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Cyclopentadienyl vs Indenyl Substituents. Organolanthanide Complexes and Biscarborane Compounds Derived from a Versatile Ligand, $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$

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A versatile compound, $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ can be conveniently converted into the monoanion $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$, the dianion $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$, and the trianion $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]K_3$ by treatment with 1 equiv or excess amounts of NaH or K metal in THF, respectively. Reaction of $LnCl_3$ with 1 equiv of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ in THF gave dichloride complexes $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]LnCl_2(THF)_3$ (Ln = Nd (**1**), Er (**2**)). They can further react with another equivalent of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ to afford monochloride complexes $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]_2LnCl(THF)_2$ (Ln = Ce (**3**), Nd (**4**), Sm (**5**), Er (**6**)), which can also be prepared by treatment of $LnCl_3$ with 2 equiv of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ in THF. **4** reacts with excess NaH in THF to produce $[Na(THF)_6][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}_2Nd]$ (**7**), which can also be prepared from the reaction of $NdCl_3$ with 2 equiv of $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$ in THF. Treatment of **2** with 2 equiv of K metal at room temperature yielded $[\eta^5{:}\eta^6\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Er(THF)_2$ (**8**). Reaction of **6** with 1 equiv of NaH afforded $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}\{\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}]Er(\mu\text{-}Cl)Na(THF)_3$ (**9**), which can also be prepared from the reaction of **2** with 1 equiv of $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$ in THF. Treatment of **9** with a mixture of 1 equiv of NaOH and excess NaH in THF generated the dinuclear complex $[Na_2(THF)_{11}][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}\{\mu\text{-}\eta^5{:}\sigma\text{-}(C_9H_6)SiMe_2O\}Er]_2$ (**10**). Treatment of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with excess NaH in THF under UV-light followed by reaction with 1 equiv of $LnCl_3$ resulted in the isolation of unprecedented biscarborane compounds $[LnCl_2(THF)_5][\mu\text{-}CH\text{-}(\textit{closo}\text{-}C_2B_{10}H_{11})\text{-}\textit{nido}\text{-}CB_{10}H_{11}]$ (Ln = Er (**11**), Y (**12**)). All of these complexes were characterized by various spectroscopic and elemental analyses. The solid-state structures of **7** and **9**−**12** were confirmed by single-crystal X-ray analyses.

Introduction

Ligand modifications have played a key role in developing new catalyst precursors for optimizing polymerization activity as well as polymer properties such as stereoregularity, molecular weight, bulky and polar comonomer incorporation, and microstructure.[1] It has been documented that a ligand containing bifunctional groups often offers complexes with some additional advantages.[1] For example, a bridging cyclic organic ligand can afford organometallic complexes with advantageous solubility, crystallizability, and thermal and kinetic stability.[2] Recently developed "constrained geometry" ligands containing both monocyclopentadienyl and σ-heteroatom components have attracted considerable attention,[3] leading to a new generation of olefin polymerization catalysts.[4]

Given the impact of the cyclopentadienyl-appended heteroatom donor groups on the catalytic performance of the complexes, we have recently designed versatile ligands[5,6] by taking advantage of carborane molecules[7] and cyclic organic groups such as cyclopentadienyl and

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indenyl groups as well as the bridging ligands. The ligand with an indenyl substituent, $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$, has shown some unique properties, leading to the isolation of a novel organolanthanide cluster[6a] and a new class of organolanthanide(II) complexes.[6b] In view of the importance of organolanthanide catalysts in olefin transformations such as hydrogenation,[8] oligomerization/polymerization,[9] hydroamination,[10] hydrosilylation,[11] hydroboration,[12] and reductive cyclization,[13] and much less studied organolanthanide indenyl complexes,[2] we have further explored organolanthanide chemistry with the $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ ligand. We report here the synthesis, reactivity, and structural characterization of new organolanthanide indenyl complexes as well as an unprecedented reaction for the preparation of the first biscarborane compounds derived from this versatile ligand. The differences between the cyclopentadienyl- and indenyl-substituted ligand systems are also discussed.

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. Anhydrous $LnCl_3$ was prepared from the hydrates by standard procedures.[14] $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$,[6] $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$,[6b] and $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$[6b] were prepared according to the procedures previously described. 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 Perkin-Elmer 1600 Fourier transform 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 the residual protons of the deuterated solvent or with respect to internal or external TMS (0.00 ppm) 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 $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]NdCl_2(THF)_3$ (1). To a suspension of $NdCl_3$ (0.25 g, 1.0 mmol) in THF (25 mL) was added a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (14.0 mL, 1.0 mmol) dropwise at room temperature, and the reaction mixture was stirred overnight. The precipitate was then filtered off, and the resulting clear blue solution was concentrated under vacuum to about 5 mL. After addition of toluene (10 mL) into the above solution, a light blue crystalline solid was obtained when this solution was allowed to stand for several days (0.43 g, 58%). ^1H NMR (pyridine-d_5): δ 14.20 (br s, 1H), 8.23 (br s, 1H), 6.80 (m, 2H), −2.69 (br s, 1H), −4.37 (br s, 1H) (C_9H_6), 4.35 (br s, 1H, C*H* of carboranyl), 3.55 (m, 12H), 1.23 (m, 12H) (OC_4H_8), 0.59 (s, 6H) (CH_3). ^{13}C NMR (pyridine-d_5): δ 155.98, 142.40, 129.39, 128.40, 126.28, 114.56, 105.03, 100.15, 95.66 (C_9H_6), 73.32, 64.67 ($C_2B_{10}H_{11}$), 70.69, 28.72 (OC_4H_8), 6.34 (CH_3). ^{11}B NMR (pyridine-d_5): δ -2.3 (1), −7.3 (2), −7.8 (2), −9.8 (1), −11.8 (2), −12.4 (2). IR (KBr, cm^{-1}): ν 3051 (w), 2966 (m), 2905 (m), 2590 (vs), 1477 (m), 1414 (m), 1387 (m), 1259 (s), 1145 (m), 1078 (m), 1038 (s), 1011 (s), 870 (s), 813 (s), 782 (s), 749 (m). Anal. Calcd for $C_{17}H_{31}B_{10}Cl_2NdOSi$ (**1** − 2THF): C, 33.88; H, 5.18. Found: C, 33.65; H, 5.30.

Preparation of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]ErCl_2(THF)_3$ (2). To a suspension of $ErCl_3$ (0.27 g, 1.0 mmol) in 20 mL of THF was added a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (14.0 mL, 1.0 mmol) dropwise at room temperature, followed by procedures similar to those used in the preparation of **1**, affording **2** as pink crystals (0.48 g, 62%). ^1H NMR (pyridine-d_5): δ 7.48 (br, 1H), 7.32 (br, 1H), 6.91 (br, 2H), −1.25 (s, 1H), −6.94 (s, 1H) (C_9H_6), 3.57 (m, 12H), 1.53 (m, 12H) (OC_4H_8), 0.64 (s, 6H, CH_3). ^{13}C NMR (pyridine-d_5): δ 146.57, 140.98, 131.58, 131.26, 122.67, 122.18, 109.27, 98.24, 96.55 (C_9H_6), 80.41, 72.42 ($C_2B_{10}H_{11}$), 76.01, 33.99 (OC_4H_8), 7.98 (CH_3). ^{11}B NMR (pyridine-d_5): δ −3.0 (2), −7.9 (3), −11.4 (2), −13.3 (3). IR (KBr, cm^{-1}): ν 3065 (w), 2977 (s), 2899 (s), 2578 (vs), 1445 (m), 1412 (m), 1383 (m), 1251 (s), 1152 (m), 1072 (m), 1026 (s), 861 (s), 815 (s), 779 (m), 737 (m), 682 (w). Anal. Calcd for $C_{21}H_{39}B_{10}Cl_2ErO_2Si$ (**2** − THF): C, 36.14; H, 5.63. Found: C, 36.20; H, 5.71.

