

Synthesis, Reactivity, and Structural Characterization of Organolanthanide Compounds Incorporating both Cyclopentadienyl and Carboranyl Groups

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Reaction of $\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)\text{Cl}$ with 1 equiv of $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ in toluene/ether at 0 °C, after hydrolysis, gave $\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)(\text{C}_2\text{B}_{10}\text{H}_{11})$ (**1**) in 79% isolated yield. **1** can be conveniently converted into the monoanion $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Na}$ (**2**), the dianion $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Li}_2$ (**3**), and the trianion $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{K}_3$ (**4**) by treatment with NaH, MeLi, and K metal in THF at room temperature, respectively. **2** reacted with 1 equiv of LnCl_3 in THF to give $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{LnCl}_2(\text{THF})_3$ ($\text{Ln} = \text{Nd}$ (**5**), Sm (**6**), Er (**7**), Yb (**8**)) in good yield. Treatment of LnCl_3 with 2 equiv of **2** or reaction of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{LnCl}_2(\text{THF})_3$ with an equimolar amount of **2** in THF resulted in the isolation of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{LnCl}(\text{THF})_2$ ($\text{Ln} = \text{Nd}$ (**9**), Sm (**10**), Y (**11**), Gd (**12**), Yb (**13**)) in good yield. Interaction of **3** with LnCl_3 in THF in a molar ratio of 1:1 or 2:1 or reaction of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{LnCl}(\text{THF})_2$ with 2 equiv of MeLi in THF gave the same compounds $[\{\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}_2\text{Ln}][\text{Li}(\text{THF})_4]$ ($\text{Ln} = \text{Nd}$ (**14**), Y (**15**), Er (**16**), Yb (**17**)). Treatment of NdCl_3 with an equimolar amount of **4** in THF or reaction of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{NdCl}_2(\text{THF})_3$ with excess K metal in THF produced $[\eta^5\text{-}\eta^6\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Nd}(\text{THF})_2$ (**18**). Under similar reaction conditions, however, interaction of LnCl_3 ($\text{Ln} = \text{Sm}, \text{Yb}$) with **4** in THF afforded the organolanthanide(II) compounds $\{[\eta^5\text{-}\eta^6\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Ln}^{\text{II}}(\text{THF})_2\}\{\text{K}(\text{THF})_2\}$ ($\text{Ln} = \text{Sm}$ (**20**), Yb (**21**)). The Sm analogue of **18**, $[\eta^5\text{-}\eta^6\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}(\text{THF})_2$ (**19**), was prepared from an unprecedented redox reaction of SmI_2 with 2 equiv of **2** in THF. Reaction of **19** with excess K metal in THF gave **20**. Unlike the SmI_2 case, interaction of YbI_2 with 2 equiv of **2** in THF gave $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{Yb}^{\text{II}}(\text{THF})_2$ (**22**). All of these compounds were characterized by various spectroscopic and elemental analyses. The solid-state structures of compounds **5**, **8**, **9**, **10**, **14**, **15**, **16**, **17**, **19**, and **22** were confirmed by single-crystal X-ray analyses. The reaction mechanism of the formation of **19** is also proposed.

Introduction

It has been documented that organolanthanide compounds are active catalysts for olefin transformations such as hydrogenation,¹ oligomerization/polymerization,² hydroamination,³ hydrosilylation,⁴ hydroboration,⁵ and reductive cyclization.⁶ To make these processes more effective, selective, and smooth, it is essential to

develop new catalysts. Although many factors will influence the performance of the catalysts, the ligand is probably the most critical one, since it controls the molecular geometry of the catalysts, which in turn affect the olefin transformations. The recently developed "constrained geometry" ligand exemplifies the importance of the ligands in olefin transformations.⁷ In view of the organolanthanide catalysts, the most popular π ligands used are cyclopentadienyl and its derivatives, in particular, C_5Me_5^- and $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2^{2-}$.^{1–6} As the isolobal analogues to the cyclopentadienyl group, C_2B_9 ,⁸ C_2B_{10} ,⁹ and C_2B_4 ¹⁰ ligand systems have recently been introduced into lanthanide chemistry, resulting in a new

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class of organolanthanide compounds. Due to the unique properties of the carborane molecules, the bondings between metal and carboranyl ligands can be varied from $2e-3c$ σ bonds to η^5 or η^6 π bonds, depending on the sizes of the bonding faces and the substituents on the bonding faces. It is rational to propose that a molecule bearing both cyclopentadienyl and carboranyl groups may have the advantages of these two units and the bridged ligands. By coupling the molecules of $C_2B_{10}H_{12}$ and cyclopentadiene, we have successfully prepared a new bridged ligand, $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$. Preliminary results have shown that it is a very versatile ligand which can offer organolanthanide compounds with some unique properties.¹¹ We now report the detailed accounts of our work on the synthesis, reactivity, and structural characterization of organolanthanide compounds with this very versatile ligand.

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.¹² $LnI_2(THF)_x$ ($Ln = Sm, Yb$),^{13a} $[(Me_3Si)_2C_5H_3]_2Sm(THF)_2$,^{13b} $(C_6H_5CH_2)_2C_2B_{10}H_{10}$,^{8c} and $Li_2C_2B_{10}H_{10}$ ¹⁴ were prepared according to the literature methods. All other

chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Melting points (decomposition points) were determined in sealed capillaries without correction. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Nicolet Magna 550 Fourier transform spectrometer. MS spectra were recorded on a Bruker APEX FTMS spectrometer. 1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker ARX-500 spectrometer at 160.46 MHz. All chemical shifts are reported in δ units with reference to internal or external TMS (0.00 ppm) or with respect to the residual protons of the deuterated solvent for proton and carbon chemical shifts and to external $BF_3 \cdot OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd, Brunel University, Middlesex, U.K.

Preparation of $Me_2Si(C_5H_5)Cl$. This compound was prepared in an analogous manner to $Me_2Si(C_5Me_4H)Cl$.¹⁵ To a suspension of Na sand (11.5 g, 0.50 mol) in THF (200 mL) was slowly added freshly distilled cyclopentadiene at 0 °C until the Na disappeared from the solution. After the solvent and excess cyclopentadiene were completely removed under vacuum, the white solid was washed with *n*-hexane three times. To a suspension of $(C_5H_5)Na$ in a mixture of solvents (200 mL) of *n*-hexane/ Et_2O (2:1) was added Me_2SiCl_2 (193.5 g, 1.50 mol) at 0 °C in one portion, and the mixture was stirred at room temperature for 20 h. The precipitate was filtered off. Fractional distillation at 134–136 °C/760 Torr gave the compound $Me_2Si(C_5H_5)Cl$ as a colorless liquid (30.0 g, 38%). 1H NMR ($CDCl_3$): δ 6.70–6.55 (m, 4H, vinyl), 3.16 (s, 1H, methine), 0.27 (s, 6H, CH_3).

Preparation of $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$ (1). To a solution of *o*- $C_2B_{10}H_{12}$ (4.0 g, 27.8 mmol) in a dry toluene/diethyl ether (2:1) mixture at 0 °C was added a 1.60 M solution of *n*-BuLi in hexane (34.7 mL, 55.5 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 cyclopentadienyldimethylsilyl chloride ($Me_2Si(C_5H_5)Cl$; 4.50 g, 28.5 mmol) in a toluene/diethyl ether (2:1) mixture was slowly added dropwise. The mixture was refluxed overnight and then quenched with 50 mL of water, transferred to the separatory funnel, and diluted with 100 mL of diethyl ether. The organic layer was separated, and the aqueous layer was extracted with additional Et_2O (3 \times 30 mL). The combined ether solutions were dried over anhydrous $MgSO_4$ and concentrated to give a crude product which was purified by column chromatography using silica gel (hexane as eluent) to yield a colorless solid (5.80 g, 79% based on the consumed *o*-carborane), mp 74–75 °C. The unreacted *o*-carborane (0.62 g, 4.3 mmol) was recovered by sublimation at 70–80 °C/0.1 Torr. 1H NMR ($CDCl_3$): δ 6.91–6.54 (m, 4H, vinyl), 3.46 (s, 1H, methine), 2.99 (m, 1H, CH of carboranyl), 0.34 (s, 6H, CH_3). ^{11}B NMR ($CDCl_3$): δ -7.4 (1), -8.9 (1), -13.9 (2), -18.1 (2), -19.2 (2), -20.6 (2). IR (cm^{-1}): ν 3060 (w), 2968 (w), 2597 (vs), 1258 (m), 1072 (m), 807 (s). High-resolution MS (FAB): m/z calcd 266.2479, found 266.2480.

Preparation of $[\eta^5-Me_2Si(C_5H_4)(C_2B_{10}H_{11})]NdCl_2(THF)_3$ (5). To a suspension of NaH (85.0 mg, 3.55 mmol) in 30 mL of THF was slowly added a solution of $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$ (1; 0.266 g, 1.00 mmol) in THF (20 mL), and the mixture was stirred at room temperature for 10 h. After removal of excess amounts of NaH, the resulting clear solution ($[Me_2Si(C_5H_4)(C_2B_{10}H_{11})]Na$ (2); ^{11}B NMR (THF) δ -4.8 (1), -5.5 (1), -9.3 (2), -12.0 (2), -14.2 (2), -15.1 (2)) was slowly added to a suspension of $NdCl_3$ (0.250 g, 1.0 mmol) in 10 mL of THF at room temperature. The mixture was then stirred for another 12 h at room temperature. The precipitate was filtered off, and the clear blue solution was concentrated under vacuum to

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about 10 mL. After addition of a few drops of *n*-hexane into the above solution, blue crystals were obtained when this solution was allowed to stand at room temperature for several days (0.43 g, 62%), mp 87 °C dec. ¹H NMR (pyridine-*d*₅): δ 4.50 (s, 1H, CH of carboranyl), 3.46 (m, 12H, THF), 1.41 (m, 12H, THF), 0.10 (s, 6H, CH₃). ¹¹B NMR (pyridine-*d*₅): δ -10.1 (2), -16.6 (2), -20.7 (4), -21.6 (2). IR (cm⁻¹): ν 3066 (w), 3045 (m), 2972 (s), 2885 (s), 2590 (br, vs), 1384 (m), 1257 (m), 1041 (vs), 861 (s), 813 (s), 775 (s). Anal. Calcd for C₁₃H₂₉B₁₀Cl₂NdOSi (5-2THF): C, 28.25; H, 5.29. Found: C, 27.91; H, 5.52.

Preparation of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]SmCl₂(THF)₃ (6). To a suspension of SmCl₃ (0.256 g, 1.0 mmol) in THF (15 mL) was slowly added a THF solution of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2; 1.0 mmol) at room temperature, followed by procedures similar to those used in the synthesis of 5, affording 6 as a yellow crystalline solid (0.44 g, 62%), mp 86 °C dec. ¹H NMR (pyridine-*d*₅): δ 4.65 (s, 1H, CH of carboranyl), 3.48 (m, 12H, THF), 1.40 (m, 12H, THF), 0.25 (s, 6H, CH₃). ¹¹B NMR (pyridine-*d*₅): δ -10.5 (2), -16.9 (2), -20.6 (4), -22.0 (2). IR (cm⁻¹): ν 3075 (w), 3046 (m), 2978 (s), 2889 (s), 2593 (br, vs), 1385 (m), 1258 (m), 1046 (vs), 862 (s), 815 (s), 779 (s). Anal. Calcd for C₂₁H₄₅B₁₀Cl₂O₃SiSm: C, 35.88; H, 6.45; Sm, 21.39. Found: C, 35.31; H, 5.83; Sm, 21.00.

