Carbon versus Silicon Bridges. Synthesis of a New Versatile Ligand and Its Applications in Organolanthanide Chemistry

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A new carbon-bridged versatile ligand $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (**1**) has been designed and successfully prepared by treatment of $Li_2C_2B_{10}H_{10}$ with 1 equiv of 6,6-dimethylbenzofulvene followed by hydrolysis with a saturated NH_4Cl aqueous solution. **1** can be conveniently converted into the monoanion $[Me_2C(C_9H_6)(C_2B_{10}H_{11})]Li$ (**2**) and the dianion $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]Li_2$ (**3**) by treatment with 1 or 2 equiv of *n*-BuLi, respectively. Both $NaNH_2$ and NaH can only convert **1** into the monoanion, but cannot deprotonate the CH proton of the carborane cage in **1**. These results differ significantly from those of a closely related analogue, $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$. Treatment of SmI_2 with 1 equiv of **3**, followed by reaction with 1 equiv of **2**, gave the redox product *rac*-$[Li(DME)_2][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Sm]$ (**4**). **4** can also be prepared by reaction of SmI_2 with 1 equiv of **3** in a relatively lower yield. These two reactions may undergo different pathways, an intramolecular electron-transfer pathway for the former and an intermolecular electron-transfer pathway for the latter. The latter reaction can be accelerated by addition of CS_2 or PhC≡CPh, which led to the isolation of *rac*-$[Li(THF)_4][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Sm]$ (**5**). Unlike the SmI_2 case, an equimolar reaction between **3** and YbI_2 afforded the Yb(II) compound $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$ (**6**). **6** can react with 1 equiv of **2** to generate a C−H bond reduction product, *rac*-$[Li(DME)_3][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]\cdot C_6H_5CH_3$ (**7**). Reaction of $LnCl_3$ with 1 or 2 equiv of **2** yielded organolanthanide dichloride and monochloride compounds, respectively, $[\eta^5\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{11})]GdCl_2(THF)_2$ (**15**) and $[\eta^5\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{11})]_2LnCl(THF)(OEt_2)$ (Ln = Y (**8**), Yb (**9**)). Treatment of **9** with 1 or 2 equiv of MeLi gave deprotonation products *rac*-$[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}\{\eta^5\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{11})\}]Yb(\mu\text{-}Cl)Li(DME)_2$ (**10**) and *rac*-$[Li(DME)_2][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]$ (**11**), respectively. Reaction of $LnCl_3$ with 2 equiv of **3** also afforded ionic compounds *rac*-$[Li(DME)_2][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Ln]$ (Ln = Yb (**11**), Nd (**12**), Er (**13**)). Recrystallization of **7** from a mixed solvent of toluene/DME (10:1) gave *meso*-$[Li(DME)_3][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]\cdot 2C_6H_5CH_3$ (**14**). All of these compounds were fully characterized by various spectroscopic and elemental analyses. The molecular structures of **4**−**7**, **11**, **12**, and **14** have been confirmed by single-crystal X-ray analyses. The structural analyses reveal that the anions in **7** (or **11**) and **14** are one pair of diastereomers.

Introduction

Ligand modifications have played a key role in developing new catalyst precursors for optimizing polymerization activity as well as polymer properties such as stereoregularity, molecular weight, bulky and polar comonomer incorporation, and microstructure.[1] Given the impact of the cyclopentadienyl-appended heteroatom donor groups on the catalytic performance of the complexes,[2,3] we have recently designed two types of silicon-bridged versatile ligands, $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$[4] and $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$,[5] by taking advantage of unique carborane molecules[6] and traditional cyclic π-ligands

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such as cyclopentadienyl and indenyl, which have led to the isolation and structural characterization of a new class of organolanthanide compounds.[4,5] Applications of these ligands, especially $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$, however, are limited due to the cleavage of the Si−C(carborane cage) bond in $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ by strong bases such as MeLi, *n*-BuLi, $NaNH_2$, and NaOH.[5,7] To improve the chemical stability of the ligand and to make comparisons between silicon- and carbon-bridged ligand systems, a Me_2C-bridged versatile ligand, $Me_2C(C_9H_7)(C_2B_{10}H_{11})$, was developed in our laboratory.

The results show that the Me_2C linkage is less susceptible to nucleophilic attack and can enhance the reducing ability of the resulting organolanthanide(II) compounds, leading to the isolation and structural characterization of several *rac*- and *meso*-lanthanocenes. This type of C_2-symmetric *ansa*-metallocenes, especially the *rac*-isomers, has received considerable attention since they could act as the precatalysts for stereospecific polymerization of α-olefins.[8,9] The separation of the chiral *rac*-isomer from the undesired, achiral *meso*-isomer is also an interesting problem.[10] We report herein the synthesis and structural characterization of *rac*- and *meso*-lanthanocenes with the new versatile ligand $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ and the differences and similarities between the $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ and $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ ligand systems.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $LnI_2(THF)_x$ (Ln = Sm, Yb),[11] $Li_2C_2B_{10}H_{10}$,[12] and 6,6-dimethylbenzofulvene[13] were prepared according to the literature methods. Anhydrous $LnCl_3$ was prepared from the hydrates by standard procedures.[14] All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker ARX-500 spectrometer at 160.46 MHz. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvent or with respect to internal or external TMS (0.00 ppm) for proton and carbon chemical shifts and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd, Brunel University, Middlesex, U.K.

Preparation of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (1). To a clear solution of *o*-$C_2B_{10}H_{12}$ (5.0 g, 34.7 mmol) in a mixed solvent of toluene/diethyl ether (30 mL, 2:1 in volume) was added a 1.60 M solution of *n*-BuLi in hexane (43.4 mL, 69.4 mmol) dropwise with stirring at 0 °C, and the mixture was warmed to room temperature and stirred for 30 min. The resulting solution was then cooled to 0 °C, and a solution of 6,6-dimethylbenzofulvene (5.4 g, 34.7 mmol) in a mixed solvent of toluene/diethyl ether (8.0 mL, 2:1 in volume) was slowly added. The reaction mixture was stirred at room temperature for 2 h and then refluxed overnight, quenched with 50 mL of a cooled saturated NH_4Cl solution, transferred to a separatory funnel, and diluted with 100 mL of diethyl ether. The organic layer was separated, and the aqueous layer was extracted with additional Et_2O (3 × 25 mL). The combined ether solutions were dried over anhydrous $MgSO_4$ and concentrated to give a crude product which was purified by recrystallization from hot *n*-hexane to afford a pale yellow crystalline solid (9.4 g, 90%). ^1H NMR ($CDCl_3$): δ 7.70 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.32 (dd, J = 7.8 and 8.7 Hz, 1H), 7.25 (dd, J = 8.7 and 8.1 Hz, 1H) (aromatic), 6.52 (t, J = 2.1 Hz, 1H) (vinyl), 3.58 (s, 1H) (C*H* of carboranyl), 3.39 (d, J = 2.1 Hz, 2H) (CH_2), 1.78 (s, 6H) (CH_3). ^{13}C NMR ($CDCl_3$): δ 148.33, 145.32, 143.84, 134.84, 127.06, 125.69, 125.08, 123.13 (aromatic and vinyl), 85.13, 63.51 ($C_2B_{10}H_{11}$), 42.91 (CH_2), 38.05, 32.74 ($(CH_3)_2C$). ^{11}B NMR ($CDCl_3$): δ −3.8 (1), −4.6 (1), −9.7 (3), −11.5 (2), −14.0 (3). IR (KBr, cm^{-1}): ν 3083 (m), 3065 (m), 2982 (m), 2959 (m), 2932 (m), 2580 (vs), 1710 (m), 1456 (s), 1386 (s), 1153 (m), 1075 (m), 1014 (s), 765 (s), 727 (s). Anal. Calcd for $C_{14}H_{24}B_{10}$: C, 55.97; H, 8.05. Found: C, 55.77; H, 8.24.

Preparation of $[Me_2C(C_9H_6)(C_2B_{10}H_{11})]Li(Et_2O)_2$ (2). To a solution of **1** (2.5 g, 8.30 mmol) in a mixed solvent of *n*-hexane/Et_2O (20 mL, 3:1) was added a 1.60 M solution of *n*-BuLi in *n*-hexane (5.20 mL, 8.30 mmol) dropwise at 0 °C, and the reaction mixture was then stirred at room temperature overnight. After removal of the solvents under vacuum, the residue was washed with *n*-hexane (2 × 10 mL). The resulting solid was recrystallized from a mixed solvent of Et_2O/*n*-hexane (10 mL, 1:2) at −30 °C to give **2** as light yellow microcrystals (3.2 g, 84%). ^1H NMR (pyridine-d_5): δ 8.15 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.20 (d, J = 3.9 Hz, 1H), 7.07 (dd, J

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= 7.8 and 8.1 Hz, 1H), 6.97 (dd, J = 8.1 and 7.8 Hz, 1H), 6.75 (d, J = 3.9 Hz, 1H) (C_9H_6), 3.87 (s, 1H) (C*H* of carboranyl), 3.38 (m, 8H), 1.14 (m, 12H) (O(CH_2CH_3)$_2$), 2.10 (s, 6H) (CH_3). ^{11}B NMR (pyridine-d_5): δ −9.6 (1), −10.4 (1), −16.2 (3), −18.8 (2), −21.7 (3). IR (KBr, cm^{-1}): ν 3078 (w), 3055 (m), 2975 (m), 2887 (m), 2583 (vs), 1451 (m), 1386 (m), 1308 (m), 1151 (m), 1074 (s), 1046 (m), 1015 (m), 740 (s), 560 (m), 440 (m).

