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Synthesis, Structural Characterization, and Olefin Polymerization Behavior of Group 4 Metal Complexes with Constrained-Geometry Carborane Ligands

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Several new group 4 metal amide complexes with recently developed constrained-geometry carborane ligands, $[\eta^5:\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]M(NR_2)_2$ and $[\eta^5:\sigma\text{-}Me_2A(C_5H_4)(C_2B_{10}H_{10})]M(NR_2)_2$ (A = C, Si; M = Ti, Zr; R = Me, Et), were prepared in good yield via amine elimination reactions of $M(NR_2)_4$ and the corresponding neutral ligands in toluene. Treatment of the amide complexes with 2.5 equiv of $Me_2NH \cdot HCl$ or $Me_3N \cdot HCl$ led to high yields of the corresponding chloride complexes, $[\{\eta^5:\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\mu\text{-}Cl)_{1.5}]_2^-$ (A = C, Si), which could also be prepared from an equimolar reaction between $ZrCl_4(THF)_2$ and $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]Li_2$. In contrast, excess Me_3SiCl could only convert $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ to $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$, due to steric effects. All these new complexes have been fully characterized by ^1H, ^{13}C, and ^{11}B NMR and IR spectroscopic data and elemental analyses. Thirteen out of fourteen newly prepared complexes have been structurally characterized by single-crystal X-ray diffraction studies. The chloride complexes exhibit a very high ethylene polymerization activity when they are activated with MMAO.

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] It has been documented that a ligand containing bifunctional groups often offers complexes with some additional advantages.[2] Recently developed "constrained-geometry" ligands containing both monocyclopentadienyl and σ-heteroatom components have attracted considerable attention.[3] Group 4 metallocenes derived from these ligands are very active catalysts (so-called constrained-geometry catalysts (CGC)) for the copolymerization of ethylene with α-olefins due to the increased electron deficiency and more open coordination environment of the central metal ions.[3] Given the impact of the cyclopentadienyl-appended heteroatom donor groups on the catalytic performance of the group 4 metal complexes, we have recently designed several silicon- and carbon-bridged versatile ligands, $Me_2A(C_5H_5)(C_2B_{10}H_{11})$ (A = C,[4] Si[5]), $Me_2A(C_9H_7)(C_2B_{10}H_{11})$ (A = C,[6] Si[7]), and $Me_2Si(C_{13}H_9)(C_2B_{10}H_{11})$,[8] which can be conveniently converted into a novel class of "constrained-geometry" ligands bearing a carboanion as σ-donor, shown in Chart 1. These ligands contain a highly electron-deficient carborane moiety, which should enhance the Lewis acidity of the central metal ion and, thus, increase the activity of the resulting group 4 metal complexes. Recent examples illustrated by Do et al. exemplify the importance of these ligands in group 4 metal chemistry.[9] We report herein our detailed study on the synthesis, structural charac-

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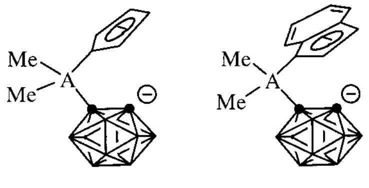
Chart 1



A = C, Si

terization, and olefin polymerization behavior of group 4 metal complexes derived from this new type of “constrained-geometry” ligands (Chart 1).[10]

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry nitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques or in a glovebox. All organic solvents (except methylene chloride) were freshly distilled from sodium benzophenone ketyl immediately prior to use. Methylene chloride was distilled from phosphorus pentoxide prior to use. $ZrCl_4(THF)_2$,[11] $M(NR_2)_4$ (M = Ti, Zr; R = Me, Et),[12] $Me_2A(C_9H_7)(C_2B_{10}H_{11})$, $Me_2A(C_5H_5)(C_2B_{10}H_{11})$ (A = C,[4,6] Si[5,7]), $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]Li_2$,[6] $Me_2NH\cdot HCl$,[13] and $Me_3N\cdot HCl$[14] 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 Nicolet Magna 550 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 internal or external TMS (0.00 ppm) or with respect 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 $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ (1a). To a toluene (20 mL) solution of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.30 g, 1.0 mmol) was added a toluene (5 mL) solution of $Ti(NMe_2)_4$ (0.225 g, 1.0 mmol) at room temperature, and the reaction mixture was refluxed for 2 days to give a red solution. A small amount of precipitate was filtered off. The resulting clear red solution was concentrated to about 5 mL. **1a** was isolated as red crystals after this solution stood at room temperature for several days (0.335 g, 77%). ^1H NMR (pyridine-d_5): δ 7.96 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.15 (m, 1H), 7.11 (m, 1H), 6.60 (m, 1H), 6.57 (m, 1H) (C_9H_6), 3.29 (s, 6H), 2.22 (s, 6H) ($N(CH_3)_2$), 1.91 (s, 3H), 1.68 (s, 3H) ($(CH_3)_2C$). ^{13}C NMR (pyridine-d_5): δ 137.67, 125.55, 125.12, 124.93, 124.01, 122.08, 118.90, 105.92, 103.7 (C_9H_6), 101.32 ($C_2B_{10}H_{10}$), 51.45, 44.01 ($N(CH_3)_2$), 34.01, 31.43, 22.15 ($(CH_3)_2C$). ^{11}B NMR (pyridine-d_5): δ −4.9 (2), −7.5 (2), −11.3 (4), −13.3 (2). IR (KBr, cm^{-1}): ν 2979 (m), 2859 (s), 2764 (m), 2593 (vs), 2547 (vs), 2314 (m), 1451 (s), 1100 (m), 1042 (s), 941 (vs), 800 (s), 743 (m), 561 (m). Anal. Calcd for $C_{18}H_{34}B_{10}N_2Ti$: C, 49.76; H, 7.89; N, 6.45. Found: C, 50.07; H, 7.86; N, 6.27.

Preparation of $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (2a). This compound was prepared as pale yellow crystals from $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.151 g, 0.5 mmol) and $Zr(NMe_2)_4$ (0.134 g, 0.5 mmol) in toluene (20 mL) by using procedures similar to those used in the synthesis of **1a**, except the reaction time was reduced to 1 day: yield 0.206 g (86%). ^1H NMR (pyridine-d_5): δ 8.05 (d, J = 8.4 Hz, 1H), 7.22 (dd, J = 6.9 and 8.4 Hz, 1H), 7.02 (dd, J = 8.4 and 6.9 Hz, 1H), 6.80 (d, J = 3.6 Hz, 1H), 6.33 (d, J = 8.4 Hz, 1H), 5.86 (d, J = 3.6 Hz, 1H) (C_9H_6), 2.99 (s, 6H), 2.35 (s, 6H) ($N(CH_3)_2$), 1.97 (s, 3H), 1.79 (s, 3H) ($(CH_3)_2C$). ^{13}C NMR (pyridine-d_5): δ 133.05, 125.31, 124.81, 124.77, 124.65, 123.57, 123.39, 121.50, 106.29 (C_9H_6), 102.43, 99.23 ($C_2B_{10}H_{10}$), 45.85, 45.03 ($N(CH_3)_2$), 35.72, 31.67, 22.80 ($(CH_3)_2C$). ^{11}B NMR (pyridine-d_5): δ −3.8 (2), −5.5 (2), −9.3 (4), −11.1 (2). IR (KBr, cm^{-1}): ν 3093 (w), 2979 (m), 2861 (s), 2822 (m), 2774 (s), 2591 (vs), 2562 (vs), 1452 (m), 1371 (m), 1333 (w), 1247 (m), 1210 (m), 1182 (m), 1129 (m), 1052 (m), 1021 (m), 932 (vs), 793 (m), 742 (s), 698 (w). Anal. Calcd for $C_{18}H_{34}B_{10}N_2Zr$: C, 45.25; H, 7.17; N, 5.86. Found: C, 45.02; H, 7.28; N, 5.78.