Preparation of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]ErCl₂(THF)₃ (7). To a suspension of ErCl₃ (0.137 g, 0.50 mmol) in THF (15 mL) was slowly added a THF solution of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2; 0.50 mmol) at room temperature, followed by procedures similar to those used in the synthesis of 5, affording 7 as a pink crystalline solid (0.24 g, 65%), mp 94–95 °C. ¹H NMR (pyridine-*d*₅): many broad, unresolved resonances. Hydrolysis of 7 in pyridine-*d*₅ with a slight molar excess of H₂O and subsequent examination by NMR methods showed the ratio of three THF molecules per ligand. ¹¹B NMR (pyridine-*d*₅): δ -14.0 (2), -16.9 (2), -22.8 (2), -29.1 (2), -32.9 (2). IR (cm⁻¹): ν 3066 (w), 3044 (m), 2976 (s), 2565 (br, vs), 1448 (m), 1256 (m), 1248 (s), 1188 (m), 1073 (s), 1030 (s), 870 (s), 782 (s), 722 (m), 675 (m), 442 (s). Anal. Calcd for C₁₉H₄₁B₁₀Cl₂ErO_{2.5}Si (7-0.5THF): C, 33.36; H, 6.04. Found: C, 33.72; H, 6.22.

Preparation of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]YbCl₂(THF)₃ (8). To a suspension of YbCl₃ (0.140 g, 0.5 mmol) in THF (15 mL) was slowly added a THF solution of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2; 0.5 mmol) at room temperature, followed by procedures similar to those used in the synthesis of 5, affording 8 as orange-yellow crystals (0.26 g, 72%), mp 109–110 °C. ¹H NMR (pyridine-*d*₅): δ 6.57 (m, 2H, C₅H₄), 6.46 (m, 2H, C₅H₄), 4.81 (s, 1H, CH of carboranyl), 3.51 (m, 12H, THF), 1.40 (m, 12H, THF), 0.46 (s, 6H, CH₃). ¹¹B NMR (pyridine-*d*₅): δ -13.8 (2), -19.3 (2), -24.7 (2), -27.0 (2), -30.2 (2). IR (cm⁻¹): ν 3069 (w), 3044 (m), 2980 (s), 2590 (br, vs), 2565 (s), 1454 (m), 1248 (s), 1030 (s), 1012 (m), 862 (s), 813 (m), 783 (s), 442 (m). Anal. Calcd for C₂₁H₄₅B₁₀Cl₂O₃SiYb: C, 33.46; H, 6.02. Found: C, 33.50; H, 6.06.

Preparation of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]₂NdCl(THF)₂ (9). To a suspension of NdCl₃ (0.125 g, 0.50 mmol) in 10 mL of THF was slowly added a THF solution of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2; 1.00 mmol). The mixture was then stirred for another 12 h at room temperature. The precipitate was filtered off, and the clear blue solution was concentrated under vacuum to about 10 mL. After addition of toluene (10 mL) to the above solution, blue crystals were obtained when this solution was allowed to stand at room temperature for several days (0.34 g, 78%), mp 174 °C dec. ¹H NMR (pyridine-*d*₅): δ 6.38–6.20 (m, 8H, C₅H₄), 4.76 (s, 2H, CH of carboranyl), 3.43 (m, 8H, THF), 1.40 (m, 8H, THF), 0.11 (br, 12H, CH₃). ¹¹B NMR (pyridine-*d*₅): δ -3.6 (4), -10.0 (4), -14.1 (8), -15.0 (4). IR (cm⁻¹): ν 3049 (w), 2963 (m), 2875 (m), 2591 (br, vs), 1384 (w), 1257 (m), 1073 (s), 1043 (s), 873 (m), 808 (s). Anal. Calcd for C₂₂H₅₀B₂₀ClNdOSi₂ (9-THF): C, 33.76; H, 6.44. Found: C, 33.54; H, 6.52.

Reaction of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]NdCl₂(THF)₃ (5) with 1 equiv of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2) in THF at room temperature gave 9 as blue crystals in 80% yield.

Preparation of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]₂SmCl(THF)₂ (10). To a suspension of SmCl₃ (0.128 g, 0.5 mmol) in 10 mL of THF was added dropwise a THF solution of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2; 1.0 mmol) at room temperature, followed by procedures similar to those used in the synthesis of 9, affording 10 as yellow crystals (0.32 g, 74%), mp 185 °C dec. ¹H NMR (pyridine-*d*₅): δ 9.20 (br, 2H, C₅H₄), 8.82 (br, 2H, C₅H₄), 7.72 (br, 2H, C₅H₄), 7.58 (br, 2H, C₅H₄), 4.74 (s, 2H, CH of carboranyl), 3.48 (m, 8H, THF), 1.45 (m, 8H, THF), 0.52 (s, 6H, CH₃), 0.36 (s, 6H, CH₃). ¹¹B NMR (pyridine-*d*₅): δ -3.6 (4), -10.0 (4), -14.1 (8), -15.0 (4). IR (cm⁻¹): ν 3049 (m), 2964 (m), 2588 (br, vs), 1255 (s), 1073 (m), 1043 (s), 1030 (s), 878 (m), 808 (s), 446 (m). Anal. Calcd for C₂₆H₅₈B₂₀ClO₂Si₂Sm: C, 36.27; H, 6.79. Found: C, 36.08; H, 6.80.

Compound 10 can also be prepared in 76% yield by an equimolar reaction of 6 with [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2) in THF at room temperature.

Preparation of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]₂YCl(THF)₂ (11). This compound was prepared as colorless crystals from YCl₃ (0.195 g, 1.0 mmol) and [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2; 23.0 mL, 2.00 mmol) in 15 mL of THF using procedures used above for 10: yield 0.53 g (81%); mp 182 °C dec. ¹H NMR (pyridine-*d*₅): δ 6.67–6.61 (m, 8H, C₅H₄), 3.44 (m, 8H, THF), 2.98 (s, 2H, CH of carboranyl), 1.43 (m, 8H, THF), 0.33 (s, 12H, CH₃). ¹³C NMR (pyridine-*d*₅): δ 121.39, 118.97, 111.86 (C₅H₄), 68.20, 26.17 (OC₄H₈), 62.85, 57.42 (C₂B₁₀), 1.93 (CH₃). ¹¹B NMR (pyridine-*d*₅): δ -9.1 (4), -14.0 (4), -18.0 (8), -20.2 (4). IR (cm⁻¹): ν 3049 (m), 2962 (m), 2891 (m), 2588 (br, vs), 1384 (m), 1256 (s), 1043 (s), 1030 (s), 873 (m), 808 (s), 792 (s), 446 (m). Anal. Calcd for C₁₈H₄₂B₂₀ClSi₂Y (11-2THF): C, 32.99; H, 6.46. Found: C, 33.22; H, 6.72.

Preparation of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]₂GdCl(THF)₂ (12). This compound was prepared as colorless crystals from GdCl₃ (0.132 g, 0.5 mmol) and [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2; 1.00 mmol) in 25 mL of THF using procedures used above for 10: yield 0.31 g (71%); mp 188 °C dec. ¹H NMR (pyridine-*d*₅): many broad, unresolved resonances. ¹¹B NMR (pyridine-*d*₅): δ -3.2 (4), -8.2 (4), -9.7 (4), -13.7 (4), -14.7 (4). IR (cm⁻¹): ν 3054 (m), 2961 (m), 2574 (br, vs), 1384 (m), 1257 (s), 1185 (m), 1072 (m), 1042 (s), 807 (s), 789 (m), 441 (m). Anal. Calcd for C₂₆H₅₈B₂₀ClGdO₂Si₂: C, 35.98; H, 6.74. Found: C, 35.65; H, 6.56.

Preparation of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]₂YbCl(THF)₂ (13). This compound was prepared as orange-yellow crystals from YbCl₃ (0.140 g, 0.50 mmol) and [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2; 11.5 mL, 1.00 mmol) in 15 mL of THF using procedures used above for 10: yield 0.35 g (85%); mp 178–180 °C. ¹H NMR (pyridine-*d*₅): δ 6.80–6.42 (m, 8H, C₅H₄), 4.61 (s, 2H, CH of carboranyl), 3.37 (m, 4H, THF), 1.30 (m, 4H, THF), 0.53 (br, 12H, CH₃). ¹¹B NMR (pyridine-*d*₅): δ -3.2 (4), -9.6 (4), -13.7 (8), -14.7 (4). IR (cm⁻¹): ν 3054 (m), 2961 (m), 2898 (m), 2573 (br, vs), 1384 (m), 1258 (s), 1185 (m), 1042 (s), 832 (m), 805 (m), 442 (m). Anal. Calcd for C₂₂H₅₀B₂₀ClOSi₂Yb (13-THF): C, 32.56; H, 6.21. Found: C, 32.98; H, 6.35.

Compound 13 can also be prepared in 80% yield by an equimolar reaction of 8 with [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (2) in THF at room temperature.

Preparation of [η⁵-σ-Me₂Si(C₅H₄)(C₂B₁₀H₁₀)]₂Nd][Li(THF)₄] (14). To a THF solution of Me₂Si(C₅H₅)(C₂B₁₀H₁₁) (1; 0.266 g, 1.0 mmol) was added MeLi (1.33 mL, 2.0 mmol) dropwise at 0 °C, and the mixture was stirred for 4 h. The resulting clear solution ([Me₂Si(C₅H₄)(C₂B₁₀H₁₀)]Li₂ (3); ¹¹B NMR (THF) δ -0.74 (2), -3.45 (2), -6.70 (4), -8.42 (2)) was slowly added to a suspension of NdCl₃ (0.125 g, 0.5 mmol) in 10 mL of THF. The reaction mixture was then stirred overnight at room temperature. After removal of the precipitates and addition of 20 mL of toluene, the clear solution was concentrated until the LiCl precipitated out. The precipitate

was filtered off, and the resulting clear blue solution was further concentrated to about 10 mL. Blue crystals were obtained when the saturated solution was allowed to stand at room temperature for 1 week (0.31 g, 64%), mp 167 °C dec. ¹H NMR (pyridine-*d*₅): δ 5.22 (m, 8H, C₅H₄), 3.60 (m, 16H, THF), 1.54 (m, 16H, THF), 0.76 (br, 12H, CH₃). ¹¹B NMR (pyridine-*d*₅): δ -3.4 (4), -10.1 (4), -13.8 (4), -16.3 (2), -21.6 (2), -32.6 (2), -36.9 (2). IR (cm⁻¹): ν 3073 (w), 2986 (s), 2883 (m), 2564 (br, vs), 1252 (m), 1184 (m), 1085 (m), 1043 (s), 889 (m), 832 (s), 807 (s), 779 (s). Anal. Calcd for C₃₀H₆₄B₂₀LiNdO₃Si₂ (**14**-THF): C, 40.20; H, 7.20. Found: C, 39.91; H, 7.12.

This compound can also be prepared from an equimolar reaction of NdCl₃ with [Me₂Si(C₅H₄)(C₂B₁₀H₁₀)]Li₂ (**3**) in THF at room temperature in 56% yield.

Alternate Method. To a THF (15 mL) solution of compound **9** (0.143 g, 0.17 mmol) was added MeLi (0.24 mL, 0.34 mmol) dropwise at 0 °C. This mixture was stirred at 0 °C for 4 h and then at room temperature overnight, followed by procedures similar to those used above, affording blue crystals identified as **14** (0.12 g, 70%).

