Organometallics **2001,** *20,* 2359−2366

Tetramethylcyclopentadienyl vs Cyclopentadienyl Substituents. Synthesis and Structural Characterization of Organolanthanide Compounds Derived from the Versatile Ligand $Me_2Si(C_5Me_4H)(C_2B_{10}H_{11})$

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Received January 16, 2001

Reaction of $Me_2Si(C_5Me_4H)Cl$ with 1 equiv of $Li_2C_2B_{10}H_{10}$ in toluene/Et_2O gave the monoanionic salt $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Li(OEt_2)_{0.5}$ (**1**), which could be conveniently converted into the dianionic salt $[\{[(\mu\text{-}\eta^5):\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]\cdot THF$ (**2**) by treatment with 1 equiv of *n*-BuLi. **1** reacted with 1 equiv of $LnCl_3$ in THF to give $[\eta^5\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]LnCl_3Li(THF)_3$ (Ln = Nd (**3**), Sm (**4**)). **3** could further react with 1 equiv of **1** to afford $[\eta^5\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]_2Nd(\mu\text{-}Cl)_2Li(OEt_2)(THF)$ (**6**), which could also be prepared from the reaction of $NdCl_3$ with 2 equiv of **1**. Partial hydrolysis of **4** resulted in the isolation of the novel cluster $[\{[\eta^5\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Sm\}_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_4Li(OEt_2)_2\text{-}Li(THF)_2Sm(\mu_4\text{-}O)]_2$ (**5**). Treatment of **1** with 4 equiv of $NaNH_2$ in THF, followed by reaction with 1 equiv of $YbCl_3$, produced $(\eta^5\text{-}C_5Me_4H)_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ (**7**). An equimolar reaction between **2** and $NdCl_3$ yielded the anionic compound $[\{\eta^5\text{:}\ \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}_2Nd]\text{-}[Li(DME)_3]$ (**11**). Interaction of $LnCl_3$ with 0.5 equiv of **2** resulted in the isolation of the lanthanocene chloride compounds $[\{\eta^5\text{:}\ \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}LnCl(\mu\text{-}Cl)]_2[Li(S)_n]_2$ (S = THF, $n = 4$, Ln = Sm (**8**), Y (**9**); S = DME, $n = 3$, Ln = Yb (**10**)). Reaction of **9** with 2 equiv of $NaN(SiMe_3)_2$ gave the unsolvated compound $[\eta^5\text{:}\ \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]YN(SiMe_3)_2$ (**12**). Treatment of LnI_2 with 0.5 equiv of **2** afforded the ionic organolanthanide(II) compounds $[\{\eta^5\text{:}\ \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}LnI_2][Li(DME)_3]_2$ (Ln = Sm (**13**), Yb (**14**)). All of these new compounds were characterized by various spectroscopic data and element analyses. The solid-state structures of compounds **2**, **5**−**7**, **10**, and **14** were further confirmed by single-crystal X-ray analyses.

Introduction

By taking advantage of unique carborane molecules[1] and traditional cyclic π-ligands as well as bridging ligands,[2] two types of silicon- and carbon-bridged versatile ligands, $Me_2A(C_5H_5)(C_2B_{10}H_{11})$ (A = Si,[3] C[4]) and $Me_2A(C_9H_7)(C_2B_{10}H_{11})$ (A = Si,[5] C[6]), were recently developed, which have led to the isolation and structural characterization of a new class of organolanthanide compounds. However, lanthanocene chloride compounds of the types $[\eta^5\text{:}\ \sigma\text{-}Me_2A(C_5H_4)(C_2B_{10}H_{10})]LnCl$ and $[\eta^5\text{:}\ \sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]LnCl$ have not been isolated, presumably due to the ligand redistribution reactions leading to the formation of the thermodynamically stable complexes $[\{\eta^5\text{:}\ \sigma\text{-}Me_2A(C_5H_4)(C_2B_{10}H_{10})\}_2Ln]^-$ and $[\{\eta^5\text{:}\ \sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})\}_2Ln]^-$.[3−6] These reactions limit the applications of the above-mentioned versatile ligands in organometallic chemistry, since lanthanocene chlorides are important intermediates for the preparation of other organolanthanide compounds.[2] To prevent such ligand redistribution reactions and to enhance the solubility of the resulting organometallic compounds in less polar organic solvents, we have extended our research to sterically demanding cyclopentadienyl analogues. A versatile ligand containing both carboranyl and tetramethylcyclopentadienyl groups was then developed in our laboratory.[7] It can indeed prevent the ligand redistribution reactions of lanthanocene chlorides and stabilize the coordinatively unsaturated organolanthanide compounds. We report herein

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10.1021/om010031i CCC: \$20.00
Publication on Web 05/04/2001

the synthesis, reactivity, and structural characterization of organolanthanide compounds derived from this ligand. The differences and similarities between the $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$ and $Me_2Si(C_5Me_4H)(C_2B_{10}H_{11})$ ligand systems are also discussed in this contribution.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry nitrogen 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.[8] $LnI_2(THF)_x$,[9] $C_5Me_4H_2$,[10] and $Me_2Si(C_5Me_4H)Cl$[11] 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. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Valian Inova 400 spectrometer at 128.32 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 solvents 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 $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Li(OEt_2)_{0.5}$ (1). To a solution of o-$C_2B_{10}H_{12}$ (7.20 g, 50.0 mmol) in a dry toluene/diethyl ether (2:1) mixture (100 mL) at 0 °C was added a 1.6 M solution of *n*-BuLi in hexane (62.5 mL, 100.0 mmol) dropwise with stirring. The mixture was warmed to room temperature and stirred for 30 min. The solution was then cooled to 0 °C, and a solution of (tetramethylcyclopentadienyl)dimethylsilyl chloride ($Me_2Si(C_5Me_4H)Cl$; 10.74 g, 50.0 mmol) in a toluene/diethyl ether (2:1) mixture (50 mL) was slowly added, and the mixture was refluxed overnight. A white precipitate (LiCl) was filtered off. Removal of the solvent gave a white solid that was recrystallized from a diethyl ether/hexane solution, affording **1** as a white solid (15.0 g, 82%). ^1H NMR (pyridine-d_5): δ 3.21 (m, 2H, OCH_2CH_3), 3.18 (br s, 1H, CH of carboranyl), 2.24 (s, 6H, CH_3), 2.04 (s, 6H, CH_3), 1.00 (m, 3H, OCH_2CH_3), 0.71 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 118.1, 115.5, 92.5 (C_5Me_4), 73.6, 63.1 ($C_2B_{10}H_{11}$), 65.7, 15.4 (Et_2O), 14.6, 11.7 (CH_3), 2.96 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ −2.9 (4), −7.6 (2), −11.2 (4). IR (KBr, cm^{-1}): ν 3052 (m), 2962 (s), 2915 (s), 2572 (vs), 1447 (m), 1382 (m), 1257 (s), 1034 (s), 806 (s). Anal. Calcd for $C_{15}H_{34}B_{10}LiO_{0.5}Si$: C, 49.28; H, 9.38. Found: C, 49.42; H, 9.52.

Preparation of $[\{[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]{\cdot}THF$ (2). To a THF (10 mL) solution of $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Li(OEt_2)_{0.5}$ (**1**; 3.66 g, 10.0 mmol) was slowly added a solution of 2.5 M *n*-BuLi in hexane (4.0 mL, 10.0 mmol) at −78 °C with stirring. The mixture was warmed to room temperature and then stirred for 30 min. Removal of the solvent gave a white product that was washed with hexane and recrystallized from a THF/hexane solution, affording **2** as colorless crystals (5.58 g, 95%). ^1H NMR (pyridine-d_5): δ 3.51 (m, 14H, THF), 2.58 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 1.42 (m, 14H, THF), 0.80 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 117.2, 114.6, 96.7 (C_5Me_4), 82.6, 77.5 ($C_2B_{10}H_{10}$), 68.0, 25.7 (THF), 15.1, 11.9 (CH_3), 3.9 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ −3.45 (4), −7.86 (6). IR (KBr, cm^{-1}): ν 2963 (s), 2882 (s), 2532 (vs), 1453 (m), 1260 (s), 1040 (s), 888 (s), 800 (s). Anal. Calcd for $C_{34}H_{72}B_{20}Li_4O_2Si_2$ (**2**−5THF): C, 50.22; H, 8.93. Found: C, 50.52; H, 8.37.

