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Sidearm Effects. Synthesis, Structural Characterization, and Reactivity of Rare Earth Complexes Incorporating a Linked Carboranyl-Indenyl Ligand with a Tethered Oxygen Atom[§]

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New ether-functionalized carboranyl-indenyl hybrid ligands were prepared. They can prevent lanthanocene chlorides from ligand redistribution reactions and offer samarium(II) complexes unusual reactivities. Treatment of Me₂SiCl(C₉H₆CH₂CH₂OMe) with 1 equiv of $Li_2C_2B_{10}H_{10}$ in toluene/Et₂O afforded the monolithium salt [Me₂Si(C₉H₅CH₂CH₂OMe)- $(C_2B_{10}H_{11})$]Li(OEt₂) (2). Interaction of 2 with 1 equiv of *n*-BuLi in Et₂O produced the dilithium salt [Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀H₁₀)]Li₂(OEt₂)₂ (3). Reaction of 3 with 1 equiv of LnCl₃ at room temperature gave the complex salts of general formula $[{[\eta^5:\sigma-Me_2Si(C_9H_5CH_2CH_2 OMe)(C_2B_{10}H_{10})]Ln(THF)(\mu-Cl)_3Ln[\eta^5:\eta^1:\sigma-Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]_2\{Li(THF)\}]-Chernel (Line)(Lin$ $[\text{Li}(\text{THF})_4]$ (Ln = Y (4), Yb (5)). Upon heating, 5 was converted into $[\eta^5:\eta^1:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_5 CH_2CH_2OMe$)($C_2B_{10}H_{10}$)]Yb(THF)(μ -Cl)₂Yb[$\eta^5:\eta^1:\sigma$ -Me₂Si($C_9H_5CH_2CH_2OMe$)($C_2B_{10}H_{10}$)] (**6**) by eliminating LiCl. Treatment of 4 or 5 with 2 equiv of group 1 metal amides gave organorare-earth amide complexes $[\eta^5:\eta^1:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀H₁₀)]Y(NHC₆H₃-2,5-'Bu₂)- $(\mu$ -Cl)Li(THF)₃ (8) or $[\eta^{5}:\eta^{1}:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀H₁₀)]Yb(NHC₆H₃-2,6-/Pr₂)(μ -Cl)Li(THF)₃ (9). An equimolar reaction of SmI_2 with 3 in THF generated, after addition of LiCl, $[\{[\eta^5:\sigma-Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]_2Sm\}\{Li(THF)\}]_n$ (10) and $[\{\eta^5:\eta^1:\eta^6-Me_2-H_2CH_2OMe\}(C_2B_{10}H_{10})]_2Sm\}\{Li(THF)\}]_n$ $Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})Sm_{2}(\mu-Cl)][Li(THF)_4]$ (11). In sharp contrast, a less reactive YbI₂ reacted with **3** in THF, producing only salt metathesis product $[\eta^5:\eta^1:\sigma-\text{Me}_2\text{Si}(C_9\text{H}_5 CH_2CH_2OMe$)($C_2B_{10}H_{10}$)[Yb(DME)(THF) (12). 12 reacted with 1 equiv of 3 to give the ionic complex {[$(\mu - \eta^5: \eta^2): \eta^1: \sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀H₁₀)]₂Yb}{Li(THF)₂}₂ (**13**). All complexes were characterized by various spectroscopic techniques and elemental analyses. The structures of **5**, **6**, and **8–13** were further confirmed by single-crystal X-ray analyses.

Introduction

Cyclopentadienyl or indenyl ligands with Lewis base functionalities have found many applications in rare earth chemistry.¹ The tethered donors can coordinate to the lanthanides, satisfying the steric requirement so as to prevent lanthanocenes from ligand redistribution reactions.² Thus a large variety of metallocene derivatives of the lanthanides have been prepared in the past decade or so.¹⁻⁴ On the other hand, the donor functionality has a strong influence on the activity of organolanthanide complexes.^{4,5} If the substrates cannot compete with the donor group of the ligand for the vacant coordination site on the metal center, a decreased catalytic activity in comparison to unfunctionalized systems would be expected. In contrast, for those substrates with a higher Lewis base strength, the functionalized sidearm just serves as a protecting unit and does not block the metal center, and increased activity would be anticipated.⁴

 $^{{}^{\$}}$ Dedicated to Prof. Changtao Qian on the occasion of his 70th birthday.

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Our previous work shows that linked carboranylindenyl ligands $[Me_2A(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ (A = C,⁶ Si⁷) cannot stabilize half-sandwich rare earth complexes of the type $[\eta^5:\sigma$ -Me₂A(C₉H₆)(C₂B₁₀H₁₀)]LnCl.⁸ Equimolar reactions between $M_2[Me_2A(C_9H_6)(C_2B_{10}H_{10})]$ (M = Li, Na) and LnCl₃ always resulted in the formation of fullsandwich complexes $[\eta^5:\sigma-Me_2A(C_9H_6)(C_2B_{10}H_{10})]_2Ln^-$, which were also formed from the reaction of M₂[Me₂A- $(C_9H_6)(C_2B_{10}H_{10})$ with SmI₂.^{6,7} However, when a functionalized sidearm MeOCH₂CH₂ was tethered to this linked ligand, the novel samaracarborane $[\{\eta^5:\eta^1:\eta^6-Me_2 Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})Sm\}_2(\mu-Cl)][Li(THF)_4]$ was isolated from an equimolar reaction of [Me₂Si(C₉H₅- CH_2CH_2OMe)($C_2B_{10}H_{10}$)]Li₂(OEt₂)₂·LiCl with SmI₂, as shown in our preliminary communication.⁹ This result demonstrated that functionalized sidearms have significant effects on the reactivity of lanthanide complexes. In this contribution, we report a full account on the synthesis, structural characterization, and reactivity of rare earth complexes with the donor-functionalized carboranyl-indenyl ligand [Me₂Si(C₉H₅CH₂CH₂OMe)- $(C_2B_{10}H_{10})]^{2-}$.

Experimental Section

General Procedures. All experiments were preformed 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. SmI₂(THF)_x,¹⁰ C₉H₇CH₂CH₂OMe,¹¹ and Li₂C₂B₁₀H₁₀⁸ were prepared according to 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 Perkin-Elmer 1600 Fourier transform spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. ¹¹B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 MHz. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external BF₃. OEt₂ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd., U.K.

Preparation of Me₂SiCl(C₉H₆CH₂CH₂OMe) (1). A 1.60 M solution of n-BuLi in hexane (36.0 mL, 57.6 mmol) was slowly added to a solution of MeOCH₂CH₂C₉H₇ (10.0 g, 57.4 mmol) in Et₂O (200 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The resulting solution was then cooled to 0 °C, and Me₂SiCl₂ (30.0 mL, 230 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 20 h. After removal of the precipitate, the solvent and excess Me₂SiCl₂ were pumped off to give 1 as a yellowish oil (14.0 g, 91%), which was pure enough for the next step of the reaction. ¹H NMR (CDCl₃): δ 7.60 (d, J = 7.2Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.35 (dd, J = 7.5 and 7.5 Hz, 1H), 7.26 (dd, J = 7.5 and 7.2 Hz, 1H), 6.42 (s, 1H), 3.69 (s, 1H) (C₉ H_6), 3.72 (t, J = 7.2 Hz, 2H), 3.41 (s, 3H), 2.96 (t, J = 7.2 Hz, 2H) (CH₂CH₂OCH₃), 0.24 (s, 3H), 0.21 (s, 3H) (Si-

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(CH₃)₂). ¹³C NMR (CDCl₃): δ 145.17, 144.01, 141.19, 129.48, 126.21, 125.05, 124.07, 119.86, 46.44 (C9H6), 72.16, 59.21, 28.77 (CH2CH2OCH3), 0.58, 0.24 (Si(CH3)2). MS (EI): 266 (M+).