Preparation of [Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$ (3). To an *n*-hexane (100 mL) solution of Me$_2$C(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (**1**) (6.7 g, 22.4 mmol) was added a 1.60 M solution of *n*-BuLi in *n*-hexane (28.0 mL, 44.8 mmol) dropwise at 0 °C, and the reaction mixture was then stirred at room temperature for 3 days. After removal of the solvent, the residue was washed with *n*-hexane (2 × 15 mL), leaving a light yellow solid which was dried under vacuum to give a light yellow product (6.6 g, 95%). ^{1}H NMR (pyridine-d_5): δ 8.41 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.23 (d, J = 3.6 Hz, 1H), 6.94 (dd, J = 7.8 and 8.4 Hz, 1H), 6.85 (dd, J = 8.4 and 7.8 Hz, 1H), 6.58 (d, J = 3.6 Hz, 1H) (C_9H_6), 2.43 (s, 3H), 2.21 (s, 3H) (CH_3). ^{11}B NMR (pyridine-d_5): δ −1.7 (1), −5.2 (3), −6.3 (2), −9.0 (3), −11.8 (1). IR (KBr, cm^{-1}): ν 3067 (w), 2955 (s), 2888 (s), 2553 (vs), 1454 (s), 1385 (m), 1366 (m), 1326 (m), 1306 (m), 1207 (m), 1168 (m), 1086 (m), 1041 (s), 885 (m), 748 (vs), 446 (m).

Preparation of *rac*-[Li(DME)$_2$][{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Sm] (4). To a THF solution of SmI$_2$(THF)$_x$ (18.5 mL, 1.0 mmol) was added a THF (15 mL) solution of **3** (0.31 g, 1.0 mmol) dropwise, and the reaction mixture was then stirred at room temperature for 24 h. The color of the solution changed from dark blue to yellow green and finally to yellow brown during the course of the reaction. The solvent was evaporated under vacuum, leaving an oily residue, to which was added 15 mL of DME, and the solvents were pumped off again, affording a brown solid that was washed with hot toluene twice (2 × 10 mL). The resulting solid was extracted with a mixed solvent of toluene and DME (3 × 10 mL, 2:1) at reflux temperature. The organic solutions were combined and concentrated to about 10 mL, from which orange crystals were obtained upon standing this solution for several days (0.17 g, 35%). They are a pure *racemic* isomer as identified by an X-ray analysis. Upon dissolving **4** in pyridine-d_5 at room temperature, a 10:1 *racemic*:*meso* ratio had already been established, and this ratio remains unchanged at room temperature after 3 days on the basis of the ^{1}H NMR spectra. ^{1}H NMR (pyridine-d_5): *racemic* isomer, δ 12.39 (br s, 1H), 10.56 (d, J = 9.0 Hz, 1H), 8.56 (br s, 1H), 7.45 (d, J = 6.0 Hz, 1H), 6.58 (dd, J = 9.0 and 6.0 Hz, 1H), 6.05 (dd, J = 6.0 and 9.0 Hz, 1H), 5.87 (m, 2H), 5.79 (m, 2H), 2.93 (br s, 1H), 1.13 (br s, 1H) (C_9H_6), 4.78 (s, 3H), 4.49 (s, 3H), 3.83 (s, 3H), 3.70 (s, 3H) (CH_3), 3.50 (m, 8H), 3.27 (s, 12H) (DME). ^{13}C NMR (pyridine-d_5): δ 132.15, 130.35, 129.03, 127.05, 126.95, 125.99, 125.44, 123.22, 122.99, 122.18, 120.92, 119.82, 118.60, 116.74, 114.98, 114.28, 113.58, 108.35 (C_9H_6), 110.65, 110.30, 81.72 ($C_2B_{10}H_{10}$), 72.41, 58.98 (DME), 38.94, 38.79, 35.95, 35.33 ((*C*H$_3$)$_2$*C*). ^{11}B NMR (pyridine-d_5): δ −4.2 (1), −6.8 (3), −8.5 (3), −10.5 (1), −14.7 (2). IR (KBr, cm^{-1}): ν 3088 (w), 2979 (m), 2933 (m), 2593 (vs), 2539 (vs), 1452 (s), 1384 (m), 1363 (m), 1333 (m), 1183 (m), 1112 (s), 1073 (vs), 1019 (s), 865 (m), 774 (s), 737 (s), 442 (w). Anal. Calcd for C$_{36}$H$_{68}$B$_{20}$LiO$_4$Sm: C, 46.07; H, 7.30. Found: C, 45.56; H, 6.86.

Alternate Method. To a THF solution of SmI$_2$(THF)$_x$ (18.5 mL, 1.0 mmol) was added a THF (15 mL) solution of **3** (0.31 g, 1.0 mmol) dropwise at room temperature followed by addition of a THF (10 mL) solution of **2** (0.46 g, 1.0 mmol), and the reaction mixture was stirred at room temperature for 24 h. Following the workup procedures similar to those used above afforded orange crystals (0.71 g, 74%) identified as **4** by both spectroscopic and X-ray analyses.

Preparation of *rac*-[Li(THF)$_4$][{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Sm] (5). To a THF solution of SmI$_2$(THF)$_x$ (18.5 mL, 1.0 mmol) was slowly added a THF (15 mL) solution of **3** (0.31 g, 1.0 mmol) followed by addition of 2.0 mL of dry CS$_2$ at room temperature. The color of the solution immediately changed from dark blue to orange-brown. The reaction mixture was then stirred at room temperature for 3 h. The solvent was removed under vacuum, leaving an oily residue, to which was added 15 mL of toluene. This suspension was stirred and filtered. The resulting solid was extracted with hot toluene (2 × 10 mL), and the toluene solutions were combined and concentrated to about 10 mL. **5** was obtained as orange crystals upon standing the solution at room temperature for days (0.19 g, 37%). **5** is a pure *racemic* isomer based on an X-ray analysis. Upon dissolving **5** in pyridine-d_5 at room temperature, a 10:1 *racemic:meso* ratio was established. ^{1}H NMR (pyridine-d_5): *racemic* isomer, δ 12.36 (br s, 1H), 10.55 (d, J = 6.0 Hz, 1H), 8.54 (br s, 1H), 7.44 (d, J = 6.0 Hz, 1H), 6.54 (dd, J = 6.0 and 3.0 Hz, 1H), 6.05 (dd, J = 3.0 and 6.0 Hz, 1H), 5.84 (m, 2H), 5.78 (m, 2H), 3.48 (br s, 1H), 2.21 (br s, 1H) (C_9H_6), 4.78 (s, 3H), 4.49 (s, 3H), 3.83 (s, 3H), 3.64 (s, 3H) (CH_3), 3.69 (m, 16H), 1.61 (m, 16H) (OC_4H_8). ^{13}C NMR (pyridine-d_5): δ 132.18, 130.28, 129.71, 128.97, 123.10, 122.92, 122.48, 122.11, 121.70, 119.76, 118.56, 116.65 (C_9H_6), 111.84, 110.59, 81.63 ($C_2B_{10}H_{10}$), 68.14, 28.75 (OC_4H_8), 55.98, 38.87, 38.73, 35.89, 35.26 ((*C*H$_3$)$_2$*C*). ^{11}B NMR (pyridine-d_5): δ −3.2 (1), −5.9 (3), −7.1 (3), −9.7 (1), −13.8 (2). IR (KBr, cm^{-1}): ν 3086 (w), 2961 (s), 2881 (m), 2580 (vs), 2544 (vs), 1452 (m), 1383 (m), 1260 (s), 1084 (s), 1041 (vs), 886 (m), 800 (s), 737 (m). Anal. Calcd for C$_{36}$H$_{60}$B$_{20}$LiO$_2$Sm (**5** − 2THF): C, 48.13; H, 6.73. Found: C, 47.65; H, 6.82.

