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Boratabenzene Complexes of Cr(III)

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We recently reported that borabenzene adducts[1] can be converted to boratabenzene ligands upon reaction with complexes of Sc, Zr, and Hf supported with σ- ligands (Scheme 1).[2,3] This reaction proceeds via coordination of borabenzene followed by an intramolecular nucleophilic attack on the boron atom, and it can be used to synthesize bis(boratabenzene)zirconium complexes.[4] Upon activation with methylaluminoxane (MAO), these complexes provide excellent single-site catalysts for the polymerization and oligomerization of olefins.[5] The reaction in Scheme 1 circumvents the use of the more reducing alkali metal boratabenzene salts and should provide an efficient means to coordinate boratabenzene in situations where metal reduction may be encountered.

Boratabenzene complexes of Cr(III) are attractive synthetic targets. Theopold has shown that $[Cp^*CrMe(THF)_2][BPh_4]$[6] ($Cp^* = C_5Me_5$) is an active ethylene polymerization catalyst which mimics the reactivity of the heterogeneous Union Carbide catalyst.[7] Efforts on our part to make isoelectronic complexes containing boratabenzene instead of Cp*, by reaction of $Li[C_5H_5B{-}Ph]$ with $CrCl_3(THF)_3$, invariably lead to the known $[C_5H_5B{-}Ph]_2Cr$.[8] Reduction to Cr(II) diminishes considerably the catalytic activity of homogeneous Cr complexes.[9] In this contribution we describe a synthesis of monoboratabenzene complexes of Cr(III) which is based on Scheme 1. These complexes can be converted into catalysts that exhibit polymerization activities similar to those of standard group 4 metallocenes.[10]

In analogy to the reactivity of $Ph_3Sc(THF)_2$,[2] $C_5H_5B{-}PMe_3$ (**1**) was added to a solution of $Ph_3Cr(THF)_3$[11] in toluene. An instantaneous darkening of the red solution occurs. Workup of the reaction affords large blood-red crystals in greater than 50% yield, which analyze correctly for $C_{26}H_{29}BCrP$. Broad signals in the −40 to 20 ppm range are observed in the ^1H NMR spectrum, and a broad peak centered at 370 ppm is observed in the ^{11}B NMR spectrum. A single-crystal X-ray diffraction study shows that the complex is $(C_5H_5B{-}Ph)CrPh_2(PMe_3)$ (**2**, in eq 1) and that it has a typical three-legged piano-stool geometry (see Supporting Information).

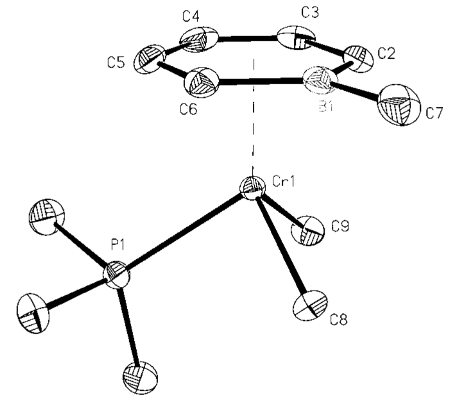


Figure 1. ORTEP view of **3**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms were omitted for clarity. Selected bond distances (Å): Cr(1)−C(2), 2.345(2); Cr(1)−C(3), 2.332(2); Cr(1)−C(4), 2.327(2); Cr(1)−C(5), 2.376(2); Cr(1)−C(6), 2.405(2); Cr(1)−C(8), 2.078(2); Cr(1)−C(9), 2.072(2); Cr(1)−B(1), 2.481(2); Cr(1)−P(1), 2.3953(5); B(1)−C(7), 1.579(3).

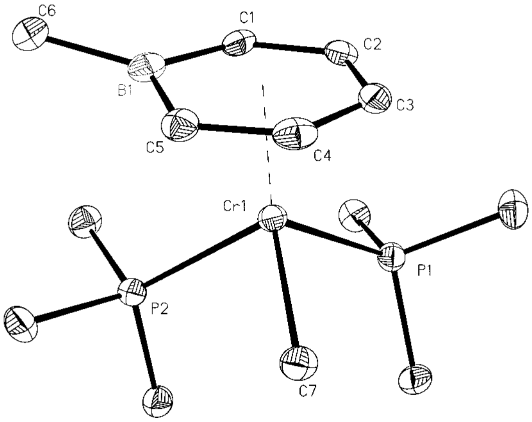
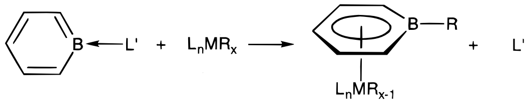
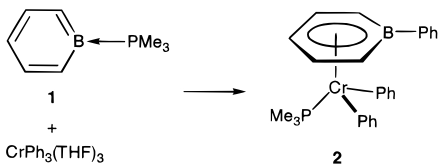


