Chelating Diamide Group IV Metal Olefin Polymerization Catalysts

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The novel group IV metal chelating diamide complexes [(2,6-diisopropylanilido)B(NMe_2)B(NMe_2)(2,6-diisopropylanilido)]MX_2, **7a** (M = Ti, X = Cl), **7b** (M = Ti, X = Me), and **8** (M = Zr, X = CH_2Ph), have been prepared and characterized by ^{1}H and ^{13}C{H} NMR spectroscopy and single-crystal X-ray structure analysis (**7a**). These complexes are active polymerization catalysts upon combining with the appropriate activator. The catalyst efficiencies, however, are considerably lower than those of Cp-based catalysts. The molecular weights of the polymers produced are activator dependent, and the polydispersities were found to be broader than those observed for Cp-based single-site catalytic systems.

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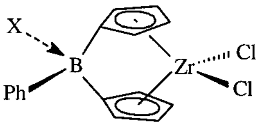
Introduction

Numerous studies of homogeneous single-site olefin polymerization catalysis have led to the rapid development of group IV cyclopentadienyl (Cp)-based complexes, which have seen extensive applications to the stereospecific polymerization of α-olefins.[1] Application of Cp-silylamido ligands to group III and group IV metals has led to complexes such as [(η^5-C_5Me_4)$SiMe_2$(N-*t*-Bu)]$TiMe_2$ (**1**) that exhibit high polymerization activity toward α-olefins and other vinyl monomers upon activation.[2]

Recent modifications to the Cp-based ligand framework have included the use of aryl- and amide-substituted boranes as the *ansa* bridge as in compounds **2**,[3] **3**,[4] and **4**,[5] which upon activation are effective olefin polymerization catalysts.

The development of non-Cp-based early transition metal complexes as homogeneous Ziegler−Natta olefin polymerization catalysts remains an active area of research.[6] One strategy that has met with considerable success involves the use of chelating diamide ligands resulting in the formation of a variety of four- and five-coordinate group 4 complexes.[7−9] Selected examples of this class of complexes are represented in Figure 1 (**5**,[9]



X = SMe_2, PMe_3

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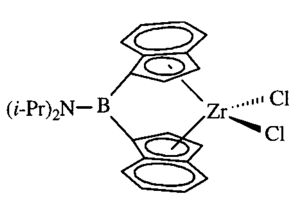

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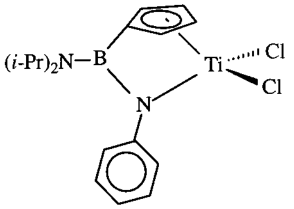

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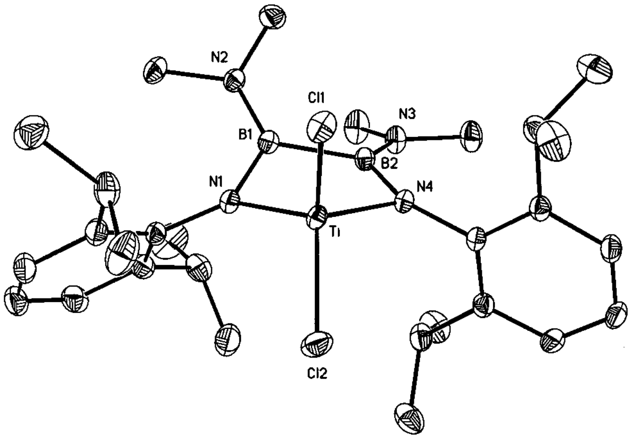
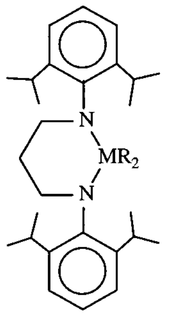


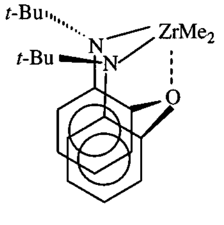
Figure 1. Molecular structure and partial numbering scheme for **7a** with 40% probability thermal elipsoids. Hydrogen atoms are omitted for clarity.

6[10]). These complexes have been shown upon activation to yield catalysts capable of the living polymerization of 1-hexene and the copolymerization of ethylene and α-olefins. In general, chelating diamide-based complexes have produced many active olefin polymerization catalysts but remain inferior to their Cp-based predecessors.

This paper describes our efforts into a new class of diborane-bridged bis(amide)-based complexes. The research is driven to determine if the inclusion of the boron–amido linkage for amide-based complexes would result in improved catalytic properties. We now report the synthesis, spectroscopy characterization, X-ray crystallographic analysis, and polymerization activity of novel electrophilic diborane-bridged diamide titanium and zirconium complexes **7** and **8**.