Preparation of $[Me_3NH][\{\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\mu\text{-}Cl)_{1.5}]_2\cdot CH_2Cl_2$ (2b). To a toluene (25 mL) solution of $[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (**2a**; 0.24 g, 0.5 mmol) was incrementally added a dry powder of Me_3NHCl (0.119 g, 1.25 mmol) over a period of several hours at 0 °C, and then the reaction mixture was stirred overnight. The solvent and the volatiles were pumped off, leaving a yellow solid. Recrystallization from a toluene/CH_2Cl_2 solution gave **2b** as yellow crystals (0.242 g, 88%). ^1H NMR (pyridine-d_5): δ 8.24 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 3.0 Hz, 2H), 7.58 (dd, J = 7.8 and 6.9 Hz, 2H), 7.13 (dd, J = 7.8 and 6.9 Hz, 2H), 6.58 (d, J = 8.7 Hz, 2H), 6.15 (d, J = 3.0 Hz, 2H) (C_9H_6), 5.66 (s, 2H) (CH_2Cl_2), 2.70 (s, 9H) ($N(CH_3)_3$), 1.99 (s, 6H), 1.87 (s, 6H) ($(CH_3)_2C$). ^{13}C NMR (pyridine-d_5): δ 144.96, 129.50, 129.18, 128.88, 127.96, 127.56, 126.13, 125.48, 110.10 (C_9H_6), 104.37, 103.83 ($C_2B_{10}H_{10}$), 55.39 (CH_2Cl_2), 45.55 ($N(CH_3)_3$), 35.43, 33.87, 23.19 ($(CH_3)_2C$). ^{11}B NMR (pyridine-d_5): δ −3.1 (2), −5.5 (2), −8.9 (4), −13.2 (2). IR (KBr, cm^{-1}): ν 3066 (w), 2954 (m), 2864 (s), 2777 (s), 2576 (vs), 1253 (s), 1158 (m), 1128 (m), 1086 (s), 1050 (m), 933 (vs), 803 (s), 745 (m). Anal. Calcd for $C_{32}H_{56}B_{20}Cl_7NZr_2$: C, 34.89; H, 5.12; N, 1.27. Found: C, 34.89; H, 5.36; N, 1.32.

Preparation of $\{[\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]ZrCl(\mu\text{-}Cl)_{1.5}\}_2\{Li(THF)_2\}\cdot C_6H_5CH_3$ (2c). To a suspension of $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]Li_2$ (0.157 g, 0.5 mmol) in diethyl ether (30 mL) was added $ZrCl_4(THF)_2$ (0.189 g, 0.5 mmol) in one portion at −30 °C with stirring, and the mixture was slowly warmed to room temperature and stirred overnight. After removal of the precipitate, the solvent was evaporated under vacuum, leaving an oily residue which was extracted with a mixed solvent of toluene and THF (10:1, 2 × 15 mL). The extractions were combined and concentrated to about 10 mL. *n*-Hexane vapor diffusion afforded **2c** as yellow crystals (0.180 g, 60%). ^1H NMR (pyridine-d_5): δ 8.25 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 3.3 Hz, 2H), 7.26 (dd, J = 6.9 and 7.8 Hz, 2H), 7.13 (dd, J = 6.9 and 7.8 Hz, 2H), 6.58 (d, J = 8.7 Hz, 2H), 6.15 (d, J = 3.3 Hz, 2H) (C_9H_6), 7.15 (m, 5H), 2.20 (s, 3H) ($C_6H_5CH_3$), 3.63 (m, 8H), 1.58 (m, 8H) (OC_4H_8), 1.99 (s, 6H), 1.87 (s, 6H) ($(CH_3)_2C$). ^{13}C NMR (pyridine-d_5): δ 145.00, 129.50, 129.19, 128.88, 127.95, 127.48, 126.09, 125.45, 110.10 (C_9H_6), 104.35, 103.75 ($C_2B_{10}H_{10}$), 129.74, 129.00, 125.27, 123.13, 23.17 ($C_6H_5CH_3$), 68.17, 26.14 (OC_4H_8), 45.55, 35.41, 33.85 ($(CH_3)_2C$). ^{11}B NMR (pyridine-d_5): δ −2.9 (2), −5.6 (2), −9.4 (4), −13.5 (2). IR (KBr, cm^{-1}): ν 2977 (m), 2954 (m), 2881 (m), 2600 (vs), 2550 (vs), 1608 (w), 1455 (m), 1374 (m), 1260 (w), 1209 (m), 1093 (m), 1042 (s), 890 (w), 828 (m), 742 (s), 696 (m). Anal. Calcd for $C_{43}H_{68}B_{20}Cl_5LiO_2Zr_2$: C, 43.04; H, 5.71. Found: C, 43.05; H, 5.46.

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Treatment of **2c** with 1 equiv of Me_3NHCl in CH_2Cl_2 gave **2b** as yellow crystals in 90% yield.

Preparation of [η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]$Zr(NEt_2)_2$ (3a). This compound was prepared as pale yellow crystals from $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.151 g, 0.50 mmol) and $Zr(NEt_2)_4$ (0.191 g, 0.50 mmol) in toluene (20 mL) by using procedures similar to those used in the synthesis of **1a**: yield 0.181 g (68%). ^{1}H NMR (pyridine-d_5): δ 8.04 (d, $J = 8.7$ Hz, 1H), 7.25 (m, 1H), 7.08 (m, 1H), 7.06 (m, 1H), 6.70 (d, $J = 3.6$ Hz, 1H), 6.32 (d, $J = 3.6$ Hz, 1H) (C_9H_6), 3.55 (q, $J = 6.9$ Hz, 2H), 2.73 (m, 4H), 2.56 (q, $J = 6.9$ Hz, 2H) ($N(CH_2CH_3)_2$), 1.92 (s, 3H), 1.72 (s, 3H) ($(CH_3)_2C$), 1.04 (t, $J = 6.9$ Hz, 6H), 0.69 (t, $J = 6.9$ Hz, 6H) ($N(CH_2CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 132.93, 124.55, 124.31, 123.97, 123.67, 120.15, 104.68, 104.37, 97.84 (C_9H_6), 42.86, 40.66, 12.79, 12.54 ($N(CH_2CH_3)_2$), 34.65, 32.56, 22.1 ($(CH_3)_2C$); the cage carbons were not observed. ^{11}B NMR (pyridine-d_5): δ −4.7 (2), −6.5 (2), −10.3 (4), −12.1 (2). IR (KBr, cm^{-1}): ν 2965 (m), 2869 (w), 2575 (vs), 2412 (m), 1592 (w), 1454 (s), 1366 (s), 1025 (vs), 786 (vs). Anal. Calcd for $C_{22}H_{42}B_{10}N_2Zr$: C, 49.49; H, 7.93; N, 5.25. Found: C, 49.61; H, 7.61; N, 5.31.

Preparation of [η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$ (4a). This compound was prepared as pale yellow crystals from $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.158 g, 0.50 mmol) and $Zr(NMe_2)_4$ (0.134 g, 0.50 mmol) in toluene (20 mL) by using procedures similar to those used in the synthesis of **2a**: yield 0.225 g (91%). ^{1}H NMR (pyridine-d_5): δ 7.86 (d, $J = 8.4$ Hz, 1H), 7.26 (dd, $J = 7.4$ and 7.8 Hz, 1H), 7.10 (dd, $J = 7.8$ and 7.4 Hz, 1H), 6.89 (d, $J = 3.5$ Hz, 1H), 6.61 (d, $J = 8.4$ Hz, 1H), 6.26 (d, $J = 3.5$ Hz, 1H) (C_9H_6), 2.99 (s, 6H), 2.35 (s, 6H) ($N(CH_3)_2$), 0.82 (s, 3H), 0.62 (s, 3H) ($(CH_3)_2Si$). ^{13}C NMR (pyridine-d_5): δ 132.30, 130.44, 128.91, 128.86, 126.26, 126.21, 125.77, 125.13, 108.43 (C_9H_6), 103.51, 82.65 ($C_2B_{10}H_{10}$), 46.86, 45.49 ($N(CH_3)_2$), 0.49, 0.00 ($(CH_3)_2Si$). ^{11}B NMR (pyridine-d_5): δ 1.4 (2), −2.8 (2), −8.5 (4), −12.0 (2). ^{1}H NMR (benzene-d_6): δ 7.51 (d, $J = 8.4$ Hz, 1H), 7.13 (m, 1H), 7.03 (m, 1H), 6.80 (m, 1H), 6.27 (d, $J = 3.6$ Hz, 1H), 6.24 (m, 1H) (C_9H_6), 2.82 (s, 6H), 1.97 (s, 6H) ($N(CH_3)_2$), 0.52 (s, 3H), 0.37 (s, 3H) ($(CH_3)_2Si$). ^{13}C NMR (benzene-d_6): δ 129.66, 128.89, 126.90, 126.63, 126.02, 125.05, 124.87, 124.47, 105.07 (C_9H_6), 97.83, 84.73 ($C_2B_{10}H_{10}$), 46.00, 41.18 ($N(CH_3)_2$), −0.86, −0.96 ($(CH_3)_2Si$). ^{11}B NMR (benzene-d_6): δ −0.8 (2), −4.4 (2), −10.0 (4), −13.6 (2). IR (KBr, cm^{-1}): ν 3066 (w), 2954 (m), 2864 (s), 2824 (m), 2777 (m), 2576 (vs), 1444 (m), 1253 (s), 1158 (m), 1128 (m), 1086 (s), 1050 (m), 934 (vs), 803 (s), 745 (m), 681 (m). Anal. Calcd for $C_{17}H_{34}B_{10}N_2SiZr$: C, 41.34; H, 6.94; N, 5.67. Found: C, 41.42; H, 7.01; N, 5.72.