Preparation of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]_2CeCl(THF)_2$ (3). To a suspension of $CeCl_3$ (0.25 g, 1.0 mmol) in THF (20 mL) was added a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (28.0 mL, 2.0 mmol) dropwise, and the reaction mixture was then stirred at room temperature overnight. The precipitate was filtered off. The solvent was removed under vacuum to give a sticky yellow product, which was then extracted with hot toluene (10 mL × 3). The toluene solutions were combined and concentrated under vacuum until a crystalline yellow product appeared on the wall of the glassware. The solid was then redissolved upon heating. Yellow crystals were obtained when this saturated solution was allowed to stand at room temperature for several days (0.57 g, 60%). ^1H NMR (pyridine-d_5): δ 7.94 (d, $J = 7.5$ Hz, 2H), 7.84 (d, $J = 7.5$ Hz, 2H), 7.29 (br s, 2H), 7.08 (m, 2H), 6.95 (m, 2H), 6.81 (br s, 2H) (C_9H_6), 4.31 (br s, 2H) (C*H* of carboranyl), 3.45 (m, 8H), 1.40 (m, 8H) (OC_4H_8), 0.59 (s, 12H, CH_3). ^{13}C NMR (pyridine-d_5): δ 138.01, 135.80, 128.03, 119.38, 119.08, 114.17, 113.65, 101.20, 90.54 (C_9H_6), 67.31, 25.28 (OC_4H_8), 63.95, 56.54 ($C_2B_{10}H_{11}$), −0.61 (CH_3). ^{11}B NMR (pyridine-d_5): δ −2.7 (1), −3.6 (2), −8.0 (2), −11.5 (1), −13.4 (2), −14.9 (2). IR (KBr, cm^{-1}): ν 3065 (w), 2959 (m), 2572 (vs),

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1444 (m), 1408 (m), 1257 (s), 1157 (m), 1145 (m), 1085 (m), 1073 (m), 1045 (m), 1030 (m), 1007 (m), 971 (m), 873 (m), 863 (m), 832 (s), 807 (s), 776 (s), 754 (s). Anal. Calcd for $C_{30}H_{54}B_{20}CeClOSi_2$ (**3** − THF): C, 41.01; H, 6.19. Found: C, 40.94; H, 6.37.

Preparation of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]_2NdCl(THF)_2$ (4). To a suspension of $NdCl_3$ (0.25 g, 1.0 mmol) in THF (20 mL) was added a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (28.0 mL, 2.0 mmol) dropwise at room temperature, followed by procedures similar to those used in the preparation of **3**, affording **4** as blue crystals (0.61 g, 64%). ^1H NMR (pyridine-d_5): δ 3.54 (m), 1.42 (m) (OC_4H_8), and other broad, unresolved resonances. ^{11}B NMR (pyridine-d_5): δ −1.7 (1), −2.7 (2), −7.1 (1), −9.4 (2), −11.3 (1), −13.9 (2), −15.1 (1). IR (KBr, cm^{-1}): ν 3060 (w), 2972 (m), 2577 (vs), 1407 (m), 1256 (s), 1157 (m), 1147 (m), 1082 (m), 1073 (m), 1030 (m), 970 (m), 833 (s), 807 (s), 780 (s), 752 (m), 682 (m). Anal. Calcd for $C_{34}H_{62}B_{20}ClNdO_2Si_2$: C, 42.76; H, 6.54. Found: C, 42.38; H, 6.21.

Complex **4** can also be prepared from the reaction of **1** with 1 equiv of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ in THF in 60% yield.

Preparation of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]_2SmCl(THF)_2$ (5). This complex was prepared as orange-yellow crystals from $SmCl_3$ (0.26 g, 1.0 mmol) and $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (28.0 mL, 2.0 mmol) in 20 mL of THF using the procedures similar to those used for **3**: yield 0.64 g (66%). ^1H NMR (pyridine-d_5): δ 9.55 (br s, 2H), 8.22 (m, 2H), 8.14 (br s, 2H), 7.27 (m, 2H), 6.94 (br s, 2H), 6.22 (br s, 2H) (C_9H_6), 4.72 (br s, 2H) (CH of carboranyl), 3.44 (m, 8H), 1.42 (m, 8H) (OC_4H_8), 0.40 (s, 12H) (CH_3). ^{11}B NMR (pyridine-d_5): δ −4.7 (2), −9.0 (2), −11.2 (2), −15.3 (3), −16.1 (1). IR (KBr, cm^{-1}): ν 3063 (m), 2961 (m), 2580 (vs), 1458 (m), 1408 (m), 1258 (s), 1157 (m), 1147 (m), 1087 (s), 1030 (s), 833 (s), 807 (s), 781 (s), 751 (m), 679 (m). Anal. Calcd for $C_{30}H_{54}B_{20}ClOSi_2Sm$ (**5** − THF): C, 40.53; H, 6.12. Found: C, 39.96; H, 6.04. The error is probably due to the partial loss of the coordinated THF molecules.

Preparation of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]_2ErCl(THF)_2$ (6). This complex was prepared as a pink crystalline solid from $ErCl_3$ (0.27 g, 1.0 mmol) and $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (28.0 mL, 2.0 mmol) in 15 mL of THF using the procedures similar to those used for **3**: yield 0.70 g (72%). ^1H NMR (pyridine-d_5): δ 3.55 (br), 1.46 (br) (OC_4H_8) and other broad, unresolved resonances. Hydrolysis of this solid in pyridine-d_5 with a slight molar excess of water and subsequent examination by ^1H NMR spectroscopy showed the presence of ligand and THF in a ratio of 1:1. ^{13}C NMR (pyridine-d_5): δ 155.01, 145.05, 136.14, 131.27, 130.78, 117.72, 105.21, 90.23, 84.40 (C_9H_6), 80.82, 76.49 ($C_2B_{10}H_{11}$), 42.32, 16.32 (OC_4H_8), −9.50 (CH_3). ^{11}B NMR (pyridine-d_5): δ −3.7 (2), −8.2 (3), −11.9 (2), −13.6 (3). IR (KBr, cm^{-1}): ν 3058 (w), 2963 (m), 2878 (m), 2576 (vs), 1449 (m), 1410 (m), 1332 (w), 1255 (s), 1152 (m), 1073 (m), 1034 (s), 866 (m), 812 (s), 786 (s), 751 (m). Anal. Calcd for $C_{30}H_{54}B_{20}ClErOSi_2$ (**6** − THF): C, 39.78; H, 6.01. Found: C, 39.45; H, 6.26.

Complex **6** can also be prepared by treatment of **2** with 1 equiv of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ in THF in 66% yield.

Preparation of $[Na(THF)_6][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}_2Nd]$ (7). To a suspension of NaH (48.0 mg, 2.0 mmol) in THF (7 mL) was slowly added a THF (20 mL) solution of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]_2NdCl(THF)_2$ (**4**; 0.40 g, 0.42 mmol), and the reaction mixture was stirred at room temperature for 2 days. The precipitate was filtered off, and the solvent was removed under vacuum to give a sticky residue, which was then extracted with hot toluene (15 mL × 3). The toluene solutions were combined and concentrated. Slow evaporation of this solution afforded blue crystals (0.32 g, 63%). ^1H NMR (pyridine-d_5): δ 10.5 (br, 2H), 8.9 (br, 2H), 1.0 (br, 2H), 0.6 (br, 2H), −4.4 (br, 2H), −11.9 (br, 2H) (C_9H_6), 3.5 (m, 24H), 1.4 (m, 24H) (OC_4H_8), −0.5 (s, 12H) (CH_3). ^{13}C NMR (pyridine-d_5): δ 128.31, 126.62, 121.12, 119.66, 115.09, 113.93, 109.30, 101.15, 99.40 (C_9H_6), 83.80, 82.96 ($C_2B_{10}H_{10}$), 67.62, 25.59 (OC_4H_8), −0.32 (CH_3). The ^{11}B NMR spectrum consisted of many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3073 (w), 2974 (m), 2877 (m), 2575 (vs), 1448 (m), 1410 (m), 1255 (m), 1159 (m), 1086 (s), 1049 (m), 887 (m), 833 (m), 808 (m), 776 (m), 745 (m), 677 (m). Anal. Calcd for $C_{50}H_{92}B_{20}NaNdO_6Si_2$: C, 48.87; H, 7.55. Found: C, 48.64; H, 7.42.

This complex can also be prepared from the reactions of $NdCl_3$ with 2 equiv of $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$ in THF at room temperature in 67% yield.

