Boratabenzene Analogues of the Constrained Geometry Polymerization Catalysts

Arthur J. Ashe, III,* Xinggao Fang, and Jeff W. Kampf

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

*Summary: (4-Dimethylsilyl-tert-butylamido)-N,N-diisopropyl-1-aminoboratabenzene ZrCl₂ (**7a**) and TiCl₂ (**7b**) complexes have been prepared. When activated by excess methylaluminoxane, **7a** and **7b** are catalysts for the polymerization of ethylene.*

Cyclopentadienyl derivatives of the group 4 metals have found important uses as homogeneous catalysts for olefin polymerization[1] and for enantioselective organic synthesis.[2] The most active and selective catalysts are those with highly constrained metal sites. The Brintzinger-type *ansa*-metallocenes, e.g. **1**,[1-4] have been most thoroughly investigated, while the "constrained geometry" catalysts based on the η^5-,η^1-$C_5Me_4SiMe_2NR$ ligand, e.g. **2**,[1e,5-7] are commercially important olefin polymerization catalysts.[8a] Recently several group 4 metal complexes which employ anionic heterocyclic ligands in place of cyclopentadienyl have been found to have catalytic activity.[9-11] For example, catalysts derived from bis(*N,N*-diisopropyl-1-aminoboratabenzene)-zirconium dichloride (**3**) and Cp_2ZrCl_2 have nearly identical activity toward polymerization of ethylene.[9a] Thus an investigation of boratabenzene complexes

analogous to **1** and **2** seems desirable. We have previously reported on bridged bis(boratabenzene)zirconium complexes **4** and **5**.[12] The recent report on bridged phospholyl dimethylsilyl-*tert*-butylamido titanium dichloride **6**[13] prompts us to report our work on the boratabenzene complexes **7** which are analogous to **2** and **6**.

1a, M = Zr
1b, M = Ti

2

3a

4a, E = CH₂CH₂
5a, E = SiMe₂

6b

7a, 7b
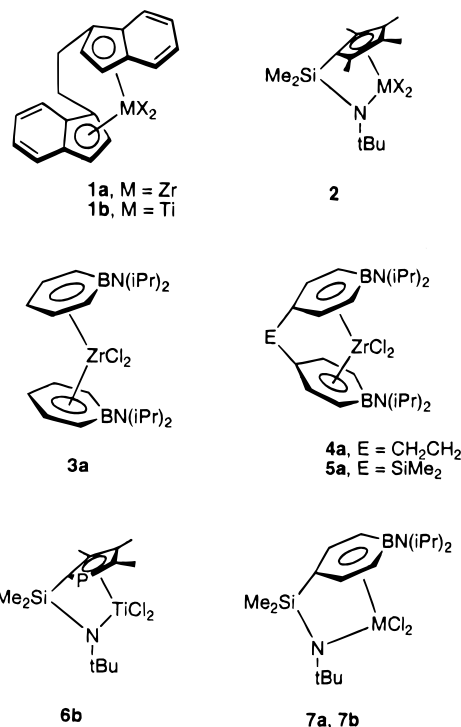
The syntheses of **7a** and **7b**, illustrated in Scheme 1, are analogous to that used to prepare **5a**.[14] Silylation of lithium *N,N*-diisopropyl-1-aminoboratabenzene with excess Me_2SiCl_2 gave 98% of **9**.[12] Treating **9** with excess

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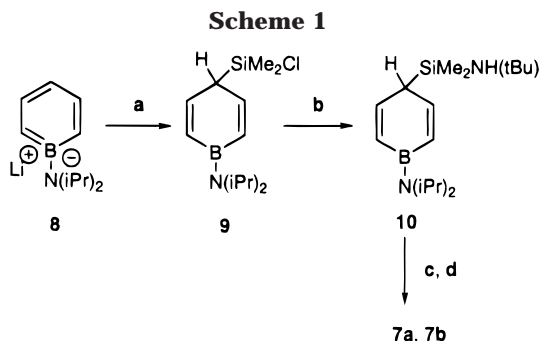
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Scheme 1

