Articles

Synthesis, Structural Characterization, and Catalytic Property of Group 4 Metal Carborane Compounds with a $^{i}Pr_2NB$-Bridged Constrained-Geometry Ligand

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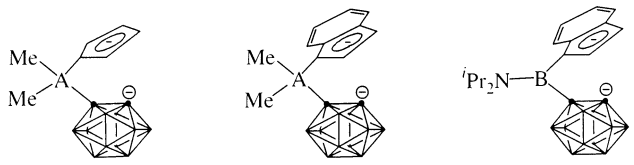
Interaction of $^{i}Pr_2NB(C_9H_7)(C_2B_{10}H_{11})$ with 1 equiv of $Zr(NMe_2)_4$ gave a constrained-geometry zirconium amide $[\eta^5:\sigma\text{-}^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (**2**). Treatment of $^{i}Pr_2NB(C_9H_7)(C_2B_{10}H_{11})$ with 1 equiv of $Ti(NMe_2)_4$, however, led to the isolation of a deborated product $(\eta^5\text{-}C_2B_9H_{11})Ti(NMe_2)_2(HNMe_2)$ (**1**). **2** reacted with excess Me_3SiCl in toluene to give the chloro derivative $[\eta^5:\sigma\text{-}^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]ZrCl_2$ (**4**). Salt metathesis reaction between $MCl_4(THF)_2$ and $[^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ afforded $[\eta^5:\sigma\text{-}^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]MCl_2$ (M = Ti (**3**), Zr (**4**), Hf (**5**)). **3** was also prepared from the reaction of $[^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ with 1 equiv of $TiCl_3(THF)_3$, followed by addition of 0.5 equiv of $PbCl_2$ in THF. Interaction of **2** with 4 equiv of Me_3Al in toluene resulted in the isolation of $[\eta^5:\sigma\text{-}^{i}Pr_2NB(C_9H_6)(C_2B_{10}H_{10})]ZrMe_2$ (**6**). **6** was also prepared via the reaction of **4** with 2 equiv of MeLi in THF. All of these compounds were fully characterized by various spectroscopic data and elemental analyses. The solid-state structures of compounds **1** and **2** were further confirmed by single-crystal X-ray analyses. Compounds **2**−**6** exhibited a moderate to very high (10^4−10^6 g mol^{-1} atm^{-1} h^{-1}) ethylene polymerization activity upon activation with MAO. The activities depended upon both the central metal ion and co-ligand and followed the order **4** > **2**, **6** > **3** > **5**.

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] Boron-bridged *ansa*-ligands have recently 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.[2] Two classes of compounds have been studied: (1) metallocenes bridged by three-coordinate boron moieties where the electrophilicity of boron is attenuated by a partial $p_\pi-p_\pi$ π-bonding[3] and (2) metallocenes bridged with four-coordinate boron-linkages.[4] Experimental results show that the R_2NB-bridged *ansa*-ligands can offer metallocenes with a very high activity in polymerization/copolymerization of α-olefins.[3c,d] We have recently developed a $^{i}Pr_2NB$-bridged carboranyl constrained-geometry ligand bearing a carboanion functionality (Chart 1, III).[5] Our recent results show that zirconocenes derived from ligands I and II (Chart 1) exhibit a very high activity in ethylene polymerization.[6] Given the impact of boron-bridged constrained-geometry ligands[3] and carboranyl moieties[6,7] on the catalytic performance of the group 4 metal compounds, we have extended our research to a newly developed $^{i}Pr_2NB$-bridged system in the hope that the electrophilic boron-linkage together with the electron-deficient carborane moiety can enhance the Lewis acidity of the central metal ions, which then in turn increases the catalytic activity of the catalysts. We report herein our detailed

Chart 1. Constrained-Geometry Carboranyl Ligands



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study on this subject. The similarities and differences among group 4 metal compounds with B-, C-, and Si-bridged ligands are also discussed in this paper.

Experimental Section

General Procedures. All experiments were preformed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents (except CH_2Cl_2) were freshly distilled from sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 was freshly distilled from CaH_2 immediately prior to use. $M(NMe_2)_4$ (M = Ti, Zr),[8] $^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$,[5] and $[^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$[5] were prepared according to literature methods. All other chemicals were purchased from either Aldrich or Acros 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. Molecular weights of the polymer were estimated by gel permeation chromatography (GPC) using a PL-GPC 200 high-temperature GPC (Polymer Laboratories Ltd.). ^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 were reported in δ units with references 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 (η^5-$C_2B_9H_{11}$)Ti(NMe_2)$_2$($HNMe_2$) (1). A toluene solution (10 mL) of $^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$ (0.37 g, 1.00 mmol) was slowly added to a toluene solution (10 mL) of $Ti(NMe_2)_4$ (0.22 g, 1.00 mmol) with stirring at room temperature. The reaction mixture was heated to 65 °C and stirred overnight to give a deep red solution. The solution was filtered and concentrated to about 5 mL, from which **1** was isolated as brick-red crystals after this solution stood at room temperature for several days (0.09 g, 29%). ^1H NMR (pyridine-d_5): δ 3.47 (s, 12H, NCH_3), 3.25 (br s, 2H, cage C*H*), 2.34 (s, 6H, HNCH_3), proton of *H*NMe_2 was not observed. ^{13}C NMR (pyridine-d_5): δ 56.43 ($C_2B_9H_{11}$), 51.01 (NCH_3), 40.53 (HNCH_3). ^{11}B NMR (pyridine-d_5): δ 6.1 (1B), −4.9 (2B), −5.6 (2B), −15.1 (3B), −20.7 (1B). IR (KBr, cm^{-1}): ν 3223 (m), 2955 (m), 2901 (s), 2858 (m), 2535 (vs), 1455 (s), 1258 (s), 1095 (vs), 1023 (vs), 803 (s). Anal. Calcd for $C_8H_{30}B_9N_3Ti$: C, 30.65; H, 9.65; N, 13.41. Found: C, 30.13; H, 9.69; N, 13.01.