Preparation of [η⁵:σ-Me₂Si(C₅H₄)(C₂B₁₀H₁₀)]₂Y][Li(THF)₄] (15**).** To a suspension of YCl₃ (0.098 g, 0.5 mmol) in THF (10 mL) was added dropwise a THF solution of [Me₂Si(C₅H₄)(C₂B₁₀H₁₀)]Li₂ (**3**; 1.0 mmol), followed by procedures similar to those used in the synthesis of **14**, affording **15** as colorless crystals (0.29 g, 63%), mp 183–184 °C. ¹H NMR (pyridine-*d*₅): δ 6.43–6.05 (m, 8H, C₅H₄), 3.42 (m, 16H, THF), 1.38 (m, 16H, THF), 0.25 (s, 12H, CH₃). ¹³C NMR (pyridine-*d*₅): δ 120.91, 116.20, 110.84 (C₅H₄), 81.07, 65.80 (C₂B₁₀), 67.66, 25.64 (OC₄H₈), -1.31 (CH₃). ¹¹B NMR (pyridine-*d*₅): δ 0.1 (2), -0.6 (2), -3.6 (6), -10.0 (2), -14.1 (6), -15.1 (2). IR (cm⁻¹): ν 3079 (w), 2979 (s), 2960 (s), 2883 (s), 2571 (br, vs), 1447 (m), 1367 (m), 1252 (s), 1186 (s), 1087 (s), 1046 (s), 887 (s), 833 (s), 808 (vs), 779 (s), 676 (m), 447 (m). Anal. Calcd for C₂₄H₄₈B₂₀-LiOSi₂Y (**15**-3THF): C, 37.92; H, 6.94. Found: C, 38.00; H, 6.83.

Reaction of YCl₃ with [Me₂Si(C₅H₄)(C₂B₁₀H₁₀)]Li₂ in THF at a molar ratio of 1:1 also gave compound **15** in 56% yield.

Alternate Method. To a colorless THF (15 mL) solution of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]₂YCl(THF)₂ (0.40 g, 0.5 mmol) was slowly added MeLi (3.2 mL, 1.0 mmol) at -30 °C, and the mixture was stirred at -30 °C for 3 h and then at room temperature overnight. The resulting clear solution was concentrated to about 5 mL, and toluene (15 mL) was then added, followed by procedures similar to those used above, giving colorless crystals identified as **15** (0.27 g, 60%).

Preparation of [η⁵:σ-Me₂Si(C₅H₄)(C₂B₁₀H₁₀)]₂Er][Li(THF)₄] (16**).** To a THF suspension (20 mL) of ErCl₃ (0.137 g, 0.5 mmol) was added dropwise a THF solution of [Me₂Si(C₅H₄)(C₂B₁₀H₁₀)]Li₂ (**3**; 8.0 mL, 1.0 mmol) at 0 °C, followed by procedures similar to those used in the synthesis of **14**, giving **16** as pink crystals (0.33 g, 67%), mp 183–185 °C. ¹H NMR (pyridine-*d*₅): δ 3.40 (br, 16H, THF), 1.40 (br, 16H, THF), 0.60 (s, 6H, CH₃), 0.40 (s, 6H, CH₃), -10.8 (br, 4H, C₅H₄), -31.0 (br, 4H, C₅H₄). ¹¹B NMR (pyridine-*d*₅): δ -6.5 (4), -9.6 (4), -16.1 (4), -20.2 (6), -21.0 (2). IR (cm⁻¹): ν 3079 (w), 2979 (m), 2960 (m), 2882 (m), 2572 (br, vs), 1251 (s), 1186 (s), 1087 (s), 1046 (s), 888 (m), 835 (s), 808 (s), 779 (s), 682 (m), 447 (m). Anal. Calcd for C₂₈H₆₀B₂₀ErLiO_{2.5}Si₂ (**16**-1.5THF): C, 38.07; H, 6.85. Found: C, 37.98; H, 7.09.

Preparation of [η⁵:σ-Me₂Si(C₅H₄)(C₂B₁₀H₁₀)]₂Yb][Li(THF)₄] (17**).** This compound was prepared as yellow crystals from YbCl₃ (0.140 g, 0.5 mmol) and [Me₂Si(C₅H₄)(C₂B₁₀H₁₀)]Li₂ (**3**; 8.0 mL, 1.0 mmol) in THF (15 mL) by using procedures similar to those used in the synthesis of **14**: yield 0.34 g (68%); mp 201–203 °C. ¹H NMR (pyridine-*d*₅): δ 6.80–6.52 (m, 8H, C₅H₄), 3.57 (m, 16H, THF), 1.41 (m, 16H, THF), 0.33 (br, 12H, CH₃). ¹¹B NMR (pyridine-*d*₅): δ 13.5 (2), 4.9 (2), 2.2 (2), -8.7 (2), -9.6 (2), -14.0 (2), -15.3 (2), -18.3 (2), -20.8 (2), -22.0 (2). IR (cm⁻¹): ν 3075 (w), 2959 (m), 2978 (m), 2882 (m), 2574 (br, vs), 1363 (m), 1251 (s), 1186 (m), 1088 (s), 1045 (s), 888

(s), 835 (s), 807 (vs), 778 (s), 676 (m), 445 (m). Anal. Calcd for C₃₀H₆₄B₂₀LiO₃Si₂Yb (**17**-THF): C, 38.95; H, 6.92. Found: C, 39.08; H, 7.35.

Preparation of [η⁵:η⁶-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]₂Nd(THF)₂ (18**).** The direct interaction of Me₂Si(C₅H₅)(C₂B₁₀H₁₁) (**1**; 0.266 g, 1.0 mmol) with K metal (0.35 g, 8.95 mmol) in THF (40 mL) at room temperature over a period of 2 days, followed by filtration, gave a pale yellow THF solution of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]K₃ (**4**; ¹¹B NMR (THF) δ -5.9 (2), -12.5 (2), -16.6 (4), -17.4 (2)). This solution was added dropwise to a stirred THF (20 mL) suspension of NdCl₃ (0.250 g, 1.0 mmol) at room temperature, and the mixture was stirred overnight. Removal of the precipitate, concentration of the solution, and *n*-hexane vapor diffusion gave compound **18** as a yellowish green crystalline solid (0.39 g, 70%), mp 146 °C dec. ¹H NMR (pyridine-*d*₅): δ 3.60 (br, THF), 1.51 (br, THF). Hydrolysis of **18** in pyridine-*d*₅ with a slight molar excess of H₂O and subsequent examination by NMR spectroscopy showed the presence of THF and ligand in a ratio of 2:1. ¹¹B NMR (pyridine-*d*₅): δ -3.1 (2), -9.6 (2), -13.8 (4), -14.6 (2). IR (cm⁻¹): ν 3066 (w), 2961 (m), 2502 (br, vs), 2361 (m), 1260 (m), 1095 (s), 1042 (s), 797 (s). Anal. Calcd for C₁₇H₃₇B₁₀NdO₂Si: C, 36.86; H, 6.73; Nd, 26.04. Found: C, 37.12; H, 6.88; Nd, 26.31.

This compound can also be prepared by the reaction of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]NdCl₂(THF)₃ (**5**) with excess K metal in THF at room temperature in 81% yield.

Preparation of [η⁵:η⁶-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Sm(THF)₂ (19**).** To a THF solution of SmI₂ (9.45 mL, 0.50 mmol) was slowly added a freshly prepared THF solution of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (**2**; 10.0 mL, 1.0 mmol) at room temperature with stirring. The reaction mixture was then stirred overnight. After removal of the solvent under vacuum, the residue was extracted with hot toluene (10 mL × 2). The combined extracts were concentrated to one-third of the original volume, affording a brownish yellow solution from which yellow crystals were obtained upon standing at room temperature for 2 days (0.045 g, 32%), mp 162 °C dec. ¹H NMR (pyridine-*d*₅): δ 3.43 (m, 8H, THF), 1.38 (m, 8H, THF), 0.14 (s, 6H, CH₃). ¹³C NMR (pyridine-*d*₅): δ 128.4, 119.2, 113.5 (C₅H₄), 67.3, 25.3 (OC₄H₈), -3.6 (CH₃). ¹¹B NMR (pyridine-*d*₅): δ -4.0 (4), -15.2 (1), -24.6 (1), -33.2 (2), -36.1 (2). IR (cm⁻¹): ν 3053 (m), 2979 (m), 2892 (m), 2528 (vs), 2498 (s), 1248 (m), 1046 (s), 1007 (s), 870 (s), 835 (s), 793 (s). Anal. Calcd for C₁₅H₃₃B₁₀O_{1.5}SiSm (**19**-0.5THF): C, 34.38; H, 6.35. Found: C, 34.60; H, 6.53.

Preparation of [η⁵:η⁶-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Sm^{II}(THF)₂{K(THF)₂} (20**).** To a stirred THF (20 mL) suspension of SmCl₃ (0.257 g, 1.0 mmol) was added a THF solution of [Me₂-Si(C₅H₄)(C₂B₁₀H₁₁)]K₃ (**4**; 12 mL, 1.0 mmol) dropwise at room temperature, and the mixture was stirred for 2 days. The color of the solution gradually changed from yellow to dark green during the course of the reaction. Removal of the precipitate, concentration of the solution, and *n*-hexane vapor diffusion gave a dark green crystalline solid (0.24 g, 65%), mp 118 °C dec. ¹H NMR (pyridine-*d*₅): δ 3.73 (br, THF), 1.56 (br, THF). Hydrolysis of this solid in pyridine-*d*₅ with a slight molar excess of H₂O and subsequent examination by ¹H NMR spectroscopy showed the presence of THF and ligand in a ratio of 4:1. The ¹¹B NMR spectrum consisted of many broad, unresolved resonances. IR (cm⁻¹): ν 3058 (m), 2975 (s), 2890 (s), 2520 (vs), 2495 (vs), 1430 (m), 1240 (m), 1009 (s), 875 (s), 833 (s), 790 (s), 630 (m). Anal. Calcd for C₂₅H₅₃B₁₀KO₄SiSm: C, 40.39; H, 7.19; Sm, 20.23. Found: C, 40.01; H, 6.76; Sm, 19.85.

This compound can also be prepared by the reaction of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]SmCl₂(THF)₃ or **19** with excess K metal in THF at room temperature in 61–70% yield.

