

Synthesis, Structure, and Olefin Polymerization Behavior of Constrained-Geometry Group 4 Metallocarboranes Incorporating Imido-Dicarbollyl Ligands

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New imido-carboranes 1-(CH=NC₆H₃R₂-2,6)-1,2-C₂B₁₀H₁₁ (R = ⁱPr (**3a**), Me (**3b**)) were successfully prepared by Schiff base condensation of 1-CHO-1,2-C₂B₁₀H₁₁ with R₂C₆H₃NH₂. They were readily converted into the corresponding imido-dicarbollyl ligands 7-(CH=NHC₆H₃R₂-2,6)-7,8-C₂B₉H₁₁ (R = ⁱPr (**4a**), Me (**4b**)) by refluxing in dry MeOH. Treatment of **3a** with Ti(NMe₂)₄ in hot toluene gave a constrained-geometry complex, [η¹:η⁵-(ⁱPr₂C₆H₃N=CH)C₂B₉H₁₀]Ti(NMe₂)₂ (**5a**). Under the same reaction conditions, interaction of **3b** with Ti(NMe₂)₄ produced a mixture of [η¹:η⁵-(Me₂C₆H₃N=CH)C₂B₉H₁₀]-Ti(NMe₂)₂ (**5b**) and [η¹:η⁵-(Me₂N)CH(NMe₂)(C₂B₉H₁₀)Ti(NMe₂)₂ (**8**). Reaction of **4a** with M(NMe₂)₄ in toluene/DME at room temperature afforded **5a** and [η¹:η⁵-(ⁱPr₂C₆H₃N=CH)C₂B₉H₁₀]M(NMe₂)₂(NHMe₂) (M = Zr (**6a**), Hf (**7a**)), respectively. Complexes **5a**, **6a**, and **7a** were active catalysts for the polymerization of ethylene in the presence of MMAO with activities of 3–16 kg/mol·h·atm. These new complexes were fully characterized by various spectroscopic techniques and elemental analyses. The molecular structures of **3a**, **3b**, **4a**, **5a**, **5b**, **6a**, **7a**, and **8** were further confirmed by single-crystal X-ray analyses.

Introduction

Constrained-geometry ligands containing both monocyclopentadienyl and *o*-heteroatom components have attracted considerable attention.¹ Group 4 metallocenes derived from these ligands (so-called constrained-geometry catalysts (CGC)) are very active catalysts for the polymerization of α -olefins due to the increased electron deficiency and more open coordination environment of the central metal ions.² As an extension of the structural variations in designing new constrained-geometry ligands, *nido*-C₂B₉H₁₁²⁻ (dicarbollide ion), an isolobal inorganic analogue of C₅H₅⁻,³ was introduced to this ligand system, leading to a carborane version of constrained-geometry ligands.⁴ Although several amido(amino)-dicarbollyl ligands were de-

veloped,⁴ the imido-dicarbollyl ligands have not been known yet. These ligands provide interesting opportunities for the design of metallocenes with new metal/charge and π/σ component combinations.⁵ In this connection, and in view of the role of imine ligands in optimizing catalytic activity of metal complexes in olefin polymerization,⁶ we designed a new type of constrained-geometry ligands incorporating both imido and dicarbollyl components. This article reports the synthesis and structure of these new ligands as well as their applications in group 4 metal chemistry. Ethylene polymerization behavior of the resultant metallocarboranes will also be described.

Experimental Section

General Procedures. All manipulations of air- and/or water-sensitive compounds were carried out under an atmosphere of dry nitrogen using standard Schlenk or cannula techniques, or in a

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glovebox. Methylene chloride was distilled from CaH_2 prior to use. All other organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Dess–Martin periodinane oxidant,⁷ $\text{M}(\text{NMe}_2)_4$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$),⁸ and $1\text{-CH}_2\text{OH-1,2-C}_2\text{B}_{10}\text{H}_{11}$ ⁹ were prepared according to literature methods. Polymerization grade ethylene was purified before use. Modified methylaluminoxane (MMAO) was purchased from Akzo Nobel with 7 wt % Al in toluene. Deuterated solvents were dried using standard procedures and stored in the glovebox. All other chemicals including silica–alumina catalyst support (grade 135) (Si-Al-135) were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM300 spectrometer at 300.0 and 75.5 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 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 $\text{BF}_3\cdot\text{OEt}_2$ (0.00 ppm) for boron chemical shifts. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 983 spectrometer. Mass spectra were obtained using the direct insertion probe method on a HP5989A instrument operating at 70 eV. Elemental analyses were performed on a Vario EL III instrument. The polymer samples for NMR spectra were prepared by dissolving the polymer in 1,2-dichlorobenzene at 120–135 °C. Molecular weights (M_w and M_n) and polydispersities of polymers were determined by a Waters high-temperature GPC 2000 at 150 °C using polystyrene calibration. 1,2,4-Trichlorobenzene was employed as a solvent.

Preparation of 1-CHO-1,2-C₂B₁₀H₁₁ (2). To a suspension of Dess–Martin periodinane oxidant (1.89 g, 4.5 mmol) in methylene chloride (7 mL) was slowly added a methylene chloride (4 mL) solution of 1-CH₂OH-1,2-C₂B₁₀H₁₁ (**1**; 0.52 g, 3.0 mmol) at room temperature. The mixture was stirred for 2 days, to which was added 40 mL of ethyl ether. The solid was removed by filtration and washed with ethyl ether (10 mL \times 3). The combined organic solutions were washed with a saturated aqueous solution of NaHCO_3 (20 mL \times 4) and deionized water (15 mL \times 3) and dried over anhydrous Na_2SO_4 . After removal of the solvents under vacuum, the residue was purified by column chromatography on silica gel using petroleum/ CH_2Cl_2 (4:1) as eluent to give **2** as a white solid

(0.44 g, 86%). ^1H NMR (CDCl_3): δ 9.27 (s, 1H, CHO), 4.05 (s, 1H, cage CH). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): δ -1.6 (2), -8.4 (2), -12.4 (4), -13.6 (2). IR (KBr, cm^{-1}): ν 3066 (s), 2590 (vs), 1734 (vs), 1368 (m), 1209 (s), 1124 (s), 1016 (m). MS (EI): 174 (M^+). These data were consistent with the literature ones.¹⁰

