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Aminoboratabenzene Derivatives of Zirconium: A New Class of Olefin Polymerization Catalysts

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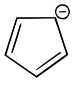
Cationic bent metallocene derivatives of the early transition and lanthanide metals are finding important uses as homogeneous catalysts for olefin polymerization.[1] Intense research efforts have centered on the design and syntheses of sterically modified metallocenes, some of which are highly stereoselective catalysts. Much less attention has been directed at the electronic modification of the catalytically active site by the substitution of heterocyclic ligands in place of cyclopentadienide (Cp, **1**).[2] Recently, the Bercaw[3] and Bazan[4] groups have prepared several early transition metal complexes of the dianionic (diisopropylamino)borollide (**2**). These complexes are capable of heterolytic bond activation and are more reactive toward certain substrates than their isoelectronic cyclopentadienide analogs. Thus, exploration of the chemistry of the early transition metal complexes of the corresponding monoanionic boratabenzene[5,6] (**3**) seems attractive. Surprisingly, the extensive prior work on boratabenzenes includes only complexes with later transition metals.[7] We report here on the synthesis of zirconium (diisopropylamino)borabenzene complexes and on their use in olefin polymerization.



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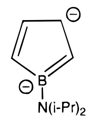

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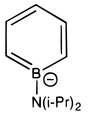

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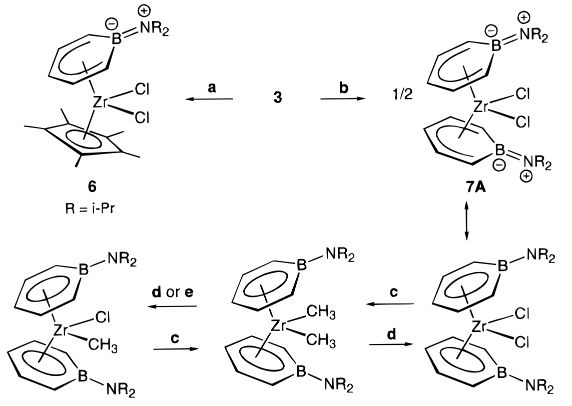
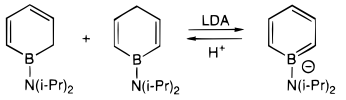
The reaction of 1-(*N*,*N*-diisopropylamino)boracyclohexa-2,5-diene (**4**) or its conjugated isomer **5** with 1 equiv of LDA in ether produces the corresponding boratabenzene lithium **3**.[8] Subsequent reaction of **3** with Cp*ZrCl$_3$ (Cp* = C$_5$Me$_5$) in ether affords, after pentane extraction, 61% of a yellow air-sensitive solid, which by ^{1}H, ^{11}B, and ^{13}C NMR spectroscopy, high-resolution mass spectroscopy, and elemental analysis is consistent with formulation as Cp*[C$_5$H$_5$BN(*i*-Pr)$_2$]ZrCl$_2$ (**6**, Scheme 1). In the same manner, the reaction of 2 equiv of **3** with ZrCl$_4$ affords red crystals of [C$_5$H$_5$BN(*i*-Pr)$_2$]$_2$ZrCl$_2$ (**7**) in 57% yield. Slow recrystallization from pentane gave crystals suitable for X-ray diffraction.[9]

Scheme 1^a



^{a} (a) Cp*ZrCl$_3$; (b) ZrCl$_4$; (c) CH$_3$Li; (d) CD$_2$Cl$_2$/$h\nu$; (e) HNMe$_3$Cl.



5 **4** **3**

The molecular structure of **7**, illustrated in Figure 1, generally resembles that of a bent metallocene. There is a crystallographically imposed C_2 axis bisecting the ClZrCl* angle, while the N(*i*-Pr)$_2$ groups are rotated to the side, pointing away from the metallocene wedge. The Zr is slip-distorted toward C(3) away from B so that the B−Zr distance (2.98 Å) is too long for effective bonding. Inspection of Zr−C distances (*i.e.*, Zr−C(1) = 2.693(5) Å; Zr−C(2) = 2.563(5) Å; Zr−C(3) = 2.483(5) Å) reveals increasing interaction further from B, to a point that the ligand adopts a slight chair-like geometry (see inset of Figure 1). Therefore, each boratabenzene ligand is only η^5-coordinated through the pentadienyl fragment of the ring in a manner similar to that of open metallocenes.[10] The very short distance between the boron and the sp^2-hybridized nitrogen (1.396(6) Å) shows that the B−N π-bonding is strong.[11] The combined effect of these structural features is that resonance contribution **7A** dominates the electronic structure of **7**.