Preparation of [Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀H₁₁)]Li-(OEt₂) (2). A 1.60 M solution of *n*-BuLi in hexane (34.7 mL, 55.6 mmol) was added dropwise with stirring to a solution of o-C₂B₁₀H₁₂ (4.00 g, 27.8 mmol) in a dry toluene/diethyl ether (2:1, 45 mL) mixture at 0 °C. The reaction mixture was warmed to room temperature and stirred for 0.5 h. The resulting solution was then cooled to 0 °C, and Me₂SiCl(C₉H₆-CH₂CH₂OMe) (1; 7.41 g, 27.8 mmol) in a toluene/diethyl ether (2:1, 10 mL) mixture was slowly added. The mixture was stirred at room temperature for 20 h. Removal of the solvents afforded a sticky solid, which was extracted with diethyl ether (20 mL \times 2). The solutions were combined and concentrated to give a pale yellow sticky solid. Recrystallization from diethyl ether/hexane produced 2 as a pale yellow crystalline solid (11.2 g, 88%). ¹H NMR (pyridine- d_5): δ 8.06 (d, J = 7.2 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.26 (s, 1H), 7.11 (m, 2H) (C₉H₅), 3.96 (t, J = 7.8 Hz, 2H), 3.64 (t, J = 7.8 Hz, 2H), 3.32 (s, 3H) $(CH_2CH_2OCH_3)$, 3.74 (br s, 1H) (cage CH), 3.36 (q, J = 6.9 Hz, 4H), 1.12 (t, J = 6.9 Hz, 6H) (O(CH₂CH₃)₂), 0.80 (s, 6H) (Si- $(CH_3)_2$). ¹³C NMR (pyridine- d_5): δ 139.51, 135.00, 128.22, 120.22, 117.71, 114.94, 113.86, 109.56, 86.82 (C9H5), 76.21, 58.45, 30.33 (CH₂CH₂OCH₃), 74.45, 64.88 (C₂B₁₀H₁₁), 66.15, 15.88 (O(CH₂CH₃)₂), 0.34 (Si(CH₃)₂). ¹¹B NMR (pyridine-d₅): δ -2.24 (2), -5.98 (1), -7.40 (2), -11.61 (3), -12.58 (2). IR (KBr, cm^-1): ν_{BH} 2563 (vs). Anal. Calcd for $C_{20}H_{39}B_{10}LiO_2Si$: C, 52.83; H, 8.65. Found: C, 52.53; H, 8.51.

Preparation of [Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀H₁₀)]-Li₂(OEt₂)₂ (3). To a suspension of [Me₂Si(C₉H₆CH₂CH₂OMe)- $(C_2B_{10}H_{11})$]Li(OEt₂) (2; 10.50 g, 23.1 mmol) in a mixed solvent of n-hexane/diethyl ether (2:1, 60 mL) was slowly added a 1.60 M solution of *n*-BuLi in hexane (14.5 mL, 23.2 mmol) at 0 °C. The mixture was stirred at 0 °C for 6 h and at room temperature overnight. The precipitate was collected and washed with *n*-hexane (3×15 mL), affording **3** as a pale yellow solid (10.30 g, 84%). ¹H NMR (pyridine- d_5): δ 8.22 (d, J = 7.5Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.23 (s, 1H), 7.02 (m, 2H) (C_9H_5) , 3.64 (t, J = 7.8 Hz, 2H), 3.31 (t, J = 7.8 Hz, 2H), 3.28 (s, 3H) ($CH_2CH_2OCH_3$), 3.36 (q, J = 6.9 Hz, 8H), 1.12 (t, J =6.9 Hz, 12H) (O(CH₂CH₃)₂), 0.92 (s, 6H) (Si(CH₃)₂). ¹³C NMR (pyridine-*d*₅): δ 137.91, 133.55, 126.60, 122.31, 118.01, 115.44, 114.38, 109.18, 89.08 (C₉H₅), 75.12, 58.19, 29.54 (CH₂CH₂OCH₃), 77.98, 63.88 (C₂B₁₀H₁₁), 66.15, 15.88 (O(CH₂CH₃)₂), 1.97 (Si- $(CH_3)_2$). ¹¹B NMR (pyridine- d_5): $\delta -1.75$ (1), -5.12 (3), -8.07(1), -9.48 (2), -10.48 (3). IR (KBr, cm⁻¹): ν_{BH} 2555 (vs). Anal. Calcd for C₂₄H₄₈B₁₀Li₂O₃Si: C, 53.91; H, 9.05. Found: C, 54.27; H, 8.87.

Preparation of $[{[\eta^5:\sigma-Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10} H_{10}]Y(THF)(\mu-Cl)_{3}Y[\eta^{5}:\eta^{1}:\sigma-Me_{2}Si(C_{9}H_{5}CH_{2}CH_{2}OMe)-$ (C₂B₁₀H₁₀)]}₂{Li(THF)}][Li(THF)₄] (4). To a suspension of YCl₃ (0.20 g, 1.0 mmol) in THF (20 mL) was slowly added a THF (15 mL) solution of 3 (0.53 g, 1.0 mmol) at room temperature, and the mixture was stirred for 6 h. Removal of the solvent gave a sticky solid, to which was added 15 mL of toluene. The mixture was heated at reflux temperature for 0.5 h. After removal of the white precipitate, the solvent was pumped off again, affording a white solid. Recrystallization from a mixed solvent of *n*-hexane/toluene (1:5) produced **4** as colorless crystals (0.49 g, 76%). ¹H NMR (pyridine- d_5): δ 8.06 (d, J = 7.8 Hz, 4H), 7.91 (d, J = 7.5 Hz, 4H), 7.21 (br s, 4H), 7.10 (m, 8H) (C₉H₅), 3.97 (t, J = 7.8 Hz, 8H), 3.60 (t, J = 7.8Hz, 8H), 3.31 (s, 12H) (CH₂CH₂OCH₃), 3.63 (m, 24H), 1.60 (m, 24H) (THF), 0.80 (s, 24H) (Si(CH₃)₂). ¹³C NMR (pyridine-d₅): δ 139.48, 134.98, 126.10, 121.74, 120.21, 117.71, 114.94, 113.86, 109.58 (C_9H_5), 76.20, 58.95, 30.31 ($CH_2CH_2OCH_3$), 86.81, 64.86 (C₂B₁₀H₁₁), 68.18, 26.16 (O(CH₂CH₂)₂), 0.34 (Si-(CH₃)₂). ¹¹B NMR (pyridine- d_5): δ -6.54 (4), -8.92 (8), -13.28 (20), -17.05 (8). IR (KBr, cm⁻¹): ν_{BH} 2567 (vs). Anal. Calcd

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for $C_{92}H_{168}B_{40}Cl_6Li_2O_{11}Si_4Y_4$: C, 42.87; H, 6.57. Found: C, 42.65; H, 6.49.

Preparation of [{[η⁵:σ-Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀-H₁₀)]Yb(THF)(μ-Cl)₃Yb[η⁵:η¹:σ-Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀-H₁₀)]₂{Li(THF)}][Li(THF)₄]·C₆H₅CH₃ (5·C₆H₅CH₃). This complex was prepared as dark red crystals from YbCl₃ (0.28 g, 1.0 mmol) and 3 (0.53 g, 1.0 mmol) in THF (30 mL) using the procedure identical to that reported for **4**: yield 0.55 g (73%). ¹H NMR (pyridine-*d*₅): δ 3.50 (s), 1.46 (s) (THF), plus many broad, unresolved resonances. ¹¹B NMR (pyridine-*d*₅): δ -0.94 (8), -6.17 (16), -9.76 (8), -11.50 (8). IR (KBr, cm⁻¹): ν_{BH} 2571 (vs). Anal. Calcd for C₉₉H₁₇₆B₄₀Cl₆Li₂O₁₁Si₄Yb₄: C, 39.56; H, 5.90. Found: C, 39.21; H, 5.98.