Preparation of [η^5:σ-^{i}Pr$_2$NB(C_9H_6)($C_2B_{10}H_{10}$)]Zr(NMe_2)$_2$ (2). A toluene solution (10 mL) of $^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$ (0.37 g, 1.00 mmol) was slowly added to a toluene solution (10 mL) of $Zr(NMe_2)_4$ (0.27 g, 1.00 mmol) with stirring at room temperature. The reaction mixture was heated to 65 °C and stirred overnight to give a yellow solution. This solution was filtered and concentrated to about 3 mL, from which **2** was isolated as yellow crystals after this solution stood at room temperature for several days (0.38 g, 70%). ^1H NMR (pyridine-d_5): δ 7.69 (d, J = 8.4 Hz, 1H, indenyl), 7.23 (t, J = 7.2 Hz, 1H, indenyl), 7.10 (t, J = 7.2 Hz, 1H, indenyl), 6.65 (d, J = 8.4 Hz, 1H, indenyl), 6.64 (d, J = 2.4 Hz, 1H, indenyl), 6.03 (d, J = 2.4 Hz, 1H, indenyl), 5.32 (m, 1H, NC*H*Me_2), 3.28 (m, 1H, NC*H*Me_2), 2.99 (s, 6H, NCH_3), 2.32 (s, 6H, NCH_3), 1.22 (d, J = 6.3 Hz, 3H, NCH(CH_3)$_2$), 1.20 (d, J = 6.3 Hz, 3H, NCH(CH_3)$_2$), 0.98 (d, J = 6.3 Hz, 3H, NCH(CH_3)$_2$), 0.55 (d, J = 6.3 Hz, 3H, NCH(CH_3)$_2$). ^{13}C NMR (pyridine-d_5): δ 130.8, 128.0, 126.8, 126.2, 126.0, 125.6, 125.3, 104.8, 103.6 (indenyl), 88.6 (cage *C*), 51.0, 49.4 (N*C*HMe_2), 47.4, 45.9 (N*C*H_3), 27.1, 26.5, 24.0, 23.1 (NCH(*C*H_3)$_2$). ^{11}B NMR (pyridine-d_5): δ 0.3 (1B), −1.8 (1B), −5.1 (3B), −9.0 (4B), −10.9 (2B). IR (KBr, cm^{-1}): ν 2959 (m), 2909 (vs), 2576 (vs), 1491 (s), 1259 (s), 1096 (vs), 1026 (vs), 801 (s). Anal. Calcd for $C_{21}H_{42}B_{11}N_3Zr$: C, 46.13; H, 7.74; N, 7.69. Found: C, 46.21; H, 7.83; N, 7.50.

Preparation of [η^5:σ-^{i}Pr$_2$NB(C_9H_6)($C_2B_{10}H_{10}$)]$TiCl_2$ (3). To a THF (10 mL) solution of $TiCl_4(THF)_2$ (0.33 g, 1.00 mmol) was slowly added a THF (10 mL) solution of $[^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (0.53 g, 1.00 mmol) with stirring at −78 °C. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was evaporated under vacuum. The oily residue was extracted with CH_2Cl_2 (10 mL × 3). The CH_2Cl_2 solutions were combined and concentrated to about 5 mL, to which *n*-hexane (15 mL) was added. **3** was isolated as red microcrystals after this solution stood at room temperature for several days (0.19 g, 40%). ^1H NMR (pyridine-d_5): δ 8.01 (d, J = 7.8 Hz, 1H, indenyl), 7.81 (d, J = 7.8 Hz, 1H, indenyl), 7.12 (d, J = 3.0 Hz, 1H, indenyl), 6.97 (t, J = 8.1 Hz, 1H, indenyl), 6.87 (t, J = 8.1 Hz, 1H, indenyl), 6.65 (d, J = 3.0 Hz, 1H, indenyl), 5.70 (m, 1H, NC*H*Me_2), 3.65 (m, 1H, NC*H*Me_2), 1.35 (d, J = 6.3 Hz, 3H, NCH(CH_3)$_2$), 1.32 (d, J = 6.3 Hz, 3H, NCH(CH_3)$_2$), 1.30 (d, J = 6.3 Hz, 3H, NCH(CH_3)$_2$), 1.17 (d, J = 6.3 Hz, 3H, NCH(CH_3)$_2$). ^{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), 82.1 (cage *C*), 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 −1.5 (1B), −3.7 (1B), −6.8 (3B), −10.8 (4B), −11.3 (2B). IR (KBr, cm^{-1}): ν 3058 (w), 2960 (s), 2915 (s), 2547 (vs), 1454 (s), 1385 (s), 1260 (s), 1088 (vs), 1027 (vs), 802 (s). Anal. Calcd for $C_{17}H_{30}B_{11}Cl_2NTi$: C, 42.00; H, 6.22; N, 2.88. Found: C, 41.87; H, 6.13; N, 2.67.

