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Application of a New Versatile Ligand to Lanthanide(II) Chemistry: Synthesis, Reactivity, and Structure of a New Class of Organolanthanide Complexes

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Reaction of $Me_2Si(C_9H_7)Cl$ with 1 equiv of $Li_2C_2B_{10}H_{10}$ gave, after hydrolysis, the new versatile ligand $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (**1**). **1** can be conveniently converted into the monoanion $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]^-$ (**2**) and the dianion $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ (**3**) by treatment with 1 equiv or excess amounts of NaH, respectively. Treatment of SmI_2 with **2** in THF gave the unexpected redox product $[\eta^5{:}\eta^6\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Sm(THF)_2$ (**4**). Reaction of SmI_2 with 1 equiv of **3** in THF, followed by reaction with **2**, gave the unexpected C−H bond reduction product $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}_2Sm][Na(THF)_6]$ (**5**). In contrast, reaction of YbI_2 with 1 or 2 equiv of **2** afforded $[\{\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}Yb(\mu\text{-}I)(THF)_2]_2$ (**6**) or $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]_2Yb(THF)_2$ (**7**), respectively. Treatment of YbI_2 with 1 equiv of **3** in THF gave $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Yb(THF)_3$ (**8**), which is the first mixed-ligand organolanthanide(II) complex containing both Ln−C π and σ bonds to be reported. **8** can also be prepared from the reaction of **6** with excess NaH in THF. Reaction of **8** with 1 equiv of **2** in THF yielded $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Yb(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na(THF)_3$ (**9**), which can also be prepared by reaction of **7** with 1 equiv of NaH in THF. These new complexes have been fully characterized by ^1H, ^{13}C, and ^{11}B NMR, IR spectroscopy, and elemental analyses. The molecular structures of **4**, **5**, **8**, and **9** have been further confirmed by single-crystal X-ray analyses.

Introduction

The chemistry of the indenyl-based organolanthanide(II) complexes is largely unexplored, although organolanthanide chemistry has witnessed an explosive growth in the past few decades.[1] To the best of our knowledge, $(C_9H_7)_2Sm(THF)_3$ is the only reported example with poor structural data.[2] In view of the remarkable and often unique reactivity exhibited by bis-ligated organolanthanide(II) complexes, especially $(C_5Me_5)_2Sm(THF)_n$ ($n = 0, 2$)[3,4] and $(ArO)_2Sm(THF)_3$ (Ar = $C_6H_2\text{-}{}^tBu_2\text{-}2,6\text{-}Me\text{-}4$),[5] we are interested in the indenyl-based organolanthanide(II) chemistry.

As the isolobal analogues to the cyclopentadienyl group, C_2B_9,[6] C_2B_{10},[7] and C_2B_4[8] ligand systems have been successively introduced to lanthanide chemistry, resulting in a new class of organolanthanide complexes. Ln(II) complexes containing the decaborate anion $[B_{10}H_{14}]^{2-}$ were also reported.[9] Due to the unique properties of the carborane molecules, the bondings between metal and carboranyl ligands can be varied from 2e−3c σ bonds to η^5 or η^6 π bonds, depending on the sizes of the bonding faces and the substituents on the bonding faces. We have recently reported the versatile ligand $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$, which possesses the properties of both cyclopentadienyl and carboranyl groups.[10] We now extend our work to indenyl systems, since the sterically demanding yet planar indenyl ring and the known diverse bonding models ($\eta^5-\eta^3-\eta^1$)

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between the central metal and five-membered ring of the indenyl ligand[11] may offer organolanthanide complexes with some unique properties. Furthermore, a bridged ligand may also afford organometallic complexes with advantageous solubility, crystallizability, thermal stability, and resistance to ligand redistribution. This work reports the synthesis, reactivity, and structure of a new class of organolanthanide complexes with the new versatile ligand $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $LnI_2(THF)_x$ (Ln = Sm, Yb),[12] $Me_2Si(C_9H_7)Cl$,[13] and $Li_2C_2B_{10}H_{10}$[14] were prepared according to the literature methods. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Nicolet Magna 550 Fourier transform spectrometer. The MS spectrum was recorded on a Bruker APEX FTMS spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker ARX-500 spectrometer at 160.46 MHz. All chemical shifts are reported in δ units with reference to internal or external TMS (0.00 ppm) or with respect to the residual protons of the deuterated solvent for proton and carbon chemical shifts and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd, Brunel University, Middlesex, U.K.

Preparation of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (1). To a solution of o-$C_2B_{10}H_{12}$ (4.0 g, 27.8 mmol) in a dry toluene/diethyl ether (2/1) mixture (60 mL) was slowly added a 1.60 M solution of n-BuLi in hexane (34.7 mL, 55.5 mmol) at 0 °C with stirring. The mixture was warmed to room temperature, stirred for 30 min, and then cooled to 0 °C again. A solution of $Me_2Si(C_9H_7)Cl$ (5.78 g, 27.8 mmol) in a toluene/diethyl ether (2/1) mixture (20 mL) was added dropwise. The mixture was refluxed overnight and then quenched with 50 mL of cold water, transferred to the separatory funnel, and diluted with 100 mL of diethyl ether. The organic layer was separated, and the aqueous layer was extracted with additional Et_2O (3×30 mL). The ether solutions were then combined and dried over anhydrous $MgSO_4$. Concentration of the filtrate gave a crude product which was purified by recrystallization from hexane to yield **1** as a white solid (6.75 g, 77%). Mp: 85−87 °C. ^1H NMR ($CDCl_3$): δ 7.50 (d, $J = 9.0$ Hz, 1H), 7.46 (d, $J = 9.0$ Hz, 1H), 7.32 (t, $J = 9.0$ Hz, 1H), 7.26 (t, $J = 9.0$ Hz, 1H), 6.99 (d, $J = 3.0$ Hz, 1H), 6.70 (dd, $J = 3.0$ Hz, 1H), 3.62 (s, 1H), 3.19 (br s, 1H), 0.46 (s, 3H), −0.04 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 145.10, 143.24, 134.74, 131.75, 126.88, 125.18, 124.34, 122.40, 66.28, 60.36, 44.40, −0.94, −4.0. ^{11}B NMR ($CDCl_3$): δ −0.4 (1), −2.2 (1), −7.5 (2), −11.6 (2), −12.7 (2), −14.0 (2). IR (cm^{-1}): ν 3062 (w), 2965 (w), 2595 (vs), 1450 (m), 1255 (m), 1073 (s), 1042 (s), 1031 (vs), 877(s), 809 (s), 775 (s), 718 (s), 461 (m). Anal. Calcd for $C_{13}H_{24}B_{10}Si$: C, 49.33; H, 7.64. Found: C, 48.92, H, 7.58. High-resolution FAB-MS (m/z): calcd, 316.2637; found, 316.2634.