5a: M = Ti, R = Me
b: M = Zr, R = CH$_2$Ph



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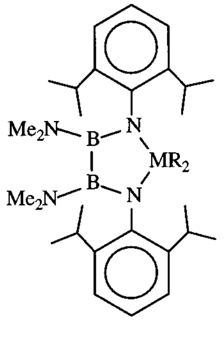

7a: M = Ti, R = Cl
b: M = Ti, R = Me
8: M = Zr, R = CH$_2$Ph

Results and Discussion

Ligand Synthesis. The preparation of the ligand is represented in Scheme 1. The initial approach to the synthesis of **9** was taken using a slight modification of a synthetic route described in the literature.[10] Solid dimethyl sulfide adduct of borontrichloride was used in the initial disproportionation reaction due to the ease of handling over the volatile boron trichloride.[11] The reaction proceeds cleanly and quantitatively at room temperature with the loss of dimethyl sulfide. Reduction of chlorobis(dimethylamido)borane with Na/K resulted in the isolation of the desired product **9** in low yield (35%) after distillation.[12] During the course of this

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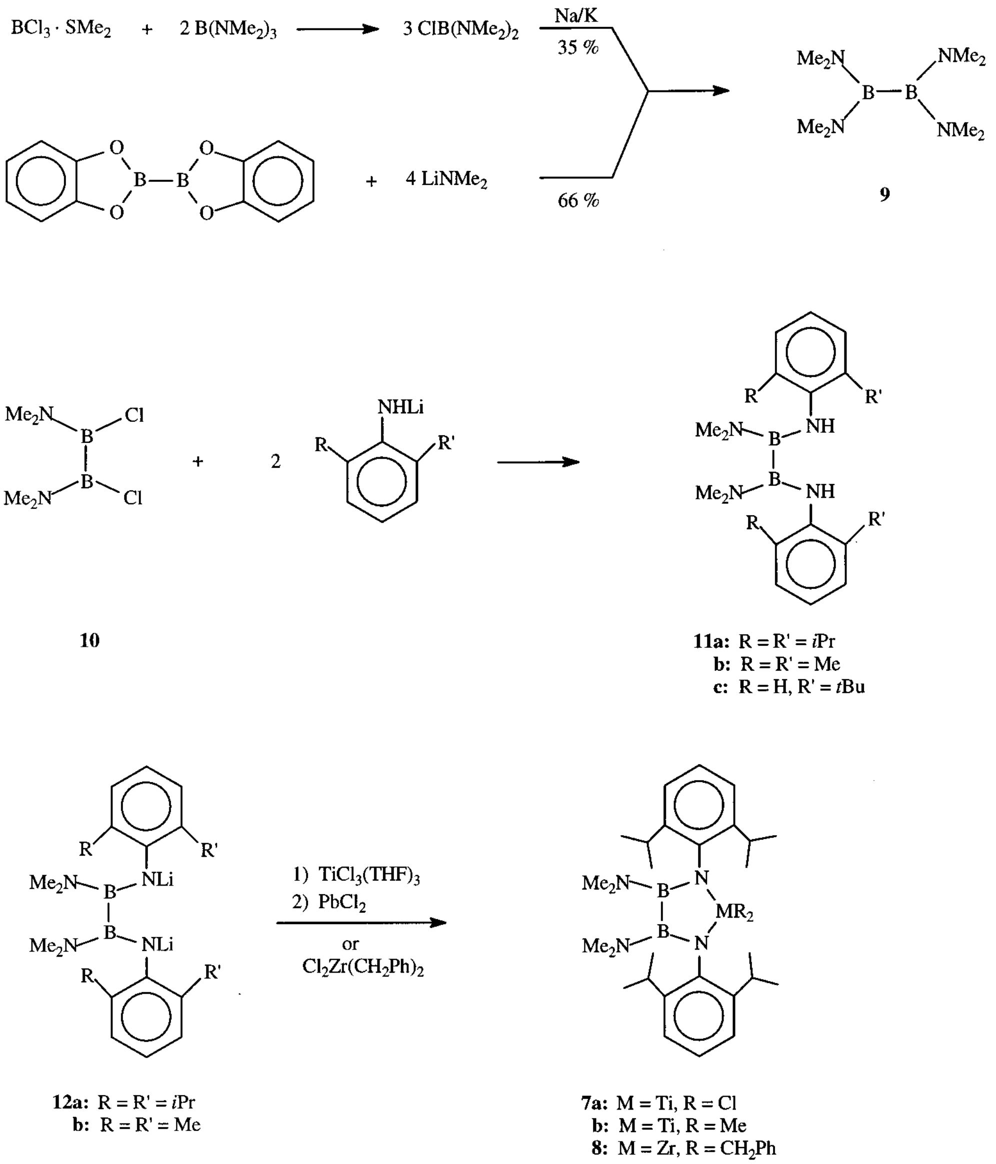
Scheme 1



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investigation a more efficient synthetic route to compound **9** was discovered from the reaction of bis(catecholato)diboron and 4 equiv of lithium dimethylamide. This reaction proceeds cleanly in a single step in 66% yield after distillation. Compound **9** was converted to **10** via reaction with 4 equiv of HCl.[13b] Compound **10** was transformed to the final ligand **11** in high yield upon mixing with 2 equiv of the respective lithium anilinide. Compounds **11a** and **11b** are then converted to the corresponding dilithium salts **12a**,**b** using 2 equiv of *n*-BuLi. The reaction of **11c** with 2 equiv of *n*-BuLi gives a mixture of unidentified products.

