Intramolecular Nucleophilic Substitution on Coordinated Borabenzenes: A New Entry into Boratabenzene Complexes

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Electrophilic complexes containing boratabenzene ligands[1] are finding applications in olefin polymerization and oligomerization reactions.[2] Most significant is the ability to control the reactivity of boratabenzene catalysts by adjusting the degree of orbital overlap between boron and its exocyclic substituent.[3] Boratabenzene catalysts have appeared with reactivities that complement those observed with standard group 4 metallocenes.[4] Furthermore, while both cyclopentadienyl (Cp) and boratabenzene are formally monoanionic 6π electron donors, boratabenzene is a weaker donor.[5] Isostructural complexes containing boratabenzene instead of Cp therefore have a greater tendency for lower oxidation states and offer altered mechanistic pathways for elementary reactions.[6]

One of the main difficulties in advancing a broader use of boratabenzene complexes in industry[7] and in noncatalytic reactions useful for organic chemistry[8] is the multistep synthesis of the boratabenzene framework.[9] Methods for coordination typically make direct analogy to Cp chemistry, namely, salt metathesis by addition of ligand salts to metal halides.[10] In this paper we report a new type of reaction that gives transition metal−*boratabenzene* complexes directly from neutral *borabenzene*−base adducts.

As shown in Scheme 1, our approach involves the reaction of a neutral borabenzene−base adduct[11] (C_5H_5B−L', **1·L'**, where L' = PMe_3 or Py) with a suitable early transition metal complex.

For example, addition of C_5H_5B−PMe_3 (**1·PMe$_3$**) to Ph_3Sc-$(THF)_2$ provides (C_5H_5B−Ph)$ScPh_2(THF)$ (**2** in eq 1) quantita-
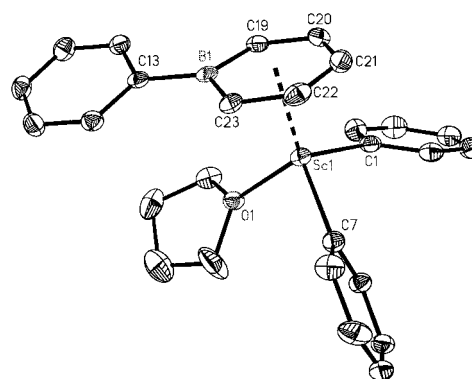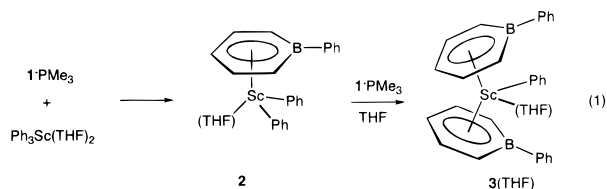

Figure 1. ORTEP view of **2**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms were omitted for clarity.

Scheme 1

1·PMe$_3$ for L' = PMe_3 M = Sc, Zr, Hf
1·Py for L' = Py

tively by ^{1}H NMR spectroscopy. A single-crystal diffraction study of **2** reveals that the molecule can be described as a three-legged piano stool and that it contains a nearly planar boratabenzene ligand (Figure 1). There is a slight slip-distortion of scandium away from boron and toward the more electron-rich carbons of the ring (in Å, average Sc−C_γ = 2.545(3), average Sc−C_β = 2.571(3), Sc−C_α = 2.613(3)). The Sc−C_{ipso} bond distances (2.214(3) and 2.231(3) Å) lie within the range of the sum of their covalent radii.[12]

Repeating the process by addition of 1 equiv of **1·PMe$_3$** to **2** in toluene affords the bis(boratabenzene)scandium complex (**3** in eq 1). In THF, **3** exists as the colorless adduct (C_5H_5B−Ph)$_2$-$ScPh(THF)$, **3(THF)**. Removal of THF by repeated chlorobenzene condensation/evaporation cycles produces green [(C_5H_5B−Ph)$_2$-$ScPh]_2$ (**3$_2$**). The nuclearity and composition of **3$_2$** was confirmed by matching the isotopic distribution obtained by mass spectrometry with calculated values. The reactions of **1·PMe$_3$** with (Me_3-$SiCH_2$)$_3Sc(THF)_2$[13] or ($PhMe_2CCH_2$)$_3Sc(THF)$ are analogous to those described for $Ph_3Sc(THF)_2$ by ^{1}H NMR spectroscopy; however, the resulting products are thermally unstable oils which are difficult to obtain in pure form.

Tetrabenzylzirconium and **1·PMe$_3$** react quickly in C_6D_6 to give (C_5H_5B−CH_2Ph)$Zr(CH_2Ph)_3$ (**4** in eq 2). With group 4 complexes, the pyridine adduct, **1·Py**, gives similar results to **1·PMe$_3$**. The formation of (C_5H_5B−CH_2Ph)$_2Zr(CH_2Ph)_2$ (**5** in eq 2) from **4** and **1·PMe$_3$** is considerably slower, requiring 3 days at room temperature. The molecular structure of **5** was confirmed by single-crystal diffraction and is included in the Supporting Information. Starting with $Hf(CH_2Ph)_4$ and **1·PMe$_3$** one obtains (C_5H_5B−CH_2-

(1)

2   **3(THF)**

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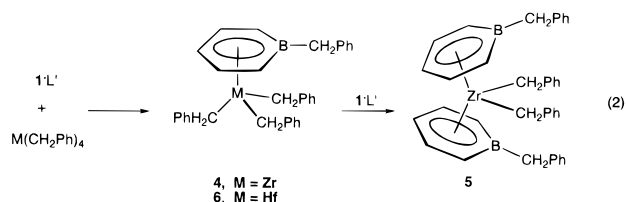
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(2)

4, M = Zr
6, M = Hf

5

Ph)Hf(CH$_2$Ph)$_3$ (**6**) as yellow crystals. Figure 2 shows that **6** is a mononuclear species and a slippage of the metal toward the carbon atoms away from boron ring (in Å, average Hf–C$_\gamma$ = 2.519(3), average Hf–C$_\beta$ = 2.575(3), Hf–C$_\alpha$ = 2.626(3). There is no reaction between **6** and either **1**·PMe$_3$ or **1**·Py.

