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

Shaowu Wang,†,‡ Hung-Wing Li,† and Zuowei Xie*,†

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China, and Institute of Organic Chemistry, School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, China

Received February 15, 2004

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 $Me_2SiCl(C_9H_6CH_2CH_2OMe)$ with 1 equiv of $Li_2C_2B_{10}H_{10}$ in toluene/Et_2O afforded the monolithium salt $[Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{11})]Li(OEt_2)$ (**2**). Interaction of **2** with 1 equiv of *n*-BuLi in Et_2O produced the dilithium salt $[Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (**3**). Reaction of **3** with 1 equiv of $LnCl_3$ at room temperature gave the complex salts of general formula $[\{[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Ln(THF)(\mu\text{-}Cl)_3Ln[\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]\}_2\{Li(THF)\}][Li(THF)_4]$ (Ln = Y (**4**), Yb (**5**)). Upon heating, **5** was converted into $[\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Yb(THF)(\mu\text{-}Cl)_2Yb[\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]$ (**6**) by eliminating LiCl. Treatment of **4** or **5** with 2 equiv of group 1 metal amides gave organo-rare-earth amide complexes $[\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Y(NHC_6H_3\text{-}2,5\text{-}{}^tBu_2)(\mu\text{-}Cl)Li(THF)_3$ (**8**) or $[\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Yb(NHC_6H_3\text{-}2,6\text{-}{}^iPr_2)(\mu\text{-}Cl)Li(THF)_3$ (**9**). An equimolar reaction of SmI_2 with **3** in THF generated, after addition of LiCl, $[\{[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]_2Sm\}\{Li(THF)\}]_n$ (**10**) and $[\{\eta^5{:}\eta^1{:}\eta^6\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})Sm\}_2(\mu\text{-}Cl)][Li(THF)_4]$ (**11**). In sharp contrast, a less reactive YbI_2 reacted with **3** in THF, producing only salt metathesis product $[\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Yb(DME)(THF)$ (**12**). **12** reacted with 1 equiv of **3** to give the ionic complex $\{[(\mu\text{-}\eta^5{:}\eta^2){:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]_2Yb\}\{Li(THF)_2\}_2$ (**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.

* Corresponding author. Fax: (852)26035057. Tel: (852)26096344. E-mail: zxie@cuhk.edu.hk.

† The Chinese University of Hong Kong.

‡ Anhui Normal University.

(1) For recent reviews, see: (a) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953. (b) Okuda, J. *J. Chem. Soc., Dalton Trans.* **2003**, 2367.

(2) For reviews, see: (a) Schumann, H.; Messe-Markscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (b) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. A. G., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 4, p 11.

(3) (a) Qian, C.; Zou, G.; Sun, J. *J. Chem. Soc., Dalton Trans.* **1998**, 1607. (b) Qian, C.; Zou, G.; Sun, J. *J. Chem. Soc., Dalton Trans.* **1999**, 519. (c) Qian, C.; Zou, G.; Nie, W.; Sun, J.; Lemenovskii, D. A.; Borzov, M. V. *Polyhedron* **2000**, *19*, 1955. (d) Qian, C.; Zou, G.; Sun, J. *J. Organomet. Chem.* **1998**, *566*, 21. (e) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4845. (f) Schumann, H.; Erbstein, F.; Hermann, K.; Demtschuk, J.; Weimann, R. *J. Organomet. Chem.* **1998**, *562*, 255. (g) Deng, D.; Qian, C.; Song, F.; Wang, Z.; Wu, G.; Zheng, P.; Jin, S.; Lin, Y. *J. Organomet. Chem.* **1993**, *458*, 83. (h) Qian, C.; Zheng, X.; Wang, B.; Deng, D.; Sun, J. *J. Organomet. Chem.* **1994**, *466*, 101. (i) Deng, D.; Qian, C.; Wu, G.; Zheng, P. *J. Chem. Soc., Chem. Commun.* **1990**, 880. (j) Van den Hende, J. R.; Hitchcock, P. B.; Lappert, M. F.; Nile, T. A. *J. Organomet. Chem.* **1994**, *472*, 79. (k) Vandeweghe, P.; Bied, C.; Collins, J.; Marcalo, J.; Santos, I. *J. Organomet. Chem.* **1994**, *475*, 121. (l) Trifonov, A.; Ferri, F.; Collins, J. *J. Organomet. Chem.* **1999**, *582*, 211. (m) Molander, G. A.; Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J. *Organometallics* **1996**, *15*, 3817. (n) Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J. *Organometallics* **1998**, *17*, 5324. (o) Cheung, M.-S.; Chan, H.-S.; Xie, Z. *Organometallics* **2004**, *23*, 517.

(4) Roesky, P. W.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4705.

(5) Xie, Z.; Qian, C.; Huang, Y.-Z. *J. Organomet. Chem.* **1991**, *412*, 61.

10.1021/om0498807 CCC: $27.50
Publication on Web 04/15/2004

Our previous work shows that linked carboranyl-indenyl ligands $[Me_2A(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ (A = C,[6] Si[7]) cannot stabilize half-sandwich rare earth complexes of the type $[\eta^5:\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]LnCl$.[8] Equimolar reactions between $M_2[Me_2A(C_9H_6)(C_2B_{10}H_{10})]$ (M = Li, Na) and $LnCl_3$ always resulted in the formation of full-sandwich complexes $[\eta^5:\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]_2Ln^-$, which were also formed from the reaction of $M_2[Me_2A(C_9H_6)(C_2B_{10}H_{10})]$ with SmI_2.[6,7] However, when a functionalized sidearm $MeOCH_2CH_2$ was tethered to this linked ligand, the novel samaracarborane $[\{\eta^5:\eta^1:\eta^6\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})Sm\}_2(\mu\text{-}Cl)][Li(THF)_4]$ was isolated from an equimolar reaction of $[Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Li_2(OEt_2)_2 \cdot LiCl$ with SmI_2, 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 $[Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]^{2-}$.

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. $SmI_2(THF)_x$,[10] $C_9H_7CH_2CH_2OMe$,[11] and $Li_2C_2B_{10}H_{10}$[8] 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 ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a 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 $BF_3 \cdot OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd., U.K.