Alternate Method. To a suspension of $TiCl_3(THF)_3$ (0.37 g, 1.00 mmol) in THF (15 mL) was slowly added a THF (10 mL) solution of $[^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]Li_2(OEt_2)_2$ (0.53 g, 1.00 mmol) with stirring at −78 °C. The reaction mixture was slowly allowed to warm to room temperature and stirred overnight. To the resulting green solution was added $PbCl_2$ (0.14 g, 0.50 mmol) as a powder at room temperature. An

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immediate color change to red with gradual precipitation of Pb^0 was observed. The reaction mixture was stirred at room temperature for 4 h, followed by the procedures used above to give **3** as red microcrystals (0.17 g, 35%).

Preparation of [η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]ZrCl$_2$ (4). A toluene solution (10 mL) of Me_3SiCl (0.54 g, 5.00 mmol) was slowly added to a toluene (20 mL) solution of **2** (0.55 g, 1.00 mmol) with stirring at −20 °C, and the mixture was slowly warmed to room temperature and stirred overnight. The solvent was evaporated under vacuum. The oily residue was extracted with CH_2Cl_2 (10 mL × 3). The CH_2Cl_2 solutions were combined and concentrated to about 8 mL, to which *n*-hexane (15 mL) was added. **4** was isolated as pale yellow microcrystals after this solution stood at room temperature for several days (0.42 g, 80%). ^{1}H NMR (pyridine-d_5): δ 8.04 (d, J = 7.2 Hz, 1H, indenyl), 7.80 (d, J = 7.2 Hz, 1H, indenyl), 7.15 (d, 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 (d, J = 3.0 Hz, 1H, indenyl), 5.72 (m, 1H, NC*H*Me$_2$), 3.44 (m, 1H, NC*H*Me$_2$), 1.35 (d, J = 6.3 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.33 (d, J = 6.3 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.31 (d, J = 6.3 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.18 (d, J = 6.3 Hz, 3H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (pyridine-d_5): δ 129.7, 126.9, 125.7, 125.0, 124.9, 124.4, 124.2, 103.7, 102.5 (indenyl), 88.8 (cage *C*), 49.9, 48.3 (N*C*HMe$_2$), 26.0, 25.4, 22.9, 22.0 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −2.5 (1B), −4.6 (1B), −8.0 (3B), −11.9 (4B), −14.1 (2B). IR (KBr, cm^{-1}): ν 2939 (s), 2564 (vs), 1473 (vs), 1368 (s), 1272 (w), 1031 (vs), 814 (s). Anal. Calcd for C$_{17}$H$_{30}$B$_{11}$Cl$_2$NZr: C, 38.56; H, 5.71; N, 2.65; Cl, 13.39. Found: C, 38.56; H, 5.77; N, 2.88; Cl, 13.72.

Alternate Method. This compound was also prepared as pale yellow microcrystals from the reaction of $ZrCl_4(THF)_2$ (0.38 g, 1.00 mmol) with [^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$(OEt$_2$)$_2$ (0.53 g, 1.00 mmol) in THF (20 mL) using procedures similar to those used in the synthesis of **3**: yield 0.24 g (46%).

Preparation of [η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]HfCl$_2$ (5). This compound was prepared as colorless microcrystals from the reaction of $HfCl_4(THF)_2$ (0.46 g, 1.00 mmol) and [^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]Li$_2$(OEt$_2$)$_2$ (0.53 g, 1.00 mmol) in THF (20 mL) using procedures similar to those used in the synthesis of **3**: yield 0.34 g (56%). ^{1}H NMR (pyridine-d_5): δ 7.98 (d, J = 8.1 Hz, 1H, indenyl), 7.71 (d, J = 8.1 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 (m, 1H, NC*H*Me$_2$), 1.26 (d, J = 6.3 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.22 (d, J = 6.3 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.18 (d, J = 6.3 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.12 (d, J = 6.3 Hz, 3H, NCH(C*H*$_3$)$_2$). ^{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*), 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 −1.7 (1B), −3.4 (1B), −6.9 (3B), −11.4 (6B). IR (KBr, cm^{-1}): ν 3062 (w), 2924 (s), 2868 (s), 2586 (vs), 1614 (m), 1453 (s), 1376 (s), 1272 (m), 1075 (s), 886 (s), 802 (s), 733 (s). Anal. Calcd for C$_{17}$H$_{30}$B$_{11}$Cl$_2$HfN: C, 33.11; H, 4.90; N, 2.27. Found: C, 32.89; H, 4.85; N, 2.36.