The ^1H NMR spectra of compounds **11a**−**c** exhibit a pair of singlets in the region of 2−3 ppm corresponding to the resonances of the dimethylamido groups. The inequivalency of the methyl resonances presumably arises from the restricted rotation about the B−N bond due to double-bond character of the B−N linkage. The coalesence temperature of these resonances is 97.5 °C for **11a**,**b** and 65.0 °C for **11c**. The corresponding free energy for this fluxional process is about 17 kcal/mol for all three compounds. Compound **11a** also exhibits fluxionality around 1 ppm, corresponding to the resonances of the isopropyl methyl groups that appear as a broad resonance at room temperature, which become a sharp doublet upon warming. In addition to the broadening of the isopropyl methyl resonances the isopropyl methine resonance is not observed at room temperature and grows in at 3.3 ppm at higher temperature. The fluxional nature of the isopropyl resonances in **11a** is consistent with a restricted rotation about the methine carbon of the isopropyl group and the C_{ipso} bond due to the steric hindrance of the isopropyl groups. The resonances of the 2,6-methyl groups in **11b** and the 2-*tert*-butyl groups in **11c** appear as sharp singlets at room temperature. The amine protons for **11a**,**b** appear as a single resonance in the region of 3.6−3.7 ppm and at 5.4 ppm for **11c**. The aromatic resonances of **11a**,**b** appear as an unresolved broad resonance in the region of 6.8−7.0 ppm. The resonances of the unsymmetrically substituted phenyl ring in **11c** appear as discrete multiplets in the range of 6.7−7.5 ppm.

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Deprotonation of **11a**,**b** gave the dilithium salts **12a**,**b.** The NMR spectra are consistent with the desired structures with the dimethylamido resonances appearing as a singlet at 2.4 ppm and the resolved aromatic resonances appearing as a doublet in the region of 6.2–6.3 ppm and a triplet at 6.7 ppm.

Complex Synthesis. Complexation of these ligands described above to group IV metals proved to be problematic. Treating **11a**–**c** with reagents such as $M(NMe_2)_4$ or $M(CH_2Ph)_4$ to form the Ti and Zr complexes was unsuccessful. The complexation to titanium was successfully accomplished by reacting **12a** with $TiCl_3(THF)_3$ followed by oxidation with $PbCl_2$ to form **12a**. Multiple reaction products were observed in the crude reaction mixture, with the desired product being isolated via recrystallization from hexane. Complex **7a** can be cleanly converted to the corresponding $TiMe_2$ complex **7b** using 2 equiv of MeMgBr. Attempts to generate the Zr analogue by reacting **12a** with zirconium halide were unsuccessful. Application of $Cl_2Zr(CH_2TMS)_2$[8k] in the reaction with **12a** also resulted in an unidentified mixture of products. Ultimately the desired product **8** was successfully synthesized by reacting $Cl_2Zr(CH_2Ph)_2(OEt_2)_x$, generated in situ, with **12a**. This reaction sequence resulted in the formation of a significant amount of unidentified byproduct, which could be removed by successive precipitations as a white solid from cold hexane. The desired product **8** was isolated as a yellow oil.

The ^1H NMR spectra of compounds **7a**,**b** exhibit a pair of singlets in the region of 2.1–2.7 ppm corresponding to the resonances of the dimethylamido groups. As in the case of the free ligands, these complexes also exhibit fluxional behavior at room temperature. The temperature of coalecense for the methyl groups of the dimethylamido fragments was found to be 100 and 80 °C for **7a** and **8**, respectively. The free energy of rotation about the B–NMe_2 bond in both cases was about 17 kcal/mol, which is the same as that observed for the free ligands, suggesting that ligand chelation has little effect on the double-bond character of the B–NMe_2 linkage. As expected, complexes **7a**,**b** exhibit similar spectral features of the ligands in their ^1H and ^{13}C NMR spectra. The Ti-Me resonance appears as a singlet at 1.05 ppm in the ^1H NMR and 57.4 ppm (J_{CH} = 119.5 Hz) in the ^{13}C NMR spectrum. It has been reported that the J_{CH} value of a Ti-Me resonance can be correlated with the electrophilicity of the Ti center as dictated by its ligand environment.[13] On the basis of this report the lower J_{CH} value (J_{CH} = 118.4 Hz) observed for Ti-Me resonance in **5a** suggests that the B–B bridged ligand imparts more electrophilicity on the Ti center in **7b**.

Table 1. Crystallographic Data for Complex 7a

chemical formula	$C_{28}H_{46}B_2Cl_2N_4Ti$
space group	$P2_1/n$
a	12.3735(6) Å
b	15.2227(7) Å
c	18.1093(9) Å
α	90°
β	107.584(1)°
γ	90°
V	3251.7(3) Å^3
fw	579.11
ρ_{calc}	1.183 mg/mm^3
Z	4
μ	0.450 mm^{-1}
T	−100 °C
λ	0.71073 Å
R1[a]	0.0320
wR2[b]	0.0815 [5769]

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ $[I > 2\sigma(I)]$.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 7a

Ti–N4	1.867(1)	N4–Ti–N1	110.59(5)
Ti–N1	1.885(1)	N4–Ti–Cl2	108.63(4)
Ti–Cl2	2.2307(5)	N1–Ti–Cl2	108.94(4)
Ti–Cl1	2.2602(5)	N4–Ti–Cl1	107.27(4)
Ti–B1	2.404(2)	N1–Ti–Cl1	111.10(4)
Ti–B2	2.456(2)	Cl2–Ti–Cl1	110.28(2)
N1–C11	1.431(2)	C11–N1–B1	132.1(1)
N1–B1	1.460(2)	C11–N1–Ti	137.0(1)
N2–B1	1.397(2)	B1–N1–Ti	90.96(9)
N2–C2	1.462(2)	B1–N2–C2	124.8(1)
N2–C1	1.462(2)	B1–N2–C1	124.1(1)
N3–B2	1.407(2)	C2–N2–C1	110.9(1)
N3–C3	1.461(2)	C5–N4–B2	133.6(1)
N3–C4	1.467(2)	C5–N4–Ti	129.44(9)
N4–C5	1.431(2)	B2–N4–Ti	94.82(9)
N4–B2	1.447(2)	N2–B1–N1	124.4(1)
B1–B2	1.800(2)	N2–B1–B2	122.6(1)
		N1–B1–B2	113.0(1)
		N3–B2–N4	123.6(1)
		N3–B2–B1	120.2(1)
		N4–B2–B1	115.9(11)