Preparation of $Me_2SiCl(C_9H_6CH_2CH_2OMe)$ (1). A 1.60 M solution of *n*-BuLi in hexane (36.0 mL, 57.6 mmol) was slowly added to a solution of $MeOCH_2CH_2C_9H_7$ (10.0 g, 57.4 mmol) in Et_2O (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 Me_2SiCl_2 (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 Me_2SiCl_2 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 ($CDCl_3$): δ 7.60 (d, *J* = 7.2 Hz, 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) (C_9H_6), 3.72 (t, *J* = 7.2 Hz, 2H), 3.41 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 2H) ($CH_2CH_2OCH_3$), 0.24 (s, 3H), 0.21 (s, 3H) ($Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 145.17, 144.01, 141.19, 129.48, 126.21, 125.05, 124.07, 119.86, 46.44 (C_9H_6), 72.16, 59.21, 28.77 ($CH_2CH_2OCH_3$), 0.58, 0.24 ($Si(CH_3)_2$). MS (EI): 266 (M^+).

Preparation of $[Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{11})]Li(OEt_2)$ (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 $o\text{-}C_2B_{10}H_{12}$ (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 $Me_2SiCl(C_9H_6CH_2CH_2OMe)$ (**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 × 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) (C_9H_5), 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 C*H*), 3.36 (q, *J* = 6.9 Hz, 4H), 1.12 (t, *J* = 6.9 Hz, 6H) ($O(CH_2CH_3)_2$), 0.80 (s, 6H) ($Si(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 139.51, 135.00, 128.22, 120.22, 117.71, 114.94, 113.86, 109.56, 86.82 (C_9H_5), 76.21, 58.45, 30.33 ($CH_2CH_2OCH_3$), 74.45, 64.88 ($C_2B_{10}H_{11}$), 66.15, 15.88 ($O(CH_2CH_3)_2$), 0.34 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): 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 $[Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (3). To a suspension of $[Me_2Si(C_9H_6CH_2CH_2OMe)(C_2B_{10}H_{11})]Li(OEt_2)$ (**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* = 7.5 Hz, 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) ($O(CH_2CH_3)_2$), 0.92 (s, 6H) ($Si(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 137.91, 133.55, 126.60, 122.31, 118.01, 115.44, 114.38, 109.18, 89.08 (C_9H_5), 75.12, 58.19, 29.54 ($CH_2CH_2OCH_3$), 77.98, 63.88 ($C_2B_{10}H_{11}$), 66.15, 15.88 ($O(CH_2CH_3)_2$), 1.97 ($Si(CH_3)_2$). ^{11}B NMR (pyridine-d_5): δ −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 $C_{24}H_{48}B_{10}Li_2O_3Si$: C, 53.91; H, 9.05. Found: C, 54.27; H, 8.87.

Preparation of $[\{[\eta^5:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Y(THF)(\mu\text{-}Cl)_3Y[\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]\}_2\{Li(THF)\}][Li(THF)_4]$ (4). To a suspension of YCl_3 (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) (C_9H_5), 3.97 (t, *J* = 7.8 Hz, 8H), 3.60 (t, *J* = 7.8 Hz, 8H), 3.31 (s, 12H) ($CH_2CH_2OCH_3$), 3.63 (m, 24H), 1.60 (m, 24H) (THF), 0.80 (s, 24H) ($Si(CH_3)_2$). ^{13}C NMR (pyridine-d_5): 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 ($C_2B_{10}H_{11}$), 68.18, 26.16 ($O(CH_2CH_2)_2$), 0.34 ($Si(CH_3)_2$). ^{11}B 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

(6) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 334.
(7) (a) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 2420. (b) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 4478. (c) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1578. (d) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **1999**, *18*, 5511.
(8) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1.
(9) Wang, S.; Li, H.-W.; Xie, Z. *Organometallics* **2001**, *20*, 3624.
(10) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.
(11) Qian, C.; Zou, G., Sun, J. *J. Organomet. Chem.* **1998**, *566*, 21.

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 [{[η^5:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]Yb(THF)(μ-Cl)$_3$Yb[η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]}$_2${Li(THF)}][Li(THF)$_4$]·C$_6$H$_5$CH$_3$ (5·C$_6$H$_5$CH$_3$). This complex was prepared as dark red crystals from $YbCl_3$ (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%). ^{1}H NMR (pyridine-d_5): δ 3.50 (s), 1.46 (s) (THF), plus many broad, unresolved resonances. ^{11}B 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 $C_{99}H_{176}B_{40}Cl_6Li_2O_{11}Si_4Yb_4$: C, 39.56; H, 5.90. Found: C, 39.21; H, 5.98.

Preparation of [{η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)}Yb(THF)(μ-Cl)$_2$Yb{η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)}]·C$_6$H$_5$CH$_3$ (6·C$_6$H$_5$CH$_3$). 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**·$C_6H_5CH_3$ as dark red crystals (0.16 g, 67%). ^{1}H NMR (pyridine-d_5): many broad, unresolved resonances. ^{11}B 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 $C_{43}H_{72}B_{20}Cl_2O_3Si_2Yb_2$: C, 38.94; H, 5.47. Found: C, 38.84; H, 5.57.

Preparation of [η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]Sm(THF)(μ-Cl)$_2$Sm[η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)-(C$_2$B$_{10}$H$_{10}$)] (7). To a suspension of $SmCl_3$ (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 $SmCl_3$. 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 orange-red crystals (0.24 g, 81%). ^{1}H NMR (pyridine-d_5): many broad, unresolved resonances. ^{11}B NMR (pyridine-d_5): δ −0.01 (4), −4.44 (4), −8.02 (6), −9.82 (2), −14.08 (4). IR (Kbr, cm^{-1}): ν_{BH} 2568 (vs). Anal. Calcd for $C_{36}H_{64}B_{20}Cl_2O_3Si_2Sm_2$: C, 36.37; H, 5.43. Found: C, 36.32; H, 5.57.

Preparation of [η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]Y(NHC$_6$H$_3$-2,5-^{t}Bu$_2$)(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 KNHC$_6$H$_3$-2,5-Bu$^t_2$ (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%). ^{1}H 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) (C$_9$*H*$_5$ and C$_6$*H*$_3$), 4.25 (br s, 1H) (N*H*), 3.55 (t, J = 7.8 Hz, 2H), 3.15 (s, 3H), 3.07 (t, J = 7.8 Hz, 2H) (C*H*$_2$C*H*$_2$OC*H*$_3$), 3.65 (m, 12H), 1.60 (m, 12H) (THF), 1.53 (br s, 9H), 1.18 (br s, 9H) (t-C$_4$*H*$_9$), 0.80 (s, 3H), 0.78 (s, 3H) (Si(C*H*$_3$)$_2$). ^{13}C NMR (pyridine-d_5): 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*$_9$H$_5$ and *C*$_6$H$_3$), 77.50, 59.87, 31.47 (*C*H$_2$*C*H$_2$O*C*H$_3$), 82.47, 63.49 (*C*$_2$B$_{10}$H$_{10}$), 69.31, 27.29 (THF), 35.62, 35.52, 33.18, 31.93 (t-*C*$_4$H$_9$), 1.69, 1.16 (Si(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −5.05 (4), −10.61 (6). IR (KBr, cm^{-1}): ν_{BH} 2568 (vs). Anal. Calcd for $C_{34}H_{58}B_{10}ClLiNO_2SiY$ (**8** − 2THF): C, 52.33; H, 7.49; N, 1.80. Found: C, 52.54; H, 7.61; N, 1.63.