Preparation of $[\eta^5\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]NdCl_3Li(THF)_3$ (3). To a suspension of $NdCl_3$ (0.125 g, 0.50 mmol) in 15 mL of THF was slowly added a THF solution (10 mL) of $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Li(OEt_2)_{0.5}$ (**1**; 0.183 g, 0.50 mmol), and the mixture was stirred overnight at room temperature. Removal of the THF gave a blue solid that was extracted with diethyl ether (3 × 10 mL). Ether solutions were combined and concentrated to yield a blue solid. Recrystallization from a THF/Et_2O solution gave **3** as blue microcrystals (0.318 g, 80%). ^1H NMR (pyridine-d_5): δ 9.09 (s, 3H, CH_3), 5.55 (s, 3H, CH_3), 4.48 (s, 1H, CH of carboranyl), 3.63 (m, 12H, THF), 1.60 (m, 12H, THF), 1.31 (s, 3H, CH_3), −0.74 (s, 6H, $Si(CH_3)_2$), −2.92 (s, 3H, CH_3). ^{13}C NMR (pyridine-d_5): δ 129.0, 128.3, 125.4 (C_5Me_4), 71.7, 62.0 ($C_2B_{10}H_{11}$), 67.4, 25.4 (THF), 18.6, 17.7, 14.7, 14.3 (CH_3), 2.1 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ −3.08 (3), −6.26 (3), −9.76 (3), −12.75 (1). IR (KBr, cm^{-1}): ν 3048 (m), 2965 (s), 2887 (s), 2585 (vs), 1633 (m), 1450 (m), 1383 (m), 1257 (m), 1037 (s), 814 (s). Anal. Calcd for $C_{15}H_{33}B_{10}Cl_3LiNdO_{0.5}Si$ (**3**−2.5THF): C, 29.29; H, 5.41. Found: C, 29.58; H, 5.26.

Preparation of $[\eta^5\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]SmCl_3Li(THF)_3$ (4). This compound was prepared as yellow microcrystals from $SmCl_3$ (0.256 g, 1.0 mmol) and $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Li(OEt_2)_{0.5}$ (**1**; 0.366 g, 1.0 mmol) in THF (15 mL) by using procedures similar to those used in the synthesis of **3**: yield 0.69 g (86%). ^1H NMR (pyridine-d_5): δ 3.63 (m, 12H, THF), 2.95 (s, 1H, CH of carboranyl), 2.50 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.60 (m, 12H, THF), 1.48 (s, 3H, CH_3), 0.78 (s, 3H, $SiCH_3$), 0.62 (s, 3H, $SiCH_3$). ^{13}C NMR (pyridine-d_5): δ 126.2, 120.9, 115.6 (C_5Me_4), 72.4, 61.7 ($C_2B_{10}H_{11}$), 67.7, 25.7 (THF), 15.7, 12.1 (CH_3), 2.4 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ −4.03 (2), −10.46 (2), −13.17 (3), −14.52 (3). IR (KBr, cm^{-1}): ν 3059 (m), 2960 (s), 2904 (s), 2573 (vs), 1445 (m), 1384 (m), 1259 (s), 1094 (s), 802 (s). Anal. Calcd for $C_{23}H_{49}B_{10}Cl_3LiO_{2.5}SiSm$ (**4**−0.5THF): C, 36.08; H, 6.45. Found: C, 35.52; H, 6.45.

Preparation of $[\{[\eta^5\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Sm\}_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_4Li(OEt_2)_2Li(THF)_2Sm(\mu_4\text{-}O)]_2$ (5). Recrystallization of **4** from a THF/Et_2O solution gave some yellow crystals identified as **5**. ^1H NMR (pyridine-d_5): δ 3.63 (m, 4H, THF), 3.32 (m, 4H, OCH_2CH_3), 2.95 (s, 1H, CH of carboranyl), 2.50 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.60 (m, 4H, THF), 1.48 (s, 3H, CH_3), 1.11 (m, 6H, OCH_2CH_3), 0.78 (s, 3H, $SiCH_3$), 0.62 (s, 3H, $SiCH_3$). ^{13}C NMR (pyridine-d_5): δ 120.3, 98.1 (C_5Me_4), 71.4, 61.6 ($C_2B_{10}H_{11}$), 67.1, 25.1 (THF), 65.1, 14.8 (Et_2O), 18.3, 14.3 (CH_3), 1.7 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ −2.9 (2), −7.9 (3), −11.1 (2), −12.9 (3). IR (KBr, cm^{-1}): ν 3052 (m), 2963 (s), 2918 (s), 2591 (vs), 1637 (vs), 1447 (m), 1380 (m), 1259 (s), 1072 (s), 813 (s). Anal. Calcd for $C_{76}H_{172}B_{40}Cl_{14}Li_4O_8Si_4Sm_6$ (**5**−2THF): C, 28.65; H, 5.44. Found: C, 28.84; H, 5.73.

Preparation of $[\eta^5\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]_2Nd(\mu\text{-}Cl)_2Li(OEt_2)(THF)$ (6). To a suspension of $NdCl_3$ (0.125 g, 0.50 mmol) in 15 mL of THF was slowly added a THF solution (10 mL) of $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Li(OEt_2)_{0.5}$ (**1**; 0.366 g, 1.0 mmol), and the mixture was stirred overnight at room temperature. Removal of THF gave a blue solid that was extracted with diethyl ether (2 × 10 mL). The ether solutions were combined and concentrated to yield a blue solid that was recrystallized from a THF/Et_2O solution, affording **6** as blue crystals (0.314 g, 62%). ^1H NMR (pyridine-d_5): δ 9.09 (s, 3H, CH_3), 5.54 (s, 3H, CH_3), 4.48 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 3.64 (m, 4H, THF), 3.33 (m, 4H, OCH_2CH_3), 2.45 (s, 2H, CH of carboranyl), 1.60 (m, 4H, THF), 1.31 (s, 3H, CH_3), 1.13 (m, 6H, OCH_2CH_3), 0.73 (s, 3H, CH_3), −0.36 (s, 3H, CH_3), −0.74 (s, 6H, $Si(CH_3)_2$), −2.00 (s, 6H, $Si(CH_3)_2$), −2.92 (s, 3H, CH_3). ^{13}C NMR (pyridine-d_5): δ 128.8, 128.0, 125.1 (C_5Me_4), 75.6,

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70.1 ($C_2B_{10}H_{11}$), 67.2, 25.2 (THF), 65.1, 14.9 (Et_2O), 5.3, 4.7, −10.3, −21.6 (CH_3), −0.5 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ 0.0 (4), −4.8 (7), −9.1 (3), −11.3 (3), −15.3 (3). IR (KBr, cm^{-1}): ν 3049 (m), 2979 (s), 2898 (s), 2574 (vs), 1637 (vs), 1447 (m), 1385 (m), 1256 (s), 1070 (s), 817 (s). Anal. Calcd for $C_{26}H_{58}B_{20}Cl_2LiNdSi_2$ (**6**−THF−Et_2O): C, 36.09; H, 6.76. Found: C, 36.51; H, 6.97.

This compound can also be prepared in 45% yield from an equimolar reaction between $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Li(OEt_2)_{0.5}$ (**1**) and $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]NdCl_3Li(THF)_3$ (**3**) in THF at room temperature.