Preparation of $[\eta^5{:}\eta^6\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Er(THF)_2$ (8). To a THF (20 mL) solution of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]ErCl_2(THF)_3$ (**2**; 0.25 g, 0.32 mmol) was added K metal (25 mg, 0.64 mmol), and the mixture was stirred at room temperature until no K metal remained. The white precipitate was filtered off, and the resulting clear orange solution was concentrated under vacuum to about 5 mL. Addition of toluene (7 mL) and slow evaporation of the solvents afforded a pink crystalline solid (0.14 g, 70%). ^1H NMR (pyridine-d_5): δ 3.46 (br), 1.42 (br) (OC_4H_8), and other broad, unresolved resonances. The ^{11}B NMR consisted of many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3058 (w), 2964 (m), 2874 (m), 2508 (vs), 1455 (m), 1386 (m), 1255 (s), 1140 (m), 1049 (s), 1012 (s), 829 (s), 798 (s), 674 (w). Anal. Calcd for $C_{17}H_{31}B_{10}ErOSi$ (**8** − THF): C, 36.79; H, 5.63. Found: C, 36.35; H, 5.45.

Alternate Method. The direct interaction of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.16 g, 0.50 mmol) with K metal (0.16 g, 4.00 mmol) in THF (20 mL) at room temperature over a period of 2 days, followed by filtration, gave a pale yellow THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]K_3$ (^{11}B NMR (THF): δ 0.8 (2), −1.6 (2), −3.6 (2), −7.2 (1), −8.2 (1), −10.3 (1), −13.9 (1)). This solution was added dropwise to a stirred THF (15 mL) suspension of $ErCl_3$ (0.14 g, 0.50 mmol) at room temperature, and the mixture was stirred overnight. The precipitate was filtered off, followed by procedures similar to those used above, giving **8** as a pink crystalline solid (0.19 g, 61%).

Preparation of $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}\{\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}]Er(\mu\text{-}Cl)Na(THF)_3$ (9). To a suspension of NaH (9 mg, 0.37 mmol) in 5 mL of THF was added a THF (25 mL) solution of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]_2ErCl(THF)_2$ (**6**; 0.35 g, 0.36 mmol), and the reaction mixture was stirred at room temperature for 2 days. The resulting clear pink solution was concentrated under vacuum to about 5 mL, and toluene (8 mL) was added. Slow evaporation of the solvents at room temperature gave pink crystals (0.32 g, 82%). ^1H NMR (pyridine-d_5): δ 8.50 (br s, 2H), 7.81 (br s, 2H), 7.35 (br s, 4H), 6.88 (br s, 4H) (C_9H_6), 3.44 (m, 12H), 1.40 (m, 12H) (OC_4H_8), 0.60 (s, 12H, CH_3). ^{13}C NMR (pyridine-d_5): δ 145.03, 134.96, 126.30, 126.04, 121.14, 120.64, 109.10, 107.67, 95.07 (C_9H_6), 80.40, 70.86 (C_2B_{10} cages), 74.28, 32.25 (OC_4H_8), 6.35 (CH_3). ^{11}B NMR (pyridine-d_5): δ −2.8 (2), −3.5 (2), −8.0 (6), −11.6 (4), −13.4 (6). IR (KBr, cm^{-1}): ν 3059 (w), 2976 (m), 2875 (m), 2584 (vs), 1447 (m), 1421 (m), 1255 (s), 1158 (m), 1145 (m), 1088 (m), 1073 (m), 1046 (s), 1030 (s), 973 (m), 890 (m), 832 (s), 808 (s), 776 (s), 748 (s). Anal. Calcd for $C_{38}H_{69}B_{20}ClErNaO_3Si_2$: C, 42.57; H, 6.49. Found: C, 42.49; H, 6.50.

Alternate Method. To a suspension of $ErCl_3$ (0.27 g, 1.0 mmol) in THF (20 mL) was added a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ (14.0 mL, 1.00 mmol) at room temperature, and the reaction mixture was stirred overnight. To the above solution (**2** in THF) was slowly added a freshly prepared THF solution of $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$ (18.0 mL, 1.00 mmol) at room temperature, and the reaction mixture was stirred at room temperature overnight. The precipitate was filtered off, and the resulting clear orange-yellow solution was then concentrated to about 10 mL. After addition of toluene (15 mL), slow evaporation of the solvents resulted in pink crystals (0.66 g, 62%) identified as **9**. A few colorless crystals were found in the pink crystals. They were identified to be $[ErCl_2(THF)_5][\mu$-CH-(*closo*-$C_2B_{10}H_{11}$)-*nido*-$CB_{10}H_{11}]$ by single-crystal X-ray analysis.

Preparation of $[Na_2(THF)_{11}][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}$-

{μ-η^5:σ-(C_9H_6)SiMe$_2$O}Er]$_2$ (10). To a mixture of NaOH/NaH (20.0 mg of NaOH, 48.0 mg of NaH) in THF (15 mL) was added a THF solution (20 mL) of [{η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$}{$\eta^5$-$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$}]Er($\mu$-Cl)Na(THF)$_3$ (**9**; 0.55 g, 0.50 mmol) at −10 °C; the mixture was then stirred at room temperature overnight. The precipitates were filtered off, and the resulting orange-red solution was concentrated under vacuum to about 10 mL. Addition of toluene (10 mL) and slow evaporation of the solvents gave pink crystals (0.29 g, 53%). ^{1}H NMR (pyridine-d_5): δ 3.43 (br s), 1.39 (br s) (OC_4H_8), and other broad, unresolved resonances. ^{13}C NMR (pyridine-d_5): δ 138.73, 128.92, 126.10, 120.38, 120.04, 114.57, 113.80, 101.31, 90.14 (C_9H_6), 74.20, 64.82 ($C_2B_{10}H_{10}$), 68.15, 26.15 (OC_4H_8), 0.30 (CH_3). The ^{11}B NMR spectrum consisted of many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3073 (w), 2971 (m), 2876 (m), 2573 (vs), 1148 (m), 1409 (m), 1254 (m), 1157 (m), 1087 (m), 1049 (s), 994 (s), 889 (m), 832 (s), 777 (s), 682 (m). Anal. Calcd for $C_{64}H_{100}B_{20}Er_2Na_2O_6Si_4$ (**10** − 7THF): C, 45.90; H, 6.02. Found: C, 45.97; H, 6.08.

Preparation of [ErCl$_2$(THF)$_5$][μ-CH-(*closo*-$C_2B_{10}H_{11}$)-*nido*-$CB_{10}H_{11}$]·THF (11·THF). To a suspension of NaH (0.10 g, 4.2 mmol) in THF (15 mL) was slowly added a THF solution of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), and the reaction mixture was stirred under UV-light for 24 h. The resulting pale yellow solution was filtered dropwise into a suspension of $ErCl_3$ (0.27 g, 1.0 mmol) in THF (20 mL), and the reaction mixture was stirred at room temperature overnight. The precipitate was filtered off, and the clear solution was concentrated to about 10 mL. *n*-Hexane vapor diffusion resulted in colorless crystals (0.23 g, 48%). ^{1}H NMR (pyridine-d_5): δ 3.65 (m), 1.57 (m) (OC_4H_8). ^{13}C NMR (pyridine-d_5): δ 67.81, 25.79 (OC_4H_8). ^{11}B NMR (pyridine-d_5): δ −1.8 (1), −3.9 (1), −6.0 (1), −8.2 (2), −12.5 (2), −16.0 (1), −19.5 (2). IR (KBr, cm^{-1}): ν 3073 (w), 2983 (m), 2902 (m), 2554 (vs), 1453 (m), 1256 (m), 1177 (m), 1071 (s), 1016 (s), 918 (m), 861 (vs), 718 (m), 674 (m). Anal. Calcd for $C_{28}H_{71}B_{20}Cl_2ErO_6$: C, 35.09; H, 7.46. Found: C, 35.28; H, 7.33.

Preparation of [YCl$_2$(THF)$_5$][μ-CH-(*closo*-$C_2B_{10}H_{11}$)-*nido*-$CB_{10}H_{11}$] (12). To a suspension of NaH (0.10 g, 4.2 mmol) in THF (10 mL) was added a THF (20 mL) solution of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), and the reaction mixture was stirred under UV-light for 24 h. The resulting pale yellow solution was filtered dropwise into a suspension of YCl_3 (0.20 g, 1.0 mmol) in THF (20 mL), followed by procedures similar to those used in the synthesis of **11**, affording colorless crystals (0.16 g, 40%). ^{1}H NMR (pyridine-d_5): δ 3.65 (m, 20H), 1.61 (m, 20H) (OC_4H_8), 3.30 (s, 1H) (μ-C*H* of cage), 2.85 (s, 1H) (C*H* of cage). ^{13}C NMR (pyridine-d_5): δ 90.18, 70.32 (cage), 67.62, 25.59 (OC_4H_8). ^{11}B NMR (pyridine-d_5): δ −1.6 (1), −3.8 (1), −5.8 (1), −8.0 (2), −12.6 (2), −16.1 (1), −19.3 (2). IR (KBr, cm^{-1}): ν 3070 (w), 2982 (m), 2902 (m), 2553 (vs), 1458 (m), 1172 (w), 1074 (m), 1017 (s), 917 (w), 862 (s), 722 (w), 669 (w). Anal. Calcd for $C_{24}H_{63}B_{20}Cl_2O_5Y$: C, 35.68; H, 7.86. Found: C, 35.78; H, 7.35.