Key: **a**, Me$_2$SiCl$_2$; **b**, (tBu)NH$_2$; **c**, tBuLi; **d**, ZrCl$_4$ or TiCl$_4$
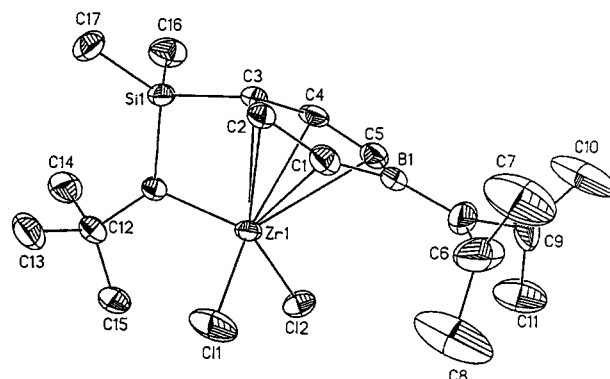

Figure 1. Solid-state structure of **7a**. Selected distances (Å) and angles (deg): ZrB, 2.877(4); ZrC(1), 2.691(3); ZrC-(2), 2.513(3); ZrC(3), 2.412(3); ZrC(4), 2.663(3); ZrC(5), 2.525(3); BC(11), 1.549(5); BC(5), 1.521(6); BN(1), 1.412-(5); C(3)Si, 1.872(3); SiN(2), 1.748(3); ZrPL(C(1,2,3,4,5)), 2.140; ZrCl(1), 2.4004(10); ZrCl(2), 2.3925(8); C(3)Si/PLC-(1,2,3,4,5), 149.8; C(3)SiN(2), 92.35(13); SiN(2)Zr, 106.62-(12).

tert-butylamine gave the amido ligand **10**. Reaction of **10** in ether with 2 equiv of *tert*-butyllithium afforded a dark red solution of the corresponding dianion, which was added to ZrCl$_4$ to afford a 26% yield of **7a** as yellow crystals. In the same manner reaction with TiCl$_4$ gave the brown **7b** in 32% yield.

Crystals of **7a** and **7b** have been characterized by ^{1}H, ^{11}B, and ^{13}C NMR spectroscopies, high-resolution mass spectroscopy, and elemental analysis. The zirconium complex **7a** has been further characterized by X-ray diffraction.[15] The molecular structure of **7a**, illustrated