Preparation of [{ $\eta^{5:}\eta^{1:}\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀-H₁₀)}**Yb(THF)**(μ -Cl)₂Yb{ $\eta^{5:}\eta^{1:}\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂-B₁₀H₁₀)}**·**C₆H₅CH₃ (6·C₆H₅CH₃). A toluene/THF (10:1, 10 mL) solution of 5 (0.27 g, 0.18 mmol) was heated at 80 °C for 1 h. After removal of the precipitate, the clear solution was slowly cooled to room temperature to give 6·C₆H₅CH₃ as dark red crystals (0.16 g, 67%). ¹H NMR (pyridine- d_5): many broad, unresolved resonances. ¹¹B NMR (pyridine- d_5): δ -0.48 (2), -3.64 (4), -8.96 (8), -11.02 (4), -13.95 (2). IR (KBr, cm⁻¹): ν_{BH} 2548 (vs). Anal. Calcd for C₄₃H₇₂B₂₀Cl₂O₃Si₂Yb₂: C, 38.94; H, 5.47. Found: C, 38.84; H, 5.57.

Preparation of $[\eta^5:\eta^1:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀-H₁₀)]Sm(THF)(μ -Cl)₂Sm[η ⁵: η ¹: σ -Me₂Si(C₉H₅CH₂CH₂OMe)-(C₂B₁₀H₁₀)] (7). To a suspension of SmCl₃ (0.13 g, 0.50 mmol) in THF (10 mL) was slowly added a THF (10 mL) solution of 3 (0.27 g, 0.50 mmol) at room temperature, and the mixture was stirred overnight. The color of the solution gradually changed from pale yellow to orange-red with disappearance of SmCl₃. After removal of THF under vacuum, toluene (15 mL) was added to the resulting orange-red solid. The mixture was heated at reflux temperature for 1 h. The precipitate (LiCl) was filtered off, and the resulting solution was concentrated to dryness, affording an orange-red solid. Recrystallization from a mixed toluene/THF (10:1) solution gave 7 as orangered crystals (0.24 g, 81%). ¹H NMR (pyridine-d₅): many broad, unresolved resonances. ¹¹B NMR (pyridine- d_5): δ –0.01 (4), -4.44 (4), -8.02 (6), -9.82 (2), -14.08 (4). IR (Kbr, cm⁻¹): $\nu_{\rm BH}$ 2568 (vs). Anal. Calcd for C₃₆H₆₄B₂₀Cl₂O₃Si₂Sm₂: C, 36.37; H, 5.43. Found: C, 36.32; H, 5.57.

Preparation of [75:71:0-Me2Si(C9H5CH2CH2OMe)(C2B10-H10)]Y(NHC6H3-2,5-'Bu2)(µ-Cl)Li(THF)3 (8). To a THF (15 mL) solution of 4 (0.35 g, 0.27 mmol) was slowly added a THF (10 mL) solution of KNHC₆H₃-2,5-Bu^t₂ (0.13 g, 0.54 mmol) at room temperature, and the mixture was stirred overnight. After removal of THF, toluene (17 mL) was added to the resulting solid. The mixture was heated at reflux temperature for 1 h. The precipitate was filtered off. The clear solution was slowly cooled to room temperature, affording 8 as colorless crystals (0.36 g, 72%). ¹H NMR (pyridine- d_5): δ 8.36 (d, J =8.1 Hz, 1H), 7.45 (dd, *J* = 6.9 and 7.2 Hz, 1H), 7.33 (br s, 1H), 7.31 (dd, J = 7.2 and 6.9 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.00 (d, J = 8.1 Hz, 1H), 6.45 (br s, 1H), 6.21 (d, J = 7.8 Hz, 1H) (C₉ H_5 and C₆ H_3), 4.25 (br s, 1H) (NH), 3.55 (t, J = 7.8 Hz, 2H), 3.15 (s, 3H), 3.07 (t, J = 7.8 Hz, 2H) ($CH_2CH_2OCH_3$), 3.65 (m, 12H), 1.60 (m, 12H) (THF), 1.53 (br s, 9H), 1.18 (br s, 9H) (t-C₄H₉), 0.80 (s, 3H), 0.78 (s, 3H) (Si(CH₃)₂). ¹³C NMR (pyridine-d₅): δ 157.64, 149.83, 135.47, 131.30, 130.65, 129.38, 129.13, 127.05, 123.38, 123.30, 122.70, 117.66, 116.43, 109.75, 104.23 (C_9H_5 and C_6H_3), 77.50, 59.87, 31.47 ($CH_2CH_2OCH_3$), 82.47, 63.49 (C₂B₁₀H₁₀), 69.31, 27.29 (THF), 35.62, 35.52, 33.18, 31.93 (t-C₄H₉), 1.69, 1.16 (Si(CH₃)₂). ¹¹B NMR (pyridine-d₅): δ -5.05 (4), -10.61 (6). IR (KBr, cm⁻¹): $\nu_{\rm BH}$ 2568 (vs). Anal. Calcd for C₃₄H₅₈B₁₀ClLiNO₂SiY (8 – 2THF): C, 52.33; H, 7.49; N, 1.80. Found: C, 52.54; H, 7.61; N, 1.63.

Preparation of $[\eta^5:\eta^1:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀-H₁₀)]**Yb**(NHC₆H₃-2,6-'Pr₂)(μ -Cl)Li(THF)₃ (9). This complex was prepared as dark red crystals from 5 (0.36 g, 0.24 mmol) and NaNHC₆H₃-2,6-'Pr₂ (0.094 g, 0.48 mmol) in THF (25 mL)

using the procedure identical to that reported for **8**: yield 0.31 g (65%). ¹H NMR (pyridine- d_5): δ 3.62 (s), 1.59 (s) (THF), plus many broad, unresolved resonances. ¹¹B NMR (pyridine- d_5): δ -1.46 (2), -5.96 (1), -7.01 (1), -11.18 (6). IR (KBr, cm⁻¹): $\nu_{\rm BH}$ 2577 (vs). Anal. Calcd for C₃₂H₅₄B₁₀ClLiNO₂SiYb (**9** – 2THF): C, 45.95; H, 6.51; N, 1.68. Found: C, 45.96; H, 6.74; N, 1.80.

Preparation of [{ $[\eta^5:\sigma-Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10} H_{10}$]₂Sm}{Li(THF)}]_n (10). To a THF solution of SmI₂(THF)_x (5.0 mL, 0.50 mmol) was slowly added a THF solution of 3 (0.27 g, 0.50 mmol) at room temperature, and the reaction mixture was stirred overnight. The color of the solution slowly changed from dark blue to dark red. After removal of THF, toluene (15 mL) was added to the resulting sticky solid, and the mixture was refluxed for 3 h. The solvent was then removed, and the resulting orange-red solid was extracted with a mixed solvent of toluene and THF (10:1, 3×10 mL). The solutions were combined and concentrated to about 15 mL. 10 was isolated as orange-red crystals after this solution stood at room temperature for 5 days (95 mg, 39% based on 3). After addition of dry LiCl (0.10 g, 2.3 mmol) to the mother liquor and the suspension was stirred at room temperature overnight, the precipitate was filtered off, giving a clear dark red solution. Dark red crystals, identified as $[\{\eta^5:\eta^1:\eta^6-Me_2Si(C_9H_5CH_2CH_2-$ OMe)($C_2B_{10}H_{10}$)Sm}₂(μ -Cl)][Li(THF)₄] (11) by a single-crystal X-ray analysis, were isolated after this solution stood at room temperature for a week (40 mg, 12%). For 10: ¹H NMR (pyridine- d_5): δ 14.36 (br s, 2H), 10.74 (d, J = 9.0 Hz, 2H), 7.35 (t, J = 9.0 Hz, 2H), 7.16 (d, J = 9.0 Hz, 2H), 6.53 (t, J =9.0 Hz, 2H) (C₉H₅), 3.63 (br s, 4H), 1.59 (br s, 4H) (THF), 4.83 (br s, 4H), 3.75 (br s, 4H), 3.40 (s, 6H) (CH₂CH₂OCH₃), 0.94 (s, 12H) (Si(CH₃)₂). ¹³C NMR (pyridine- d_5): δ 138.37, 136.18, $129.00, 126.10, 121.21, 120.23, 119.52, 116.22, 103.55 (C_9H_5),$ 85.07 (C2B10H11), 76.21, 58.75, 30.91 (CH2CH2OCH3), 68.17, 26.15 (THF), 2.60, 0.37 (Si(CH₃)₂). ¹¹B NMR (pyridine-d₅): 32.50 (4), -5.15 (16). IR (KBr, cm⁻¹): ν_{BH} 2572 (vs). Anal. Calcd for C₅₄H₈₈B₂₀LiO₄Si₂Sm: C, 44.37; H, 6.62. Found: C, 44.15; H, 6.38.