Preparation of [η⁵:η⁶-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Yb^{II}(THF)₂{K(THF)₂} (21**).** To a stirred THF (30 mL) suspension of YbCl₃ (0.279 g, 1.0 mmol) was added a THF solution of

Table 1. Crystal Data and Summary of Data Collection and Refinement for 5, 8, 9, 10, and 14

	5	8	9	10	14
formula	C ₂₁ H ₄₅ B ₁₀ Cl ₂ NdO ₃ Si	C ₂₁ H ₄₅ B ₁₀ Cl ₂ O ₃ SiYb	C ₂₆ H ₅₈ B ₂₀ ClNdO ₂ Si ₂	C ₂₆ H ₅₈ B ₂₀ ClO ₂ Si ₂ Sm	C ₃₄ H ₇₂ B ₂₀ LiNdO ₄ Si ₂
cryst size (mm)	0.15 × 0.40 × 0.40	0.20 × 0.20 × 0.28	0.12 × 0.16 × 0.16	0.20 × 0.22 × 0.26	0.12 × 0.12 × 0.24
fw	696.90	725.70	854.79	860.90	968.48
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	14.877(1)	14.651(3)	7.878(2)	7.866(2)	14.700(3)
<i>b</i> , Å	16.566(1)	16.562(3)	24.140(5)	24.073(5)	22.574(5)
<i>c</i> , Å	14.713(1)	14.512(3)	11.610(2)	11.650(2)	15.965(3)
β, deg	111.77(1)	111.35(3)	92.00(3)	92.07(3)	92.76(3)
<i>V</i> , Å ³	3367.4(4)	3279.4(11)	2206.6(8)	2204.6(8)	5292(2)
<i>Z</i>	4	4	2	2	4
<i>D</i> _{calcd} , Mg/m ³	1.375	1.470	1.287	1.297	1.216
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	3.0–55.0	3.0–52.0	3.0–53.0	3.0–52.0	4.0–52.0
μ, mm ⁻¹	1.758	3.074	1.317	1.472	1.060
<i>F</i> (000)	1412	1452	870	874	1996
<i>T</i> , K	293	293	293	293	293
no. of indep rflns	7062	5608	3722	6649	9123
no. of obsd rflns (<i>I</i> > 2σ(<i>I</i>))	7061	4614	3722	6646	9123
no. of params refined	496	347	552	479	754
goodness of fit	1.097	1.493	0.951	1.041	1.183
R1	0.039	0.048	0.043	0.046	0.049
wR2	0.100	0.182	0.106	0.119	0.126
Δρ _{max} , Δρ _{min} , e/Å ³	0.60, -0.84	1.00, -0.73	0.51, -0.38	0.58, -0.65	0.53, -0.32

[Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]K₃ (**4**; 12 mL, 1.0 mmol) dropwise at room temperature, and the mixture was stirred at room temperature for 2 days. The color of the solution gradually changed from orange-yellow to green during the course of the reaction. After removal of the precipitate, the clear green solution was concentrated to about 5 mL. *n*-Hexane vapor diffusion afforded a green crystalline solid (0.18 g, 62%), mp 138 °C dec. ¹H NMR (pyridine-*d*₅): δ 6.75 (m, 2H, C₅H₄), 6.25 (m, 2H, C₅H₄), 5.61 (s, 1H, CH of carboranyl), 3.44 (m, 12H, THF), 1.40 (m, 12H, THF), 0.92 (s, 6H, CH₃). ¹³C NMR (pyridine-*d*₅): δ 114.57, 112.74, 110.08 (C₅H₄), 67.27, 25.24 (OC₄H₈), -1.64 (CH₃). ¹¹B NMR (pyridine-*d*₅): δ 1.7 (2), -3.1 (2), -10.1 (2), -15.9 (2), -21.0 (2). IR (cm⁻¹): ν 3066 (w), 2959 (m), 2878 (m), 2515 (vs), 2480 (s), 1244 (m), 1172 (m), 1038 (s), 876 (m), 827 (m), 803 (s), 769 (s), 688 (m). Anal. Calcd for C₁₅H₃₃B₁₀KO_{1.5}SiYb (**21**-1.5THF): C, 31.51; H, 5.82; Yb, 24.96. Found: C, 31.07; H, 5.90; Yb, 24.38.

This compound can also be prepared in 65% yield by the reaction of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]YbCl₂(THF)₃ with excess K metal at room temperature, followed by procedures similar to those used for **21**.

Preparation of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]₂Yb(THF)₂ (22**).** To a THF solution of YbI₂ (16.40 mL, 0.50 mmol) was slowly added a freshly prepared THF solution of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (**2**; 10.0 mL, 1.0 mmol) with stirring. The reaction mixture was then stirred overnight. After removal of the solvent under vacuum, the residue was extracted with hot toluene (10 mL × 2). The combined extracts were concentrated, and *n*-hexane vapor diffusion gave compound **22** as red crystals (0.28 g, 66%), mp 136 °C dec. ¹H NMR (pyridine-*d*₅): δ 6.20 (m, 4H, C₅H₄), 6.08 (m, 4H, C₅H₄), 3.43 (m, 8H, THF), 2.64 (br, s, 2H, CH of carboranyl), 1.38 (m, 8H, THF), 0.20 (s, 12H, CH₃). ¹³C NMR (pyridine-*d*₅): δ 116.8, 111.6, 107.3 (C₅H₄), 69.7, 62.5 (C₂B₁₀), 67.3, 25.3 (OC₄H₈), -2.94 (CH₃). ¹¹B NMR (pyridine-*d*₅): δ -3.5 (4), -7.8 (4), -14.1 (8), -15.0 (4). IR (cm⁻¹): ν 3073 (w), 3038 (m), 2961 (m), 2591 (br, vs), 1254 (m), 1037 (s), 807(s), 760 (s). Anal. Calcd for C₂₆H₅₈B₂₀O₂Si₂Yb (**22**): C, 36.82; H, 6.89; Yb, 20.40. Found: C, 36.43; H, 6.71; Yb, 20.12.

Reaction of SmI₂(THF)_x with Carboranes. An NMR tube was charged with equimolar amounts of SmI₂(THF)_x and C₂B₁₀H₁₂ or (C₆H₅CH₂)₂C₂B₁₀H₁₀ in THF/pyridine-*d*₅, and the mixture was shaken at room temperature for 2 days. No color change was observed. ¹¹B NMR spectra showed no reaction between SmI₂(THF)_x and C₂B₁₀H₁₂ or (C₆H₅CH₂)₂C₂B₁₀H₁₀.

Reaction of [(Me₃Si)₂C₅H₃]₂Sm(THF)₂ with C₂B₁₀H₁₂. An NMR tube was charged with equimolar amounts of [(Me₃Si)₂C₅H₃]₂Sm(THF)₂ and C₂B₁₀H₁₂ in THF/pyridine-*d*₅, and the mixture was shaken at room temperature for 2 days. The color of the solution changed from dark blue to orange-yellow. This reaction was monitored by ¹¹B NMR. ¹¹B NMR (THF/pyridine-*d*₅) after 0.5 h: δ 14.9, 10.6, -0.7, -4.9, -7.2, -9.3, -11.4, -15.4, -23.9. Among these resonances, the peaks at -4.9, -11.4, and -15.4 are attributable to C₂B₁₀H₁₂. ¹¹B NMR (THF/pyridine-*d*₅) after 2 h: δ 14.9 (2), 10.6 (2), -0.7 (2), -7.2 (2), -9.3 (1), -23.9 (1).

X-ray Structure Determination. All single crystals were immersed in Paratone-N oil and sealed under N₂ 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.¹⁶ 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, on *F*² using the Siemens SHELXTL program package (PC version).^{17a} Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. For noncentrosymmetric structures, the appropriate enantiomorph was chosen by refining Flack's parameter *χ* toward zero.^{17a,b} Crystal data and details of data collection and structure refinements are given in Tables 1 and 2. Selected bond distances and angles are listed in Table 3. Further details are included in the Supporting Information.

Results and Discussion

Synthesis of Me₂Si(C₅H₅)(C₂B₁₀H₁₁) (1**).** Treatment of Me₂Si(C₅H₅)Cl with 1 equiv of Li₂C₂B₁₀H₁₀ in toluene/ether at 0 °C, after hydrolysis, gave Me₂Si(C₅H₅)(C₂B₁₀H₁₁) (**1**) in 79% isolated yield (Scheme 1). The ¹H NMR spectrum indicates that **1** is a mixture of isomers

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

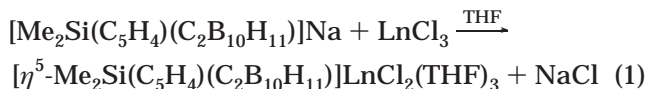
(17) (a) SHELXTL V 5.03 Program Package; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995. (b) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881.

Table 2. Crystal Data and Summary of Data Collection and Refinement for 15, 16, 17, 19, and 22

	15	16	17	19	22
formula	C ₃₄ H ₇₂ B ₂₀ LiO ₄ Si ₂ Y	C ₃₄ H ₇₂ B ₂₀ ErLiO ₄ Si ₂	C ₃₄ H ₇₂ B ₂₀ LiO ₄ Si ₂ Yb	C ₁₇ H ₃₇ B ₁₀ O ₂ SiSm	C ₂₆ H ₅₈ B ₂₀ O ₂ Si ₂ Yb
cryst size (mm)	0.20 × 0.20 × 0.24	0.12 × 0.14 × 0.22	0.20 × 0.30 × 0.30	0.10 × 0.10 × 0.14	0.20 × 0.22 × 0.32
fw	913.15	991.50	997.28	560.0	848.14
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁	<i>Pbca</i>
<i>a</i> , Å	14.719(3)	14.716(3)	14.712(3)	10.030(2)	12.938(3)
<i>b</i> , Å	22.601(5)	22.540(5)	22.571(5)	17.933(4)	16.832(5)
<i>c</i> , Å	15.932(3)	15.882(3)	15.863(3)	14.368(3)	40.341(8)
β, deg	93.52(3)	93.85(3)	93.86(5)	91.43(3)	90.00
<i>V</i> , Å ³	5290(2)	5256(2)	5256(1)	2583(9)	8785(3)
<i>Z</i>	4	4	4	2	8
<i>D</i> _{calcd} , Mg/m ³	1.146	1.253	1.260	1.440	1.283
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	3.0–52.0	3.0–52.0	3.0–52.0	3.0–52.0	3.0–52.0
μ, mm ⁻¹	1.181	1.676	1.859	2.332	2.208
<i>F</i> (000)	1912	2028	2036	1124	3424
<i>T</i> , K	293	293	293	293	293
no. of indep rflns	4856	7240	6512	5859	7008
no. of obsd rflns (<i>I</i> > 2σ(<i>I</i>))	3606	7240	6510	5039	7006
no. of params refined	600	660	591	560	561
goodness of fit	1.196	1.140	1.317	0.909	1.002
R1	0.074	0.069	0.065	0.067	0.054
wR2	0.138	0.178	0.134	0.168	0.153
Δρ _{max} , Δρ _{min} , e/Å ³	0.24, -0.27	0.64, -0.38	0.56, -0.79	0.64, -0.86	0.91, -0.97

in which the silicon atom bonds to the sp³ or sp² carbons of the cyclopentadienyl ring, respectively. The ¹¹B NMR spectrum exhibits a 1:1:2:2:2 splitting pattern, which is similar to that of Me₂Si(*t*-Bu)(C₂B₁₀H₁₁).¹⁴ Since compound **1** contains both cyclopentadiene and carborane groups, it may possess some properties of both units. Indeed, **1** can be conveniently converted into the monoanion (**2**), dianion (**3**), and trianion (**4**) by treatment with NaH, MeLi, and K in THF, respectively (Scheme 2). Among these anions, **3** is a novel "constrained geometry" ligand in which a carbon atom rather than a heteroatom functions as the second binding site. The ¹¹B NMR spectrum of the monoanion (**2**) exhibits the same splitting pattern as that of **1**, but their chemical shifts are different from each other. Unlike **1** and **2**, ¹¹B NMR spectra of both the dianion (**3**) and trianion (**4**) show a 1:1:2:1 splitting pattern, but their chemical shifts are quite different.

Synthesis and Characterization of [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]LnCl₂(THF)₃ (Ln = Nd (5**), Sm (**6**), Er (**7**), Yb (**8**)).** Treatment of LnCl₃ with an equimolar amount of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na (**2**) in THF at room temperature, removal of the precipitates, and *n*-hexane vapor diffusion gave organolanthanide dichloride compounds of the general formula [η⁵-Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]LnCl₂(THF)₃ in good yield (eq 1).