Preparation of $[\eta^5{:}\eta^6\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Sm(THF)_2$ (4). A mixture of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.317 g, 1.0 mmol) and NaH (0.024 g, 1.0 mmol) in THF (25 mL) was stirred at room temperature overnight. The resulting clear colorless solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (**2**) was slowly added to a THF solution of SmI_2 (9.85 mL, 1.0 mmol) at room temperature. The reaction mixture was then stirred at room temperature for 8 h. The solvent was pumped off, and 20 mL of toluene was added to the residue. The brownish yellow suspension was heated to 100 °C, and this temperature was maintained for 3 h. After hot filtration, the hot solution was slowly cooled to room temperature, affording **4** as orange-red crystals (0.24 g, 39%). ^1H NMR (pyridine-d_5): δ 15.07 (br s, 1H), 11.25 (br s, 1H), 7.69 (br, 1H), 7.00 (br, 1H), 5.35 (br, 2H), 4.05 (m, 8H), 2.63 (br, 1H), 2.00 (m, 8H), 1.56 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (pyridine-d_5): δ 138.72, 138.19, 130.62, 127.98, 124.20, 121.12, 120.78, 119.74, 109.97, 67.99, 65.90, 25.92, 1.06, −0.56. The ^{11}B NMR spectrum consisted of very broad, unresolved resonances. IR (cm^{-1}): ν 3060 (w), 2964 (m), 2899 (m), 2534 (vs), 2500 (s), 1458 (m), 1405 (m), 1384 (m), 1254 (s), 1156 (m), 1064 (s), 1035 (vs), 863 (s), 832 (s), 801 (vs), 675 (m), 454 (m). Anal. Calcd for $C_{25}H_{47}B_{10}O_3SiSm$ (**4** + THF): C, 44.01; H, 6.94. Found: C, 44.45; H, 7.05.

The reaction of SmI_2 with $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ in THF in a molar ratio of 1:2, followed by procedures similar to those used above, gave **4** in 40% yield.

Preparation of $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}_2Sm][Na(THF)_6]$ (5). A suspension of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.317 g, 1.0 mmol) and NaH (0.072 g, 3.0 mmol) in THF (20 mL) was refluxed overnight. The resulting clear colorless solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$ (**3**) was slowly added to a THF solution of SmI_2 (9.85 mL, 1.0 mmol) at 0 °C, and the mixture was stirred at room temperature for 4 h. To this dark blue solution was then added a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (1.0 mmol) at room temperature. The reaction mixture was stirred at room temperature overnight. After removal of the solvent and addition of toluene (25 mL), the brownish yellow suspension was heated to 100 °C; this temperature was maintained for 0.5 h. After hot filtration, **5** was crystallized out as orange-yellow crystals (0.74 g, 60%) upon slow cooling to room temperature. ^1H NMR (pyridine-d_5): δ 14.54 (br s, 2H), 13.24 (br s, 2H), 9.92 (d, $J = 9.0$ Hz, 2H), 7.30 (t, $J = 9.0$ Hz, 2H), 5.31 (t, $J = 9.0$ Hz, 2H), 3.41 (m, 24H), 2.18 (s, 6H), 1.38 (m, 24H), 1.12 (d, $J = 9.0$ Hz, 2H), 0.57 (s, 6H). ^{13}C NMR (pyridine-d_5): δ 129.03, 126.06, 123.26, 121.64, 120.55, 120.10, 117.62, 115.17, 101.70, 86.35, 68.31, 64.98, 26.28, 2.56, 0.40. ^{11}B NMR (pyridine-d_5): δ −3.6 (4), −8.0 (4), −10.0 (4), −14.1 (6), −15.0 (2). IR (cm^{-1}): ν 3073 (w), 2971 (m), 2878 (m), 2573 (vs), 1446 (m), 1410 (m), 1256 (s), 1159 (m), 1087 (s), 1046 (vs), 1022 (s), 886 (m), 833 (s), 807 (s), 779 (s), 743 (m), 682 (m), 446 (m). Anal. Calcd for $C_{42}H_{76}B_{20}NaO_4Si_2Sm$ (**5** − 2THF): C, 46.24; H, 7.02. Found: C, 46.33; H, 7.19.

Preparation of $[\{\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}Yb(\mu\text{-}I)(THF)_2]_2$ (6). To a THF solution of YbI_2 (25.0 mL, 1.0 mmol)

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was added dropwise a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (**2**) (15.0 mL, 1.0 mmol) with stirring at 0 °C, and the mixture was stirred overnight at room temperature. The color of the solution was changed from yellow to orange and finally to red. After removal of the solvent, the residue was extracted with toluene (3 × 10 mL). The toluene solutions were combined and concentrated to about 15 mL. **6** was isolated as a red crystalline solid when the solution stood at room temperature for several days (0.48 g, 70%). ^1H NMR (pyridine-d_5): δ 7.65 (d, $J = 6.3$ Hz, 1H), 7.42 (d, $J = 6.3$ Hz, 1H), 7.16 (br s, 1H), 6.90 (m, 2H), 6.73 (br s, 1H), 3.63 (m, 8H), 2.87 (br s, 1H), 1.61 (m, 8H), 0.59 (s, 6H). ^{13}C NMR (pyridine-d_5): δ 131.68, 127.30, 122.13, 121.63, 121.31, 118.76, 118.14, 101.10, 92.49, 70.59, 67.16, 61.91, 25.14, −1.57. ^{11}B NMR (pyridine-d_5): δ −3.5 (2), −8.0 (2), −11.8 (2), −13.0 (2), −14.1 (2). IR (cm^{-1}): ν 3065 (m), 3042 (m), 2959 (m), 2888 (m), 2585 (vs), 1447 (m), 1409 (s), 1321 (m), 1289 (m), 1253 (s), 1145 (s), 1072 (m), 1027 (s), 970 (m), 870 (m), 838 (m), 808 (s), 747 (s), 677 (m), 442 (m). Anal. Calcd for $C_{46}H_{86}B_{20}I_2O_5Si_2Yb_2$ (**6** + THF): C, 34.72; H, 5.45. Found: C, 34.50; H, 5.68.