Preparation of 1-(CH=NC₆H₃Pr₂-2,6)-1,2-C₂B₁₀H₁₁ (3a). A mixture of Si-Al-135 (1.05 g) and 4 Å molecular sieves powder (2.10 g) was activated by heating at 200 °C in vacuo for 9 h. A toluene solution (35 mL) of **2** (1.80 g, 10.5 mmol) was added to this solid. To the resultant suspension was slowly added 2,6-diisopropylaniline (2.34 g, 12.1 mmol) at room temperature, and the mixture was stirred at 90 °C for 36 h. After removal of the solid, the clear solution was concentrated to dryness. Recrystallization from CH_2Cl_2 /hexane gave **3a** as yellow crystals (2.82 g, 81%). Mp: 116–118 °C. ^1H NMR (CDCl_3): δ 7.57 (s, 1H, CHN), 7.11 (m, 3H, aromatic H), 4.49 (s, 1H, cage CH), 2.66 (sept, $J = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.14 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 155.2 (CHN), 145.3, 137.0, 125.5, 123.1 (aromatic C), 72.2 (cage CCHN), 55.7 (cage CH), 27.8 ($\text{CH}(\text{CH}_3)_2$), 23.2 ($\text{CH}(\text{CH}_3)_2$). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): δ -2.0 (1), -3.0 (1), -8.9 (2), -11.2 (2), -12.8 (4). IR (KBr, cm^{-1}): ν 3059 (m), 2962 (s), 2634 (w), 2584 (vs), 2561 (w), 2553 (w), 1656 (s), 1459 (w), 1436 (w), 796 (w), 761 (m), 709 (w). Anal. Calcd for $\text{C}_{15}\text{H}_{29}\text{B}_{10}\text{N}$: C, 54.35; H, 8.82; N, 4.23. Found: C, 54.31; H, 8.72; N, 4.14. MS (EI): 333 (M^+).

Preparation of 1-(CH=NC₆H₃Me₂-2,6)-1,2-C₂B₁₀H₁₁ (3b). This compound was prepared from **2** (2.01 g, 11.7 mmol) and 2,6-dimethylaniline (1.61 g, 13.1 mmol) in toluene (40 mL) in the presence of Si-Al-135 (1.17 g) and 4 Å molecular sieves powder (2.33 g) using the same procedures as those for **3a**. The product was further purified by column chromatography on silica gel using petroleum/ CH_2Cl_2 (6:1) as eluent to give **3b** as a white solid (2.67 g, 83%). X-ray-quality crystals were obtained from recrystallization in CH_2Cl_2 /hexane. Mp: 104–105 °C. ^1H NMR (CDCl_3): δ 7.62 (s, 1H, CHN), 6.99 (m, 3H, aromatic H), 4.52 (s, 1H, cage CH), 2.03 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 155.9 (CHN), 147.1, 128.3, 126.5, 125.1 (aromatic C), 72.2 (cage CCHN), 55.8 (cage CH), 17.9 (CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): δ -1.6 (1), -2.8 (1), -8.6 (2), -10.5 (2), -12.4 (4). IR (KBr, cm^{-1}): ν 3052 (s), 2635 (w), 2625 (w), 2604 (m), 2577 (s), 1658 (s), 1468 (m), 1188 (m), 1121 (w), 1010 (w), 774 (m), 721 (w), 703 (w). Anal. Calcd for $\text{C}_{11}\text{H}_{21}\text{B}_{10}\text{N}$: C, 47.97; H, 7.69; N, 5.09. Found: C, 48.09; H, 7.54; N, 4.99. MS (EI): 277 (M^+).

Preparation of 7-(CH=NHC₆H₃Pr₂-2,6)-7,8-C₂B₉H₁₁ (4a). A dry methanol (20 mL) solution of 1-(CH=NC₆H₃Pr₂-2,6)-1,2-C₂B₁₀H₁₁ (**3a**; 333 mg, 1.00 mmol) was heated to reflux for 12 h. After removal of methanol and volatile molecules, **4a** was obtained as a pale yellow solid (318 mg, 99%). X-ray-quality crystals were obtained from recrystallization in dry CH_2Cl_2 . ^1H NMR (acetone- d_6): δ 11.90 (br, 1H, NH), 8.72 (s, 1H, CHN), 7.44 (m, 3H, aromatic H), 3.01 (sept, $J = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.65 (s, 1H, cage CH), 1.22 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.21 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6): δ 188.8 (CHN), 144.6, 133.6, 131.4, 124.8 (aromatic C), 28.8 ($\text{CH}(\text{CH}_3)_2$), 23.2, 23.1 ($\text{CH}(\text{CH}_3)_2$), the cage carbons were not observed. $^{11}\text{B}\{^1\text{H}\}$ NMR (acetone- d_6): δ -4.2 (1), -5.1 (1), -9.9 (1), -11.3 (1), -16.3 (2), -22.2 (1), -28.5 (1), -31.1 (1). IR (KBr, cm^{-1}): ν 3298 (w), 3194 (m), 3033 (w), 2969 (m), 2952 (m), 2537 (vs), 1626 (vs), 1459 (m), 1289 (s). Anal. Calcd for $\text{C}_{15}\text{H}_{30}\text{B}_9\text{N}$: C, 56.00; H, 9.40; N, 4.35. Found: C, 56.31; H, 9.28; N, 4.25. MS (EI): 323 (M^+).

Preparation of 7-(CH=NHC₆H₃Me₂-2,6)-7,8-C₂B₉H₁₁ (4b). This compound was prepared as a pale yellow solid from **3b** (138 mg, 0.50 mmol) in dry methanol (13 mL) using the same procedures

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as those for **4a**: yield 132 mg (99%). ^1H NMR (acetone- d_6): δ 11.66 (br, 1H, NH), 8.66 (s, 1H, CHN), 7.30 (m, 3H, aromatic H), 2.62 (s, 1H, cage CH), 2.30 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6): δ 189.0 (CHN), 136.3, 134.2, 130.6, 129.6 (aromatic C), 17.6 (CH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (acetone- d_6): δ -3.9 (1), -4.7 (1), -9.4 (1), -10.9 (1), -16.0 (2), -21.9 (1), -28.2 (1), -30.6 (1). IR (KBr, cm^{-1}): ν 3227 (m), 2535 (vs), 1630 (s), 1588 (w), 1474 (w), 1288 (m), 1163 (m), 784 (m). Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{B}_9\text{N}$: C, 49.74; H, 8.35; N, 5.27. Found: C, 49.56; H, 8.33; N, 5.06. MS (EI): 267 (M^+).