Ln = Nd (**5**), Sm (**6**), Er (**7**), Yb (**8**)

These compounds are soluble in polar organic solvents such as THF and pyridine, slightly soluble in toluene, and insoluble in *n*-hexane. They are characterized by various spectroscopic and elemental analyses as well as X-ray analyses (for **5** and **8**). ¹¹B NMR spectra of compounds **5** and **6** exhibit a 1:1:2:1 splitting pattern, while those of compounds **7** and **8** show a 1:1:1:1 splitting pattern. ¹H NMR spectra of all four compounds

support the ratio of three THF molecules per ligand. IR spectra of the four compounds are similar, showing a typical strong and broad characteristic B–H absorption at about 2590 cm⁻¹.

The solid-state structures of compounds **5** and **8** have been confirmed by single-crystal X-ray analyses. They are isostructural and isomorphous. Figure 1 shows the representative structure of **8**. The lanthanide ion is η⁵-bound to the cyclopentadienyl ring and σ-bound to two chloride atoms and three oxygen atoms from the coordinated THF molecules in a pseudo-octahedral geometry, typical of CpLnCl₂(THF)₃ compounds.¹⁸ There is no intramolecular interaction between the B–H bonds of the carborane cage and metal ion presumably because, on the one hand, a B–H bond is a weaker σ-donor than THF and, on the other hand, the C–H bond of the cage has some π interactions with the cyclopentadienyl ring. The distances from the centroid of the cyclopentadienyl ring to the H atom on the carbon atom of the cage are 2.848 Å in **5** and 2.678 Å in **8**, respectively, resulting in the smaller C(1)–Si(1)–C(5) angles of 103.3(1)° in **5** and 103.5(1)° in **8**. These measured distances can be compared to those (2.184–2.765 Å) found in the adduct of *o*-C₂B₁₀H₁₂ with cyclotrimeratrylene.¹⁹ The nonclassical hydrogen bonds can stabilize the conformation of the cage in both compounds **5** and **8**, which is consistent with the acidic nature of the protons attached to the carbon atoms of the carborane.

The Yb–C distances range from 2.651(3) to 2.703(2) Å (Table 3) with an average value of 2.679(3) Å, which is about 0.109 Å shorter than the average Nd–C distance of 2.788(3) Å. The average Yb–O distance of 2.394(2) Å is 0.116 Å shorter than that of Nd–O in **5**.

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(19) Blanch, R. J.; Williams, M.; Fallon, G. D.; Gardiner, M. G.; Kaddour, R.; Raston, C. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 504–506.

Table 3. Selected Interatomic Distances (Å) and Angles (deg)^a

Compound 5							
Nd(1)–C(5)	2.803(3)	Nd(1)–C(8)	2.787(3)	Nd(1)–O(2)	2.497(2)	Nd(1)–Cl(2)	2.6753(9)
Nd(1)–C(6)	2.781(3)	Nd(1)–C(9)	2.784(3)	Nd(1)–O(3)	2.585(2)	Nd(1)–Cent	2.518
Nd(1)–C(7)	2.785(3)	Nd(1)–O(1)	2.448(2)	Nd(1)–Cl(1)	2.701(1)	av Nd(1)–C(C ₅ ring)	2.788(3)
O(1)–Nd(1)–O(3)	77.28(9)	O(1)–Nd(1)–Cl(2)	89.55(5)	O(3)–Nd(1)–Cl(1)	78.68(6)	Cent–Nd(1)–O(3)	178.5
O(1)–Nd(1)–O(2)	153.94(9)	O(1)–Nd(1)–Cl(1)	87.31(6)	Cent–Nd(1)–O(2)	103.2	Cent–Nd(1)–Cl(2)	103.7
O(2)–Nd(1)–O(3)	76.77(9)	O(3)–Nd(1)–Cl(2)	77.77(6)	Cent–Nd(1)–O(1)	102.6	Cent–Nd(1)–Cl(1)	99.8
C(1)–Si(1)–C(5)	103.3(1)						
Compound 8							
Yb(1)–C(5)	2.703(2)	Yb(1)–C(8)	2.651(3)	Yb(1)–O(2)	2.495(2)	Yb(1)–Cl(2)	2.561(1)
Yb(1)–C(6)	2.690(2)	Yb(1)–C(9)	2.688(3)	Yb(1)–O(3)	2.327(2)	Yb(1)–Cent	2.394
Yb(1)–C(7)	2.661(3)	Yb(1)–O(1)	2.360(2)	Yb(1)–Cl(1)	2.584(1)	av Yb(1)–C(C ₅ ring)	2.679(3)
O(1)–Yb(1)–O(2)	76.43(6)	O(1)–Yb(1)–Cl(2)	86.83(5)	O(3)–Yb(1)–Cl(2)	87.98(5)	Cent–Yb(1)–O(3)	103.1
O(1)–Yb(1)–O(3)	153.18(4)	O(1)–Yb(1)–Cl(1)	86.02(5)	Cent–Yb(1)–O(2)	178.3	Cent–Yb(1)–Cl(1)	100.6
O(2)–Yb(1)–O(3)	76.76(6)	O(3)–Yb(1)–Cl(1)	87.76(5)	Cent–Yb(1)–O(1)	103.7	Cent–Yb(1)–Cl(2)	104.1
C(1)–Si(1)–C(5)	103.5(1)						
Compound 9							
Nd(1)–O(1)	2.592(1)	Nd(1)–C(8)	2.833(3)	Nd(1)–C(18)	2.776(2)	Nd(1)–C(22)	2.794(2)
Nd(1)–O(2)	2.590(1)	Nd(1)–C(9)	2.760(3)	Nd(1)–C(19)	2.814(2)	Nd(1)–Cent(1)	2.492
Nd(1)–Cl(1)	2.670(1)	Nd(1)–C(10)	2.672(3)	Nd(1)–C(20)	2.779(2)	Nd(1)–Cent(2)	2.534
Nd(1)–C(7)	2.808(2)	Nd(1)–C(11)	2.713(3)	Nd(1)–C(21)	2.797(2)	av Nd(1)–C(C ₅ ring)	2.775(3)
O(1)–Nd(1)–O(2)	162.09(4)	Cent(1)–Nd(1)–Cl(1)	119.0	Cent(1)–Nd(1)–O(2)	89.6	Cent(1)–Nd(1)–Cent(2)	125.4
O(1)–Nd(1)–Cl(1)	81.05(4)	Cent(2)–Nd(1)–Cl(1)	115.5	Cent(1)–Nd(1)–O(1)	96.2	C(1)–Si(1)–C(7)	103.5(1)
O(2)–Nd(1)–Cl(1)	81.31(3)	Cent(2)–Nd(1)–O(2)	98.0	Cent(2)–Nd(1)–O(1)	92.4	C(3)–Si(2)–C(18)	105.5(1)
Compound 10							
Sm(1)–O(1)	2.580(2)	Sm(1)–C(8)	2.767(3)	Sm(1)–C(18)	2.779(2)	Sm(1)–C(22)	2.771(3)
Sm(1)–O(2)	2.594(2)	Sm(1)–C(9)	2.692(3)	Sm(1)–C(19)	2.779(3)	Sm(1)–Cent(1)	2.450
Sm(1)–Cl(1)	2.639(1)	Sm(1)–C(10)	2.673(3)	Sm(1)–C(20)	2.771(3)	Sm(1)–Cent(2)	2.500
Sm(1)–C(7)	2.792(3)	Sm(1)–C(11)	2.735(3)	Sm(1)–C(21)	2.766(3)	av Sm(1)–C(C ₅ ring)	2.752(4)
O(1)–Sm(1)–O(2)	161.96(5)	Cent(1)–Sm(1)–Cl(1)	115.6	Cent(1)–Sm(1)–O(1)	93.7	Cent(1)–Sm(1)–Cent(2)	126.4
O(1)–Sm(1)–Cl(1)	81.11(5)	Cent(2)–Sm(1)–Cl(1)	118.0	Cent(1)–Sm(1)–O(2)	92.2	C(1)–Si(1)–C(7)	105.9(1)
O(2)–Sm(1)–Cl(1)	81.01(4)	Cent(2)–Sm(1)–O(1)	94.1	Cent(2)–Sm(1)–O(2)	95.9	C(3)–Si(2)–C(18)	103.9(2)
Compound 14							
Nd(1)–C(1)	2.619(1)	Nd(1)–C(7)	2.740(1)	Nd(1)–C(16)	2.733(1)	Nd(1)–Cent(1)	2.457
Nd(1)–C(11)	2.583(1)	Nd(1)–C(8)	2.743(1)	Nd(1)–C(17)	2.710(1)	Nd(1)–Cent(2)	2.449
Nd(1)–C(5)	2.711(1)	Nd(1)–C(9)	2.727(1)	Nd(1)–C(18)	2.731(1)	av Nd(1)–C(C ₅ ring)	2.728(1)
Nd(1)–C(6)	2.723(1)	Nd(1)–C(15)	2.734(1)	Nd(1)–C(19)	2.728(1)		
C(1)–Nd(1)–C(11)	117.53(3)	Cent(1)–Nd(1)–Cent(2)	127.0	C(1)–Nd(1)–Cent(2)	106.7	C(1)–Nd(1)–Cent(1)	101.2
C(11)–Nd(1)–Cent(2)	100.5	C(11)–Nd(1)–Cent(1)	105.1				
Compound 15							
Y(1)–C(1)	2.525(9)	Y(1)–C(7)	2.624(13)	Y(1)–C(16)	2.637(9)	Y(1)–Cent(1)	2.346
Y(1)–C(11)	2.566(10)	Y(1)–C(8)	2.640(11)	Y(1)–C(17)	2.653(10)	Y(1)–Cent(2)	2.357
Y(1)–C(5)	2.641(9)	Y(1)–C(9)	2.646(9)	Y(1)–C(18)	2.664(10)	av Y(1)–C(C ₅ ring)	2.640(13)
Y(1)–C(6)	2.616(11)	Y(1)–C(15)	2.648(9)	Y(1)–C(19)	2.632(9)		
C(1)–Y(1)–C(11)	112.2(4)	Cent(1)–Y(1)–Cent(2)	128.2	C(1)–Y(1)–Cent(2)	104.8	C(1)–Y(1)–Cent(1)	102.8
C(11)–Y(1)–Cent(2)	104.0	C(11)–Y(1)–Cent(1)	104.9				
Compound 16							
Er(1)–C(1)	2.553(2)	Er(1)–C(7)	2.599(2)	Er(1)–C(16)	2.630(2)	Er(1)–Cent(1)	2.338
Er(1)–C(11)	2.502(2)	Er(1)–C(8)	2.652(3)	Er(1)–C(17)	2.632(3)	Er(1)–Cent(2)	2.329
Er(1)–C(5)	2.626(2)	Er(1)–C(9)	2.595(2)	Er(1)–C(18)	2.607(3)	av Er(1)–C(C ₅ ring)	2.618(3)
Er(1)–C(6)	2.613(2)	Er(1)–C(15)	2.626(2)	Er(1)–C(19)	2.606(3)		
C(1)–Er(1)–C(11)	110.71(8)	Cent(1)–Er(1)–Cent(2)	127.9	C(1)–Er(1)–Cent(1)	104.2	C(1)–Er(1)–Cent(2)	104.9
C(11)–Er(1)–Cent(1)	104.4	C(11)–Er(1)–Cent(2)	104.3				
Compound 17							
Yb(1)–C(1)	2.518(9)	Yb(1)–C(7)	2.598(9)	Yb(1)–C(16)	2.597(8)	Yb(1)–Cent(1)	2.311
Yb(1)–C(11)	2.497(8)	Yb(1)–C(8)	2.594(10)	Yb(1)–C(17)	2.589(8)	Yb(1)–Cent(2)	2.315
Yb(1)–C(5)	2.582(10)	Yb(1)–C(9)	2.604(10)	Yb(1)–C(18)	2.639(9)	av Yb(1)–C(C ₅ ring)	2.601(10)
Yb(1)–C(6)	2.614(8)	Yb(1)–C(15)	2.588(8)	Yb(1)–C(19)	2.607(9)	C(13)–Yb(1)–Cent(2)	104.7
C(1)–Yb(1)–C(11)	110.3(3)	Cent(1)–Yb(1)–Cent(2)	127.8	C(13)–Yb(1)–Cent(1)	104.6		
C(11)–Yb(1)–Cent(1)	104.5	C(11)–Yb(1)–Cent(2)	104.4				
Compound 19							
Sm(1)–O(1)	2.409(2)	Sm(1)–C(11)	2.582(2)	Sm(1)–C(2)	2.693(3)	Sm(1)–B(6)	2.635(4)
Sm(1)–O(2)	2.517(2)	Sm(1)–C(12)	2.808(2)	Sm(1)–B(3)	2.880(3)	Sm(1)–Cent	2.390
Sm(1)–C(9)	2.679(2)	Sm(1)–C(13)	2.640(2)	Sm(1)–B(4)	2.961(4)	Sm(1)–Bent	2.298
Sm(1)–C(10)	2.610(2)	Sm(1)–C(1)	3.018(3)	Sm(1)–B(5)	2.861(3)	av Sm(1)–C(C ₅ ring)	2.664(2)
						av Sm(1)–atom(C ₂ B ₄ ring)	2.856(2)