Preparation of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]_2Yb(THF)_2$ (7). To a THF solution of YbI_2 (12.5 mL, 0.50 mmol) was slowly added a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (**2**; 25 mL, 1.0 mmol) at room temperature, and the mixture was stirred at room temperature for 6 h. After removal of the solvent and addition of toluene (20 mL), the suspension was refluxed for 3 h. Hot filtering and cooling to room temperature yielded **7** as a red crystalline solid (0.32 g, 67%). ^1H NMR (pyridine-d_5): δ 7.96 (d, $J = 7.5$ Hz, 2H), 7.87 (d, $J = 7.5$ Hz, 2H), 7.32 (d, $J = 3.3$ Hz, 2H), 7.03 (t, $J = 7.5$ Hz, 2H), 6.95 (t, $J = 7.5$ Hz, 2H), 6.85 (d, $J = 3.3$ Hz, 2H), 4.62 (br s, 2H), 3.45 (m, 8H), 1.40 (m, 8H), 0.60 (s, 12H). ^{13}C NMR (pyridine-d_5): δ 137.80, 130.10, 126.00, 124.30, 121.47, 121.18, 116.27, 115.75, 102.81, 69.31, 66.02, 58.52, 27.27, 1.44. ^{11}B NMR (pyridine-d_5): δ −3.6 (6), −8.0 (2), −10.1 (2), −14.1 (8), −15.0 (2). IR (cm^{-1}): ν 3065 (w), 3035 (w), 2973 (m), 2876 (m), 2564 (vs), 1448 (m), 1385 (m), 1324 (w), 1254 (s), 1148 (m), 1085 (s), 1047 (s), 832 (m), 807 (s), 769 (s), 749 (m), 675 (m). Anal. Calcd for $C_{30}H_{54}B_{20}OSi_2Yb$ (**7** − THF): C, 41.12; H, 6.21. Found: C, 40.76; H, 7.13.

Reaction of **6** with an equimolar amount of **2** in THF at room temperature, followed by procedures similar to those used above, gave red crystals identified as **7** in 70% yield.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Yb(THF)_3$ (8). To a THF solution of YbI_2 (25.0 mL, 1.0 mmol) was added dropwise a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$ (**3**; 20 mL, 1.0 mmol) at room temperature, and the mixture was stirred at room temperature for 8 h. After removal of the solvent and addition of toluene (25 mL), the suspension was refluxed for 3 h. Hot filtering and slow cooling to room temperature afforded **8** as red crystals (0.37 g, 53%). ^1H NMR (pyridine-d_5): δ 7.93 (d, $J = 8.0$ Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 6.97 (d, $J = 3.0$ Hz, 1H), 6.88 (t, $J = 8.0$ Hz, 1H), 6.68 (t, $J = 8.0$ Hz, 1H), 6.31 (d, $J = 3.0$ Hz, 1H), 3.45 (m, 12H), 1.41 (m, 12H), 0.67 (s, 3H), 0.48 (s, 3H). ^{13}C NMR (pyridine-d_5): δ 134.86, 132.53, 128.08, 122.66, 119.68, 119.60, 114.29, 102.06, 100.70, 81.45, 68.61, 26.58, 1.19, 1.03. ^{11}B NMR (pyridine-d_5): δ −0.4 (1), −1.5 (1), −3.7 (2), −8.5 (4), −10.0 (1), −10.9 (1). IR (cm^{-1}): ν 3069 (w), 2977 (m), 2961 (m), 2891 (m), 2565 (vs), 1448 (m), 1407 (m), 1249 (m), 1159 (m), 1084 (m), 1032 (s), 874 (s), 833 (s), 808 (s), 754 (s), 675 (m), 447 (m). Anal. Calcd for $C_{21}H_{38}B_{10}O_2SiYb$ (**8** − THF): C, 39.93; H, 6.06. Found: C, 40.22; H, 6.22.

Reaction of **6** with excess amounts of NaH in THF at room temperature, followed by procedures similar to those used above, gave red crystals identified as **8** in 50% yield.

Preparation of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Yb(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na(THF)_3$ (9). To a THF solution (20 mL) of $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Yb(THF)_3$ (**8**; 0.20 g, 0.029 mmol) was added dropwise a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (**2**; 10 mL, 0.029 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 10 h. After removal of the solvent and addition of toluene (20 mL), the suspension was refluxed for 3 h. Hot filtering and slow cooling to room temperature afforded **9** as red crystals (0.243 g, 77%). ^1H NMR (pyridine-d_5): δ 7.95 (d, $J = 7.0$ Hz, 2H), 7.83 (d, $J = 7.0$ Hz, 2H), 7.30 (br s, 2H), 7.02 (m, 2H), 6.94 (m, 2H), 6.82 (br s, 2H), 4.35 (br s, 1H), 3.45 (m, 16H), 1.41 (m, 16H), 0.61 (m, 12H). ^{13}C NMR (pyridine-d_5): δ 138.37, 135.00, 128.64, 122.92, 121.46, 121.20, 115.40, 114.88, 101.51, 89.25, 73.82, 67.96, 64.44, 57.19, 25.93, 0.03. ^{11}B NMR (pyridine-d_5): δ −3.2 (1), −3.7 (6), −7.9 (2), −10.1 (2), −11.5 (1), −13.4 (1), −14.1 (6), −14.9 (1). IR (cm^{-1}): ν 3066 (w), 3037 (w), 2974 (m), 2877 (m), 2566 (vs), 1462 (m), 1404 (m), 1325 (m), 1290 (m), 1255 (s), 1149 (m), 1084 (m), 1048 (s), 1030 (s), 868 (m), 833 (s), 808 (s), 773 (s), 750 (s), 675 (m), 447 (m), 420 (m). Anal. Calcd for $C_{38}H_{69}B_{20}NaO_3Si_2Yb$ (**9** − THF): C, 43.79; H, 6.67. Found: C, 43.34; H, 6.73.

Treatment of **7** with an equimolar amount of NaH in THF at room temperature, followed by procedures similar to those used above, gave a red crystalline solid identified as **9** in 60% yield.

X-ray Structure Determination. All single crystals were immersed in Paratone-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on an MSC/Rigaku RAXIS-IIC imaging plate using Mo Kα radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program.[15] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the Siemens SHELXTL program package (PC version).[16] Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinement are given in Table 1. Selected bond distances and angles are listed in Table 2. Further details are included in the Supporting Information.

Results and Discussion

Ligand Synthesis. Treatment of $Me_2Si(C_9H_7)Cl$ with 1 equiv of $Li_2C_2B_{10}H_{10}$ in toluene/ether at 0 °C gave, after hydrolysis, $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ **(1)** in 77% isolated yield (Scheme 1). The ^1H NMR spectrum indicates that **1** is a pure compound in which the silicon atom bonds only to the sp^3 carbon of the five-membered ring. Two methyl groups at the silicon atom are not equivalent, as indicated by ^1H and ^{13}C NMR spectra. ^1H NMR chemical shifts of the CH vertex of the cage and the sp^3 CH of the indenyl group are 3.19 and 3.62 ppm, respectively. The ^{11}B NMR spectrum exhibits a 1:1:2:2:2:2 splitting pattern that is similar to those of $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$[10a] and $Me_2Si(^tBu)(C_2B_{10}H_{11})$.[14] It is noted that the ^{11}B NMR spectrum of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$,[17] an analogue of $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$, shows a 1:1:1:2 splitting pattern, indicating that the ^{11}B NMR of the icosahedral cage is very sensitive to the substituents.