Preparation of $[\eta^1:\eta^5\text{-}(\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_2\text{B}_9\text{H}_{10}]\text{Ti}(\text{NMe}_2)_2$ (5a**).** A mixture of 1-($\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2$ -2,6)-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (**3a**; 332 mg, 1.00 mmol) and $\text{Ti}(\text{NMe}_2)_4$ (224 mg, 1.00 mmol) in toluene (20 mL) was heated at 70 °C for 8 h. After removal of the precipitate, the resultant clear deep red solution was concentrated to about 7 mL. Complex **5a** was isolated as brick-red crystals after this solution stood at room temperature for 2 days (263 mg, 58%). ^1H NMR (CD_2Cl_2): δ 8.03 (s, 1H, CHN), 7.24 (m, 3H, aromatic H), 3.68 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.38 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.25 (s, 1H, cage CH), 2.89 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 2.14 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.25 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.06 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 176.1 (CHN), 139.5, 128.4, 124.0, 123.8 (aromatic C), 53.8, 53.5 (cage C), 49.3, 47.5 ($\text{N}(\text{CH}_3)_2$), 28.2, 27.4, 26.0, 24.3, 22.7, 21.9 ($\text{CH}(\text{CH}_3)_2$). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 8.8 (1), 1.1 (1), -2.5 (1), -4.4 (1), -5.5 (1), -15.2 (3), -17.8 (1). IR (KBr, cm^{-1}): ν 2962 (m), 2869 (w), 2528 (vs), 1638 (s), 1590 (w), 1461 (m), 1438 (w), 1161 (w), 1019 (m). Anal. Calcd for $\text{C}_{19}\text{H}_{40}\text{B}_9\text{N}_3\text{Ti}$: C, 50.08; H, 8.85; N, 9.22. Found: C, 49.58; H, 8.35; N, 9.13.

This complex was also prepared in 69% yield from **4a** (100 mg, 0.31 mmol) and $\text{Ti}(\text{NMe}_2)_4$ (70 mg, 0.31 mmol) at room temperature in toluene/DME (DME = dimethoxyethane).

Preparation of $[\eta^1:\eta^5\text{-}(\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_2\text{B}_9\text{H}_{10}]\text{Zr}(\text{NMe}_2)_2\text{-}(\text{NHMe}_2)\cdot 0.5\text{DME}$ (6a**·0.5DME).** To a DME solution (4 mL) of 7-($\text{CH}=\text{NHC}_6\text{H}_3\text{Pr}_2$ -2,6)-7,8- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (**4a**; 100 mg, 0.31 mmol) was added a toluene (4 mL) solution of $\text{Zr}(\text{NMe}_2)_4$ (83 mg, 0.31 mmol) with stirring at room temperature, and the reaction mixture was stirred for 10 min. Slow evaporation of the solvent gave **6a**·0.5DME as pale yellow crystals (120 mg, 66%). ^1H NMR (CD_2Cl_2): δ 8.61 (s, 1H, CHN), 7.39 (m, 3H, aromatic H), 3.64 (s, 2H, DME), 3.35 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.25 (s, 3H, DME), 3.01 (s, 12H, $\text{N}(\text{CH}_3)_2$), 2.38 (s, 6H, $\text{HN}(\text{CH}_3)_2$), 1.15 (m, 12H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 175.6 ($\text{CH}=\text{N}$), 144.2, 139.3, 127.0, 123.2 (aromatic C), 71.4, 57.9 (DME), 52.5, 50.1 (cage C), 43.9, 41.5 ($\text{N}(\text{CH}_3)_2$), 26.7 ($\text{CH}(\text{CH}_3)_2$), 23.9 ($\text{CH}(\text{CH}_3)_2$). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 1.8 (1), -4.5 (1), -7.2 (4), -14.5 (1), -16.8 (1), -22.1 (1). IR (KBr, cm^{-1}): ν 3257 (m), 2960 (s), 2779 (m), 2534 (vs), 2516 (s), 1633 (s), 1460 (s), 1167 (m), 1015 (m), 928 (s). Anal. Calcd for $\text{C}_{21}\text{H}_{47}\text{B}_9\text{N}_4\text{Zr}$ (**6a**): C, 46.35; H, 8.71; N, 10.30. Found: C, 46.17; H, 8.47; N, 10.55.

Preparation of $[\eta^1:\eta^5\text{-}(\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_2\text{B}_9\text{H}_{10}]\text{Hf}(\text{NMe}_2)_2\text{-}(\text{NHMe}_2)\cdot 0.5\text{DME}$ (7a**·0.5DME).** This complex was prepared as pale yellow crystals from **4a** (100 mg, 0.31 mmol) and $\text{Hf}(\text{NMe}_2)_4$ (110 mg, 0.31 mmol) in a mixed solvent of DME (4 mL) and toluene (4 mL) using the same procedures as those for **6a**: yield 160 mg (76%). ^1H NMR (CD_2Cl_2): δ 8.84 (s, 1H, CHN), 7.35 (m, 3 H, aromatic H), 3.64 (s, 2H, DME), 3.41 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.25 (s, 3H, DME), 2.91 (s, 12H, NMe_2), 2.38 (s, 6H, $\text{HN}(\text{CH}_3)_2$), 1.20 (m, 12H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 175.5 ($\text{CH}=\text{N}$), 144.2, 139.5, 127.2, 123.2 (aromatic C), 71.4, 57.9 (DME), 52.1, 49.5 (cage C), 43.3, 41.7 ($\text{N}(\text{CH}_3)_2$), 26.7 ($\text{CH}(\text{CH}_3)_2$), 23.9 ($\text{CH}(\text{CH}_3)_2$). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 1.4 (1), -5.3 (1), -7.1 (4), -15.2 (1), -17.1 (1), -22.9 (1). IR (KBr, cm^{-1}): ν 3250 (m), 2962 (s), 2780 (m), 2532 (vs), 1639 (s), 1623 (s), 1461 (s), 1116 (m), 1023 (m), 931 (m). Anal. Calcd for $\text{C}_{21}\text{H}_{47}\text{HfB}_9\text{N}_4$ (**7a**): C, 39.95; H, 7.50; N, 8.87. Found: C, 39.66; H, 7.54; N, 8.69.