Preparation of [η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]Yb(NHC$_6$H$_3$-2,6-^{i}Pr$_2$)(μ-Cl)Li(THF)$_3$ (9). This complex was prepared as dark red crystals from **5** (0.36 g, 0.24 mmol) and NaNHC$_6$H$_3$-2,6-^{i}Pr$_2$ (0.094 g, 0.48 mmol) in THF (25 mL) using the procedure identical to that reported for **8**: yield 0.31 g (65%). ^{1}H NMR (pyridine-d_5): δ 3.62 (s), 1.59 (s) (THF), plus many broad, unresolved resonances. ^{11}B NMR (pyridine-d_5): δ −1.46 (2), −5.96 (1), −7.01 (1), −11.18 (6). IR (KBr, cm^{-1}): ν_{BH} 2577 (vs). Anal. Calcd for $C_{32}H_{54}B_{10}ClLiNO_2SiYb$ (**9** − 2THF): C, 45.95; H, 6.51; N, 1.68. Found: C, 45.96; H, 6.74; N, 1.80.

Preparation of [{[η^5:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]$_2$Sm}{Li(THF)}]$_n$ (10). To a THF solution of SmI$_2$(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 [{η^5:η^1:η^6-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$-OMe)(C$_2$B$_{10}$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**: ^{1}H 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) (C$_9$*H*$_5$), 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) (C*H*$_2$C*H*$_2$OC*H*$_3$), 0.94 (s, 12H) (Si(C*H*$_3$)$_2$). ^{13}C NMR (pyridine-d_5): δ 138.37, 136.18, 129.00, 126.10, 121.21, 120.23, 119.52, 116.22, 103.55 (*C*$_9$H$_5$), 85.07 (*C*$_2$B$_{10}$H$_{11}$), 76.21, 58.75, 30.91 (*C*H$_2$*C*H$_2$O*C*H$_3$), 68.17, 26.15 (THF), 2.60, 0.37 (Si(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): 32.50 (4), −5.15 (16). IR (KBr, cm^{-1}): ν_{BH} 2572 (vs). Anal. Calcd for $C_{54}H_{88}B_{20}LiO_4Si_2Sm$: C, 44.37; H, 6.62. Found: C, 44.15; H, 6.38.

Preparation of [{η^5:η^1:η^6-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)Sm}$_2$(μ-Cl)][Li(THF)$_4$] (11). To a THF solution of SmI$_2$-(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%). ^{1}H 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$_9$*H*$_5$), 3.86 (s, 6H), 3.36 (br s, 4H), 3.17 (br s, 4H) (C*H*$_2$C*H*$_2$OC*H*$_3$), 3.65 (m, 16H), 1.59 (m, 16H) (THF), −0.28 (s, 6H), −0.51 (s, 6H) (Si(C*H*$_3$)$_2$). ^{13}C NMR (pyridine-d_5): δ 129.35, 128.60, 125.70, 122.69, 121.33, 120.84, 119.98, 119.32 (*C*$_9$H$_5$), 69.50, 58.67, 31.65 (*C*H$_2$*C*H$_2$O*C*H$_3$), 88.43, 65.73 (*C*$_2$B$_{10}$H$_{11}$), 67.79, 22.78 (THF), 0.24, 0.08 (Si(*C*H$_3$)$_2$). ^{11}B 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$_2$Si(C$_9$H$_5$CH$_2$CH$_2$-OMe)(C$_2$B$_{10}$H$_{10}$)]Li$_2$(OEt$_2$)$_2$·LiCl prepared directly from **1** and C$_2$B$_{10}$H$_{10}$Li$_2$ followed by treatment with 1 equiv of n-BuLi.[9]

Preparation of [η^5:η^1:σ-Me$_2$Si(C$_9$H$_5$CH$_2$CH$_2$OMe)(C$_2$B$_{10}$H$_{10}$)]Yb(DME)(THF) (12). To a THF solution of YbI$_2$(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	$C_{99}H_{176}B_{40}Cl_6Li_2O_{11}Si_4Yb_4$	$C_{43}H_{72}B_{20}Cl_2O_3Si_2Yb_2$	$C_{42}H_{74}B_{10}ClLiNO_4SiY$	$C_{40}H_{70}B_{10}ClLiNO_4SiYb$
cryst size (mm)	0.66 × 0.13 × 0.05	0.50 × 0.40 × 0.25	0.60 × 0.25 × 0.17	0.52 × 0.20 × 0.06
fw	3005.9	1326.4	924.5	980.6
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
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)
c, 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)
Z	4	2	2	4
D_{calcd}, Mg/m^3	1.215	1.532	1.170	1.268
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (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%). ^{1}H NMR (pyridine-d_5): δ 8.15 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.00 (m, 2H), 6.80 (dd, J = 8.1 Hz, 1H) (C_9H_5), 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-OCH_3), 1.62 (m, 4H) (THF), 0.84 (s, 3H), 0.70 (s, 3H), ($Si(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 144.43, 131.77, 127.98, 121.57, 120.21, 119.78, 114.52, 111.56, 98.29 (C_9H_5), 76.82, 73.51, 60.10, 60.62, 29.95, 27.28 ($CH_2CH_2OCH_3$, THF, DME), 82.27, 69.31 ($C_2B_{10}H_{11}$), 2.14, 1.52 ($Si(CH_3)_2$). ^{11}B 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 {[(μ-η^5:η^2):η^1:σ-$Me_2Si(C_9H_5CH_2CH_2OMe)$-$(C_2B_{10}H_{10})]_2Yb$}{$Li(THF)_2$}$_2$·$C_7H_8$ (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**·C_7H_8 as red crystals (0.45 g, 69%). ^{1}H 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) (C_9H_5 and $C_6H_5CH_3$), 3.97 (m, 4H), 3.35 (m, 4H), 3.27 (s, 6H) (CH_2CH_2-OCH_3), 2.20 (s, 3H) ($C_6H_5CH_3$), 3.64 (m, 16H), 1.59 (m, 16H) (THF), 0.94 (s, 6H), 0.66 (s, 6H) ($Si(CH_3)_2$). ^{13}C 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 (C_9H_5 and C_6H_5-CH_3), 75.61, 58.46, 29.56 ($CH_2CH_2OCH_3$), 68.19, 26.16 (THF), 80.76, 67.07 ($C_2B_{10}H_{11}$), 23.19 ($C_6H_5CH_3$), 1.99, 0.44 ($Si(CH_3)_2$). ^{11}B 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 N_2 in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα 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 least-squares 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 $Li[C_9H_6CH_2CH_2OMe]$ with excess Me_2SiCl_2 in Et_2O gave $Me_2SiCl(C_9H_6CH_2CH_2OMe)$ (**1**) in 91% yield. Treatment of **1** with 1 equiv of $Li_2C_2B_{10}H_{10}$ in toluene/Et_2O afforded the monolithium salt $[Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{11})]Li(OEt_2)$ (**2**) in 88% yield. Interaction of **2** with 1 equiv of n-BuLi in Et_2O produced the dilithium salt $[Me_2Si(C_9H_5CH_2CH_2$-$OMe)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (**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 ^{1}H NMR spectra of both **2** and **3** exhibit the same splitting pattern with slightly different chemical shifts and support one Et_2O molecule per carboranyl in **2** and two Et_2O molecules per carboranyl in **3**, respectively. In addition, the ^{1}H NMR spectrum of **2** displays a broad singlet at δ = 3.74 ppm attributable to the cage CH proton, supporting that **2** is a monolithium salt. The ^{13}C NMR data are in line with the results from the corresponding ^{1}H NMR spectra. The ^{11}B 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 $LnCl_3$. 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. Crystal Data and Summary of Data Collection and Refinement for 10−13

