Aminoboranediyl-Bridged Zirconocenes: Highly Active Olefin Polymerization Catalysts

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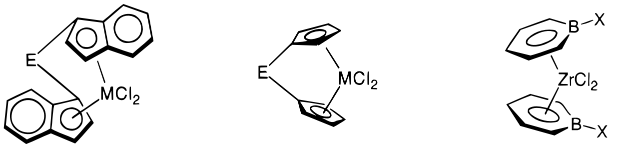
*Summary: Novel aminoboranediyl-bridged zirconocenes [i-Pr$_2$NB(η^5-C$_5$H$_4$)$_2$]ZrCl$_2$ (**8b**) and [i-Pr$_2$NB(η^5-1-C$_9$H$_8$)$_2$]ZrCl$_2$ (**4b**) have been prepared and structurally characterized. When activated by excess methylaluminoxane, **4b** and **8b** form highly active catalysts for the polymerization of ethylene. The catalyst derived from **4b** converts propylene to isotactic polypropylene.*

The Brintzinger type of chiral group 4 bridged metallocenes (**1**[1] and **2**[2]) have been widely used as stereoselective homogeneous catalysts for olefin polymerization[3] and in organic synthesis.[4] Although a number of different bridging groups have been studied,[5] the CH$_2$-CH$_2$ and SiMe$_2$ bridges are most commonly used.[6] Bridges by first-row elements other than carbon are particularly rare. Boron-bridged **3b**[7] and a related bis Cp complex **5b**[8] have been reported by Rufanov, Lorberth, and co-workers, while Shapiro et al. have examined the coordinated boron-bridged **6b**.[9] Compounds **3b** and **5b** are rather labile and were poorly characterized, while the relatively more stable **6b** (L = PMe$_3$) showed only a low activity toward polymerization of ethylene. Very recently Braunschweig et al. have prepared and structurally characterized the BN(SiMe$_3$)$_2$-bridged titanium complex **7a**.[10,11]



a, M = Ti
b, M = Zr

1, E = CH$_2$-CH$_2$
2, E = SiMe$_2$
3, E = BC(SiMe$_3$)$_3$
4, E = BN(iPr)$_2$

5, E= PhB
6, E = PhBL (L = SMe$_2$, PMe$_3$)
7, E = BN(SiMe$_3$)$_2$
8, E = BN(iPr)$_2$

9, X = N(iPr)$_2$
10, X = Ph

Our prior work on olefin polymerization using boratabenzene zirconium complexes **9**[12] and **10**[13] showed that a change of the B-substituent from Ph to N(i-Pr)$_2$ markedly effected their polymerization activities.[14] Thus we felt that the use of aminoborane bridges might result in *ansa*-zirconocenes with novel properties. Specifically, the aminoboron bridge should (1) mask the electrophilicity of boron by B−N π-bonding, (2) offer a more rigid bridge, and (3) result in an electron-rich boron which should diminish the electrophilicity of Zr. On the basis of these considerations we have prepared and structurally characterized **4b** and **8b**. On activation by excess methylaluminoxane (MAO), these complexes give olefin polymerization catalysts with remarkably high activities.

The reaction of (i-Pr)$_2$NBCl$_2$[15] with 2 equiv of CpLi gave a quantitative yield of **11** as a mixture of double-bond isomers (Scheme 1).[16] Deprotonation of **11** with LDA followed by reaction with ZrCl$_4$ in ether gave **8b** as colorless crystals in 38% yield. **8b** was characterized by NMR and mass spectroscopy, elemental analysis, and X-ray crystallography.[17] The molecular structure of **8b** is displayed in Figure 1.