Preparation of [Me_2NH_2][{η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$}-$ZrCl(\mu$-$Cl)_{1.5}$]$_2$·$0.5CH_2Cl_2$ (4b). To a toluene (20 mL) solution of [η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$ (**4a**; 0.247 g, 0.50 mmol) was added a toluene (5 mL) solution of Me_3SiCl (0.434 g, 4.0 mmol), and the reaction mixture was then stirred at room temperature overnight. The solvent was pumped off along with excess Me_3SiCl, leaving a yellow solid. Recrystallization from a toluene/CH_2Cl_2 solution afforded a yellow powder (2.10 g). The ^{1}H NMR spectrum of this product is complicated, showing many peaks in the aromatic region and the presence of an amido group. This solid was then treated with Me_2NH·HCl (0.082 g, 1.0 mmol) in toluene (20 mL) by using procedures similar to those used in the synthesis of **2b** to afford **4b** as yellow crystals (0.137 g, 51%). ^{1}H NMR (pyridine-d_5): δ 8.06 (d, $J = 8.6$ Hz, 2H), 7.89 (dd, $J = 3.5$ and 5.7 Hz, 2H), 7.51 (dd, $J = 5.7$ and 3.5 Hz, 2H), 7.26 (d, $J = 3.3$ Hz, 2H), 6.72 (d, $J = 8.6$ Hz, 2H), 6.35 (d, $J = 3.3$ Hz, 2H) (C_9H_6), 4.37 (m, 6H) ($(CH_3)_2NH_2$), 0.91 (s, 6H), 0.86 (s, 6H) ($(CH_3)_2Si$). ^{13}C NMR (pyridine-d_5): δ 132.00, 130.41, 128.94, 128.46, 126.11, 126.01, 125.71, 124.13, 108.41 (C_9H_6), 103.31, 82.45 ($C_2B_{10}H_{10}$), 46.90 ($N(CH_3)_2$), 0.48, 0.00 ($(CH_3)_2Si$). ^{11}B NMR (pyridine-d_5): δ −1.7 (2), −5.1 (2), −8.7 (4), −10.3 (2). IR (KBr, cm^{-1}): ν 3080 (w), 2960 (m), 2862 (w), 2572 (vs), 1604 (m), 1489 (m), 1444 (s), 1255 (s), 1228 (m), 1158 (m), 1154 (m), 1090 (s), 1060 (m), 1042 (m), 1008 (m), 960 (m), 836 (s), 809 (s), 756 (s), 698 (s), 670 (m), 629 (m). Anal. Calcd for $C_{28}H_{52}B_{20}Cl_5NSi_2Zr_2$ (**4b**−$0.5CH_2Cl_2$): C, 32.50; H, 5.07; N, 1.35. Found: C, 31.93; H, 5.50; N, 1.52.

This complex could be prepared in 81% yield by direct treatment of **4a** with 2.5 equiv of Me_2NH·HCl in toluene.

Preparation of [Me_3NH][η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$-$ZrCl(\mu$-$Cl)_{1.5}$]$_2$· THF (4c). This compound was prepared as yellow crystals from [η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$ (**4a**; 0.247 g, 0.5 mmol) and Me_3NHCl (0.119 g, 1.25 mmol) in toluene (25 mL) by using procedures similar to those used in the synthesis of **2b**: yield 0.238 g (85%). ^{1}H NMR (pyridine-d_5): δ 8.06 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 3.2$ Hz, 2H), 7.63 (t, $J = 7.5$ Hz, 2H), 7.27 (t, $J = 7.5$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 2H), 6.36 (d, $J = 3.2$ Hz, 2H) (C_9H_6), 3.63 (m, 4H), 1.59 (m, 4H) (OC_4H_8), 2.87 (s, 9H) ($N(CH_3)_3$), 0.78 (s, 6H), 0.71 (s, 6H) ($(CH_3)_2Si$). ^{13}C NMR (pyridine-d_5): δ 134.91, 129.30, 129.11, 128.00, 127.91, 127.51, 126.10, 125.41, 110.00 (C_9H_6), 103.85 ($C_2B_{10}H_{10}$), 68.10, 26.16 (OC_4H_8), 45.61 ($N(CH_3)_3$), 0.30, −0.21 ($(CH_3)_2Si$). ^{11}B NMR (pyridine-d_5): δ −1.7 (2), −5.1 (2), −8.7 (4), −10.6 (2). IR (KBr, cm^{-1}): ν 3066 (w), 2954 (m), 2869 (s), 2576 (vs), 1449 (m), 1252 (s), 1158 (m), 1129 (m), 1080 (s), 1055 (m), 936 (vs), 808 (s), 747 (m), 681 (m). Anal. Calcd for $C_{33}H_{62}B_{20}Cl_5NOSi_2Zr_2$: C, 35.36; H, 5.58; N, 1.25. Found: C, 35.04; H, 5.35; N, 1.28.

Preparation of [η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]$Zr(NEt_2)_2$ (5a). This compound was prepared as pale yellow crystals from $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.162 g, 0.51 mmol) and $Zr(NEt_2)_4$ (0.195 g, 0.51 mmol) in toluene (20 mL) by using procedures similar to those used in the synthesis of **1a**: yield 0.152 g (54%). ^{1}H NMR (pyridine-d_5): δ 7.90 (d, $J = 8.4$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.31 (m, 1H), 7.28 (m, 1H), 6.86 (d, $J = 3.3$ Hz, 1H), 6.79 (d, $J = 3.3$ Hz, 1H) (C_9H_6), 3.57 (m, 4H), 2.70 (m, 2H), 2.53 (m, 2H) ($N(CH_2CH_3)_2$), 1.05 (t, $J = 6.9$ Hz, 6H), 0.68 (t, $J = 6.9$ Hz, 6H) ($N(CH_2CH_3)_2$), 0.74 (s, 3H), 0.56 (s, 3H) ($(CH_3)_2Si$). ^{13}C NMR (pyridine-d_5): δ 131.55, 128.46, 126.60, 125.63, 125.31, 124.44, 124.31, 108.11, 104.70 (C_9H_6), 98.33, 84.30 ($C_2B_{10}H_{10}$), 42.86, 40.32 ($N(CH_2CH_3)_2$), 13.20, 13.11 ($N(CH_2CH_3)_2$), −1.60, −1.98 ($(CH_3)_2Si$). ^{11}B NMR (pyridine-d_5): δ −0.3 (2), −4.1 (2), −9.4 (4), −12.5 (2). ^{1}H NMR (benzene-d_6): δ 7.62 (d, $J = 8.1$ Hz, 1H), 7.24 (d, $J = 8.1$ Hz, 1H), 6.85 (m, 2H), 6.32 (m, 2H) (C_9H_6), 3.40 (m, 4H), 2.60 (m, 2H), 2.35 (m, 2H) ($N(CH_2CH_3)_2$), 0.89 (t, $J = 6.9$ Hz, 6H), 0.60 (t, $J = 6.9$ Hz, 6H) ($N(CH_2CH_3)_2$), 0.51 (s, 3H), 0.36 (s, 3H) ($(CH_3)_2Si$). ^{13}C NMR (benzene-d_6): δ 132.12, 128.68, 126.44, 125.96, 125.67, 125.09, 124.58, 109.40, 104.27 (C_9H_6), 98.25, 84.47 ($C_2B_{10}H_{10}$), 43.43, 40.90 ($N(CH_2CH_3)_2$), 13.90, 13.86 ($N(CH_2CH_3)_2$), −0.95, −1.34 ($(CH_3)_2Si$). ^{11}B NMR (benzene-d_6): δ −0.4 (2), −4.4 (2), −9.9 (4), −13.4 (2). IR (KBr, cm^{-1}): ν 2967 (s), 2567 (vs), 1446 (s), 1364 (s), 1256 (s), 1138 (m), 1093 (s), 1000 (m), 798 (vs). Anal. Calcd for $C_{21}H_{42}B_{10}N_2SiZr$: C, 45.86; H, 7.70; N, 5.09. Found: C, 45.51; H, 7.47; N, 4.97.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$Ti(NMe_2)_2$ (6a). This compound was prepared as red crystals from $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.250 g, 1.0 mmol) and $Ti(NMe_2)_4$ (0.225 g, 1.0 mmol) in toluene (30 mL) by using procedures similar to those used in the synthesis of **1a**: yield 0.309 g (80%). ^{1}H NMR (pyridine-d_5): δ 6.15 (m, 2H), 6.01 (m, 2H) (C_5H_4), 3.10 (s, 12H) ($N(CH_3)_2$), 1.56 (s, 6H) ($(CH_3)_2C$). ^{13}C NMR (pyridine-d_5): δ 148.01, 113.10, 110.48 (C_5H_4), 103.81, 101.45 ($C_2B_{10}H_{10}$), 47.46 ($N(CH_3)_2$), 31.57, 22.52 ($(CH_3)_2C$). ^{11}B NMR (pyridine-d_5): δ −4.4 (2), −7.3 (2), −11.2 (4), −12.9 (2). IR (KBr, cm^{-1}): ν 2972 (m), 2858 (s), 2597 (vs), 2561 (vs), 1622 (m), 1454 (s), 1098 (s), 1044 (s), 930 (s), 816 (s), 520 (vs). Anal. Calcd for $C_{14}H_{32}B_{10}N_2Ti$: C, 43.74; H, 8.39; N, 7.29. Found: C, 43.90; H, 8.34; N, 7.29.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$TiCl(NMe_2)$ (6b). To a toluene solution (20 mL) of **6a** (0.309 g, 0.80 mmol) was added Me_3SiCl (1.3 mL, 10 mmol), and the reaction mixture was stirred overnight. The solvent was pumped off along with excess Me_3SiCl, leaving a red solid which was