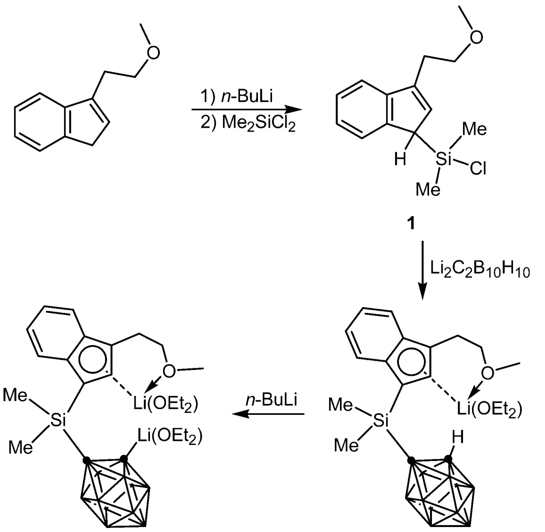
	10	**11**	**12**	**13**·toluene
formula	$C_{36}H_{64}B_{20}LiO_3Si_2Sm$	$C_{48}H_{88}B_{20}ClLiO_6Si_2Sm_2$	$C_{24}H_{46}B_{10}O_4SiYb$	$C_{55}H_{96}B_{20}Li_2O_6Si_2Yb$
cryst size (mm)	0.54 × 0.46 × 0.30	0.10 × 0.03 × 0.02	0.43 × 0.43 × 0.08	0.50 × 0.37 × 0.13
fw	974.5	1376.7	707.8	1312.6
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	*Pnc*2	$P2_1/c$	$P2_1$	*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)
c, 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)
Z	2	4	2	4
D_{calcd}, Mg/m^3	1.097	1.279	1.437	1.244
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (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
R1	0.033	0.088	0.029	0.031
wR2	0.097	0.181	0.058	0.073

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

	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.

