Synthesis, Structural Characterization, and Reactivity of Organolanthanide Complexes Derived from a New, Versatile Boron-Bridged Ligand, $^{i}Pr_2NB(C_9H_7)(C_2B_{10}H_{11})$†

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New boron-bridged ligands incorporating both indenyl and carboranyl moieties have been prepared. Reaction of $^{i}Pr_2NB(C_9H_7)Cl$ with 1 equiv of $Li_2C_2B_{10}H_{10}$ gave, after treatment with 1 equiv of *n*-BuLi, the dilithium salt $[^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (**1**), which was conveniently converted into its neutral counterpart $^{i}Pr_2NB(C_9H_7)(C_2B_{10}H_{11})$ (**2**) via reaction with excess C_5H_6. Mixing **1** and **2** in a 1:1 molar ratio quantitatively afforded the monolithium salt $[^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{11})]Li(THF)_2$ (**3**). Treatment of LnI_2 with 1 equiv of **1** generated the trivalent organolanthanide complexes *meso*-$[\{\eta^5{:}\sigma\text{-}^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})\}_2Ln][Li(S)_n]$ (Ln = Sm, Yb; S = THF, $n = 4$; S = DME, $n = 3$), which was also prepared in a much higher yield by reaction of LnI_2 with 1 equiv of **1** followed by treatment with 1 equiv of **3**. Both inter- and intramolecular electron-transfer pathways are proposed for these reactions. Reaction of $LnCl_3$ with 1 or 2 equiv of **1** gave the same ionic complexes *meso*-$[\{\eta^5{:}\sigma\text{-}^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})\}_2Ln][Li(S)_n]$ (Ln = Nd, Y, Yb; S = THF, $n = 4$; S = DME, $n = 3$). Silylamine elimination reactions of **2** and $Ln[N(SiHMe_2)_2]_3(THF)_2$ resulted in clear formation of $[\eta^5{:}\sigma\text{-}^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]LnN(SiHMe_2)_2(THF)_2$ (Ln = Nd (**8**), Er (**9**), Y (**10**)). Treatment of **8** with Me_3NHCl or Me_3SiCl led to the isolation of **2** and $NdCl_3(DME)_2$ (**11**), respectively. The new complexes were fully characterized by various spectroscopic data and element analyses. Some were further confirmed by single-crystal X-ray analyses. Complex **8** is an active catalyst for the polymerization of methyl methacrylate (MMA) in toluene, affording syn-rich poly(MMA)s.

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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] To meet the requirements of different purposes, a large number of bridged ancillary ligands have been developed. Among different bridging groups in these ligands, carbon and silicon moieties are most common and have served a primarily structual role, that of fixing the cyclic organic units in a specific orientation with respect to the active site of the catalyst.[2]

Very recently, boron-bridged *ansa* ligands have attracted much attention, since the electrophilic boron linkage may affect the property of the active metal center via geometry changes and intramolecular Lewis acid coactivation.[3] Two classes of complexes have been studied: (1) metallocenes bridged by three-coordinate boron moieties where the electrophilicity of boron is attenuated by partial $p_\pi-p_\pi$ π-bonding[4] and (2) metallocenes bridged with four-coordinate boron linkages.[5] Experimental results show that R_2NB-bridged *ansa* ligands can offer metallocenes with a very high activity in polymerization/copolymerization of α-olefins.[4c,d]

To take advantage of unique carborane molecules,[6] and traditional cyclic π-ligands as well as bridging ligands,[7] we have developed several versatile carbon- and silicon-bridged ligands, $Me_2A(C_5R_4H)(C_2B_{10}H_{11})$ (A = C, R = H;[8] A = Si, R = H,[9] Me[10]), $Me_2A(C_9RH_6)(C_2B_{10}H_{11})$ (A = C, R = H;[11] A = Si, R = H,[12] CH_2CH_2OMe,[13] $CH_2CH_2NMe_2$[13]), and $Me_2Si(C_{13}H_9)(C_2B_{10}H_{11})$.[14] Our results show that both the cyclic organic groups and the bridging atoms have a large influence on the properties of these ligand systems and the resulting organometallic compounds.[8−14] Besides the electronic effects, the bridging atoms also play an important role in directing the stereochemistry of ring addition during complex formation.[15] With these in mind and given the impact of the boron-bridged *ansa* ligands on the catalytic performance of the metallocenes, we have incorporated

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the R_2NB linkage into our ligand systems. We report herein the synthesis and properties of a new, versatile boron-bridged ligand, $^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$, as well as its applications in lanthanide chemistry. The similarities and differences among organolanthanide complexes with B-, C-, and Si-bridged ligands are also discussed in this paper.

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. $C_9H_7SiMe_3$,[16] $Ln[N(SiHMe_2)_2]_3(THF)_2$,[17] and $Li_2C_2B_{10}H_{10}$[9] were prepared according to the literature methods. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a 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., Brunel University, Middlesex, U.K.

Preparation of $Cl_2B(C_9H_7)$. To a CH_2Cl_2 (50 mL) solution of BCl_3 (2.25 g, 19.2 mmol) was added a CH_2Cl_2 (20 mL) solution of $C_9H_7SiMe_3$ (3.62 g, 19.2 mmol) dropwise with stirring at 0 °C, and the mixture was stirred for 2 h at room temperature. Removal of the solvent and fractional distillation at 88−90 °C/1 Torr yielded $Cl_2B(C_9H_7)$ as a colorless liquid (2.26 g, 60%). ^1H NMR (benzene-d_6): δ 8.11 (d, J = 6.0 Hz, 1H), 7.33−7.04 (m, 4H), 2.86 (m, 2H). ^{11}B NMR (benzene-d_6): δ 51.3.

Preparation of $^iPr_2NB(C_9H_7)Cl$. To a *n*-hexane (50 mL) solution of $Cl_2B(C_9H_7)$ (2.95 g, 15.0 mmol) was added a *n*-hexane (10 mL) solution of $^iPr_2NH$ (3.03 g, 30.0 mmol) dropwise with stirring at 0 °C. The mixture was refluxed for 2 h. The white precipitate ($^iPr_2NH \cdot HCl$) was filtered off. Removal of the solvent and fractional distillation at 128−130 °C/1 Torr yielded $^iPr_2NB(C_9H_7)Cl$ as a white solid (1.96 g, 50%). ^1H NMR (benzene-d_6): δ 7.59 (d, J = 6.0 Hz, 1H, indenyl), 7.30 (d, J = 6.0 Hz, 1H, indenyl), 7.24 (t, J = 9.0 Hz, 1H, indenyl), 7.13 (m, 1H, indenyl), 6.37 (m, 1H, indenyl), 3.77 (m, 1H, NC*H*Me_2), 3.45 (m, 1H, NC*H*Me_2), 3.11 (s, 2H, indenyl), 1.40 (m, 6H, NCH(C*H*$_3$)$_2$), 0.84 (m, 6H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (benzene-d_6): δ 149.5, 147.8, 144.5, 137.5, 126.9, 125.2, 124.2, 122.6, 40.7 (indenyl), 51.7, 47.2 (N*C*HMe_2), 23.5, 22.6 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (benzene-d_6): δ 35.2. IR (KBr, cm^{-1}): ν 3064 (m), 2971 (vs), 1582 (m), 1486 (s), 1376 (s), 1264 (s), 1051 (vs), 807 (vs), 755 (vs), 717 (s).