Table 3 (Continued)

Compound 19							
O(1)–Sm(1)–O(2)	76.76(6)	Cent–Sm(1)–Bent	123.4	Cent–Sm(1)–O(1)	99.9		
Bent–Sm(1)–O(1)	123.1	Bent–Sm(1)–O(2)	114.3	Cent–Sm(1)–O(2)	109.7		
Sm(2)–O(3)	2.434(2)	Sm(2)–C(16)	2.892(2)	Sm(2)–C(4)	2.610(4)	Sm(2)–B(16)	2.623(4)
Sm(2)–O(4)	2.350(2)	Sm(2)–C(17)	2.751(2)	Sm(2)–B(13)	2.795(3)	Sm(2)–Cent	2.465
Sm(2)–C(14)	2.619(3)	Sm(2)–C(18)	2.760(2)	Sm(2)–B(14)	2.957(4)	Sm(2)–Bent	2.226
Sm(2)–C(15)	2.720(2)	Sm(2)–C(3)	2.748(3)	Sm(2)–B(15)	2.839(3)	av Sm(2)–C(C ₅ ring)	2.748(3)
						av Sm(2)–atom(C ₂ B ₄ ring)	2.762(4)
O(3)–Sm(2)–O(4)	83.63(6)	Cent–Sm(2)–Cent(6)	126.7	Cent–Sm(2)–O(3)	106.4		
Bent–Sm(2)–O(3)	106.4	Bent–Sm(2)–O(4)	117.8	Cent–Sm(2)–O(4)	106.6		
Compound 22							
Yb(1)–O(1)	2.391(2)	Yb(1)–C(11)	2.726(2)	Yb(1)–C(15)	2.708(2)	Yb(1)–Cent(1)	2.455
Yb(1)–O(2)	2.459(1)	Yb(1)–C(12)	2.742(2)	Yb(1)–C(16)	2.718(2)	Yb(1)–Cent(2)	2.447
Yb(1)–C(9)	2.728(2)	Yb(1)–C(13)	2.712(2)	Yb(1)–C(17)	2.734(2)	av Yb(1)–C(C ₅ ring)	2.725(2)
Yb(1)–C(10)	2.728(2)	Yb(1)–C(14)	2.715(2)	Yb(1)–C(18)	2.735(2)	O(1)–Yb(1)–Cent(2)	106.5
O(1)–Yb(1)–O(2)	83.27(7)	Cent(1)–Yb(1)–Cent(2)	134.0	O(1)–Yb(1)–Cent(1)	104.5	C(3)–Si(2)–C(14)	104.8(1)
O(2)–Yb(1)–Cent(1)	110.4	O(2)–Yb(1)–Cent(2)	106.4	C(1)–Si(1)–C(9)	107.2(1)		

^a Cent = the centroid of the cyclopentadienyl ring; Bent = the centroid of the C₂B₄ bonding face.

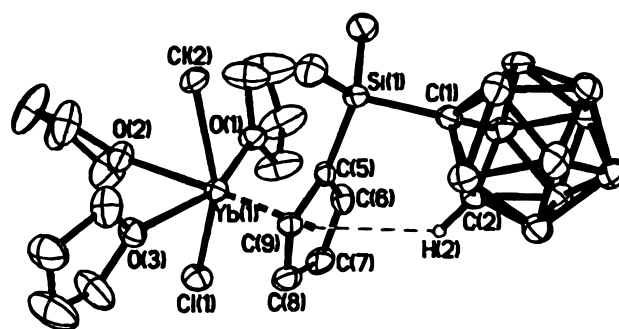
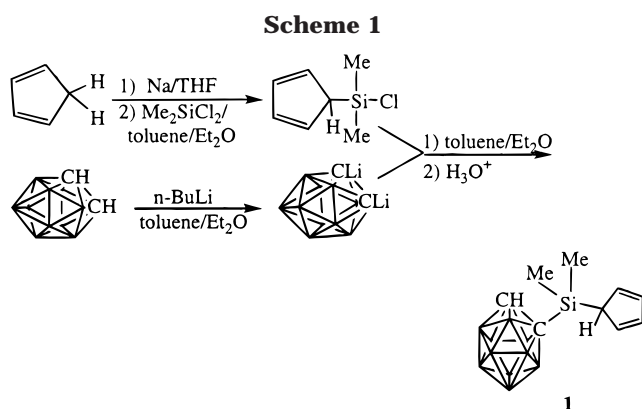
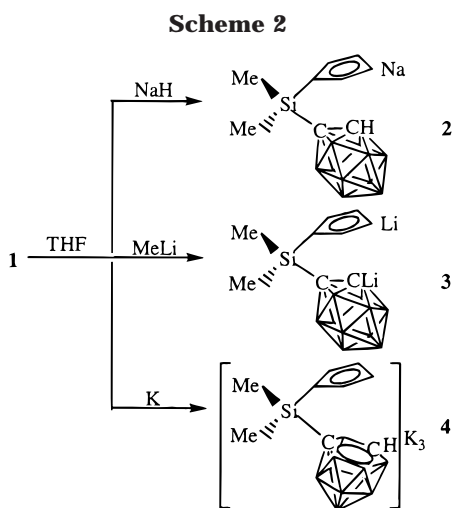
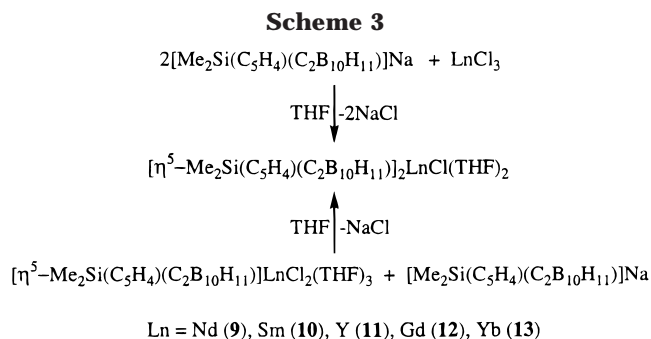


Figure 1. Molecular structure of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})\text{-YbCl}_2(\text{THF})_3$ (**8**) (thermal ellipsoids drawn at the 35% probability level).



These differences can be compared to the 0.124 Å difference between Shannon's ionic radii of eight-coordinate Yb^{3+} and Nd^{3+} .²⁰

Synthesis and Characterization of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{LnCl}(\text{THF})_2$ (Ln = Nd (9**), Sm (**10**), Y (**11**), Gd (**12**), Yb (**13**)).** Treatment of LnCl_3 with 2 equiv of $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Na}$ (**2**) in THF at room temperature or reaction of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{LnCl}_2(\text{THF})_3$ with an equimolar amount of **2** in THF at room temperature afforded organolanthanide chloride compounds of the general formula $[\eta^5\text{-}$



$\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{LnCl}(\text{THF})_2$ in good yield (Scheme 3).

These compounds are soluble in THF and Et₂O, slightly soluble in toluene, and insoluble in *n*-hexane. Their ¹H NMR spectra support the ratio of two THF molecules per ligand. ¹¹B NMR spectra of compounds **9**, **10**, **11**, and **13** exhibit a 1:1:2:1 splitting pattern, while that of **12** shows a 1:1:1:1:1 splitting pattern. IR spectra of all five compounds are similar, showing a very strong characteristic B–H absorption at about 2580 cm⁻¹.

The solid-state structures of **9** and **10** as derived from single-crystal X-ray diffraction studies reveal that they are isostructural and isomorphous; the lanthanide ion is η^5 -bound to each of two cyclopentadienyl rings and σ -bound to one chloride atom and two oxygen atoms from the coordinated THF molecules in a distorted-trigonal-bipyramidal geometry (Figure 2). Such an arrangement around the lanthanide ion is not common

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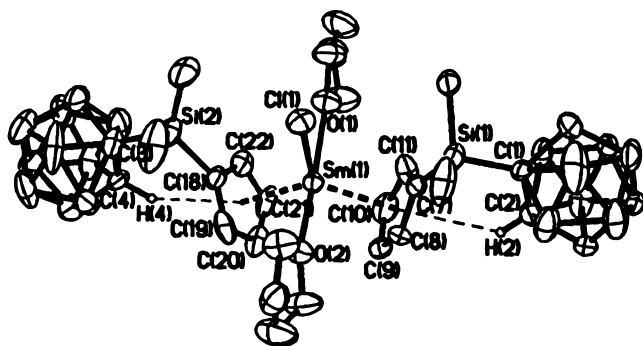
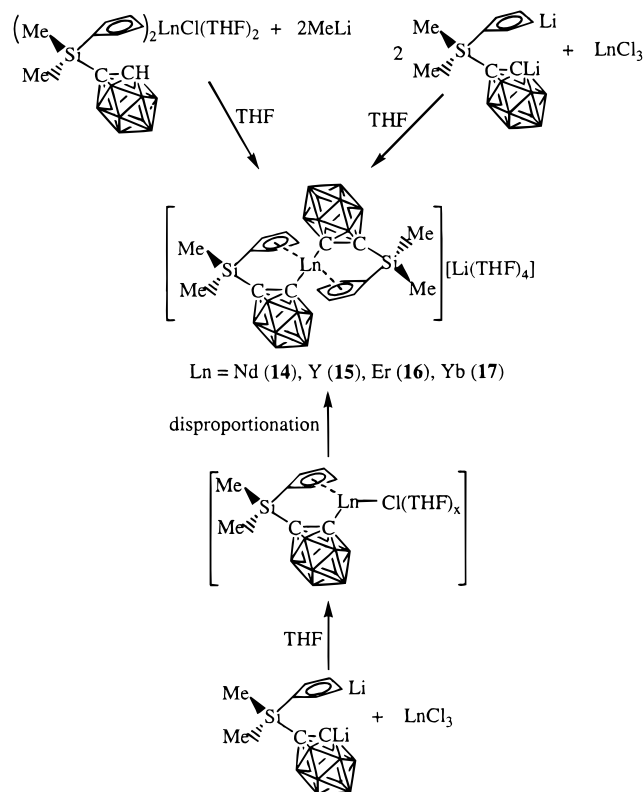


Figure 2. Molecular structure of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{SmCl}(\text{THF})_2$ (**10**) (thermal ellipsoids drawn at the 35% probability level).