Alternate Method. To a THF solution of SmI$_2$(THF)$_x$ (18.5 mL, 1.0 mmol) was added a THF (15 mL) solution of **3** (0.31 g, 1.0 mmol) dropwise followed by addition of PhC≡CPh (0.2 g, 1.1 mmol), and the reaction mixture was then stirred at room temperature overnight. The color of the solution slowly changed from dark blue to orange-brown. Following the workup procedures similar to those used above gave orange crystals identified as **5** in 32% yield.

Preparation of [η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Yb(DME)$_2$ (6). To a THF solution of YbI$_2$(THF)$_x$ (24.6 mL, 1.0 mmol) was slowly added a THF (15 mL) solution of **3** (0.31 g, 1.0 mmol) at room temperature. The color of the solution immediately changed from yellow to red. The reaction mixture was then stirred at room temperature overnight. The solvent was removed under vacuum, affording an oily residue, to which was added 15 mL of toluene. The suspension was heated and filtered. The resulting orange-red solid was extracted with a mixed solvent of toluene and DME (5:1, 3 × 10 mL). The solutions were then combined and concentrated to 15 mL, from which orange-red crystals were obtained upon standing this solution at room temperature for several days (0.39 g, 60%). ^{1}H NMR (pyridine-d_5): δ 8.16 (br s, 1H), 6.87 (br s, 1H), 6.79 (br s, 1H), 6.70 (br s, 1H), 6.35 (br s, 1H), 6.20 (br s, 1H) (C_9H_6), 3.51 (m, 8H), 3.29 (s, 12H) (DME), 2.17 (s, 3H), 1.95 (s, 3H) (CH_3). ^{13}C NMR (pyridine-d_5): δ 129.75, 129.01, 126.10, 124.18, 123.89, 123.52, 123.14, 121.98, 117.51 (C_9H_6), 72.39, 58.96 (DME), 44.98, 37.51, 35.00 ((*C*H$_3$)$_2$*C*). ^{11}B NMR (pyridine-d_5): δ −4.7 (2), −5.3 (1), −6.6 (2), −11.1 (2), −15.2 (2), −16.1 (1). IR (KBr, cm^{-1}): ν 3073 (w), 2981 (m), 2940 (m), 2567 (vs), 1451 (s), 1386 (m), 1189 (m), 1108 (s), 1063 (vs), 1017 (s), 861 (s), 741 (s), 440 (m). Anal. Calcd for C$_{22}$H$_{44}$B$_{10}$O$_4$Yb: C, 40.54; H, 6.50. Found: C, 40.64; H, 6.13.

Preparation of *rac*-[Li(DME)$_3$][{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Yb]·C$_6$H$_5$CH$_3$ (7). To a THF solution of **6** (0.24 g, 0.37 mmol) was added a THF (10 mL) solution of **2** (0.17 g, 0.37 mmol) dropwise with stirring at room temperature. The color of the solution immediately changed from orange-red to dark blue. The mixture was then stirred at room temperature for 7 h. The solvent was pumped off to give an oily residue, which was extracted with a mixed solvent of toluene and DME (5:1, 3 × 10 mL). The organic solutions were combined and concentrated to about 15 mL, from which dark blue crystals were obtained upon standing the solution for several days at room temperature (0.31 g, 74%). These crystals were identified to be a pure *racemic* isomer by an X-ray analysis. Upon

dissolving **7** in pyridine-d_5, a 10:1 *racemic*:*meso* ratio was established. ^{1}H NMR (pyridine-d_5): *racemic* isomer, δ 54.7 (s, 1H), 40.1 (s, 1H), 33.8 (s, 1H), 30.3 (s, 1H), 26.7 (s, 1H), 24.2 (s, 1H), 19.9 (s, 1H), 1.1 (s, 1H), 1.08 (s, 1H), 0.8 (s, 1H), 0.4 (s, 1H), −8.5 (s 1H) (C_9H_6), 7.1 (m, 5H), 2.2 (s, 3H) ($C_6H_5CH_3$), 4.0 (m, 12H), 3.3 (m, 18H) (DME), −27.6 (s, 3H), −35.1 (s, 3H), −38.1 (s, 3H), −45.1 (s, 3H) ((CH_3)$_2$C). ^{13}C NMR (pyridine-d_5): δ 165.79, 162.17, 161.47, 147.05, 141.34, 140.13, 130.33, 128.54, 127.26, 123.49 (C_9H_6), 94.44, 91.94, 69.96, 59.16 ($C_2B_{10}H_{10}$), 131.51, 130.77, 127.86, 23.43 ($C_6H_5CH_3$), 74.17, 60.72 (DME), 33.81, 26.75, 24.94, 24.77, 16.34 ((CH_3)$_2C$). ^{11}B NMR (pyridine-d_5): many very broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3066 (w), 2981 (m), 2933 (m), 2581 (vs), 2547 (vs), 1452 (s), 1385 (m), 1338 (m), 1246 (m), 1185 (m), 1122 (s), 1084 (vs), 1025 (s), 867 (m), 785 (s), 733 (s), 696 (m). Anal. Calcd for $C_{47}H_{82}B_{20}LiO_6Yb$: C, 49.55; H, 7.25. Found: C, 49.10; H, 7.32.

Preparation of [η^5-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]$_2$YCl(THF)(OEt$_2$) (8). To a suspension of NaH (0.11 g, 4.6 mmol) in THF (10 mL) was added a THF (15 mL) solution of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.30 g, 1.0 mmol). The mixture was then stirred at room temperature overnight. The resulting THF solution of [$Me_2C(C_9H_6)(C_2B_{10}H_{11})$]Na was slowly filtered into a suspension of YCl_3 (0.10 g, 0.5 mmol) in THF (10 mL), and the reaction mixture was stirred at room temperature for 24 h. The precipitate was filtered off, and the solvent was evaporated under vacuum to afford a sticky oil, to which was added 5 mL of Et_2O. The solvent was removed again under vacuum to give a pale yellow solid. Recrystallization of this solid from a mixed solvent of toluene, THF, and Et_2O (4:1:1) gave colorless microcrystals (0.27 g, 63%). ^{1}H NMR (pyridine-d_5): δ 7.76 (d, J = 7.5 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 6.96 (m, 2H), 6.80 (m, 2H), 6.55 (br s, 2H), 5.64 (br s, 2H) (C_9H_6), 4.85 (br s, 2H) (C*H* of carboranyl), 3.67 (m, 4H), 1.67 (m, 4H) (OC_4H_8), 3.36 (m, 4H), 1.15 (m, 6H) (O(CH_2CH_3)$_2$), 2.52 (s, 12H) ((CH_3)$_2$C). ^{13}C NMR (pyridine-d_5): δ 148.59, 142.37, 137.94, 124.61, 124.11, 122.93, 122.72, 121.90, 121.56, 121.34, 103.24 (C_9H_6), 68.06, 26.00 (OC_4H_8), 65.98, 15.74 (O(CH_2CH_3)$_2$), 87.5, 65.42 ($C_2B_{10}H_{11}$), 25.07, 23.02 ((CH_3)$_2C$). ^{11}B NMR (pyridine-d_5): δ −5.3 (2), −6.3 (2), −10.4 (4), −12.5 (2). IR (KBr, cm^{-1}): ν 3061 (m), 2970 (s), 2876 (s), 2555 (vs), 1448 (s), 1366 (m), 1335 (m), 1210 (m), 1172 (m), 1072 (s), 1044 (vs), 1021 (s), 861 (s), 751 (s), 444 (m). Anal. Calcd for $C_{32}H_{54}B_{20}ClOY$ (**8** − Et_2O): C, 48.32; H, 6.84. Found: C, 47.73; H, 6.79.

Preparation of [η^5-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]$_2$YbCl(THF)(OEt$_2$) (9). To a suspension of $NaNH_2$ (0.28 g, 7.2 mmol) in THF (10 mL) was added a THF (15 mL) solution of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.60 g, 2.0 mmol), and the reaction mixture was then stirred at room temperature overnight. The resulting THF solution of [$Me_2C(C_9H_6)(C_2B_{10}H_{11})$]Na was slowly filtered into a suspension of $YbCl_3$ (0.28 g, 1.0 mmol) in THF (10 mL), and the reaction mixture was stirred at room temperature overnight. Following the workup procedures similar to those used in the preparation of **8** afforded an orange-red crystalline solid (0.66 g, 70%). ^{1}H NMR (pyridine-d_5): δ 7.74 (m, 2H), 7.15 (m, 2H), 7.09 (m, 2H), 6.92 (m, 2H), 6.78 (m, 2H), 6.50 (m, 2H) (C_9H_6), 5.53 (br, 2H) (C*H* of carboranyl), 3.65 (m, 4H), 1.62 (m, 4H) (OC_4H_8), 3.34 (m, 4H), 1.12 (m, 6H) (Et_2O), 2.43 (s, 12H) (CH_3). ^{13}C NMR (pyridine-d_5): δ 151.58, 145.68, 144.34, 143.67, 141.78, 125.14, 124.94, 122.10, 121.76, (C_9H_6), 96.34, 65.66 ($C_2B_{10}H_{11}$), 68.21, 26.18 (OC_4H_8), 66.15, 15.89 (O(CH_2-CH_3)$_2$), 25.20, 23.15 ((CH_3)$_2C$). ^{11}B NMR (pyridine-d_5): δ −4.1-(1), −9.4 (5), −12.9 (2), −14.2 (2). IR (KBr, cm^{-1}): ν 3065 (w), 2970 (s), 2878 (m), 2557 (vs), 1449 (s), 1377 (m), 1366 (m), 1170 (m), 1074 (s), 1045 (s), 1022 (s), 870 (m), 752 (s), 720 (m), 444 (m). Anal. Calcd for $C_{36}H_{64}B_{20}ClO_2Yb$: C, 45.34; H, 6.76. Found: C, 45.34; H, 6.86.