Preparation of $[^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (1). To a solution of *o*-$C_2B_{10}H_{12}$ (7.20 g, 50.0 mmol) in a dry toluene/diethyl ether (2:1) mixture (100 mL) at 0 °C was slowly added a 1.6 M solution of *n*-BuLi in *n*-hexane (62.5 mL, 100.0 mmol) with stirring. The mixture was warmed to room temperature and stirred for 30 min. The resulting solution of $Li_2C_2B_{10}H_{10}$ was then cooled to 0 °C, to which was slowly added a solution of $^iPr_2NB(C_9H_7)Cl$ (13.1 g, 50.0 mmol) in a toluene/diethyl ether (2:1) mixture (50 mL). The reaction mixture was then refluxed overnight. The white precipitate (LiCl) was filtered off. A 1.6 M solution of *n*-BuLi in *n*-hexane (32 mL, 50.0 mmol) was added dropwise with stirring at −78 °C, leading to the formation of a yellow solid. This suspension was then stirred at room temperature overnight. The precipitate was collected and washed with ether (20 mL × 3), giving **1** as a pale yellow solid (19.8 g, 75%). ^1H NMR (pyridine-d_5): δ 7.96 (d, J = 9.0 Hz, 1H, indenyl), 7.73 (d, J = 9.0 Hz, 1H, indenyl), 7.12 (d, J = 3.0 Hz, 1H, indenyl), 6.90 (t, J = 6.6 Hz, 1H, indenyl), 6.81 (t, J = 6.6 Hz, 1H, indenyl), 6.61 (d, J = 3.0 Hz, 1H, indenyl), 5.66 (m, 1H, NC*H*Me_2), 3.45 (br, 1H, NC*H*Me_2), 3.32 (q, J = 4.5 Hz, 8H, Et_2O), 1.25 (m, 9H, NCH(C*H*$_3$)$_2$), 1.12 (d, J = 6.9 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.06 (t, J = 4.5 Hz, 12H, Et_2O). ^{13}C NMR (pyridine-d_5): δ 130.3, 129.0, 128.7, 124.9, 121.2, 120.5, 114.6, 114.3, 94.7 (indenyl), 82.1 (cage *C*), 66.2, 15.9 (Et_2O), 49.0, 48.4 (N*C*HMe_2), 26.4, 26.3, 23.5, 22.8 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −1.6 (1B), −6.5 (1B), −8.6 (3B), −11.3 (5B), −13.9 (1B). IR (KBr, cm^{-1}): ν 3066 (m), 2969 (vs), 2552 (vs), 1452 (s), 1382 (s), 1321 (s), 1185 (s), 1090 (s), 1065 (s), 754 (s). Anal. Calcd for $C_{21}H_{40}B_{11}Li_2NO$ (**1** − Et_2O): C, 55.39; H, 8.86; N, 3.07. Found: C, 55.15; H, 8.60; N, 2.73.

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Preparation of ^{i}Pr$_2$NB(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (2). To a THF (100 mL) solution of [^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$(OEt$_2$)$_2$ (**1**; 2.65 g, 5.0 mmol) was slowly added a THF (20 mL) solution of freshly distilled cyclopentadiene (C$_5$H$_6$; 1.32 g, 20.0 mmol) with stirring at −78 °C. This reaction mixture was warmed to room temperature and stirred overnight. Removal of the solvent afforded a white solid that was extracted with *n*-hexane (30 mL × 3). Removal of *n*-hexane generated a white solid. Recrystallization from *n*-hexane gave **2** as colorless crystals (1.61 g, 87%). ^{1}H NMR (benzene-d_6): δ 7.23 (t, J = 7.8 Hz, 1H, indenyl), 7.16 (m, 2H, indenyl), 7.05 (t, J = 7.8 Hz, 1H, indenyl), 6.04 (m, 1H, indenyl), 4.93 (m, 1H, NC*H*Me$_2$), 3.14 (s, 1H, cage C*H*), 3.00 (m, 1H, NC*H*Me$_2$), 2.94 (m, 2H, indenyl), 0.90 (m, 9H, NCH(C*H*$_3$)$_2$), 0.66 (d, J = 7.4 Hz, 3H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (benzene-d_6): δ 148.3, 143.5, 139.8, 126.9, 125.7, 124.5, 62.8, 50.1, 40.6 (indenyl), 72.5 (cage *C*), 48.4 (N*C*HMe$_2$), 25.7, 25.5, 22.4, 21.5 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (benzene-d_6): δ 36.1 (1B), −0.2 (1B), −2.8 (1B), −8.2 (1B), −8.9 (1B), −10.4 (1B), −11.4 (1B), −13.7 (4B). IR (KBr, cm^{-1}): ν 3068 (s), 2964 (vs), 2582 (vs), 1484 (s), 1373 (s), 1338 (s), 1184 (s), 1076 (s), 1024 (s), 717 (s). Anal. Calcd for C$_{17}$H$_{32}$B$_{11}$N: C, 55.28; H, 8.73; N, 3.79. Found: C, 55.54; H, 8.48; N, 3.98.

Preparation of [^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{11}$)]Li(THF)$_2$ (3). To a THF (100 mL) solution of [^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$(OEt$_2$)$_2$ (**1**; 2.65 g, 5.0 mmol) was slowly added a THF (20 mL) solution of ^{i}Pr$_2$NB(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (**2**; 1.85 g, 5.0 mmol) with stirring at −78 °C. This mixture was warmed to room temperature and stirred overnight. Removal of the solvent gave a yellow solid that was washed with *n*-hexane (30 mL × 3) to give **3** as a yellow solid (4.94 g, 95%). ^{1}H NMR (pyridine-d_5): δ 7.79 (d, J = 7.8 Hz, 1H, indenyl), 7.70 (d, J = 7.8 Hz, 1H, indenyl), 7.09 (t, J = 6.6 Hz, 1H, indenyl), 6.83 (t, J = 6.6 Hz, 1H, indenyl), 6.75 (d, J = 3.0 Hz, 1H, indenyl), 6.72 (d, J = 3.0 Hz, 1H, indenyl), 3.55 (m, 8H, THF), 3.51 (m, 2H, NC*H*Me$_2$), 2.93 (s, 1H, cage C*H*), 1.42 (m, 8H, THF), 1.27 (br, 6H, NCH(C*H*$_3$)$_2$), 1.18 (d, J = 6.0 Hz, 6H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (pyridine-d_5): δ 134.9, 132.8, 128.4, 125.7, 121.9, 119.3, 113.2, 112.9, 96.1 (indenyl), 78.5 (cage *C*), 68.2, 26.1 (THF), 49.3 (N*C*HMe$_2$), 26.1 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −3.9 (1B), −5.8 (1B), −8.3 (1B), −11.2 (5B), −14.6 (3B). IR (KBr, cm^{-1}): ν 3037 (s), 2968 (vs), 2598 (vs), 2559 (vs), 1475 (s), 1370 (s), 1326 (s), 1185 (s), 1042 (vs), 890 (s), 737 (s). Anal. Calcd for C$_{25}$H$_{43}$B$_{11}$LiNO$_{1.5}$ (**3** − 0.5THF): C, 57.14; H, 8.97; N, 2.90. Found: C, 56.85; H, 9.22; N, 2.69.

Preparation of *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Sm][Li(DME)$_3$] (4a). To a THF solution of SmI$_2$(THF)$_x$ (18.5 mL, 1.0 mmol) was added a THF (15 mL) solution of **1** (0.53 g, 1.0 mmol) dropwise, and the reaction mixture was then stirred at room temperature for 2 days. The color of the solution changed from dark blue to yellowish green and finally to dark red during the course of the reaction. The solvent was evaporated under vacuum. The oily residue was extracted with DME (10 mL × 3). The DME solutions were combined and concentrated to about 10 mL, from which **4a** was obtained as orange crystals after this solution stood at −20 °C for several days (0.19 g, 32%). ^{1}H NMR (pyridine-d_5): δ 3.48 (s, 4H), 3.25 (s, 6H) (DME), plus many unresolved peaks ranging from 14.3 to 0.5 ppm. ^{13}C NMR (pyridine-d_5): δ 137.4, 128.7, 128.0, 125.3, 114.0, 113.3, 112.7, 111.7, 93.0 (indenyl), 90.9 (cage *C*), 71.4, 57.9 (DME), 49.2, 49.0 (N*C*HMe$_2$), 25.7, 25.1, 24.6, 22.2 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −3.2 (2B), −5.9 (4B), −10.5 (3B), −16.2 (2B). IR (KBr, cm^{-1}): ν 3073 (m), 2960 (vs), 2575 (vs), 1459 (s), 1375 (s), 1329 (s), 1193 (s), 1077 (vs), 1027 (s), 867 (s), 805 (s), 750 (s). Anal. Calcd for C$_{46}$H$_{90}$B$_{22}$LiN$_2$O$_6$Sm: C, 47.53; H, 7.80; N, 2.41. Found: C, 47.21; H, 7.58; N, 2.44.