Reaction of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with $LnCl_3$ (Ln = Y, Er) under UV-Light. An NMR tube was charged with an equimolar amount of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ and $LnCl_3$ (Ln = Y, Er) in THF/pyridine-d_5, and the mixture was shaken under UV-light for 24 h. The ^{11}B NMR spectra showed that no reactions occurred.

[$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]Na under UV-Light. An NMR tube was charged with 0.5 mL of THF solution of [$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]Na in THF/pyridine-$d_5$ solution, and the tube was placed under UV-light for 24 h. The ^{11}B NMR (THF/pyridine-d_5) spectrum exhibits a 1:1:2:2:2:2 splitting pattern at δ 4.1, 2.7, −1.4, −5.1, −6.8, −7.6, which is identical with that of [$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]Na.

[$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]Na$_2$ under UV-Light. An NMR tube was charged with 0.5 mL of [$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]Na$_2$ in THF/pyridine-d_5, and the tube was placed under UV-light for 24 h. ^{11}B NMR (THF/pyridine-d_5): δ 0.8, −0.1, −1.1, −3.1, −5.3, −6.5, −8.0, −9.3, −10.0, −12.9, −16.3. Among these, the resonances at 0.8, −1.1, −3.1, −5.3, −9.3, −12.9, −16.3 ppm were attributable to the biscarborane monoanion.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on an MSC/Rigaku RAXIS−II 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 directed methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares 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. The precision of the X-ray structure determination of compound **12** is affected by the large anomalous scattering effects of Y with Mo radiation. Crystal data and details of data collection and structure refinements 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. Compound $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ can be conveniently converted into the monoanion [$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]Na, the dianion [$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]Na$_2$, and the trianion [$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]K$_3$ by treatment with 1 equiv or excess amounts of NaH[6b] or K metal in THF at room temperature, respectively (Scheme 1). It is noteworthy that the CH proton of the carborane cage in $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ can be deprotonated by NaH, indicating that the acidity of this proton is higher than that in $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$,[5] perhaps due to the electron-withdrawing nature of the indenyl group. This result is also supported by the ^{1}H NMR spectra, $\delta_{\mathrm{CH\ of\ cage}}$ 3.19 ppm in $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ vs $\delta_{\mathrm{CH\ of\ cage}}$ 2.99 ppm in $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$. It is suggested that two groups, carboranyl and indenyl, in $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ communicate with each other, which results in some unique properties of the complexes bearing this ligand.

Organolanthanide Complexes. Treatment of $LnCl_3$ with 1 equiv of [$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]Na in THF at room temperature afforded [η^5-$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]LnCl$_2(THF)_3$ (Ln = Nd (**1**), Er (**2**)) in about 60% yield (Scheme 2). These monoindenyl complexes can react with another equivalent of [$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]Na at room temperature to give bisindenyl complexes [η^5-$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]$_2$LnCl(THF)$_2$ (Ln = Ce (**3**), Nd (**4**), Sm (**5**), Er (**6**)), which can also be prepared by treatment of $LnCl_3$ with 2 equiv of [$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]Na in 60−70% yield. The ^{1}H NMR spectra support the ratio of three THF molecules per ligand for monoindenyl complexes **1** and **2** and one THF molecule per ligand for bisindenyl complexes **3**−**6**. Comparison of the chemical shifts of the CH protons of the carborane cages in **1**−**6** (4.35−4.72 ppm) to the 3.19 ppm chemical shift in $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ suggests the presence of the nonclassical hydrogen bonds between the H atoms on carbon atoms of the carborane cages and the five-

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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.

Table 1. Crystal Data and Summary of Data Collection and Refinement for 7 and 9−12

	7	**9**	**10**	**11**	**12**
formula	$C_{50}H_{92}B_{20}NaNdO_6Si_2$	$C_{38}H_{69}B_{20}ClErNaO_3Si_2$	$C_{92}H_{156}B_{20}Er_2Na_2O_{13}Si_4$	$C_{28}H_{71}B_{20}Cl_2ErO_6$	$C_{24}H_{63}B_{20}Cl_2O_5Y$
crystal size (mm)	0.30 × 0.36 × 0.38	0.12 × 0.20 × 0.32	0.14 × 0.15 × 0.15	0.18 × 0.27 × 0.38	0.20 × 0.20 × 0.24
fw	1228.9	1072.0	2179.2	958.2	807.8
crystal class	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a, Å	31.167(2)	25.345(1)	31.820(1)	13.108(1)	13.116(1)
b, Å	10.995(1)	12.299(1)	20.445(1)	13.844(1)	13.857(1)
c, Å	20.829(1)	17.629(1)	19.202(1)	15.449(1)	15.356(2)
α, deg				93.22(1)	93.09(1)
β, deg	109.72(1)	100.52(1)	115.19(1)	107.62(1)	107.58(1)
γ, deg				102.27(1)	102.41(1)
V, $Å^3$	6719.1(7)	5403.0(3)	11304.1(8)	2589.0(3)	2577.2(4)
Z	4	4	4	2	2
D_{calcd}, Mg/m^3	1.215	1.318	1.280	1.228	1.262
radiation (λ), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2θ range, deg	4.0−50.0	3.0−50.0	3.0−51.0	3.0−50.0	3.0−50.0
μ, mm^{-1}	0.857	1.690	1.578	1.757	1.262
$F(000)$	2556	2180	4504	978	840
no. of indep reflns	5024	7999	8290	7897	4827
no. of obsd reflns	4995	7947	8290	7878	4827
no. of params refnd	364	596	602	490	470
goodness of fit	1.035	1.053	1.060	1.050	0.991
R1	0.080	0.077	0.055	0.059	0.108
wR2	0.221	0.194	0.129	0.173	0.277

membered rings of indenyl groups, similar to those observed in $[\eta^5\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})]LnCl_2(THF)_3$ and $[\eta^5\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})]_2LnCl(THF)_2$.[5] The ^{13}C NMR spectra are consistent with the results of ^1H NMR spectra and indicate that the two indenyl groups in **3**−**6** are identical in solution. The IR spectra of all six complexes exhibit a very strong characteristic B−H absorption at about 2575 cm^{-1}. The ^{11}B NMR spectra are dependent upon the central atom ions and surrounding ligands showing various splitting patterns. All attempts to grow single crystals suitable for X-ray analyses failed due to severe twinning problems.

Reaction of **4** with excess NaH or treatment of $NdCl_3$ with 2 equiv of $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$ in THF at room temperature yielded the same complex, $[Na(THF)_6][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}_2Nd]$ (**7**), in about 65% yield. The ^1H NMR spectrum supports the ratio of three THF molecules per ligand and the deprotonation of the CH protons of the cages. An X-ray analysis reveals that **7** is an ionic complex consisting of well-separated, alternating layers of discrete tetrahedral anions $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}_2Nd]^-$ and octahedral cations $[Na(THF)_6]^+$, isostructural to $[Na(THF)_6][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}_2Sm]$, which was prepared from a redox reaction between SmI_2, $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$, and $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ in THF.[6b] Figure 1 shows the molecular structure of the anion, in which the Nd atom sits on a crystallographic C_2 axis and is η^5-bound to each of two indenyl groups and σ-bound to two carbon atoms from two carborane cages in a distorted-tetrahedral geometry with Cnt−Nd−Cnt, Cnt−Nd−C(1), and C(1)−Nd−C(1A) angles of 112.9°, 102.4°, and 108.6(2)°, respectively (Cnt: the centroid of the five-membered ring of the indenyl group). Two phenyl rings of the indenyl groups are located on the same side, indicating that **7** is a *meso* isomer.