Strong B−N π-bonding is independently indicated by the high rotational barrier about the B−N bond. The slow B−N rotation at 25 °C makes pairs of *i*-Pr methyl groups diastereotopic. On heating **7** in C$_6$D$_6$ to 62 °C, the ^{13}C NMR signals (δ 23.56, 23.497 ppm) coalesce, indicating a barrier to B−N rotation of $\Delta G^{\ddagger} = 18.2 \pm 0.5$ kcal/mol.[12] Although there are no structural data for **6**, the identical B−N rotation barrier ($\Delta G^{\ddagger} = 17.7 \pm$

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[1] For recent reviews, see: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. A., Eds.; Springer-Verlag: Berlin, 1995. (c) Thayer, A. M. *Chem. Eng. News* **1995**, *73* (37), 15.

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[9] Crystal data for ZrC$_{22}$H$_{38}$B$_2$Cl$_2$N$_2$: space group *Pbnc* (No. 60) with $a = 27.816(7)$ Å, $b = 6.924(2)$ Å, $c = 12.772(2)$ Å, $Z = 4$, FW = 514.3, and $\rho = 1.39$ g/cm^3. A total of 2490 reflections (h, k, l) were collected in the range $4° < 2\theta < 50°$ with the 1319 having $I > 3.00\sigma(I)$ being used in the structure refinement by full-matrix least-squares techniques (132 variables) using the TEXSAN crystallographic package from Molecular Structures Corporation. Final $R_1 = 0.040$, $R_2 = 0.042$.

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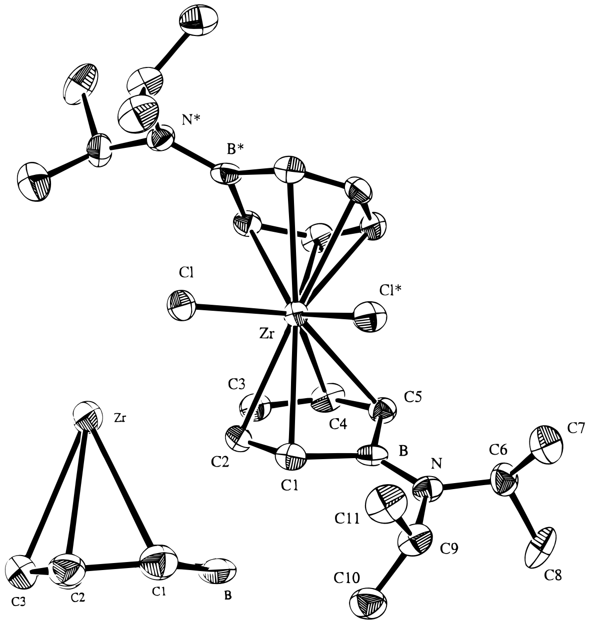

Figure 1. ORTEP view of **7**, showing the atom-numbering scheme. Hydrogen atoms were omitted for clarity. Selected bond distances (Å): Zr−C(4), 2.582(4); Zr−C(5), 2.649(4); N−B, 1.396(6); C(1)−B, 1.549(7); C(5)−B, 1.554(6). The inset shows a profile view of one of the rings juxtaposed to the Zr.

0.5 kcal/mol) and near identical ^{11}B NMR chemical shift to that of **7** suggest the same coordination of its boratabenzene moiety. We note here that all structurally characterized late transition metal−boratabenzene complexes are η^6-coordinated, even though metal bonding is consistently weaker to boron than to carbon.[7b,13] We suggest that the distortion toward η^5-binding in **6** and **7** is due to the high electron demand of Zr(IV), which prefers coordination to the more electron rich carbons. The steric consequence of this electronic preference is to confine the boron with its large pendant group to the open entrance of the metallocene wedge.

