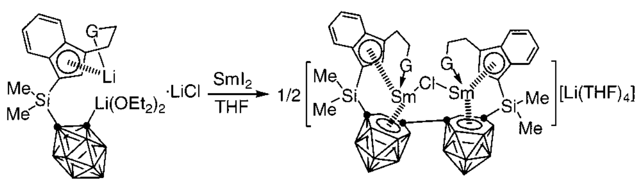
*Summary: New metallacarboranes bearing a (nido-$RC_2B_{10}H_{10})_2^{4-}$ ligand, $[\{\eta^5:\eta^1:\eta^6\text{-}Me_2Si(C_9H_5CH_2CH_2G)(C_2B_{10}H_{10})Sm\}_2(\mu\text{-}Cl)][Li(THF)_4]$ ($G = NMe_2$ (**1**), OMe (**2**)), have been prepared and structurally characterized by treatment of $SmI_2(THF)_x$ with 1 equiv of $[Me_2Si(C_9H_5CH_2CH_2G)(C_2B_{10}H_{10})]Li_2(OEt_2)_2\cdot LiCl$ in THF via unexpected samarium-mediated tandem reactions.*

Transition metal-mediated oxidative coupling and oxidative fusion reactions of carboranes, boranes, and metallacarboranes have been extensively studied.[1] In sharp contrast, metal-mediated reductive coupling of these cage molecules are largely unknown.[2] We recently reported a reductive coupling reaction of $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$ promoted by UV-light leading to the isolation of a biscarborane species.[3] It has been well-documented that *o*-carborane can be readily reduced by group 1 metals to form *nido*-carborane dianions.[4] Our previous work showed that organosamarium(II) compounds can also reduce *o*-carborane, leading to successful preparation of mixed samaracarboranes.[5] We have found new ligand systems that are able to induce reduction and coupling of the cage in a tandem manner. These new findings are reported in this paper.

Scheme 1



$G = NMe_2$ (**1**), OMe (**2**)

Treatment of $[Me_2Si(C_9H_5CH_2CH_2G)(C_2B_{10}H_{10})]Li_2(OEt_2)_2\cdot LiCl$[6] with 1 equiv of $SmI_2(THF)_x$ in THF gave, after workup, novel samaracarboranes $[\{\eta^5:\eta^1:\eta^6\text{-}Me_2Si(C_9H_5CH_2CH_2G)(C_2B_{10}H_{10})Sm\}_2(\mu\text{-}Cl)][Li(THF)_4]$ ($G = NMe_2$ (**1**), OMe (**2**)) as red crystals in about 50% isolated yield,[7] shown in Scheme 1. These two compounds are extremely air- and moisture-sensitive. They are soluble in polar organic solvents such as THF and pyridine, sparely soluble in toluene, and insoluble in hexane. They have been characterized by various spectroscopic data and elemental analyses.[7] The NMR spectra do not offer much information about the bonding and molecular structures of these compounds due to their paramagnetic properties. It is necessary to perform single-crystal X-ray diffraction studies in order to confirm the molec-

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(6) It was prepared from an equimolar reaction between $Me_2Si(C_9H_6CH_2CH_2G)Cl$ and $C_2B_{10}H_{10}Li_2$ followed by treatment with 1 equiv of *n*-BuLi; see Supporting Information for complete synthetic procedures and compound characterization data.