Preparation of $(\eta^5\text{-}C_5Me_4H)_2Yb(\mu\text{-}Cl)_2Li(THF)_2$ (7). To a suspension of $NaNH_2$ (0.160 g, 4.0 mmol) in THF (20 mL) was added a THF solution (10 mL) of $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Li(OEt_2)_{0.5}$ (**1**; 0.366 g, 1.0 mmol), and the mixture was stirred at room temperature for 24 h. The resulting colorless solution was filtered into a stirred suspension of $YbCl_3$ (0.280 g, 1.0 mmol) in THF (10 mL) at room temperature, and this reaction mixture was then stirred overnight. After the solvent was removed under vacuum, the residue was extracted with *n*-hexane (3 × 10 mL). The hexane solutions were combined, concentrated to about 10 mL, and cooled to −20 °C, affording **7** as red crystals (0.080 g, 25%). ^1H NMR (benzene-d_6): δ 1.90 (s, 1H, C_5Me_4H), 1.21 (m, 8H, THF), 0.90 (m, 8H, THF), 0.21 (s, 1H, C_5Me_4H), −3.71 (br s, 6H, CH_3), −4.01 (br s, 9H, CH_3), −18.01 (s, 9H, CH_3). ^{13}C NMR (benzene-d_6): δ 136.2, 131.6, 89.8 (C_5Me_4H), 64.5, 25.6 (THF), 23.0, 19.6, 14.3 (CH_3). IR (KBr, cm^{-1}): ν 2962 (s), 2904 (s), 1615 (m), 1444 (m), 1261 (s), 1096 (vs), 1022 (vs), 800 (vs). Anal. Calcd for $C_{20}H_{30}Cl_2LiO_{0.5}Yb$ (**7**−1.5THF): C, 45.38; H, 5.71. Found: C, 45.66; H, 6.09.

Preparation of $[\{\eta^5\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}SmCl(\mu\text{-}Cl)]_2[Li(THF)_4]_2$ (8). A THF (20 mL) solution of $[\{[(\mu\text{-}\eta^5)\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]\cdot THF$ (**2**; 0.293 g, 0.25 mmol) was slowly added to a suspension of $SmCl_3$ (0.128 g, 0.50 mmol) in 10 mL of THF, and the reaction mixture was stirred overnight at room temperature. After removal of the precipitate and addition of 10 mL of toluene, the clear solution was then concentrated until the LiCl precipitated out. The precipitate was filtered off, and the resulting clear yellow solution was further concentrated to about 12 mL. Yellow microcrystals were obtained when this solution stood at room temperature for several days (0.23 g, 56%). ^1H NMR (pyridine-d_5): δ 3.51 (m, 16H, THF), 3.30 (s, 3H, CH_3), 3.08 (s, 6H, CH_3), 2.95 (s, 3H, CH_3), 1.42 (m, 16H, THF), 0.87 (s, 3H, $SiCH_3$), 0.82 (s, 3H, $SiCH_3$). ^{13}C NMR (pyridine-d_5): δ 126.2, 123.1, 118.0 (C_5Me_4), 72.5, 61.7 ($C_2B_{10}H_{10}$), 67.7, 25.7 (THF), 15.7, 14.2, 12.1 (CH_3), 2.5, 1.3 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ −2.0 (2), −9.5 (2), −14.2 (4), −15.5 (2). IR (KBr, cm^{-1}): ν 2954 (s), 2916 (s), 2542 (vs), 1604 (m), 1454 (m), 1253 (m), 1039 (vs), 808 (m). Anal. Calcd for $C_{42}H_{88}B_{20}Cl_4Li_2O_4Si_2Sm_2$ (**8**−4THF): C, 36.39; H, 6.40. Found: C, 36.56; H, 6.73.

Preparation of $[\{\eta^5\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}YCl(\mu\text{-}Cl)]_2[Li(THF)_4]_2$ (9). This compound was prepared as colorless microcrystals from YCl_3 (0.195 g, 1.0 mmol) and $[\{[(\mu\text{-}\eta^5)\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]\cdot THF$ (**2**; 0.587 g, 0.50 mmol) in THF (15 mL) by using procedures similar to those used in the synthesis of **8**: yield 0.33 g (43%). ^1H NMR (pyridine-d_5): δ 3.66 (m, 16H, THF), 2.63 (s, 6H, CH_3), 2.11 (s, 6H, CH_3), 1.62 (m, 16H, THF), 0.90 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 129.1, 121.1, 110.3 (C_5Me_4), 83.5 ($C_2B_{10}H_{10}$), 68.3, 26.2 (THF), 18.5, 12.8 (CH_3), 4.0 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ 0.02 (1), −2.87 (3), −8.52 (6). IR (KBr, cm^{-1}): ν 2970 (s), 2884 (s), 2549 (vs), 1614 (m), 1454 (m), 1251 (m), 1042 (vs), 888 (s). Anal. Calcd for $C_{58}H_{120}B_{20}Cl_4Li_2O_8Si_2Y_2$: C, 44.90; H, 7.80. Found: C, 45.04; H, 7.96.

Preparation of $[\{\eta^5\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}YbCl(\mu\text{-}Cl)]_2[Li(DME)_3]_2$ (10). A THF (20 mL) solution of $[\{[(\mu\text{-}\eta^5)\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]\cdot THF$ (**2**; 0.293 g, 0.25 mmol) was slowly added to a suspension of $YbCl_3$ (0.140 g, 0.5 mmol) in 10 mL of THF, and the reaction mixture was stirred overnight at room temperature. After removal of the solvent, the residue was extracted with DME (2 × 10 mL). The DME solutions were combined and concentrated to about 8 mL. **10** was isolated as red crystals when the solution stood at room temperature for several days (0.29 g, 70%). ^1H NMR (pyridine-d_5): δ 5.31 (s, 3H, CH_3), 4.62 (s, 6H, CH_3), 3.91 (s, 6H, CH_3), 3.52 (s, 12H, DME), 3.31 (s, 18H, DME), −6.62 (s, 3H, CH_3). ^{13}C NMR (pyridine-d_5): δ 71.4, 58.0 (DME); other carbon atoms were not observed. ^{11}B NMR (pyridine-d_5): δ −4.55 (2), −8.87 (1), −11.04 (2), −15.11 (3), −15.94 (2). IR (KBr, cm^{-1}): ν 2912 (s), 2575 (vs), 1616 (m), 1455 (m), 1383 (vs), 1255 (m), 1082 (vs), 805 (s). Anal. Calcd for $C_{46}H_{106}B_{20}Cl_4Li_2O_{10}Si_2Yb_2$ (**10**−DME): C, 34.67; H, 6.70. Found: C, 34.41; H, 7.10.

Preparation of $[\{\eta^5\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}_2Nd][Li(DME)_3]$ (11). A THF (10 mL) solution of $[\{[(\mu\text{-}\eta^5)\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]\cdot THF$ (**2**; 0.587 g, 0.50 mmol) was slowly added to a suspension of $NdCl_3$ (0.125 g, 0.50 mmol) in 10 mL of THF, and the reaction mixture was stirred overnight at room temperature. After removal of the solvent, the residue was extracted with DME (2 × 10 mL). The DME solutions were combined and concentrated to give a blue solid that was recrystallized from a DME solution, affording **11** as blue microcrystals (0.28 g, 53%). ^1H NMR (pyridine-d_5): δ 3.64 (s, 3H, CH_3), 3.48 (s, 12H, DME), 3.25 (s, 18H, DME), 2.34 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.33 (br, 6H, CH_3), 0.81 (br, 9H, CH_3), 0.31 (s, 6H, CH_3). ^{13}C NMR (pyridine-d_5): δ 122.5, 119.6, 114.7 (C_5Me_4), 71.7, 58.3 (DME), 67.5 ($C_2B_{10}H_{10}$), 31.4, 28.9, 25.5, 22.5, 22.3, 13.9, 11.2, 1.6 (CH_3). ^{11}B NMR (pyridine-d_5): δ −3.7 (3), −9.0 (3), −10.1 (2), −14.2 (2). IR (KBr, cm^{-1}): ν 2954 (s), 2918 (m), 2564 (vs), 1611 (m), 1454 (m), 1384 (m), 1257 (s), 1082 (s), 805 (s). Anal. Calcd for $C_{32}H_{71}B_{20}NdLiO_3Si_2$ (**11**−1.5DME): C, 41.44; H, 7.72. Found: C, 41.23; H, 7.52.