Since compound **1** contains both indenyl and carboranyl groups, it is expected to have some properties of both units. For instance, **1** can be conveniently converted into the monoanion $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]^-$ (**2**)

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(15) Higashi, T. ABSCOR−An Empirical Absorption Correction Based on Fourier Coefficient Fitting; Rigaku Corp., Tokyo, 1995.

(16) SHELXTL V 5.03 Program Package; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.

(17) Hong, E.; Kim, Y.; Do, Y. *Organometallics* **1998**, *17*, 2933.

Table 1. Crystal Data and Summary of Data Collection and Refinement Details for 4, 5, 8, and 9

	4	**5**	**8**	**9**
formula	$C_{21}H_{39}B_{10}O_2SiSm$	$C_{50}H_{92}B_{20}NaO_6Si_2Sm$	$C_{25}H_{46}B_{10}O_3SiYb$	$C_{42}H_{77}B_{20}NaO_4Si_2Yb$
cryst size (mm)	0.06 × 0.09 × 0.20	0.07 × 0.25 × 0.38	0.30 × 0.32 × 0.36	0.20 × 0.24 × 0.30
fw	610.06	1234.96	703.85	1114.45
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$C2/c$	$P2_1/n$	$P\bar{1}$
a, Å	10.344(1)	31.186(9)	11.125(4)	10.717(1)
b, Å	11.848(1)	11.015(2)	17.564(4)	14.908(1)
c, Å	23.604(1)	20.767(8)	17.333(4)	19.450(1)
α, deg				73.06(1)
β, deg	99.74(1)	109.83(2)	101.59(2)	85.55(1)
γ, deg				72.31(1)
V, Å^3	2851.1(5)	6711(3)	3318(2)	2831.9(3)
Z	4	4	4	2
D_{calcd}, Mg/m^3	1.421	1.222	1.409	1.307
radiation (λ), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2θ range, deg	3.0−51.0	3.0−50.0	4.0−50.0	2.0−52.0
μ, mm^{-1}	2.119	0.959	2.880	1.739
F(000)	1228	2564	1416	1140
T, K	293	293	293	293
no. of indep rflns	3836	5889	5837	8878
no. of obsd rflns	3836	5834	5806	8868
no. of params refined	317	477	362	597
goodness of fit	1.109	0.885	0.875	1.001
R1	0.058	0.054	0.044	0.050
wR2	0.119	0.127	0.112	0.144
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	0.62, −0.76	0.47, −1.18	1.30, −1.55	1.22, −1.33

Table 2. Selected Interatomic Distances (Å) and Angles (deg)[a]

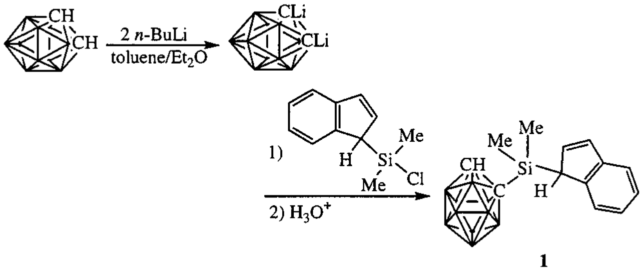
			Complex **4**				
Sm(1)−C(11)	2.617(3)	Sm(1)−C(19)	2.866(4)	Sm(1)−C(2)	2.720(4)	Sm(1)−B(6)	2.639(3)
Sm(1)−C(12)	2.696(3)	Sm(1)−O(1)	2.419(2)	Sm(1)−B(3)	2.863(4)	Sm(1)−Cnt5	2.468
Sm(1)−C(13)	2.828(4)	Sm(1)−O(2)	2.393(2)	Sm(1)−B(4)	2.993(5)	Sm(1)−Cnt6	2.298
Sm(1)−C(18)	2.748(3)	Sm(1)−C(1)	2.866(3)	Sm(1)−B(5)	2.855(4)	av Sm(1)−C(C_5 ring)	2.751(4)
						av Sm(1)−cage atom	2.823(4)
O(1)−Sm(1)−O(2)	82.68(7)	O(1)−Sm(1)−Cnt5	105.5	O(1)−Sm(1)−Cnt6	107.1	Cnt5−Sm(1)−Cnt6	126.0
			Complex **5**				
Sm(1)−C(11)	2.711(3)	Sm(1)−C(18)	2.840(3)	Na(1)−O(1)	2.360(2)	Sm(1)−Cnt5	2.478
Sm(1)−C(12)	2.686(3)	Sm(1)−C(19)	2.818(3)	Na(1)−O(2)	2.394(2)	av Sm(1)−C(C_5 ring)	2.757(2)
Sm(1)−C(13)	2.729(3)	Sm(1)−C(1)	2.606(3)	Na(1)−O(3)	2.495(2)		
C(1)−Sm(1)−C(1A)	109.2(12)	Cnt5−Sm(1)−C(1)	102.3	Cnt5−Sm(1)−Cnt5(A)	112.6		
			Complex **8**				
Yb(1)−O(1)	2.529(2)	Yb(1)−C(2)	2.584(3)	Yb(1)−C(43)	2.814(3)	av Yb(1)−C(C_5 ring)	2.750(3)
Yb(1)−O(2)	2.372(2)	Yb(1)−C(41)	2.702(3)	Yb(1)−C(48)	2.671(3)	av Yb(1)−O	2.432(2)
Yb(1)−O(3)	2.395(2)	Yb(1)−C(42)	2.800(3)	Yb(1)−C(49)	2.765(3)	Yb(1)−Cnt5	2.473
O(1)−Yb(1)−O(2)	78.36(7)	O(2)−Yb(1)−O(3)	113.59(7)	O(3)−Yb(1)−O(1)	75.09(7)	C(2)−Yb(1)−O(3)	86.19(8)
O(2)−Yb(1)−C(2)	91.36(8)	O(1)−Yb(1)−C(2)	152.52(8)	Cnt5−Yb(1)−O(1)	103.6	Cnt5−Yb(1)−O(2)	112.3
Cnt5−Yb(1)−O(3)	132.6	Cnt5−Yb(1)−C(2)	103.9				
			Complex **9**				
Yb(1)−C(11)	2.754(2)	Yb(1)−C(21)	2.763(2)	Na(1)−C(23)	3.042(3)	av Yb(1)−C(C_5 ring1)	2.817(3)
Yb(1)−C(12)	2.744(3)	Yb(1)−C(22)	2.706(2)	Na(1)−C(28)	2.878(2)	av Yb(1)−C(C_5 ring2)	2.820(3)
Yb(1)−C(13)	2.834(3)	Yb(1)−C(23)	2.812(3)	Na(1)−C(29)	3.014(2)	av Na(1)−C(C_5 ring2)	2.934(3)
Yb(1)−C(18)	2.826(3)	Yb(1)−C(28)	2.889(2)	Na(1)−O(2)	2.306(2)	av H(2)−C(C_5 ring1)	2.786
Yb(1)−C(19)	2.926(3)	Yb(1)−C(29)	2.929(3)	Na(1)−O(3)	2.374	Yb(1)−Cnt5(1)	2.546
Yb(1)−O(1)	2.403(2)	Na(1)−C(21)	2.831(3)	Na(1)−O(4)	2.314	Yb(1)−Cnt5(2)	2.549
Yb(1)−C(4)	2.594(2)	Na(1)−C(22)	2.903(3)	ave Na(1)−O	2.331	Na(1)−Cnt5(2)	2.674
						H(2)−Cnt5(1)	2.514
O(1)−Yb(1)−C(4)	102.09(7)	O(1)−Yb(1)−Cnt5(1)	105.9	Cnt5(2)−Na(1)−O(2)	105.8	O(3)−Na(1)−O(4)	90.55(9)
Cnt5(1)−Yb(1)−C(4)	108.1	O(1)−Yb(1)−Cnt5(2)	103.1	Cnt5(2)−Na(1)−O(3)	134.6	O(2)−Na(1)−O(4)	110.2(1)
Cnt5(2)−Yb(1)−C(4)	103.6	Cnt5(1)−Yb(1)−Cnt5(2)	130.8	Cnt5(2)−Na(1)−O(4)	119.0	O(3)−Na(1)−O(2)	93.30(8)