Scheme 4



for Cp_2LnCl types of compounds.²¹ The two carborane cages stay away from each other, and there is no direct interaction between the cages and the Ln^{3+} ion. As in the compounds **5** and **8**, the nonclassical hydrogen bonds between the H atoms on carbon atoms of the carborane cages and the cyclopentadienyl rings are also present with distances of 2.743 and 2.970 Å in **9** and 2.771 and 2.902 Å in **10** from the H atoms to the centroids of the cyclopentadienyl rings, respectively, which again result in the smaller C(1)–Si(1)–C(7) and C(18)–Si(2)–C(3) angles.

The average Nd–C, Nd–O, and Nd–Cl distances of 2.775(3), 2.591(1), and 2.670(1) Å in **9** compare with the corresponding values of 2.788(3), 2.510(2), and 2.688(1)

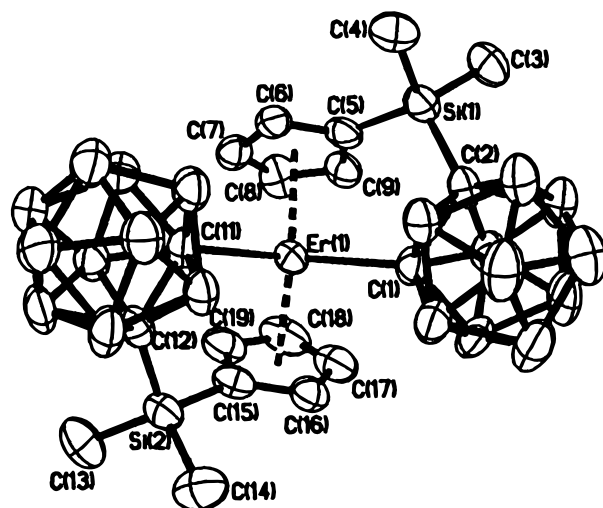


Figure 3. Molecular structure of the anion $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]_2\text{Er}^-$ in **16** (thermal ellipsoids drawn at the 35% probability level).

Å in **5**, respectively. The average Sm–C distance of 2.752(3) Å is 0.023 Å shorter than the Nd–C distance in **9**, which is consistent with the lanthanide contraction.²⁰

It should be noted that the carborane cage in both organolanthanide dichloride (**5–8**) and organolanthanide chloride (**9–13**) compounds serves only as a bulky substituent which prevents early-lanthanocene chloride compounds from disproportionation.²¹

Synthesis and Characterization of $[\{\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}_2\text{Ln}][\text{Li}(\text{THF})_4]$ (Ln = Nd (14**), Y (**15**), Er (**16**), Yb (**17**)).** Treatment of $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Li}_2$ (**3**) with LnCl_3 in a molar ratio of 2:1 or 1:1 in THF afforded the same compounds of the general formula $[\{\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}_2\text{Ln}][\text{Li}(\text{THF})_4]$ (Scheme 4). The equimolar reaction did not give the stable monochloride compounds $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{LnCl}(\text{THF})_x$, indicating that such an intermediate is very reactive and undergoes disproportionation to yield thermodynamically more stable products. Reaction of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{LnCl}(\text{THF})_2$ with 2 equiv of MeLi in THF also produced $[\{\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}_2\text{Ln}][\text{Li}(\text{THF})_4]$. Here, **3** serves as a bifunctional monocyclopentadienyl ligand with an appended anionic carboanion functionality, which is a novel constrained-geometry ligand.

¹H NMR spectra support the ratio of four THF molecules per ligand in these compounds, and IR spectra show the characteristic B–H absorption at about 2570 cm^{-1} . ¹¹B NMR spectra of these compounds are complicated, showing a different splitting pattern for each compound. For example, a 2:2:2:1:1:1:1 splitting pattern was observed in compound **14** and a 1:1:3:1:3:1 splitting pattern in **15**.

Molecular structures of compounds **14–17** have been confirmed by single-crystal X-ray analyses. They are isostructural and isomorphous. Figure 3 shows the representative structure of these four molecules. All of them consist of well-separated, alternating layers of the discrete tetrahedral cation $\text{Li}(\text{THF})_4^+$ and anion $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]_2\text{Ln}^-$. In each anion, the lanthanide ion is η^5 -bound to each of two cyclopentadienyl rings and σ -bound to each of two carbon atoms from two

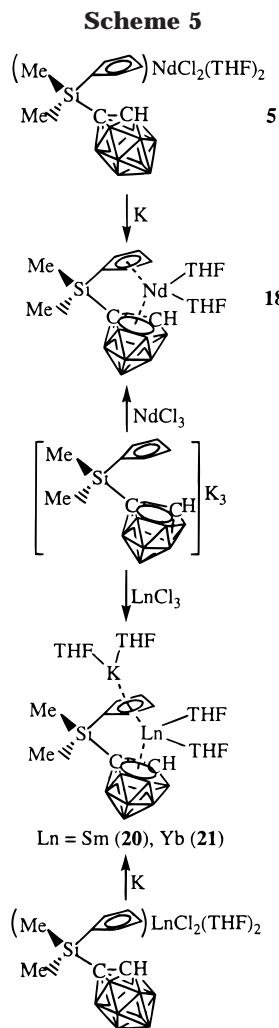
(21) For reviews, see: (a) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, U.K., 1995; Vol. 4, pp 11–812. (b) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865–986. (c) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081–1124.

carborane cages in a distorted-tetrahedral arrangement with C(1)–Ln–C(11) angles ranging from 110.3(3) to 117.5(1)° and the Cent–Ln–Cent angles ranging from 127.0 to 128.2°, respectively. The formal coordination number of Ln³⁺ is 8.

The average Ln–C(C₅ ring) distances are 2.728(1) Å in **14**, 2.640(13) Å in **15**, 2.618(3) Å in **16**, and 2.601(10) Å in **17**. The average Ln–C(σ) distances are 2.601(1) Å in **14**, 2.546(10) Å in **15**, 2.528(2) Å in **16**, and 2.508(9) Å in **17**. The differences in the above distances are in good agreement with the lanthanide contraction.²⁰ It is noteworthy that the intramolecular Ln–C(σ) bonds in **14**–**17** are significantly longer than the corresponding terminal Ln–C(σ) bonds but are similar to the bridging Ln–C(σ) bonds,²² probably indicating steric and/or electronic effects. For instance, the average Y–C(σ) distance of 2.546(10) Å in **15** is significantly longer than that of 2.468(7) Å in (C₅Me₅)₂YCH(SiMe₃)₂^{22c} but is very close to the value of 2.545(10) Å in [(C₅H₅)₂Y(μ -Me)]₂.^{22e}

Synthesis and Characterization of [η^5 : η^6 -Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Ln(THF)₂ (Ln = Nd (18**), Sm (**19**)), { [η^5 : η^6 -Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Ln(THF)₂}₂·{K(THF)₂} (Ln = Sm (**20**), Yb (**21**)), and [η^5 -Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Yb(THF)₂ (**22**).** Treatment of NdCl₃ with an equimolar amount of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]K₃ (**4**) in dry THF at room temperature gave a yellowish green air- and moisture-sensitive compound, [η^5 : η^6 -Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Nd(THF)₂ (**18**), in good yield (Scheme 5). Reaction of **5** with excess K metal in THF at room temperature also afforded **18**, which involves a redox reaction between K metal and carborane and an intramolecular metathesis reaction.

Under similar reaction conditions, reaction of LnCl₃ (Ln = Sm, Yb) with **4** in a molar ratio of 1:1 in THF, however, did not afford analogous compounds of **18**; instead, intensely colored compounds with the formula [[η^5 : η^6 -Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Ln(THF)₂ }₂·{K(THF)₂} (Ln = Sm (**20**, dark green), Yb (**21**, green)) were isolated. This color change indicates that the oxidation state of Ln has changed from +3 to +2.²¹ The reason for that is due to the powerful reducing agent C₂B₁₀H₁₀R₂²⁻, which has been known to reduce M(IV) to M(III) (M = Ti, Zr, Hf)²³ and Eu(III) to Eu(II).⁹ Reaction of compound **6** or **8** with excess K metal in THF also gave **20** or **21**, respectively, which indicates that both K metal and **4** can reduce Ln³⁺ to Ln²⁺ (Ln = Sm, Yb). These transformations are outlined in Scheme 5.



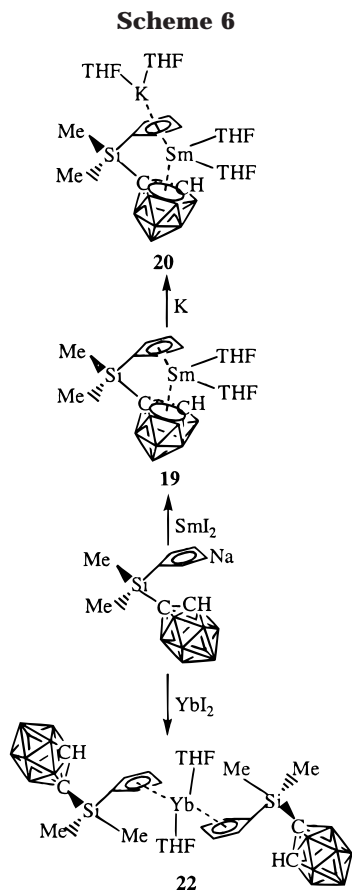
The above results imply that it is rather difficult to prepare the Sm and Yb analogues of compound **18** by the metathesis reactions due to the reducing property of the ligand **4** and oxidizing ability of the Sm(III) and Yb(III). A new methodology is definitely desirable. As the ligand was applied to Ln(II) chemistry, an unprecedented redox reaction was discovered, which led to the isolation of [η^5 : η^6 -Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Sm(THF)₂ (**19**).

Treatment of a dark green THF solution of SmI₂ with 2 equiv of [Me₂Si(C₅H₄)(C₂B₁₀H₁₁)]Na in THF at room temperature gave compound **19** as yellow crystals (Scheme 6). This color change indicates that the oxidation state of Sm has been changed from 2+ to 3+, which goes in the opposite direction of the previous reaction as shown in Scheme 5. Reaction of **19** with excess K metal in THF produced **20**.

These new compounds have been characterized by spectroscopic and elemental analyses as well as X-ray analysis (for **19**). ¹H NMR spectra of the hydrolysis products of four compounds are essentially identical and show the ratio of two THF molecules per ligand for compounds **18** and **19** and the ratio of four THF molecules per ligand for compounds **20** and **21**, respectively. Their IR spectra all exhibit a unique doublet centered at about 2510 cm⁻¹, typical of the ionic interaction of a positive metal center and an anionic carborane ligand of C₂B₁₀ systems.^{9,24} The ¹¹B NMR spectrum of **18** shows a 1:1:2:1 splitting pattern. Compound **21** gives a 1:1:1:1:1 splitting pattern in its ¹¹B NMR spectrum.

