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Group-4 Transition-Metal Boryl Complexes: Syntheses, Structures, Boron−Metal Bonding Properties, and Application as a Polymerization Catalyst

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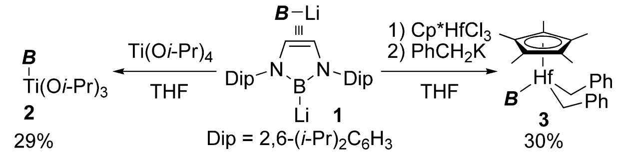
Metal−boron σ bonds in transition-metal boryl complexes[1] have been proved to possess remarkable donor ability[2,3] and a unique reactivity toward C−H bonds of hydrocarbons.[4] Although group-5 boryl complexes[5] and group-4 σ-borane complexes[6] have been reported, there has been no example of group-4 transition-metal boryls.[7,8] The reason for the lack of group-4 boryl complexes could be that synthetic methods for boryl complexes have been limited. All three conventional methodologies,[1] (1) reactions of anionic complexes with haloboranes, (2) oxidative addition of B−X bonds (X = B, H, halogen) to low-valent metal complexes, and (3) σ-bond metathesis of metal alkyls, hydrides, and alkoxides with boron-containing reagents, are not applicable to the syntheses of group-4 boryl complexes because (1, 2) anionic group-4 metal complexes and low-valent group-4 metal complexes are not easily available as precursors, (3) a Lewis acidic boron reagent may abstract an anionic ligand from a group-4 metal complex to form a borate complex rather than undergo σ-bond metathesis, and (4) it is not easy to obtain boryl anionic equivalents to do metal halide substitution, which is a standard approach for making metal−carbon bonds. In this context, our recent success in nucleophilic introduction[3] of a boryl ligand to group-11 transition-metal centers using boryllithium **1**[9−12] prompted us to synthesize group-4 transition-metal boryl complexes. Herein, we report syntheses, structures, and B−metal bonding properties of boryltitanium and borylhafnium complexes and their application as catalyst precursors for polymerization.

Boryltitanium triisopropoxide (**2**) was synthesized by reaction of boryllithium **1** with $Ti(Oi\text{-}Pr)_4$ (Scheme 1). Introduction of the boryl group to Cp^*HfCl_3 using **1** and the following reaction with benzylpotassium gave $HfCp^*(boryl)Bn_2$ (**3**).[13] Complexes **2** and **3** are the first examples of group-4 metal boryl complexes.[14] Boryltitanium **2** is also the first example of a borylmetal alkoxide.[15] It is noteworthy that all attempted reactions of **1** with MCl_4 (M = Ti, Zr, Hf) gave the corresponding protonated hydroboranes **4**,[9,10] probably via proton abstraction by **1** from THF activated by the Lewis acidic metal center. In the ^1H NMR spectrum of **2**, the six methyl groups of the three isopropoxide ligands are equivalent, as are the four methyl groups of the Dip moieties. Borylhafnium **3** has two distinct methyl protons in the isopropyl groups, and two geminal protons on the benzylic carbon were separately observed. A broad ^{11}B signal was observed at the typical region for borylmetal complexes in both cases (δ_B 38.2 for **2**, δ_B 70.0 for **3**). No significant change was observed for either **2** or **3** in their $^1H\{^{11}B\}$ and non-proton-decoupled ^{11}B NMR spectra. These results suggest that the resulting complexes have no borane-type hydrogen atom around the metal center.[6,16]

Crystallographic studies of **2** and **3** revealed a slightly distorted tetrahedral structure of **2** and a typical three-leg piano-stool structure of **3** (Figure 1). Selected bond distances and angles are summarized in Table 1. The B−Ti bond length of 2.258(2) Å in **2** is in the mid to lower end of the range of B−Ti interatomic distances in hydroborane−Ti[6] and hydroborate−Ti[17] complexes and is significantly shorter than those in Ti−carbollide complexes.[17] The B−Hf bond length of 2.497(4) Å in **3** is close to the lower end of the reported B−Hf contact in carbollide−Hf complexes.[17] Both B−metal bonds in **2** and **3** are slightly longer than the sum of the covalent radii of the atoms (B−Ti, 2.20 Å; B−Hf, 2.32 Å).[18] The remarkably short Ti−O bonds (av 1.758 Å) and large Ti−O−C angles (av 164.9°) in **2** reflect double-bond character of the Ti−O bonds, which could be attributed to pπ−dπ interactions between titanium and oxygen atoms.[19] The two Hf−benzylic carbon bonds (av 2.219 Å) and five Hf−C(Cp*) bonds (av 2.494 Å) in **3** are similar to those observed in conventional Cp*Hf−alkyl complexes.[20]

Scheme 1. Syntheses of Boryltitanium **2** and Borylhafnium **3** from Boryllithium **1**



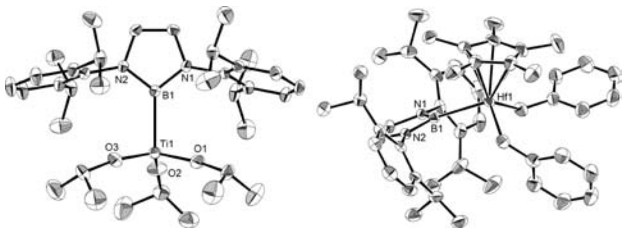
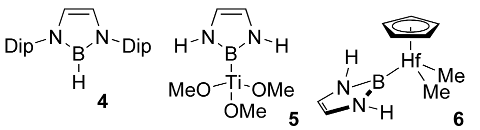