Table 1. Crystal Data and Summary of Data Collection and Refinement Details for **3a, **3b**, and **4a****

	3a	3b	4a
formula	$\text{C}_{15}\text{H}_{29}\text{B}_{10}\text{N}$	$\text{C}_{11}\text{H}_{21}\text{B}_{10}\text{N}$	$\text{C}_{15}\text{H}_{30}\text{B}_9\text{N}$
cryst size (mm)	$0.50 \times 0.40 \times 0.30$	$0.50 \times 0.50 \times 0.40$	$0.25 \times 0.15 \times 0.15$
fw	331.5	275.4	321.7
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
<i>a</i> , Å	10.235(2)	7.775(2)	7.081(2)
<i>b</i> , Å	10.932(2)	18.751(3)	10.503(2)
<i>c</i> , Å	11.000(2)	11.870(2)	27.287(5)
α , deg	114.94(1)	90	90
β , deg	100.51(1)	96.70(1)	96.51(1)
γ , deg	103.88(1)	90	90
<i>V</i> , Å ³	1025.7(2)	1718.7(5)	2016.3(6)
<i>Z</i>	2	4	4
<i>D</i> _{calc} , Mg/m ³	1.073	1.064	1.060
radiation (λ), Å	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)
2θ range, deg	4.3 to 50.0	4.1 to 50.0	4.2 to 48.0
μ , mm ⁻¹	0.054	0.052	0.054
<i>F</i> (000)	352	576	688
no. of obsd rflns	3557	3022	2642
no. of params refnd	239	202	230
goodness of fit	0.982	0.826	0.983
<i>R</i> 1	0.067	0.058	0.091
<i>wR</i> 2	0.171	0.124	0.219

Preparation of $[\eta^1:\eta^5\text{-}(\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_2\text{B}_9\text{H}_{10}]\text{Ti}(\text{NMe}_2)_2\cdot 0.5\text{C}_7\text{H}_8$ (5b**·0.5C₇H₈) and $[\eta^1:\eta^5\text{-}(\text{Me}_2\text{N})\text{CH}(\text{NMe}_2)(\text{C}_2\text{B}_9\text{H}_{10})]\text{-Ti}(\text{NMe}_2)_2\cdot 0.5\text{C}_7\text{H}_8$ (**8**·0.5C₇H₈).** A mixture of 1-($\text{CH}=\text{NC}_6\text{H}_3\text{Me}_2$ -2,6)-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ (**3b**; 275 mg, 1.00 mmol) and $\text{Ti}(\text{NMe}_2)_4$ (224 mg, 1.00 mmol) in toluene (20 mL) was heated at 90 °C for 24 h. After removal of the precipitate, the clear solution was concentrated to about 7 mL. A red crystalline solid together with some red crystals were obtained after this solution stood at room temperature for a week. Both ^1H and ^{11}B NMR spectra indicated that it was a mixture of products. Many attempts to separate them by fractional recrystallization failed. There were two slightly different shapes of crystals under the microscope. The block ones were identified as **5b**·0.5C₇H₈ and the prism ones as **8**·0.5C₇H₈ by single-crystal X-ray diffraction studies. The spectroscopic data could not be taken.

Ethylene Polymerization. A flame-dried Schlenk flask was charge with the catalyst (10 μmol) together with MMAO (20 mmol) and toluene (25 mL) under nitrogen atmosphere. The mixture was stirred at 50 °C for 1 h. Ethylene gas was then introduced to the flask, and its pressure was maintained continuously at 1 atm by means of bubbling. The polymerization was terminated by addition of acidic ethanol. The white precipitate was filtered off, washed with ethanol, and then dried at 50 °C under vacuum until constant weight.

X-ray Structure Determination. All single crystals were sealed under N₂ in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo K α radiation. An empirical absorption correction was applied using the SADABS program.¹¹ 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 (PC version).¹² The solvated toluene molecule in **8**·0.5C₇H₈ was seriously disordered, and only its arene plane was well defined by using rigid body refinement procedures, leading to a relatively high *R* index. All 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. Selected bond distances and angles are compiled in Tables 3 and 4. Further details are included in the Supporting Information.

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

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

Table 2. Crystal Data and Summary of Data Collection and Refinement Details for 5a, 5b, 6a, 7a, and 8

	5a	5b·0.5C ₇ H ₈	6a·0.5DME	7a·0.5DME	8·0.5C ₇ H ₈
formula	C ₁₉ H ₄₀ B ₉ N ₃ Ti	C _{18.50} H ₃₆ B ₉ N ₃ Ti	C ₂₃ H ₅₂ B ₉ N ₄ OZr	C ₂₃ H ₅₂ B ₉ HfN ₄ O	C _{14.50} H ₃₉ B ₉ N ₄ Ti
cryst size (mm)	0.50 × 0.35 × 0.20	0.50 × 0.50 × 0.45	0.50 × 0.40 × 0.40	0.40 × 0.40 × 0.30	0.50 × 0.30 × 0.20
fw	455.7	445.7	589.2	676.5	414.7
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	16.128(2)	10.219(2)	10.004(2)	10.165(2)	29.625(3)
<i>b</i> , Å	13.205(2)	10.679(2)	17.188(3)	17.424(4)	10.671(1)
<i>c</i> , Å	12.639(2)	12.657(2)	18.834(4)	20.250(4)	18.426(2)
α , deg	90	106.78(1)	90	90	90
β , deg	91.33(1)	91.44(1)	98.64(3)	111.00(3)	125.60(1)
γ , deg	90	103.30(1)	90	90	90
<i>V</i> , Å ³	2691.1(5)	1280.6(3)	3202(1)	3349(1)	4735.8(7)
<i>Z</i>	4	2	4	4	2
<i>D</i> _{calcd} , Mg/m ³	1.125	1.155	1.222	1.342	0.291
radiation (λ), Å	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)
2 θ range, deg	2.5 to 50.0	3.4 to 48.0	4.4 to 50.0	4.7 to 50	3.4 to 48.0
μ , mm ⁻¹	0.330	0.346	0.367	3.138	0.092
<i>F</i> (000)	968	470	1244	1372	442
no. of obsd rflns	4731	3329	5633	5284	3716
no. of params refnd	297	296	343	343	246
goodness of fit	0.982	1.436	1.035	1.137	1.013
<i>R</i> 1	0.053	0.117	0.052	0.055	0.069
<i>wR</i> 2	0.120	0.328	0.136	0.149	0.201