Preparation of [$\{\eta^5: \eta^1: \eta^6: Me_2Si(C_9H_5CH_2CH_2OMe\})(C_2B_{10}-C_2B_$ $H_{10}Sm_{2}(\mu-Cl)$ [Li(THF)₄] (11). To a THF solution of SmI₂-(THF)_x (10.0 mL, 1.0 mmol) was slowly added a THF (20 mL) solution of 3 (0.53 g, 1.0 mmol) at room temperature, to which was added LiCl (0.10 g, 2.3 mmol). The reaction mixture was stirred at room temperature overnight. The color of the solution changed from dark blue to dark red. Workup using the procedure identical to that reported for 10 gave 11 as dark red crystals (0.30 g, 43%). ¹H NMR (pyridine- d_5): δ 13.89 (br s, 1H), 10.48 (d, J = 9.0 Hz, 1H), 9.82 (d, J = 9.0 Hz, 1H), 6.93 (br s, 1H), 6.52 (m, 1H), 6.20 (m, 1H), 5.91 (m, 1H), 5.12 (br s, 1H), 4.40 (br s, 1H), 4.03 (br s, 1H) (C_9H_5), 3.86 (s, 6H), 3.36 (br s, 4H), 3.17 (br s, 4H) (CH₂CH₂OCH₃), 3.65 (m, 16H), 1.59 (m, 16H) (THF), -0.28 (s, 6H), -0.51 (s, 6H) (Si(CH₃)₂). ¹³C NMR (pyridine-*d*₅): δ 129.35, 128.60, 125.70, 122.69, 121.33, 120.84, 119.98, 119.32 (C_9H_5), 69.50, 58.67, 31.65 $(CH_2CH_2OCH_3)$, 88.43, 65.73 $(C_2B_{10}H_{11})$, 67.79, 22.78 (THF), 0.24, 0.08 (Si(CH_3)₂). ¹¹B NMR (pyridine- d_5): δ -3.5 (4), -9.8-(4), -14.5(8), -15.0(4). IR (KBr, cm⁻¹): ν_{BH} 2538 (vs), 2450 (m). Anal. Calcd for $C_{48}H_{88}B_{20}ClLiO_6Si_2Sm_2$: C, 41.87; H, 6.44. Found: C, 41.66; H, 6.57.

This complex was also obtained in 47% yield via the equimolar reaction of $SmI_2(THF)_x$ with $[Me_2Si(C_9H_5CH_2CH_2-OMe)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ ·LiCl prepared directly from **1** and $C_2B_{10}H_{10}Li_2$ followed by treatment with 1 equiv of *n*-BuLi.⁹

Preparation of $[\eta^{5}:\eta^{1}:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀-H₁₀)]**Yb(DME)(THF)** (12). To a THF solution of YbI₂(THF)_x (19.0 mL, 1.0 mmol) was slowly added a THF solution of **3** (0.53 g, 1.0 mmol) at room temperature. The color of the solution immediately changed from yellow to orange-red. The reaction mixture was then stirred at room temperature overnight. After removal of THF, the resulting solid was washed with hot toluene (3 × 5 mL) to remove LiI. The orange-

Table 1. Crystal Data and Summary of Data Collection and Refinement for 5, 6, 8, and 9

	5-toluene	6-toluene	8	9		
formula	$C_{99}H_{176}B_{40}Cl_6Li_2O_{11}Si_4Yb_4$	C43H72B20Cl2O3Si2Yb2	C42H74B10ClLiNO4SiY	C40H70B10ClLiNO4SiYb		
cryst size (mm)	0.66 imes 0.13 imes 0.05	0.50 imes 0.40 imes 0.25	0.60 imes 0.25 imes 0.17	0.52 imes 0.20 imes 0.06		
fw	3005.9	1326.4	924.5	980.6		
cryst syst	monoclinic	triclinic	triclinic	monoclinic		
space group	C2/c	$P\overline{1}$	$P\overline{1}$	$P2_{1}/c$		
a, Å	33.129(1)	9.918(1)	10.104(2)	21.775(3)		
b, Å	11.238(1)	14.955(1)	12.881(3)	12.155(2)		
<i>c</i> , Å	45.825(2)	21.076(1)	21.254(4)	19.751(3)		
α, deg	90	69.87(1)	90.99(3)	90		
β , deg	105.61(1)	84.99(1)	100.25(3)	100.72(1)		
γ , deg	90	78.39(1)	104.97(3)	90		
V, Å ³	16431.8(11)	2874.5(3)	2623.8(9)	5136.4(13)		
Ζ	4	2	2	4		
D_{calcd} , Mg/m ³	1.215	1.532	1.170	1.268		
radiation (λ), Å	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)		
2θ range, deg	2.6 to 50.0	2.0 to 50.0	3.2 to 50.0	3.8 to 52.0		
μ , mm ⁻¹	2.424	3.405	1.222	1.932		
F(000)	6008	1312	976	2012		
no. of obsd reflns	10 626	13 550	4340	10 075		
no. of params refnd	672	649	555	543		
goodness of fit	0.937	0.969	1.212	0.875		
R1	0.056	0.028	0.115	0.039		
wR2	0.147	0.069	0.276	0.089		

red solid was then extracted with a mixed solvent of toluene and DME (10:1, 3×10 mL). The solutions were combined and concentrated to 15 mL, from which orange crystals were obtained after this solution stood at room temperature for 5 days (0.51 g, 72%). ¹H NMR (pyridine- d_5): δ 8.15 (d, J = 8.1Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.00 (m, 2H), 6.80 (dd, J = 8.1 Hz, 1H) (C₉H₅), 3.66 (m, 4H) (THF), 3.47 (s, 4H) (DME), 3.25 (br s, 9H) (DME + $CH_2CH_2OCH_3$), 3.18 (m, 4H) (CH_2CH_2 -OCH₃), 1.62 (m, 4H) (THF), 0.84 (s, 3H), 0.70 (s, 3H), $(Si(CH_3)_2)$. ¹³C NMR (pyridine- d_5): δ 144.43, 131.77, 127.98, 121.57, 120.21, 119.78, 114.52, 111.56, 98.29 (C₉H₅), 76.82, 73.51, 60.10, 60.62, 29.95, 27.28 (CH₂CH₂OCH₃, THF, DME), 82.27, 69.31 (C2B10H11), 2.14, 1.52 (Si(CH3)2). 11B NMR (pyridine- d_5): δ -3.60 (2), -10.13 (2), -14.22 (6). IR (KBr, cm⁻¹): ν_{BH} 2562 (vs). Anal. Calcd for $C_{20}H_{38}B_{10}O_3SiYb$ (12 - THF): C, 37.78; H, 6.03. Found: C, 37.66; H, 6.33.