Preparation of $[\eta^5\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]YN(SiMe_3)_2$ (12). To a THF (10 mL) solution of $[\{\eta^5\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}YCl(\mu\text{-}Cl)]_2[Li(THF)_4]_2$ (**9**; 0.39 g, 0.25 mmol) was slowly added a toluene (15 mL) solution of $NaN(SiMe_3)_2$ (0.095 g, 0.50 mmol) at −78 °C, and the reaction mixture was stirred overnight at room temperature. The precipitate was filtered off, and the resulting clear colorless solution was concentrated under vacuum to about 10 mL. **12** was isolated as colorless microcrystals when this solution stood at −20 °C for several days (0.25 g, 87%). ^1H NMR (pyridine-d_5): δ 2.59 (s, 6H, CH_3), 2.07 (s, 6H, CH_3), 0.79 (s, 6H, $Si(CH_3)_2$), 0.22 (s, 18H, $N[Si(CH_3)_3]_2$). ^{13}C NMR (pyridine-d_5): δ 117.1, 114.6, 96.7 (C_5Me_4), 77.6, 62.7 ($C_2B_{10}H_{10}$), 15.1, 12.0 (CH_3), 6.6 ($Si(CH_3)_3$), 3.9 ($N[Si(CH_3)_3]_2$). ^{11}B NMR (pyridine-d_5): δ 0.35 (4), −5.20 (6). IR (KBr, cm^{-1}): ν 2949 (s), 2885 (s), 2552 (vs), 1450 (m), 1247 (m), 1017 (vs), 824 (vs). Anal. Calcd for $C_{19}H_{46}B_{10}NSi_3Y$: C, 40.04; H, 8.14; N, 2.46. Found: C, 39.70; H, 7.95; N, 2.23.

Preparation of $[\{\eta^5\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}SmI_2][Li(DME)_3]_2$ (13). A THF solution of $[\{[(\mu\text{-}\eta^5)\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]\cdot THF$ (**2**; 0.293 g, 0.25 mmol) was slowly added to a dark green THF solution of SmI_2 (10 mL of 0.05 M, 0.50 mmol), and the reaction mixture was stirred overnight at room temperature. After removal of the solvent, the residue was extracted with DME (2 × 10 mL). The DME solutions were combined and concentrated to about 8 mL. Green microcrystals were obtained after this solution was kept at 0 °C for 1 week (0.46 g, 72%). ^1H NMR (pyridine-d_5): δ 3.45 (s, 24H, DME), 3.21 (s, 36H, DME), 2.62 (s, 6H, CH_3), 2.07 (s, 6H, CH_3), 0.79 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 129.4, 128.6, 125.7 (C_5Me_4), 89.7 ($C_2B_{10}H_{10}$), 72.0, 58.6 (DME), 31.7, 21.3 (CH_3), 14.2 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ 0.35 (4), −5.20 (6). IR (KBr, cm^{-1}): ν 2962 (s), 2915 (m), 2572 (vs), 1447 (m), 1382 (m), 1257 (s), 1086 (s), 1034 (vs), 806 (vs). Anal. Calcd for $C_{29}H_{68}B_{10}I_2Li_2O_8SiSm$ (**13**−2DME): C, 31.69; H, 6.24. Found: C, 31.38; H, 5.94.

Preparation of $[\{\eta^5\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}YbI_2][Li(DME)_3]_2$ (14). This compound was prepared as red crystals from YbI_2 (10 mL of 0.05 M, 0.50 mmol) and $[\{[(\mu\text{-}\eta^5)\text{:}\sigma\text{-}Me_2\text{-}$

Table 1. Crystal Data and Summary of Data Collection and Refinement for 2, 5, and 6

	2	**5**	**6**
formula	$C_{54}H_{112}B_{20}$-$Li_4O_7Si_2$	$C_{84}H_{188}B_{40}Cl_{14}$-$Li_4O_{10}Si_4Sm_6$	$C_{34}H_{76}B_{20}Cl_2$-$LiNdO_2Si_2$
cryst size (mm)	0.40 × 0.40 × 0.20	0.38 × 0.22 × 0.20	0.40 × 0.14 × 0.12
fw	1173.6	3329.3	1011.4
cryst syst	monoclinic	monoclinic	monoclinic
space group	*Cc*	$P2_1/c$	$P2_1/c$
a, Å	38.213(8)	18.830(1)	10.280(1)
b, Å	10.460(2)	24.187(1)	24.893(1)
c, Å	18.533(4)	17.076(1)	21.402(1)
β, deg	90.00(3)	109.81(1)	92.29(1)
V, Å^3	7408(3)	7316.9(7)	5472.4(3)
Z	4	2	4
D_{calcd}, Mg/m^3	1.052	1.511	1.228
radiation (*λ*, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2*θ* range, deg	4.6−50.0	4.0−50.0	2.5−50.0
μ, mm^{-1}	0.091	2.701	1.119
F(000)	2528	3300	2084
no. of obsd rflns	4683	10 823	7585
no. of params refnd	805	648	560
goodness of fit	1.195	1.084	1.114
R1	0.109	0.056	0.067
wR2	0.278	0.132	0.166

Table 2. Crystal Data and Summary of Data Collection and Refinement for 7, 10, and 14

	7	**10**	**14**
formula	$C_{26}H_{42}Cl_2Li$-O_2Yb	$C_{25}H_{58}B_{10}Cl_2Li$-O_6SiYb	$C_{37}H_{88}B_{10}I_2$-$Li_2O_{12}SiYb$
cryst size (mm)	0.40 × 0.24 × 0.18	0.50 × 0.40 × 0.25	0.30 × 0.28 × 0.10
fw	637.5	841.8	1302.0
cryst syst	trigonal	monoclinic	orthorhombic
space group	$P\bar{3}$	$P2_1/c$	$P2_12_12_1$
a, Å	29.950(4)	16.478(1)	14.026(1)
b, Å	29.950(4)	15.147(1)	15.837(1)
c, Å	12.983(1)	16.965(1)	27.756(1)
β, deg	90.00	102.54(1)	90.00
V, Å^3	10085(2)	4133.3(5)	6165.4(4)
Z	12	4	4
D_{calcd}, Mg/m^3	1.260	1.353	1.403
radiation (*λ*), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2*θ* range, deg	3.5−50.0	3.7−50.0	2.9−50.0
μ, mm^{-1}	2.957	2.454	2.583
F(000)	3852	1708	2608
no. of obsd rflns	7273	5729	5735
no. of params refnd	562	415	588
goodness of fit	1.192	1.129	0.984
R1	0.085	0.051	0.053
wR2	0.204	0.140	0.110

$Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]\cdot THF$ (**2**; 0.293 g, 0.25 mmol) in THF (15 mL) by using procedures similar to those used in the synthesis of **13**: yield 0.42 g (64%). ^1H NMR (pyridine-d_5): *δ* 3.49 (s, 24H, DME), 3.26 (s, 36H, DME), 2.45 (s, 6H, CH_3), 1.92 (s, 6H, CH_3), 0.73 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (pyridine-d_5): *δ* 121.3, 117.0, 104.2 (C_5Me_4), 81.3 ($C_2B_{10}H_{10}$), 71.4, 58.0 (DME), 14.7, 11.3 (CH_3), 2.9 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): *δ* −1.63 (1), −3.18 (1), − 4.89 (3), −9.47 (5). IR (KBr, cm^{-1}): *ν* 2925 (s), 2560 (vs), 1452 (m), 1383 (m), 1250 (s), 1081 (s), 868 (s). Anal. Calcd for $C_{23}H_{53}B_{10}I_2Li_2O_5SiYb$ (**14**−3.5DME): C, 28.00; H, 5.42. Found: C, 27.94; H, 5.67.