Table 1. Crystal Data and Summary of Data Collection and Refinement for 1a, 3a−7a, and 9a

	1a	**3a**	**4a**	**5a**	**6a**	**7a**	**9a**
formula	$C_{18}H_{34}B_{10}$-N_2Ti	$C_{22}H_{42}B_{10}$-N_2Zr	$C_{17}H_{34}B_{10}$-N_2SiZr	$C_{21}H_{42}B_{10}$-N_2SiZr	$C_{14}H_{32}B_{10}$-N_2Ti	$C_{14}H_{32}B_{10}$-N_2Zr	$C_{17}H_{40}B_{10}$-N_2SiZr
cryst size (mm)	0.56 × 0.45 × 0.23	0.58 × 0.45 × 0.40	0.45 × 0.36 × 0.24	0.54 × 0.28 × 0.25	0.25 × 0.21 × 0.20	0.42 × 0.23 × 0.20	0.63 × 0.59 × 0.45
fw	434.47	533.90	493.87	549.98	384.42	427.74	499.92
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	9.394(2)	14.381(1)	9.603(2)	10.321(2)	9.182(2)	9.915(1)	9.171(1)
b, Å	13.723(2)	11.257(1)	13.971(3)	15.679(4)	13.594(2)	13.811(1)	19.792(1)
c, Å	18.675(3)	16.974(1)	19.096(4)	18.018(4)	17.701(2)	16.936(1)	14.722(1)
β, deg	99.38(1)	90.54(1)	99.35(3)	90.00	97.22(1)	105.79(1)	98.23(1)
V, Å^3	2375.3(7)	2747.8(3)	2527.9(9)	2915.7(12)	2191.9(5)	2231.67(14)	2644.9(2)
Z	4	4	4	4	4	4	4
D_{calcd}, Mg/m^3	1.215	1.291	1.298	1.253	1.165	1.273	1.255
radiation (λ, Å)	Mo Kα (0.710 73)						
2θ range, deg	3.70−52.00	2.84−52.00	3.62−50.00	3.44−52.00	3.78−52.00	3.86−52.00	3.48−52.00
μ, mm^{-1}	0.369	0.416	0.491	0.433	0.392	0.494	0.470
F(000)	912	1112	1016	1144	808	880	1040
no. of obsd rflns	4659	5382	3156	5713	4309	4359	5188
no. of params refined	281	317	321	313	245	244	271
goodness of fit	1.052	1.099	1.060	0.998	1.105	1.081	1.069
R1	0.067	0.025	0.075	0.039	0.047	0.044	0.025
wR2	0.187	0.071	0.187	0.086	0.136	0.131	0.067

washed with *n*-hexane (3 × 5 mL). Recrystallization from a toluene solution at −20 °C gave **6b** as red crystals (0.195 g, 65%). ^{1}H NMR (pyridine-d_5): δ 6.85 (m, 1H), 6.60 (m, 1H), 6.50 (m, 1H), 6.23 (m, 1H) (C_5H_4), 3.61 (s, 6H) ($N(CH_3)_2$), 1.60 (s, 3H), 1.50 (s, 3H) ($(CH_3)_2C$). ^{13}C NMR (pyridine-d_5): δ 151.86, 117.22, 117.10, 116.58, 115.38 (C_5H_4), 102.71 ($C_2B_{10}H_{10}$), 49.50 ($N(CH_3)_2$), 31.37, 30.51, 22.17 ($(CH_3)_2C$). ^{11}B NMR (pyridine-d_5): δ −4.4 (2), −7.6 (2), −10.7 (4), −12.9 (2). IR (KBr, cm^{-1}): ν 2992 (w), 2590 (vs), 2341 (m), 1462 (m), 1252 (m), 1048 (s), 915 (m), 823 (s), 547 (m). Anal. Calcd for $C_{12}H_{26}B_{10}ClNTi$: C, 38.35; H, 6.97; N, 3.73. Found: C, 38.68; H, 7.04; N, 3.70.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$ (7a). This compound was prepared as yellow crystals from $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.50 g, 2.0 mmol) and $Zr(NMe_2)_4$ (0.54 g, 2.0 mmol) in toluene (40 mL) by using procedures similar to those used in the synthesis of **2a**: yield 0.58 g (68%). ^{1}H NMR (pyridine-d_5): δ 6.31 (m, 2H), 5.62 (m, 2H) (C_5H_4), 2.95 (s, 12H) ($N(CH_3)_2$), 1.65 (s, 6H) ($(CH_3)_2C$). ^{13}C NMR (pyridine-d_5): δ 145.05, 113.00, 110.17 (C_5H_4), 104.11, 100.73 ($C_2B_{10}H_{10}$), 45.71 ($N(CH_3)_2$), 32.60, 22.00 ($(CH_3)_2C$). ^{11}B NMR (pyridine-d_5): δ −5.2 (2), −7.2 (2), −11.0 (4), −12.4 (2). IR (KBr, cm^{-1}): ν 2986 (w), 2864 (s), 2776 (m), 2598 (vs), 2561 (vs), 1450 (m), 1253 (m), 1184 (w), 1142 (w), 1052 (s), 1024 (m), 921 (s), 862 (w), 808 (vs), 704 (w), 547 (m). Anal. Calcd for $C_{14}H_{32}B_{10}N_2Zr$: C, 39.31; H, 7.54; N, 6.55. Found: C, 39.01; H, 7.21; N, 6.23.

Preparation of [η^5:σ-$Me_2Si(C_5H_4)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$ (8a). This compound was prepared as pale yellow crystals from $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$ (0.142 g, 0.53 mmol) and $Zr(NMe_2)_4$ (0.142 g, 0.53 mmol) in toluene (20 mL) by using procedures similar to those used in the synthesis of **2a**: yield 0.15 g (64%). ^{1}H NMR (pyridine-d_5): δ 6.53 (m, 2H), 5.96 (m, 2H) (C_5H_4), 2.94 (s, 12H) ($N(CH_3)_2$), 0.38 (s, 6H) ($(CH_3)_2Si$). ^{13}C NMR (pyridine-d_5): δ 120.17, 115.80, 112.96 (C_5H_4), 100.62, 79.91 ($C_2B_{10}H_{10}$), 45.10 ($N(CH_3)_2$), −2.66 ($(CH_3)_2Si$). ^{11}B NMR (pyridine-d_5): δ −0.5 (2), −4.6 (2), −10.4 (4), −12.2 (2). IR (KBr, cm^{-1}): ν 2970 (m), 2870 (s), 2569 (vs), 2415 (m), 2308 (m), 1485 (s), 1260 (m), 1056 (s), 925 (m), 806 (vs), 702 (w), 517 (s). Anal. Calcd for $C_{13}H_{32}B_{10}N_2SiZr$: C, 35.18; H, 7.27; N, 6.31. Found: C, 34.88; H, 7.48; N, 6.36.