Reaction of Zr(NMe$_2$)$_4$ with **1**·PMe$_3$ in C$_6$D$_6$ at 80 °C for 12 h gives (C$_5$H$_5$B–NMe$_2$)Zr(NMe$_2$)$_3$ (**7** in eq 3). A second equivalent

(3)

7
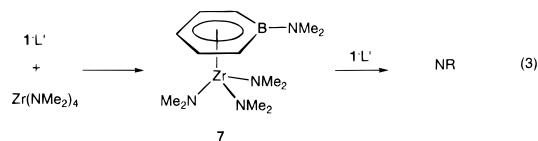
of borabenzene adduct does not react with **7**, even after heating to 80 °C for 48 h. The synthesis of **5** in high yield opens the opportunity to examine for the first time how different activators (i.e., MAO, B(C$_6$F$_5$)$_3$,[14] and [Ph$_3$C][B(C$_6$F$_5$)$_4$][15]) affect the reactivity of the catalytic species. Polymer precipitation is observed for the catalysts **5**/B(C$_6$F$_5$)$_3$ (76 kg PE/(mol Zr·h), [Zr] = 4.8 × 10^{-4} M) and **5**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (250 kg PE/(mol Zr·h), [Zr] = 4.8 × 10^{-4} M), while ethylene oligomers are produced by **5**/MAO (440 kg OE/mol Zr·h), [Zr] = 4.2 × 10^{-4} M, 1000 Al/Zr ratio) upon addition of 1 atm ethylene. Activators therefore control not only the rate of ethylene consumption but also the molecular weight of the resulting products.[16]

In view of the reactivity of Cp*$_2$ScR complexes,[17] our expectation was that the scandium complexes would behave as single component catalysts. However, no reaction was detected when ethylene was added to **3**(THF) or **3**$_2$. It appears that the smaller size and weaker donating abilities of boratabenzene relative to Cp* discourage breakup of **3**$_2$ into active mononuclear species. Addition of 1 atm ethylene to a solution of **3**$_2$ that has been pretreated with H$_2$ results in the production of 1-alkenes (7.4 kg 1-alkenes/(mol Sc·h); [Sc] = 1.75 × 10^{-3} M).

The pathway by which neutral borabenzene converts into the formally monoanionic boratabenzene ligand, in conjunction with the metal ligand exchange is novel and merits examination. The following observations have been made: (a) the reaction is first order in **1** and in the metal complex and proceeds without formation of detectable intermediates; (b) **1**·Py reacts considerably faster than **1**·PMe$_3$; and (c) the addition of bases, such as THF or Py, retards product formation.

Figure 2. ORTEP view of **6**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms were omitted for clarity.

Scheme 2

A

Our current thinking is that the boratabenzene ligand forms as a result of an intramolecular nucleophilic attack on boron upon coordination of borabenzene (Scheme 2). There is ample literature precedent for the coordination of neutral arene rings to d^0 metal complexes.[18] Since borabenzene adducts can be considered to have a partial negative charge on the ring, such adducts should be more favored. The tetraamide of zirconium is considerably slower than the corresponding tetrabenzyl species, probably due to its existence as a dimer in the solid state and solution.[19] Addition of THF or Py, which compete for sites on the metal, retards the reaction.[20] That the more electron-rich and smaller **1**·Py reacts faster than **1**·PMe$_3$ suggests that ring coordination is rate-determining. Exchange of exocyclic groups most likely occurs via a Meisenheimer-type[21] intermediate of type **A**, in which borate formation is accompanied by the binding of the metal to the back of the ring in a pentadienyl-like fashion. Precedent also exists for attack by external nucleophiles on the boron atom in **1**·PMe$_3$[22] and in (**1**·PMe$_3$)Cr(CO)$_3$.[11b]

In summary, we have developed a new reaction for the synthesis of boratabenzene complexes which takes advantage of the unique reactivity of the borabenzene ring and departs form conventional Cp-based methodology. Scandium species as well as alkylated zirconium and hafnium complexes are easily accessed. The availability of compound **5** allows for the comparison of the effect of different activators on the activity of ethylene polymerization catalysts. The high yield of reactions represented in Scheme 1 should encourage further applications of boratabenzene complexes.

Supporting Information Available: Complete details for the synthesis of all compounds, the polymerization conditions, and the crystallographic studies of **2**, **5**, and **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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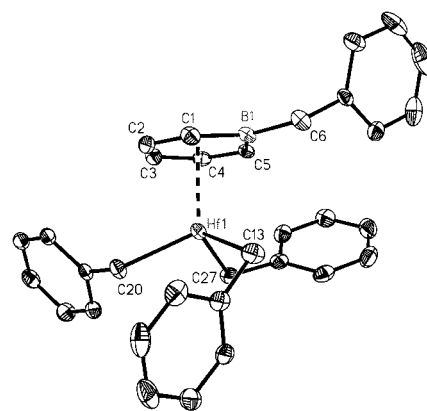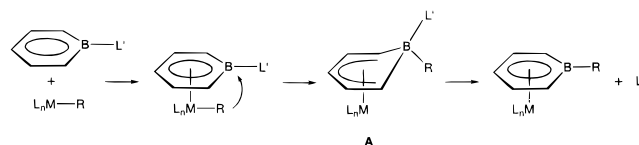
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