The average Nd−C(C_5 ring) distance of 2.777(4) Å is very close to the 2.767(6) Å in $[CH_3OCH_2CH_2C_9H_6]_2NdCl$[17] and 2.780(6) Å in $[O(CH_2CH_2C_9H_6)_2]NdCl(THF)$,[18] but is slightly longer than the 2.728(1) Å in $[Li(THF)_4][\{\eta^5{:}\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})\}_2Nd]$[5] perhaps due to steric effects of the indenyl groups. The intramolecular Nd−C (σ) bond distance of 2.635(4) Å is slightly longer than that of 2.601(1) Å in $[Li(THF)_4][\{\eta^5{:}\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})\}_2Nd]$[5] and is significantly longer than the terminal Nd−C (σ) bond distances such as 2.517(7) Å in $(C_5Me_5)_2NdCH(SiMe_3)_2$[19] and 2.506(7) Å in $[Me_2Si(C_5Me_4)_2]NdCH(SiMe_3)_2$,[20] but is comparable to the bridging Nd−C (σ) bond distances such as 2.622(5) Å in $[(Bu^tC_5H_4)_2Nd(C{\equiv}CC_6H_5)]_2$.[21]

Reaction of **2** with 2 equiv of K metal in THF at room temperature gave $[\eta^5{:}\eta^6\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Er(THF)_2$ (**8**), which can also be prepared by treatment of $ErCl_3$ with 1 equiv of $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]K_3$ in THF in 60−70% yield. The ^1H NMR spectrum supports the ratio of two THF molecules per ligand. The ^{11}B NMR spectrum consists of many broad, unresolved resonances, which differs from those of **2** and $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]$-

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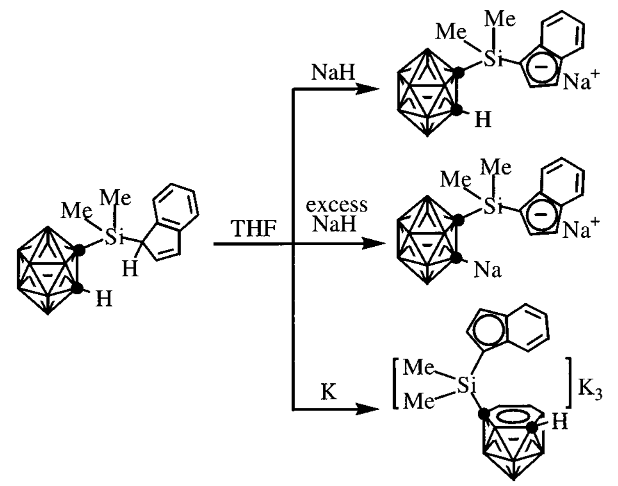
Table 2. Selected Interatomic Distances (Å) and Angles (deg)[a]

		Complex **7**			
Nd(1)−C(1)	2.635(4)	Nd(1)−C(13)	2.745(3)	Na(1)−O(1)	2.476(4)
Nd(1)−C(11)	2.699(4)	Nd(1)−C(18)	2.872(4)	Na(1)−O(2)	2.453(4)
Nd(1)−C(12)	2.740(3)	Nd(1)−C(19)	2.828(4)	Na(1)−O(3)	2.445(4)
C(1A)−Nd(1)−C(1)	108.6(2)	C(1)−Nd(1)−Cnt	102.4	Cnt−Nd(1)−Cnt	112.9
		Complex **9**			
Er(1)−C(11)	2.677(3)	Er(1)−C(21)	2.632(3)	Er(1)−C(1)	2.520(3)
Er(1)−C(12)	2.636(3)	Er(1)−C(22)	2.583(3)	Na(1)−O(1)	2.297(4)
Er(1)−C(13)	2.626(3)	Er(1)−C(23)	2.646(3)	Na(1)−O(2)	2.328(3)
Er(1)−C(18)	2.756(3)	Er(1)−C(28)	2.738(3)	Na(1)−O(3)	2.310(3)
Er(1)−C(19)	2.716(3)	Er(1)−C(29)	2.757(3)	H(4A)-Cnt	2.874
Er(1)−Cl(1)	2.545(1)	Na(1)−Cl(1)	2.633(2)		
Cl(1)−Er(1)−C(1)	96.42(7)	Cnt-Er(1)−Cnt	129.4		
		Complex **10**			
Er(1)−C(1)	2.566(2)	Er(1)−O(1A)	2.051(2)	Na(1)−O(3)	2.428(3)
Er(1)−C(11)	2.690(3)	Er(1)−C(21)	2.728(3)	Na(1)−O(4)	2.459(3)
Er(1)−C(12)	2.611(3)	Er(1)−C(22)	2.639(3)	Na(1)−O(5)	2.457(2)
Er(1)−C(13)	2.693(3)	Er(1)−C(23)	2.614(3)	Na(2)−O(6)	2.377(4)
Er(1)−C(18)	2.847(3)	Er(1)−C(28)	2.798(3)	Na(2)−O(7)	2.282(4)
Er(1)−C(19)	2.864(3)	Er(1)−C(29)	2.712(3)	Na(2)−O(8)	2.315(4)
O(1A)−Er(1)−C(1)	98.30(8)	C(1)−Er(1)−Cnt(1)	103.6	C(1)−Er(1)−Cnt(2)	107.3
Si(2)−O(1)−Er(1A)	167.9(1)				
		Compound **11**			
Er(1)−O(1)	2.382(2)	Er(1)−O(4)	2.375(2)	C(1)−C(3)	1.628(8)
Er(1)−O(2)	2.379(2)	Er(1)−O(5)	2.393(2)	C(3)−B(15)	1.678(12)
Er(1)−O(3)	2.382(2)	Er(1)−Cl(1)	2.548(1)	C(3)−B(16)	1.991(11)
		Er(1)−Cl(2)	2.541(1)		
O(1)−Er(1)−O(5)	72.11(6)	O(2)−Er(1)−O(3)	71.60(6)	O(4)−Er(1)−O(1)	71.56(6)
O(5)−Er(1)−O(2)	72.00(6)	O(3)−Er(1)−O(4)	72.56(6)	Cl(1)−Er(1)−Cl(2)	179.62(2)
		Compound **12**			
Y(1)−O(2)	2.379(3)	Y(1)−O(5)	2.382(3)	C(1)−C(3)	1.657(9)
Y(1)−O(3)	2.390(3)	Y(1)−O(6)	2.395(3)	C(3)−B(14)	1.816(13)
Y(1)−O(4)	2.385(3)	Y(1)−Cl(1)	2.559(1)	C(3)−B(15)	1.908(11)
		Y(1)−Cl(2)	2.558(1)		
O(4)−Y(1)−O(6)	71.17(10)	O(2)−Y(1)−O(5)	71.82(10)	O(3)−Y(1)−O(4)	72.61(10)
O(6)−Y(1)−O(2)	72.13(10)	O(5)−Y(1)−O(3)	72.36(10)	Cl(1)−Y(1)−Cl(2)	179.53(4)

[a] Cnt: the centroid of the five-membered ring of the indenyl group.

Scheme 1



K$_3$. The IR spectrum shows a unique doublet centered around 2508 cm^{-1}, typical of the ionic interaction of a positive metal center and an anionic carboranyl ligand.[5,6b,22] It is reasonable to suggest that the solid-state structure of **8** is similar to that of [η^5:η^6-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]Sm(THF)$_2$ prepared from an unexpected redox reaction between SmI$_2$ and [Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]Na in THF.[6b]

Reaction of **6** with 1 equiv of NaH or treatment of **2** with 1 equiv of [Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Na$_2$ in THF at room temperature yielded the same complex [{η^5:σ-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}{η^5-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)}]Er(μ-Cl)Na(THF)$_3$ (**9**) in 80% yield (Scheme 3). The ^{1}H NMR spectrum of the hydrolysis products supports the ratio of 1.5 THF molecules per ligand. The ^{11}B NMR spectrum exhibits a 1:1:2:2:4 splitting pattern that differs from those of **2** and **6**. Its molecular structure has been confirmed by single-crystal X-ray analysis.