Preparation of [η^5:σ-$Me_2Si(C_5H_4)(C_2B_{10}H_{10})$]$Zr(NEt_2)_2$ (9a). This compound was prepared as pale yellow crystals from $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$ (0.133 g, 0.50 mmol) and $Zr(NEt_2)_4$ (0.191 g, 0.50 mmol) in toluene (20 mL) by using procedures similar to those used in the synthesis of **1a**: yield 0.182 g (73%). ^{1}H NMR (pyridine-d_5): 6.57 (m, 2H), 6.51 (m, 2H) (C_5H_4), 3.36 (m, 8H) ($N(CH_2CH_3)_2$), 0.99 (t, J = 6.9 Hz, 12H) ($N(CH_2CH_3)_2$), 0.49 (s, 6H) ($(CH_3)_2Si$). ^{13}C NMR (pyridine-d_5): δ 121.26, 119.54, 113.64 (C_5H_4), 96.51, 82.50 ($C_2B_{10}H_{10}$), 41.88 ($N(CH_2CH_3)_2$), 13.51 ($N(CH_2CH_3)_2$), −2.90 ($(CH_3)_2Si$). ^{11}B NMR (pyridine-d_5): δ −0.3 (2), −3.9 (2), −8.9 (4), −12.1 (2). IR (KBr, cm^{-1}): ν 2956 (s), 2868 (s), 2573 (vs), 2341 (m), 1652 (m), 1450 (m), 1362 (m), 1264 (m), 802 (vs), 673 (m). Anal. Calcd for $C_{17}H_{40}B_{10}N_2SiZr$: C, 40.84; H, 8.07; N, 5.60. Found: C, 40.63; H, 7.82; N, 5.54.

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 (3.0 μmol) together with MMAO (4.5 mmol) and toluene (50 mL). The mixture was stirred at 60 °C 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 Paratone-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on an MSC/Rigaku RAXIS-IIC imaging plate diffractometer using Mo Kα radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA or on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS 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 calculations on F^2 using the Siemens SHELXTL program package (PC version).[16] Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. For noncentrosymmetric structures, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[17] Crystal data and details of data collection and structure refinement are given in Tables 1 and 2, respectively. Some key structural parameters are listed in Table 3. Further details are included in the Supporting Information.

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

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

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

Table 2. Crystal Data and Summary of Data Collection and Refinement for 2a, 8a, 2b, 2c, 4b and 6b

	2a	**8a**	**2b**	**2c**	**4b**	**6b**
formula	$C_{18}H_{34}B_{10}$-N_2Zr	$C_{13}H_{32}B_{10}$-N_2SiZr	$C_{32}H_{56}B_{20}$-Cl_7NZr_2	$C_{43}H_{68}B_{20}$-$Cl_5LiO_2Zr_2$	$C_{28.5}H_{53}B_{20}$-$Cl_6NSi_2Zr_2$	$C_{12}H_{26}B_{10}$-$ClNTi$
cryst size (mm)	0.36 × 0.28 × 0.08	0.48 × 0.32 × 0.27	0.40 × 0.20 × 0.18	0.25 × 0.20 × 0.20	0.30 × 0.30 × 0.20	0.60 × 0.25 × 0.20
fw	477.79	443.82	1101.57	1199.80	1077.24	375.79
cryst syst	triclinic	rhombohedral	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$R3$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	10.135(2)	26.404(2)	11.935(2)	12.423(3)	12.043(2)	9.557(2)
b, Å	10.357(2)	26.404(2)	12.085(2)	13.692(3)	12.102(2)	14.472(2)
c, Å	13.572(3)	10.181(1)	20.557(4)	18.266(4)	20.301(4)	14.346(2)
α, deg	68.69(3)	90.00	88.87(3)	95.73(3)	86.89(3)	90.00
β, deg	83.77(3)	90.00	86.66(3)	94.89(3)	87.95(3)	96.74(1)
γ, deg	67.38(3)	120.00	76.34(3)	113.84(3)	76.99(3)	90.00
V, Å^3	1224.4(4)	6146.8(10)	2876.2(10)	2800.6(10)	2877.7(10)	1970.4(4)
Z	2	9	2	2	2	4
D_{calcd}, Mg/m^3	1.296	1.079	1.272	1.423	1.243	1.267
radiation (λ), Å	Mo Kα (0.710 73)					
2θ range, deg	3.22–50.00	4.38–50.00	3.46–50.00	3.28–50.00	4.02–48.00	4.02–52.00
μ, mm^{-1}	0.458	0.447	0.712	0.647	0.705	0.564
F(000)	492	2052	1108	1220	1082	776
no. of obsd rflns	2615	4248	4338	5500	3739	3867
no. of params refined	281	246	545	580	566	226
goodness of fit	1.042	1.067	1.136	1.075	1.273	1.128
R1	0.074	0.038	0.087	0.074	0.132	0.038
wR2	0.195	0.102	0.244	0.192	0.314	0.116

Table 3. Summary of Key Structural Data

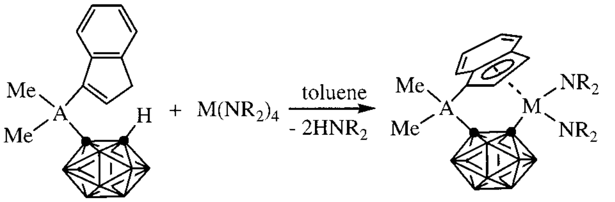
compd	M^{4+}	M–C(C$_5$ ring) (Å)	M–C(σ) (Å)	M–N (Å)	M-Cl(μ) (Å)	M–Cl(terminal) (Å)	C(C$_5$ ring)–A–C(cage) (deg)	N–M–N (deg)	Cent–M–C(cage) (deg)[a]
1a	Ti	2.391(3)	2.196(3)	1.896(3)			108.7(2)	104.5(2)	105.4
2a	Zr	2.521(8)	2.326(7)	2.016(8)			109.4(6)	108.0(3)	101.6
3a	Zr	2.538(2)	2.361(2)	2.030(2)			110.5(2)	106.6(1)	100.6
4a	Zr	2.541(5)	2.348(5)	2.019(4)			104.8(2)	107.3(2)	109.9
5a	Zr	2.561(4)	2.362(4)	2.029(4)			105.0(2)	107.6(2)	107.5
6a	Ti	2.369(3)	2.209(2)	1.894(2)			108.5(2)	106.1(2)	105.0
7a	Zr	2.510(3)	2.343(3)	2.024(3)			110.7(2)	113.1(2)	100.3
8a	Zr	2.519(5)	2.353(4)	2.015(4)			105.2(2)	110.6(2)	108.4
9a	Zr	2.543(2)	2.384(2)	2.031(2)			104.7(1)	110.1(1)	107.6
2b	Zr	2.539(14)	2.367(12)		2.634(3)	2.449(4)	111.0(14)		98.4
2c	Zr	2.527(9)	2.375(9)		2.641(3)	2.424(3)	109.6(7)		99.5
4b	Zr	2.545(12)	2.393(10)		2.622(3)	2.401(3)	104.1(4)		105.4
6b	Ti	2.341(2)	2.179(2)	1.862(2)		2.277(1)	108.5(2)		105.7
10[b]	Zr	2.544(6)	2.355(5)	2.028(5)			105.8(2)	104.5(2)	110.3
11[c]	Ti	2.365(5)	2.178(4)			2.234(1)	102.0(1)		115.4

[a] Cent = centroid of the five-membered ring of the indenyl or cyclopentadienyl group. [b] [η^5:σ-$Me_2Si(C_5Me_4)(C_2B_{10}H_{10})$]$Zr(NMe_2)_2$.[9b] [c] [$\eta^5$:$\sigma$-$Me_2Si(C_5Me_4)(C_2B_{10}H_{10})$]$TiCl_2$.[9b]

Results and Discussion

Amide Complexes. Lappert's eariler observation shows that group 4 metallocene compounds can be prepared by an amine elimination reaction.[18] This methodology has then been adopted by several groups to synthesize many group 4 metal amide complexes.[13,14,19,20] Treatment of $M(NR_2)_4$ with 1 equiv of $Me_2A(C_9H_7)(C_2B_{10}H_{11})$ or $Me_2A(C_5H_5)(C_2B_{10}H_{11})$ (A = C, Si) in toluene at reflux temperature gave, after workup, group 4 metal amides of the general formula [η^5:σ-$Me_2A(C_9H_6)(C_2B_{10}H_{10})$]$M(NR_2)_2$ (Scheme 1) and [η^5:σ-$Me_2A(C_5H_4)(C_2B_{10}H_{10})$]$M(NR_2)_2$ (Scheme 2) in good isolated yields, respectively. It is noteworthy that $Ti(NEt_2)_4$ does not react with any one of the neutral ligands mentioned above, due to the steric effects. The prolonged reaction would lead to an intensive color of the resulting solution and a lower isolated yield. These complexes are very soluble in polar organic solvents such as THF, DME, pyridine, and ether and soluble in toluene but insoluble in n-hexane. They were fully characterized by various spectroscopic data, elemental analyses, and X-ray diffraction studies.