[a] Cnt5 = centroid of the C_5 ring of the indenyl group; Cnt6 = centroid of the hexagonal C_2B_4 bonding face.

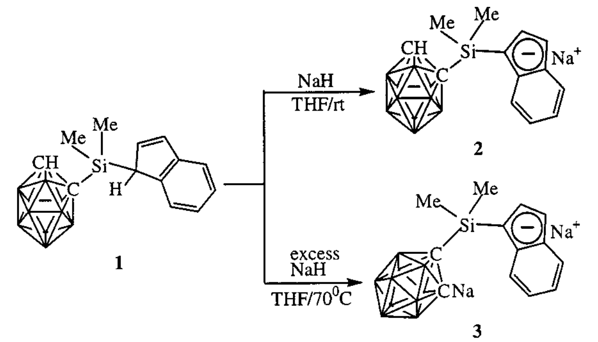
and the dianion $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ (**3**) by treatment with an equimolar amount of NaH in THF at room temperature or excess NaH in refluxing THF, respectively (Scheme 2). It is noteworthy that both MeLi and *n*-BuLi will lead to the cleavage of the Si−C(carborane) bond in **1**. These results are significantly different from those of $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$, in which the CH proton of the carborane cannot be deprotonated by NaH, and on the other hand, the Si−C(carborane) bond is not sensitive to either MeLi or *n*-BuLi. It is clear that the indenyl group is responsible for these differences, probably due to electronic effects.

Organosamarium Complexes. Treatment of SmI_2 with 1 or 2 equiv of $Na[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]$ (**2**) in

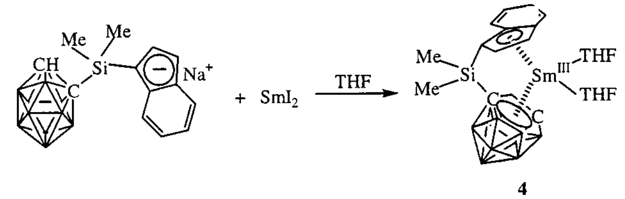
Scheme 1



Scheme 2



Scheme 3



THF gave the same redox product, [η^5:η^6-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]Sm(THF)$_2$ (**4**), as orange-red[18] crystals in about 39% yield (Scheme 3). Neither [{η^5-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)}SmI(THF)$_2$]$_2$[19] nor [η^5-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]$_2$Sm(THF)$_2$ was isolated, but they may serve as the active intermediates which reduce the carboranyl group to the dianion, and meanwhile, Sm^{2+} was oxidized to Sm^{3+}. A similar redox reaction was also observed between SmI$_2$ and Na[Me$_2$Si(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)].[10b] This type of redox reaction may be a general method to prepare the mixed samaracarboranes that are not accessible via other methods.

The IR spectrum of **4** exhibits a unique doublet centered at about 2510 cm^{-1}, typical of the ionic interaction of a positive metal center and the anionic carborane ligand of C$_2$B$_{10}$ systems.[7,10,20] The ^{1}H NMR spectrum supports the ratio of two THF molecules per ligand and shows that two methyl groups at the silicon atom are not equivalent, which is also reflected in its ^{13}C NMR spectrum. The ^{11}B NMR spectrum consists of extremely broad, unresolved resonances, which is similar to the case for other samaracarboranes.[10]

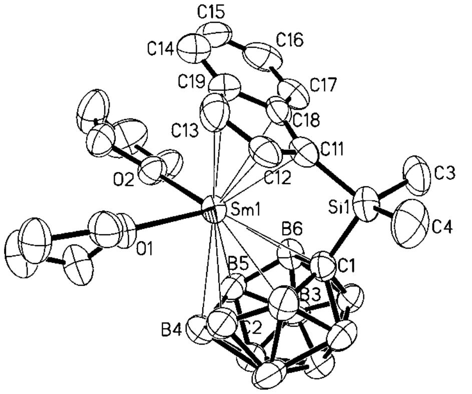


Figure 1. Molecular structure of [η^5:η^6-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]Sm(THF)$_2$ (**4**). Thermal ellipsoids are drawn at the 35% probability level.

The molecular structure of **4** has been confirmed by single-crystal X-ray analyses, which represents the first mixed lanthanacarborane containing an indenyl group. As shown in Figure 1, the Sm ion is η^5-bound to indenyl, η^6-bound to the hexagonal C$_2$B$_4$ face of the C$_2$B$_{10}$ cage, and coordinated to two THF molecules in a distorted-tetrahedral geometry. The angles Cnt5−Sm−Cnt6 (126.0°) (Cnt5 = centroid of the five-membered ring of indenyl; Cnt6 = centroid of the C$_2$B$_4$ bonding face), O(1)−Sm−O(2) (82.68°), Cnt5−Sm−O, and Cnt6−Sm−O are all similar to the corresponding values found in [η^5:η^6-Me$_2$Si(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]Sm(THF)$_2$.[10b] The average Sm−C(C$_5$ ring) distance of 2.751(4) Å is very close to that of 2.75(1) Å in (C$_9$H$_7$)$_3$Sm[21] and to those values found in [O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]LnCl(THF) and [CH$_3$OCH$_2$CH$_2$C$_9$H$_6$]$_2$LnCl types of complexes[22] if the differences in Shannon's ionic radii[23] are taken into account. This measured value can be compared with the average Sm−C(C$_5$ ring) distances of 2.664(2) and 2.748(2) Å in [η^5:η^6-Me$_2$Si(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]Sm(THF)$_2$. The average Sm−cage atom (C$_2$B$_4$ face) distance of 2.823(4) Å compares with those of 2.764(3) and 2.841(3) Å in [η^5:η^6-Me$_2$Si(C$_5$H$_4$)(C$_2$B$_{10}$H$_{11}$)]Sm(THF)$_2$. The average Sm−O distance of 2.406(2) Å falls in the range normally observed in THF-coordinated organosamarium(III) complexes.[1]

Comparison of the 2.617(3) Å Sm−C(11) distance to the adjacent Sm−C distances in the five-membered ring (2.696(3) Å for Sm−C(12) and 2.748(3) Å for Sm−C(18)) and the two nonadjacent Sm−C distances (2.828(4) Å for Sm−C(13) and 2.866(4) Å for Sm−C(19)) suggests that this ring is beginning to move toward an η^3-indenyl orientation.