Preparation of { $[(\mu - \eta^5: \eta^2): \eta^1: \sigma - Me_2Si(C_9H_5CH_2CH_2OMe) (C_2B_{10}H_{10})]_2Yb$ { $Li(THF)_2$ } C_7H_8 (13 C_7H_8). To a THF (16) mL) solution of 12 (0.35 g, 0.50 mmol) was slowly added a THF solution of 3 (0.26 g, 0.50 mmol) at room temperature. The color of the solution immediately changed from orange to red. The reaction mixture was then stirred at room temperature overnight. Workup using the procedure identical to that reported for 12 gave 13·C₇H₈ as red crystals (0.45 g, 69%). ¹H NMR (pyridine- d_5): δ 8.23 (d, J = 7.5 Hz, 2H), 8.14 (d, J =7.5 Hz, 2H), 8.09 (dd, J = 7.5 Hz, 2H), 7.94 (br s, 2H), 7.76 (dd, J = 7.5 Hz, 2H), 7.16 (m, 2H), 7.05 (m, 3H) (C₉H₅ and C₆H₅CH₃), 3.97 (m, 4H), 3.35 (m, 4H), 3.27 (s, 6H) (CH₂CH₂-OCH₃), 2.20 (s, 3H) (C₆H₅CH₃), 3.64 (m, 16H), 1.59 (m, 16H) (THF), 0.94 (s, 6H), 0.66 (s, 6H) (Si(CH₃)₂). ¹³C NMR (pyridine d_5): δ 133.54, 129.76, 128.24, 126.61, 123.16, 122.33, 120.24, 118.97, 117.73, 115.45, 114.95, 114.38, 110.45 (C9H5 and C6H5-CH₃), 75.61, 58.46, 29.56 (CH₂CH₂OCH₃), 68.19, 26.16 (THF), 80.76, 67.07 (C₂B₁₀H₁₁), 23.19 (C₆H₅CH₃), 1.99, 0.44 (Si(CH₃)₂). ¹¹B NMR (pyridine- d_5): δ -3.38 (8), -8.86 (12). IR (KBr, cm⁻¹): ν_{BH} 2565 (vs). Anal. Calcd for $C_{55}H_{96}B_{20}Li_2O_6Si_2Yb$: C, 50.32; H, 7.37. Found: C, 50.55; H, 7.15.

This complex was also obtained in 65% yield from the reaction of $YbI_2(THF)_x$ with 2 equiv of **3** in THF, followed by the same procedures used above.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N₂ in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo K α radiation. An empirical absorption correction was applied using the SADABS 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 leastsquares calculations on F^2 using the SHELXTL program package.¹³ For noncentrosymmetric structures, the appropriate enantiomorph was chosen by refining Flack's parameter *x* toward zero.¹⁴ Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Tables 1 and 2, respectively. Selected bond lengths and angles are compiled in Table 3. Further details are included in the Supporting Information.

Results and Discussion

Ligand. Reaction of $\text{Li}[C_9H_6CH_2CH_2OMe]$ with excess Me₂SiCl₂ in Et₂O gave Me₂SiCl($C_9H_6CH_2CH_2OMe$) (1) in 91% yield. Treatment of 1 with 1 equiv of $\text{Li}_2C_2B_{10}H_{10}$ in toluene/Et₂O afforded the monolithium salt [Me₂Si($C_9H_5CH_2CH_2OMe$)($C_2B_{10}H_{11}$)]Li(OEt₂) (2) in 88% yield. Interaction of 2 with 1 equiv of *n*-BuLi in Et₂O produced the dilithium salt [Me₂Si($C_9H_5CH_2CH_2OMe$)($C_2B_{10}H_{10}$)]Li₂(OEt₂)₂ (3) in 84% yield. 3 is insoluble in ether, whereas 2 is soluble. Therefore, they were easily separated. These transformations are outlined in Scheme 1.

The ¹H NMR spectra of both **2** and **3** exhibit the same splitting pattern with slightly different chemical shifts and support one Et₂O molecule per carboranyl in **2** and two Et₂O molecules per carboranyl in **3**, respectively. In addition, the ¹H NMR spectrum of **2** displays a broad singlet at $\delta = 3.74$ ppm attributable to the cage CH proton, supporting that **2** is a monolithium salt. The ¹³C NMR data are in line with the results from the corresponding ¹H NMR spectra. The ¹¹B NMR spectra show a 2:1:2:3:2 splitting pattern for **2** and a 1:3:1:2:3 splitting pattern for **3**, respectively.

Reaction with LnCl₃. Treatment of **3** with 1 equiv of $LnCl_3$ at room temperature gave the complex salts of

⁽¹²⁾ Sheldrick, G. M. *SADABS*: Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

⁽¹³⁾ *SHELXTL* V 5.03 Program Package; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1995.

⁽¹⁴⁾ Flack, H. D. Acta Crystallogr. 1983, A39, 876.

Table 2. C	rystal Data	and Summary	of Data	Collection	and Refinement	: for	10 - 13
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	U	U		
	10	11	12	13-toluene
formula	C ₃₆ H ₆₄ B ₂₀ LiO ₃ Si ₂ Sm	C48H88B20ClLiO6 Si2Sm2	C24H46B10O4SiYb	C55H96B20Li2O6Si2Yb
cryst size (mm)	0.54 imes 0.46 imes 0.30	0.10 imes 0.03 imes 0.02	0.43 imes 0.43 imes 0.08	0.50 imes 0.37 imes 0.13
fw	974.5	1376.7	707.8	1312.6
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	Pnc2	$P2_1/c$	$P2_1$	Pbcn
a, Å	9.322(1)	10.18(1)	9.402(1)	15.946(1)
b, Å	13.569(1)	21.06(4)	17.047(1)	19.129(1)
<i>c</i> , Å	23.332(1)	33.39(6)	10.350(1)	22.969(1)
α, deg	90	90	90	90
β , deg	90	93.04(14)	99.62(1)	90
γ , deg	90	90	90	90
V, Å ³	2951.1(2)	7148(19)	1635.5(1)	7006.3(4)
Ζ	2	4	2	4
D_{calcd} , Mg/m ³	1.097	1.279	1.437	1.244
radiation (λ), Å	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
2θ range, deg	3.5 to 50.0	4.1 to 50.0	4.0 to 56.0	3.3 to 52.0
μ , mm ⁻¹	1.064	1.737	2.924	1.413
F(000)	994	2784	712	2712
no. of obsd reflns	3962	9156	7563	6892
no. of params refnd	290	637	361	390
goodness of fit	1.090	0.807	0.997	0.997
Ř1	0.033	0.088	0.029	0.031
wR2	0.097	0.181	0.058	0.073

Tabl	e 3.	Selected	Bond	Lengths	(A) and	Ang	les (deg)a
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	5	6	8	9	10	11	12	13
(Ln)	(Yb)	(Yb)	(Y)	(Yb)	(Sm)	(Sm)	(Yb)	(Yb)
av Ln–C(ring)	2.688(12)	2.641(3)	2.684(12)	2.660(3)	2.779(7)	2.75(2)	2.814(7)	2.845(4)
av Ln-C(cage)	2.527(12)	2.494(3)	2.540(10)	2.488(2)	2.635(7)		2.638(5)	2.654(4)
av Ln-Cl	2.692(3)	2.664(1)	2.625(3)	2.558(1)		2.645(4)		
av Ln–O (sidearm)	2.387(7)	2.439(3)	2.466(9)	2.463(2)		2.49(2)	2.631(4)	
av Ln–O (THF)	2.323(8)	2.342(3)					2.432(4)	
av C(ring)-Si-C(cage)	107.4(6)	105.9(1)	108.7(5)	107.9(1)	109.1(3)		109.8(2)	111.5(2)
av Cent-Ln-C(cage)	103.3	103.7	105.5	105.3	104.1		102.5	104.1

^{*a*} Cent: the centroid of the five-membered ring of the indenyl group.





general formula [{ $[\eta^5: \sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀-H₁₀)]-Ln(THF)(μ -Cl)₃Ln[$\eta^5: \eta^1:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)-(C₂B₁₀H₁₀)]₂{Li(THF)}][Li(THF)₄] (Ln = Y (**4**), Yb (**5**)) in good yields. The coordinated LiCl was able to be removed upon heating in toluene solution. For instance, **5** was converted into [$\eta^5: \eta^1:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)-(C₂B₁₀H₁₀)]Yb(THF)(μ -Cl)₂Yb[$\eta^5: \eta^1:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)-(C₂B₁₀H₁₀)]Yb(THF)(μ -Cl)₂Yb[$\eta^5: \eta^1:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀H₁₀)] (**6**) by heating its toluene/THF (10:1) solution at 80 °C for 1 h. The samarium analogue of **6**, [$\eta^5: \eta^1:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀H₁₀)]Sm-(THF)(μ -Cl)₂Sm[$\eta^5: \eta^1:\sigma$ -Me₂Si(C₉H₅CH₂CH₂OMe)-

 $(C_2B_{10}H_{10})]$ (7), was also prepared from the reaction of **3** with 1 equiv of SmCl₃ at room temperature, followed by extraction with hot toluene. These transformations are summarized in Scheme 2.