As shown in Figure 2, **9** is a *racemic* isomer and the Er atom lies in a distorted-tetrahedral environment, η^5-bound to each of the two indenyl ligands and σ-bound to the C atom of the carborane cage and with a doubly bridging Cl atom. The Er−C(C$_5$ ring) distances range from 2.583(3) to 2.757(3) Å with an average value of 2.676(3) Å. This measured value can be compared to that of 2.704(7) Å in [{(η^5:μ_2−C$_9$H$_6$SiMe$_2$NH)Er}$_2$(μ_3-Cl)(THF)]$_2$(μ_4-NH),[6a] and those observed in [CH$_3$OCH$_2$CH$_2$C$_9$H$_6$]$_2$LnCl[17] and [O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]LnCl(THF)[18] if Shannon's ionic radii are taken into account.[23] The Er−Cl distance of 2.545(1) Å is comparable to those normally

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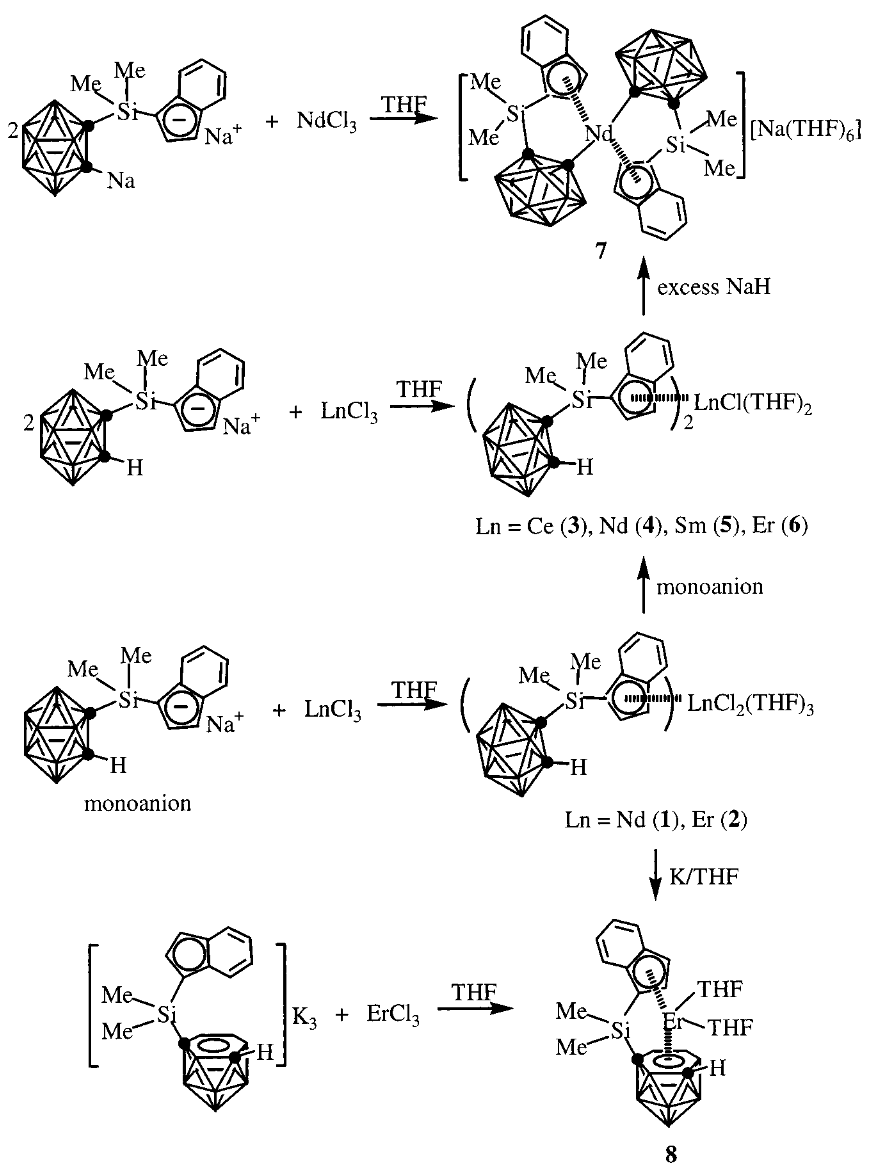
(22) (a) Khattar, R.; Knobler, C. B.; Johnson, S. E.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 1970. (b) Khattar, R.; Manning, M. J.; Knobler, C. B.; Johnson, S. E.; Hawthorne, M. F. *Inorg. Chem.* **1992**, *31*, 268. (c) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1990**, *29*, 2191. (d) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4962. (e) Oki, A. R.; Zhang, H.; Hosmane, N. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 432. (f) Hosmane, N. S.; Wang, Y.; Oki, A. R.; Zhang, H.; Maguire, J. A. *Organometallics* **1996**, *15*, 626. (g) Hosmane, N. S.; Wang, Y.; Zhang, H.; Maguire, J. A.; McInnis, M.; Gray, T. G.; Collins, J. D.; Kremer, R. K.; Binder, H.; Waldh, E.; Kaim, W. *Organometallics* **1996**, *15*, 1006. (h) Hosmane, N. S.; Wang, Y.; Zhang, H.; Oki, A. R.; Maguire, J. A.; Waldh, E.; Kaim, W.; Binder, H.; Kremer, R. K. *Organometallics* **1995**, *14*, 1101. (i) Hosmane, N. S.; Oki, A. R.; Zhang, H. *Inorg. Chem. Commun.* **1998**, *1*, 101. (j) Hosmane, N. S.; Zhu, D.; Zhang, H.; Oki, A. R.; Maguire, J. A. *Organometallics* **1998**, *17*, 3196. (k) Hosmane, N. S.; Zhang, H.; Jia, L.; Colacot, T. J.; Maguire, J. A.; Wang, X.; Hosmane, S. N.; Brooks, K. A. *Organometallics* **1999**, *18*, 516.

Scheme 2



observed in organoerbium chloride complexes.[2a] The intramolecular Er–C (σ) bond distance of 2.520(3) Å is very close to that of 2.528(2) Å in $[Li(THF)_4][\{\eta^5{:}\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})\}_2Er]$[5c] and 2.526(6) Å in $[(C_5H_5)_2Er(\eta^2\text{-}CH{=}N\text{-}{}^tBu)]_2$,[24] but is longer than that of 2.458(19) Å in $[(C_5H_5)_2Er(\mu\text{-}Me)_2Li(tmed)]$[25] and 2.44(2) Å in $[(C_5H_5)_2Er(\mu\text{-}C{\equiv}C\text{-}{}^tBu)]_2$.[26]

Similar to $[\eta^5\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})]LnCl_2(THF)_3$, $[\eta^5\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})]_2LnCl(THF)_2$,[5] and $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Yb(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na(THF)_3$,[6b] the nonclassical hydrogen bond between the H(4A) atom on the carbon atom of the carborane cage and the five-membered ring of one of the indenyl groups is present in **9** with a distance of 2.874 Å, resulting in the smaller C(3)–Si(2)–C(11) angle of 105.87(3)°. The formation of complexes **7** and **9** indicates that the CH protons of the carborane cages in $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]_2LnCl(THF)_2$ can be deprotonated step by step.

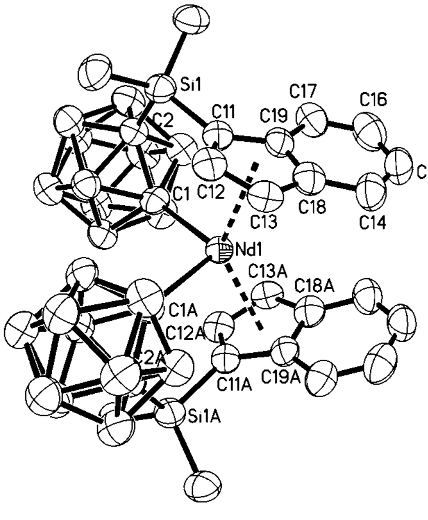


Figure 1. Molecular structure of the anion $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]_2Nd^-$ in **7** (thermal ellipsoids drawn at the 35% probability level).