Preparation of *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Sm][Li(THF)$_4$]·0.25C$_6$H$_6$ (4b). To a THF solution of SmI$_2$(THF)$_x$ (18.5 mL, 1.0 mmol) was added a THF (15 mL) solution of **1** (0.53 g, 1.0 mmol) dropwise, and the reaction mixture was then stirred at room temperature for 4 h. To the resulting solution was then added a THF (15 mL) solution of **3** (0.52 g, 1.0 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 days. The color of the solution changed from dark blue to yellowish green and finally to dark red during the course of the reaction. The solvent was evaporated under vacuum. The oily residue was extracted with hot benzene (10 mL × 3). The benzene solutions were combined and concentrated to about 15 mL, from which **4b** was obtained as orange crystals after this solution stood at room temperature for several days (0.84 g, 70%). ^{1}H NMR (pyridine-d_5): δ 3.63 (m, 4H), 1.60 (m, 4H) (THF), plus many unresolved peaks ranging from 14.3 to 0.2 ppm. ^{13}C NMR (pyridine-d_5): δ 138.4, 129.8, 129.0, 126.3, 115.1, 114.4, 113.7, 112.7, 94.0 (indenyl), 128.0 (*C*$_6$H$_6$), 91.9 (cage *C*), 68.2, 26.2 (THF), 50.5, 50.0 (N*C*HMe$_2$), 26.7, 25.9, 24.4, 22.9 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −3.2 (2B), −5.9 (4B), −10.5 (3), −16.2 (2). IR (KBr, cm^{-1}): ν 3080 (w), 2961 (vs), 2890 (vs), 2547 (vs), 1470 (s), 1378 (s), 1331 (s), 1186 (s), 1098 (vs), 1033 (s), 880 (s), 801 (s), 744 (s). Anal. Calcd for C$_{50}$H$_{92}$B$_{22}$LiN$_2$O$_4$Sm (**4b** − 0.25C$_6$H$_6$): C, 50.87; H, 7.86; N, 2.37. Found: C, 50.92; H, 7.71; N, 2.40.

Preparation of *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Yb][Li(DME)$_3$] (5a). This compound was prepared as green crystals from the reaction of YbI$_2$(THF)$_x$ (25 mL, 1.0 mmol) with **1** (0.53 g, 1.0 mmol) in THF (15 mL) by using procedures similar to those used in the synthesis of **4a**: yield 0.21 g (36%). ^{1}H NMR (pyridine-d_5): δ 3.51 (s, 4H), 3.21 (s, 6H) (DME), plus many unresolved peaks ranging from 2.2 to −16.7 ppm. ^{13}C NMR (pyridine-d_5): δ 71.4, 57.9 (DME), plus many unresolved peaks. ^{11}B NMR (pyridine-d_5): δ 16.0 (2B), −3.6 (2B), −5.4 (3B), −12.1 (1B), −16.2 (1B), −19.8 (2B). IR (KBr, cm^{-1}): ν 3050 (w), 2961 (vs), 2576 (vs), 1642 (s), 1478 (s), 1380 (s), 1329 (s), 1192 (s), 1082 (vs), 1026 (s), 801 (s). Anal. Calcd for C$_{40}$H$_{75}$B$_{22}$LiN$_2$O$_3$Yb (**5a** − 1.5DME): C, 45.76; H, 7.20; N, 2.67. Found: C, 45.32; H, 7.31; N, 2.49.

Preparation of *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Yb][Li(THF)$_4$]·0.5C$_6$H$_6$ (5b). This compound was prepared as green crystals from the reaction of YbI$_2$(THF)$_x$ (25 mL, 1.0 mmol) with **1** (0.53 g, 1.0 mmol) followed by addition of **3** (0.52 g, 1.0 mmol) in THF (15 mL) by using procedures similar to those used in the synthesis of **4b**: yield 0.92 g (74%). ^{1}H NMR (pyridine-d_5): δ 7.12 (s, 3H, C$_6$*H*$_6$), 3.61 (m, 16H, THF), 1.61 (m, 16H, THF), plus many unresolved peaks ranging from 2.2 to −15.6 ppm. ^{13}C NMR (pyridine-d_5): δ 128.7 (*C*$_6$H$_6$), 67.2, 25.1 (THF); plus many unresolved peaks. ^{11}B NMR (pyridine-d_5): δ 16.0 (2B), −3.6 (2B), −5.4 (3B), −12.1 (1B), −16.2 (1B), −19.8 (2B). IR (KBr, cm^{-1}): ν 3070 (w), 2963 (vs), 2579 (vs), 1632 (s), 1479 (s), 1377 (s), 1332 (s), 1193 (s), 1094 (vs), 1040 (s), 889 (s), 744 (s). Anal. Calcd for C$_{50}$H$_{92}$B$_{22}$LiN$_2$O$_4$Yb (**5b** − 0.5C$_6$H$_6$): C, 49.92; H, 7.71; N, 2.33. Found: C, 49.89; H, 7.81; N, 2.59.

Preparation of *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Nd][Li(DME)$_3$] (6). To a suspension of NdCl$_3$ (0.13 g, 0.50 mmol) in THF (15 mL) was added a THF (10 mL) solution of **1** (0.53 g, 1.0 mmol) dropwise with stirring at room temperature. The reaction mixture was stirred at room temperature for 2 days. The solvent was evaporated under vacuum. The oily residue was extracted with DME (10 mL × 3). The DME solutions were combined and concentrated to about 10 mL, from which **6** was obtained as blue microcrystals after this solution stood at −20 °C for several days (0.40 g, 70%). ^{1}H NMR (pyridine-d_5): δ 6.78 (m, 1H), 6.24 (m, 1H), 4.95 (m, 1H), 3.61 (s, 6H, DME), 3.49 (s, 9H, DME) 3.26 (s, 6H), 2.22 (m, 1H) 1.88 (m, 1H), 1.67 (m, 1H), 1.25 (m, 1H), 0.81 (m, 1H), 0.35 (s, 6H). ^{13}C NMR (pyridine-d_5): δ 134.4, 132.2, 129.2, 128.1, 119.6, 114.7, 113.7, 111.9, 107.3 (indenyl), 90.9 (cage *C*), 71.7, 58.3 (DME), 55.8, 53.2 (NCHMe$_2$), 27.7, 25.5, 22.5 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ 0.0 (3B), −4.6 (3B), −7.5 (3B), −9.7 (1B), −10.6 (1B). IR (KBr, cm^{-1}): ν 3060 (w), 2958 (vs), 2557 (vs), 1453 (s), 1371 (s), 1329 (s), 1190 (s), 1077 (vs), 1028 (s), 863 (s), 800 (s), 742 (s). Anal. Calcd for C$_{36}$H$_{65}$B$_{22}$LiN$_2$NdO (**6** − 2.5DME): C, 46.45; H, 7.04; N, 3.01. Found: C, 46.47; H, 7.09; N, 2.85.

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Preparation of *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Y][Li(DME)$_3$] (7). This compound was prepared as colorless microcrystals from the reaction of YCl_3 (0.10 g, 0.50 mmol) with **1** (0.53 g, 1.0 mmol) in THF (15 mL) by using procedures similar to those used in the synthesis of **6**: yield 0.41 g (74%). ^{1}H NMR (pyridine-d_5): δ 8.03 (d, J = 7.2 Hz, 1H, indenyl), 7.80 (d, J = 7.2 Hz, 1H, indenyl), 7.15 (t, J = 3.0 Hz, 1H, indenyl), 7.00 (t, J = 6.3 Hz, 1H, indenyl), 6.87 (t, J = 6.3 Hz, 1H, indenyl), 6.68 (t, J = 3.0 Hz, 1H, indenyl), 5.72 (m, 1H, NC*H*Me$_2$), 3.49 (m, 1H, NC*H*Me$_2$), 3.48 (s, 6H, DME), 3.27 (s, 9H, DME), 1.34 (m, 9H, NCH(C*H*$_3$)$_2$), 1.18 (d, J = 6.0 Hz, 3H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (pyridine-d_5): δ 131.6, 130.3, 125.9, 125.3, 122.2, 121.6, 115.6, 115.4, 95.8 (indenyl), 89.5 (cage *C*), 73.5, 60.1 (DME), 50.2, 49.3 (N*C*HMe$_2$), 27.5, 27.3, 24.6, 23.8 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −5.2 (1B), −1.9 (1B), −6.8 (2B), −8.9 (1B), −11.5 (5B), −14.4 (1B). IR (KBr, cm^{-1}): ν 3060 (w), 2953 (m), 2908 (vs), 2571 (vs), 1633 (s), 1455 (s), 1381 (s), 1258 (s), 1094 (s), 1025 (s), 801 (s). Anal. Calcd for $C_{46}H_{90}B_{22}LiN_2O_6Y$: C, 50.18; H, 8.24; N, 2.55. Found: C, 50.43; H, 8.45; N, 2.38.