Complexes **5**–**7** are paramagnetic species and do not offer useful ¹H and ¹³C NMR information. For the diamagnetic yttrium complex **4**, the ¹H NMR spectrum exhibits only one set of ligand proton signals, suggesting a fluxional process may be present in the solution, namely, the tethered sidearm can reversibly coordinate to the central metal ion. As expected, both **3** and **4** show very similar splitting patterns for the ligand protons. The ¹³C NMR data are consistent with the ¹H NMR results. The ¹¹B NMR spectrum of **4** displays a 1:2:2 splitting pattern, which is different from that of **3**.

The molecular structure of **5**, an analogue of **4**, was 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 $[\{[\eta^5: \sigma - Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Yb(THF)(\mu Cl)_{3}Yb[\eta^{5}:\eta^{1}:\sigma-Me_{2}Si(C_{9}H_{5}CH_{2}CH_{2}OMe)(C_{2}B_{10}H_{10})]_{2}$ $\{Li(THF)\}]^{-}$ and shows one toluene of solvation in the crystal lattice. In the anion, the disordered Li(2) atom links to two dimeric units of $\{ [\eta^5: \sigma - Me_2Si(C_9H_5CH_2CH_2 - Me_2Si(C_9H_5CH_2 - Me_2Si$ OMe)(C₂B₁₀H₁₀)]Yb(THF)(μ -Cl)₃Yb[η ⁵: η ¹: σ -Me₂Si(C₉H₅- $CH_2CH_2OMe)(C_2B_{10}H_{10})]^-$ via the oxygen atom of one of the sidearms from each unit, as shown in Figure 1. Each Yb atom in the dimeric unit is η^5 -bound to one five-membered ring of the indenyl group and σ -bound to one cage carbon atom, three doubly bridging Cl atoms, and one oxygen atom from either THF or the sidearm in a distorted-octahedral coordination environ-



ment (Figure 2). The other sidearm in the dimeric unit does not coordinate to the Yb atom probably because of steric reasons.

Figure 3 shows the dimeric structure of **6**, which is a neutral species generated by elimination of LiCl from **5**. Unlike the structure of **5**, both sidearm oxygen atoms coordinate to the Yb atoms. In addition, each Yb atom is also bound to either one THF or a B–H bond, leading to an asymmetric structure. As expected, the average Yb–Cl(μ_2 -Cl) distance of 2.664(1) Å in **6** is shorter than

the average Yb–Cl(μ_3 -Cl) distance of 2.692(3) Å in **5** and is identical with the Yb–Cl(μ_2 -Cl) distance of 2.666(1) Å found in [{ η^5 : σ -Me₂Si(C₅Me₄)(C₂B₁₀H₁₀)}YbCl(μ -Cl)]₂-[Li(DME)₃]₂.¹⁵ The average Yb–C(ring) and Yb–C(cage) distances in both **5** and **6** (Table 3) are comparable to those observed in this family of complexes.^{2,8} The average Yb–O(sidearm) distances are 2.387(7) in **5** and 2.439(3) Å in **6**, respectively, which compare to the 2.468(9) Å in (η^5 : η^1 -C₅H₄CH₂CH₂OMe)₂YbCl¹⁶ and the 2.450(12) Å in (η^5 : η^1 -C₅H₄CH₂CH₂OMe)₂YbL^{3g}



Figure 1. Molecular structure of the anion $[\{[\eta^5:\sigma-Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Yb(THF)(\mu-Cl)_3Yb[\eta^5:\eta^1:\sigma-Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]\}_2\{Li(THF)\}]^-$ in **5**. Note that the Li2 atom is disordered over two sets of positions with 0.5:0.5 occupancies.



Figure 2. Coordinating sphere around the Yb atoms in **5**. Selected bond distances (Å) and angles (deg): Yb1-C1 = 2.519(12), Yb1'-C1' = 2.535(11), Yb1-Cl1 = 2.704(3), Yb1-Cl2 = 2.700(3), Yb1-Cl3 = 2.624(3), Yb1-O1 = 2.387(7), Yb1'-Cl1 = 2.656(3), Yb1'-Cl2 = 2.683(3), Yb1'-Cl3 = 2.787(3), Yb1'-O2 = 2.323(8), av Yb1-C(ring) = 2.666(12), av Yb1'-C(ring) = 2.689(12), Cent-Yb1-C1 = 103.1, Cent'-Yb1'-C1' = 103.5.



Figure 3. Molecular structure of $[\eta^5:\eta^1:\sigma$ -Me₂Si(C₉H₅CH₂-CH₂OMe)(C₂B₁₀H₁₀)]Yb(THF)(μ -Cl)₂Yb[$\eta^5:\eta^1:\sigma$ -Me₂Si(C₉H₅-CH₂CH₂OMe)(C₂B₁₀H₁₀)] **(6**). Selected bond distances (Å) and angles (deg): Yb1-C1 = 2.460(3), Yb1-O1 = 2.369-(3), Yb1-Cl1 = 2.642(1), Yb1-Cl2 = 2.654(1), Yb1-H4' = 2.62, av Yb1-C(ring) = 2.627(3), Yb2-C1' = 2.528(3), Yb2-O2 = 2.509(2), Yb2-O3 = 2.342(3), Yb2-Cl1 = 2.692-(1), Yb2-Cl2 = 2.669(1), av Yb2-C(ring) = 2.655(3), Yb1-Cl1-Yb2 = 103.39(3), Yb1-Cl2-Yb2 = 103.67(3), Cent-Yb1-C1 = 104.1, Cent'-Yb2-C1' = 103.3.

Complexes **5**, **6**, $[\{\eta^{5}:\sigma-\text{Me}_2\text{Si}(C_5\text{Me}_4)(C_2\text{B}_{10}\text{H}_{10})\}$ -LnCl $(\mu$ -Cl)]₂[Li(DME)₃]₂ (Ln = Sm, Y, Yb),¹⁵ and $[\{[\eta^{5}:\sigma^{-l}\text{Pr}_2\text{NP}(C_9\text{H}_6)(C_2\text{B}_{10}\text{H}_{10})]\text{LnCl}\}_2(\mu$ -Cl)₃Li(DME)]-[Li(DME)₃]₂ (Ln = Er, Y)¹⁷ represent new structure types of contrained-geometry organo-rare-earth complexes.¹ The bridging atom, substituent on the cyclic five-membered ring, and reaction condition have influences on the structures of the resulting metal complexes.

Our previous work shows that $[Me_2A(C_9H_6)(C_2-B_{10}H_{10})]^{2-}$ (A = C, Si)⁷ and $[{}^{l}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]^{2-}$



Figure 4. Molecular structure of $[\eta^{5:}\eta^{1:}\sigma$ -Me₂Si(C₉H₅CH₂-CH₂OMe)(C₂B₁₀H₁₀)]Y(NHC₆H₃-2,5-'Bu₂)(μ -Cl)Li(THF)₃ (**8**). Selected bond distances (Å) and angles (deg): Y1-C1 = 2.540(10), Y1-N1 = 2.222(9), Y1-Cl1 = 2.625(3), Y1-O1 = 2.466(9), av Y1-C(ring) = 2.684(12), Cent-Y1-C1 = 105.5.

ligands¹⁸ cannot stabilize lanthanocene chlorides, and only $[\{\eta^5:\sigma-L(C_9H_6)(C_2B_{10}H_{10})\}_2Ln]^-$ type of complexes (L = Me₂C, Me₂Si, 'Pr₂NB) were isolated, regardless of the molar ratios of the reactants and the sizes of the lanthanides. Present examples indicate that modification of these ligands with a Lewis-base-functionalized sidearm leads to a new version of this type of ligands which can efficiently stabilize lanthanocene chlorides. Such sidearm effects were previously observed mainly in early lanthanocene chloride complexes.² The chlorine atoms in these complexes are expected to be replaced by other groups via salt metathesis reactions.