Preparation of *rac*-[{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}{η^5-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)}]Yb(μ-Cl)Li(DME)$_2$ (10). To a THF solution (10 mL) of [η^5-$Me_2C(C_9H_6)(C_2B_{10}H_{11})$]$_2$YbCl(THF)(OEt$_2$) (**9**; 0.43 g, 0.45 mmol) was slowly added a 1.68 M solution of MeLi in ether (0.28 mL, 0.45 mmol) at 0 °C. The mixture was then stirred at room temperature overnight. The solvents were pumped off, leaving an oily residue, to which was added a mixed solvent of toluene and DME (8 mL, 6:1). Slow evaporation of the solvents gave **10** as dark blue microcrystals (0.33 g, 74%). ^{1}H NMR (pyridine-d_5): δ 55.0 (s, 1H), 40.5 (s, 1H), 35.9 (s, 1H), 30.6 (s, 1H), 26.9 (s, 1H), 24.4 (s, 1H), 19.0 (s, 1H), 16.4 (s, 1H), −8.5 (s, 1H), −10.8 (s, 1H), −18.5 (s, 1H), −50.8 (s, 1H) (C_9H_6), −27.7 (s, 3H), −35.2 (s, 3H), −38.3 (s, 3H), −45.3 (s, 3H) ((CH_3)$_2$C), 3.6 (m, 8H), 3.3 (s, 12H) (DME). ^{13}C NMR (pyridine-d_5): δ 160.54, 160.00, 145.44, 139.83, 137.10, 129.75, 129.01, 126.10, 125.80, 122.00, 114.78, 90.13 (C_9H_6), 72.53, 59.09 (DME), 32.19, 29.24, 25.32, 23.27, 14.73 ((CH_3)$_2C$). ^{11}B NMR (pyridine-d_5): δ −2.0 (1), −4.0 (1), −6.0 (2), −10.0 (4), −12.0 (2). IR (KBr, cm^{-1}): ν 3093 (w), 3059 (w), 2980 (m), 2935 (s), 2598 (vs), 2545 (vs), 1452 (s), 1383 (s), 1185 (m), 1112 (s), 1075 (vs), 1020 (s), 865 (s), 786 (s), 740 (s), 440 (m). Anal. Calcd for $C_{38}H_{65}B_{20}ClLiO_4Yb$: C, 43.52; H, 6.60. Found: C, 43.14; H, 7.00.

Preparation of *rac*-[Li(DME)$_2$][{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Yb] (11). To a THF (15 mL) solution of **10** (0.22 g, 0.22 mmol) was added a 1.68 M solution of MeLi in ether (0.14 mL, 0.23 mmol) dropwise at 0 °C, and the mixture was then stirred at room temperature for 12 h. Following the workup procedures similar to those used in the preparation of **10** gave dark blue crystals (0.14 g, 67%). These crystals were identified to be a pure *racemic* isomer by an X-ray analysis. Similar to **7**, upon dissolving **11** in pyridine-d_5, a 10:1 *racemic*:*meso* ratio was established. ^{1}H NMR (pyridine-d_5): *racemic* isomer, δ 54.7 (s, 1H), 40.1 (s, 1H), 33.8 (s, 1H), 30.3 (s, 1H), 26.7 (s, 1H), 24.2 (s, 1H), 19.9 (s, 1H), 1.1 (s, 1H), 1.08 (s, 1H), 0.8 (s, 1H), 0.4 (s, 1H), −8.5 (s, 1H) (C_9H_6), 4.0 (m, 8H), 3.3 (m, 12H) (DME), −27.6 (s, 3H), −35.1 (s, 3H), −38.1 (s, 3H), −45.1 (s, 3H) ((CH_3)$_2$C). ^{13}C NMR (pyridine-d_5): δ 165.79, 162.17, 161.47, 147.05, 141.34, 140.13, 130.33, 128.54, 127.26, 123.49 (C_9H_6), 94.44, 91.94, 69.96, 59.16 ($C_2B_{10}H_{10}$), 74.17, 60.72 (DME), 33.81, 26.75, 24.94, 24.77, 16.34 ((CH_3)$_2C$). The ^{11}B NMR (pyridine-d_5) spectrum consisted of many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3065 (w), 2958 (m), 2591 (vs), 2542 (vs), 1451 (s), 1383 (vs), 1261 (s), 1075 (s), 1021 (s), 865 (m), 795 (s), 737 (m). Anal. Calcd for $C_{36}H_{68}B_{20}LiO_4Yb$: C, 44.99; H, 7.13. Found: C, 44.79; H, 7.49.

This compound can also be prepared in 71% yield from reaction of $YbCl_3$ with 2 equiv of **3** in THF at room temperature.

Preparation of *rac*-[Li(DME)$_2$][{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Nd] (12). To a suspension of $NdCl_3$ (0.13 g, 0.50 mmol) in THF (15 mL) was added a THF (10 mL) solution of **3** (0.31 g, 1.0 mmol) dropwise at 0 °C, and the mixture was stirred overnight at room temperature. Following the workup procedures similar to those used in the preparation of **4** afforded green crystals (0.32 g, 70%). **12** was identified to be a pure *racemic* isomer by an X-ray analysis. No *meso* isomer was observed upon dissolving **12** in pyridine-d_5. ^{1}H NMR (pyridine-d_5): δ 9.01 (br s, 1H), 8.42 (br s, 1H), 8.17 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.78 (m, 3H), 6.92 (d, J = 5.4 Hz, 2H), 6.87 (d, J = 5.4 Hz, 2H), 6.77 (br s, 1H) (C_9H_6), 4.87 (s, 3H), 2.00 (s, 3H), −0.82 (s, 3H), −1.02 (s, 3H) ((CH_3)$_2$C), 3.48 (m, 8H), 3.25 (m, 12H) (DME). ^{13}C NMR (pyridine-d_5): δ 143.88, 141.70, 138.14, 125.15, 124.95, 122.12, 121.77, 115.39, 112.87, 111.56 (C_9H_6), 72.40, 58.96 (DME), 68.18 ($C_2B_{10}H_{10}$), 38.38, 37.79, 25.19, 23.15, 21.67. ((CH_3)$_2C$). The ^{11}B NMR spectrum consisted of many very broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3086 (w), 2980 (m), 2935 (m), 2593 (vs), 2541 (vs), 1452 (s), 1386 (m), 1364 (m), 1333 (m), 1184 (m), 1111 (s), 1073 (vs), 1019 (s), 865 (m), 771 (s), 742 (s), 551 (m). Anal. Calcd for $C_{36}H_{68}B_{20}LiNdO_4$: C, 46.38; H, 7.35. Found: C, 45.82; H, 6.90.

Preparation of *rac*-[Li(DME)$_2$][{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Er] (13). This compound was prepared as yellow crystals in 73% yield from reaction of $ErCl_3$ (0.14 g, 0.5 mmol)

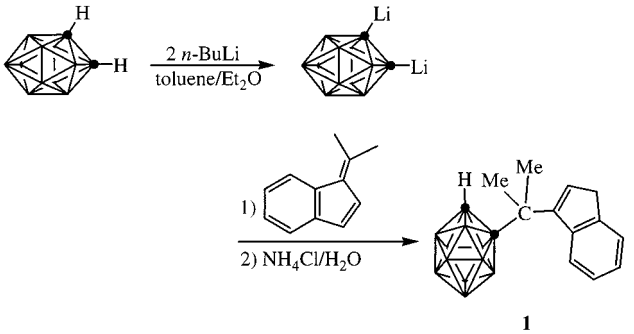
with **3** (0.31 g, 1.0 mmol) in THF (30 mL) followed by procedures similar to those used in the preparation of **12**. ^{1}H NMR (pyridine-d_5): δ 85.6 (s), 65.8 (s), 55.7 (s), 50.6 (s), 43.7 (s), 34.8 (s), 17.6 (br), −1.0 (br), −10.2 (br), −20.6 (br), −29.0 (br), −31.1 (s), −40.4 (s), −48.0 (br), −60.9 (s), −92.1 (s) (unable to be assigned), 3.4 (m), 3.2 (m) (DME). ^{13}C NMR (pyridine-d_5): δ 143.46, 142.74, 139.82, 136.17, 135.40, 102.49 (C_9H_6, other carbons were not observed), 86.16, 72.69 (DME), 79.86, 75.82 ($C_2B_{10}H_{10}$), 45.71, 36.84, 28.25 ($(CH_3)_2C$). ^{11}B NMR (pyridine-d_5): δ 79 (1), 58 (1), 35 (1), 4 (5), −5 (4), −15 (1), −25 (1), −37 (1), −46 (1), −69 (1), −76 (1), −91 (1), −152 (1). IR (KBr, cm^{-1}): ν 3093 (w), 2978 (m), 2935 (s), 2834 (m), 2587 (vs), 2543 (vs), 1452 (s), 1384 (m), 1363 (m), 1336 (m), 1184 (m), 1112 (s), 1073 (vs), 1020 (s), 864 (s), 785 (s), 737 (s), 441 (m). Anal. Calcd for $C_{36}H_{68}B_{20}ErLiO_4$: C, 45.26; H, 7.17. Found: C, 45.29; H, 6.64.