Preparation of *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Yb][Li(THF)$_4$] (5c). To a suspension of $YbCl_3$ (0.13 g, 0.50 mmol) in THF (15 mL) was added a THF (10 mL) solution of **1** (0.53 g, 1.0 mmol) dropwise with stirring at room temperature. The reaction mixture was stirred at room temperature for 2 days. The solvent was evaporated under vacuum. The oily residue was extracted with toluene (10 mL × 3). The toluene solutions were combined and concentrated to about 15 mL from which **5c** was isolated as green crystals after this solution stood at room temperature for several days (0.42 g, 70%). ^{1}H NMR (pyridine-d_5): δ 3.61 (m, 4H), 1.61 (m, 4H) (THF), plus many unresolved peaks ranging from 2.2 to −16.8 ppm. ^{13}C NMR (pyridine-d_5): δ 68.2, 26.2 (THF), plus many unresolved peaks. ^{11}B NMR (pyridine-d_5): δ 16.0 (2B), −3.6 (2B), −5.4 (3B), −12.1 (1B), −16.2 (1B), −19.8 (2B). IR (KBr, cm^{-1}): ν 3050 (w), 2961 (vs), 2577 (vs), 1453 (s), 1378 (s), 1330 (s), 1192 (s), 1081 (vs), 1027 (s), 866 (s), 800 (s), 740 (s). Anal. Calcd for $C_{42}H_{76}B_{22}LiN_2O_2Yb$ (**5c** − 2THF): C, 47.64; H, 7.24; N, 2.65. Found: C, 47.35; H, 7.43; N, 2.35.

Alternate Method. To a suspension of $YbCl_3$ (0.28 g, 1.0 mmol) in THF (15 mL) was added a THF (10 mL) solution of **1** (0.53 g, 1.0 mmol) dropwise with stirring at room temperature, and the reaction mixture was stirred at room temperature for 2 days. Following workup procedures similar to those used above afforded green crystals (0.38 g, 64% based on **1**) identified as **5c** by both spectroscopic and X-ray analyses.

Preparation of [η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]NdN(SiHMe$_2$)$_2$(THF)$_2$ (8). A toluene solution (10 mL) of **2** (0.37 g, 1.0 mmol) was slowly added to a toluene solution (10 mL) of Nd[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (0.69 g, 1.0 mmol) with stirring at room temperature. The resulting solution was refluxed overnight to give a yellow solution. This solution was filtered and concentrated to about 1 mL to which was added *n*-hexane (10 mL). **8** was isolated as green crystals after this solution stood at room temperature for several days (0.58 g, 73%). ^{1}H NMR (benzene-d_6): many broad, unresolved peaks ranging from 13.3 to −5.0 ppm. ^{13}C NMR (benzene-d_6): δ 68.2, 26.2 (THF), plus many unresolved peaks. ^{11}B NMR (benzene-d_6): δ 17.3 (2B), 13.3 (2B), 8.5 (3B), 2.8 (3B), −36.4 (1B). IR (KBr, cm^{-1}): ν 3050 (w), 2961 (vs), 2570 (vs), 1458 (s), 1376 (s), 1252 (s), 1096 (vs), 1024 (vs), 907 (s). Anal. Calcd for $C_{29}H_{60}B_{11}N_2NdO_2Si_2$: C, 44.19; H, 7.67; N, 3.56. Found: C, 44.13; H, 7.64; N, 3.21.

Preparation of [η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]ErN(SiHMe$_2$)$_2$(THF)$_2$ (9). This compound was prepared as pink crystals from the reaction of **2** (0.37 g, 1.0 mmol) with Er[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (0.71 g, 1.0 mmol) in toluene (20 mL) by using procedures similar to those used in the synthesis of **8**: yield 0.54 g (67%). ^{1}H NMR (benzene-d_6): many broad, unresolved peaks ranging from 7.2 to −26.8 ppm. ^{13}C NMR (benzene-d_6): δ 69.3, 27.0 (THF), plus many unresolved peaks. ^{11}B NMR (benzene-d_6): δ −9.0 (3B), −14.9 (3B), −20.8 (3B), −28.8 (2B). IR (KBr, cm^{-1}): ν 3067 (w), 2958 (vs), 2579 (vs), 1487 (s), 1377 (s), 1246 (s), 1024 (vs), 897 (vs). Anal. Calcd for $C_{29}H_{60}B_{11}ErN_2O_2Si_2$: C, 42.94; H, 7.46; N, 3.45. Found: C, 43.02; H, 7.53; N, 3.10.

Preparation of [η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]YN(SiHMe$_2$)$_2$(THF)$_2$ (10). This compound was prepared as yellow microcrystals from the reaction of **2** (0.37 g, 1.0 mmol) with Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (0.63 g, 1.0 mmol) in toluene (20 mL) by using procedures similar to those used in the synthesis of **8**: yield 0.40 g (54%). ^{1}H NMR (benzene-d_6): δ 8.01 (d, J = 7.8 Hz, 1H, indenyl), 7.81 (d, J = 7.8 Hz, 1H, indenyl), 7.12 (d, J = 3.3 Hz, 1H, indenyl), 6.97 (t, J = 7.8 Hz, 1H, indenyl), 6.87 (t, J = 7.8 Hz, 1H, indenyl), 6.65 (d, J = 3.3 Hz, 1H, indenyl), 5.70 (m, 1H, NC*H*Me$_2$), 5.43 (m, 2H, YNSi*H*(CH$_3$)$_2$), 3.66 (m, 8H, THF), 3.50 (m, 1H, NC*H*Me$_2$), 1.64 (m, 8H, THF), 1.34 (br, 9H, NCH(C*H*$_3$)$_2$), 1.17 (d, J = 6.9 Hz, 3H, NCH(C*H*$_3$)$_2$), 0.54 (s, 12H, SiC*H*$_3$). ^{13}C NMR (benzene-d_6): δ 130.4, 129.2, 124.7, 124.3, 121.1, 120.5, 114.5, 114.3, 94.7 (indenyl), 49.1, 48.5 (N*C*HMe$_2$), 68.2, 26.4 (THF), 26.2, 23.5, 22.7 (NCH(*C*H$_3$)$_2$), 4.3 (Si*C*H$_3$). ^{11}B NMR (benzene-d_6): δ −1.0 (1B), −3.2 (1B), −6.3 (3B), −10.3 (4B), −11.9 (2B). IR (KBr, cm^{-1}): ν 3060 (w), 2960 (s), 2570 (vs), 1471 (s), 1347 (s), 1249 (s), 1032 (s), 898 (s). Anal. Calcd for $C_{29}H_{60}B_{11}N_2YO_2Si_2$: C, 47.53; H, 8.25; N, 3.82. Found: C, 47.21; H, 8.48; N, 3.94.

Reaction of 8 with Me$_3$SiCl. A toluene solution (10 mL) of Me$_3$SiCl (0.22 g, 2.0 mmol) was added to a toluene (10 mL) solution of **8** (0.16 g, 0.2 mmol) dropwise with stirring and the reaction mixture was stirred overnight at room temperature. After removal of the solvent and excess Me$_3$SiCl, the residue was extracted with DME (5 mL × 3). The DME solutions were combined and concentrated to about 2 mL, from which blue crystals were isolated after this solution stood at room temperature for several days. These crystals were identified as NdCl$_3$(DME)$_2$ (**11**): 0.06 g, 70%. IR (KBr, cm^{-1}): ν 2963 (vs), 2905 (vs), 1633 (m), 1452 (s), 1348 (s), 1249 (s), 1173 (s), 1040 (s), 990 (vs), 918 (vs), 818 (vs), 680 (s). Anal. Calcd for $C_8H_{20}Cl_3NdO_4$: C, 22.30; H, 4.68. Found: C, 22.20; H, 4.35.

Reaction of 8 with Me$_3$NHCl. To a THF (10 mL) solution of **8** (0.24 g, 0.3 mmol) was added a dry powder of Me$_3$NHCl (0.03 g, 0.3 mmol) with stirring, and the reaction mixture was stirred overnight at room temperature. After removal of the solvent, the residue was extracted with toluene (5 mL × 3). The toluene solutions were combined and concentrated to about 1 mL, from which a small amount of colorless crystals was isolated, which was identified as ^{i}Pr$_2$NB(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (**2**) by both spectroscopic and X-ray analyses.

Polymerization of MMA. A toluene (2 mL) solution of **8** (0.029 g, 0.037 mmol) was adjusted to a constant temperature using an external bath. Into the well-stirred solution was syringed 2.0 mL (1.86 g, 18.6 mmol) of methyl methacrylate, and the reaction mixture was vigorously stirred for 3 h at that temperature. The polymerization was quenched by the addition of acidified methanol. The resulting precipitated poly(MMA) was collected, washed with methanol several times, and dried in vacuo at 50 °C overnight.