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.[12] 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).[13a] Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. For the noncentrosymmetric structure, the appropriate enantiomorph was chosen by refining Flack's parameter *x* toward zero.[13b] Crystal data and details of data collection and structure refinements are given in Tables 1 and 2, respectively. Selected bond distances and angles are listed in Table 3. Further details are included in the Supporting Information.

Results and Discussion

Ligand. Treatment of $Me_2Si(C_5Me_4H)Cl$[11] with 1 equiv of $Li_2C_2B_{10}H_{10}$ in toluene/ether (2:1) at 0 °C gave, after recrystallization from an ether solution, the monoanionic salt $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Li(OEt_2)_{0.5}$ (**1**) in 82% yield. Like its cyclopentadienyl and indenyl analogues, hydrolysis of this compound with a saturated aqueous solution of NH_4Cl at −20 °C in THF afforded its neutral counterpart $Me_2Si(C_5Me_4H)(C_2B_{10}H_{11})$.[7] The hydrolysis must be done at low temperature; otherwise, the silicon−C(cage) bond would be broken, leading to a mixture of products. Reaction of **1** with an equimolar amount of *n*-BuLi gave, after recrystallization from a THF solution, the dianionic salt $[\{[(\mu\text{-}\eta^5)\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]\cdot THF$ (**2**). It is noted that the reaction between **1** and excess Na metal in THF was very slow and did not proceed to completion even under reflux temperature according to the ^{11}B NMR spectroscopic analyses; this behavior differs significantly from that of its cyclopentadienyl analogue.[3] These transformations are summarized in Scheme 1.

Compounds **1** and **2** are soluble in polar organic solvents such as THF, ether, and pyridine but insoluble in *n*-hexane. The ^{11}B NMR spectrum of **1** exhibits a 2:1:2 splitting pattern, while that of **2** shows a 4:6 splitting pattern. The ^1H NMR spectra support the ratio of 0.5 molecule of ether per carboranyl ligand for **1** and 3.5 THF molecules per carboranyl ligand for **2**. The ^1H NMR chemical shift of the CH vertex in **1** at 3.18 ppm is absent from the ^1H NMR spectrum of **2**, which also supports the formation of the dianionic salt. The IR spectra of compounds **1** and **2** show typical characteristic B−H absorptions at 2572 and 2532 cm^{-1}, respectively.

The solid-state structure of compound **2** was further confirmed by single-crystal X-ray analyses. It consists of well-separated, alternating layers of the discrete tetrahedral cations $[Li(THF)_4]^+$ and the complex anions $[\{[(\mu\text{-}\eta^5)\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li]^-$ and shows one THF of solvation. This complex anion is composed of two $\{[\eta^5\text{:}\ \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}^-$ units that are connected by a Li^+ cation via η^5 bonding (Figure 1). In each of these units, the Li^+ ion is η^5-bound to one tetramethylcyclopentadienyl ring and *σ*-bound to one cage carbon atom and to one oxygen

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

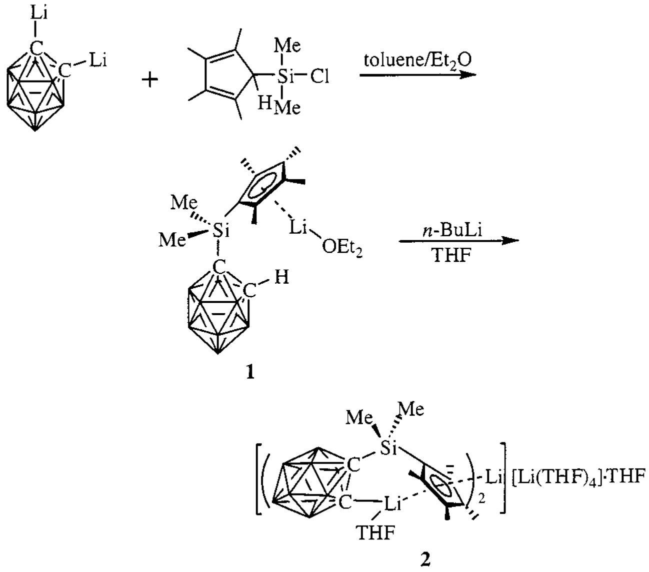
(13) (a) SHELXTL V 5.03 Program Package; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995. (b) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

Table 3. Average Bond Lengths (Å) and Angles (deg)[a]

	2	5	6	7	10	14
M^{n+}	Li^+	Sm^{3+}	Nd^{3+}	Yb^{3+}	Yb^{3+}	Yb^{2+}
M−C(C_5 ring)	2.332(8)	2.757(2)	2.775(3)	2.604(6)	2.609(3)	2.723(5)
M−C(σ)	2.140(7)				2.505(2)	2.531(4)
M−X(μ_2)		2.746(1)	2.710(1)	2.598(2)	2.666(1)	3.048(1)[b]
C(C_5 ring)-Si−C(cage)	109.20(2)	108.02(2)	107.32(2)		108.47(2)	112.2(2)
cent−M−C(cage)	128.1				107.8	107.4

[a] cent = the centroid of the cyclopentadienyl ring. [b] The distance of Yb−I(terminal).

Scheme 1



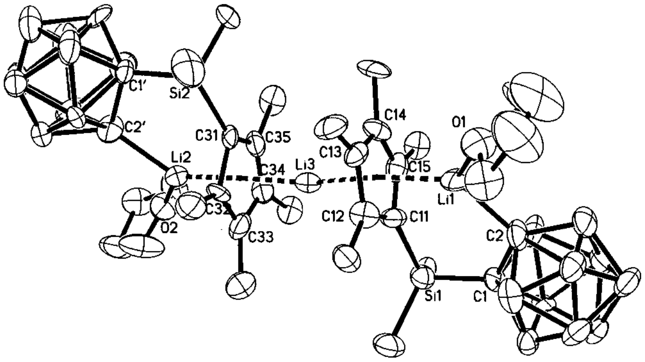


Figure 1. Molecular structure of the anion $[\{[(\mu\text{-}\eta^5):\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]\text{-}Li(THF)\}_2Li]^-$ in **2** (thermal ellipsoids drawn at the 35% probability level).

atom from the coordinated THF molecule in a distorted-trigonal arrangement. The two centroids of the cyclopentadienyl rings and three Li atoms (Li1, Li2, Li3) almost form a straight line. This is a very rare example of a lithium complex containing both full- and half-sandwich lithocene units. The average Li−C(cage carbon) distance of 2.140(7) Å is close to that of 2.176(8) Å in $(C_2B_{10}H_{10}Me)Li\{MeN(CH_2CH_2NMe_2)_2\}$.[14] The average Li−C($C_5$ ring) distance of 2.332(8) Å is comparable to that of 2.318(4) Å in $[(\eta^5\text{-}C_5H_5)_2Li][Ph_4P]$.[15]

Organolanthanide Compounds Derived from 1. Treatment of $LnCl_3$ with an equimolar amount of $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Li(OEt_2)_{0.5}$ (**1**) in THF at room temperature gave, after removal of the solvent, extraction with ether, and recrystallization from a THF/ether solution, organolanthanide compounds of the general formula $[\eta^5\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]LnCl_3Li(THF)_3$ (Ln = Nd (**3**), Sm (**4**)) in good yields. These compounds are soluble in polar organic solvents such as THF, ether, and pyridine, slightly soluble in toluene, and insoluble in n-hexane. They were characterized by various spectroscopic data and elemental analyses. The ^{11}B NMR spectrum of compound **3** exhibits a 3:3:3:1 splitting pattern, while that of compound **4** shows a 2:2:3:3 splitting pattern. Their ^1H NMR spectra support the ratio of three THF molecules per ligand. The IR spectra show a typical strong and broad characteristic B−H absorption at about 2580 cm^{-1}.