Scheme 1

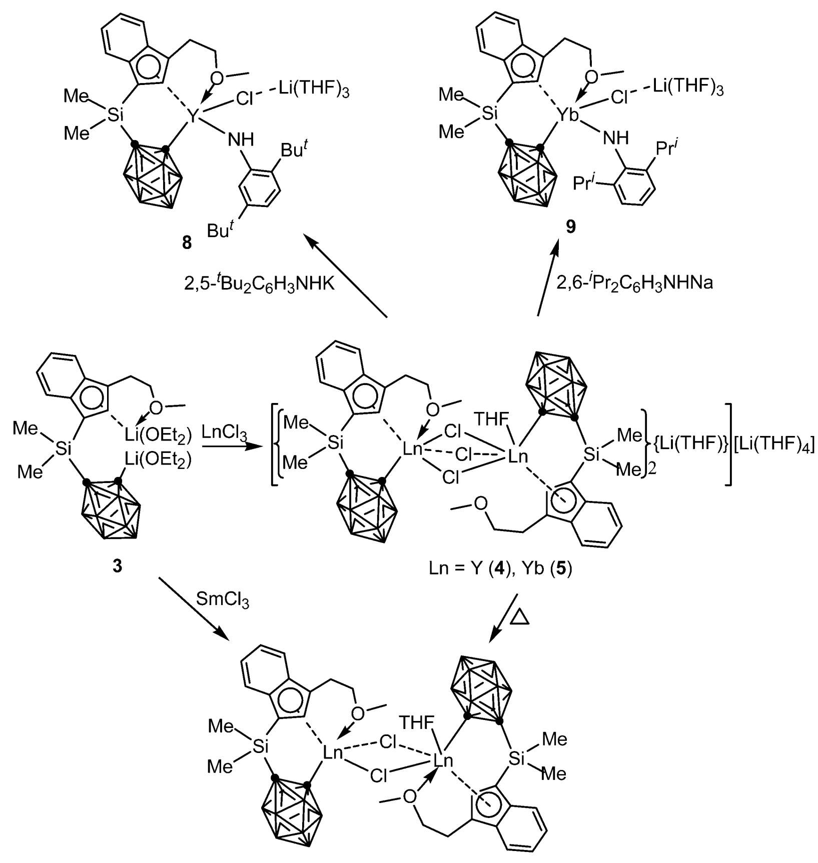


general formula [{[η^5: σ-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$]-Ln(THF)($\mu$-Cl)$_3$Ln[$\eta^5$: η^1:σ-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$]}$_2${Li(THF)}][Li(THF)$_4$] (Ln = Y (**4**), Yb (**5**)) in good yields. The coordinated LiCl was able to be removed upon heating in toluene solution. For instance, **5** was converted into [η^5: η^1:σ-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$]Yb(THF)($\mu$-Cl)$_2$Yb[$\eta^5$: η^1:σ-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$] (**6**) by heating its toluene/THF (10:1) solution at 80 °C for 1 h. The samarium analogue of **6**, [η^5: η^1:σ-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$]Sm(THF)($\mu$-Cl)$_2$Sm[$\eta^5$:$\eta^1$:$\sigma$-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$] (**7**), was also prepared from the reaction of **3** with 1 equiv of $SmCl_3$ 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 ^{1}H and ^{13}C NMR information. For the diamagnetic yttrium complex **4**, the ^{1}H 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 ^{13}C NMR data are consistent with the ^{1}H NMR results. The ^{11}B 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 [{[η^5: σ-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$]Yb(THF)($\mu$-Cl)$_3$Yb[$\eta^5$:$\eta^1$:$\sigma$-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$]}$_2$-{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 {[η^5:σ-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$]Yb(THF)($\mu$-Cl)$_3$Yb[$\eta^5$:$\eta^1$:$\sigma$-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$]}$^-$ 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-

Scheme 2



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-$Me_2Si(C_5Me_4)(C_2B_{10}H_{10})$}YbCl($\mu$-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-$C_5H_4CH_2CH_2OMe$)$_2$YbCl[16] and the 2.450(12) Å in (η^5:η^1-$C_5H_4CH_2CH_2OMe$)$_2$YbI.[3g]

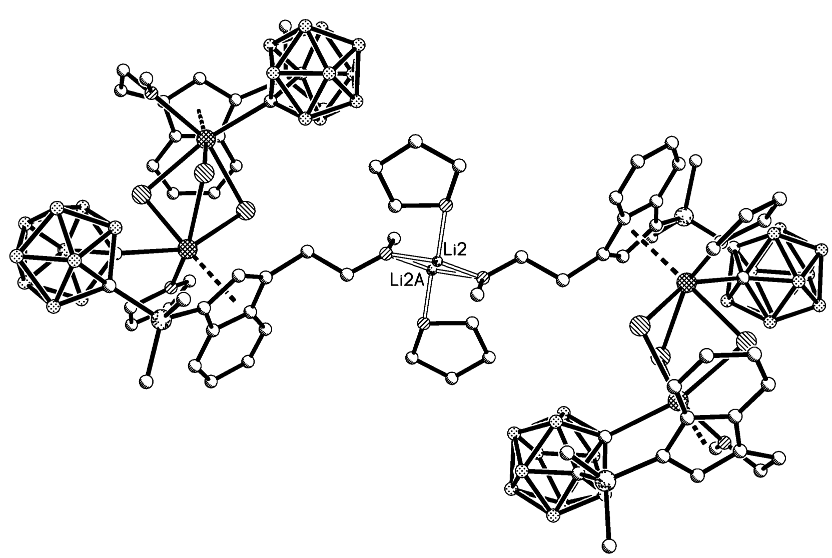


Figure 1. Molecular structure of the anion [{[η^5:σ-$Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$]Yb(THF)($\mu$-Cl)$_3$Yb[$\eta^5$:$\eta^1$:$\sigma$-$Me_2Si$-($C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})$]}$_2${Li(THF)}]$^-$ in **5**. Note that the Li2 atom is disordered over two sets of positions with 0.5:0.5 occupancies.

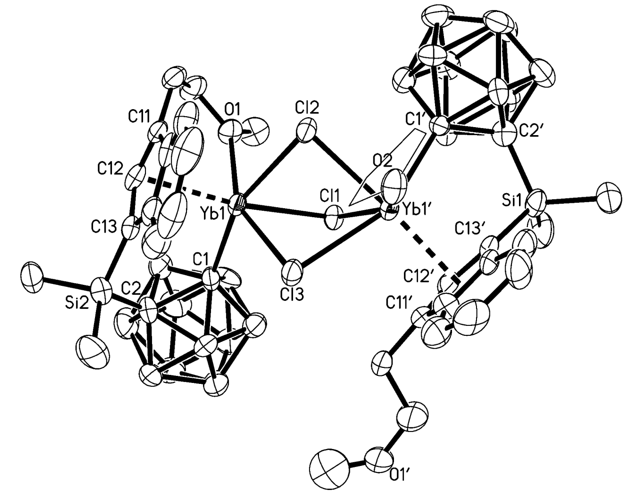


Figure 2. Coordinating sphere around the Yb atoms in **5**. Selected bond distances (Å) and angles (deg): Yb1−C1 = 2.519(12), Yb1′-C1′ = 2.535(11), Yb1−Cl1 = 2.704(3), Yb1−Cl2 = 2.700(3), Yb1−Cl3 = 2.624(3), Yb1−O1 = 2.387(7), Yb1′−Cl1 = 2.656(3), Yb1′−Cl2 = 2.683(3), Yb1′−Cl3 = 2.787(3), Yb1′−O2 = 2.323(8),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