Preparation of *meso*-[Li(DME)$_3$][{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Yb]·2C$_6$H$_5$CH$_3$ (14). A suspension of **7** (0.10 g, 0.09 mmol) in a mixed solvent of toluene and DME (15 mL, 10:1) was refluxed for 3 h. Dark blue crystals were obtained upon slowly cooling the clear solution to room temperature (0.09 g, 82%). These crystals were identified to be a pure *meso* isomer by an X-ray analysis. Upon dissolving **14** in pyridine-d_5, a 10:1 *racemic*:*meso* ratio was established. The ^{1}H, ^{13}C, and ^{11}B NMR spectra are identical with those of **7** in pyridine-d_5. IR (KBr, cm^{-1}): ν 3086 (w), 2931 (s), 2828 (m), 2587 (vs), 2546 (vs), 1451 (s), 1384 (m), 1186 (m), 1120 (s), 1083 (vs), 1024 (s), 866 (s), 765 (s), 734 (s), 695 (m), 567 (m). Anal. Calcd for $C_{43.5}H_{78}B_{20}LiO_6Yb$ (**14** − 1.5$C_6H_5CH_3$): C, 47.79; H, 7.19. Found: C, 47.63; H, 6.93.

Preparation of [η^5-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]GdCl$_2$(THF)$_2$ (15). To a suspension of $GdCl_3$ (0.13 g, 0.50 mmol) in THF (15 mL) was slowly added a freshly prepared THF solution of [Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]Na (15 mL, 0.50 mmol) at room temperature. The mixture was then stirred for 12 h. The precipitate was filtered off and the solution was concentrated under vacuum to about 5 mL, to which was added 10 mL of toluene. A yellow crystalline solid was obtained upon slow evaporation of the solvents at room temperature for several days (0.23 g, 62%). The ^{1}H and ^{13}C NMR (pyridine-d_5) spectra were unable to be taken due to the lack of lock signals. ^{11}B NMR (pyridine-d_5): δ -5.3 (1), −10.2 (3), −14.7 (2), −22.1 (2), −25.7 (1), −37.4 (1). IR (KBr, cm^{-1}): ν 3062 (w), 2982 (s), 2899 (s), 2553 (vs), 1451 (s), 1343 (m), 1256 (m), 1172 (m), 1073 (s), 1015 (vs), 917 (m), 860 (vs), 734 (s), 671 (m), 444 (m). Anal. Calcd for $C_{22}H_{39}B_{10}Cl_2GdO_2$: C, 39.33; H, 5.85. Found: C, 39.34; H, 5.62.

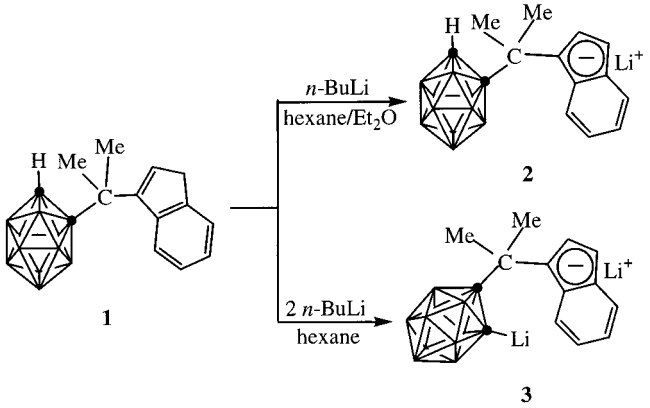
X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on an MSC/Rigaku RAXIS-II imaging plate using Mo Kα radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program.[15] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 using the Siemens SHELXTL program package (PC version).[16a] Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. For non-centrosymmetric structures, the appropriate enantiomorph was chosen by refining Flack's parameter *x* toward zero.[16b] Two DME molecules in **4** and one DME molecule in **12** are disordered over two sets of positions with 0.5:0.5 occupancies. Two DME molecules in **11** are disordered over two sets of positions with 0.5:0.5 and 0.8:0.2 occupancies, respectively. Two methyl groups of the two DME molecules in **7** are disordered over two sets of positions with 0.5:0.5 and 0.75:0.25 occupancies, respectively. The relatively higher *R*-values for **11** and **14** are due to badly disordered DME molecules in **11** and the labile solvated toluene molecules in **14**. Further details are included in the Supporting Information.

Scheme 1



1

Scheme 2



Results and Discussion

Ligand Synthesis. Treatment of 6,6-dimethylbenzofulvene[13] with 1 equiv of $Li_2C_2B_{10}H_{10}$[12] in a mixed solvent of toluene/ether gave, after hydrolysis with a saturated NH_4Cl aqueous solution, Me$_2$C(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (**1**) in 90% isolated yield (Scheme 1). The ^{1}H and ^{13}C NMR spectra show that **1** is a pure compound in which the CMe_2 group bonds only to the sp^2 carbon of the five-membered ring of the indenyl group. The ^{11}B NMR spectrum of **1** shows a 1:1:3:2:3 splitting pattern, which differs from that of Me$_2$C(C$_5$H$_5$)(C$_2$B$_{10}$H$_{11}$)[17] and Me$_2$Si(R)(C$_2$B$_{10}$H$_{11}$) (R = *t*-Bu,[12] C$_5$H$_5$,[4] C$_9$H$_7$[5]), indicating that the ^{11}B NMR of the carborane cage in this type of compounds is very sensitive to the substituents.

Compound **1** can be conveniently converted into the monoanion [Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]$^-$ and the dianion [Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]$^{2-}$ by treatment with 1 equiv of *n*-BuLi in hexane/Et_2O or 2 equiv of *n*-BuLi in *n*-hexane, respectively (Scheme 2).

The ^{1}H NMR spectra exhibit the same splitting pattern for the indenyl groups in two anions. The two methyl groups in the monoanion are equivalent, while those in the dianion are nonequivalent. Both NaH and $NaNH_2$ are also able to convert **1** into the monoanion [Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]$^-$ in THF at room temperature. They, however, cannot deprotonate the CH proton of the

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carborane cage and cannot break the C−C(carborane) bond even under UV light or reflux conditions. These results are significantly different from those of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$,[5,7] indicating that the C−C(carborane) bond is much stronger than the Si−C(carborane) bond.

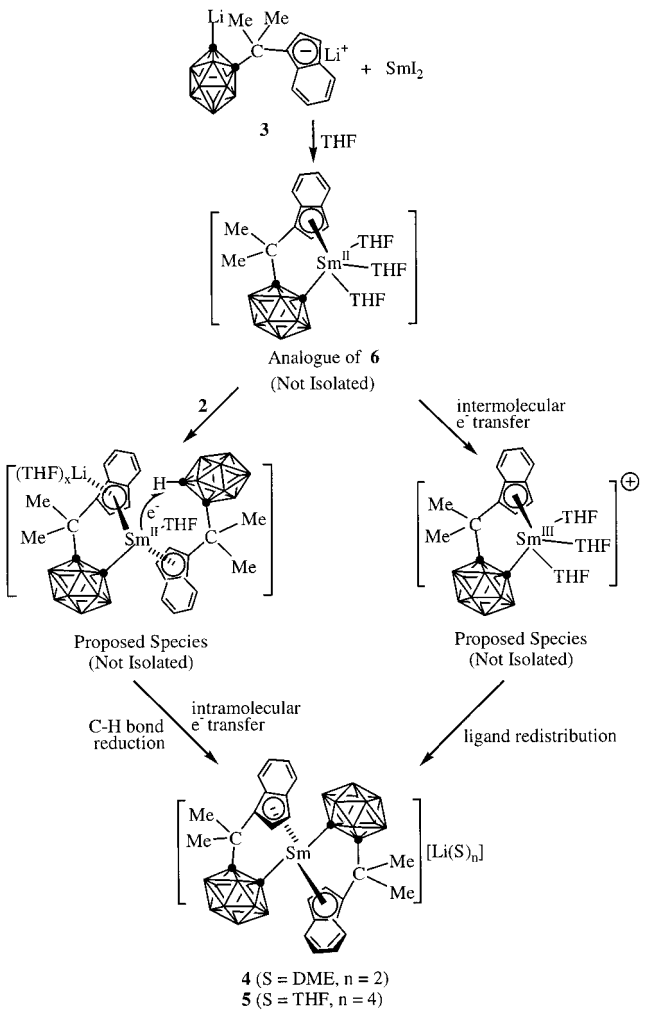
Comparison of the properties of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$[5] to those of $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$[4] seems to imply that the indenyl group can enhance the acidity of the CH proton of the carborane cage. However, the acidity of the CH proton of the carborane cage in **1** is obviously lower than that in $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ and is similar to that in $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$ with respect to the reactions with NaH in THF, indicating that the bridging groups also play an important role in these reactions. It seems that the Si atom functions as an "electron conductor", while the C atom functions as an "electron insulator" in these ligand systems, perhaps due to the empty 3d orbitals of the Si atom.