Preparation of [η^5:σ-^{i}Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]ZrMe$_2$ (6). A 2.0 M solution of $AlMe_3$ in *n*-hexane (2.0 mL, 4.0 mmol) was slowly added to a toluene (20 mL) solution of **2** (0.55 g, 1.00 mmol) with stirring at −20 °C, resulting in the formation of a yellow precipitate. This suspension was then stirred at room temperature overnight. The precipitate was collected and washed with *n*-hexane (20 mL × 3), giving **6** as a yellow solid (0.38 g, 78%). ^{1}H NMR (pyridine-d_5): δ 7.87 (d, J = 6.0 Hz, 1H, indenyl), 7.34 (d, J = 6.0 Hz, 1H, indenyl), 7.18 (t, J = 9.0 Hz, 1H, indenyl), 6.98 (t, J = 9.0 Hz, 1H, indenyl), 6.36 (d, J = 6.0 Hz, 1H, indenyl), 6.14 (d, J = 6.0 Hz, 1H, indenyl), 5.37 (m, 1H, NC*H*Me$_2$), 3.32 (m, 1H, NC*H*Me$_2$), 1.25 (d, J = 6.0 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.21 (d, J = 6.0 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.16 (d, J = 6.0 Hz, 3H, NCH(C*H*$_3$)$_2$), 0.58 (d, J = 6.0 Hz, 3H, NCH(C*H*$_3$)$_2$), −0.38 (s, 6H, ZrC*H*$_3$). ^{13}C NMR (pyridine-d_5): δ 131.4, 126.7, 126.4, 126.1, 122.6, 120.2, 106.0, 100.5, 98.2 (indenyl), 91.9 (cage *C*), 49.7, 48.7 (N*C*HMe$_2$), 43.0 (Zr*C*H$_3$), 25.9, 25.3, 23.2, 23.0 (NCH(*C*H$_3$)$_2$). ^{11}B NMR (pyridine-d_5): δ −1.4 (1B), −3.2 (1B), −6.6 (3B), −11.0 (6B). IR (KBr, cm^{-1}): ν 3060 (w), 2961 (vs), 2904 (s), 2582 (vs), 1454 (s), 1381 (s), 1255 (s), 1089 (vs), 1029 (vs), 797 (s). Anal. Calcd for C$_{19}$H$_{36}$B$_{11}$NZr: C, 46.70; H, 7.43; N, 2.87. Found: C, 46.37; H, 7.53; N, 3.01.

Table 1. Crystal Data and Summary of Data Collection and Refinement for 1 and 2

	1	2
formula	C$_8$H$_{30}$B$_9$N$_3$Ti	C$_{21}$H$_{42}$B$_{11}$N$_3$Zr
cryst size (mm)	0.46 × 0.39 × 0.31	0.65 × 0.60 × 0.56
fw	313.5	546.7
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$
a, Å	8.847(1)	9.436(1)
b, Å	12.298(1)	15.829(1)
c, Å	16.931(2)	10.562(1)
β, deg	105.15	110.80(1)
V, Å^3	1778.2(3)	1474.8(2)
Z	4	2
D_{calcd}, Mg/m^3	1.171	1.231
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	4.1 to 56.2	4.6 to 56.1
μ, mm^{-1}	0.470	0.389
F(000)	664	568
no. of obsd reflns	4318	5169
no. of params refnd	203	327
goodness of fit	1.038	1.041
R1	0.048	0.023
wR2	0.153	0.067

Alternate Method. A 1.5 M solution of MeLi in Et_2O (1.4 mL, 2.1 mmol) was slowly added to a THF (15 mL) solution of **4** (0.53 g, 1.00 mmol) with stirring at −78 °C. The reaction mixture was warmed to room temperature and stirred overnight. This solution was filtered and concentrated to about 10 mL, to which *n*-hexane (10 mL) was added. **6** was isolated as yellow microcrystals after this solution stood at room temperature for several days (0.27 g, 56%).

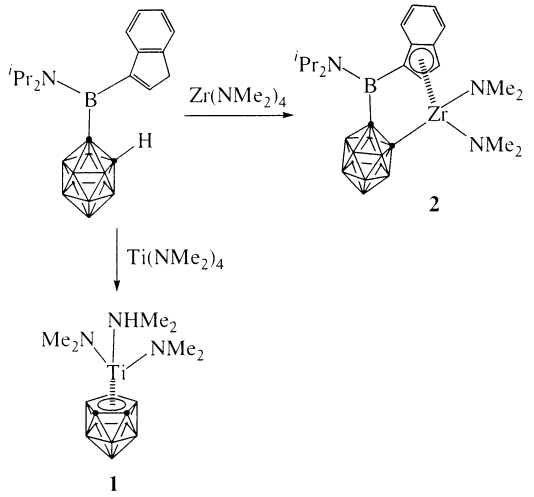
Ethylene Polymerization. This experiment was carried out in a 150 mL glass reactor equipped with a magnetic stirrer and gas inlets. The reactor was charged with the catalyst together with MAO and toluene (50 mL). The mixture was stirred at room temperature for 1 h. Ethylene gas was then introduced to the reactor, and its pressure was maintained continuously at 1 atm by means of bubbling. The polymerization was terminated by addition of acidic ethanol (100 mL). The white precipitate was filtered off and washed with ethanol and acetone. The resulting powder was finally dried in a vacuum oven at 80 °C overnight.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[9] 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.[10a] For the non-centrosymmetric structure **2**, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[10b] Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 1. Further details are included in the Supporting Information.