(7) Preparation of $\mathbf{1}\cdot C_7H_8$. To a THF solution of $SmI_2(THF)_x$ (9.7 mL, 1.0 mmol) was slowly added a THF solution of $[Me_2Si(C_9H_5CH_2CH_2NMe_2)(C_2B_{10}H_{10})]Li_2(OEt_2)_2\cdot LiCl$[6] (0.59 g, 1.0 mmol) at room temperature, and the reaction mixture was stirred at room temperature overnight. The solvent was then pumped off, leaving a sticky dark purple solid, to which was added 15 mL of toluene. The mixture was refluxed for several hours. Removal of the solvent afforded a dark red solid that was washed with toluene (3 × 5 mL). The red solid was then extracted with a mixed solvent of toluene and THF (10:1, 3 × 10 mL). The solutions were combined and concentrated to about 15 mL, from which $\mathbf{1}\cdot C_7H_8$ was isolated as red crystals after the solution stood at room temperature for a week (0.36 g, 53%). ^1H NMR (pyridine-d_5): δ 12.27 (br s, 1H), 11.72 (br s, 1H), 10.38 (d, $J = 6.0$ Hz, 1H), 10.17 (d, $J = 9.0$ Hz, 1H), 9.96 (br s, 1H), 7.83 (br s, 1H), 7.29 (br s, 5H), 6.92 (br s, 1H), 6.01 (br s, 1H), 5.73 (br s, 1H), 5.63 (br s, 1H) ($C_9\mathit{H}_5$ and $C_6\mathit{H}_5CH_3$), 2.87 (m, 4H), 2.68 (m, 4H) ($C\mathit{H}_2C\mathit{H}_2N(CH_3)_2$), 2.18 (br s, 15H) ($N(C\mathit{H}_3)_2$ and $C_6H_5C\mathit{H}_3$), 3.66 (m, 16H), 1.59 (m, 16H) (THF), 0.68 (s, 6H), −0.01 (s, 6H) ($Si(C\mathit{H}_3)_2$). ^{13}C NMR (pyridine-d_5): δ 147.77, 146.11, 142.24, 138.52, 134.74, 129.75, 128.99, 126.10, 124.81, 123.13, 120.45, 120.09, 119.26, 114.05 (C_9H_5 and $\mathit{C}_6H_5CH_3$), 59.83, 45.87, 27.01 ($\mathit{C}H_2\mathit{C}H_2N(\mathit{C}H_3)_2$), 90.16, 58.45 ($\mathit{C}_2B_{10}H_{11}$), 68.18, 26.15 (THF), 23.19 ($C_6H_5\mathit{C}H_3$), −0.37, −4.45 ($Si(\mathit{C}H_3)_2$). ^{11}B NMR (pyridine-d_5): δ −4.54 (4), −11.00 (4), −15.04 (8), −15.92 (4). IR (KBr, cm^{-1}): ν_{BH} 2527 (vs), 2444 (s). Anal. Calcd for $C_{42}H_{78}B_{20}ClLiN_2O_2Si_2Sm_2$ (**10** − 2THF − toluene): C, 40.08; H, 6.25; N, 2.23. Found: C, 39.75; H, 6.47; N, 2.50. **2** was prepared as red crystals from $SmI_2(THF)_x$ (9.7 mL, 1.0 mmol) and $[Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Li_2(OEt_2)_2\cdot LiCl$[6] (0.58 g, 1.0 mmol) in THF using the procedures similar to those used for **1**: yield 0.32 g (47%). ^1H NMR (pyridine-d_5): δ 13.89 (br s, 1H), 10.48 (d, $J = 9.0$ Hz, 1H), 9.82 (d, $J = 9.0$ Hz, 1H), 6.93 (br s, 1H), 6.52 (m, 1H), 6.20 (m, 1H), 5.91 (m, 1H), 5.12 (br s, 1H), 4.40 (br s, 1H), 4.03 (br s, 1H) ($C_9\mathit{H}_5$), 3.86 (s, 6H), 3.36 (m, 4H), 3.17 (m, 4H) ($C\mathit{H}_2C\mathit{H}_2OC\mathit{H}_3$), 3.65 (m, 16H), 1.59 (m, 16H) (THF), −0.28 (s, 6H), −0.51 (s, 6H) ($Si(C\mathit{H}_3)_2$). ^{13}C NMR (pyridine-d_5): δ 129.35, 128.60, 125.70, 122.69, 121.33, 120.84, 119.98, 119.32 (C_9H_5; other carbons are overlapped with those of solvent), 69.50, 58.67, 31.65 ($\mathit{C}H_2\mathit{C}H_2O\mathit{C}H_3$), 88.43, 65.73 ($\mathit{C}_2B_{10}H_{11}$), 67.79, 22.78 (THF), 0.24, 0.08 ($Si(\mathit{C}H_3)_2$). ^{11}B NMR (pyridine-d_5): δ −3.5 (4), −9.8(4), −14.5(8), −15.0(4). IR (KBr, cm^{-1}): ν_{BH} 2538 (vs), 2450 (m). Anal. Calcd for $C_{48}H_{88}B_{20}ClLiO_6Si_2Sm_2$: C, 41.87; H, 6.44. Found: C, 41.66; H, 6.57.