X-ray Structure Determination. All single crystals were immersed in Paratone-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[18] 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.[19] Most of the carborane hydrogen atoms were located

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Table 1. Crystal Data and Summary of Data Collection and Refinement for 2, 4a,b, and 5a

	2	4a	4b	5a
formula	$C_{17}H_{32}B_{11}N$	$C_{46}H_{90}B_{22}LiN_2O_6Sm$	$C_{51.5}H_{93.5}B_{22}LiN_2O_4Sm$	$C_{46}H_{90}B_{22}LiN_2O_6Yb$
cryst size (mm)	0.34 × 0.35 × 0.92	0.10 × 0.14 × 0.42	0.43 × 0.38 × 0.33	0.76 × 0.37 × 0.19
fw	369.4	1162.3	1199.9	1185.0
cryst syst	monoclinic	orthorhombic	triclinic	orthorhombic
space group	*C*2/*c*	*Pbca*	$P\bar{1}$	*Pbca*
a, Å	25.264(2)	22.112(1)	12.615(3)	22.231(1)
b, Å	25.864(2)	21.537(1)	14.785(3)	21.264(1)
c, Å	14.098(1)	27.987(1)	19.744(4)	27.965(1)
α, deg	90	90	72.51(1)	90
β, deg	93.52(1)	90	81.54(1)	90
γ, deg	90	90	89.08(1)	90
V, Å^3	9194.8(9)	13328.1(4)	3472.4(14)	13220(1)
Z	16	8	2	8
D_{calcd}, Mg/m^3	1.067	1.158	1.147	1.191
radiation (*λ*), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2*θ* range, deg	3.0−50.0	3.4−51.2	3.0−50.0	3.4−52.0
μ, mm^{-1}	0.054	0.922	0.885	1.456
F(000)	3136	4824	1245	4888
no. of obsd rflns	7220	11 137	10 856	12 917
no. of params refnd	532	704	718	698
goodness of fit	0.933	1.015	0.934	1.068
R1	0.076	0.061	0.070	0.047
wR2	0.201	0.168	0.152	0.118

Table 2. Crystal Data and Summary of Data Collection and Refinement for 5b,c, 8, and 11

	5b	5c	8	11
formula	$C_{53}H_{95}B_{22}LiN_2O_4Yb$	$C_{50}H_{92}B_{22}LiN_2O_4Yb$	$C_{29}H_{60}B_{11}N_2NdO_2Si_2$	$C_8H_{20}Cl_3NdO_4$
cryst size (mm)	0.92 × 0.74 × 0.42	0.25 × 0.14 × 0.13	0.55 × 0.40 × 0.25	0.35 × 0.32 × 0.25
fw	1242.1	1203.1	788.1	430.8
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a, Å	12.658(1)	14.662(4)	11.505(1)	11.653(1)
b, Å	14.913(1)	12.708(4)	11.851(1)	9.000(1)
c, Å	19.584(1)	36.851(11)	16.412(1)	15.736(1)
α, deg	72.68(1)	90	101.57(1)	90
β, deg	80.76(1)	93.74(1)	99.88(1)	105.30(1)
γ, deg	88.64(1)	90	98.59(1)	90
V, Å^3	3482.2(2)	6852(3)	2120.2(2)	1591.7(1)
Z	2	4	2	4
D_{calcd}, Mg/m^3	1.185	1.166	1.235	1.798
radiation (*λ*), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2*θ* range, deg	4.1−50.0	2.9−50.0	2.6−56.0	5.3−56.1
μ, mm^{-1}	1.383	1.404	1.308	3.762
F(000)	1284	2484	814	844
no. of obsd rflns	10 837	8906	9964	3831
no. of params refnd	674	590	432	146
goodness of fit	1.150	0.793	0.994	1.009
R1	0.034	0.084	0.031	0.025
wR2	0.090	0.169	0.074	0.065

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. Further details are included in the Supporting Information.

Results and Discussion

Ligands. Our target molecule is a tricoordinate boron compound with three different substituents that have to be introduced step by step. The carboranyl moiety is the most expensive one among these three groups, which should be introduced in the last step. Treatment of BCl_3 with 1 equiv of $C_9H_7SiMe_3$ in CH_2Cl_2 gave $Cl_2B(C_9H_7)$ in 60% yield. Interaction between $Cl_2B(C_9H_7)$ and $^iPr_2NH$ in a molar ratio of 1:2 in *n*-hexane afforded $^iPr_2NB(C_9H_7)Cl$ in 50% yield. It reacted with 1 equiv of $Li_2C_2B_{10}H_{10}$ in toluene/ether (2:1) at 0 °C to give, after treatment with 1 equiv of *n*-BuLi, the dilithium salt $[^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (**1**) in 75% yield. Since the B−C bond is moisture sensitive, the neutral counterpart $^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$ cannot be prepared by hydrolysis. A new method is desirable. Treatment of **1** with excess cyclopentadiene in THF gave, after extraction with *n*-hexane, the neutral ligand $^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$ (**2**) in 87% yield. The monolithium salt $[^iPr_2NB(C_9H_6)(C_2B_{10}H_{11})]Li(THF)_2$ (**3**) was quantitatively prepared by mixing **1** and **2** in a 1:1 molar ratio in THF. The synthetic routes are summarized in Scheme 1. The driving force for these protonation reactions is the differences in acidities between cyclopentadiene, indene, and *o*-carborane.[20] The solubilities of these compounds in various organic solvents follow the trend **2** > **3** > **1**. **2** is even soluble in *n*-hexane, and **3** is soluble in ether, but **1** is insoluble in ether. Therefore, they could be easily separated and purified. It is noted that the initially formed **3** from the reaction of $^iPr_2NB(C_9H_7)Cl$ with $Li_2C_2B_{10}H_{10}$ always contains some impurities

(20) (a) Shatenshtein, A. I.; Zakharkin, L. I.; Petrov, E. S.; Yakoleva, E. A.; Yakushin, F. S.; Vukmirovich, Z.; Isaeva, G. G.; Kalinin, V. N. *J. Orgamomet. Chem.* **1970**, *23*, 313. (b) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: New York, 1972; p 494.

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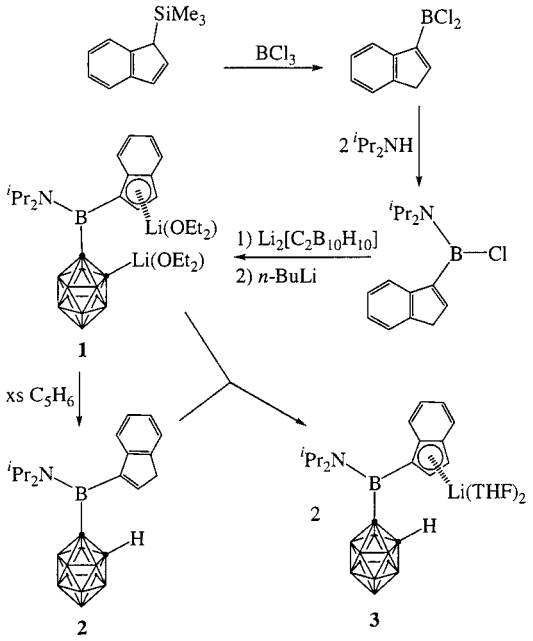
Scheme 1

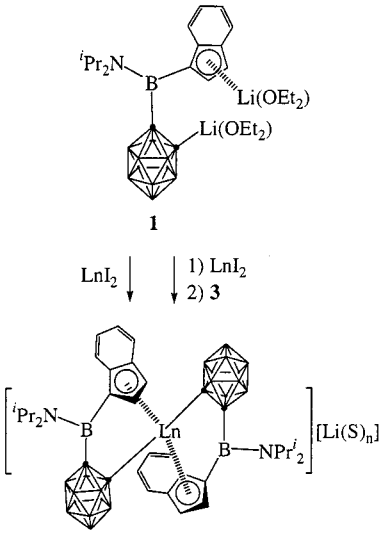


that can only be removed by washing with ether after converting **3** to **1**.

Compounds **1**−**3** were fully characterized by various spectroscopic data and elemental analyses. The solid-state structure of **2** is further confirmed by single-crystal X-ray analyses. The ^{11}B NMR spectra exhibit 1:1:3:5:1, 1:1:1:1:1:1:1:4, and 1:1:1:5:3 splitting patterns for **1**−**3**, respectively. The ^{11}B NMR is a very powerful tool to monitor the transformations among **1**−**3**. The three-coordinate bridging boron atom has some π-interactions with the sp^2 C of the indenyl group. The negative charge on the indenyl moiety can significantly strengthen such $p_\pi-p_\pi$ interactions, which is reflected in the ^{11}B chemical shift of the bridging boron atom: 36.1 ppm in **2** vs <-1.6 ppm in **1** and **3** (note that it is infeasible to assign the ^{11}B chemical shift of the bridging boron atom in both **1** and **3** due to the overlapping with the cage boron atoms). Both ^{1}H and ^{13}C NMR spectra support that the bridging B atom is only bound to the sp^2 C of the indenyl moiety in **2**. The ^{1}H NMR spectra also support the ratio of two ether molecules per carboranyl ligand for **1** and two THF molecules per carboranyl ligand for **3**. The IR spectra of three compounds all show a typical characteristic B−H absorption at about 2570 cm^{-1}.