Treatment of **4** or **5** with 2 equiv of group 1 metal amides gave organo-rare-earth amide complexes $[\eta^{5}:\eta^{1}:$ σ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀H₁₀)]Y(NHC₆H₃-2,5-'Bu₂)(μ -Cl)Li(THF)₃ (**8**) or $[\eta^{5}:\eta^{1}:\sigma$ -Me₂Si(C₉H₅CH₂CH₂-OMe)(C₂B₁₀H₁₀)]Yb(NHC₆H₃-2,6-^{*i*}Pr₂)(μ -Cl)Li(THF)₃ (**9**) in good yields, shown in Scheme 2. It is noted that reactions of **4** with alkylating reagents such as CH₃Li, Me₃SiCH₂M (M = Li, K), and Me₃SiCH₂MgCl were complicated and no pure products were isolated. Unlike complex **5**, the coordinated LiCl cannot be removed by recrystallization from hot toluene, suggesting very high electron deficiency of the central metal ions.

The ¹H NMR spectrum of the diamagnetic yttrium complex **8** shows the presence of the hybrid ligand, the 2,5-'Bu₂C₆H₃NH unit, and THF in a molar ratio of 1:1: 3. The ¹¹B NMR spectrum exhibits a 2:3 splitting pattern, which is different from those of **3** and **4**. These data indicate that the splitting patterns of the ¹¹B NMR spectra of this type of complexes are very sensitive to the coordination environments of central metal ions and are hardly predictable.

Single-crystal X-ray analyses confirm the molecular structures of both **8** and **9**, shown in Figures 4 and 5, respectively. Both exhibit a distorted-trigonal-bipyramidal arrangement of ligands with the cage carbon atom and the tethered oxygen atom occupying the axial positions. The average Yb-C(ring), Yb-C(cage), and

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Scheme 3



Yb–O distances in **9** are comparable to those in **5** and **6** (Table 3). The Ln–Cl distances of 2.558(1) Å in **9** and 2.625(3) Å in **8** are close to the Er–Cl(μ) distance of 2.563(4) Å observed in $[\{\eta^{5:}\eta^{6-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}$ -Er(THF)(μ -Cl)Na(THF)₂]_n¹⁹ and the Yb–Cl(μ) distance of 2.552(2) Å found in $[(Me_3Si)_2N]_3Yb(\mu$ -Cl)Li(THF)₃²⁰ if the differences in Shannon's ionic radii are taken into account.²¹ The Yb–N distance of 2.157(2) Å compares to the corresponding values of 2.188(5) Å in $\{(Pr_2C_6H_3N)(Pr_2C_6H_3NH)Yb(\mu$ -NC₆H₃ $Pr_2)_2\{[Li(THF)]-[Na(THF)]_2^{22}$ and 2.211(5) Å in $[(Me_3Si)_2N]_3Yb(\mu$ -Cl)Li(THF)]-Li(THF)₃.²⁰ The Y–N distance of 2.222(9) Å falls in the range 2.211–2.382 Å normally observed in organo-yttrium amide complexes.^{3e}

Reaction with LnI₂. Treatment of SmI₂ with 1 equiv of **3** in THF at room temperature gave, after extraction with hot toluene, $[\{[\eta^5:\sigma-Me_2Si(C_9H_5CH_2CH_2OMe)-(C_2B_{10}H_{10})]_2Sm\}\{Li(THF)\}]_n$ (**10**) as orange-red crystals in 39% yield (based on **3**). Addition of LiCl to the mother liquor led to the isolation of $[\{\eta^5:\eta^1:\eta^6-Me_2Si(C_9H_5CH_2-CH_2OMe)(C_2B_{10}H_{10})Sm\}_2(\mu-Cl)][Li(THF)_4]$ (**11**) as dark red crystals in 12% yield (based on **3**). **11** was originally isolated from an equimolar reaction of $[Me_2Si(C_9H_5CH_2-CH_2OMe)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ ·LiCl with SmI₂ in THF.⁹ These transformations are outlined in Scheme 3.



Figure 5. Molecular structure of $[\eta^5: \eta^1:\sigma$ -Me₂Si(C₉H₅CH₂-CH₂OMe)(C₂B₁₀H₁₀)]Yb(NHC₆H₃-2,6-Pr₂)(μ -Cl)Li(THF)₃ (**9**). Selected bond distances (Å) and angles (deg): Yb1-C1 = 2.488(2), Yb1-N1 = 2.157(2), Yb1-C11 = 2.558(1), Yb1-O1 = 2.463(2), av Yb1-C(ring) = 2.660(3), Cent-Yb1-C1 = 105.3.

Both **10** and **11** are the trivalent samarium complexes as confirmed by single-crystal X-ray diffraction studies. Complex **10** is a coordination polymer with Li(THF) as a linkage connecting two $[\{\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_5\text{CH}_2\text{CH}_2\text{-OMe})(\text{C}_2\text{B}_{10}\text{H}_{10})\}_2\text{Sm}]^-$ fragments together via the tethered oxygen atoms, shown in Figure 6. The coordination geometry of this fragment (shown in Figure 7) is very close to that of $[\{\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\}_2\text{Sm}]^{-,7a}$ Slightly longer Sm–C(ring) and Sm–C(cage) distances are observed in **10** in comparison with literature data because of steric reasons.

Complex 11 consists of well-separated, alternating layers of discrete tetrahedral cations $[Li(THF)_4]^+$ and complex anions $[\{\eta^5:\eta^1:\eta^6-Me_2Si(C_9H_5CH_2CH_2OMe) (C_2B_{10}H_{10})Sm\}_2(\mu$ -Cl)]⁻. In the anion, each Sm³⁺ ion is η^6 -bound to the *nido*-C₂B₁₀H₁₀ unit via a six-membered C_2B_4 bonding face, η^5 -bound to the five-membered ring of the indenyl group, and coordinated to a doubly bridging Cl atom and one O atom from the appended ether group of indenyl in a highly distorted-tetrahedral geometry with the formal coordination number of eight (Figure 8). The two *nido*-C₂B₁₀H₁₀ units are connected to each other through a C-C single bond at a distance of 1.53(3) Å, and the dihedral angle between two sixmembered C₂B₄ rings is 69.6°. This complex represents a very rare example of metallacarboranes bearing a $(nido-RC_2B_{10}H_{10})_2^{\hat{4}-}$ tetraanion ligand.²³

The average Sm-C(ring) and Sm-cage atom distances of 2.75(2) and 2.84(3) Å in **11** are very close to the corresponding values of 2.751(4) and 2.823(4) Å observed in $[\eta^5:\eta^6-\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}(\text{THF})_2$,^{7a} respectively. The average Sm-Cl(μ) distance of 2.645-(4) Å in **11** is much shorter than the corresponding values of 2.76(1) Å in [{ $(\eta^5-\text{C}_5\text{Me}_5)_2\text{SmCl}_2(\mu-\text{Cl})]^-$ and

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Figure 6. Perspective view of $[\{[\eta^5:\sigma-Me_2Si(C_9H_5CH_2CH_2-OMe)(C_2B_{10}H_{10})]_2Sm\}\{Li(THF)\}]_n$ (**10**) revealing a portion of the infinite polymeric chain.