Compound **8** exhibits fluxionality due to restricted rotation about the B–NMe_2 bond. The isopropyl methine protons appear as two multiplets at 3.1 and 3.4 ppm, which coalesce at 50 °C. The benzylic protons appear as a pair of doublets at 1.7 and 1.8 ppm, which coalesce at 45 °C. The rotational barriers for these processes were about 17 kcal/mol, which is the same as determined for the barrier for the B–NMe_2 bond rotation. It seems that the observed fluxional processes are dependent on the ability of the dimethylamide to rotate about the B–N bond to a conformation that in turn allows the isopropyl groups and the benzyl groups to rotate to provide steric relief. The isopropyl methyl resonances appear as a sharp doublet at 1.1 ppm and a broad resonance at 1.2 ppm at room temperature. These resonances sharpened to a pair of resolved doublets at higher temperature. The ortho aromatic protons of the benzyl groups appear as a sharp doublet at 6.59 ppm, which remains unchanged at −50 °C. The upfield chemical shift of these protons suggests that the phenyl π systems of the benzyl groups may be interacting with the zirconium center.[14] In the closely related compound, **5b**, the ortho protons of the benzyl groups appear as a doublet at 6.65 ppm, and an η^2 benzyl–zirconium interaction was proposed.[8a]

X-ray Crystal Structure Analysis. The molecular structure of **7a** was confirmed by a single-crystal X-ray structure analysis. The thermal ellipsoid drawing is shown in Figure 1. Crystal data are presented in Table 1, while selected bond distances and angles are included in Table 2. The B–B bond distance of 1.800(2) Å is slightly longer than that of reported series of compounds of the type $(Cp)(NMe_2)B–B(NMe_2)(Cp)$ (1.72–1.76 Å).[15] This lengthening of the B–B bond reflects a more

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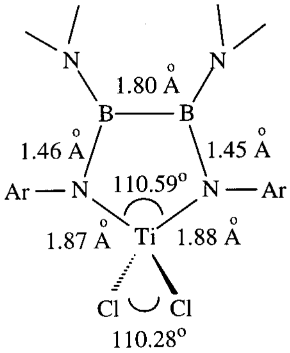
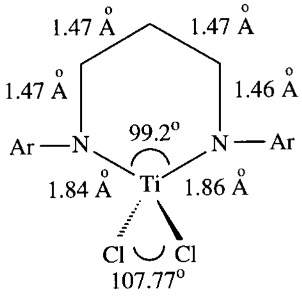


7a



5a

Figure 2. Schematic comparison of bond angles and distances for **7a** and **5a**.

electron-rich amido substituent weakening the B−B bond. The B−NMe$_2$ bond distances of 1.397(2) and 1.407(2) Å suggest some degree of double-bond character and are similar to those observed in the (Cp)(NMe$_2$)B−B(NMe$_2$)(Cp) compounds (1.386−1.429 Å). The sum of the angles about the N atoms of these fragments equals 359.85° and 359.81°, indicating sp^2 hybridization of these N atoms. The distances of 1.447(2) and 1.460(2) Å observed for the B−N(aniline) bonds are in the range for B−N single-bond linkage. Figure 2 depicts selected structural comparisons between complexes **5a** as the dichloride and **7a**. The Ti−N(aniline) bond distances of 1.867(1) and 1.885(1) Å are slightly longer than those observed for **5a** (1.839 and 1.856 Å), suggesting a weaker Ti−N interaction, which is consistent with the electron-deficient nature of the B−B bond linkage relative to the propyl linkage for **5a**.[11d] The N1−Ti−N4 and Cl−Ti−Cl bond angles of 110.59(5)° and 110.28(2)°, respectively, for **7a** compared to the analogous values of 99.2° and 107.77° for **5a** suggest that **7a** possesses a more symmetrically substituted tetrahedral Ti metal center than **5a**. The Ti−Cl bond distances for **7a** and **5a** are essentially the same. Another notable feature of **7a** is the observed envelope conformation of the five-member metallacycle. The plane consisting of atoms Ti−N1−B1 lies 34.08(9)° out of the Ti−N4−B2−B1 plane, resulting in the puckering of one of the ring anilido groups of the metallacycle. The aryl rings are positioned from the metalloheterocycle plane with dihedral angles of 89.75(5)° and 60.80(4)°.

Polymerization Results. Complexes **7a**,**b** and **8** provide active polymerization catalysts upon combination with appropriate activators. In the cases of B(C$_6$F$_5$)$_3$ (1 equiv) and MAO (1000 equiv) each complex was activated by mixing the appropriate catalyst and activator solutions immediately prior to injection to the reactor. The polymerizations were conducted for 15 min with ethylene on demand. The polymerization results for ethylene/octene are summarized in Table 3 and show that the catalysts generated from **7** and **8** exhibit significantly lower activities compared to those derived from **1** and **5a**. The polydispersities of the polymers produced from **7** and **8** were broader than those produced from **1** and **5a**, presumably as a result of the formation of multiple catalyst sites.