(14) Experimental procedures and characterization of new compounds are as follows: (a) **10**: *tert*-Butylamine (0.46 mL, 4.44 mol) was added to a solution of **9** (0.30 g, 1.11 mmol) in 10 mL of THF at −78 °C. The mixture was allowed to warm to 25 °C for 12 h. The solvent was removed under reduced pressure. Pentane (15 mL) was added, and the resulting suspension was filtered through a sintered glass frit. The precipitate was washed with pentane (5 mL), and solvent was removed from the combined filtrate to afford 0.34 g (100%) of **10** as a yellow oil. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.12 (s, 6H, SiMe$_2$), 1.08 (s, 9H, t-Bu); 1.22 (d, J = 6.9 Hz, 12H, i-Pr), 3.14 (t, J = 4.1 Hz, 1H, H(4)), 3.81 (m, 2H, NCH), 6.62 (d, J = 12.4 Hz, 2H, H(2, 6), 7.07 (dd, J = 12.4, 3.8 Hz, 2H, H(3, 5)). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 0.4 (SiMe$_2$); 24.0 (Me), 24.3 (Me), 34.4 (Me), 46.7, 47.3, 49.4 (t-Bu), 130.3 (br, C(2, 6)), 148.0 (C(3, 5)). ^{11}B NMR (115.5 MHz, C$_6$D$_6$): δ 31.9 HRMS (CI with NH$_3$): calcd for C$_{17}$H$_{35}^{11}$BN$_2$Si (MH$^+$), 307.2741; found, 307.2725. (b) **7a**: A 1.7 M pentane soluton of *tert*-butyllithium (6.30 mL, 10.7 mmol) was added dropwise to a solution of **10** (1.64 g, 5.36 mmol) in 20 mL of ether at −78 °C. The mixture was allowed to warm to 25 °C with stirring over 3 h. The resulting red solution was cooled to −78 °C and added via cannula to a suspension of ZrCl$_4$ (1.28 g, 5.36 mmol) in ether at −78 °C. The reaction mixture was allowed to warm to 25 °C with stirring for 12 h. The solvent was removed under reduced pressure. The residue was extracted with pentane (4 × 7 mL), and the extracts were filtered. Concentration of the filtrate to a volume of about 15 mL followed by cooling to −78 °C gave the crude product as a yellow solid. Recrystallization from pentane afforded 0.66 g (26%) of **7a** as yellow crystals, mp 200−200.5 °C. ^{1}H NMR (360 MHz, C$_6$D$_6$): δ 0.26 (s, 6H, SiMe$_2$), 1.21 (d, J = 6.8 Hz, 6H, i-Pr), 1.25 (d, J = 6.8 Hz, 6H, i-Pr′), 1.35 (s, 9H, t-Bu), 3.69 (m, 2H, NCH), 6.73 (d, J = 11.2 Hz, 2H, H(2,6)), 7.08 (d, J = 11.3 Hz, 2H, H(3, 5)). ^{11}B NMR (115.5 MHz, C$_6$D$_6$): δ 29.2. ^{13}C NMR (90 MHz, C$_6$D$_6$, T = 25 °C): δ 0.4 (SiMe$_2$), 22.8 (i-Pr), 23.8 (i-Pr′), 33.3 (t-Bu), 47.2, 58.0, 95.7, 130.3 (br, C(2, 6)), 144.4 (C(3, 5)). The signals at δ 22.8, 23.8 coalesce at 52 °C to δ 23.1. HRMS (EI): calcd for C$_{16}$H$_{30}^{11}$B$_{35}$Cl$_2$N$_2$SiZr (M − CH$_3$), 449.0695; found, 449.0697. Anal. Calcd for C$_{17}$H$_{33}$BCl$_2$N$_2$SiZr: C, 43.68; H, 7.28; N, 6.00. Found: C, 44.00; H, 7.39; N, 5.64. (c) In the same manner as above **7b** was prepared in 32% yield as brownish crystals, mp 123−125 °C. ^{1}H NMR (360 MHz, C$_6$D$_6$): δ 0.17 (s, 6H, SiMe$_2$), 1.15 (d, J = 6.8 Hz, 6H, i-Pr), 1.20 (d, J = 6.7 Hz, 6H, i-Pr′), 3.64 (m, 2H, NCH), 7.04 (d, J = 10.3 Hz, 2H), 7.12 (d, J = 10.1 Hz, 2H). ^{11}B NMR (115.5 MHz, C$_6$D$_6$): δ 28.6. ^{13}C NMR (90.5 MHz, C$_6$D$_6$, T = 25 °C): δ −0.6 (SiMe$_2$), 22.9 (i-Pr), 23.1 (i-Pr′), 32.4 (t-Bu), 47.3 (NCH), 63.8 (NC), 102.5 (C(4)), 139.6 (br, C(2, 6)), 142.3 (C(3, 5)). At 65 °C the signals at δ 22.9, 23.1 coalesce to δ 23.0. HRMS (EI): calcd for C$_{16}$H$_{30}^{11}$B$_{35}$Cl$_2$N$_2$-SiTi (M − CH$_3$), 422.1362; found, 422.1357. Anal. Calcd for C$_{17}$H$_{33}$-BCl$_2$N$_2$SiTi: C, 48.38; H, 7.82; N, 6.64. Found: C, 48.64; H, 7.81; N, 6.32.

(15) Crystal data for **7d**: C$_{17}$H$_{34}$BCl$_2$N$_2$SiZr, monoclinic, $P2(1)/c$, a = 8.309(2) Å, b = 12.7608(11) Å, c = 21.394(2) Å, β = 92.363(9)°, V = 2266.4(5) Å^3, Z = 4, D_c = 1.370 g cm^{-3}, T = 178(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$_1$ = 0.0377, wR$_2$ = 0.0952. R indices (all data): R$_1$ = 0.0518, wR$_2$ = 0.0999. GOF on F^2 = 1.023.

in Figure 1, generally resembles the constrained geometry complexes **2** and **6b**. These compounds exhibit a pseudo-tetrahedral geometry about the metal consisting of the π-bound ring with its *ansa*-dimethylsilyl-*tert*-butylamido group and the two terminal chlorine atoms. The bond angles and bond distances of the corresponding bridge atoms are nearly identical for **7a** and **2a**,[7a,8] whereas the geometry of the *N,N*-diisopropyl-1-aminoboratabenzene group closely resembles that of **3a**. The corresponding intra-ring C−C and B−C distances vary by no more than 0.02 Å, indicating that bridging exerts little perturbation on the ring. In contrast the Zr−ring atom distances average 0.05 Å closer for **7a** than for **2a**.