Figure 2. ORTEP view of **4**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms and the $[MeB(C_6F_5)_3]$ anion were omitted for clarity. Selected bond distances (Å): Cr(1)−C(1), 2.403(3); Cr(1)−C(2), 2.331(3); Cr(1)−C(3), 2.245(3); Cr(1)−C(4), 2.266(3); Cr(1)−C(5), 2.326(3); Cr(1)−C(7), 2.074(3); Cr(1)−B(1), 2.545(4); Cr(1)−P(1), 2.4466(12); Cr(1)−P(2), 2.4295(11); B(1)−C(6), 1.570(5).

Scheme 1





(1)

To prepare the methyl analogue of **2**, we resorted to making "Me_3Cr" in situ by treating a slurry of $CrCl_3(THF)_3$ with 3 equiv of MeMgBr (THF, −45 °C). Subsequent addition of **1** results in an instantaneous color change from red to green. Stirring for an

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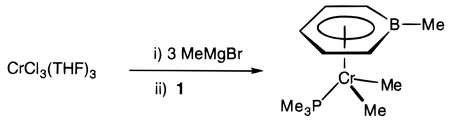
Table 1. Ethylene Polymerization Results[a]

entry	precatalyst	activator	activity[b]	M_n (× 10^{-3})	M_w (× 10^{-3})	PDI[c]	T_m (°C)
1	**2**	MAO	71.5	6.46	28.7	4.43	130.2
2	**2**	$B(C_6F_5)_3$	0	–	–	–	–
3	**3**	MAO	83.4	2.97	12.1	4.07	130.5
4	**3**	$B(C_6F_5)_3$	27.5	10.6	38.5	3.63	127.4
5	**3**	$2B(C_6F_5)_3$	71.7	16.6	53.9	3.25	128.7
6	**3**	$3B(C_6F_5)_3$	65.9	13.8	59.8	4.33	129.7
7	**3**	$[Ph_3C][B(C_6F_5)_4]$	50.5	39.5	114.1	2.89	130.0
8	$Cp^*CrMe_2(PMe_3)$[d]	MAO	73.8	–	–	–	–
9	$Cp^*CrMe_2(PMe_3)$	$B(C_6F_5)_3$	44.2	14.7	56.7	3.87	129.5
10	Cp_2ZrCl_2	MAO	85.4	9.87	22.3	2.55	132.5

[a] Conditions for polymerizations: [M] = 1 × 10^{-3}M, M = Cr, Zr; 30 min; 1 atm ethylene; 23 °C; for MAO polymerizations, [Al]/[M] = 1000. [b] Activity measured in kg [product]/mol M•hr. [c] M_w/M_n. [d] Only low molecular weight products were obtained from this reaction.

additional 30 min at −45 °C gives a dark purple solution. Purple-black needles that analyze for $C_{11}H_{23}BCrP$ can be obtained in nearly 70% yield. Structural characterization (Figure 1) shows that the product is $(C_5H_5B{-}Me)CrMe_2(PMe_3)$ (**3**), as shown in eq 2. The ^{11}B NMR spectrum of **3** displays a broad resonance centered at 219 ppm.



3

(2)

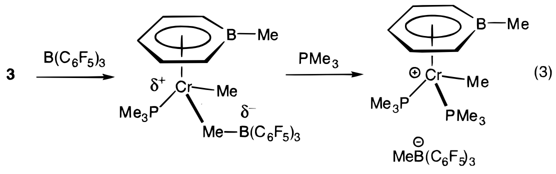
The molecular structures of **2** and **3** are similar. Minor differences are observed in the Cr−B distances (d(Cr−B) = 2.565(3) Å in **2** and d(Cr−B) = 2.481(2) Å in **3**). However, because the rings are rotated differently relative to the $CrR_2(PMe_3)$ tripod, it is not obvious whether variations in Cr−B distances are due to steric or electronic preferences.