Conclusions

Novel group IV metal complexes comprising diborane-bridged amido ligands have been synthesized. Complex **7b** was prepared by reacting the dilithium ligand salt with TiCl$_3$(THF)$_3$ followed by oxidation with PbCl$_2$. This TiCl$_2$ complex was then converted to the corresponding TiMe$_2$ complex via reaction with MeMgBr. Complex **8** was synthesized by the reaction of the dilithium ligand salt with the disproportionation product of Zr(CH$_2$Ph)$_4$ and ZrCl$_4$. These complexes have been shown to be active catalysts upon combination with the appropriate activator. Additionally, efforts to examine the structure−activity relationships of B-bridged amide-based complexes are currently underway.

Experimental Section

The ^{1}H (300 MHz) and ^{13}C{H} NMR (75 MHz) spectra were recorded on Varian Mercury Vx and Inova 300 spectrometers. The ^{1}H and ^{13}C NMR spectra are referenced to the residual solvent peaks and are reported in ppm relative to tetramethylsilane. All *J* values are given in Hz. Tetrahydrofuran (THF), diethyl ether, toluene, and hexane were used following passage through double columns charged with activated alumina and Q-5 catalyst. The compounds BCl$_3$−SMe$_2$, B(NMe$_2$)$_3$, *n*-BuLi, 2,6-dimethylaniline, 2-*tert*-butylaniline, bis(catecholato)diboron, LiNMe$_2$, and 2,6-diisopropylaniline were used as purchased from Aldrich. The compound B(C$_6$F$_5$)$_3$ was used as purchased from Boulder Scientific. The compounds TiCl$_3$(THF)$_3$[16] and Zr(CH$_2$Ph)$_4$[17] were prepared as described in the literature. All syntheses were performed under dry nitrogen or argon atmosphere using a combination of glovebox and high-vacuum techniques. High-resolution mass spectroscopy (HRMS) was performed by the University of Florida. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY, and the University of Michigan, Ann Arbor, MI.

Single-Crystal X-ray Analysis of Dichloro[1,2-bis(2,6-diisopropylanilide)-1,2-bis(dimethylamido)diborane]titanium (7a). Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). Cell parameters were refined using 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was <1%). Absorption corrections by integration were applied on the basis of measured indexed crystal faces.

The structure was solved by the direct methods in SHELXTL5 and refined using full-matrix least squares.[18] The non-H atoms were refined with anisotropic thermal parameters, and all of the H atoms were calculated in idealized positions and

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Table 3. Ethylene/Octene Copolymerization Results

complex	activator	T (°C)	efficiency (g P/g M)	exotherm (°C)	M_w/M_n (PDI)
1	MAO	70	1 561 195	2.7	220 000/102 000 (2.16)
1	$B(C_6F_5)_3$	140	1 070 000	2.8	65 500/24 300 (2.69)
5a	MAO	70	163 504	2.2	120 000/28 600 (4.20)
5a	$B(C_6F_5)_3$	140	36 000	0.6	76 300/11 300 (6.77)
7a	MAO	70	23 571	1.1	22 600/5500 (4.13)
7b	MAO	70	9548	0.9	58 800/1600 (37.9)
7b	$B(C_6F_5)_3$	140	20 000	0.3	31 000/4300 (7.25)
8	MAO	70	15 973	1.0	101 000/2600 (38.9)
8	$B(C_6F_5)_3$	140	1000	0.9	

refined riding on their parent atoms. In the final cycle of refinement, 5769 observed reflections with $I > 2\sigma(I)$ were used to refine 335 parameters, and the resulting R1 and wR2 were 3.20% and 8.15%, respectively. Refinement was done using F^2.

Ethylene/Octene Copolymerizations. All feeds were passed though columns of activated alumina and Q-5 catalyst prior to introduction to the reactor. A stirred 2 L Parr reactor was charged with 740 g of Isopar-E solvent and 118 g of 1-octene comonomer. Hydrogen was added as a molecular weight control agent by differential pressure expansion from a 75 mL addition tank at 25 psi. The reactor contents were then heated to the polymerization temperature of 140 °C and saturated with ethylene at 500 psig. The metal complexes and activators were mixed as dilute toluene solutions, transferred to a catalyst addition tank, and injected into the reactor through a stainless steel transfer line. The polymerization conditions were maintained for 15 min with ethylene added on demand. Heat was continually removed from the reaction with an internal cooling coil. The resulting solution was removed from the reactor, quenched with isopropyl alcohol, and stabilized by the addition of 10 mL of a toluene solution containing approximately 67 mg of a hindered phenol antioxidant (Irganox 1010 from Ciba Geigy Corp.) and approximately 133 mg of a phosphorus stabilizer (Irgafos 168 from Ciba Geigy Corp.). Between polymerization runs a wash cycle was conducted in which 850 g of mixed alkanes was added to the reactor, which was then heated to 150 °C and then emptied of the heated solvent immediately prior to a new polymerization run.