Application to Lanthanide(II) Chemistry. Reaction of a dark blue THF solution of SmI_2 with 1 equiv of $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]Li_2$ (**3**) in THF at room temperature, followed by extraction with a mixed solvent of DME and toluene, did not produce the expected compound, $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Sm(DME)_2$; instead, the Sm(III) compound *rac*-$[Li(DME)_2][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Sm]$ (**4**) was isolated as orange crystals in 35% yield. This color change indicates that the oxidation state of Sm has been changed from 2+ to 3+.[4c,5] Treatment of SmI_2 with 1 equiv of **3** in THF followed by addition of 1 equiv of **2** gave, after extraction with a mixed solvent of DME and toluene, the same compound **4** in a much higher yield. To gain some insight into the reactive intermediates, the reactions between the generated samarium(II) species and CS_2 or PhC≡CPh were examined since they have been reported to react with organosamarium(II) species to afford the insertion products.[18,19] Addition of CS_2 into the Sm(II) solution generated in situ causes an immediate color change from dark blue to orange-brown, while the reaction between the Sm(II) species and PhC≡CPh is relatively slow on the basis of the color change. In both cases, only *rac*-$[Li(THF)_4][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Sm]$ (**5**) was crystallized out; neither CS_2 nor PhC≡CPh insertion products were isolated. But it is very clear that both CS_2 and PhC≡CPh do accelerate the redox reactions. All these transformations are summarized in Scheme 3.

Both intramolecular and intermolecular electron-transfer pathways are proposed for the above reactions as shown in Scheme 3 after successful isolation of compound $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$ (**6**). The intramolecular pathway offers a higher yield, while the yield is relatively lower for the intermolecular pathway. Such an intermolecular electron transfer could be accelerated by electron acceptors; the higher the electron-accepting ability is, the faster the reaction will be, which could explain why CS_2 can dramatically enhance the reaction rate.

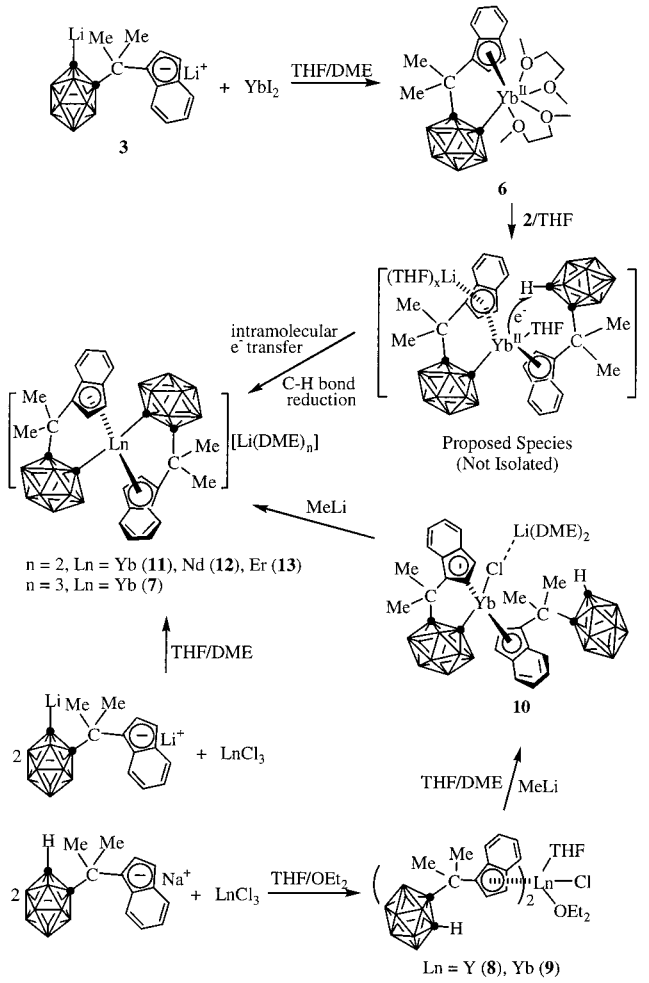
Treatment of YbI_2 with 1 equiv of **3** in THF afforded, after extraction with a mixed solvent of DME and toluene, an orange-red Yb(II) compound, $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$ (**6**). Unlike the SmI_2 case, no redox reaction was observed. Reaction of **6** with 1 equiv of $[Me_2C(C_9H_6)(C_2B_{10}H_{11})]Li$ (**2**) in THF at room temperature immediately generated a dark blue solution, from which *rac*-$[Li(DME)_3][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]\cdot C_6H_5CH_3$ (**7**) was isolated in good yield after extraction with a mixed solvent of toluene and DME. It is noteworthy that the expected Yb(II) compound $[\eta^5\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{11})]Yb(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Li(THF)_x$, an analogue of $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Yb(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na(THF)_3$,[5] was not isolated. But it may serve as an intermediate in which the Yb(II) reduces the C−H bond of the carborane cage via an intramolecular electron-transfer pathway to form the final product **7**, as shown in Scheme 4. This is one of few examples showing that an organoytterbium(II) compound can reduce the C−H bond[20] since Yb(II) is usually considered to be a less powerful reducing agent.[21] Comparing the reactivity of $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$ (**6**) with that of $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Yb(THF)_3$[5] suggests that the bridging atom has a large influence on the reactivity of the resulting compounds.

Scheme 3



(18) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.
(19) Evans, W. J.; Seibel, C. A.; Ziller, J. W.; Doedens, R. J. *Organometallics* **1998**, *17*, 2103.
(20) Boncella, J. M.; Tilley, T. D.; Anderson, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 710.
(21) The reduction potentials for the Ln^{3+}/Ln^{2+} couple are −1.1 V for Yb and −1.5 V for Sm, respectively; see: Evans, W. J. *Polyhedron* **1987**, *6*, 803.

Scheme 4



Compounds **4**−**7** have been fully characterized by various spectroscopic and elemental analyses. Their solid-state structures have all been confirmed by X-ray diffraction studies. Compounds **4**, **5**, and **7** are all pure *racemic* isomers based on their solid-state structures. They crystallize out from the solution in the shape of plates. Upon dissolving them in pyridine-d_5, a 10:1 *racemic*:*meso* ratio had already been established at room temperature for all three compounds according to the ^{1}H NMR spectra, and this ratio remains unchanged after 3 days at room temperature. The *racemic* isomer exhibits four types of Me resonances and two sets of indenyl protons in its ^{1}H NMR spectrum, while the *meso* isomer displays two Me resonances and one set of indenyl protons. The *racemic*−*meso* interconversion for *ansa*-metallocenes has been reported, and such an interchange may be promoted by donor solvents and salts.[22]

Application to Lanthanide(III) Chemistry. Treatment of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (**1**) with excess NaH or $NaNH_2$ in THF at room temperature gave the monoanion $[Me_2C(C_9H_6)(C_2B_{10}H_{11})]Na$ (**2**). This was followed by reaction with 0.5 equiv of $LnCl_3$ at room temperature, after recrystallization from a mixed solvent of toluene, THF, and Et_2O, to afford organolanthanide monochloride compounds that have been formulated as $[\eta^5$-$Me_2C(C_9H_6)(C_2B_{10}H_{11})]_2LnCl(THF)(OEt_2)$ (Ln = Y(**8**), Yb (**9**)) on the basis of spectroscopic data and elemental analyses (Scheme 4). These results further indicate the differences between the two ligand systems, $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ and $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$.[5,7] All attempts to grow single crystals suitable for X-ray analyses failed due to severe twinning problems.