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

(10) (a) Sheldrick, G. M. *SHELXTL 5.10 for Windows NT*: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997. (b) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

Scheme 1

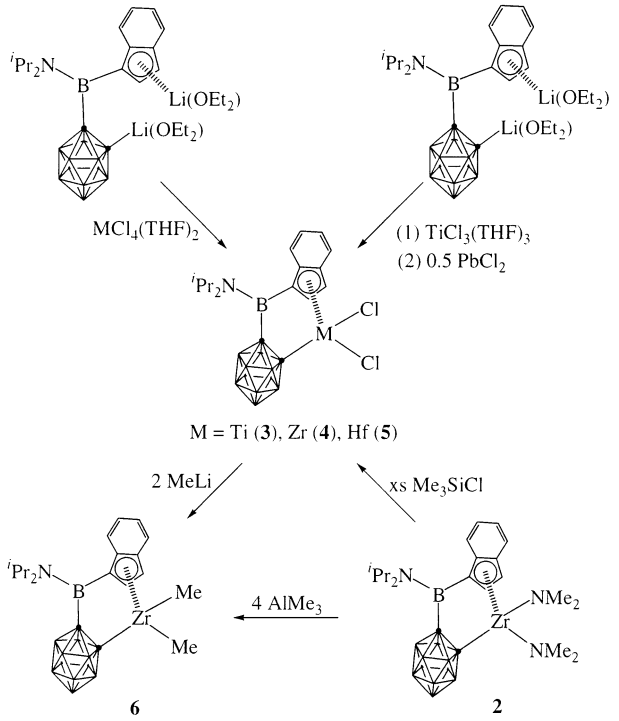


Results and Discussion

Synthesis. Our previous work showed that interaction between $Me_2A(C_9H_7)(C_2B_{10}H_{11})$ or $Me_2A(C_5H_5)(C_2B_{10}H_{11})$ (A = C, Si) and $M(NMe_2)_4$ in toluene resulted in the clean formation of the corresponding organo group 4 metal amide compounds.[6] The two acidic protons in ^{i}Pr$_2$NB$(C_9H_7)(C_2B_{10}H_{11})$ would allow similar amine elimination to occur between ^{i}Pr$_2$NB$(C_9H_7)(C_2B_{10}H_{11})$ and metal amides. In fact, treatment of ^{i}Pr$_2$NB$(C_9H_7)(C_2B_{10}H_{11})$ with 1 equiv of $Zr(NMe_2)_4$ in toluene at 65 °C gave the desired compound $[\eta^5{:}\sigma$-^{i}Pr$_2$NB$(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (**2**) in 70% yield. Under similar reaction conditions, however, interaction between ^{i}Pr$_2$NB$(C_9H_7)(C_2B_{10}H_{11})$ and an equimolar amount of $Ti(NMe_2)_4$ in toluene did not lead to the isolation of the expected compound $[\eta^5{:}\sigma$-^{i}Pr$_2$NB$(C_9H_6)(C_2B_{10}H_{10})]Ti(NMe_2)_2$; instead, the deborated product $(\eta^5$-$C_2B_9H_{11})Ti(NMe_2)_2(HNMe_2)$ (**1**) was isolated in 29% yield. This compound was reported earlier from the reaction of $C_2B_9H_{13}$ with $Ti(NMe_2)_4$.[11] These reactions were closely monitored by the unique ^{11}B chemical shift (δ 36.1 ppm) of the bridging B atom in ^{i}Pr$_2$NB$(C_9H_7)(C_2B_{10}H_{11})$.[5] As indicated by ^{11}B NMR, such amine elimination reactions did not proceed at all at room temperature. Upon heating, **2** was formed cleanly, while the reaction of $Ti(NMe_2)_4$ with ^{i}Pr$_2$NB$(C_9H_7)(C_2B_{10}H_{11})$ was very complicated. It was assumed that NMe_2^- in $Ti(NMe_2)_4$ might attack the bridging B atom and the cage B atom, leading to the formation of **1**. It was unlikely for the formed $HNMe_2$ to attack the B atoms; otherwise, **2** would not be isolated in high yield. These transformations are outlined in Scheme 1.