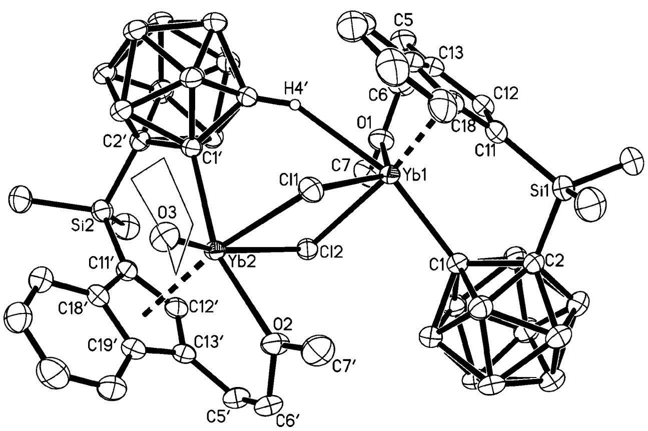


Figure 3. Molecular structure of $[\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Yb(THF)(\mu\text{-}Cl)_2Yb[\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]$ (**6**). Selected bond distances (Å) and angles (deg): Yb1−C1 = 2.460(3), Yb1−O1 = 2.369(3), Yb1−Cl1 = 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**, $[\{\eta^5:\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})\}LnCl(\mu\text{-}Cl)]_2[Li(DME)_3]_2$ (Ln = Sm, Y, Yb),[15] and $[\{[\eta^5:\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]LnCl\}_2(\mu\text{-}Cl)_3Li(DME)][Li(DME)_3]_2$ (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 $[Me_2A(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ (A = C, Si)[7] and $[{}^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ ligands[18] cannot stabilize lanthanocene chlorides, and only $[\{\eta^5:\sigma\text{-}L(C_9H_6)(C_2B_{10}H_{10})\}_2Ln]^-$ type of complexes (L = Me_2C, Me_2Si, ${}^iPr_2NB$) 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 $[\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Y(NHC_6H_3\text{-}2,5\text{-}{}^tBu_2)(\mu\text{-}Cl)Li(THF)_3$ (**8**) or $[\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Yb(NHC_6H_3\text{-}2,6\text{-}{}^iPr_2)(\mu\text{-}Cl)Li(THF)_3$ (**9**) in good yields, shown in Scheme 2. It is noted that reactions of **4** with alkylating reagents such as CH_3Li, Me_3SiCH_2M (M = Li, K), and Me_3SiCH_2MgCl 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 $2,5\text{-}{}^tBu_2C_6H_3NH$ unit, and THF in a molar ratio of 1:1:3. The ^{11}B 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 ^{11}B 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

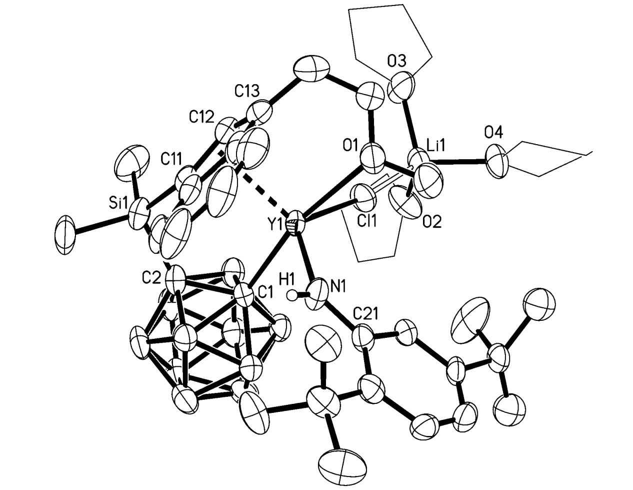
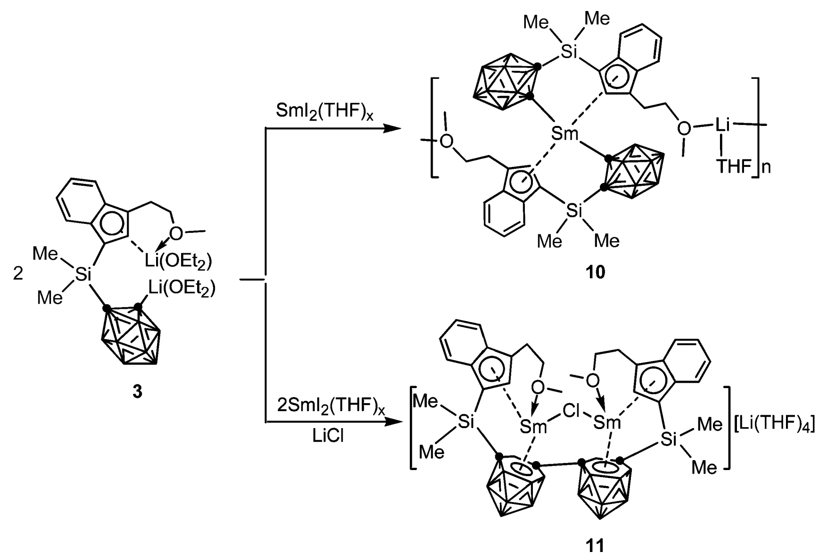


Figure 4. Molecular structure of $[\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Y(NHC_6H_3\text{-}2,5\text{-}{}^tBu_2)(\mu\text{-}Cl)Li(THF)_3$ (**8**). Selected bond distances (Å) and angles (deg): Y1−C1 = 2.540(10), Y1−N1 = 2.222(9), Y1−Cl1 = 2.625(3), Y1−O1 = 2.466(9), av Y1−C(ring) = 2.684(12), Cent−Y1−C1 = 105.5.

(15) Zi, G.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2001**, *20*, 2359.
(16) Qian, C.; Wang, B.; Deng, D.; Hu, J.; Chen, J.; Wu, G.; Zheng, P. *Inorg. Chem.* **1994**, *33*, 3382.
(17) Wang, H.; Wang, H.; Li, H.-W.; Xie, Z. *Organometallics* **2004**, *23*, 875.
(18) Zi, G.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 1136.

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 [{η^5:η^6-$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$}-Er(THF)($\mu$-Cl)Na$(THF)_2]_n$[19] and the Yb−Cl($\mu$) distance of 2.552(2) Å found in $[(Me_3Si)_2N]_3$Yb(μ-Cl)Li$(THF)_3$[20] 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 {(^{i}Pr$_2$C$_6$H$_3$N)(^{i}Pr$_2$C$_6$H$_3$NH)Yb(μ-NC$_6$H$_3$^{i}Pr$_2$)}$_2${[Li(THF)]-[Na(THF)}$_2$[22] and 2.211(5) Å in $[(Me_3Si)_2N]_3$Yb(μ-Cl)-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 organoyttrium amide complexes.[3e]

Reaction with LnI$_2$. Treatment of SmI_2 with 1 equiv of **3** in THF at room temperature gave, after extraction with hot toluene, [{[η^5:σ-$Me_2Si(C_9H_5CH_2CH_2OMe)$-$(C_2B_{10}H_{10})]_2$Sm}{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 [{η^5:η^1:η^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 SmI_2 in THF.[9] These transformations are outlined in Scheme 3.