Table 1 shows the results from a series of polymerization experiments. Complexes **2** and **3** react with excess methylaluminoxane (MAO) ([Cr] = 1 × 10^{-3} M, 30 min reaction time, the reaction vessel was submerged in a water bath at 23 °C, 1000 Al/Cr, 1 atm C_2H_4) to give active ethylene polymerization catalysts (entries 1 and 3). The result from Cp_2ZrCl_2/MAO under similar conditions (entry 10) shows that the reactivities of **2**/MAO and **3**/MAO are similar to group 4 metallocenes. The well-defined activator $B(C_6F_5)_3$[12] is suitable for **3** but fails in the case of **2** (entries 2 and 4). For **3**/$B(C_6F_5)_3$, the best results are observed with a borane-to-**3** ratio of approximately 2 (entries 4, 5, and 6). Excellent activity is also observed with **3**/$[Ph_3C][B(C_6F_5)_4]$[13] (entry 7). Finally, the activities of $Cp^*CrMe_2(PMe_3)$[14] with MAO and $B(C_6F_5)_3$ are shown in entries 8 and 9 for comparison. In all cases, melting points typical for linear polyethylene were obtained.

Studies on $[Cp^*CrMe(THF)_2][BPh_4]$ and on bis(boratabenzene)$ZrCl_2$/MAO[15] systems suggest that the catalysts derived from **3** are cations of the type $[(C_5H_5B{-}Me)CrMe(PMe_3)]^+$. However, it is important to rule out the possibility of phosphine abstraction for the **3**/$B(C_6F_5)_3$ catalysts. In particular, it has been shown that $B(C_6F_5)_3$ can remove phosphine from nickel complexes to generate neutral ethylene polymerization catalysts.[16]

A series of experiments were conducted to resolve some of the uncertainties raised above. Addition of excess THF-d_8 to a solution of **3**/$B(C_6F_5)_3$ in C_6D_6 generates a sharp resonance at −14.5 ppm in the ^{11}B NMR spectrum attributed to free $[MeB(C_6F_5)_3]^-$.[17] Addition of MeMgBr to **3**/$B(C_6F_5)_3$ regenerates the signal at 219 ppm which is characteristic of **3**. These observations are consistent with the formation of $[(C_5H_5B{-}Me)CrMe(PMe_3)][MeB(C_6F_5)_3]$ instead of $[(C_5H_5B{-}Me)CrMe_2]$ and $[Me_3P{-}B(C_6F_5)_3]$.

In another set of experiments, a slight excess of PMe_3 was added to **3**/$B(C_6F_5)_3$ in toluene, resulting in a color change from green to red. After removal of toluene and residual PMe_3, the product was dissolved in 3:1 C_6D_6/chlorobenzene and examined by ^{11}B NMR spectroscopy. A signal was clearly observed at −14.4 ppm due to $[MeB(C_6F_5)_3]^-$. Slow evaporation of an ether solution gave single crystals suitable for structural characterization (Figure 2). The product of the reaction is therefore $[(C_5H_5B\text{-}Me)CrMe(PMe_3)_2][MeB(C_6F_5)_3]$ (**4**), as shown in eq 3.



4

(3)

The solid-state structure of **4** resembles closely that of **3**, with some subtle differences. A slight increase in Cr−B distance is observed (d(Cr−B) = 2.545(4) Å in **4** vs d(Cr−B) = 2.481(2) Å in **3**) as well as a decrease in chromium-ring carbon distances (d(Cr−C_{ave}) = 2.357(2) Å in **3** and d(Cr−C_{ave}) = 2.314(3) Å in **4**). The positively charged Cr therefore binds more tightly to the electron-rich carbons, despite the presence of the bulkier PMe_3 ligand. At the same time, the Cr−B overlap is reduced.

In summary, we have shown that monoboratabenzene−Cr(III) complexes such as **2** and **3** are readily accessible by reaction of **1** with either $Ph_3Cr(THF)_3$ or "$CrMe_3$" made in situ. Complexes **2** and **3** are precursors to ethylene polymerization catalysts that have activities competitive with those prepared from standard metallocenes. Furthermore, it is possible to activate **3** with $B(C_6F_5)_3$ to give single component catalysts of the type $[(C_5H_5B{-}Me)CrMe(PMe_3)][MeB(C_6F_5)_3]$. There is ample precedent for the modulation of reactivity in boratabenzene-supported catalysts by choice of the boron substituent. A similar control is anticipated for these Cr(III) catalysts.

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Supporting Information Available: Complete details for the synthesis of all compounds, the polymerization conditions, and the crystallographic studies of **2**, **3**, and **4** (PDF). The material is available free of charge via the Internet at http://pubs.acs.org.

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