It has been well-documented that organolanthanide(III) complexes containing a Ln−C σ bond are active catalysts in olefin transformations.[1b] In contrast, organolanthanide(II) complexes containing both Ln−C π and σ bonds have not been reported yet, presumably due to the ligand redistribution of such mixed-ligand complexes leading to the formation of homoleptic complexes. To prevent the ligand redistribution, a bridged ligand such as **3**, a novel "constrained geometry" ligand, should be a good choice. Treatment of SmI$_2$ with 1 equiv

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(18) Organosamarium(II) complexes are often dark green or dark purple, while organosamarium(III) complexes are usually orange-yellow.[1,3a]

(19) (a) Reaction of SmI$_2$ with an equimolar amount of KC$_5$Me$_5$ in THF gave [(C$_5$Me$_5$)Sm(μ-I)(THF)$_2$]$_2$; see: Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941. (b) Swamy, S. J.; Schumann, H. *J. Organomet. Chem.* **1987**, *334*, 1.

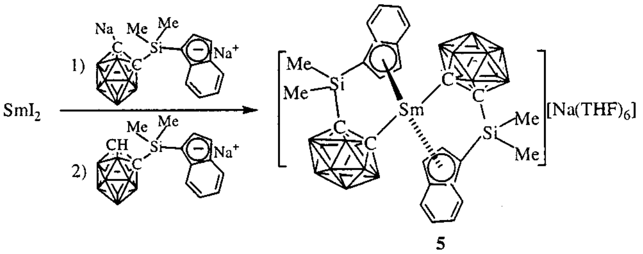
(20) (a) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1990**, *29*, 2191. (b) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4962.

(21) Atwood, J. L.; Burns, J. H.; Laubereau, P. G. *J. Am. Chem. Soc.* **1973**, *95*, 1830.

(22) (a) Qian, C.; Zou, G.; Sun, J. *J. Chem. Soc., Dalton Trans.* **1998**, 1607. (b) Qian, C.; Zou, G.; Sun, J. *J. Organomet. Chem.* **1998**, *566*, 21.

(23) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Scheme 4



5

of a THF solution of the dianion $Na_2[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]$ (**3**) presumably yielded $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Sm(THF)_3$, which when followed by reaction with 1 equiv of the monoanion $Na[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]$ (**2**) gave the unexpected intramolecular C−H bond reduction product $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}_2Sm][Na(THF)_6]$ (**5**) as orange-yellow crystals in 60% yield (Scheme 4). Attempts to isolate the pure complex $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Sm(THF)_3$ failed, and neither $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Sm(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na(THF)_3$ nor complex **4** was isolated. This result indicates that (1) the Sm(II) species generated in the above reactions are very reactive and (2) the reduction of the C−H bond of the carborane cage by Sm(II) species is superior to that of the carboranyl to the dianion.

The ^1H NMR spectrum supports the ratio of three THF molecules per ligand and shows two sets of methyl proton resonances, one set of indenyl proton resonances, and the absence of a resonance attributable to the CH proton of the cage. The ^{13}C NMR spectrum exhibits two peaks attributable to the methyl groups at the silicon atom and one set of indenyl carbon resonances, respectively, which is consistent with the results from the ^1H NMR spectrum. The ^{11}B NMR spectrum exhibits five peaks at −3.6, −8.0, −10.0, −14.1, and −15.0 ppm in the ratio 2:2:2:3:1. The color[18] of the product indicates that it should be an organosamarium(III) complex. Spectroscopic data support that only anion **3** bonds to the Sm^{3+} and only one isomer (either *meso* or *rac*) is present.[22]

The molecular structure of complex **5** has been confirmed by single-crystal X-ray analysis, which represents the first structurally characterized example of an organolanthanide indenyl complex containing a Ln−C σ bond. The solid-state structure of **5** consists of alternating layers of discrete tetrahedral anions and octahedral cations, which is somewhat similar to that of $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})\}_2Nd][Li(THF)_4]$.[10a] Figure 2 shows the structure of the anion, in which the Sm atom sits on a C_2 axis and is η^5-bound to each of two indenyl rings and σ-bound to two carbon atoms from two carborane cages in a distorted-tetrahedral geometry with Cnt5−Sm−C(1), Cnt5−Sm−Cnt5(A), and C(1)−Sm−C(1A) angles of 102.3, 112.6, and 109.2(1)°, respectively. Two phenyl rings of the indenyl ligands are located on the same side, indicating that **5** is a *meso* isomer.

The average Sm−C(C_5 ring) distance of 2.757(3) Å is almost identical with the 2.751(4) Å average in **4**. However, the 2.686(3)−2.840(3) Å range of Sm−C(C_5 ring) distances is much smaller than the range for **4**, perhaps indicating that the tendency to form the η^3-indenyl orientation in **5** is much lower than that for **4**.

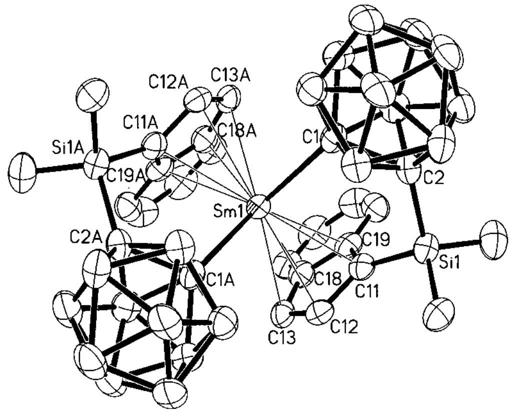


Figure 2. Molecular structure of the anion $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]_2Sm^-$ in **5**. Thermal ellipsoids are drawn at the 35% probability level.