Preparation of Chlorobis(dimethylamido)borane. BCl_3-SMe_2 (62.000 g, 345.78 mmol) and $B(NMe_2)_3$ (98.921 g, 691.56 mmol) were stirred together at room temperature overnight under a nitrogen bubbler. The mixture was then heated to reflux for 1 h to drive off any residual SMe_2. Allowing the pale yellow liquid to stir to room temperature followed by filtration resulted in the isolation of the desired product (139.436 g, 93.3% yield). ^{1}H NMR (C_6D_6): δ 2.49 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 39.86.

Preparation of Tetrakis(dimethylamido)diborane (9) via ClB(NMe)₂. Chlorobis(dimethylamido)borane (30.000 g, 223.19 mmol) was refluxed in hexane (200 mL) as Na/K alloy [Na (1.539 g, 66.96 mmol)/K (8.726 g, 223.19 mmol)] was added dropwise to the solution. After the first several drops the reaction initiated, as evidenced by a sudden increase in the reflux. The heat was then turned off and the alloy added slowly to maintain a reflux. After the addition was complete the reaction mixture was heated to reflux for an additional hour and then stirred at room temperature for 3 h. The mixture was then filtered through a Celite pad, and the volatiles were removed, resulting in the isolation of a yellow liquid. Fractional vacuum distillation resulted in the isolation of the desired compound as a pale yellow liquid (7.756 g, 35.1% yield). ^{1}H NMR (C_6D_6): δ 2.73 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 41.37.

Preparation of Tetrakis(dimethylamido)diborane (9) via Bis(catecholato)diboron. Lithium dimethylamide (10.70 g, 210.0 mmol) was added slowly as a solid to a solution of bis(catecholato)diboron (10.00 g, 42.00 mmol) in diethyl ether (200 mL) at −20 °C. This mixture was then allowed to stir for an additional 40 h at room temperature. After the reaction period ether was removed under vacuum and the residue was extracted and filtered using hexane. Solvent removal and fractional vacuum distillation resulted in the isolation of the desired compound as a pale yellow liquid (5.493 g, 66.0% yield).

Preparation of Bis(dimethylamido)diborondichloride (10). Tetrakis(dimethylamido)diborane (7.756 g, 39.19 mmol) was stirred in diethyl ether (100 mL) at −78 °C as HCl (156.75 mmol, 156.75 mL of 1.0 M solution in diethyl ether) was added dropwise. This mixture was then allowed to stir for 6 h at room temperature. After the reaction period the volatiles were removed and the residue was extracted and filtered using hexane. The product was obtained as a pale yellow liquid after solvent removal and vacuum distillation (4.722 g, 66.7% yield). ^{1}H NMR (C_6D_6): δ 2.40 (s, 6 H), 2.50 (s, 6 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 37.62, 41.78.

Preparation of 2,6-Dimethylaniline, Lithium Salt. *n*-BuLi (49.54 mmol, 30.94 mL of 1.6 M solution in hexane) was added dropwise to a solution of 2,6-dimethylaniline (6.000 g, 49.54 mmol) in hexane (100 mL). This mixture was allowed to stir for 3 h, during which time a white precipitate formed. After the reaction period the white salt that formed was filtered and washed with hexane, dried under vacuum, and used without further purification or analysis (5.954 g, 94.6% yield).

Preparation of 2-*tert*-Butylaniline, Lithium Salt. *n*-BuLi (24.12 mmol, 15.08 mL of 1.6 M solution in hexane) was added dropwise to a solution of 2-*tert*-butylaniline (3.600 g, 24.12 mmol) in hexane (50 mL). This mixture was allowed to stir overnight, during which time a precipitate formed. After the reaction period the white salt that formed was filtered and washed with hexane, dried under vacuum, and used without further purification or analysis (2.961 g, 79.1% yield).

Preparation of 2,6-Diisopropylaniline, Lithium Salt. *n*-BuLi (56.40 mmol, 35.25 mL of 1.6 M solution in hexane) was added dropwise to a solution of 2,6-diisopropylaniline (10.00 g, 56.40 mmol) in hexane (100 mL). This mixture was allowed to stir for 3 h, during which time a white precipitate formed. After the reaction period the white salt that formed was filtered and washed with hexane, dried under vacuum, and used without further purification or analysis (9.988 g, 96.7% yield).

Preparation of 1,2-Bis(2,6-diisopropylanilide)-1,2-bis(dimethylamido)diborane (11a). Bis(dimethylamido)diborondichloride (2.350 g, 13.00 mmol) in diethyl ether (10 mL) was added dropwise to a solution of 2,6-diisopropylaniline, lithium salt (4.765 g, 26.01 mmol) in diethyl ether (50 mL) at 0 °C. This mixture was then allowed to stir overnight at room temperature. After the reaction period the volatiles were removed and the residue was extracted and filtered using hexane. Removal of the hexane resulted in the isolation of the desired product as a white solid (5.322 g, 88.9% yield). ^{1}H NMR (C_6D_6): δ 0.9−1.4 (br m, 24 H), 2.29 (s, 6 H), 2.85 (s, 6 H), 3.71 (s, 2 H), 7.08 (br m, 6 H). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 22.51, 24.03 (br), 28.17, 36.82, 42.67, 123.19, 124.78, 140.71, 145.02 (br). HRMS(EI): calcd for $C_{28}H_{48}N_4B_2$ m/z 460.4026, found 460.4025. Anal. Calcd for $C_{28}H_{48}N_4B_2$: C, 72.74; H, 10.46; N, 12.12. Found: C, 72.76; H, 10.34; N, 11.72.