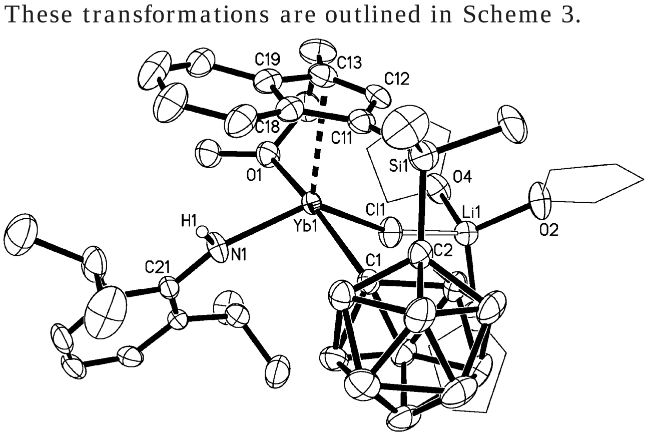


Figure 5. Molecular structure of [η^5: η^1:σ-$Me_2Si(C_9H_5CH_2$-$CH_2OMe)(C_2B_{10}H_{10})$]Yb(NHC$_6H_3$-2,6-^{i}Pr$_2$)($\mu$-Cl)Li$(THF)_3$ (**9**). Selected bond distances (Å) and angles (deg): Yb1−C1 = 2.488(2), Yb1−N1 = 2.157(2), Yb1−Cl1 = 2.558(1), Yb1−O1 = 2.463(2), av Yb1−C(ring) = 2.660(3), 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 [{η^5:σ-$Me_2Si(C_9H_5CH_2CH_2$-$OMe)(C_2B_{10}H_{10})$}$_2$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 [{η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$}$_2$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 [{η^5:η^1:η^6-$Me_2Si(C_9H_5CH_2CH_2OMe)$-$(C_2B_{10}H_{10})$Sm}$_2$($\mu$-Cl)]$^-$. In the anion, each Sm^{3+} ion is η^6-bound to the *nido*-$C_2B_{10}H_{10}$ 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*-$C_2B_{10}H_{10}$ 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 six-membered C_2B_4 rings is 69.6°. This complex represents a very rare example of metallacarboranes bearing a (*nido*-$RC_2B_{10}H_{10})_2^{4-}$ 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 [η^5:η^6-$Me_2Si(C_9H_6)(C_2B_{10}H_{11})$]Sm$(THF)_2$,[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 [{(η^5-$C_5Me_5)_2$SmCl}$_2$(μ-Cl)]$^-$ and

(19) Wang, S.; Wang, Y.; Cheung, M.-S.; Chan, H.-S.; Xie, Z. *Tetrahedron Sym.-in-Print* **2003**, *59*, 10373.
(20) Sheng, E.; Wang, S.; Yang, G.; Zhou, S.; Cheng, L.; Zhang, K.; Huang, Z. *Organometallics* **2003**, *22*, 684.
(21) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
(22) Chan, H.-S.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2002**, 652.
(23) For reviews, see: (a) Xie, Z. *Coord. Chem. Rev.* **2002**, *231*, 23. (b) Grimes, R. N. *Coord. Chem. Rev.* **2000**, *200/202*, 773. (c) Saxena, A. K.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **1997**, *97*, 2421. (d) Grimes, R. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. A. G., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 1, p 371. (e) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081. (f) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251.

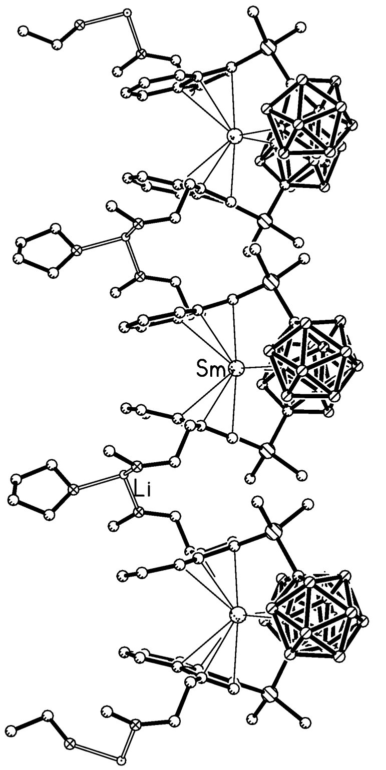


Figure 6. Perspective view of $[\{[\eta^5:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]_2Sm\}\{Li(THF)\}]_n$ (**10**) revealing a portion of the infinite polymeric chain.

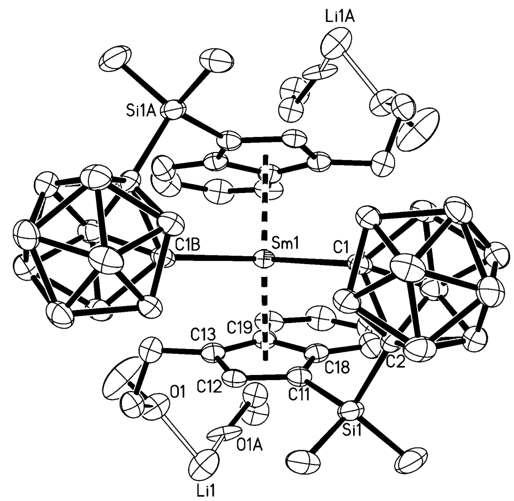


Figure 7. Coordinating sphere around the Sm atom in **10**. Selected bond distances (Å) and angles (deg): Sm1−C1 = 2.635(7), av Sm1−C(ring) = 2.779(7), Cent−Sm1−C1 = 104.1, Cent−Sm1−Cent = 129.6.

2.88(2) Å in $[(\eta^5\text{-}C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$,[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 $[\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Sm^{II}$,[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

(24) Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 3928.

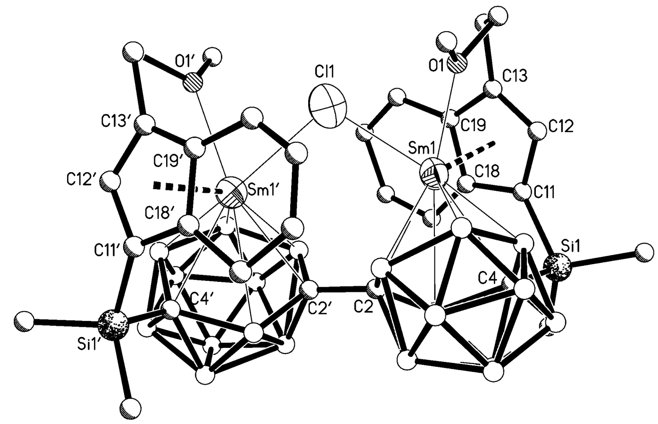


Figure 8. Molecular structure of the anion $[\{\eta^5:\eta^1:\eta^6\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})Sm\}_2(\mu\text{-}Cl)]^-$ in **11**. Selected bond distances (Å) and angles (deg): C2−C2′ = 1.53(3), Sm1−Cl1 = 2.643(4), Sm1′−Cl1 = 2.647(5), Sm1−O1 = 2.49(2), Sm1′−O1′ = 2.48(2), av Sm1−C(ring) = 2.77(2), av Sm1−cage atom = 2.82(2), av Sm1′−C(ring) = 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*-$RC_2B_{10}H_{10})_2^{4-}$, which bonds to the Sm^{3+} 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.