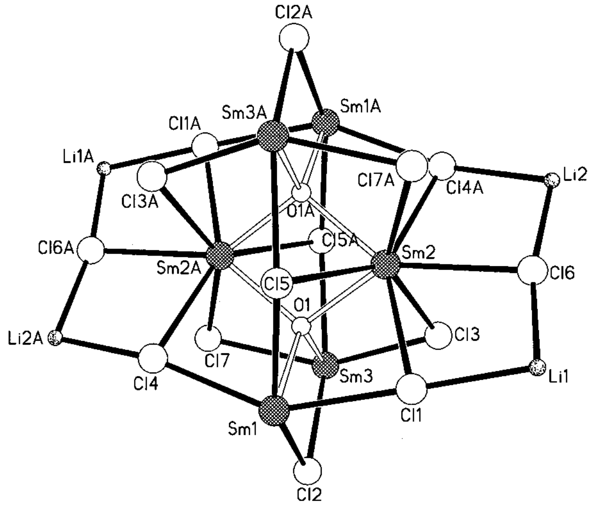


Figure 2. Core structure of **5**.

Recrystallization of **4** from a THF/Et_2O solution resulted in the isolation of some yellow crystals that were identified as $[\{[\eta^5\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]Sm\}_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_4Li(OEt_2)_2Li(THF)_2Sm(\mu_4\text{-}O)]_2$ (**5**) by spectroscopic data and X-ray analyses. They result from partial hydrolysis of **4** during the recrystallization process.

Compound **5** is a centrosymmetric cluster containing two μ_4-O units. Each of the two μ_4-O atoms coordinates to four Sm atoms in a tetrahedral geometry. These two tetrahedrons share one edge to form the core structure of the cluster (Figure 2). The arrangement of the eight atoms O_2Sm_6 in the core is very similar to that of diborane(6) (B_2H_6). Each of the two Sm atoms on the common edge coordinates to two μ_4-O atoms, four triply bridging μ_3-Cl atoms, and two doubly bridging μ_2-Cl atoms. Each of the other four Sm atoms is η^5-bound to one tetramethylcyclopentadienyl ring and σ-bound to one μ_4-O atom and coordinates to either three triply bridging μ_3-Cl atoms and one doubly bridging μ_2-Cl atom or three doubly bridging μ_2-Cl atoms and one triply

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(14) Clegg, W.; Brown, D. A.; Bryan, S. J.; Wade, K. *Polyhedron* **1984**, *3*, 307.

(15) Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744.

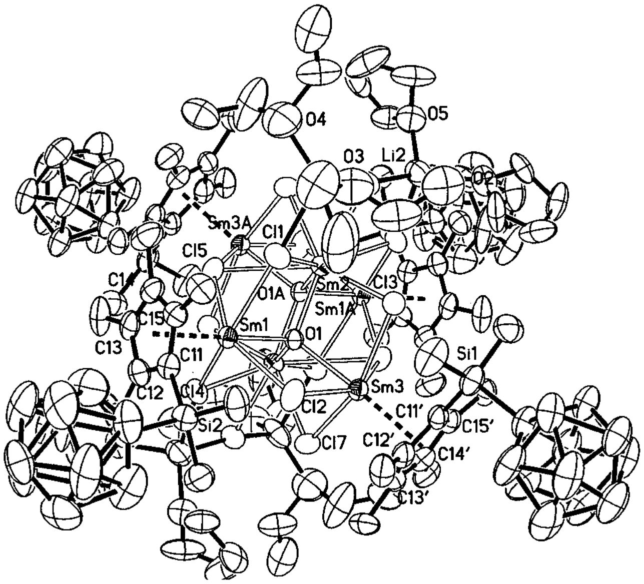

Figure 3. Molecular structure of $[\{[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}\}_2(\mu_2\text{-Cl})_3(\mu_3\text{-Cl})_4\text{Li}(\text{OEt}_2)_2\text{Li}(\text{THF})_2\text{Sm}(\mu_4\text{-O})]_2$ (**5**) (thermal ellipsoids drawn at the 35% probability level).

bridging μ_3-Cl atom in a distorted-octahedral geometry. Each of the four Li atoms coordinates to two triply bridging μ_3-Cl atoms and two O atoms to balance the charge, resulting in a neutral cluster (Figure 3). The average Sm−C(C_5 ring) distance of 2.757(2) Å is comparable to those normally observed in organosamarium compounds.[2] The average Sm−O(μ_4-O) distance of 2.346(1) Å is greater than the value of 2.211(8) Å found in $[\{\eta^5\text{-}(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_4\}\text{Sm}]_3[\{(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_4\text{Li}\}_3(\mu_3\text{-OMe})][\mu_2\text{-Li}(\text{THF})]_3(\mu_3\text{-O})$[16] and the 2.094 Å in $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}]_2(\mu_2\text{-O})$.[17] The average Sm−Cl($\mu_3$-Cl) distance of 2.880(1) Å is longer than the average Sm−Cl(μ_2-Cl) distance of 2.746(1) Å. These observations are all consistent with the decrease in the coordination number of O and Cl atoms.

$[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{NdCl}_3\text{Li}(\text{THF})_3$ (**3**) could further react with another 1 equiv of **1** in THF at room temperature to afford, after recrystallization from an ether solution, the bis-ligated compound $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)(\text{THF})$ (**6**). This compound could also be prepared by treatment of NdCl_3 with 2 equiv of **1** in THF at room temperature. Its ^{11}B NMR spectrum exhibits a 4:7:3:3:3 splitting pattern, which is quite different from that of **3** or **1**. The ^{1}H NMR spectrum supports the ratio of 0.5 THF and 0.5 ether molecule per ligand. Its IR spectrum shows a typical strong and broad characteristic B−H absorption at 2574 cm^{-1}.

The solid-state structure of **6** derived from single-crystal X-ray diffraction studies reveals that the Nd^{3+} ion is η^5-bound to each of two tetramethylcyclopentadienyl rings and σ-bound to two doubly bridging chlorine atoms in a distorted-tetrahedral arrangement (Figure 4). Such an arrangement around the lanthanide ion is typical for $\text{Cp}_2\text{Ln}(\mu\text{-Cl})_2\text{Li}(\text{S})_n$ type of compounds.[2] The two carborane cages stay away from each other, and there is no direct interaction between the cage and the Nd^{3+} ion. It is noted that the acidic C−H proton of the cage has only a very weak asymmetric interaction with the cyclopentadienyl ring through the C51 and C52 or C61 and C62 atoms, which differs significantly from that observed in the unsubstituted-cyclopentadienyl analogues.[3,4] The average Nd−C(C_5 ring) and Nd−Cl distances are 2.775(3) and 2.710(1) Å, respectively, which fall in a range normally observed for organoneodymium compounds.[2]

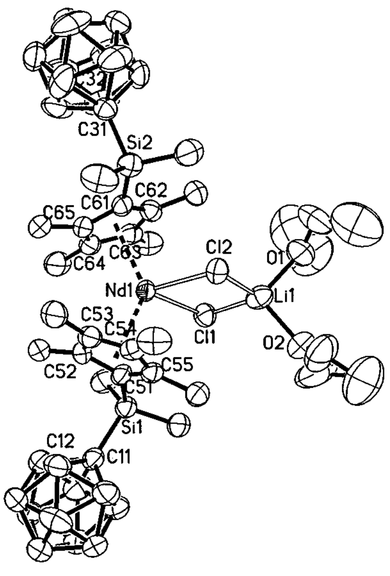

Figure 4. Molecular structure of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)(\text{THF})$ (**6**) (thermal ellipsoids drawn at the 35% probability level).

It has been reported that treatment of $\text{Me}_2\text{Si}(\text{C}_9\text{H}_7)(\text{C}_2\text{B}_{10}\text{H}_{11})$ with 4 equiv of NaNH_2 in THF led to the complete cleavage of the Si−C(cage) bond, which resulted in the isolation of new organolanthanide clusters after reaction with LnCl_3 in THF.[5c] However, treatment of $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Li}(\text{OEt}_2)_{0.5}$ (**1**) with 4 equiv of NaNH_2 in THF, followed by reaction with 1 equiv of YbCl_3, afforded the compound $(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Yb}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**7**), suggesting the cleavage of the Si−C(C_5Me_4) bond, a reactivity pattern that is significantly different from the one previously mentioned.