Preparation of 1,2-Bis(2,6-dimethylanilide)-1,2-bis(dimethylamido)diborane (11b). Bis(dimethylamido)dibo-

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ron dichloride (1.000 g, 5.530 mmol) in diethyl ether (10 mL) was added dropwise to a solution of 2,6-dimethylaniline, lithium salt (1.407 g, 11.07 mmol) in diethyl ether (50 mL) at 0 °C. This mixture was then allowed to stir overnight at room temperature. After the reaction period the volatiles were removed and the residue was extracted and filtered using hexane. Removal of the hexane resulted in the isolation of the desired product as a white solid (1.785 g, 92.1% yield). ^{1}H NMR (toluene-d_8): δ 1.87 (s, 12 H), 2.32 (s, 6 H), 2.79 (s, 6 H), 3.58 (s, 2 H), 6.8−6.9 (m, 6 H). ^{13}C{H} NMR (toluene-d_8): δ 19.00, 35.91, 42.64, 123.14, 128.21, 133.44, 143.56. HRMS(EI): calcd for $C_{20}H_{32}N_4B_2$ *m/z* 348.2773, found 348.2777.

Preparation of 1,2-Bis(2-*tert*-butylanilide)-1,2-bis(dimethylamido)diborane (11c). Bis(dimethylamido)diborondichloride (0.833 g, 4.61 mmol) in diethyl ether (10 mL) was added dropwise to a solution of 2-*tert*-butylaniline, lithium salt (1.431 g, 9.22 mmol) in diethyl ether (40 mL) at 0 °C. This mixture was then allowed to stir at room temperature overnight. After the reaction period the volatiles were removed and the residue was extracted and filtered using hexane. Removal of the hexane resulted in the isolation of the desired product as a white solid (1.419 g, 75.7% yield). ^{1}H NMR (toluene-d_8): δ 1.34 (s, 9 H), 2.61 (s, 6 H), 2.71 (s, 6 H), 5.44 (s, 2 H), 6.80 (t, $^3J_{HH}$ = 7.1 Hz, 2 H), 7.03 (m, 2 H), 7.20 (d, $^3J_{HH}$ = 7.7 Hz, 2 H), 7.42 (d, $^3J_{HH}$ = 8.0 Hz, 2 H). ^{13}C{H} NMR (toluene-d_8): δ 30.37, 34.33, 36.37, 41.99, 120.45, 126.12, 127.00, 136.54, 144.94. HRMS(EI): calcd for $C_{24}H_{40}N_4B_2$ *m/z* 404.3399, found 404.3406. Anal. Calcd for $C_{24}H_{40}N_4B_2$: C, 70.96; H, 9.92; N, 13.79. Found: C, 68.96; H, 9.88; N, 13.77.

Preparation of 1,2-Bis(2,6-diisopropylanilide)-1,2-bis(dimethylamido)diborane, Dilithium Salt (12a). 1,2-Bis(2,6-diisopropylanilide)-1,2-bis(dimethylamido)diborane (1.820 g, 3.950 mmol) was stirred in hexane (75 mL) as *n*-BuLi (7.91 mmol, 4.94 mL of 1.6 M solution in hexane) was added dropwise. This mixture was then allowed to stir overnight. After the reaction period the mixture was filtered and the salt was washed with hexane and dried under vacuum, resulting in the isolation of the desired product as a white powder (1.6878 g, 90.4% yield). ^{1}H NMR (THF-d_8): δ 1.04 (d, $^3J_{HH}$ = 6.9 Hz, 6 H), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 6 H), 2.45 (s, 12 H), 3.66 (septet, $^3J_{HH}$ = 6.9 Hz, 4 H), 6.29 (t, $^3J_{HH}$ = 7.5 Hz, 2 H), 6.73 (d, $^3J_{HH}$ = 7.5 Hz, 4 H). ^{13}C{H} NMR (THF-d_8): δ 24.88, 25.34, 28.00, 40.91, 114.40, 121.95, 137.21, 158.76.

Preparation of 1,2-Bis(2,6-dimethylanilide)-1,2-bis(dimethylamido)diborane, Dilithium Salt (12b). 1,2-Bis(2,6-dimethylanilide)-1,2-bis(dimethylamido)diborane (1.500 g, 4.280 mmol) was stirred in hexane (75 mL) as *n*-BuLi (8.57 mmol, 5.36 mL of 1.6 M solution in hexane) was added dropwise. This mixture was then allowed to stir overnight. After the reaction period the mixture was filtered and the salt was washed well with hexane and dried under vacuum, resulting in the isolation of the desired product as a white powder (1.413 g, 91.1% yield). ^{1}H NMR (THF-d_8): δ 2.09 (s, 12 H), 2.48 (s, 12 H), 6.17 (t, $^3J_{HH}$ = 7.2 Hz, 2 H), 6.73 (d, $^3J_{HH}$ = 7.2 Hz, 4 H). ^{13}C{H} NMR (THF-d_8): δ 21.22, 40.86, 123.19, 127.53, 128.28, 162.05.