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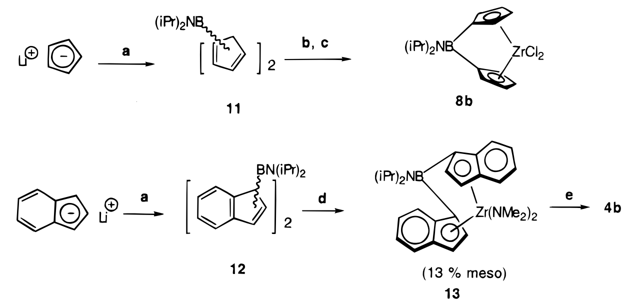
Scheme 1



Key: **a**, $(iPr)_2NBCl_2$; **b**. LDA; **c**, $ZrCl_4$; **d**, $Zr(NMe_2)_4$; **e**, TMSCl

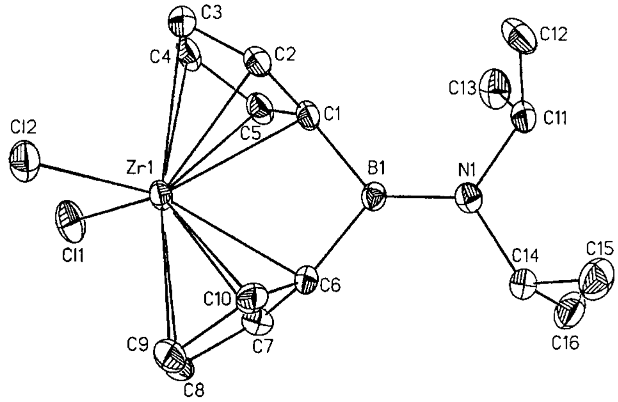


Figure 1. ORTEP view of **8b**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): B−C(1), 1.578(6); B−C(6), 1.584(6); ZrCp(c), 2.20; Cp/Cp, 65.5; Cp(c)−Zr−Cp(c), 119.6, Cl(1)−Zr−Cl(2), 97.9; C(1)−B−C(6), 103.9(3).

Encouraged by this facile synthesis, we attempted a similar preparation of **4b**. The reaction of indenyllithium with $(i\text{-}Pr)_2NBCl_2$ afforded a quantitative yield of bis(indenyl)diisopropylaminoborane **12** as a mixture of double-bond isomers. Reaction of **12** with LDA followed by $ZrCl_4$ gave **4b** as a mixture of isomers in the ratio of 4:6. The minor isomer, subsequently identified as *meso*, could be isolated in 14% yield by repeated recrystallization from toluene. The desired *rac* isomer was obtained by an adaption of the aminolysis procedure used by Jordan et al. for stereoselective synthesis of pure *rac*-**1b**.[18] Reaction of **12** with $Zr(NMe_2)_4$ in toluene at 65 °C for 2 h afforded *rac*-**13** containing only 13% of the *meso* isomer. Recrystallization from toluene gave pure *rac*-**13** as red crystals in 33% yield. Reaction of **13** with TMSCl followed by recrystallization afforded pure *rac*-**4b** in 83% yield. The molecular structure of **4b** is illustrated in Figure 2.[19]