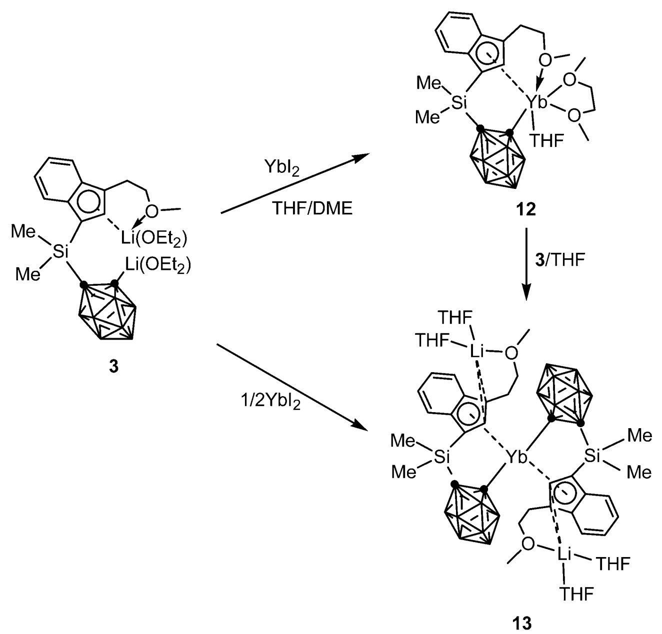
To get some insight into the reaction intermediates, SmI_2 was replaced by a less reactive YbI_2. An equimolar reaction of YbI_2 with **3** in THF produced, after recrystallization from a THF/DME solution, the divalent ytterbium complex $[\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Yb(DME)(THF)$ (**12**) in 72% yield. Treatment of **12** with 1 equiv of **3** gave the ionic complex $\{[(\mu\text{-}\eta^5:\eta^2):\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]_2Yb\}\{Li(THF)_2\}_2$ (**13**) in 69% yield. Complex **13** was also directly prepared from the reaction of YbI_2 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 YbI_2, 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 ^{11}B 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 eight-coordinate $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$[6] and $[\eta^5:\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$.[17] The average Yb−C(ring) distance of 2.814(7) Å, the average Yb−O

Scheme 4



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-^{i}Pr$_2$NP-(C_9H_6)($C_2B_{10}H_{10}$)]Yb(DME)$_2$ and 2.789(8), 2.445(5), and 2.561(6) Å observed in [η^5:σ-Me$_2$C(C_9H_6)($C_2B_{10}H_{10}$)]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**.

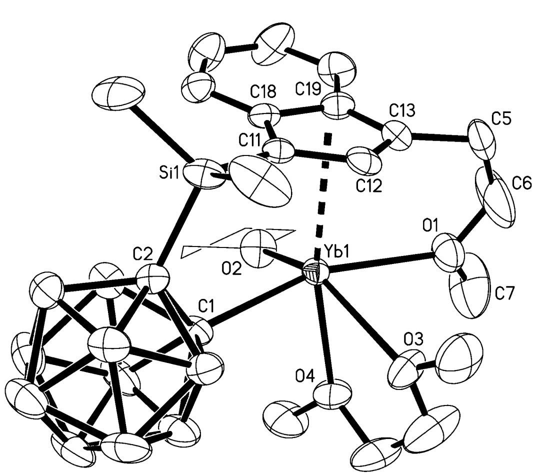


Figure 9. Molecular structure of [η^5:η^1:σ-Me$_2$Si($C_9H_5CH_2$-CH_2OMe)($C_2B_{10}H_{10}$)]Yb(DME)(THF) (**12**). Selected bond distances (Å) and angles (deg): Yb1−C1 = 2.638(5), Yb1−O1 = 2.631(4), Yb1−O2 = 2.432(4), Yb1−O3 = 2.546(4), Yb1−O4 = 2.506(3), av Yb1−C(ring) = 2.814(7), Cent−Yb1−C1 = 102.5.

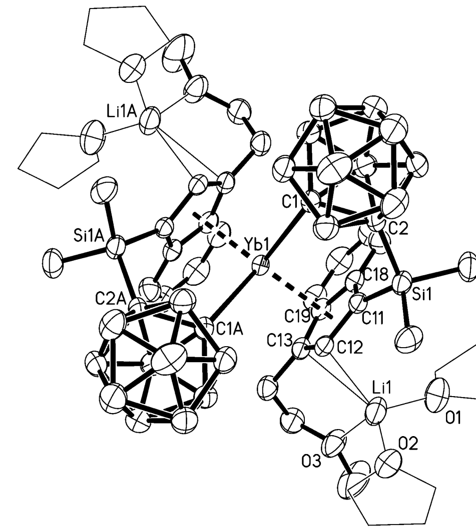


Figure 10. Molecular structure of {[(μ-η^5:η^2):η^1:σ-Me$_2$Si-($C_9H_5CH_2CH_2$OMe)($C_2B_{10}H_{10}$)]$_2$Yb}{Li(THF)$_2$}$_2$ (**13**). Selected bond distances (Å) and angles (deg): Yb1−C1 = 2.654(4), av Yb1−C(ring) = 2.845(4), Li1−C12 = 2.365(9), Li1−C13 = 2.611(9), Cent−Yb1−C1 = 104.1, Cent−Yb1−Cent = 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 [{[(μ-η^5):σ-Me$_2$Si-(C_5Me_4)($C_2B_{10}H_{10}$)]Li(THF)}$_2$Li][Li(THF)$_4$][15] and 2.318-(4) Å in [(η^5-C_5H_5)$_2$Li][Ph$_4$P].[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$_2$Si($C_9H_5CH_2CH_2$OMe)($C_2B_{10}H_{10}$)]$^{2-}$ 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 ether-functionalized ligand can offer divalent samarium complexes unusual reactivities, resulting in the formation of unexpected reduction/coupling products.

Acknowledgment. The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administration Region (Project No. CUHK4026/02P). Z.X. acknowledges the Croucher Foundation for a Senior Research Fellowship Award. S.W. thanks the Excellent Young Scholars Foundation of Anhui Province and the Postdoctoral Fellowship of the Chinese University of Hong Kong.

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.

OM0498807

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