Organolanthanide Complexes. The dilithium salt [^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$(OEt$_2$)$_2$ (**1**) is a new "constrained-geometry" ligand bearing a carboanion functionality. An equimolar reaction between LnI$_2$ and **1** in THF at room temperature gave, after recrystallization from a DME solution, the trivalent organolanthanide compounds *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln][Li(DME)$_3$] (Ln = Sm (**4a**), Yb (**5a**)), in ca. 35% yield. They were also prepared in a much higher yield (70%) by treatment of LnI$_2$ with 1 equiv of **1** in THF followed by the addition of 1 equiv of **3**. Recrystallization from a THF/benzene solution afforded the THF-coordinated complexes *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln][Li(THF)$_4$]·nC$_6$H$_6$ (n = 0.25, Ln = Sm (**4b**); n = 0.5, Ln = Yb (**5b**)). These transformations are summarized in Scheme 2.

Scheme 2



S = DME, n = 3, Ln = Sm (**4a**), Yb (**5a**);
S = THF, n =4, Ln = Sm (**4b**), Yb (**5b**)

No organoytterbium(II) complexes were isolated, though they are believed to be much less reactive than their organosamarium(II) analogues.[7] These results suggest that the ^{i}Pr$_2$NB-bridged ligand can offer organoytterbium(II) complexes with a high reactivity in redox reactions. Both intra- and intermolecular electron-transfer pathways that are similar to those proposed for the reaction of [Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$ with SmI$_2$[12a] are suggested for the formation of organolanthanide(III) complexes, shown in Scheme 3. The intramolecular pathway offers a higher yield, while the yield is relatively lower for the intermolecular pathway.

Interaction between LnCl$_3$ and 1 or 2 equiv of **1** in THF gave, after recrystallization from a DME/toluene or THF/toluene solution, the ionic compounds *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln][Li(S)$_n$] (S = DME, n = 3, Ln = Nd (**6**), Y (**7**); S = THF, n = 4, Ln = Yb (**5c**)), in a typical yield of 70% (Scheme 4). No organolanthanide chloride complexes of the type [η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]LnCl(THF)$_n$ were isolated, regardless of the molar ratios of the reactants and the sizes of the lanthanide ions. Although the ^{i}Pr$_2$NB linkage is more sterically demanding than the Me$_2$Si and Me$_2$C linkages, the organolanthanide chloride complexes can still not be stabilized. These compounds are soluble in polar organic solvents such as THF, DME, and pyridine, slightly soluble in toluene, and insoluble in *n*-hexane. They were fully characterized by various spectroscopic data, elemental analyses, and single-crystal X-ray analyses (for Sm and Yb complexes). They are all *meso* isomers. Unlike the Me$_2$C-bridged analogues [{η^5:σ-Me$_2$C(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln][Li(DME)$_3$],[11] the ^{i}Pr$_2$NB-bridged species [{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln][Li(S)$_n$] do not show any *rac*−*meso* interconversion in solution, as indicated by ^{1}H NMR. The sterically demanding ^{i}Pr$_2$NB linkage may be responsible for this. Since the salt metathesis does not offer the desirable half-sandwich complexes, an alternate method is then sought.

It has been documented that lanthanocenes can be efficiently prepared via silylamine elimination reactions

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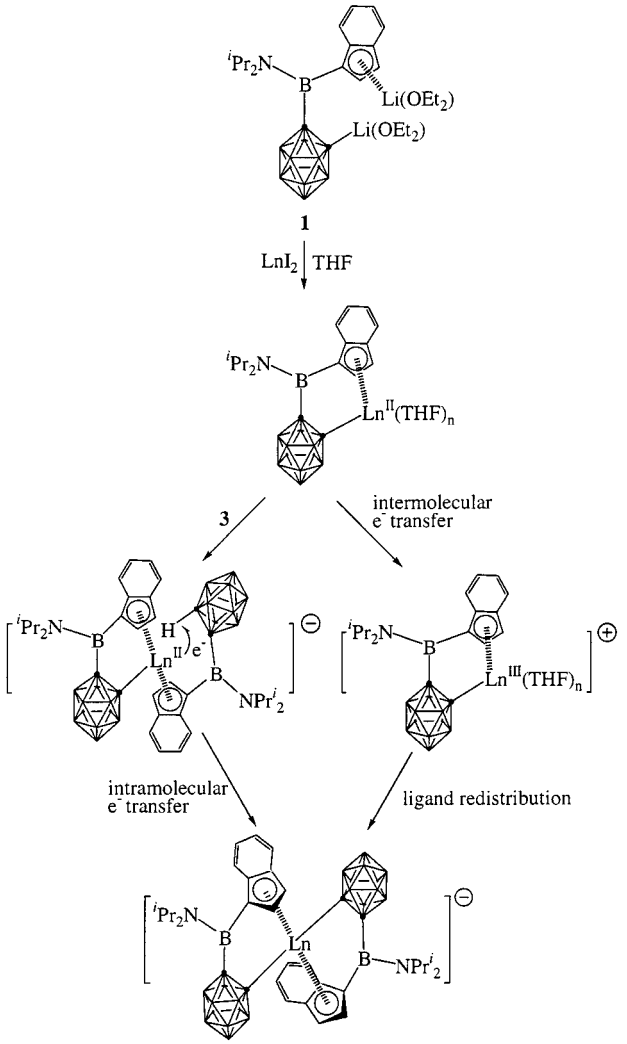
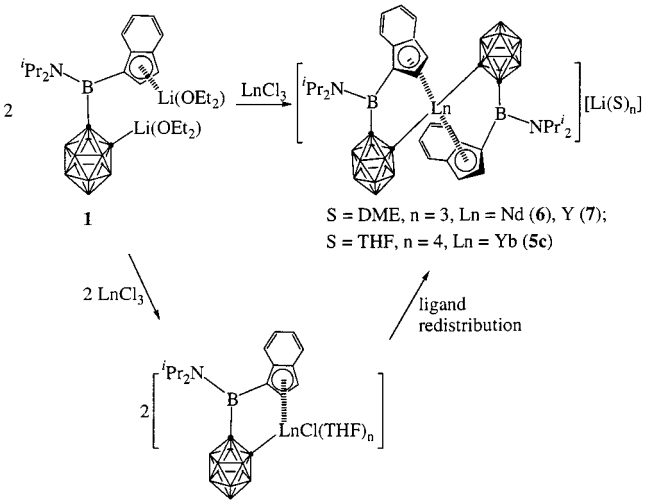
Scheme 3



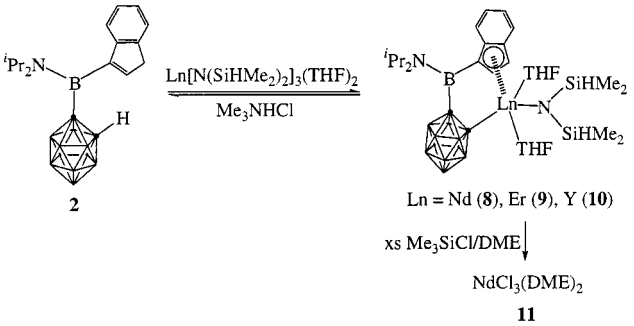
Scheme 4



of $Ln[N(SiHMe_2)_2]_3(THF)_2$ and protic reagents.[21] It is rational to propose that two acidic protons in **2** would allow the similar silylamine elimination to occur between **2** and metal amides. In fact, treatment of **2** with 1 equiv of $Ln[N(SiHMe_2)_2]_3(THF)_2$ in toluene at reflux

(21) Eppinger, J.; Spiegler, M.; Hieringer, W.; Herrmann, W. A.; Anwander, R. *J. Am. Chem. Soc.* **2000**, *122*, 3080.