(22) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110. (c) Haan, K. H. D.; Boer, J. L. D.; Teuben, J. H. Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726–1733. (d) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagne, M. R.; Sabat, M.; Rheingold, A.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212–10240 and references therein. (e) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1979**, 54–61. (f) Evans, W. J.; Hanusa, T. P.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1987**, *6*, 295–301. (g) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1979**, 45–46. (h) Schumann, H.; Lauke, H.; Hahn, E.; Heeg, M. J.; van der Helm, D. *Organometallics* **1985**, *4*, 321–324. (i) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115–4119.

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In contrast, the ^{11}B NMR spectra of compounds **19** and **20** are complicated, consisting of extremely broad, unresolved resonances.

The solid-state structure of compound **19** has been confirmed by single-crystal X-ray analysis, showing two crystallographically independent molecules in the unit cell. Each Sm ion is η^5 -bound to the cyclopentadienyl ring and η^6 -bound to the hexagonal C_2B_4 face of the $\text{C}_2\text{B}_{10}\text{H}_{11}$ cage and two coordinated THF molecules in a distorted-tetrahedral geometry with Cent-Ln-Bent angles of 123.4 and 126.7° (Figure 4; Bent = centroid of the C_2B_4 bonding face; Cent = centroid of the cyclopentadienyl ring).

The average Sm–C(C_5 ring) distances of $2.664(2)$ and $2.748(2)$ Å compare rather well with those found in other Me_2Si -bridged cyclopentadienyl samarium(III) complexes.²⁵ The average Sm–cage atom (C_2B_4 face) distances of $2.764(3)$ and $2.841(3)$ Å are close to the values of 2.805 – 2.859 Å that would be expected by subtracting the difference, 0.171 Å, between Shannon's ionic radii²⁰ of Sm^{3+} (1.079 Å) and Eu^{2+} (1.250 Å) from the average Eu–cage atom distances, 2.976 and 2.989 Å in $[(\text{C}_2\text{B}_{10}\text{H}_{12})\text{Eu}(\text{MeCN})_3]_n$ ⁹ or 3.03 Å in $[(\text{C}_2\text{B}_{10}\text{H}_{12})_2\text{Eu}(\text{THF})_2]^{2-}$.⁹ On the other hand, the Sm–Cent distances (2.390 and 2.465 Å) are significantly longer than those (2.226 and 2.298 Å) of Sm–Bent. These differences should be due to the much larger C_2B_4 face of the carborane cage, not to the ligating properties of the anions. Otherwise, the

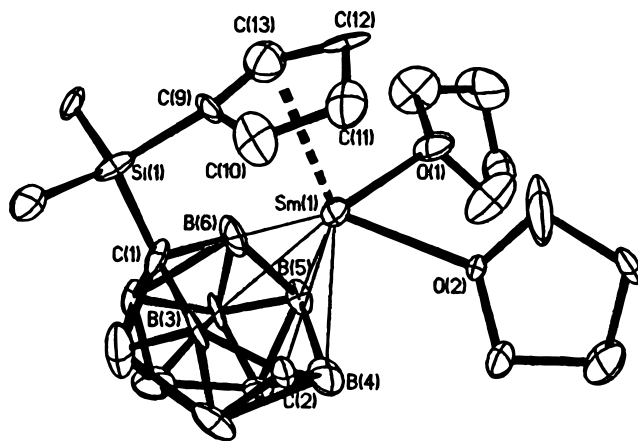


Figure 4. Molecular structure of $[\eta^5:\eta^6\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)\text{-(C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}(\text{THF})_2$ (**19**) (thermal ellipsoids drawn at the 35% probability level).

ligand redistribution products would be expected to be isolated.⁹ The average Sm–O distances of $2.463(2)$ and $2.392(2)$ Å fall in the range normally observed in THF-coordinated organosamarium(III) compounds.²¹

On the basis of the spectroscopic studies and elemental analyses as well as the similarities between the lanthanide analogues, it is reasonable to conclude that compound **18** has the same structure as **19**, and compounds **20** and **21** may have a structure similar to that of **19**.

The formation of compound **19** is an interesting question. Apparently, it was formed via an unexpected redox reaction in which Sm^{2+} was oxidized to Sm^{3+} and, meanwhile, the neutral carborane was reduced to the dianion. To gain some insight into this new reaction, ^{11}B NMR was used as a probe to examine some reactions. The results show that there are no reactions between SmI_2 and $\text{C}_2\text{B}_{10}\text{H}_{12}$ or $(\text{CH}_2\text{C}_6\text{H}_5)_2\text{C}_2\text{B}_{10}\text{H}_{10}$ in THF, although SmI_2 is a well-known reducing reagent in organic synthesis.²⁶ $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Sm}(\text{THF})_2$, however, can reduce $\text{C}_2\text{B}_{10}\text{H}_{12}$ in THF to the corresponding dianions. The ^{11}B NMR spectrum of the latter reaction product exhibited six new peaks at the chemical shifts δ 14.9 , 10.6 , -0.7 , -7.2 , -9.3 , and -23.9 , with a 2:2:2:2:1:1 splitting pattern, and the intensities of these resonances increased as the time of the reaction was prolonged. On the other hand, the color of the solution changed from dark green to orange-yellow. These results indicate that $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Sm}(\text{THF})_2$ is a stronger reducing reagent than SmI_2 ; in other words, cyclopentadienyl can enhance the reducing ability of Sm^{2+} . To get further evidence of the reaction intermediate, another experiment was performed. Interaction of YbI_2 with 2 equiv of $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Na}$ in THF at room temperature yielded the red compound $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{Yb}(\text{THF})_2$ (**22**) in 66% yield (Scheme 6). Unlike the SmI_2 case, no redox reaction was observed between the less powerful reducing reagent YbI_2 ²⁷ and $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Na}$ in THF. Compound **22** has been fully characterized by spectroscopic and elemental analyses as well as X-ray crystallography.

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(27) The reduction potentials for the $\text{Ln}^{3+}/\text{Ln}^{2+}$ couple are -1.1 V for Yb and -1.5 V for Sm, respectively; see: Evans, W. J. *Polyhedron* **1987**, *6*, 803–835.

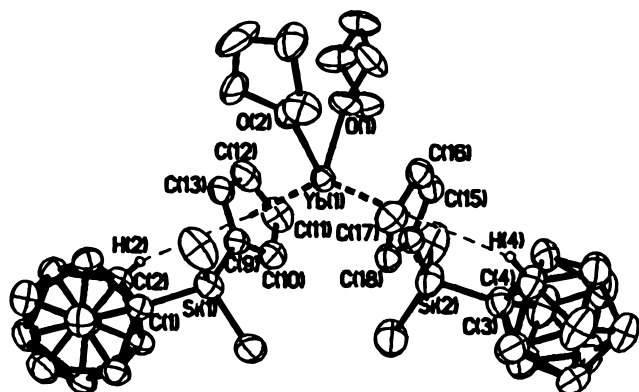


Figure 5. Molecular structure of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{Yb}(\text{THF})_2$ (**22**) (thermal ellipsoids drawn at the 35% probability level).

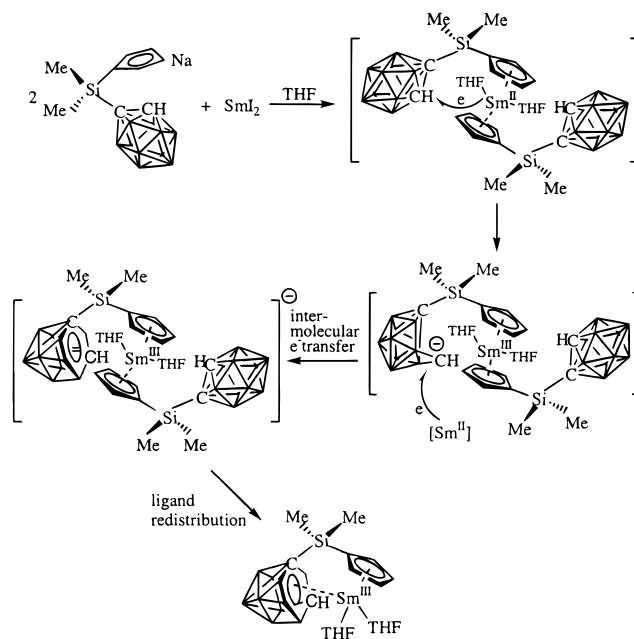
As shown in Figure 5, the compound adopts the pseudo-tetrahedral, bent metallocene motif commonly observed for $\text{Cp}_2\text{Yb}^{\text{II}}\text{L}_2$ complexes.²⁸ There is no direct interaction between Yb^{2+} and any one of the B–H bonds from the carboranes, and the two cages stay away from each other. Similar to compounds $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{LnCl}(\text{THF})_2$ and $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{-LnCl}_2(\text{THF})_3$, the nonclassical hydrogen bonds between the H atoms on carbon atoms of the carborane cages and the cyclopentadienyl rings are present in **22** with distances of 2.690 and 3.161 Å, resulting in the smaller C(3)–Si(2)–C(14) and C(1)–Si(1)–C(9) angles of 104.82(8) and 107.21(7)°, respectively. It is notable that the smaller C(3)–Si(2)–C(14) angle is associated with the shorter H–Cent distance. The average Yb–C distance of 2.725(2) Å, the average Yb–O distance of 2.426(2) Å, the Cent–Yb–Cent angle of 134.0°, and the O(1)–Yb–O(2) angle of 83.3(1)° all fall in the range normally observed for $\text{Cp}_2\text{Yb}^{\text{II}}\text{L}_2$ types of compounds.²⁸

On the basis of the above results, it is reasonable to suggest that $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{Sm}(\text{THF})_2$ may serve as the first intermediate in the formation of **19**. Intramolecular one-electron transfer from the Sm(II) intermediate to the cage gives $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})][\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}^{\text{III}}(\text{THF})_2$,²⁹ followed by intermolecular one-electron transfer from the Sm(II) center to the monoanion, generating $\{[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})][\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}^{\text{III}}(\text{THF})_2\}^-$. Ligand redistribution affords $[\eta^5\text{-}\eta^6\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}(\text{THF})_2$ (**19**) and other unidentified compounds. This plausible reaction mechanism is outlined in Scheme 7.

Conclusion

By using the advantages of the cyclopentadienyl group, icosahedral carborane, and the bridged ligand, a very versatile ligand has been designed and successfully prepared. It can be conveniently converted into the monoanion, dianion, and trianion by treatment with

Scheme 7



various reagents. Applications of this ligand to Ln(III) and Ln(II) chemistry have resulted in the isolation and structural characterization of a series of organolanthanide compounds including organolanthanide dichloride and monochloride, carboranyl, and lanthanacarboranes, where the carborane serves as a bulky substituent, or a σ ligand, or a π ligand, respectively. This ligand not only offers organolanthanide compounds with high versatility but also prevents the mixed lanthanacarboranes from undergoing disproportionation reactions.³⁰ The relationships between various types of compounds were also investigated.

Nonclassical hydrogen bonds between the H atoms on carbon atoms of the carborane cages and the cyclopentadienyl rings in the solid-state structures of $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{LnCl}_2(\text{THF})_3$, $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{LnCl}(\text{THF})_2$, and $[\eta^5\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Yb}(\text{THF})_2$ are very informative, which helps to distinguish the C atoms from the boron atoms in the carborane cages. As shown by the ¹¹B NMR spectra, the solution structures of these organolanthanide compounds may differ from their solid-state structures, and a fluxional process may be present in the solutions.^{9,23}

As evidenced by a very recent publication,³¹ this ligand should have a rich chemistry with d-transition metals.

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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 **8**, **10**, and **15–17**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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