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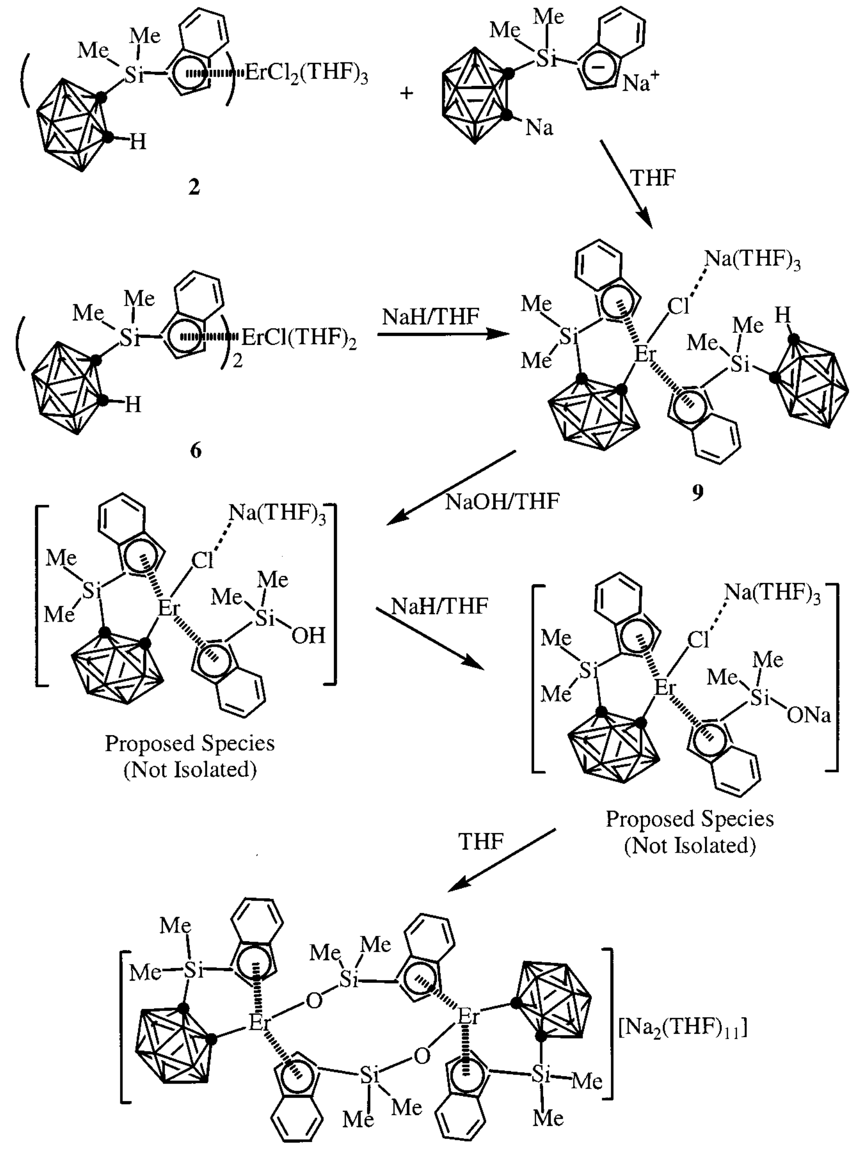
Scheme 3



10

Reaction of **9** with 1 equiv of NaOH in THF resulted in an oily product. No pure compound was isolated. It is proposed that the OH^- group may attack the Si atom to form the silanol, which may further react with Er–C bonds affording a mixture of products. For simultaneous deprotonation of the forming silanol, NaH was then used. Treatment of **9** with a mixture of 1 equiv of NaOH and excess NaH in THF at room temperature gave $[Na_2(THF)_{11}][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}\{\mu\text{-}\eta^5{:}\sigma\text{-}(C_9H_6)SiMe_2O\}Er]_2$ (**10**) in 53% yield (Scheme 3). Spectroscopic data on **10** show the presence of indenyl, carboranyl, and methyl groups as well as THF molecules. Its molecular structure as derived from single-crystal X-ray analysis is shown in Figure 3. It is an ionic complex consisting of one discrete dianion $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}\{\mu\text{-}\eta^5{:}\sigma\text{-}(C_9H_6)SiMe_2O\}Er]_2^{2-}$ and two discrete cations of the octahedral $[Na(THF)_6]^+$ and the trigonal-bipyramidal $[Na(THF)_5]^+$. It is not clear why two Na^+ ions adopt a different coordination environment. The dianion has a crystallographic C_2 axis through the center of the two Er atoms and retains the structural motif of $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Er$ in **9**. Each of the Er atoms is η^5-bound to two indenyl rings and σ-bound to one carbon atom of the carborane cage and one oxygen atom of the silyloxyl group in a distorted-tetrahedral geometry with Cnt(1)–Er–Cnt(2), Cnt(1)–Er–C(1), Cnt(2)–Er–C(1), Cnt(1)–Er–O, and C(1)–Er–O angles of 126.9°, 103.6°, 107.3°, 107.1°, and 98.30(8)°, respectively.

The range of the Er–C distances in the C(11)–C(19) ring (2.611(3)–2.864(3) Å) is larger than that in the C(21)–C(29) ring (2.614(3)–2.798(3) Å), indicating that the tendency to form an η^3-orientation is higher in the C(11)–C(19) ring. The average Er–C(C(11)–C(19)) ring distance of 2.741(3) Å is longer than that of 2.698(3) Å in the C(21)–C(29) ring and 2.676 (3) Å in **9**. The intramolecular Er–C (σ) bond distance of 2.566(2) Å is longer than that of 2.520(3) Å in **9** and is perhaps the longest Er–C (σ) bond distance reported in the literature,[27] implying steric effects.

The Er–O(Si) distance of 2.051(2) Å is comparable to the Ln–O(Si) distances normally observed in organo-

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[27] Cotton, S. A. *Coord. Chem. Rev.* **1997**, *160*, 93.

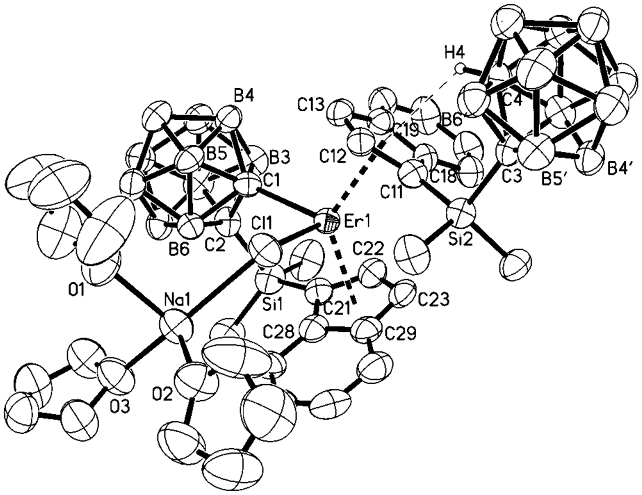


Figure 2. Molecular structure of $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}\{\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}]Er(\mu\text{-}Cl)Na(THF)_3$ (**9**) (thermal ellipsoids drawn at the 35% probability level).

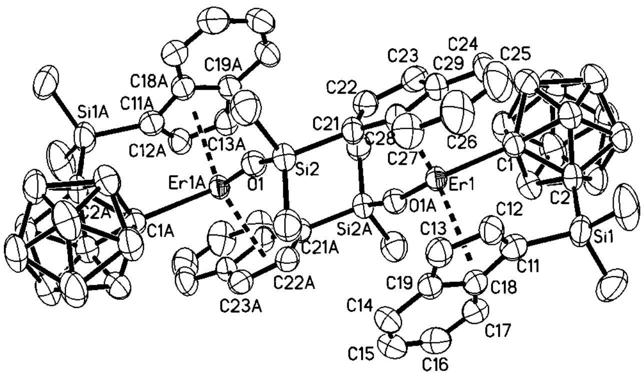
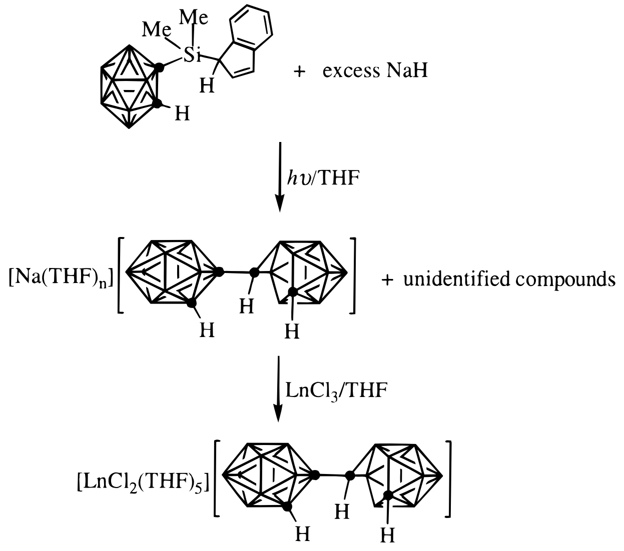


Figure 3. Molecular structure of the dianion $[\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}\{\mu\text{-}\eta^5{:}\sigma\text{-}(C_9H_6)SiMe_2O\}Er]_2^{2-}$ in **10** (thermal ellipsoids drawn at the 35% probability level).

lanthanide silyloxide complexes, for example, 2.170(2) Å in $[(C_6H_5)_3SiO]_3Sm(THF)_3$,[28] 2.13(2) Å in $[(C_6H_5)_3SiO]_3Y(THF)_3$,[29] 2.222(4) Å in $[(C_6H_5)_3SiO]_3Ce(THF)_3$,[30] and 2.225(7) Å in $[(C_6H_5)_3SiO]_3La(THF)_3$.[31] The differences in the above distances are close to those in their ionic radii.[23] The Er−O−Si angle of 167.9(1)° falls in the range 158−180° normally observed for the M−O−Si angle. The relatively short Er−O(Si) distance and large Er−O−Si angle suggest the presence of metal d_π−oxygen p_π interactions,[31] which is probably the reason (at least one of the reasons) that the dimeric anion is formed.