Scheme 1



	1a	**2a**	**3a**	**4a**	**5a**
A	C	C	C	Si	Si
M	Ti	Zr	Zr	Zr	Zr
R	Me	Me	Et	Me	Et

In addition to six multiplets observed in the aromatic region of ^{1}H NMR spectra of **1a**–**5a**, there are two sets

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(18) (a) Chandra, G.; Lappert, M. F. *J. Chem. Soc. A* **1968**, 1940. (b) Lappert, M. F.; Power, P. B.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amines*; Ellis Horwood: Chichester, West Sussex, U.K., 1980.

(19) Herrmann, W. A.; Morawietz, M. J. A. *J. Organomet. Chem.* **1994**, *482*, 169.

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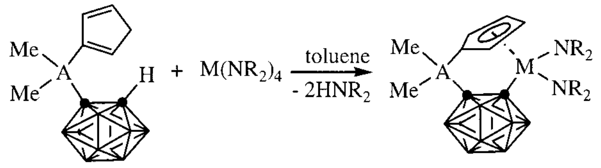
Scheme 2



	6a	7a	8a	9a
A	C	C	Si	Si
M	Ti	Zr	Zr	Zr
R	Me	Me	Me	Et

of singlets in the region 0.5−3.5 ppm corresponding to two diastereotopic bridging atom and nitrogen methyl groups for **1a**, **2a**, and **4a**, and there are two singlets, two triplets, and two quartets in the region 0.5−3.5 ppm attributable to two diastereotopic bridging atoms and nitrogen ethyl groups for **3a** and **5a**. Such diastereotopic splittings are also observed in benzene-*d* solution. These results are consistent with their ^{13}C NMR spectra, suggesting that complexes **1a**−**5a** exhibit C_1 symmetry in both pyridine and benzene solutions. The ^{11}B NMR spectra all display a 1:1:2:1 splitting pattern regardless of the central metal ions and R groups.

The ^{1}H NMR spectra of **6a**−**9a** show a simpler splitting pattern than those of **1a**−**5a** due to the higher symmetry. Besides two multiplets corresponding to the cyclopentadienyl ring, there are two singlets in the region 0.3−3.0 ppm observed in **6a**−**8a** attributable to the bridging Me_2A and $M(NMe_2)_2$ units, and there are one singlet, one triplet, and one quartet observed in **9a** assignable to Me_2Si and $Zr(NEt_2)_2$ groups, respectively. These results are consistent with their ^{13}C NMR. Their ^{11}B NMR spectra exhibit the same splitting pattern (1:1:2:1) as that observed in **1a**−**5a**.

The solid-state structures of **1a**−**9a** confirm that they are all constrained-geometry complexes. The metal is η^5-bound to one five-membered ring of either the cyclopentadienyl or the indenyl group and σ-bound to a cage carbon atom and two amido groups (NR_2) in a distorted-tetrahedral geometry. Some are isostructural but not isomorphous. Their representative structures are shown in Figures 1−4, respectively.

Overall, the key structural parameters observed in **2a**−**5a**, **7a**−**9a**, and $[\eta^5{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$[9b] (Table 3) are close to each other, suggesting that the central Zr atom adopts very similar geometries in these complexes. On the other hand, some trends do exist: (1) slightly longer Zr−C(C_5 ring), Zr−C(σ), and Zr−N bond distances are observed in $Zr(NEt_2)_2$-containing complexes and (2) larger C(C_5 ring)−A−C(cage) angles are also observed in complexes with a Me_2C linkage, which are probably due to the greater steric bulk of NEt_2 versus NMe_2 and Me_2Si versus Me_2C, respectively.

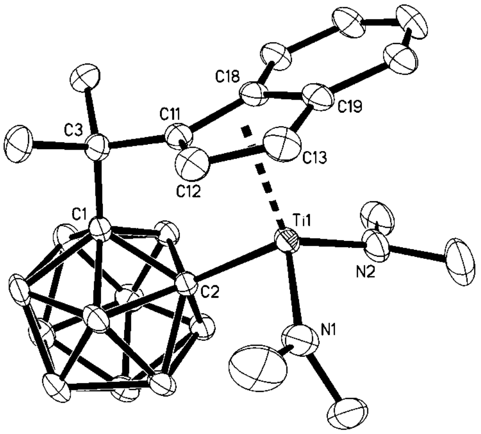


Figure 1. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ (**1a**) (thermal ellipsoids drawn at the 35% probability level).

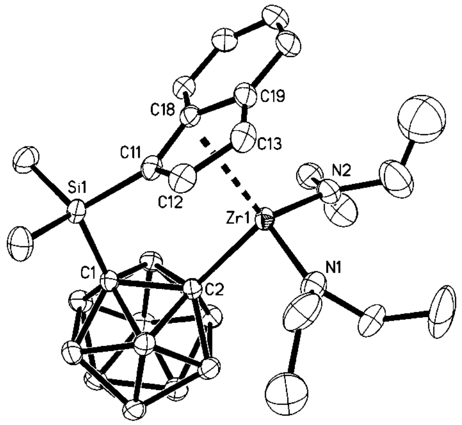


Figure 2. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(NEt_2)_2$ (**5a**) (thermal ellipsoids drawn at the 35% probability level).

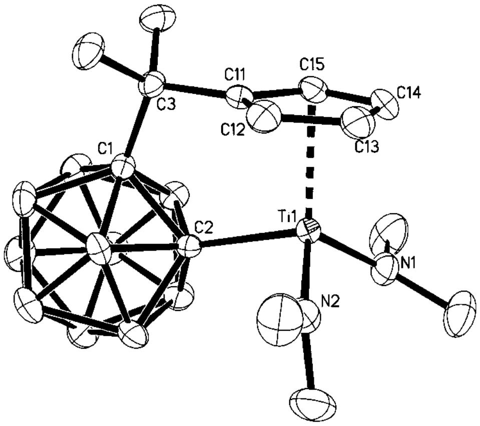


Figure 3. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ (**6a**) (thermal ellipsoids drawn at the 35% probability level).