Compound **9** reacted with 1 equiv of MeLi in THF at room temperature to give, after recrystallization from a mixed solvent of toluene and DME, *rac*-$[\{\eta^5$:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})\}\{\eta^5$-$Me_2C(C_9H_6)(C_2B_{10}H_{11})\}]Yb(\mu$-Cl)-$Li(DME)_2$ (**10**), an analogue of *rac*-$[\{\eta^5$:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}\{\eta^5$-$Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}]Er(\mu$-Cl)Na-$(THF)_3$,[7b] as dark blue microcrystals in good yield. Further reaction of **10** with 1 equiv of MeLi in THF, after recrystallization from a mixed solvent of toluene and DME, produced *rac*-$[Li(DME)_2][\{\eta^5$:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]$ (**11**) in good yield. These results imply that the two CH cage protons in **9** can be deprotonated step by step.

Treatment of $LnCl_3$ with 2 equiv of $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]Li_2$ (**3**) in THF at room temperature generated, after workup, ionic compounds *rac*-$[Li(DME)_2][\{\eta^5$:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Ln]$ (Ln = Yb (**11**), Nd (**12**), Er (**13**)) in good yield. As shown in Scheme 4, compound **11** can be prepared in three different ways, indicating the versatility of the ligand and the resulting compounds.

Compounds **7**−**13** have been fully characterized by various spectroscopic and elemental analyses. The solid-state structures of **11** and **12** have been further confirmed by single-crystal X-ray analyses. They are all *racemic* isomers. The ^{1}H NMR spectra of **7** and **11** are identical except the relative intensity of DME resonances.

***Racemic*−*Meso* Interconversion of $[Li(DME)_3][\{\eta^5$:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]$.** The solid-state structures show that all isolated compounds are pure *racemic* isomers. Upon dissolving them into pyridine-d_5, a 10:1 *racemic*:*meso* ratio had already been established. Such an epimerization process is very common for *ansa*-metallocenes, and the isomer ratio is dependent on solvent, substituent, metal ion, and salt.[22] Dissolution of *rac*-$[Li(DME)_3][\{\eta^5$:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]$ (**7**) in hot toluene/DME (10:1) and slowly cooling to room temperature gave *meso*-$[Li(DME)_3][\{\eta^5$:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]\cdot 2C_6H_5CH_3$ (**14**). Thus, both *racemic* and *meso* isomers of $[\{\eta^5$:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]^-$ have been successfully isolated and structurally characterized. Their ^{1}H NMR spectra are identical in pyridine-d_5 solution, indicating the *racemic*−*meso* interconversion is very fast in pyridine-d_5 solution. This process can be explained by a plausible mechanism proposed by Marks (Scheme 5).[22a] It involves coordination of DME molecules to the Yb center with Li^+ assistance to encourage Yb−indenyl heterolysis, rotation about the C−indenyl bond of the detached indenyl group, and recoordination of the opposite face.

Molecular Structure. The solid-state structures of **4**−**7**, **11**, **12**, and **14** have been confirmed by single-

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Scheme 5

crystal X-ray analyses. Crystal data and details of data collection and structure refinement are given in Table 1. Selected bond distances and angles are listed in Table 2.

The molecular structure of **6** is shown in Figure 1. The Yb(II) ion is η^5-bound to indenyl, σ-bound to the carbon atom of the carborane cage, and coordinated to four oxygen atoms from two DME molecules in a distorted-octahedral geometry with a formal coordination number of 8, which compares with the seven-coordinate [η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]Yb$(THF)_3$.[5] The average Yb−C($C_5$ ring) distance of 2.789(8) Å, the average Yb−O distance of 2.445(5) Å, and the Yb−C(2) σ bond distance of 2.561(6) Å are comparable to the corresponding values of 2.750(3), 2.432(2), and 2.584(3) Å in [η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]Yb$(THF)_3$.[5] The Yb−C(2) σ bond distance of 2.561(6) Å in **6** falls in a range normally observed for organoytterbium(II) compounds, for instance, 2.580(2) Å in [η^5-$Me_2Si(C_9H_6)$-$(C_2B_{10}H_{11})$]Yb(THF)[(μ-η^5):σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]Na-$(THF)_3$,[5] 2.501(9) Å in Yb[$C(SiMe_3)_3]_2$,[23a] 2.47(2) Å in [Yb{$CH(SiMe_3)_2$}I$(OEt_2)]_2$,[23a,b] 2.573(13) Å in [Yb(CR_3)-(μ-OEt)$(OEt_2)]_2$,[23c] and 2.55(6) Å in (Tp)Yb{$CH(SiMe_3)_2$} (Tp = hydridotris(3-*tert*-butyl-5-methylpyrazolyl)-borate).[23d] The C(2)−Yb−Cent (Cent: the centroid of the

Table 1. Crystal Data and Summary of Data Collection and Refinement for 4−7, 11, 12, and 14

	4	**5**	**6**	**7**	**11**	**12**	**14**
formula	$C_{36}H_{64}B_{20}LiO_4Sm$	$C_{44}H_{52}B_{20}LiO_4Sm$	$C_{22}H_{42}B_{10}O_4Yb$	$C_{47}H_{82}B_{20}LiO_6Yb$	$C_{36}H_{64}B_{20}LiO_4Yb$	$C_{36}H_{64}B_{20}LiNdO_4$	$C_{54}H_{90}B_{20}LiO_6Yb$
crystal size (mm)	0.07 × 0.26 × 0.38	0.08 × 0.26 × 0.32	0.13 × 0.16 × 0.40	0.40 × 0.45 × 0.46	0.03 × 0.07 × 0.36	0.17 × 0.35 × 0.36	0.08 × 0.16 × 0.26
fw	934.4	1018.4	651.7	1139.3	957.1	928.3	1231.4
cryst syst	triclinic	triclinic	orthorhombic	orthorhombic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$Pca2_1$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	11.624(1)	11.994(3)	20.354(2)	12.716(3)	11.551(3)	11.645(1)	11.874(2)
b, Å	12.928(1)	13.266(4)	9.642(1)	21.471(4)	12.899(3)	12.959(1)	31.547(6)
c, Å	16.753(1)	17.716(5)	15.400(1)	22.011(4)	16.805(4)	16.732(1)	18.809(4)
α, deg	80.01(1)	76.83(2)	90.0	90.0	79.91(1)	79.92(1)	90.0
β, deg	77.00(1)	76.13(2)	90.0	90.0	76.46(2)	77.13(1)	105.16(1)
γ, deg	84.93(1)	85.86(2)	90.0	90.0	83.45(2)	84.87(1)	90.0
V, Å^3	2412.6(3)	2664(1)	3022.1(5)	6010(2)	2390(1)	2420.2(2)	6800(2)
Z	2	2	4	4	2	2	4
D_{calcd}, Mg/m^3	1.286	1.269	1.432	1.259	1.330	1.274	1.203
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.0−50.0	3.0−51.0	4.0−51.0	3.0−51.0	3.0−50.0	3.0−50.0	3.0−50.0
μ, mm^{-1}	1.253	1.141	3.120	1.599	1.993	1.109	1.418
F(000)	954	1026	1304	2340	970	950	2540
no. of indep reflns	7304	7737	2657	5858	4677	7572	6648
no. of obsd reflns	6917	6843	2408	5858	4677	7315	6405
no. of params refnd	541	632	335	698	565	528	741
goodness of fit	1.054	1.013	1.141	1.059	1.171	1.025	1.099
R1	0.051	0.074	0.067	0.057	0.096	0.058	0.096
wR2	0.140	0.207	0.167	0.148	0.245	0.169	0.235

(23) (a) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12071. (b) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Lu, Z.-R.; Smith, J. D. *Organometallics* **1996**, *15*, 4783. (c) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2691. (d) Hasinoff, L.; Takats, J.; Zhang, X.-W.; Bond, A. H.; Rogers, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 8833.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

	compound (Ln)						
	4 (Sm)	**5** (Sm)	**7** (Yb)	**11** (Yb)	**12** (Nd)	**14** (Yb)	**6** (Yb)
Ln−C(11)	2.759(2)	2.741(4)	2.689(4)	2.600(9)	2.771(3)	2.644(6)	2.747(6)
Ln−C(12)	2.644(2)	2.645(4)	2.504(4)	2.538(9)	2.754(3)	2.535(7)	2.779(7)
Ln−C(13)	2.645(2)	2.661(4)	2.539(4)	2.587(8)	2.711(3)	2.576(6)	2.720(8)
Ln−C(18)	2.859(2)	2.816(4)	2.820(4)	2.707(9)	2.784(3)	2.629(7)	2.876(7)
Ln−C(19)	2.798(2)	2.788(4)	2.749(5)	2.668(8)	2.786(3)	2.691(7)	2.825(7)
Ln−C(21)	2.729(2)	2.712(5)	2.640(4)	2.677(9)	2.773(3)	2.647(7)	
Ln−C(22)	2.688(2)	2.690(4)	2.578(5)	2.544(7)	2.683(2)	2.525(7)	
Ln−C(23)	2.694(2)	2.695(4)	2.585(5)	2.583(9)	2.670(3)	2.582(7)	
Ln−C(28)	2.768(2)	2.766(4)	2.693(5)	2.783(8)	2.881(3)	2.730(6)	
Ln−C(29)	2.765(2)	2.751(4)	2.726(4)	2.765(7)	2.801(3)	2.746(6)	
Ln−C(1)	2.529(2)	2.540(4)	2.442(3)	2.440(7)	2.549(3)	2.502(6)	2.561(6)
Ln−C(3)	2.577(2)	2.580(4)	2.451(4)	2.447(10)	2.603(3)	2.505(6)	
C(1)−Ln−C(3)	115.7(1)	113.0(1)	106.3(1)	106.6(3)	117.0(1)	106.2(2)	
Cent−Ln−Cent	127.6	128.4	127.5	127.9	127.6	136.6	