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(16) Experimental procedures: (a) Bis(cyclopentadienyl) *N*,*N*-diisopropylaminoborane (**11**). A solution of lithium cyclopentadienide (0.31 g, 2.1 mmol) in THF (10 mL) was added dropwise at −78 °C to a solution of diisopropylaminoboron dichloride (0.39 g, 2.1 mmol) in THF (5 mL) at −78 °C. The mixture was slowly warmed and stirred 15 h at room temperature to give a red solution. After solvent removal, the residue was extracted with pentane (3×), and combined extracts were filtered. Solvent was then removed to give product (0.55 g, 100%) as a yellow syrup: ^1H NMR spectrum was rather complicated, which suggested the product was a mixture of isomers. ^{11}B NMR (115 MHz, C_6D_6): δ 39.8 (major), 30.4 (minor). MS (EI, *m*/*e* (intensity)): 241 (M^+, 47), 226 (40), 176 (16), 93 (100). (b) *N*,*N*-Diisopropylaminoboranediyl bis(1-cyclopentadienyl) zirconium dichloride (**8b**). A solution of LDA (6.93 mmol) in ether (10 mL) was added to a solution of **11** (0.71 g, 2.95 mmol) in Et_2O (15 mL) at −78 °C. The mixture was warmed and stirred for 2 h at room temperature to give a slightly turbid solution. The solution was then added to a suspension of $ZrCl_4$ (0.69 g, 2.95 mmol) in Et_2O (15 mL) at −78 °C. The resulting mixture was warmed and stirred 15 h at room temperature to give a yellowish suspension. After solvent was removed, residue was extracted with toluene and the extracts were filtered. The toluene solution was concentrated and cooled to −78 °C to give product (0.50 g, 38%) as colorless crystals: Mp = 222 °C (dec). ^1H NMR (400 MHz, $CDCl_3$): δ 1.32 (d, 12H, J = 7.0 Hz), 2.92 (m, 2H), 5.65 (t, 4H, J = 2.4 Hz), 6.80 (t, 4H, J = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 49.6, 111.4, 125.7. ^{11}B NMR (115 MHz, $CDCl_3$): δ 37.6. HRMS (EI) Calcd for $C_{16}H_{22}{}^{11}B^{35}Cl_2NZr$: 399.0269, found 399.0272. Anal. Calcd for $C_{16}H_{22}BCl_2NZr$: C, 47.88; H, 5.49; N, 3.49. Found: C, 46.95; H, 5.44; N, 3.12. Single crystals suitable for X-ray diffraction analysis were grown from a mixed solvent of CH_2Cl_2 and hexane. (c) Bis(1-indenyl) *N*,*N*-diisopropylaminoborane (**12**). A solution of lithium indenide (1.50 g, 12.3 mmol) in THF (40 mL) at −78 °C was added dropwise to a solution of diisopropylaminoboron dichloride (1.10 g, 6.0 mmol) in THF (10 mL) at −78 °C. The mixture was slowly warmed and stirred 15 h at room temperature to give a red solution. After solvent removal, residue was extracted with CH_2Cl_2 (3×), and the extracts were filtered. Removal of solvent gave product (2.12 g, 100%) as a white solid: ^1H NMR spectrum was very complicated, which indicated product as a mixture of double isomers. ^{11}B NMR (115 MHz, C_6D_6): δ 41.4. MS (EI, *m*/*e* (intensity)): 341 (M^+, 8), 226 (100). HRMS (EI), Calcd for $C_{24}H_{28}{}^{11}BN$: 341.2315, found 341.2310. (d) *meso*-*N*,*N*-Diisopropylaminoboranediyl bis(1-indenyl) zirconium dichloride (*meso*-**4b**). A solution of LDA (2.62 mmol) in ether (8 mL) was added to a suspension of **12** (0.39 g, 1.41 mmol) in Et_2O (10 mL) at −78 °C. The mixture was warmed and stirred 15 h at room temperature to give an orange suspension. After solvent was