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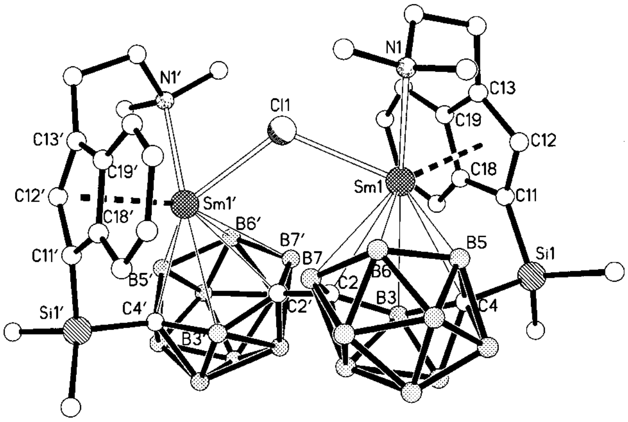

Figure 1. Molecular structure of $[\{\eta^5:\eta^1:\eta^6\text{-Me}_2\text{Si}(\text{C}_9\text{H}_5\text{CH}_2\text{CH}_2\text{NMe}_2)(\text{C}_2\text{B}_{10}\text{H}_{10})\text{Sm}\}_2(\mu\text{-Cl})]^-$ in **1**. Selected bond distances (Å) and angle (deg): Sm1−Cl1 = 2.688(3); Sm1−N1 = 2.709(8); av Sm1−C$_5$ ring = 2.731(8); av Sm1−cage atom = 2.815(9); Sm1′−Cl1 = 2.668(3); Sm1′−N1′ = 2.665(8); av Sm1′−C$_5$ ring = 2.732(8); av Sm1′−cage atom = 2.803(9); C2−C2′ = 1.509(10); Sm1−Cl1−Sm1′ = 120.07(10).

ular structures and elucidate the metal−ligand bonding in these metallacarboranes.

X-ray analyses[8] reveal that compounds **1** and **2** have similar solid-state structures, but **1** shows one toluene of solvation, leading to a lower symmetry of its crystal system compared with that of **2**. Both of them consist of well-separated, alternating layers of discrete tetrahedral cations $[\text{Li(THF)}_4]^+$ and complex anions $[\{\eta^5:\eta^1:\eta^6\text{-Me}_2\text{Si}(\text{C}_9\text{H}_5\text{CH}_2\text{CH}_2\text{G})(\text{C}_2\text{B}_{10}\text{H}_{10})\text{Sm}\}_2(\mu\text{-Cl})]^-$. In the anion, each Sm^{3+} ion is η^6-bound to a *nido*-$\text{C}_2\text{B}_{10}\text{H}_{10}$ unit via a six-membered C_2B_4 bonding face, η^5-bound to the five-membered ring of the indenyl group, and coordinated to a doubly bridging Cl atom and either the N atom in **1** or the O atom in **2** from the appended group of indenyl in a highly distorted tetrahedral geometry with the formal coordination number of eight (Figure 1). It is noted that two *nido*-$\text{C}_2\text{B}_{10}\text{H}_{10}$ units are connected to each other through a C−C single bond, and the dihedral angles between the two six-membered C_2B_4 rings are 63.3° for **1** and 69.6° for **2**, respectively. These large angles presumably result from the steric effects. As far as we are aware, these are rare examples of metallacarboranes bearing a $(nido\text{-RC}_2\text{B}_{10}\text{H}_{10})_2^{4-}$ tetraanion ligand.