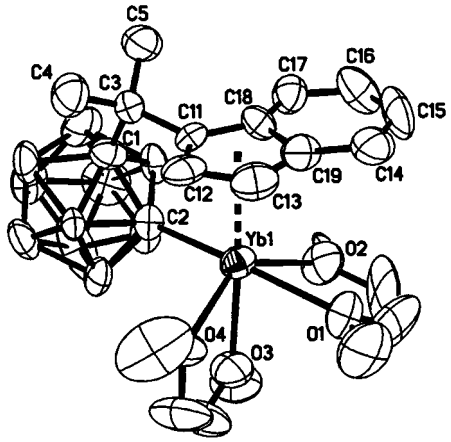

Figure 1. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$ (**6**) (thermal ellipsoids drawn at the 35% probability level).

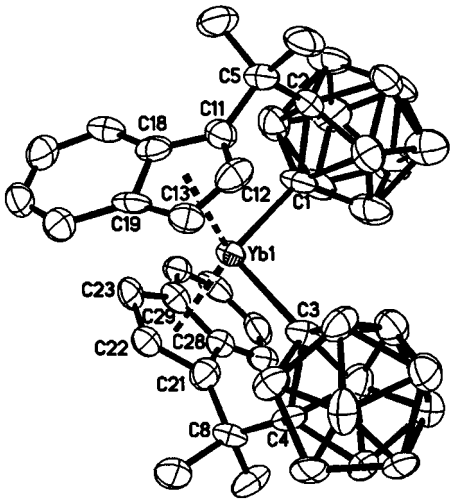

Figure 2. Molecular structure of the anion *rac*-$[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]_2Yb^-$ in **11** (thermal ellipsoids drawn at the 35% probability level).

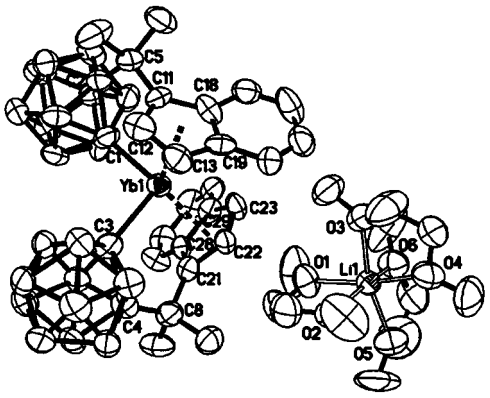

Figure 3. Molecular structure of *rac*-$[Li(DME)_3][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Yb]$ (**7**) (the solvated toluene molecule is not shown; thermal ellipsoids drawn at the 35% probability level).

five-membered ring of indenyl) angle of 90.6° is significantly smaller than the corresponding value of 103.9° in both $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Yb(THF)_3$[5] and $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Yb(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na(THF)_3$,[5] due to the difference in the coordination environment of the Yb atom.

The solid-state structures of compounds **4**, **5**, **7**, **11**, **12**, and **14** as derived from single-crystal X-ray diffraction studies consist of well-separated, alternating layers of discrete tetrahedral anions of $[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Ln]^-$ and cations of $[Li(solvent)_n]^+$ and show one or two toluenes of solvation for **7** and **14**, respectively. For the anions $[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}_2Ln]^-$, except that in **14**, they are all *racemic* isomers; the anions in **7** (or **11**) and **14** are one pair of diastereomers. Compounds **4**, **5**, **11**, and **12** are isomorphous, and the anions in these compounds are isostructural. Figure 2 shows their representative structures. Figures 3 and 4 display the molecular structures of **7** and **14**, respectively. Compound **7** crystallizes in the non-centrosymmetric space group $P2_12_12_1$, but the absolute structure could not be determined from the X-ray data, as the Flack parameter *x* refined to a value of 0.51(3).[16b] This can be rationalized by the fact that the enantiomeric forms of **7** differ only in regard to a minor portion of their similar molecular skeletons. An alternative explanation is that the crystal is a racemic twin composed of an equal mixture of domains of different chirality.

In all structures, the Ln ion is η^5-bound to two indenyl rings and σ-bound to two carbon atoms from two carborane cages in a distorted-tetrahedral geometry with Cent−Ln−Cent angle of around 128° (except *meso* isomer **14**). The C(1)−Ln−C(3) angle ranges from 106° to 117°.

As listed in Table 2, on going from Nd to Sm to Yb, the Ln−C distance decreases, which is consistent with the lanthanide contraction and Shanonn's ionic radii.[24]

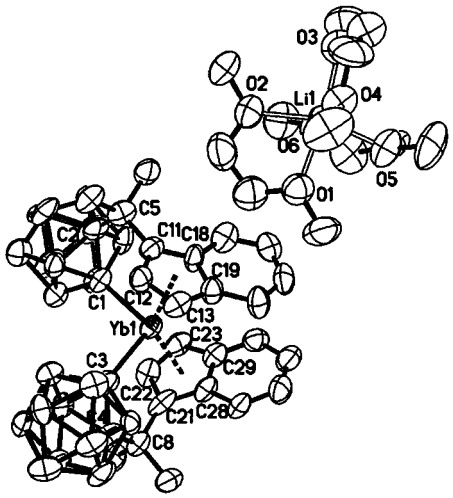

Figure 4. Molecular structure of *meso*-[Li(DME)$_3$][{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Yb] (**14**) (the solvated toluene molecules are not shown; thermal ellipsoids drawn at the 35% probability level).

Both Ln−C π and σ bond distances are comparable to those observed in [{η^5:σ-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln]$^-$ and [{η^5:σ-Me$_2$Si(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln]$^-$ anions.[4,5] The differences in C−C and Si−C bond distances seem to have only a little effect on the structural parameters of the resulting organolanthanide compounds. It, however, may affect the *racemic*:*meso* ratio in solution with respect to the isolation of *meso*-[{η^5:σ-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln][Na(THF)$_6$] (Ln = Sm,[5] Nd[7b]) and *rac*-[{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln][Li(solvent)$_n$] and the ^{1}H NMR spectra in pyridine-d_5.

Conclusion

Despite being close analogues, Me$_2$C(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (**1**) and Me$_2$Si(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) exhibit different reactivity patterns. The C−C(carborane) bond cannot be broken by NaNH$_2$ or organolithium reagents such as MeLi and *n*-BuLi, and the CH proton of the cage in **1** cannot be deprotonated by NaH and NaNH$_2$. In contrast, the Si−C(carborane) bond is very sensitive to NaNH$_2$ and organolithium reagents, and the CH proton of the cage in Me$_2$Si(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) can be deprotonated by NaH.[5,7]

Comparison of the acidity of the CH proton of the carborane cage in **1** to that in Me$_2$Si(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$)[5] and Me$_2$Si(C$_5$H$_5$)(C$_2$B$_{10}$H$_{11}$)[4] suggests that the Si atom may function as an "electron conductor" and the C atom as an "electron insulator" in this type of ligand system probably due to the empty 3d orbitals of the Si atom.

The bridging group has also some effects on the reactivity of the resulting organolanthanide compounds. For example, [η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Yb(DME)$_2$ (**6**) can reduce the C−H bond of the carborane cage, indicating that **6** is a stronger reducing agent than its analogue [η^5:σ-Me$_2$Si(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Yb(THF)$_3$.[5] This, together with the higher stability of the C−C bond toward nucleophilic attack, will certainly make **1** a more applicable ligand than its silicon analogue Me$_2$Si(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$).

The isolation and structural characterization of both *rac*- and *meso*-isomers of [{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Yb]$^-$ and their ^{1}H NMR spectra in pyridine imply that *rac*-[{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln]$^-$ predominates in polar solvents such as pyridine, THF, and DME.

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Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures giving atom-numbering schemes for compounds **4**−**7**, **11**, **12**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990648O

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