Scheme 5



temperature generated organolanthanide amides of the general formula $[\eta^5{:}\sigma\text{-}^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]$-$LnN(SiHMe_2)_2(THF)_2$ (Ln = Nd (**8**), Er (**9**), Y (**10**)) in good yield (Scheme 5). The unique ^{11}B chemical shift of the bridging B atom in **2** serves as an excellent spectroscopic probe to monitor the progress of these reactions. As indicated by ^{11}B NMR, such silylamine elimination reactions do not proceed either at room temperature or with $Ln[N(SiMe_3)_2]_3$. The coordinated THF molecules come from the metal amide complexes and cannot be removed, even by recrystallizing again from a refluxing toluene solution. It is clear that the sterically less demanding dimethylsilyl group and THF dissociation favor the ligand approach and proton transfer, leading to the formation of half-sandwich organolanthanide amide complexes.[21]

Reactivity. It has been documented that the addition of excess Me_3SiCl or a stoichiometric amount of $Me_3N{\cdot}HCl$ to the metal amide complexes results in the clear formation of chloride derivatives.[22] Treatment of $[\eta^5{:}\sigma\text{-}^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]NdN(SiHMe_2)_2(THF)_2$ (**8**) with excess Me_3SiCl in toluene at room temperature gave, after extraction with DME, the DME-coordinated metal trichloride complex $NdCl_3(DME)_2$ (**11**) in 70% yield. The ^{11}B NMR shows the formation of a neutral ligand, presumably $^iPr_2NB(C_9H_6SiMe_3)(C_2B_{10}H_{10}SiMe_3)$, during the reaction. The same complex **11** was isolated even if only 1 equiv of Me_3SiCl was used for the reaction. An equimolar reaction between **8** and $Me_3N{\cdot}HCl$ also afforded $NdCl_3(DME)_2$ (**11**) and the neutral ligand $^iPr_2$-$NB(C_9H_7)(C_2B_{10}H_{11})$ (**2**). The primarily ionic bonding between Nd^{3+} and ligands and the formation of strong Nd−Cl bonds are the driving forces for these reactions. These transformations are summarized in Scheme 5.

The reaction between **8** and Me_3Al is very complicated, and no pure product is isolated. These results show that organolanthanide amide complexes exhibit very different reactivity patterns from their d-block transition metal counterparts due to the difference in bonding between metal ions and ligands.

To examine the catalytic ability of compound **8** toward polar monomers, polymerization of methyl methacrylate (MMA) has been tested under the conditions given in Table 3. The polymerization data show that conversion of MMA is low over the various reaction temperatures. The sterically encumbered environment around the

(22) (a) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045. (b) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (c) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572. (d) Wang, H.; Wang, Y.; Li, H.-W.; Xie, Z. *Organometallics* **2001**, *20*, 5110.

Table 3. MMA Polymerization Results by 8[a]

entry	T_p (°C)	conversn (%)	*rr* (%)[b]	*mr* (%)[b]	*mm* (%)[b]
1	−15	2.4	72	13	15
2	0	4.0	71	14	15
3	25	7.8	69	14	17

[a] Conditions: **8**/MMA (mol/mol) = 1/500; polymerization time, 3 h; solvent, 2 mL of toluene; MMA/solvent (v/v) = 1/1. [b] Triad values from methyl region of ^{1}H NMR spectra in $CDCl_3$ at 25 °C.

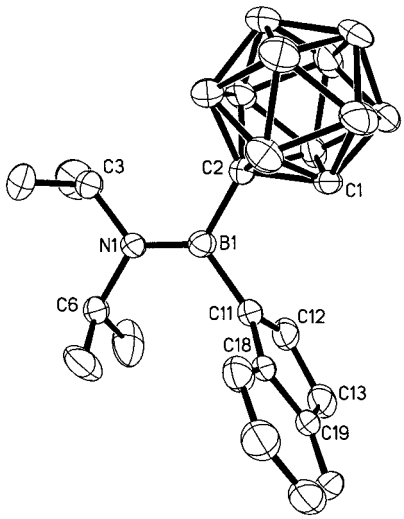


Figure 1. Molecular structure of ^{i}Pr$_2$NB(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) (**2**) (thermal ellipsoids drawn at the 35% probability level).

metal center coupled with the relatively low reactivity of the amide complex compared to the situation for the corresponding alkyl or hydride derivations[23] seems to act as a major reason for such a low conversion. The resulting poly(MMA)s are all syn-rich under the conditions examined. Our results show that the catalytic activity of **8** resembles that of *ansa*-[Me$_2$Si(η^3-C$_{13}$H$_8$)(η^5-C$_5$Me$_4$)]YN(SiMe$_3$)$_2$,[24] while the microstructure of the resulting poly(MMA)s are similar to those initiated by *ansa*-[Me$_2$Si(η^5-C$_{13}$H$_8$)(η^5-C$_5$H$_4$)]LnE(SiMe$_3$)$_2$ (E = CH, N).[25] It is noted that the resulting poly(MMA)s are either insoluble in THF or cannot pass through the columns of GPC, which makes the measurements of molecular weight and molecular weight distributions of these polymers infeasible.

Molecular Structure. The solid-state structures of **2**, **4a**,**b**, **5a**−**c**, **8**, and **11** have all been confirmed by single-crystal X-ray analyses. Table 4 lists selected bond distances and angles. Some key structural data of the corresponding Me$_2$Si- and Me$_2$C-bridged organolanthanide complexes are compiled in Table 5 for comparison.

An X-ray analysis reveals there are two crystallographically independent molecules in the unit cell of **2**. One of them is shown in Figure 1. Both the bridging boron and nitrogen atoms are in a trigonal-planar environment (sum of angles around N and B ∼360°). This geometry together with a short boron−nitrogen distance of 1.395(5) Å indicate the presence of a N(p$_\pi$)→B(p$_\pi$) double bond.[4f] The differences in both carbon−carbon bond distances of the indenyl moiety (C(11)−C(12) = 1.352(5) Å versus C(12)−C(13) = 1.480(6) Å) and boron−carbon bond distances (B(1)−C(11) = 1.577(6) Å vs B(1)−C(2) = 1.616(6) Å) suggest (1) a possible π-interaction between the bridging boron and the vinylic system of the indenyl group and (2) the bridging boron atom binding only to an sp^2 C of the indenyl moiety.

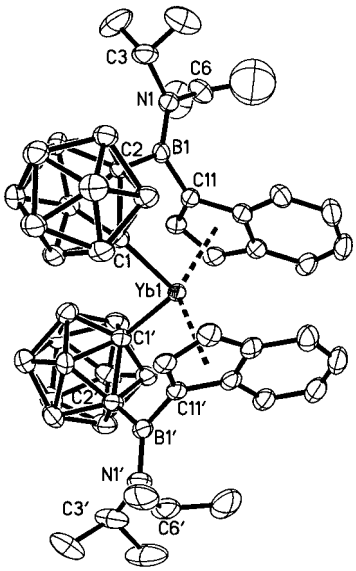


Figure 2. Molecular structure of *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Yb]$^-$ in **5a** (thermal ellipsoids drawn at the 35% probability level).

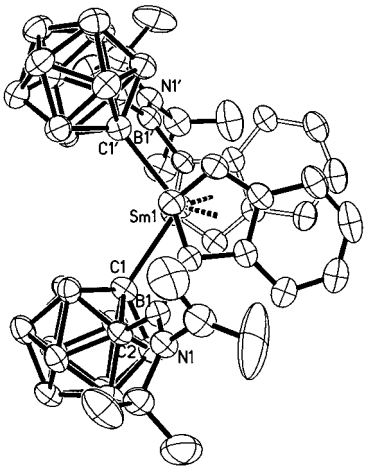


Figure 3. Molecular structure of *meso*-[{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Sm]$^-$ in **4a** (thermal ellipsoids drawn at the 35% probability level).

The solid-state structures of **4a**,**b** and **5a**−**c** as derived from single-crystal X-ray diffraction studies confirm that they are all *meso* isomers consisting of well-separated, alternating layers of discrete tetrahedral anions of [{η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)}$_2$Ln]$^-$ and cations of [Li(solvent)$_n$]$^+$ and show one-fourth and half benzene of solvation for **4b** and **5b**, respectively. The anions in these complexes are isostructural. Figures 2 and 3 show their representative structures with different views, respectively. The Ln^{3+} ion is η^5-bound to each of two indenyl groups and σ-bound to two cage carbon atoms from two carboranyl moieties in a distorted-tetrahedral geometry with a Cent−Ln−Cent angle of ∼139° for Sm or of ∼135° for Yb complexes, respectively. The C(cage)−Ln−C(cage) angles are ∼109° for Sm and ∼107° for Yb

(23) Yasuda, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1955.
(24) Lee, M.-H.; Hwang, J.-W.; Kim, Y.; Kim, J.; Han, Y.; Do, Y. *Organometallics* **1999**, *18*, 5124.
(25) Qian, C.; Nie, W.; Sun, J. *Organometallics* **2000**, *19*, 4134.