The solid-state structure of **7** derived from single-crystal X-ray analyses reveals that the Yb^{3+} ion is η^5-bound to each of two tetramethylcyclopentadienyl rings and σ-bound to two doubly bridging chlorine atoms in a distorted-tetrahedral arrangement (Figure 5). The average Yb−C(C_5 ring) distance of 2.604(6) Å and the average Yb−Cl(μ_2-Cl) distance of 2.598(2) Å are comparable to those reported in the literature.[2] All transformations discussed in this section are summarized in Scheme 2.

Organolanthanide Compounds Derived from 2. An equimolar reaction between NdCl_3 and **2** in THF gave, after recrystallization from a DME solution, the ionic compound $[\{\eta^5{:}\ \sigma\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}_2\text{Nd}][\text{Li}(\text{DME})_3]$ (**11**) in 53% yield. This compound is soluble in polar organic solvents such as THF, DME, and pyridine, slightly soluble in ether, and insoluble in *n*-hexane. The ^{11}B NMR spectrum of compound **11** exhibits a 3:3:2:2 splitting pattern. Its ^{1}H NMR spectrum supports the ratio of 1.5 DME molecules per ligand. The solid-state IR spectrum shows a typical strong and broad charac-

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(16) Hosmane, N. S.; Wang, Y.; Oki, A. R.; Zhang, H.; Maguire, J. A. *Organometallics* **1996**, *15*, 626.

(17) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405.

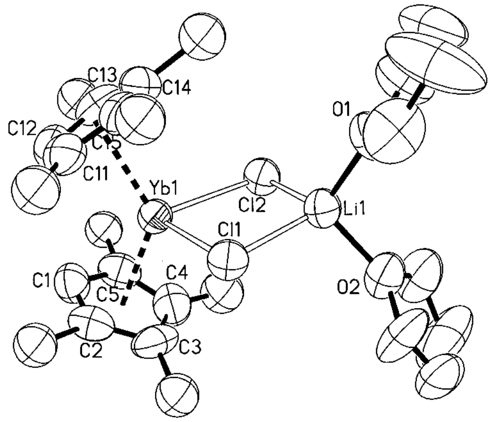
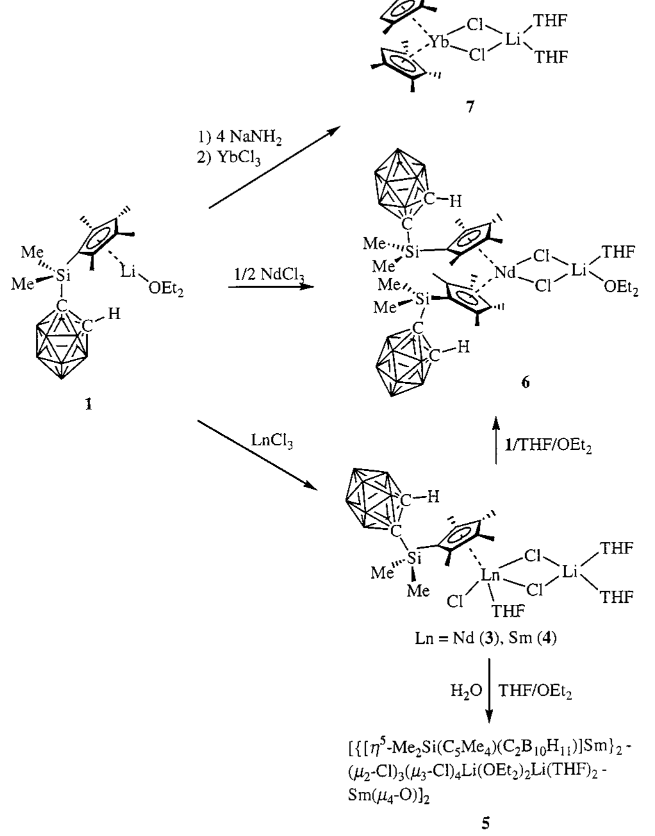


Figure 5. Molecular structure of (η^5-$C_5Me_4H)_2Yb(\mu$-$Cl)_2Li(THF)_2$ (**7**) (thermal ellipsoids drawn at the 35% probability level).

Scheme 2



teristic B−H absorption at 2564 cm^{-1}. The elemental analyses indicate that this compound does not contain any chlorine atom. It is likely that this compound would have a structure which is similar to $[\{\eta^5\text{:}\ \sigma\text{-}Me_2A(C_5H_4)(C_2B_{10}H_{10})\}_2Ln][Li(S)_n]$ (A = Si,[3] C[4]).

Treatment of $LnCl_3$ with 0.5 equiv of **2** in THF gave, after recrystallization from a THF or DME solution, organolanthanide compounds of the general formula $[\{\eta^5\text{:}\ \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}LnCl(\mu\text{-}Cl)]_2[Li(S)_n]_2$ (S = THF, $n = 4$, Ln = Sm (**8**), Y (**9**); S = DME, $n = 3$, Ln = Yb (**10**)) in good yields. This result differs significantly from our previous work, in which treatment of $LnCl_3$ with $[Me_2A(C_5H_4)(C_2B_{10}H_{10})]^{2-}$ or $[Me_2A(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ (A = Si, C) always afforded $[\{\eta^5\text{:}\ \sigma\text{-}Me_2A(C_5H_4)(C_2B_{10}H_{10})\}_2Ln]^-$ or $[\{\eta^5\text{:}\ \sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})\}_2Ln]^-$ regardless of the molar ratios of the reactants.[3−6] It is clear that the present ligand bearing a bulky tetramethylcyclopentadienyl group can effectively prevent the ligand redistribution reactions. The resulting half-sandwich lanthanocene chloride compounds are important intermediates for the preparation of Ln−C- and Ln−heteroatom-containing organolanthanide compounds.[2]

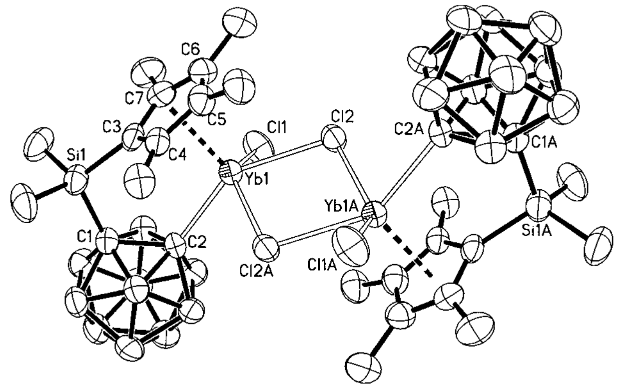


Figure 6. Molecular structure of the anion $[\{\eta^5\text{:}\ \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}YbCl(\mu\text{-}Cl)]_2^{2-}$ in **10** (thermal ellipsoids drawn at the 35% probability level).