The average Sm−C(C$_5$ ring) and Sm−cage atom distances of 2.732(8) and 2.809(8) Å in **1** and 2.75(2) and 2.84(3) Å in **2** are close to the corresponding values of 2.751(4) and 2.823(4) Å observed in $[\eta^5:\eta^6\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm(THF)}_2$,[5b] respectively. The average Sm−Cl distances of 2.678(3) Å in **1** and 2.645(4) Å in **2**, the average Sm−N distance of 2.687(8) Å in **1**, and the average Sm−O distance of 2.49(2) Å in **2** fall within the range of Sm−Cl, Sm−N, and Sm−O distances found in the literature, respectively.[9]

It is clear that the formation of **1** and **2** involves two-electron reduction and coupling of the carborane cages. It may be suggested that the reaction of $\text{SmI}_2(\text{THF})_x$ with $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_5\text{CH}_2\text{CH}_2\text{G})(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Li}_2(\text{OEt}_2)_2\cdot\text{LiCl}$ gives the first intermediate $[\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_5\text{CH}_2\text{CH}_2\text{G})(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Sm}^{\text{II}}$,[5b] followed by intramolecular electron transfer from the Sm^{II} to the cage, leading to the cleavage of the Sm-cage carbon and the cage C−C bonds; coupling of the two cages via the formation of a C−C single bond generates the thermodynamically stable *nido*-species $(nido\text{-RC}_2\text{B}_{10}\text{H}_{10})_2^{4-}$, which then bonds to the Sm^{3+} ions in a η^6-fashion to form the final product.

Comparisons between $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_5\text{CH}_2\text{CH}_2\text{G})(\text{C}_2\text{B}_{10}\text{H}_{10})]^{2-}$ and $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]^{2-}$ may conclude that the appended heteroatom group has very large effects on the reactivity of the resulting organosamarium(II) compounds. In an equimolar reaction with $\text{SmI}_2(\text{THF})_x$, for example, the former gives **1** or **2** and the latter affords $[\{\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\}_2\text{Sm}]^-$.[10]

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Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates, figures containing the atom-numbering schemes for **1** and **2**, and text giving experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] Crystal data for **1**·C_7H_8 ($\text{C}_{57}\text{H}_{102}\text{B}_{20}\text{ClLiN}_2\text{O}_4\text{Si}_2\text{Sm}_2$; fw, 1494.9): triclinic, space group $P\bar{1}$, $a = 10.662(2)$ Å, $b = 15.748(3)$ Å, $c = 24.832(5)$ Å, $\alpha = 104.00(3)°$, $\beta = 99.43(3)°$, $\gamma = 103.29(3)°$, $V = 3829(1)$ Å^3, $d_{\text{calcd}} = 1.297$ g/cm^3, $Z = 2$, $R_1 = 0.065$ ($I > 2.0\sigma(I)$), $wR_2 = 0.179$ on F^2. Crystal data for **2** ($\text{C}_{48}\text{H}_{88}\text{B}_{20}\text{ClLiO}_6\text{Si}_2\text{Sm}_2$; fw, 1376.7): monoclinic, space group $P2_1/c$, $a = 10.18(1)$ Å, $b = 21.06(4)$ Å, $c = 33.39(6)$ Å, $\beta = 93.04(14)°$, $V = 7148(19)$ Å^3, $d_{\text{calcd}} = 1.279$ g/cm^3, $Z = 4$, $R_1 = 0.088$ ($I > 2.0\sigma(I)$), $wR_2 = 0.181$ on F^2.

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