As had been previously noted for other *N,N*-diisopropyl-1-aminoboratabenzene zirconium complexes[9a,12] the Zr atom of **7a** is slip distorted away from the B atom so that the Zr−B distance (2.877(4) Å) is rather long for strong B−Zr bonding. Therefore the Zr atom is η^5-bound to the ring carbon atoms which are coplanar. The B atom is displaced out of this plane away from Zr by 0.09 Å. The sp^2-hybridized boron (sum of bond angles, 359.8°) is π-bound to the pendant sp^2-hybridized nitrogen (sum of bond angles, 360.1°). The short B−N bond (1.412(5) Å) is consistent with B−N π bonding. The B−N π bonding is independently indicated by the sizable barrier to rotation about this bond. At 25 °C the ^{13}C NMR spectrum shows two peaks (δ 22.8, 23.8) for the pairs of diastereotopic isopropyl methyl groups. On heating

(16) Ethylene/Octene Copolymerization: A 2 L reactor is charged with mixed alkane solvent (Isopar-E) and 1-octene. Hydrogen is added by differential pressure expansion from a 75 mL addition tank from 300 psig (2.1 MPa) to near 275 psig (1.9 MPa). The reactor and contents are then heated to and maintained at 140 °C, the polymerization temperature, and saturated with ethylene at 500 psig (3.4 MPa). In an inert atmosphere glovebox the appropriate quantities of metal complex and methylalumoxane (MAO) cocatalyst solutions (0.00500 and 1.5 M, respectively, in toluene) are combined, and this catalyst solution is transferred to a catalyst addition tank. The polymerization is initiated by injecting this catalyst solution into the contents of the reactor. The polymerization conditions are maintained for the run time with ethylene provided on demand at 500 psig (3.4 MPa). Additional catalyst solution prepared and transferred in the same way may be added to the reactor throughout the course of the reaction. The polymer solution is removed from the reactor and combined with a hindered phenol antioxidant and isopropyl alcohol. Volatile components are removed from the polymer in a vacuum oven set at 140 °C for about 20 h. Results are contained in Table 1.

**Table 1. Summary of Ethylene/1-Octene
Polymerization Data for 7a and 7b**

complex (μmol)	polymer yield (g)	efficiency (g/μmol)	octene (mol %)
7a (12.0)	20.8	1.73	1.1
7b (3.0)	21.3	7.1	0.8

to 52 °C, these peaks coalesce to a single peak (δ 23.1). A barrier of 16.1 ± 0.5 kmol/mol is indicated, while the Ti complex **7b** shows a barrier of 17.2 ± 0.5 kcal/mol.

It was found that on activation by a 300 M excess of methylaluminoxane (MAO) that **7a** and **7b** are active in the polymerization of mixtures of ethylene and 1-octene.[16] See Table 1. The activity of **7b** is 4 times that of **7a**. Cp-based constrained geometry catalysts also generally show higher activities for the titanium over the zirconium analogues.[1e,8] It is significant that the polyethylene derived for **7a** and **7b** had incorporated only about 1 mol % of octene. The Cp-based constrained

geometry catalysts give ethylene−octene copoloymers with substantially higher octene incorporation.[1e,7,17] We propose that the lower polymerization activity of **7b** toward α-olefins may be due to steric hindrance. The bridging in the 4-position forces the diisopropylamino group to occupy the central position above the middle of the metal wedge. It has been suggested that steric hindrance at this point is particularly effective at blocking insertion of α-olefins into the polymer chains.[1a] Bridging at another ring position would push the boron substituents to the side and might result in more active catalysts.

Supporting Information Available: Tables of crystallographic data for **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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