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3a, 3b, and 4a

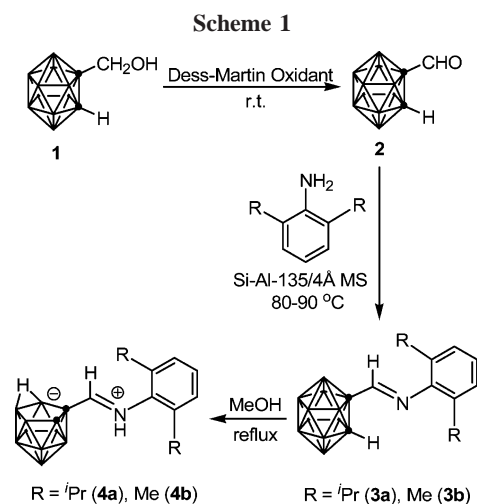
	3a	3b	4a
C(1)–C(2)	1.606(3)	1.617(3)	1.580(8)
C(1)–C(3)	1.496(3)	1.488(3)	1.496(8)
C(3)–N(1)	1.247(3)	1.242(3)	1.248(2)
N(1)–C(4)	1.435(2)	1.433(3)	1.526(7)
C(4)–N(1)–C(3)	117.8(2)	118.6(2)	126.5(7)
N(1)–C(3)–C(1)	121.3(2)	123.5(2)	118.1(7)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 5a, 5b, 6a, 7a, and 8

	5a (Ti)	5b (Ti)	6a (Zr)	7a (Hf)	8 (Ti)
C(1)–C(3)	1.480(4)	1.521(10)	1.469(6)	1.511(11)	1.534(6)
C(3)–N(1)	1.261(3)	1.301(11)	1.273(6)	1.275(11)	1.555(5)
M–N(1)	2.196(2)	2.128(4)	2.538(3)	2.535(6)	2.202(3)
M–N(2)	1.894(3)	1.920(4)	2.036(4)	2.057(7)	1.887(4)
M–N(3)	1.878(2)	1.901(4)	2.043(4)	2.060(7)	1.902(4)
M–N(4)			2.461(4)	2.462(7)	
M–C(1)	2.365(3)	2.361(7)	2.625(4)	2.648(7)	2.368(4)
M–C(2)	2.393(3)	2.392(8)	2.650(4)	2.667(8)	2.362(4)
M–B(3)	2.410(3)	2.421(10)	2.599(5)	2.622(10)	2.390(5)
M–B(4)	2.436(3)	2.403(10)	2.588(5)	2.601(9)	2.453(5)
M–B(5)	2.372(3)	2.362(9)	2.582(5)	2.608(8)	2.409(5)
av M–cage atom	2.395(3)	2.389(10)	2.601(5)	2.629(10)	2.396(5)
M–Cent	1.925	1.918	2.188	2.197	1.920
N(1)–C(3)–C(1)	112.6(3)	112.4(6)	115.3(4)	114.1(7)	102.8(3)
C(3)–N(1)–M	100.4(2)	100.2(4)	100.2(3)	101.7(5)	98.5(2)
N(2)–M–N(3)	101.8(2)	88.5(5)	115.8(1)	115.3(3)	103.3(2)
N(1)–M–Cent	95.8	100.6	84.7	84.9	99.9

Results and Discussion

Ligands. Imines were generally prepared from the reactions of aldehydes (ketones) with amines. The aldehyde 1-CHO-1,2-(C₂B₁₀H₁₁) (**2**) was synthesized in 86% yield from 1-CH₂OH-1,2-C₂B₁₀H₁₁ by a modified method using Dess–Martin periodinane oxidant. The easy workup and high-yielding procedure were the advantage of this route.^{10a} Treatment of **2** with a slightly excess amount of disubstituted aniline at 80–90 °C in the presence of silica–alumina catalyst support (grade 135) (Si–Al-135) and 4 Å molecular sieves powder gave the corresponding imines 1-(CH=N₂C₆H₃R₂)-1,2-C₂B₁₀H₁₁ (R = ⁱPr (**3a**), Me (**3b**)) in ~80% yield. It was noteworthy that Si–Al-135 was crucial to this reaction. Other reaction conditions proceeded with very poor yields. They were quantitatively converted into the corresponding zwitterionic dicarbollide salt 7-(CH=NHC₆H₃R₂–



2,6)-7,8-C₂B₉H₁₁ (R = ⁱPr (**4a**), Me (**4b**)) just by refluxing in dry MeOH. These transformations are outlined in Scheme 1.

Compounds **3a** and **3b** were stable in air and moisture and were soluble in common organic solvents such as CH₂Cl₂, CHCl₃, and THF. The zwitterionic salts **4a** and **4b** were, however, sensitive to moisture, resulting in the formation of the corresponding aldehyde and anilines. They were soluble only in highly polar organic solvents such as MeOH, acetone, and pyridine.

Compounds **3a,b** and **4a,b** were characterized by ¹H, ¹³C, and ¹¹B NMR spectroscopy and elemental analyses. The unique proton chemical shifts $\delta_{CH=N}$ were observed at 7.57 and 7.62 ppm in **3a,b**, which were downfield shifted to 8.72 and 8.66 ppm in **4a,b**, respectively. Accordingly, their ¹³C chemical shifts were also moved from ca. 155 ppm in **3a,b** to ca. 189 ppm in **4a,b**. A broad singlet at δ = 11.90 ppm in **4a** and 11.66 ppm in **4b** assignable to the NH proton was observed. The ¹¹B NMR spectra exhibited a 1:1:2:2:4 splitting pattern for **3a,b** and 1:1:1:1:2:1:1:1 for **4a,b**, respectively. Therefore, the deboration reactions were closely monitored by ¹¹B NMR spectroscopy.