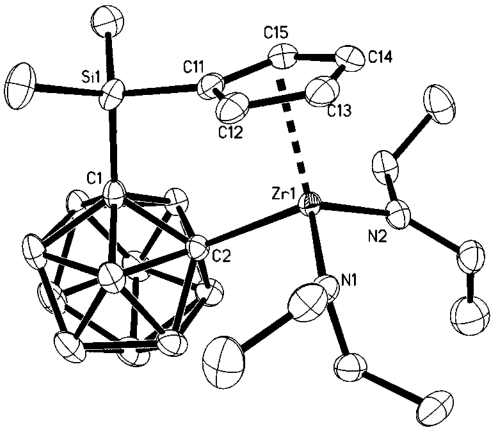
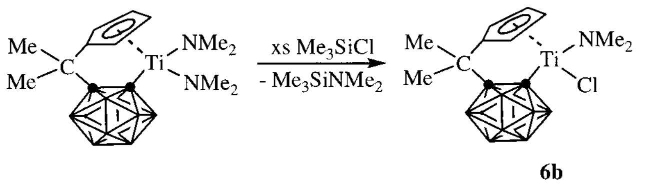
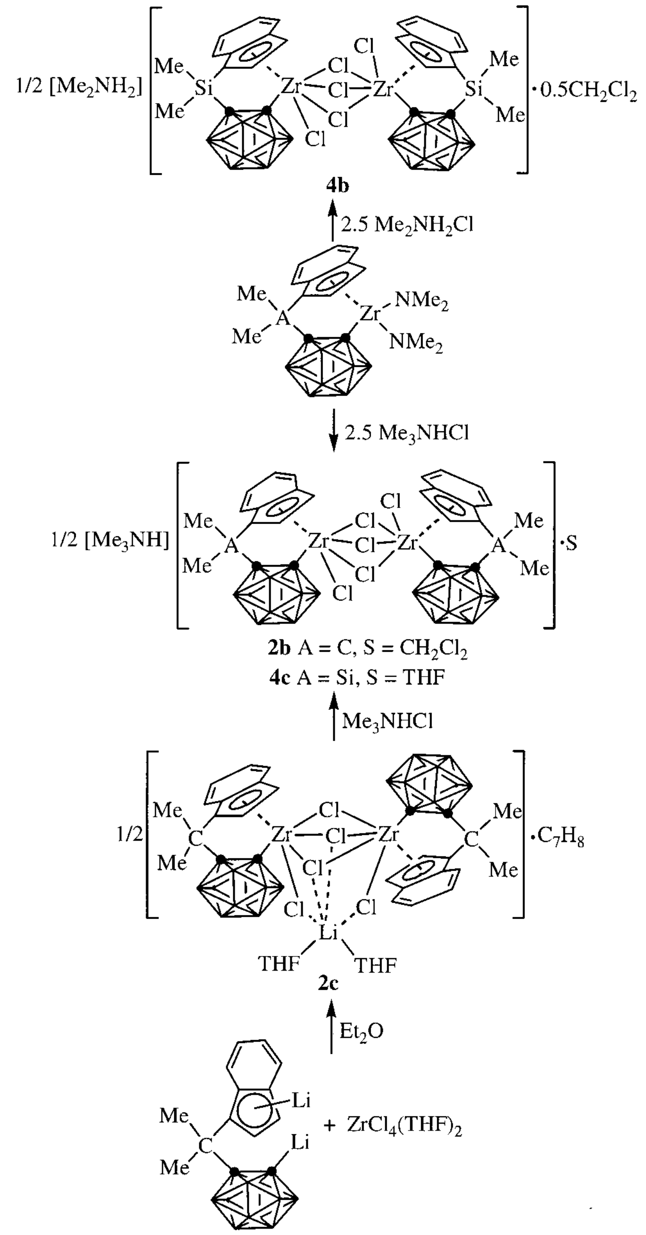


Figure 4. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})]Zr(NEt_2)_2$ (**9a**) (thermal ellipsoids drawn at the 35% probability level).

Scheme 3



Scheme 4



The nitrogen atoms (N(1) and N(2)) in **1a**−**9a** are flat (sum of angles around N ∼360°), which indicates the sp^2 hybridization at N and partial $N(p_\pi) \rightarrow M(d_\pi)$ (M = Ti, Zr) interactions. The lack of additional electron donation from the carboranyl group to the M center strengthens this $p_\pi \rightarrow d_\pi$ interactions, leading to noticeably shorter M−N bond distances (see Table 3) compared with the corresponding Zr−N bond distances of 2.062(5) Å in $[Me_2Si(C_5Me_4)(NBu^t)]Zr(NMe_2)_2$,[14] 2.057(9) Å in *rac*-$[C_2H_4(C_9H_6)_2]Zr(NMe_2)_2$,[21] 2.07 Å in $Zr(NMe_2)_4$,[22] and 2.06 Å in $(Me_2N)_2Zr(\mu\text{-}NBu^t)_2Zr(NMe_2)_2$[23] and Ti−N bond distances of 1.915(4) Å in $[Me_2Si(C_5H_4)(NBu^t)]Ti(NMe_2)_2$,[14] 1.921(14) Å in $(C_5Me_5)Ti(NMe_2)_3$,[24] and 1.940(10) Å in $Ti[N(SiMe_3)_2]_3Cl$.[25]

Chloride Complexes. It is documented that treatment of $Cp_2Zr(NMe_2)_2$ with excess Me_3SiCl results in a clean formation of Cp_2ZrCl_2.[26] However, reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ (**6a**) with excess Me_3SiCl in toluene or CH_2Cl_2 at room temperature generated $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$ (**6b**) in 65% isolated yield. The same product was isolated even at reflux temperature, suggesting that **6b** does not react further with Me_3SiCl (Scheme 3). Similarly, reaction of $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (A = C (**2a**), Si (**4a**)) with excess Me_3SiCl in toluene at room temperature or at 100 °C overnight did not lead to a complete conversion of $Zr(NMe_2)_2$ to $ZrCl_2$ on the basis of spectroscopic and elemental analyses, presumably due to steric reasons. We then turned our attention to other method.

It is reported that the stoichiometric addition of acid (HCl) in the form of $Me_2NH{\cdot}HCl$ or $Me_3N{\cdot}HCl$ to the amide complexes results in the clean formation of chloride derivatives.[13,14] Reaction of $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (**4a**) with excess Me_3SiCl in toluene at room temperature overnight followed by treatment with 2 equiv of $Me_2NH{\cdot}HCl$ gave, after recrystallization from a CH_2Cl_2 solution, the ionic complex $[Me_2NH_2][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\mu\text{-}Cl)_{1.5}]_2{\cdot}0.5CH_2Cl_2$ (**4b**) in 51% isolated yield. This yield can be greatly improved up to 81% by direct treatment of **4a** with 2.5 equiv of $Me_2NH{\cdot}HCl$ in toluene. If $Me_3N{\cdot}HCl$ was used to replace $Me_2NH{\cdot}HCl$, the corresponding Me_3NH^+ salts $[Me_3NH][\{\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\mu\text{-}Cl)_{1.5}]_2{\cdot}S$ (A = C, S = CH_2Cl_2 (**2b**); A = Si, S = THF (**4c**)) were isolated in a typical yield of 85%. It is surprising that the Zr−C(cage) bond remains intact. The chloride derivative can also be prepared by a salt metathesis reaction. An equimolar reaction between $ZrCl_4(THF)_2$ and $[Me_2C(C_9H_6)(C_2B_{10}H_{10})]Li_2$ in ether produced, after recrystallization from a toluene/THF solution, $\{[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]ZrCl(\mu\text{-}Cl)_{1.5}\}_2\{Li(THF)_2\}{\cdot}C_7H_8$ (**2c**) in 60% yield. Treatment of **2c** with 1 equiv of $Me_3N{\cdot}HCl$ in CH_2Cl_2 resulted in the clean formation of **2b**. The above-mentioned transformations are outlined in Scheme 4.

The ^1H NMR spectra of **2b**,**c** and **4b,c** all show six multiplets in the aromatic region and two singlets corresponding to the bridging Me_2A group, which is similar to those observed in their parent amide complexes. These results are supported by the ^{13}C NMR spectra. Replacement of one NMe_2 group by a Cl atom in **6a** reduces its symmetry, resulting in the observation of four multiplets of the cyclopentadienyl ring and two singlets of the Me_2C unit in the ^1H NMR spectrum of **6b** compared with two multiplets of the cyclopentadienyl

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(26) For examples, see: Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045 and refs 13, 14, and 21.

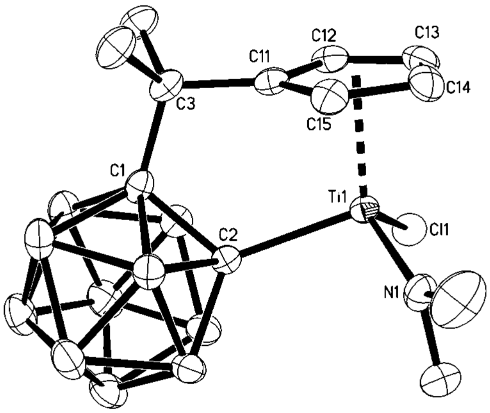

Figure 5. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$ (**6b**) (thermal ellipsoids drawn at the 35% probability level).