Figure 7. Coordinating sphere around the Sm atom in **10**. Selected bond distances (Å) and angles (deg): Sm1–C1 = 2.635(7), av Sm1–C(ring) = 2.779(7), Cent–Sm1–C1 = 104.1, Cent–Sm1–Cent = 129.6.

2.88(2) Å in $[(\eta^5-C_5Me_5)_2Sm(\mu-Cl)]_{3,}^{24}$ implying that steric repulsion plays an important role.

The formation of complexes **10** and **11** results from the electron transfer from samarium(II) to the cage. It may be suggested that the reaction of $SmI_2(THF)_x$ with **3** gives the first intermediate $[\eta^5:\eta^1:\sigma$ -Me₂Si(C₉H₅CH₂-CH₂OMe)(C₂B₁₀H₁₀)]Sm^{II},^{7a} followed by intermolecular electron transfer and then ligand redistribution to afford **10**. Either intermolecular or intramolecular electron transfer from the Sm^{II} to the cage leads to the cleavage



Figure 8. Molecular structure of the anion $[\{\eta^{5}:\eta^{1}:\eta^{6}\cdot\text{Me}_{2}:\text{Si}(C_{9}H_{5}CH_{2}CH_{2}OMe)(C_{2}B_{10}H_{10})\text{Sm}\}_{2}(\mu-Cl)]^{-}$ in **11**. Selected bond distances (Å) and angles (deg): C2-C2' = 1.53(3), Sm1-Cl1 = 2.643(4), Sm1'-Cl1 = 2.647(5), Sm1-O1 = 2.49(2), Sm1'-O1' = 2.48(2), av Sm1-C(ring) = 2.77-(2), av Sm1-cage atom = 2.82(2), av Sm1'-Cl1-Sm1' = 2.74(2), av Sm1'-cage atom = 2.84(2), Sm1-Cl1-Sm1' = 107.4(2).

of the Sm-cage carbon and the cage C–C bonds; coupling of the two cages via the formation of a C–C single bond generates the *nido*-species (*nido*-RC₂-B₁₀H₁₀)₂^{4–}, which bonds to the Sm³⁺ ions in a η^6 -fashion to form complex **11**. Addition of LiCl leads to the substitution of an iodo with a chloro atom, facilitating the crystallization of the product.

To get some insight into the reaction intermediates, SmI₂ was replaced by a less reactive YbI₂. An equimolar reaction of YbI₂ with **3** in THF produced, after recrystallization from a THF/DME solution, the divalent ytterbium complex [η^5 : η^1 : σ -Me₂Si(C₉H₅CH₂CH₂CH₂OMe)-(C₂B₁₀H₁₀)]Yb(DME)(THF) (**12**) in 72% yield. Treatment of **12** with 1 equiv of **3** gave the ionic complex {[(μ - η^5 : η^2): η^1 : σ -Me₂Si(C₉H₅CH₂CH₂OMe)(C₂B₁₀H₁₀)]₂Yb{Li-(THF)₂}₂ (**13**) in 69% yield. Complex **13** was also directly prepared from the reaction of YbI₂ with 2 equiv of **3** in THF. These reactions are summarized in Scheme 4.

The isolation of **12** supports the above proposed intermediate in the reaction of SmI_2 with **3**. In sharp contrast to the SmI_2 case, only the salt metathesis product was isolated and no redox reactions were detected in the case of YbI₂, which offers useful information of the reaction pathways.

The ¹H NMR spectra show the presence of the hybrid ligand, THF, and DME in a molar ratio of 1:1:1 for **12** and support the molar ratio of two THF molecules per hybrid ligand in **13**, respectively. The splitting patterns of the ¹¹B NMR spectra are 1:1:3 in **12** and 2:3 in **13**, respectively. Their solid-state IR spectra display a characteristic B–H absorption of a *closo*-carborane at about 2562 cm⁻¹.

The molecular structure of **12** is shown in Figure 9. The Yb atom is η^5 -bound to the five-membered ring of the indenyl group, σ -bound to the carborane cage carbon atom, and coordinated to four oxygen atoms from the sidearm, one DME, and one THF molecule, respectively, in a distorted-octahedral geometry with a formal coordination number of 8, which is similar to the eightcoordinate [η^5 : σ -Me₂C(C₉H₆)(C₂B₁₀H₁₀)]Yb(DME)₂⁶ and [η^5 : σ -Pr₂NP(C₉H₆)(C₂B₁₀H₁₀)]Yb(DME)₂.¹⁷ The average Yb-C(ring) distance of 2.814(7) Å, the average Yb-O

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distance of 2.529(4) Å, and the Yb–C(cage) distance of 2.638(5) Å are all longer than the corresponding values of 2.790(8), 2.494(6), and 2.587(7) Å in [η^{5} : σ -Pr₂NP-(C₉H₆)(C₂B₁₀H₁₀)]Yb(DME)₂ and 2.789(8), 2.445(5), and 2.561(6) Å observed in [η^{5} : σ -Me₂C(C₉H₆)(C₂B₁₀H₁₀)]Yb-(DME)₂, probably because of steric reasons.

The solid-state structure of **13** was confirmed by single-crystal X-ray analysis, shown in Figure 10. The asymmetric unit contains one toluene of solvation. The Yb atom is η^5 -bound to each of two five-membered rings of the indenyl groups and σ -bound to each of two carborane cage carbon atoms in a distorted-tetrahedral geometry, which is similar to that of **10**. The charge is then compensated by two Li⁺ ions. Each Li atom is asymmetrically η^2 -bound to the five-membered ring and coordinated to three oxygen atoms from the sidearm and two THF molecules, respectively. As expected, both Yb– C(ring) and Yb–C(cage) distances in **13** are slightly longer than the corresponding values observed in **12**.



Figure 9. Molecular structure of $[\eta^5:\eta^1:\sigma$ -Me₂Si(C₉H₅CH₂-CH₂OMe)(C₂B₁₀H₁₀)]Yb(DME)(THF) (**12**). Selected bond distances (Å) and angles (deg): Yb1-C1 = 2.638(5), Yb1-O1 = 2.631(4), Yb1-O2 = 2.432(4), Yb1-O3 = 2.546(4), Yb1-O4 = 2.506(3), av Yb1-C(ring) = 2.814(7), Cent-Yb1-C1 = 102.5.



Figure 10. Molecular structure of { $[(u-\eta^5:\eta^2):\eta^{1:}\sigma-Me_2Si-(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]_2Yb$ }{Li(THF)₂}₂ (13). Selected bond distances (Å) and angles (deg): Yb1-C1 = 2.654(4), av Yb1-C(ring) = 2.845(4), Li1-C12 = 2.365(9), Li1-C13 = 2.611(9), Cent-Yb1-C1 = 104.1, Cent-Yb1-Cent = 126.1.

The Li–C distances are 2.365(9) and 2.611(9) Å, suggesting a slip distortion from η^2 to η^1 . These measured values compare to the 2.332(8) Å in [{[$(\mu - \eta^5):\sigma$ -Me₂Si-(C₅Me₄)(C₂B₁₀H₁₀)]Li(THF)}₂Li][Li(THF)₄]¹⁵ and 2.318-(4) Å in [$(\eta^5$ -C₅H₅)₂Li][Ph₄P].²⁵

Conclusion

The ether substituent on the five-membered ring of the indenyl unit in linked carboranyl-indenyl hybrid ligands has significant effects on the stability and reactivity of the resulting organo-rare-earth complexes via temporarily and reversibly coordinating to the metal ion. For example, $[Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]^{2-}$ can prevent lanthanocene chlorides from ligand redistribution reactions by satisfying the steric requirements, which offers opportunities for further studies on this class of organolanthanide complexes.^{1,2} This etherfunctionalized ligand can offer divalent samarium complexes unusual reactivities, resulting in the formation of unexpected reduction/coupling products.

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Supporting Information Available: Crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **5**, **6**, and **8**–**13**. This material is available free of charge via the Internet at http:/pubs.acs.org.

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