removed, the residue was extracted with toluene and filtered. Solvent was then removed to give an orange solid, which consists mostly of a mixture of two stereoisomers (*rac*/*meso*, ca. 6:4). Repeated recrystallization (3×) from toluene at −78 °C gave the pure *meso* isomer (0.08 g, 14%) as an orange solid: Mp = 250−254 °C (dec). ^1H NMR (500 MHz, $CDCl_3$): δ 1.54 (d, 6H, J = 6.6 Hz), 1.57 (d, 6H, J = 6.8 Hz), 4.27 (m, 2H, NCH), 5.91 (d, 2H, J = 3.0 Hz), 6.9 (m, 4H), 7.17 (t, 2H, J = 7.6 Hz), 7.31 (dd, 2H, J = 8.3, 3.6 Hz), 7.53 (d, 2H, J = 8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.7, 25.0 (NCH*CH*$_3$), 49.7, 100.2 (BC), 115.7, 117.2, 125.2, 125.3, 125.6, 125.9, 126.5, 131.4. ^{11}B NMR (115 MHz, $CDCl_3$): δ 39.5. HRMS (EI) Calcd for $C_{24}H_{26}{}^{11}B^{35}Cl_2Zr$: 499.0582, found 499.0606. (e) *rac*-Bis(dimethylamido)-*N*,*N*-diisopropylaminoboranediyl bis(1-indenyl) zirconium (**13**). Toluene (15 mL) was added to a mixture of **12** (1.01 g, 2.96 mmol) and $Zr(NMe_2)_4$ (0.79 g, 2.96 mmol). The resulting solution was heated to 65 °C and stirred for 2 h to give a bright red solution. The reaction vessel was open to the manifold with a moderate N_2 flow. ^1H NMR spectroscopic analysis of an aliquot showed that the product consists of two isomers with a ratio of 6.7:1. The solution was filtered, concentrated, and cooled to −78 °C to give the pure *rac* isomer (0.50 g, 33%) as red crystals. The structure was confirmed by X-ray diffraction analysis on single crystals grown from toluene/hexane at −20 °C. Mp = 220 °C (dec). ^1H NMR (500 MHz, C_6D_6): δ 1.20 (d, 6H, J = 6.8 Hz), 1.27 (d, 6H, J = 6.6 Hz), 2.61 (s, 12H), 3.86 (m, 2H), 6.04 (d, 2H, J = 2.9 Hz), 6.74 (m, 4H), 7.00 (t, 2H, J = 7.6 Hz), 7.37 (dd, 2H, J = 8.5, 0.9 Hz), 7.52 (d, 2H, J = 8.5 Hz). ^{13}C NMR (90 MHz, C_6D_6): δ 24.6, 24.9, 47.9 (NCH_3), 49.6, 105.6, 112.4, 123.1, 123.2, 124.0, 124.2, 126.3, 129.1. ^{11}B NMR (115 MHz, C_6D_6): δ 40.8. HRMS (EI) Calcd for $C_{28}H_{38}{}^{11}BN_3Zr$: 517.2206, found 517.2217. (f) *rac*-*N*,*N*-Diisopropylaminoboranediyl bis(1-indenyl) zirconium dichloride (*rac*-**4b**). TMSCl (2.0 mL, 15.76 mmol) was added to a solution of **13** (0.50 g, 0.96 mmol) in toluene (35 mL) at room temperature. The solution was stirred for 8 h at room temperature to give an orange suspension. Solvent was removed, and residue was washed with pentane (2×) to give the desired product (0.40 g, 83%) as an orange powder. Single crystals suitable for X-ray structural analysis were grown from mixed solvents of CH_2Cl_2 and hexane at −20 °C. Mp = 242 °C (dec). ^1H NMR (500 MHz, $CDCl_3$): δ 1.50 (d, 6H, J = 6.8 Hz), 1.55 (d, 6H, J = 6.6 Hz), 4.24 (hept, 2H, J = 7.7 Hz), 5.79 (d, 2H, J = 3.0 Hz), 6.80 (dd, 2H, J = 3.2, 0.7 Hz), 7.07 (t, 2H, J = 7.6 Hz), 7.28 (dd, 2H, J = 7.0, 0.7 Hz), 7.38 (t, 2H, J = 8.0 Hz), 7.58 (d, 2H, J = 8.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.7, 25.0, 49.6, 98.4 (BC), 113.1, 114.1, 122.0, 123.0, 125.8, 126.4, 127.2, 131.9. ^{11}B NMR (115 MHz, $CDCl_3$): δ 39.2. HRMS (EI) Calcd for $C_{24}H_{26}{}^{11}B^{35}Cl_2NZr$: 499.0582, found 499.0606. Anal. Calcd for $C_{24}H_{26}BNCl_2Zr$: C, 57.48; H, 5.19; N, 2.79. Found: C, 57.46; H, 5.32; N, 2.68.