The molecular structures of **3a,b** are shown in Figures 1 and 2. These imines adopt the *trans* configuration with typical N(1)–C(3) double bond distances of 1.247(3) Å in **3a** and 1.242(3) Å in **3b** (Table 3). The four atoms C(4), N(1), C(3), and C(1) are coplanar with the angles C(4)–N(1)–C(3) and N(1)–C(3)–

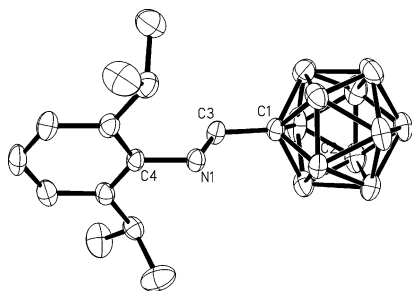


Figure 1. Molecular structure of 1-(CH=NC₆H₃ⁱPr₂-2,6)-1,2-C₂B₁₀H₁₁ (**3a**).

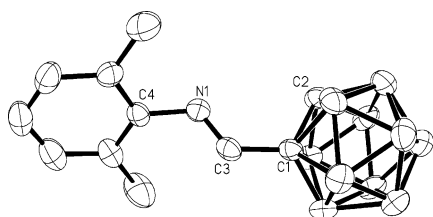


Figure 2. Molecular structure of 1-(CH=NC₆H₃Me₂-2,6)-1,2-C₂B₁₀H₁₁ (**3b**).

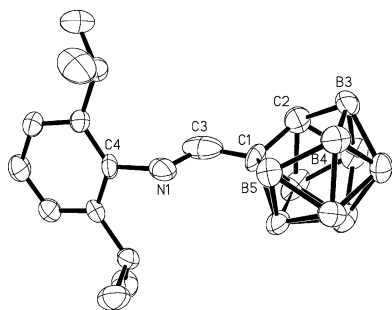


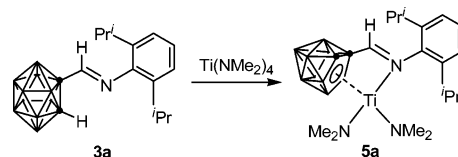
Figure 3. Molecular structure of 7-(CH=NHC₆H₃ⁱPr₂-2,6)-7,8-C₂B₉H₁₁ (**4a**).

C(1), being 117.8(2)° and 121.3(2)° in **3a** and 118.6(2)° and 123.5(2)° in **3b**.

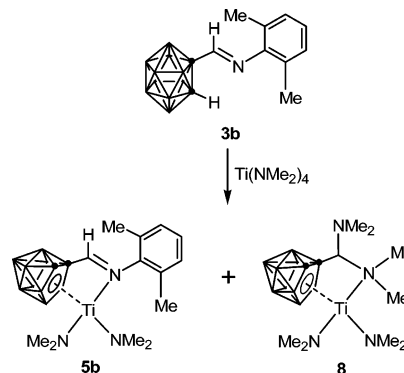
Single-crystal X-ray analyses reveal that **4a** is a zwitterionic salt, shown in Figure 3. The N(1)–C(3) distance of 1.248(2) Å is almost identical with that of 1.247(3) Å observed in its parent compound **3a**. On the other hand, protonation of N(1) results in the disappearance of the lone-pair electrons, which leads to a much longer N(1)–C(4) distance and a larger C(3)–N(1)–C(4) angle than those observed in **3a** (Table 3). The B–B and C–B distances in **3a,b** and **4a** are normal and very comparable to the literature data.³

Group 4 Metal Complexes. Amine elimination reactions have been proved to be an efficient method for the preparation of group 4 metal amides supported by various ancillary ligands including functional carboranes.^{4,5,13} It has been documented that the carborane cage CH proton can be deprotonated by M(NMe₂)₄.^{14,15} For example, treatment of Me₂C(C₅H₅)(C₂B₁₀H₁₁) with M(NMe₂)₄ gave [η⁵:σ-Me₂C(C₅H₄)(C₂B₁₀H₁₀)]M(NMe₂)₂ (M = group 4 metals) in good yields.^{15c} We attempted to prepare

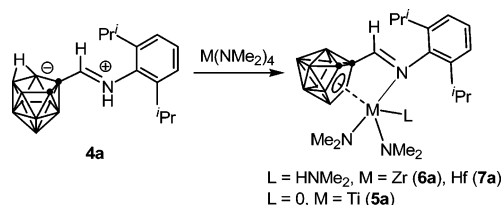
Scheme 2



Scheme 3



Scheme 4



[η¹:σ-(R₂C₆H₃N=CH)C₂B₁₀H₁₀]MX₃ (X = NMe₂, Cl) for comparison with [η¹:η⁵:σ-(Ph₂PC₆H₃N=CH(^tBu)₂C₆H₂O)]TiCl₃ in olefin polymerization.⁶¹ The latter was an extremely active catalyst recently developed in our laboratory for the polymerization/copolymerization of ethylene with α-olefins upon activation with MMAO.⁶¹

Reaction of **3a** with 1 equiv of Ti(NMe₂)₄ in toluene at 70 °C gave an unexpected titanacarborane, [η¹:η⁵-(ⁱPr₂C₆H₃N=CH)C₂B₉H₁₀]Ti(NMe₂)₂ (**5a**), in 58% isolated yield (Scheme 2). The ¹¹B NMR indicated that this reaction did not proceed at room temperature at all, and both deprotonation and deboration reactions occurred as the reaction temperature was increased. After heating at 70 °C for 8 h, **5a** became the major product. The in situ-generated Me₂NH might act as a deborating agent for the formation of **5a**.¹⁶ A similar deboration reaction was previously observed in the reaction of ⁱPr₂NB(C₉H₇)-(C₂B₁₀H₁₁) with Ti(NMe₂)₄.^{15b} On the other hand, treatment of **3a** with 1 equiv of M(NMe₂)₄ (M = Zr, Hf) under the same or forced reaction conditions always afforded a mixture of products according to the ¹¹B NMR analyses. Many attempts to isolate the pure product from this mixture failed. Salt metathesis reaction of [(R₂C₆H₃N=CH)C₂B₁₀H₁₀]K with MCl₄ in THF also generated a mixture of inseparable products.