Preparation of Dichloro[1,2-bis(2,6-diisopropylanilide)-1,2-bis(dimethylamido)diborane]titanium (7a). 1,2-Bis(2,6-diisopropylanilide)-1,2-bis(dimethylamido)diborane, dilithium salt (0.600 g, 1.27 mmol) in THF (20 mL) was added dropwise to a slurry of $TiCl_3(THF)_3$ (0.471 g, 1.27 mmol) in THF (50 mL) at 0 °C. This mixture was then allowed to stir at room temperature for 45 min. $PbCl_2$ (0.177 g, 0.640 mmol) was then added as a solid and the mixture allowed to stir for an additional 30 min. After the reaction period the volatiles were removed and the residue was extracted and filtered using hexane. The solution was concentrated and cooled to −10 °C overnight, resulting in the formation of orange X-ray quality crystals (0.156 g, 21.3% yield). ^{1}H NMR (toluene-d_8): δ 1.23 (d, $^3J_{HH}$ = 6.6 Hz, 6 H), 1.45 (d, $^3J_{HH}$ = 6.6 Hz, 6 H), 2.17 (s, 6 H), 2.76 (s, 6 H), 3.53 (septet, $^3J_{HH}$ = 6.6 Hz, 4 H), 7.11 (s, 6 H). ^{13}C{H} NMR (toluene-d_8): δ 24.94, 24.67, 29.48, 39.33, 42.93, 124.08 (br), 17.23, 150.64. HRMS (EI): calcd for $C_{28}H_{46}N_2B_2TiCl_2$ *m/z* 578.2781, found 578.2789. Anal. Calcd for $C_{28}H_{46}N_2B_2TiCl_2$: C, 58.07; H, 8.01; N, 9.67. Found: C, 58.28; H, 8.20; N, 9.42.

Preparation of Dimethyl[1,2-bis(2,6-diisopropylanilide)-1,2-bis(dimethylamido)diborane]titanium (7b). Dichloro[1,2-bis(2,6-diisopropylanilide)-1,2-bis(dimethylamido)diborane]titanium (0.272 g, 0.470 mmol) was stirred in diethyl ether (40 mL) as MeMgBr (0.940 mmol, 0.313 mL of 3.0 M solution in diethyl ether) was added dropwise. This mixture was allowed to stir for 1 h. After the reaction period the volatiles were removed and the residue was extracted and filtered using hexane. Removal of the hexane resulted in the isolation of the desired product as a dark yellow oil (0.209 g, 82.5% yield). ^{1}H NMR (C_6D_6): δ 1.05 (s, 6 H), 1.21 (d, $^3J_{HH}$ = 6.9 Hz, 16 H), 1.32 (d, $^3J_{HH}$ = 6.3 Hz, 16 H), 2.19 (s, 6 H), 2.69 (s, 6 H), 3.58 (br, 2 H), 7.0−7.2 (m, 6 H). ^{13}C{H} NMR (C_6D_6): δ 24.06, 24.83, 29.31, 39.58, 42.93, 57.38, 123.97, 125.18, 139.5 (br), 149.45. HRMS (EI): calcd for $C_{30}H_{52}N_2B_2Ti$ *m/z* 538.3793, found 538.3858.

Preparation of Dibenzyl[1,2-bis(2,6-diisopropylanilide)-1,2-bis(dimethylamido)diborane]zirconium (8). Zirconium tetrachloride (0.100 g, 0.440 mmol) and zirconium tetrabenzyl (0.192 g, 0.440 mmol) were stirred together in diethyl ether (30 mL) for 1 h. 1,2-Bis(2,6-diisopropylanilide)-1,2-bis(dimethylamido)diborane, dilithium salt (0.400 g, 0.842 mmol) in diethyl ether (30 mL) was then added dropwise, and the mixture was allowed to stir for 3 h. After the reaction period the volatiles were removed under vacuum and the residue was extracted and filtered using hexane. The filtrate was then concentrated and cooled to −10 °C overnight, during which time a white powder precipitated. The mixture was again filtered, and the volatiles were removed, resulting in the isolation of the desired product as a yellow oil (0.123 g, 19.8% yield). ^{1}H NMR (toluene-d_8): δ 1.14 (d, $^3J_{HH}$ = 6.6 Hz, 6 H), 1.22 (br, 6 H), 1.70 (d, $^3J_{HH}$ = 9.0 Hz, 2 H), 1.83 (d, $^3J_{HH}$ = 9.6 Hz, 2 H), 2.10 (s, 6 H) 2.71 (s, 6 H), 3.0−3.2 (br, 2 H), 3.3−3.5 (br, 2 H), 6.59 (d, $^3J_{HH}$ = 7.2 Hz, 4 H), 6.77 (t, $^3J_{HH}$ = 7.2 Hz, 2 H), 6.9−7.1 (m, 10 H). ^{13}C{H} NMR (toluene-d_8): δ 23.96 (br), 24.22 (br), 24.36 (br), 25.23 (br), 29.47, 39.72, 43.05, 62.23, 122.70, 123.73 (br), 124.08 (br), 124.33, 127.23, 130.82, 139.26 (br), 140.16 (br), 144.90, 144.92, 149.03. HRMS(EI): calcd for $C_{42}H_{60}N_2B_2Zr$ (M^+) 732.4037; found {M − [CH_2Ph]} *m/z* 641.3469, {M − [$Zr(CH_2Ph)_2$] + H} *m/z* 461.3976.

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Supporting Information Available: ORTEP diagram and tables of crystal data, data collection, and refinement parameters, atomic coordinates, bond distances and angles, and isotropic displacement parameters for complex **7a** and ^{1}H NMR spectra for **7a** and **11c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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