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Table 4. Selected Average Bond Lengths (Å) and Angles (deg)[a]

	2	4a	4b	5a	5b	5c	8
Ln		Sm	Sm	Yb	Yb	Yb	Nd
B(bridging)−N	1.385(6)	1.408(3)	1.407(7)	1.391(9)	1.400(2)	1.354(11)	1.402(4)
B(bridging)−C(cage)	1.626(6)	1.625(3)	1.622(8)	1.623(11)	1.610(2)	1.649(12)	1.607(4)
B(bridging)−C(ring)	1.583(7)	1.568(3)	1.568(9)	1.569(11)	1.574(2)	1.629(12)	1.578(4)
Ln−C(ring)		2.727(2)	2.730(6)	2.637(7)	2.643(2)	2.596(9)	2.760(4)
Ln−C(cage)		2.581(2)	2.574(6)	2.495(7)	2.499(1)	2.359(9)	2.598(3)
C(cage)−Ln−C(cage)		108.83(7)	109.2(2)	107.1(2)	107.4(1)	106.1(3)	
Cent−Ln−Cent		138.4	139.3	135.1	135.3	135.4	
Cent−Ln−C(cage)		95.8	95.0	98.7	98.3	97.9	93.2
C(cage)−B−C(ring)	115.3(3)	115.8(2)	116.1(4)	115.0(6)	114.9(1)	114.0(6)	115.6(2)
∑∠B(bridging)	359.9(3)	360.0(2)	360.0(6)	360.0(7)	360.0(2)	360.0(8)	360.0(3)
∑∠N	360.1(4)	360.0(2)	360.0(6)	360.0(7)	360.0(2)	359.9(7)	360.1(3)

[a] Cent = the centroid of the five-membered ring of the indenyl group.

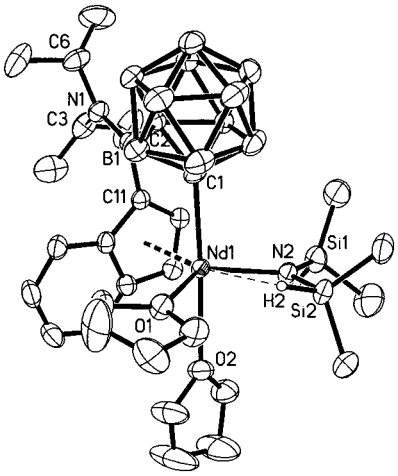
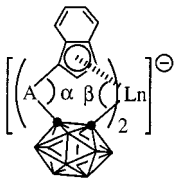


Figure 4. Molecular structure of $[\eta^5{:}\sigma\text{-}^i Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]NdN(SiHMe_2)_2(THF)_2$ (**8**) (thermal ellipsoids drawn at the 35% probability level).

complexes, respectively. Both N and bridging B atoms in **4a**,**b** and **5a**−**c** are flat. The B(bridging)−N, B(bridging)−C(cage) and B(bridging)−C(ring) distances in these complexes are all very close to the corresponding values in **2**. These structure data show that the geometry around the bridging B atom remains unchanged after complexation with lanthanides. These measured values (Table 4) compare with the B−N distance of 1.381(2) Å, the B−C(ring) distance of 1.588(2) Å, and the C(ring)−B−C(ring) angle of 104.9(1)° in $[^i Pr_2NB(\eta^5\text{-}C_9H_6)_2]ZrCl_2$.[4c] The average Ln−C(cage) and Ln−C(ring) distances are all very close to the corresponding values found in $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]_2Ln^-$ (A = Si, Ln = Sm;[12a] A = C, Ln = Sm,[11] Yb[11]). The C(ring)−B−C(cage) (α) and Cent−Ln−C(cage) (β) angles in **4a**,**b** and **5a**−**c** are close to the corresponding values found in $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]_2Ln^-$ but are significantly different from those in $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]_2\text{-}Ln^-$ (see Table 5), probably due to the size of the bridging atoms.

The molecular structure of **8** is shown in Figure 4. The Nd^{3+} ion is η^5-bound to the five-membered ring of the indenyl group, σ-bound to the cage carbon atom and nitrogen atom of $N(SiHMe_2)_2$, and coordinated to two THF molecules in a distorted-trigonal-bipyramidal geometry with the cage carbon atom and O(2) occupying the axial sites. The structure data in Table 4 indicate that the geometry of the bridging B atom in **8** is the same as that in **2**, **4a**,**b** or **5a**−**c**. The average Nd−C(ring) distance of 2.760(4) Å and Nd−C(cage) distance of 2.598(3) Å are close to the corresponding values of 2.761(3) and 2.576(3) Å found in $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]_2Nd^-$ [11] and 2.777(4) and 2.635(4) Å in $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]_2Nd^-$,[12b] respectively. The Nd−N distance of 2.326(2) Å is very close to the corresponding value of 2.343(5) Å found in the starting material $Nd[N(SiHMe_2)]_3(THF)_2$.[17]

Table 5. Structural Data for $[\eta^5{:}\sigma\text{-}A(C_9H_6)(C_2B_{10}H_{10})]_2Ln^-$



	Sm		Yb		
A	α	β	α	β	ref
$^i Pr_2NB$	115.8−116.1	95.0−95.8	114.0−115.0	97.9−98.7	this work
Me_2C	111.3−111.5	93.0−93.5	110.4−111.8	96.7−97.5	11
Me_2Si	108.1	102.5			12a

The most interesting structural feature in **8** is the asymmetric coordination mode of the silylamide moiety, as indicated by a significantly smaller Nd(1)−N(2)−Si(2) angle of 101.95(10)° versus an Nd(1)−N(2)−Si(1) angle of 134.92(13)°, shorter Nd(1)···Si(2) distance of 3.147(1) Å versus the Nd(1)···Si(1) distance of 3.729(1) Å and shorter Nd(1)···H(2) distance of 2.63(3) Å versus the Nd(1)···H(1) distance of 4.41(3) Å. Such an asymmetric β-Si agostic interaction is often observed in $L_2Ln-N(SiMe_3)_2$ types of complexes (L_2 = *ansa* ligands)[24,25] but not in $L_2Ln-N(SiHMe_2)_2$ systems, where only symmetric β-SiH agostic interactions are observed.[21] If the metal size and coordination number are taken into account,[26] the above measured values for **8** are quite comparable with the corresponding values found in $L_2Ln-N(SiHMe_2)_2$ types of complexes (Ln···Si, 3.03−3.28 Å; Ln···H, 2.38−3.05 Å; Ln-N−Si, 99.5−117.1°).[21]

Figure 5 shows the molecular structure of $NdCl_3(DME)_2$ (**11**). The Nd^{3+} ion is bound to three terminal chloro groups and coordinated to two DME molecules in a distorted-pentagonal-bipyramidal geometry with the Cl(2) and Cl(3) atoms occupying the axial sites, which is very similar to the structure of $NdCl_3(THF)_4$.[27]

(26) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
(27) Chen, W.; Jin, Z.; Xing, Y. *Inorg. Chim. Acta* **1987**, *130*, 125.

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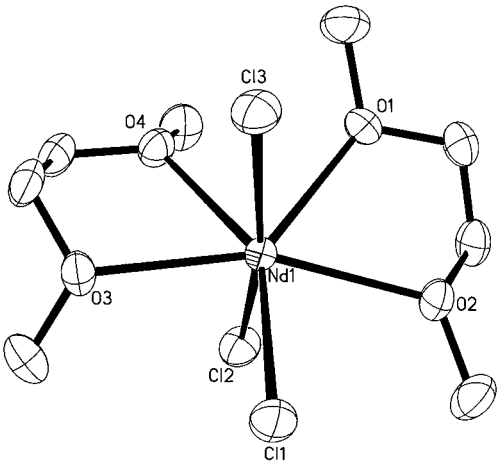

Figure 5. Molecular structure of $NdCl_3(DME)_2$ (**11**) (thermal ellipsoids drawn at the 35% probability level).

Summary

New boron-bridged ligands have been prepared, which can enhance the reducing ability of organoytterbium(II) complexes. The resulting organolanthanide complexes resemble those derived from the Me_2C-bridged ligand $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ with respect to the molecular structures and reactivity patterns.

Silylamine elimination reactions of the neutral ligand and $Ln[N(SiHMe_2)]_3(THF)_2$ are very effective methods for the preparation of half-sandwich lanthanocene amide complexes. The ^{11}B chemical shift of the bridging B atom serves as an excellent spectroscopic probe to closely monitor the progress of these types of reactions. These amide complexes can initiate the polymerization of MMA, leading to syn-rich poly(MMA)s, but the reactivity is very low.

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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 complexes **2**, **4a**,**b**, **5a**−**c**, **8**, and **11**; data are also available in CIF format for these compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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