The substituents on the aromatic ring played a role in the reaction of Ti(NMe₂)₄ with imine ligands. Interaction of **3b** with 1 equiv of Ti(NMe₂)₄ in toluene gave, after recrystallization, a mixture of [η¹:η⁵-(Me₂C₆H₃N=CH)C₂B₉H₁₀]Ti(NMe₂)₂·0.5C₇H₈ (**5b**·0.5C₇H₈) and [η¹:η⁵-(Me₂N)CH(NMe₂)(C₂B₉H₁₀)Ti(NMe₂)₂·0.5C₇H₈ (**8**·0.5C₇H₈) on the basis of ¹H NMR spectroscopy (Scheme 3). Many attempts to separate **5b** and **8** by fractional crystallization failed. They always crystallized out together as red crystals in slightly different shapes: block for **5b**·0.5C₇H₈ and prism for **8**·0.5C₇H₈. The spectroscopic data for pure

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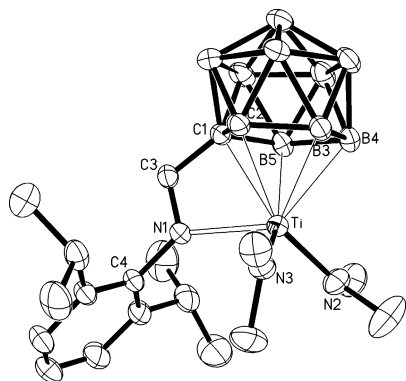


Figure 4. Molecular structure of $[\eta^1:\eta^5-(i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_2\text{B}_9\text{H}_{10}]\text{-Ti}(\text{NMe}_2)_2$ (**5a**).

complexes were not obtainable. They were identified by single-crystal X-ray analyses (vide infra).

Comparing the results obtained from the reactions of $\text{Ti}(\text{NMe}_2)_4$ with **3a,b**, it was reasonable to suggest that **5b** may serve as an intermediate for the formation of **8**. The Me_2NH generated in situ attacked the less protected $\text{C}=\text{N}$ bond in **5b**,¹⁷ followed by an amine exchange reaction to produce **8** and aniline.¹⁸ Other possibilities cannot be ruled out at this stage. The two bulky isopropyl groups at the 2,6-positions of the phenyl ring may prevent the $\text{C}=\text{N}$ double bond in **5a** from the nucleophilic attack of Me_2NH .

Complex **5a** was also directly prepared from **4a** via an amine elimination reaction. Treatment of $\text{M}(\text{NMe}_2)_4$ with 1 equiv of **4a** in toluene/DME at room temperature produced, after workup, the metallocarboranes **5a** and $[\eta^1:\eta^5-(i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_2\text{B}_9\text{H}_{10}]\text{-M}(\text{NMe}_2)_2(\text{NHMe}_2)$ ($\text{M} = \text{Zr}$ (**6a**), Hf (**7a**)) in good yields. It was noted that reactions of $\text{M}(\text{NMe}_2)_4$ with 1 equiv of **4b** gave a mixture of inseparable products under similar or forced reaction conditions.

The ^1H NMR spectrum of **5a** exhibited a singlet at 8.03 ppm assignable to the $\text{HC}=\text{N}$ proton and two singlets at 3.68 and 3.38 ppm attributable to the two NMe_2 groups in addition to the $i\text{Pr}_2\text{C}_6\text{H}_3$ protons. The ^1H NMR spectra of **6a** and **7a** were very similar, showing the presence of DME and HNMe_2 in a molar ratio of 0.5:1 besides the common spectroscopic features of **5a**. No proton exchange between the coordinated HNMe_2 and two amido groups was observed. The unique $\text{CH}=\text{N}$ carbon shift at $\delta_{\text{C}} \approx 176$ ppm was also found in the ^{13}C NMR spectra of three complexes. The ^{11}B NMR spectra showed a 1:1:1:1:1:3:1 splitting pattern for **5a** and a 1:1:4:1:1:1:1 splitting pattern for **6a** and **7a**.

Single-crystal X-ray analyses revealed that the Ti atoms in **5a,b** and **8** adopt a characteristic three-legged piano stool arrangement by an η^5 -dicarbollyl group, two amido units, and one nitrogen from the sidearm, shown in Figures 4–6, respectively. The structures of both **5b** and **8** show a half toluene of solvation. The overall geometry is similar to that found in $[\eta^1:\eta^5-(\text{Me}_2\text{NCH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NMe}_2)_2$,^{5f} and $[\eta^1:\eta^5-(\text{C}_6\text{H}_5\text{CH}_2)_2\text{-N}(\text{CH}_2\text{CH}_2)\text{C}_2\text{B}_9\text{H}_{10}]\text{Ti}(\text{NMe}_2)_2$.^{5e} As shown in Table 4, the average Ti–cage atom, the Ti–Cent (Cent: the centroid of the open C_2B_3 bonding face), and Ti–N distances in **5a,b** and **8**

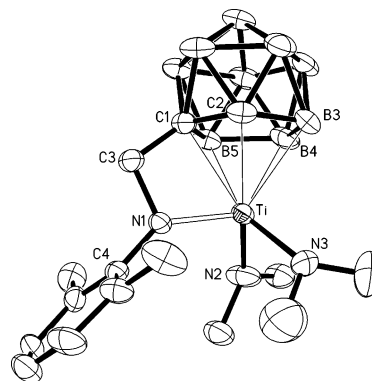


Figure 5. Molecular structure of $[\eta^1:\eta^5-(\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_2\text{B}_9\text{H}_{10}]\text{-Ti}(\text{NMe}_2)_2$ (**5b**).

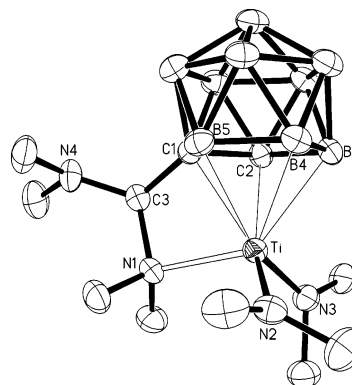


Figure 6. Molecular structure of $[\eta^1:\eta^5-(\text{NMe}_2)\text{CH}(\text{NMe}_2)(\text{C}_2\text{B}_9\text{H}_{10})\text{-Ti}(\text{NMe}_2)_2$ (**8**).