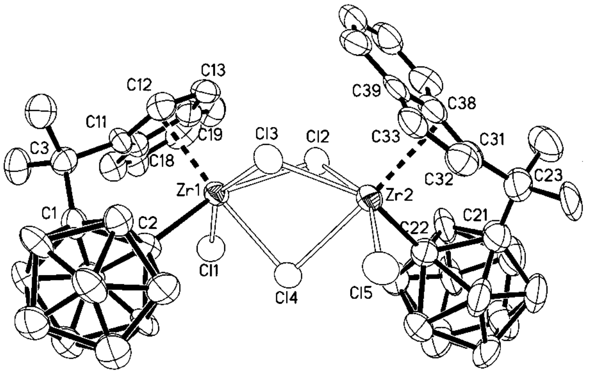

Figure 6. Molecular structure of the anion $[\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\mu\text{-}Cl)_{1.5}]_2^-$ in **2b** (thermal ellipsoids drawn at the 35% probability level).

ring and one singlet of the Me_2C unit found in the ^1H NMR spectrum of its parent complex **6a**. This is further supported by the ^{13}C NMR spectrum of **6b**. The ^{11}B NMR spectra of all chloride complexes exhibit a 1:1:2:1 splitting pattern that is the same as their parent amide complexes.

An X-ray analysis reveals that **6b** adopts a monomeric structure, shown in Figure 5. The structural features are similar to those of its parent amide complex **6a**, except for the replacement of one NMe_2 group with one chlorine atom. The average Ti$-$C(C_5 ring) distance of 2.341(2) Å and Ti$-$C(σ) distance of 2.179(2) Å are comparable to the corresponding distances of 2.365(5) and 2.178(4) Å found in $[\eta^5{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]TiCl_2$, respectively.[9b] The Ti$-$N distance of 1.862(2) Å is shorter than the corresponding value of 1.894(2) Å in its parent complex **6a** and the 1.896(3) Å in the closely related complex **1a**. On the other hand, the Ti$-$Cl distance of 2.277(1) Å is longer than the corresponding distance of 2.234(1) Å in $[\eta^5{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]TiCl_2$[9b] and 2.264(1) Å in $[Me_2Si(C_5H_4)NBu^t]TiCl_2$.[14] The shorter Ti$-$N and longer Ti$-$Cl distances in **6b** clearly indicate the presence of $p_\pi \rightarrow d_\pi$ interactions.

X-ray diffraction studies show that **4b** and **2b** are isostructural and isomorphous. Figure 6 shows their representative structure. It is noted that the structure of **4b** is relatively poorly refined in comparison with that of **2b**, due to the disorder problems of both $Me_2NH_2^+$ and CH_2Cl_2. Their solid-state structures consist of alternating layers of discrete cations $[Me_2NH_2]^+$ or $[Me_3NH]^+$ and anions $\{[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]ZrCl(\mu\text{-}Cl)_{1.5}\}_2^-$. The anion is a dimeric species bearing the $Zr(\mu\text{-}Cl)_3Zr$ moiety. Each Zr atom is η^5-bound to one five-membered ring of the indenyl group and σ-bound to a cage carbon atom, one terminal chlorine atom, and three doubly bridging chlorine atoms in a distorted-octahedral geometry. They are formally 16-electron complexes. These results differ significantly from the Ti complexes **6b** and $[\eta^5{:}\sigma\text{-}Me_2Si(C_5Me_4)(C_2B_{10}H_{10})]TiCl_2$[9b] probably due to steric reasons.

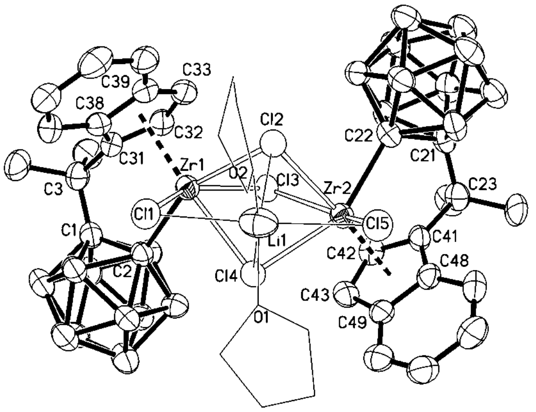

Figure 7. Molecular structure of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]ZrCl(\mu\text{-}Cl)_{1.5}\}_2\{Li(THF)_2\}$ (**2c**) (the solvated toluene molecule is not shown; thermal ellipsoids drawn at the 35% probability level).

Replacement of $[Me_3NH]^+$ with Li^+ results in the formation of the new complex **2c**. As shown in Figure 7, the Li⋯Cl interactions force two terminal chlorine atoms to be on the same side, although the coordination environment of each Zr atom in **2c** is very similar to that of **2b** or **4b**. These electrostatic interactions lead to a dramatic decrease of the Cl(1)Zr(1)Zr(2)Cl(5) torsion angles from 102.9° in **2b** and 98.4° in **4b** to 17.2° in **2c**.

The average Zr$-$Cl(μ) and Zr$-$Cl(terminal) distances fall in the ranges 2.622(3)$-$2.641(3) and 2.401(3)$-$2.449(4) Å, respectively. There is no other example of such $[Zr_2(\mu\text{-}Cl)_3]$ bridges containing zirconium in oxidation state IV. The measured Zr$-$Cl(μ) distances can be compared to the 2.6288(8) and 2.6797(9) Å in $[\{C_5H_4(CH_2)_3NMe\}Zr(CH_2C_6H_5)(\mu\text{-}Cl)]_2$[13] and 2.692(2) and 2.579(2) Å in $[(C_5Me_5)Zr(CH_2CH_2SiMe_3)Cl(\mu\text{-}Cl)]_2$.[27] The measured terminal Zr$-$Cl distances are comparable to the 2.408(1) Å in $[Me_2Si(C_5Me_4)(NBu^t)]ZrCl_2$,[14] 2.450(1) Å in $[Me_2Si(C_5Me_4)(NCH_2CH_2NMe_2)]ZrCl_2$,[28] and 2.410(2) Å in $[(C_5H_5)Zr(NPr^i{}_2)Cl_2$.[29]

Ethylene Polymerizations. Group 4 metal chloride complexes **2b**,**c** and **4b**,**c** underwent preliminary testing for catalytic activity, using modified methylalumoxane (MMAO) as cocatalyst (Al/Zr = 1500) in toluene at 60 °C (30 min., 1 atm of ethylene). The results are compiled in Table 4. All four complexes exhibit very high ethylene polymerization activity in the presence of MMAO. No clear ligand and cation effects on activity are evident from the data yet available. Molecular weights of the polymer samples could not be measured because of very

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Table 4. Ethylene Polymerization Results[a]

catalyst	yield (g)	activity (10^6 g/(mol atm h))	T_m (°C)[b]
2b	5.01	3.34	130.5
2c	4.10	2.73	131.2
4b	3.92	2.61	129.8
4c	4.36	2.91	129.5

[a] Conditions: toluene (50 mL), 1 atm of ethylene, $T = 60$ °C, catalyst (3.0 μmol), MMAO (4.5 mmol), Al/Zr = 1500, time 30 min. [b] Measured by DSC.

low solubility in polar organic solvents. However, melting temperatures (T_m) measured by differential scanning calorimetry (DSC) are typical of high-density polyethylene. No methyl bending resonances at around 1376 cm^{-1} were observed in the IR spectra of the resulting polymers, suggesting that the branching might be absent.[30]

Summary

Several new group 4 metal amide and chloride complexes with recently developed constrained-geometry carborane ligands $[Me_2A(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ and $[Me_2A(C_5H_4)(C_2B_{10}H_{10})]^{2-}$ (A = C, Si) have been prepared and structurally characterized. The chloride derivatives exhibit a very high ethylene polymerization activity when they are activated with MMAO.

This work shows that the aminolysis reaction is very sensitive to the steric crowding of reactants. For example, there is no reaction between $Ti(NEt_2)_4$ and $Me_2A(C_9H_7)(C_2B_{10}H_{11})$ or $Me_2A(C_5H_5)(C_2B_{10}H_{11})$, although both $Zr(NEt_2)_4$ and $Ti(NMe_2)_4$ react readily with these neutral ligands to give amide complexes in good yield.

Unlike most of the reported examples,[26] excess Me_3SiCl can only convert one M−NMe_2 to M−Cl; the second M−NMe_2 group remains intact even at higher temperatures. Again, steric factors play a role in these reactions. On the other hand, $Me_2NH{\cdot}HCl$ or $Me_3N{\cdot}HCl$ can effectively convert the $M(NMe_2)_2$ moiety to the MCl_2 group without attacking the M−C(cage) bond.

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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 **1a**−**9a**, **2b**,**c**, **4b**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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