Biscarborane Compounds. The biscarborane compound $[ErCl_2(THF)_5][\mu\text{-}CH\text{-}(\textit{closo}\text{-}C_2B_{10}H_{11})\text{-}\textit{nido}\text{-}CB_{10}H_{11}]$ (**11**) was initially isolated as a byproduct from "one-pot" synthesis of **9** by treatment of $ErCl_3$ with $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ and then $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$ in THF at room temperature. As far as we are aware, this is the first biscarborane monoanion compound to be reported. The formation of this compound interests us. To gain some insight into this reaction, the ^{11}B NMR was used as a probe to examine some reactions. The results show that no biscarborane anion was formed after mixing $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ or $[Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Na$ with $ErCl_3$ in THF even under UV-light for 24 h. Disodium salt $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na_2$, however, can lead to the formation of biscarborane monoanion $[\mu\text{-}CH\text{-}(\textit{closo}\text{-}C_2B_{10}H_{11})\text{-}\textit{nido}\text{-}CB_{10}H_{11}]^-$ under UV-light in over 50% yield after 24 h. Attempts to isolate the sodium salt $[Na(THF)_x][\mu\text{-}CH\text{-}(\textit{closo}\text{-}C_2B_{10}H_{11})\text{-}\textit{nido}\text{-}CB_{10}H_{11}]$ from the reaction mixture turned out to be very difficult probably due to the solubility problems. A larger cation is desirable in order to crystallize out a larger anion. The successful isolation of **11** suggests that $[LnCl_2(THF)_5]^+$ should be the suitable cation for this purpose and can be generated in situ by dissolving $LnCl_3$ in THF in some cases.[32−35] The mechanism of the formation of such a biscarborane anion is not clear, but it may be similar to the Wurtz reaction[36] to some extent. A method for the preparation of biscarborane monoanion compounds is then developed.

Scheme 4



Ln = Er (**11**), Y (**12**)

Treatment of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with excess NaH in THF under UV-light followed by reaction with 1 equiv of $LnCl_3$ at room temperature afforded biscarborane compound $[LnCl_2(THF)_5][\mu\text{-}CH\text{-}(\textit{closo}\text{-}C_2B_{10}H_{11})\text{-}\textit{nido}\text{-}CB_{10}H_{11}]$ (Ln = Er (**11**), Y (**12**)) in about 40% yield (Scheme 4). The IR spectra exhibit a very strong broad B−H absorption at about 2550 cm^{-1}. The ^1H NMR spectrum of **12** shows the presence of THF molecules and two types of carborane CH protons and the absence of indenyl and methyl groups. The ^{11}B NMR spectra display a 1:1:1:2:2:1:2 splitting pattern.

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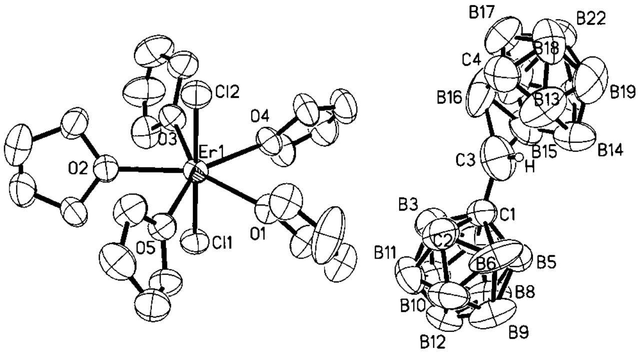

Figure 4. Molecular structure of $[ErCl_2(THF)_5][\mu$-CH-(*closo*-$C_2B_{10}H_{11}$)-*nido*-$CB_{10}H_{11}]$ (**11**) (the solvated THF molecule is not shown; thermal ellipsoids drawn at the 35% probability level).

Molecular structures of both compounds **11** and **12** have been confirmed by single-crystal X-ray analyses. They are isostructural and isomorphous. Figure 4 shows their representative structure. Both of them consist of well-separated, alternating layers of discrete cations $[LnCl_2(THF)_5]^+$ and biscarborane monoanions $[\mu$-CH-(*closo*-$C_2B_{10}H_{11}$)-*nido*-$CB_{10}H_{11}]^-$. The cation adopts a pentagonal-bipyramidal geometry with two chloro ligands at the axial positions and the five THF molecules at the equatorial positions, similar to that of $[SmI_2(THF)_5]^+$,[32] $[YCl_2(THF)_5]^+$,[33] $[TbCl_2(THF)_5]^+$,[34] and $[CeCl_2(THF)_5]^+$.[35] The anion consists of two carborane cages that are connected to each other through a C(1)−C(3) single bond. One of them is an icosahedral cage with normal C−B and B−B distances observed in C_2B_{10} cage systems.[5−7] The other is a *nido*-carborane monoanion with a bridging CH group. The two C(3)−B distances are 1.678(12) and 1.991(11) Å in **11** and 1.816(14) and 1.908(11) Å in **12**, respectively. The C(1)−C(3) distance is 1.628(8) Å in **11** and 1.657(9) Å in **12**, respectively. These differences may be due to the crystal packing forces, as discussed in the literature.[37]

In comparison with the structures of $[C_2B_{10}H_{11}]_2^{2-}$,[37] $[C_2B_{10}H_{12}]_2^{2-}$,[37a] and $[C_2B_{10}H_{13}]^-$,[38] it may be better to describe the biscarborane monoanion as $[\mu$-CH-(*closo*-$C_2B_{10}H_{11}$)-*nido*-$CB_{10}H_{11}]^-$ rather than as $[C_2B_{10}H_{11}]_2^-$. Single-electron reduction of biscarborane $[C_2B_{10}H_{11}]_2$ to form $[C_2B_{10}H_{11}]_2^-$ seems unlikely according to the electron-counting rules, although two-electron reduction of $[C_2B_{10}H_{11}]_2$ to $[C_2B_{10}H_{11}]_2^{2-}$ was reported.[37] The μ-CH hydrogen atom in the monoanion $[\mu$-CH-(*closo*-$C_2B_{10}H_{11}$)-*nido*-$CB_{10}H_{11}]^-$ should be from the reaction mixture rather than from the H_2O molecule since the experiments were repeatable and very carefully carried out in an oxygen- and moisture-free N_2 atmosphere.

Conclusion

Applications of a versatile ligand $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ to Ln(III) chemistry have resulted in the isolation and structural characterization of a series of organolanthanide indenyl complexes including the monochloride, dichloride, carboranyl, silyloxide, and lanthanacarboranes. Due to the electronic and steric effects of the indenyl group, the resulting organolanthanide complexes show some different reactivity patterns from their cyclopentadienyl analogues.[5]

This study shows that the two units, the carboranyl and cyclic organic groups, in this type of bridging ligand communicate with each other, indicating that the acidity of the CH proton of the carborane cage is dependent upon the substituents on the cyclopentadienyl rings, which in turn affects the property of the resulting complexes. Therefore, fine-tuning is possible by changing the substituents on the cyclic organic groups.

Unexpected coupling of the carborane cages led to the isolation and structural characterization of the first example of a biscarborane monoanion compound, which offers the first method to prepare biscarborane monoanion compounds.

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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 complexes **7** and **9**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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