(17) Crystal data for $C_{16}H_{22}BCl_2NZr$ (**8b**): monoclinic, $P2_1/n$, a = 12.1342(2) Å, b = 10.4836(1) Å, c = 14.3648(2) Å, β = 107.9462(5)°, V = 1738.44(4) Å^3, Z = 4, D_c = 1.553 g cm^{-3}, T = 158(2) K, λ(Mo Kα) = 0.710 73 Å. Data were collected on a Siemens SMART CCD. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0555, wR_2 = 0.1071. R indices (all data): R_1 = 0.0711, wR_2 = 0.1123.

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(19) Crystal data for $C_{24}H_{26}BCl_2NZr$ (**4b**): triclinic, $P\bar{1}$, a = 8.5588(1) Å, b = 10.3633(2) Å, c = 13.9398(2) Å, α = 100.919(1)°, β = 94.946(1)°, γ = 108.19(1)°, V = 1139.26(3) Å^3, Z = 2, D_c = 1.462 g cm^{-3}, T = 158(2) K, λ(Mo Kα) = 0.710 73 Å. Data were collected on a Siemens SMART CCD. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0217, wR_2 = 0.0575. R indices (all data): R_1 = 0.0238, wR_2 = 0.0591.

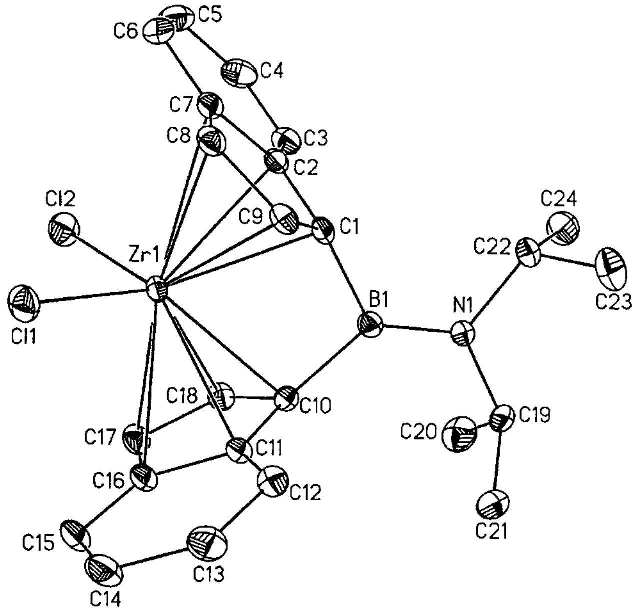

Figure 2. ORTEP view of **4b**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): B−C(1), 1.586 (2); B−C(10), 1.589 (2); Zr−Cp(c), 2.216; Cp/Cp, 66.8; C(1)−B−C(10), 104.9 (1).

The crystal structure of **4b** closely resembles that of **2b** in that both compounds have a C_2-symmetrically bridged bis indenyl system about the $ZrCl_2$ group. The most important difference is the larger angle between the two coordinated rings, 67° for **4b** vs 62° for **2b**, due to the smaller size of the bridging atom. There is a consequent increase in the accessibility of the $ZrCl_2$ group, which is likely to affect the relative catalytic activities. The structures of **4b** and **8b** show very short B−N distances (1.38 Å), which indicates strong B−N π-bonding. This trigonal π-bonding at boron contrasts with the quarternary coordinate bonding shown by **6b**. However the geometries of the remaining parts of **6b** and **8b** are remarkably similar. The dihedral angles between coordinated Cp rings (65.4° for **8b** and 65.8° for **6b**) and the corresponding CBC angles (104° for **8b** and 101° for **6b**) are nearly identical. This close structural similarity suggests that any chemical differences must be due to different bonding at boron.

When activated by excess MAO as a cocatalyst, complexes **8b** and **4b** are highly active olefin polymerization catalysts. Under typical conditions **8b** and **4b** effect the copolymerization of mixtures of 1-octene/ethylene with activities of 0.7×10^6 g/(mol Zr·atm) and 17×10^6 g/(mol Zr·atm), respectively.[20] Complexes **8b** and **4b** effect the polymerization of propylene with activities of 0.64×10^5/(mol Zr·atm) and 2.2×10^6 g/(mol Zr·atm), respectively.[21] The polypropylene resulting from polymerization by **4b** had mp = 113 °C with triad ratios of 82:12:6 (mm/mr/rr) and thus had a modest isotacticity.[22] These catalytic activities are in the range shown by Me_2Si-bridged zirconocenes.[1,23,24] It seems likely that modifications of the indenyl moieties of **4** will give rise to even more active and selective catalysts.[24] Further research on borane-bridged metallocenes is under way in our laboratory.

Acknowledgment. This work was supported by the Dow Chemical Company and the National Science Foundation. We are grateful to the Dow Chemical Company for running the polymerization experiments.

Supporting Information Available: X-ray crystallographic data of the structures of compounds of **4b** and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) For conditions of ethylene polymerization see: Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 1363.

(21) Conditions for the propylene polymerization were similar except the pressure was 23.3 atm and the temperature was 70 °C.

(22) The isotacticity of the polypropylene must derive from the diastereoselectivity of the catalyst. This result implies that the chiral aminoboranediyl bridge of **4b** remains intact in the active form of the catalyst. See ref 3a.

(23) Precise comparison is not possible since the literature polymerizations were run under different conditions. However, see footnote 24c.

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