It had been known that treatment of $Cp_2Zr(NMe_2)_2$ with excess Me_3SiCl resulted in clean formation of Cp_2ZrCl_2.[12] Reaction of **2** with excess Me_3SiCl led to the isolation of a zirconocene chloride compound $[\eta^5{:}\sigma$-^{i}Pr$_2$NB$(C_9H_6)(C_2B_{10}H_{10})]ZrCl_2$ (**4**) in 80% yield. Salt metathesis reaction between $MCl_4(THF)_2$ and $[^i$Pr$_2$NB$(C_9H_6)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ in a 1:1 molar ratio also afforded constrained-geometry compounds of the general formula $[\eta^5{:}\sigma$-^{i}Pr$_2$NB$(C_9H_6)(C_2B_{10}H_{10})]MCl_2$ (M = Ti (**3**), Zr (**4**), Hf (**5**)) in good yields. **3** was also prepared in 35% yield from the reaction of $[^i$Pr$_2$NB$(C_9H_6)(C_2B_{10}H_{10})]Li_2(Et_2O)_2$ with 1 equiv of $TiCl_3(THF)_3$ followed by addition of 0.5 equiv of $PbCl_2$ in THF. Interaction of **2** with 4 equiv of Me_3Al in toluene resulted in the isolation of the methyl derivative $[\eta^5{:}\sigma$-^{i}Pr$_2$NB$(C_9H_6)(C_2B_{10}H_{10})]ZrMe_2$ (**6**) in 78% yield. **6** was also prepared in 56% yield from the reaction of **4** with 2 equiv of MeLi in THF. These synthetic routes are summarized in Scheme 2.

Scheme 2



These new constrained-geometry group 4 metal compounds were all very soluble in polar organic solvents such as THF, DME, and pyridine, sparely soluble in toluene, and insoluble in *n*-hexane. They were fully characterized by various spectroscopic data and elemental analyses. The solid-state structures of compounds **1** and **2** were further confirmed by single-crystal X-ray analyses.

Spectroscopic Characterization. The ^{1}H NMR spectra show that compounds **1**−**6** are all unsolvated species. In addition to six multiplets observed in the aromatic region of the ^{1}H NMR spectra of **2**−**6**, there are two multiplets (∼5.5 and ∼3.3 ppm), four doublets in the region 0.5−1.3 ppm corresponding to two diastereotopic isopropanyl groups of the ^{i}Pr$_2$N unit. This phenomenon is also observed in $[\eta^5{:}\sigma$-^{i}Pr$_2$NB$(C_9H_6)(C_2B_{10}H_{10})]YN(SiHMe_2)_2(THF)_2$.[5] The ^{1}H NMR spectrum of **2** also exhibits two singlets at 2.99 and 2.32 ppm attributable to two diastereotopic NMe_2 groups. These two singlets disappear upon treatment of **2** with excess Me_3SiCl, supporting the formation of **4**. A new singlet at −0.38 ppm ($ZrMe_2$ unit) is generated after reaction of **4** with 2 equiv of MeLi, confirming the formation of **6**. These results are in line with their ^{13}C NMR spectra. Their ^{11}B NMR spectra are similar, showing a 1:1:3:4:2 splitting pattern for **2**−**4** and a 1:1:3:6 splitting pattern for **5** and **6** (two resonances at higher field cannot be resolved), respectively. The IR spectra of **2**−**6** show a typical strong and broad characteristic B-H absorption

(11) Bowen, D. E.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3630.

(12) For examples, see: Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045, and references therein.

Table 2. Key Structural Data for [η^5:σ-A(C_9H_6)($C_2B_{10}H_{10}$)]Zr(NMe_2)$_2$ and [η^5:σ-$Me_2Si(C_5Me_4)(C_2B_{10}H_{10})$]Zr($NMe_2$)$_2$ (7)[a]

A	Zr−C (C_5 ring)	Zr−C (σ)	Zr−N	Cent−Zr−C(cage)[b]	C(C_5 ring)−A−C(cage)	N−Zr−N	ref
^{i}Pr$_2$NB	2.522(2)	2.345(2)	2.026(2)	103.0	114.0(2)	106.4(1)	this work
Me_2C	2.521(8)	2.326(7)	2.016(8)	101.6	109.4(6)	108.0(3)	6
Me_2Si	2.541(5)	2.348(5)	2.019(4)	109.9	104.8(2)	107.3(2)	6
Me_2Si (**7**)	2.544(6)	2.355(5)	2.028(5)	110.3	105.8(2)	104.5(2)	18

[a] All distances are in Å and angles in deg. [b] Cent = centroid of the five-membered ring of the indenyl or tetramethylcyclopentadienyl group.

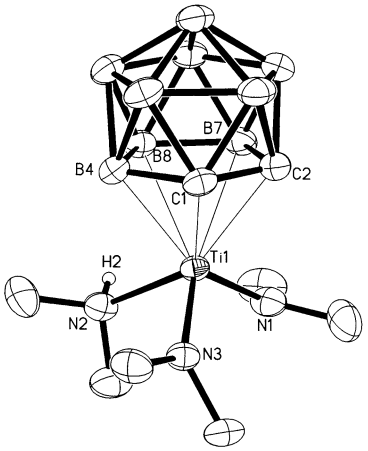


Figure 1. Molecular structure of (η^5-$C_2B_9H_{11}$)Ti(NMe_2)$_2$-($HNMe_2$) (**1**) (thermal ellipsoids drawn at the 35% probability level).