Alkylation of zirconium proceeds without complications. Adding 2 equiv of methyllithium to **7** in ether affords 83% of $[C_5H_5BN(i\text{-}Pr)_2]_2ZrMe_2$ (**8**) as a yellow oil, which slowly crystallized on standing. Photolysis of **8** in CD_2Cl_2 initially gives the monomethyl chloride **9**, which is ultimately converted to **7** upon further irradiation. Trimethylammonium chloride with **8** in CH_2Cl_2 also provides **9** along with methane and the boracyclohexadienes **4** and **5**. The latter two products appear to derive from ring protonation followed by decomplexation. The unsymmetrical **9** is recognizable from its first-order ^{1}H NMR spectrum, which shows signals for five nonequivalent boratabenzene ring protons. Reaction of **9** with methyllithium regenerates **8**.

Addition of a large excess of methylaluminoxane (MAO)[14] to **6** and **7** results in a color change to red for **6** and to intense magenta in the case of **7**. These solutions polymerize ethylene (1 atm and 23 °C) with activities of 52 kg of PE/(h [Zr] mol) for **6** and 105 kg of PE/(h [Zr] mol) for **7**.[15] Since reactivity in these reactions is sensitive to a variety of interrelated variables such as monomer quality and pressure, reaction temperature, MAO quality, etc., we standardized our protocol using Cp_2ZrCl_2, obtaining an activity of 90 kg of PE/(h [Zr] mol). It is most likely that MAO serves its standard role, namely, methylation at zirconium followed by methyl anion abstraction and generation of a highly electrophilic zirconium cation.

In summary, boratabenzene zirconium(IV) derivatives analogous to Cp_2ZrCl_2 are easily prepared and undergo similar functional group manipulation. The pronounced structural deviation to open pentadienyl-like bonding observed in **7** is likely to be a general feature, especially for situations where the metal is in its highest oxidation state and a strong π donor is attached to boron. The observation that **6** and **7** have similar polymerization activities to Cp_2ZrCl_2 is highly significant. Existing synthetic methodology allows preparation of both C-substituted boratabenzene[13,16] and boratabenzenes in which B is substituted with different donor character.[17] Therefore, boratabenzene analogs of sterically constrained, more catalytically active metallocenes should be readily obtainable. Moreover, boron interacts strongly with its exocyclic substituents,[18] implying that electron density and consequent reactivity at the metal center could be modulated in a manner not readily achievable using cyclopentadienide ligands. We believe that novel electrophilic boratabenzene−early transition metal complexes will find innovative applications that complement the function of cyclopentadienide-based reagents.

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Supporting Information Available: Complete experimental details for the preparation of all new compounds and X-ray crystallographic determination of the structure of compound **7** (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(12) Alternative processes involving interconversion of the enantiomeric crystallographic conformations or rotations about C−N bonds must be fast at 62 °C since only single signals are observed for the pairs of atoms C_2−C_4 and C_6−C_9. For comparison, see ref 8.

(13) Maier, G.; Wolf, H.-J.; Boese, R. *Chem. Ber.* **1990**, *123*, 505.

(14) MAO (6.4 wt % Al, density = 0.88 g/mL) was obtained from Akzo Chemicals.

(15) α-Olefins polymerize as well. For example, reaction of **6**/MAO with 1,5-hexadiene produces poly(methylene-1,5-cyclopentane) (M_n = 2200, polydispersity = 1.2; relative to polystyrene) with close to 70% cis linkages. For a comparison to other metallocenes, see: Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91.

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(17) For functional manipulation of related borole complexes, see: (a) Herberich, G. E.; Englert, U.; Hostalek, M.; Laven, R. *Chem. Ber.* **1991**, *124*, 17. (b) For related borepins, see: Ashe, A. J., III; Klein, W.; Rousseau, R. *Organometallics* **1993**, *12*, 3225.

(18) The strength of the boron−metal interaction decreases as the π overlap of boron with its pendant substituent increases. For a detailed discussion, see refs 7a, 8, and 17a.