Figure 1. ORTEP drawings of (left) **2** and (right) **3** with 50% thermal ellipsoids. Hydrogens and minor parts of the disordered isopropoxide groups have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) in **2** and **3** and Reference Molecules **4**, **5**, and **6**



	2	**3**	**4**	**5**	**6**
B−metal	2.258(2)	2.497(4)		2.226	2.394
B−N	1.446(3)	1.458(4)	1.418(3)	1.442	1.451
	1.447(3)	1.477(4)	1.423(3)		1.453
N−B−N	102.85(16)	100.6(3)	105.25(16)	102.2	100.9

To elucidate the nature of the group-4 transition metal−boron bond, DFT studies were conducted. The structural parameters of model borylmetal complexes **5** and **6**, except for the orientation of the diazaborole ring in **6**,[21] were close to those of **2** and **3** (Table 1). The optimized structures of **5** and **6** are illustrated with their

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HOMO and HOMO−1 orbitals in Figure 2. Both **5** and **6** have HOMO character similar to a π orbital of the diazaborole ring, like hydroborane **4**.[10,11] The shape of HOMO−1 seems to be similar to the HOMO of boryllithium **1**·$(\mathrm{THF})_2$, which has lone-pair character on the central boron atom.[10,11] Natural bond order (NBO) analyses of **5** and **6** suggest that both of the HOMO−1 orbitals have a shared two-center−two-electron bonding character with hybridizations of $\mathrm{B{-}Ti} = 0.5668(\mathrm{sp}^{1.49})\mathrm{B} + 0.4332(\mathrm{sp}^{0.92}\mathrm{d}^{1.06})\mathrm{Ti}$ for **5** and $\mathrm{B{-}Hf} = 0.6265(\mathrm{sp}^{1.06})\mathrm{B} + 0.3745(\mathrm{sp}^{0.54}\mathrm{d}^{2.01})\mathrm{Hf}$ for **6**.[22] Atoms-in-molecule analyses also afforded the same conclusion. Negative $\nabla^2\rho(r)$ values ($-0.03079\ e/a_0^5$ in **5**; $-0.33061\ e/a_0^5$ in **6**) at the bond critical point between the boron and metal atoms indicated covalent character for these B−metal bonds.[23]

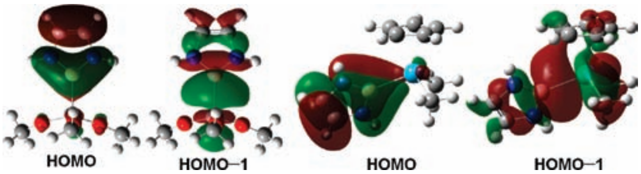

Figure 2. HOMO and HOMO−1 of (left) **5** and (right) **6**.

Preliminary studies of the catalytic activity of **3** for polymerization of ethylene and hex-1-ene were performed (see the Supporting Information for details). An admixture of **3** with $\mathrm{Ph_3CB(C_6F_5)_4}$ in toluene could polymerize ethylene to form a linear polyethylene (PE) [turnover frequency (TOF) = 110 kg of PE (mol of Hf)$^{-1}$ h^{-1}, $M_\mathrm{n} = 4800$, polydispersity index (PDI) = 2.1, 2 branches per 1000 C]. The present system was also active for polymerization of hex-1-ene to afford an atactic poly(hex-1-ene) (PHex) (TOF = 21 kg of PHex (mol of Hf)$^{-1}$ h^{-1}, $M_\mathrm{n} = 3100$, PDI = 2.2). Activities of **3**/$\mathrm{Ph_3CB(C_6F_5)_4}$ toward polymerization were comparable to those of previously reported hafnium half-sandwich complex-derived catalyst systems.[24]

In conclusion, two group-4 boryl complexes, boryltitanium **2** and borylhafnium **3**, were synthesized via nucleophilic borylation using boryllithium **1**. Complexes **2** and **3** are the first examples of group-4 borylmetals. Theoretical calculations on model molecules **5** and **6** indicated that the boron−metal bond in both complexes has covalent character. Complex **3** has an activity for polymerization of ethylene and hex-1-ene. Further studies on polymerization and modification of the boryl ligand are ongoing.

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Supporting Information Available: Details about preparations and characterizations of **2** and **3**, polymerization procedures, X-ray crystallography (CIF), and the computational study. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The stability of **2** and **3** shows that the boryl ligand can coexist in the coordination sphere with other nucleophilic ligands such as alkoxides and alkyls.

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(21) It was confirmed that this difference in the orientation angles of the diazaborole rings in **3** and **6** did not affect the bonding character. See the Supporting Information.

(22) For comparison, an NBO analysis of boryllithium **1**·$(\mathrm{THF})_2$ with cc-pvdz basis sets was independently performed in this study. The analysis indicates that the boron center of boryllithium **1**·$(\mathrm{THF})_2$ has LP character in its $\mathrm{sp}^{1.237}$ hybridized orbital.

(23) This is in contrast to the case of **1**·$(\mathrm{THF})_2$, which has positive $\nabla^2\rho(r)$ values, indicating ionic character of the B−Li bond. See ref 10 and the Supporting Information.

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