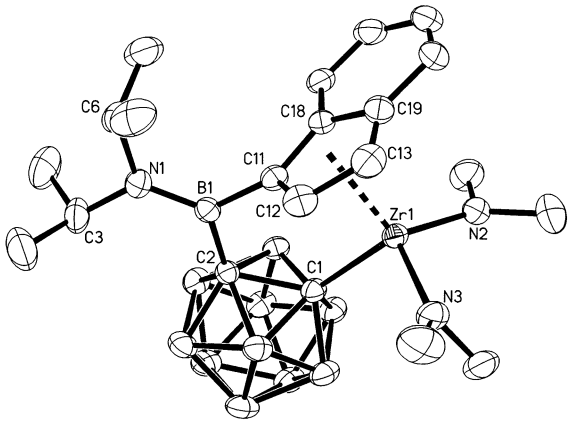


Figure 2. Molecular structure of [η^5:σ-^{i}Pr$_2$NB(C_9H_6)-($C_2B_{10}H_{10}$)]Zr(NMe_2)$_2$ (**2**) (thermal ellipsoids drawn at the 35% probability level).

at about 2560 cm^{-1}. The spectroscopic data of **1** are identical to those reported.[11]

Molecular Structure. The solid-state structure of **1** derived from single-crystal X-ray analyses shows that it adopts a monomeric three-legged piano stool structure containing an η^5-dicarbollide ligand with two amido and one amine ligand in the basal positions, a structure that is similar to (η^5-$C_2B_9H_{11}$)Zr(NEt_2)$_2$($HNEt_2$),[11] shown in Figure 1. The short Ti−N(1) and Ti−N(3) bond distances (1.886(2) and 1.913(2) Å) and the planar geometry around the N(1) and N(3) nitrogen atoms indicate that both nitrogen atoms with sp^2 hybridization are engaged in N(p_π)→Ti(d_π) interactions. As expected, the Ti−N(2) distance of 2.215(2) Å is much longer than the Ti−N(amido) distance and the N(2) adopts a pyramidal geometry. The average Ti−cage atom distance is 2.423-(2) Å. These structural data are very close to those found in [(η^5-C_5Me_5)(η^5-$C_2B_9H_{11}$)]Ti(N=CMe_2).[13]

The solid-state structure of **2** is shown in Figure 2. The Zr^{4+} ion is η^5-bound to the five-membered ring of the indenyl group and σ-bound to two amido ligands and one cage carbon atom in a distorted-tetrahedral geometry. Both the bridging boron and nitrogen (N(1)) atoms are in a trigonal planar environment (sum of angles around N(1) and B(1) ∼360°). This geometry together with a short boron−nitrogen distance of 1.396(3) Å indicates the presence of a N(p_π)→B(p_π) double-bond character. The B(bridging)−N (1.396(3) Å), B(bridging)−C(cage) (1.626(3) Å), and B(bridging)−C(ring) (1.587(3) Å) distances in **2** are very close to the corresponding values found in [η^5:σ-^{i}Pr$_2$NB(C_9H_6)($C_2B_{10}H_{10}$)]$_2$Ln$^-$.[5] The short Zr−N(2) and Zr−N(3) bond distances (2.041(2) and 2.011(2) Å) and the planar geometry around the N(2) and N(3) nitrogen atoms indicate that both nitrogen atoms with sp^2 hybridization are engaged in N(p_π)→Zr(d_π) interactions. The lack of additional electron donation from the *o*-carboranyl carbon atom to the Zr center also strengthens this N(p_π)→Zr(d_π) interaction, resulting in substantial decrease in Zr−N bond distances compared with the corresponding Zr−N bond distances of 2.062(5) Å in [$Me_2Si(C_5H_4)(NBu^t)$]Zr-(NMe_2)$_2$,[14] 2.057(9) Å in *rac*-[$C_2H_4(C_9H_6)_2$]Zr(NMe_2)$_2$,[15] 2.07 Å in Zr(NMe_2)$_4$,[16] and 2.06 Å in (Me_2N)$_2$Zr(μ-NBu^t)$_2$-Zr(NMe_2)$_2$.[17] For a comparison with similar constrained-geometry zirconium compounds, Table 2 summarizes the key structural data of [η^5:σ-Me_2A(C_9H_6)($C_2B_{10}H_{10}$)]-Zr(NMe_2)$_2$ with various linkage units A and [η^5:σ-Me_2-$Si(C_5Me_4)(C_2B_{10}H_{10})$]Zr($NMe_2$)$_2$.[18] The cent−Zr−C(cage) angles increase in the order Me_2C < ^{i}Pr$_2$NB < Me_2Si. The C(C_5 ring)−A−C(cage) angles decrease in the order ^{i}Pr$_2$NB > Me_2C > Me_2Si. Other structural parameters are similar.