The intramolecular Sm−C σ bond distance of 2.606(3) Å is significantly longer than those found in the monomeric $(C_5Me_5)_2SmR(THF)$ complexes (R = Me, 2.464(14) Å; R = C_6H_5, 2.511(8) Å; R = $CH_2C_6H_5$, 2.525(8) Å)[24] but is closer to those observed in the dimeric organosamarium(III) complexes (2.55(1) Å for $[(CH_3C_5H_4)_2SmC{\equiv}CBu^t]_2$[25a] and 2.59(1) Å for $[(Bu^tC_5H_4)_2SmC{\equiv}CC_6H_5]_2$[25b]). This measured value is also close to the value of 2.571 Å which would be expected by subtracting the difference, 0.03 Å, between Shannon's ionic radii[23] of Nd^{3+} and Sm^{3+} from the average Nd−C σ bond distance of an eight-coordinate neodymium analogue, 2.601 Å in $[\{Me_2Si(C_5H_4)(C_2B_{10}H_{10})\}_2Nd][Li(THF)_4]$.[10a]

The above results have shown that organosamarium(II) species of this new ligand are too reactive to be isolated; only the final products of organosamarium(III) complexes are obtained. To gain some insight into these unique redox reactions and reaction intermediates, a less reactive ytterbium element[26] was chosen for the study.

Organoytterbium Complexes. Treatment of YbI_2 with 1 equiv of $Na[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]$ (**2**) in THF at 0 °C gave $[\{\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}Yb(\mu\text{-}I)(THF)_2]_2$ (**6**) as a red crystalline solid in 70% yield (Scheme 5). The ^1H NMR spectrum supports the ratio of two THF molecules per ligand and exhibits one set of indenyl proton resonances and one peak at 0.59 ppm attributable to the Me_2Si unit. The ^{13}C NMR spectrum also shows the presence of the ligand and THF. The ^{11}B NMR spectrum exhibits a 1:1:1:1:1 splitting pattern. The IR spectrum shows the characteristic B−H absorption at 2585 cm^{-1}. The NMR data suggest that **6** is a diamagnetic complex, which implies that no redox reaction proceeded in the above-mentioned reaction. On the basis of the spectroscopic data and elemental analyses, it is reasonable to suggest that **6** may have a structure similar to that of $[(\eta^5\text{-}C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$.[19a]

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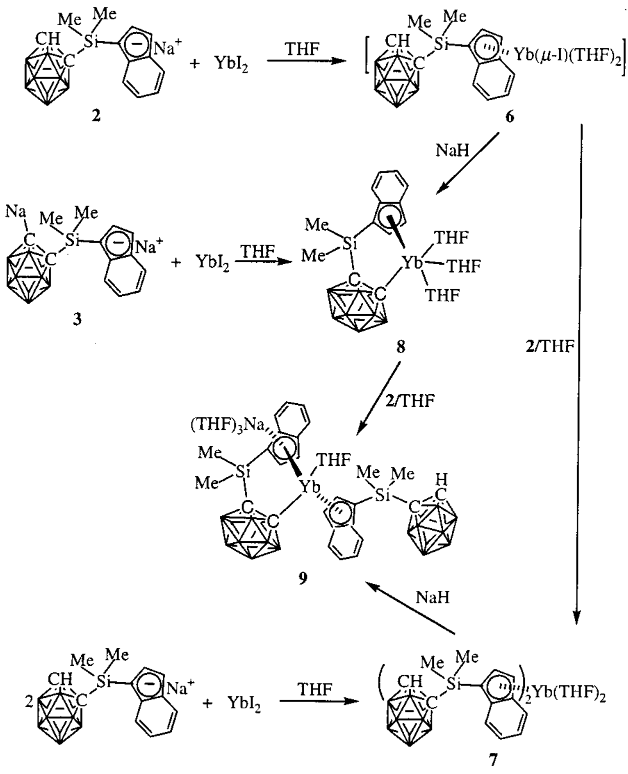
[24] (a) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112. (b) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423. (c) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134.

[25] (a) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 709. (b) Shen, Q.; Zheng, D.; Lin, L.; Lin, Y. *J. Organomet. Chem.* **1990**, *391*, 307.

[26] The reduction potentials for the Ln^{3+}/Ln^{2+} couple are −1.1 V for Yb and −1.5 V for Sm, respectively.[3a]

Scheme 5



Reaction of **6** with $\mathrm{Na[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]}$ (**2**) in THF in a molar ratio of 1:1 or treatment of $\mathrm{YbI_2}$ with 2 equiv of **2** in THF afforded $[\eta^5\text{-}\mathrm{Me_2Si(C_9H_6)(C_2B_{10}H_{11})}]_2$-$\mathrm{Yb(THF)_2}$ (**7**), after simple workup, as red crystals in good yield (Scheme 5). Unlike the $\mathrm{SmI_2}$ case, no redox product was isolated even in refluxing toluene. Complex **7** was fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR and IR spectroscopy as well as elemental analyses. Unfortunately, the crystal structure could not be solved, since all crystals obtained suffered from severe twinning.

Reaction of **6** with excess NaH in THF or treatment of $\mathrm{YbI_2}$ with a THF solution of $\mathrm{Na_2[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]}$ (**3**) gave the novel constrained-geometry complex $[\eta^5{:}\sigma\text{-}\mathrm{Me_2Si(C_9H_6)(C_2B_{10}H_{10})}]\mathrm{Yb(THF)_3}$ (**8**), after workup, as red crystals in good yield. It is extremely air- and moisture-sensitive but is stable even in hot toluene under dry $\mathrm{N_2}$. The ^{1}H NMR spectrum supports the ratio of three THF molecules per ligand. In contrast with the ^{1}H NMR spectrum of **6**, the broad singlet peak at 2.87 ppm attributable to the CH of the carborane cage did not appear in the ^{1}H NMR spectrum of **8**; two sets of methyl proton resonances at 0.67 and 0.48 ppm were observed. The ^{13}C NMR spectrum shows the presence of the ligand, THF, and two different methyl groups. The ^{11}B NMR spectrum exhibits a 1:1:2:4:1:1 splitting pattern. The monomeric nature of this complex has been confirmed by single-crystal X-ray analysis.

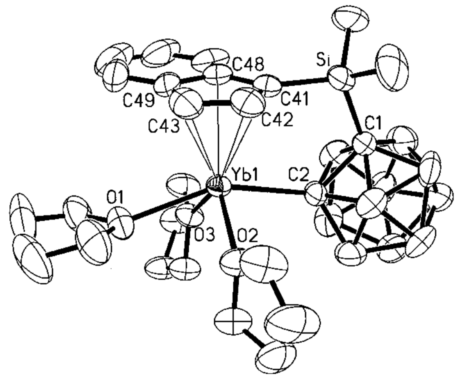


Figure 3. Molecular structure of $[\eta^5{:}\sigma\text{-}\mathrm{Me_2Si(C_9H_6)}$-$\mathrm{(C_2B_{10}H_{10})}]\mathrm{Yb(THF)_3}$ (**8**). Thermal ellipsoids are drawn at the 35% probability level.