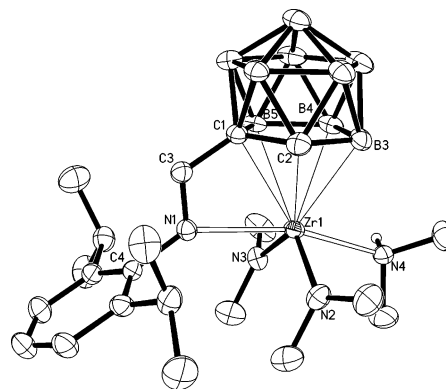


Figure 7. Molecular structure of $[\eta^1:\eta^5-(i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_2\text{B}_9\text{H}_{10}]\text{-Zr}(\text{NMe}_2)_2(\text{NHMe}_2)$ (**6a**).

are very close to the literature data.^{4,5e,f,15} The Ti–N(imine) distances (2.196(2), 2.128(4) Å) in **5a,b** are marginally shorter than the Ti–N(amine) distances of 2.202(3) Å in **8**, 2.225(2) Å in $[\eta^2-(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NEt}_2)_2(\text{NHET}_2)$,¹⁹ and 2.240(3) Å in $[\eta^1:\eta^5-(\text{Me}_2\text{NCH}_2)_2\text{C}_2\text{B}_9\text{H}_9]\text{Ti}(\text{NMe}_2)_2$,^{5f} suggesting that the tethered N atom is coordinated to the Ti center in a strained manner. The $\text{C}(3)\text{--N}(1)$ double bond distances in **5a,b** are longer than those observed in **3a,b**, but are significantly shorter than the corresponding C–N single bond distance found in **8**.

X-ray diffraction studies indicated that **6a** and **7a** are isomorphous and isostructural, each with a half DME of solvation. Figure 7 shows the representative structure of **6a**. It has a four-legged piano stool geometry, with the coordinated amine and the imine unit in a *trans* position, which is different

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Table 5. Ethylene Polymerization Results^a

catalyst	activity (kg/mol·h·atm)	$M_w/10^4$ (g/mol)	M_w/M_n^b
5a (Ti)	9.2	1.57	2.27
6a (Zr)	15.8	13.10	1.63
7a (Hf)	3.0	2.27	1.69

^a Conditions: toluene (25 mL), 1 atm of ethylene, $T = 50\text{ }^\circ\text{C}$, catalyst (10.0 μmol), MMAO (20.0 mmol), Al/M = 2000, aging time = 1 h, reaction time = 30 min. ^b Measured by GPC relative to polystyrene standard.

from that of **5a**, most likely resulting from the larger size of Zr and Hf atoms. It was noted that the N atom of the sidearm in $[\eta^5\text{-}\{(\text{C}_6\text{H}_5\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{10}\}]\text{Zr}(\text{NMe}_2)_2(\text{NHMe}_2)$ did not coordinate to the Zr.^{5e} The average Zr–/Hf–cage atom distances (2.601(5)/2.629(10) Å) are much longer than the corresponding values of 2.546(5) Å in $[\eta^5\text{-}\{(\text{C}_6\text{H}_5\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_{10}\}]\text{Zr}(\text{NMe}_2)_2(\text{NHMe}_2)$,^{5e} 2.568(4) Å in $[\eta^1\text{-}\eta^5\text{-}\{(\text{C}_6\text{H}_5\text{CH}_2)\text{NH}(\text{CH}_2\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9(\text{Me})\}]\text{ZrCl}_2(\text{THF})$,^{5e} 2.564(5) Å in $(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{Zr}(\text{NEt}_2)_2(\text{NHMe}_2)$,²⁰ and 2.505(7) Å in $(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})(\text{Cp}^*)\text{Hf}(\mu\text{-}\eta^2\text{-C}_2\text{B}_9\text{H}_{11})\text{HfMe}_2(\text{Cp}^*)$ ²¹ probably owing to the higher coordination number and steric congestion of the central metal ion. Consequently, the Zr–/Hf–N distances are longer than the corresponding values reported in the literatures.^{4,19,20} The Zr–/Hf–N(imine) distances (2.538(3)/2.535(6) Å) are significantly longer than the Zr–/Hf–N(amine) distances (2.461(4)/2.462(7) Å), indicative of weak interactions between the tethered imine and the metal center.

Ethylene Polymerization. Complexes **5a**, **6a**, and **7a** underwent preliminary testing for catalytic activity in ethylene polymerization, using modified methylaluminoxane (MMAO) as cocatalyst (Al/M = 2000) in toluene at 50 °C under 1 atm of ethylene. The results are compiled in Table 5. They were active catalysts with an activity of 3.0–15.8 kg/mol·h·atm, and the following trend in activity was observed: Zr > Ti > Hf. The molecular weights (M_w) of the polymers ranged from 1.57×10^4 to 13.10×10^4 , and the polydispersities determined by

GPC were between 1.63 and 2.27. The ^{13}C NMR analyses of the polymer generated by **5a** revealed that it was the highly linear polyethylene with no detectable branches. These results showed that complexes **5a**, **6a**, and **7a** had activities in ethylene polymerization comparable to those of amine-tethered analogues $[\eta^1\text{-}\eta^5\text{-}\{\text{R}'_2\text{N}(\text{CH}_2)_n\}\text{RC}_2\text{B}_9\text{H}_9]\text{MCl}_2$ ^{5e,i} ($n = 1$, M = Ti, R' = Me, R = H, Me; $n = 2$, M = Ti, Zr, R' = C₆H₅CH₂, R = H, Me). The low activities of this type of constrained-geometry complexes might be ascribed to the instability of the active species.^{5e}

Conclusion

New imine-carboranyl compounds were successfully prepared by Schiff base condensation of carboranyl aldehyde with anilines in the presence of Si-Al-135 and 4 Å molecular sieves. They were readily converted into the corresponding imido-dicarbollyl ligands by simply refluxing in dry methanol solution. Several constrained-geometry group 4 metallocarborane amide complexes were prepared via amine elimination reactions of 7-(CH=NHC₆H₃Pr₂-2,6)-7,8-C₂B₉H₁₁ with M(NMe₂)₄ in toluene/DME. A sterically bulky imine sidearm was necessary to prevent the C=N double bond from the nucleophilic attack of the in situ-generated amine.

In the presence of MMAO, these group 4 metal complexes were active catalysts for the polymerization of ethylene to produce highly linear polymers with narrow polydispersities, but the activities were low.

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Supporting Information Available: Crystallographic data in CIF format for **3a**, **3b**, **4a**, **5a**, **5b**, **6a**, **7a**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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