Ethylene Polymerization. Compounds **2**−**6** underwent preliminary testing for catalytic activity, using methylalumoxane (MAO) as cocatalyst (Al/cat. = 1500) in toluene at room temperature (1 atm of ethylene). The activity of (C_5H_5)$_2$ZrCl_2 was also tested under the same experimental conditions for comparison. The results are compiled in Table 3. All five compounds could catalyze the polymerization of ethylene with moderate to very high activities in the presence of MAO. Both the central metal ion and co-ligand affected the catalytic perfor-

(13) Kreuder, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993.

(14) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572.

(15) Christopher, J. N.; Diamond, G. M.; Jordan, R. F. *Organometallics* **1996**, *15*, 4038.

(16) Hagen, K.; Holwill, C. J.; Rice, D. A.; Runnacles, J. D. *Inorg. Chem.* **1988**, *27*, 2032.

(17) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030.

(18) Lee, M. H.; Hwang, J.-W.; Kim, Y.; Han, Y.; Do, Y. *Organometallics* **2000**, *19*, 5514.

Table 3. Ethylene Polymerization Results[a]

catalyst	time (min)	yield (g)	activity (10^6 g/(mol atm h))	$M_w/10^3$	M_w/M_n[c]	T_m[d] (°C)
$(C_5H_5)_2ZrCl_2$	60	3.75	1.25	103	2.28	130.0
2 (Zr)	60	0.60	0.20	465	14.0	135.5
3 (Ti)	60	0.22	0.07	372	21.5	131.3
4 (Zr)	10	1.97	3.94	346	2.88	137.0
4[b] (Zr)	60	1.05	3.50	359	4.78	137.1
5 (Hf)	60	0.09	0.03	107	17.7	129.6
6 (Zr)	60	0.61	0.20	110	20.3	130.6

[a] Conditions: toluene (50 mL), 1 atm of ethylene, $T = 25$ °C, catalyst (3.0 μmol), MAO (4.5 mmol), Al/M = 1500. [b] Conditions: toluene (50 mL), 1 atm of ethylene, $T = 25$ °C, catalyst (0.3 μmol), MAO (0.45 mmol), Al/Zr = 1500. [c] Measured by GPC (using polystyrene standards in 1,2,4-trichlorobenzene at 150 °C.) [d] Measured by DSC (heating rate: 10 °C/min).

mance of the catalysts, and the following trends were observed: (1) Zr ≫ Ti > Hf and (2) Cl > Me ≈ NMe_2. Note that two polymerization conditions were examined for **4** since a large amount of polyethylene precipitates caused difficulty in stirring. Among these catalysts, **4** exhibited the highest activity in ethylene polymerization. Its activity was slightly higher than the corresponding zirconium compounds derived from the Me_2C- and Me_2Si-bridged constrained-geometry ligands $[Me_2A(C_9H_5)(C_2B_{10}H_{10})]^{2-}$ (Chart 1)[6] and was at the high end for constrained-geometry metallocene catalysts reported in the literature.[1]

The melting temperatures (T_m) of the polyethylenes prepared with the catalysts listed in Table 3 were between 129.6 and 137.1 °C, values typical for linear high-density polyethylenes. This result was supported by the IR spectra of the polymers showing no sign of branching.[19] Molecular weights and polydispersities of the polymers produced ranged from 110 000 to 465 000 g mol^{-1} and 2.88 to 20.3, respectively. These data indicated that **4** might be a single-site catalyst and the others might probably have more than one active site after activation with MAO.

(19) Koenig, J. L. *Chemical Microstructure of Polymer Chains*; Wiley: New York, 1982; p 63.

Conclusion

Several new group 4 metal compounds with a $^iPr_2$-NB-bridged constrained-geometry carboranyl ligand were prepared. They exhibited a moderate to very high ethylene polymerization activity when activated with MAO. The activities depended upon both the central metal ion and co-ligand. The following trends were observed: (1) Zr ≫ Ti > Hf and (2) Cl > Me ≈ NMe_2. Compound **4** showed the highest ethylene polymerization activity among the five compounds examined. This work also showed that the B-bridged system offered zirconium compounds with a slightly higher ethylene polymerization activity than the corresponding C- and Si-bridged systems, which might suggest that the $^iPr_2$-NB-linkage played a role in enhancing the catalytic activity of the resulting catalysts.

On changing from the Me_2A- (A = Si, C) to $^iPr_2NB$-linkage, $Me_2A(C_9H_7)(C_2B_{10}H_{11})$ (A = Si, C) and $^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$ exhibited some different reactivity patterns. For example, the reaction of $^iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$ with $Ti(NMe_2)_4$ did not give the expected compound $[^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]Ti(NMe_2)_2$, while $Ti(NMe_2)_4$ reacted readily with $Me_2A(C_9H_7)(C_2B_{10}H_{11})$ (A = Si, C) to give the corresponding amide compounds in good yields.[6] Unlike $[Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (A = Si, C),[6] treatment of $[^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ with excess Me_3SiCl led to the complete conversion of the $M(NMe_2)_2$ moiety to the MCl_2 group.

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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 **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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