Figure 3 shows the solid-state structure of complex **8**. As far as we are aware, this is the first mixed-ligand organolanthanide(II) complexes containing both Ln−C π and σ bonds to be reported and is also the first structurally well-characterized example of an organolanthanide(II) indenyl complex.[2] In this structure, the Yb ion is η^5-bound to indenyl, σ-bound to the carbon atom of the carborane cage, and coordinated to three THF molecules in a distorted-square-pyramidal geometry with the centroid of the pentagonal ring (Cnt5) occupying the axial site, the Cnt5−Yb(1)−C(2) angle being 103.9°. The Yb(1)−C(2) σ bond distance of 2.584(3) Å is longer than the 2.501(9) Å for $\mathrm{Yb\{C(SiMe_3)_3\}_2}$,[27a] 2.47(2) Å for $\mathrm{[Yb\{C(SiMe_3)_3\}I(OEt_2)]_2}$,[27a,b] 2.573(13) Å for $\mathrm{[Yb(CR_3)(\mu\text{-}OEt)(OEt_2)]_2}$,[27c] and 2.55(6) Å for (Tp)-$\mathrm{Yb\{CH(SiMe_3)_2\}}$ (Tp = hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borate).[27d] The Yb−C(C$_5$ ring) distances range from 2.671(3) to 2.814(3) Å with an average value of 2.750(3) Å. This measured value is somewhat longer than the typical Yb−C distance of 2.67 Å in $\mathrm{Cp_2YbL}$ complexes.[28] It is not possible to make further comparison, since no other data on Yb−indenyl bond distances are available.

Complex **8** is a reactive species. Further reaction with another 1 equiv of $\mathrm{Na[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]}$ (**2**) in THF at room temperature yielded, after workup, $[\eta^5$-$\mathrm{Me_2Si(C_9H_6)(C_2B_{10}H_{11})}]\mathrm{Yb(THF)}[(\mu\text{-}\eta^5){:}\sigma\text{-}\mathrm{Me_2Si(C_9H_6)}$-$\mathrm{(C_2B_{10}H_{10})}]\mathrm{Na(THF)_3}$ (**9**) as red crystals in 77% yield (Scheme 5). Unlike the $\mathrm{SmI_2}$ case, no C−H bond reduction product was found, even in refluxing toluene for several hours. **9** can also be prepared from the reaction of **7** with 1 equiv of NaH in THF at room temperature.

The ^{1}H NMR spectrum supports the ratio of two THF molecules per ligand and shows the chemical shift of carborane CH at 4.35 ppm, which is greatly downfield-shifted in comparison with those observed in **1** and **6,** probably due to the nonclassical hydrogen bonding between the acidic proton of the carborane and the C$_5$ ring of the indenyl group.[29] Both ^{1}H and ^{13}C NMR spectra indicate the diamagnetic nature of complex **9**. The ^{11}B NMR spectrum exhibits a 1:6:2:2:1:1:6:1 splitting pattern. The IR spectrum shows the characteristic B−H absorption at 2566 cm^{-1}. The molecular structure of this complex has been confirmed by single-crystal X-ray analysis.

An X-ray diffraction study of **9** reveals that it is a *meso* isomer and the Yb atom lies in a distorted-tetrahedral environment, η^5-bound to each of two indenyl ligands

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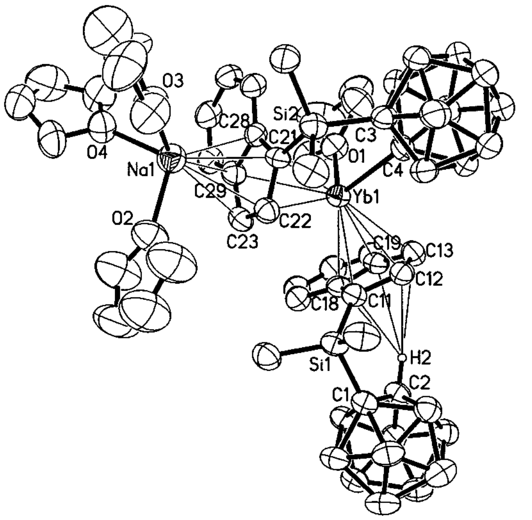

Figure 4. Molecular structure of [η^5-$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]-Yb(THF)[($\mu$-$\eta^5$):$\sigma$-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]Na(THF)$_3$ (**9**). Thermal ellipsoids are drawn at the 35% probability level.

and σ-bound to the C atom of the carborane cage and the O atom of the THF molecule (Figure 4). One of the indenyl ligands is bonded to both Yb^{2+} and Na^+ in a η^5 fashion. The Yb(1)−C(4) (σ bond) distance of 2.580(2) Å, the average Yb−C(C_5 ring) distances of 2.820(3) and 2.817(3) Å, and the C(4)−Yb(1)−Cnt5 angle of 103.9° are close enough to the corresponding values in **8**, suggesting that the structural motif of **8** is retained in **9**. The ranges of the Yb−C(C_5 ring) distances (2.744(3)−2.926(3) and 2.706(2)−2.929(3) Å) indicate that the tendency to form the η^3-indenyl coordination exists in **9**.

It is interesting to note that the distances from the five-membered ring of one of the indenyl groups to the H atom on the carbon atom of the cage range from 2.616 to 2.980 Å, with an average value of 2.786 Å. The distance from the centroid of this C_5 ring to the H(2) atom is 2.514 Å, which can be compared with those (2.184−2.765 Å) found in the adduct of *o*-$C_2B_{10}H_{12}$ with cyclotriveratrylene,[29] consistent with the acidic nature of the protons attached to the carbon atoms of the carborane. This nonclassical hydrogen bonding has resulted in (1) a much smaller C(1)−Si(1)−C(11) angle of 105.3(1)° in comparison with the corresponding C(3)−Si(2)−C(21) angle of 110.2(1)°, (2) the Na^+ being coordinated to another indenyl ligand, (3) a greatly downfield-shifted CH proton of the carborane cage in the ^{1}H NMR spectrum, and (4) the definitive assignment of the second carbon atom on the cage.

Conclusion

By taking advantage of the properties of the indenyl group, icosahedral carborane, and the bridged ligand, the very versatile ligand $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (**1**) has been designed and successfully prepared. Reactions of LnI_2 with the anions derived from **1** have resulted in the isolation and structural characterization of a new class of organolanthanide indenyl complexes with novel structural features.

Organosamarium(II) species of this ligand are extremely reactive, which can reduce the C−H bond of the carborane cage to the monoanion by a one-electron reductive process or reduce the carboranyl to carborane dianion by two-electron reductive processes. As a result, only samarium(III) products are isolated. The ytterbium(II) analogues, however, are stable and well-characterized. Their structural information can help us to better understand the reaction mechanisms of the formation of samarium(III) complexes. Organosamarium(II) and organoytterbium(II) chemistry are complementary to each other.

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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 and figures giving atom-numbering schemes for **4**, **5**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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