These compounds were fully characterized by various spectroscopic data and elemental analyses. The solid-state structure of **10** was further confirmed by X-ray analyses. It consists of well-separated, alternating layers of the discrete octahedral cations $[Li(DME)_3]^+$ and anions $[\{\eta^5\text{:}\ \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}YbCl(\mu\text{-}Cl)]_2^{2-}$. In the centrosymmetric anion, each Yb^{3+} ion is η^5-bound to one tetramethylcyclopentadienyl ring and σ-bound to one cage carbon atom, one terminal Cl atom, and two doubly bridging Cl atoms in a distorted-square-pyramidal arrangement (Figure 6). The formal coordination number for each Yb atom is 7. **10** represents one of the very rare structurally characterized examples of organolanthanide compounds bearing both Ln−C π and σ bonds and Ln−Cl bonds.[2]

The average Yb−C(C_5 ring) distance of 2.609(3) Å and Yb−C(σ) distance of 2.505(2) Å are very close to the values found in $[\{\eta^5\text{:}\ \sigma\text{-}Me_2A(C_5H_4)(C_2B_{10}H_{10})\}_2Yb]^-$ [3,4] and $[\{\eta^5\text{:}\ \sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]^-$ (A = Si, C).[5,6] The average Yb−Cl(μ_2-Cl) distance of 2.666(1) Å is longer than the Yb−Cl(terminal) distance of 2.522(1) Å because of the difference in the coordination number of Cl atoms. These measured values are comparable to the corresponding values reported in the literature.[2]

The chlorine atoms in these lanthanocene chlorides can be replaced by other groups via metathesis reactions. In fact, treatment of **9** with 2 equiv of $NaN(SiMe_3)_2$ in toluene/THF gave the corresponding amido complex $[\eta^5\text{:}\ \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]YN(SiMe_3)_2$ (**12**). The spectroscopic data and elemental analyses all support the fact that **12** is an unsolvated compound, which may indicate the presence of interactions between the electron-deficient metal center and the electron-donating property of the Si−C bond. This phenomenon is often observed in $Cp_2LnE(SiMe_3)_2$ (E = CH, N) types of compounds.[18]

Treatment of LnI_2 with 0.5 equiv of $[\{[(\mu\text{-}\eta^5)\text{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Li(THF)\}_2Li][Li(THF)_4]\cdot THF$ (**2**) in

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[18] (a) Qian, C.; Nie, W.; Sun, J. *Organometallics* **2000**, *19*, 4134. (b) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 108. (c) Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 3195.

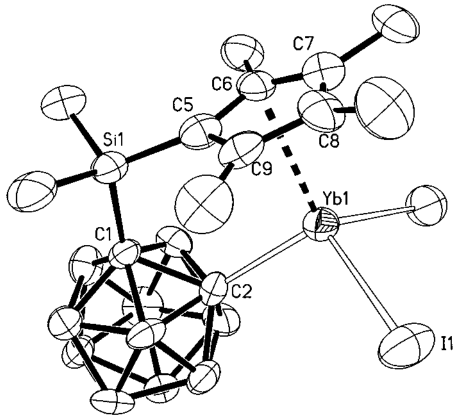
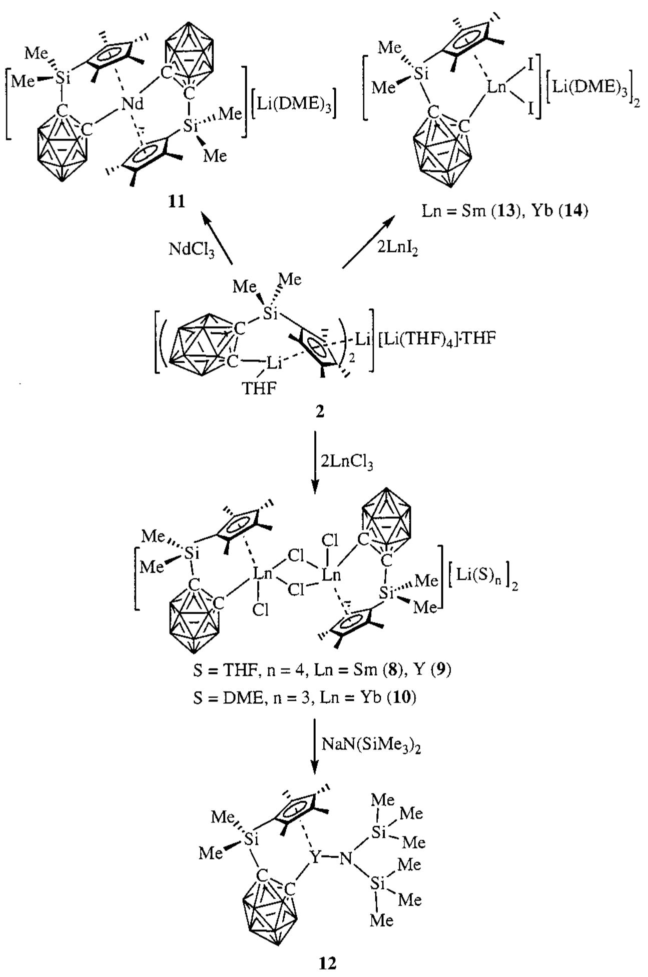


Figure 7. Molecular structure of the anion $[\{\eta^5\!: \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}YbI_2]^{2-}$ in **14** (thermal ellipsoids drawn at the 35% probability level).

THF gave, after recrystallization from a DME solution, organolanthanide compounds of the general formula $[\{\eta^5\!: \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}LnI_2][Li(DME)_3]_2$ (Ln = Sm (**13**), Yb (**14**)) in good yields. **13** and **14** were isolated as green and red crystals, respectively. They are soluble in polar organic solvents such as THF, DME, and pyridine and insoluble in toluene and *n*-hexane. They were characterized by various spectroscopic data and elemental analyses. Their ^1H NMR spectra support the ratio of six DME molecules per ligand. Compound **14** was further confirmed by X-ray analyses.

The solid-state structure of **14** consists of well-separated, alternating layers of the discrete octahedral cations $[Li(DME)]_3^+$ and anions $[\{\eta^5\!: \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}YbI_2]^{2-}$, which is comparable to the packing in the seven-coordinate $[\eta^5\!: \sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Yb(THF)_3$[5a] and eight-coordinate $[\eta^5\!: \sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$.[6] In the anion, the Yb^{2+} ion is η^5-bound to the tetramethylcyclopentadienyl ring and σ-bound to two iodo ligands and one cage carbon atom in a distorted-tetrahedral geometry (Figure 7). The coordination environment of the Yb^{2+} is similar to that of Ti^{4+} in $[\eta^5\!: \sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]TiCl_2$.[7b] The average Yb−C($C_5$ ring) distance of 2.723(5) Å and the Yb−C(σ) distance of 2.531(4) Å are comparable to the corresponding values found in $[\eta^5\!: \sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Yb(THF)_3$ (2.750(3) and 2.584(3) Å)[5a] and $[\eta^5\!: \sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$ (2.789(8) and 2.561(6) Å).[6] The average Yb−I distance of 3.048(1) Å is comparable to the 3.103(1) Å in $YbI_2(THF)_4$[19] and the 3.155(1) Å in $[(\eta^5\text{-}C_5Me_5)Yb(\mu\text{-}I)(THF)_2]_2$.[20] The differences in the above-mentioned bond distances are due to the differences in the coordination number of the Yb^{2+} ion. It is noted that $[Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]^{2-}$ and $[Me_2A(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ (A = Si, C)[5,6] resulted in the formation of different types of organolanthanide(II) compounds, although the reaction conditions used in the preparation are the same, which suggests the effect of the cyclopentadienyl ring substituents on the formation and reactivity of organometallic compounds. All reactions discussed in this section are summarized in Scheme 3.

Scheme 3



Conclusion

When a change is made from C_5H_4 to C_5Me_4, $[Me_2Si(C_5H_4)(C_2B_{10}H_{11})]^-$ and $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]^-$ exhibit different reactivity patterns. For example, reaction of $[Me_2Si(C_5Me_4)(C_2B_{10}H_{11})]^-$ with excess Na metal is very slow and does not proceed to completion even under reflux temperature. The tetramethylcyclopentadienyl analogue can effectively prevent lanthanocene chlorides from ligand redistribution reactions, which offers important intermediates for the preparation of organolanthanide compounds containing the Ln−C or Ln−X (X = heteroatom) bonds. This sterically demanding ligand can also stabilize organosamarium(II) and coordinatively unsaturated compounds. The present work shows that this ligand can decrease the coordination number of the central metal ions by 2 units.

Acknowledgment. The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administration Region (Project No. CUHK 4210/99P).

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 compounds **2**, **5**−**7**, **10**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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