Reactions of Bis(pentafluorophenyl)borane with Titanocene Dialkyls: Synthesis and Structure of $Cp_2Ti[\eta^2\text{-}H_2B(C_6F_5)_2]$

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Summary: Clean reactions of Cp_2TiR_2 (R = CH_3, CH_2Ph) with $HB(C_6F_5)_2$ occur when 2.5 equiv of borane are used. The products of the reaction are the Ti(III) complex $Cp_2Ti[\eta^2\text{-}H_2B(C_6F_5)_2]$, which has been fully characterized, RH, and $RB(C_6F_5)_2$. A plausible explanation for these observations, which contrast with other reactions of boranes with group 4 metallocenes, is presented.

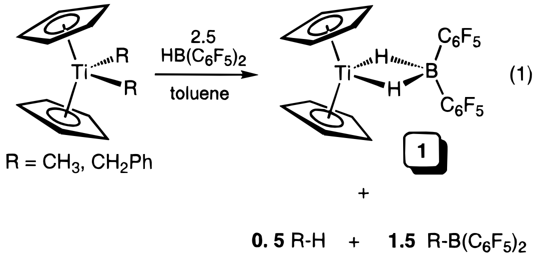
Introduction

Since the discovery of rhodium-catalyzed hydroboration[1] of alkenes with otherwise unreactive boranes (e.g., HB(catecholate)), there has been growing interest in the fundamental chemistry involved in the interaction of boranes with organotransition metal compounds.[2] Organotitanium compounds have received particular attention.[3] The tendency of such titanium compounds to undergo facile reduction renders these catalyst systems mechanistically complex, and the nature of the "true catalyst" is highly dependent on conditions and catalyst precursors. It now appears that titanium-mediated hydroboration involves low-valent titanocene species.

Although the highly electrophilic borane bis(pentafluorophenyl)borane, $HB(C_6F_5)_2$, requires no catalyst to react with unsaturated functionalities,[4] we have been exploring its reactivity with early transition metal organometallic compounds to compare and contrast its behavior with that of less reactive boranes. Having explored such reactions with organozirconium[5] and organotantalum[6] compounds, we have extended these studies to include the reactions of $HB(C_6F_5)_2$ with simple bisalkyl titanocenes Cp_2TiR_2 (R = CH_3, CH_2Ph).

Results and Discussion

The reactions of $HB(C_6F_5)_2$ with Cp_2ZrR_2[5c] were found to be highly sensitive to variation in the equivalency of borane and the solvent medium; in contrast, clean reactions with the analogous dialkyl titanocenes were only observed when 2.5 equiv of borane was used, and the solvent did not appear to influence the course of the reaction. Accordingly, red-orange solutions of the Ti(IV) $Cp_2Ti(CH_3)_3$ starting material, gradually changed color to purple upon treatment with 2.5 equiv of $HB(C_6F_5)_2$, indicative of reduction of the titanium to Ti(II) or Ti(III). When the reaction involving the dibenzyl titanocene is followed by ^1H NMR spectroscopy, it is apparent from the relative integrals of the benzylic protons that 0.5 equiv of H_3CPh and 1.5 equiv of $PhCH_2B(C_6F_5)_2$ are also produced in this reaction. Similar byproducts are seen in the $Cp_2Ti(CH_3)_3$ reaction, although the methane (δ = 0.16 ppm in C_6D_6) produced was not quantified. The boranes $RB(C_6F_5)_2$ were identified by spectroscopic comparison to authentic samples.[5c] Light purple microcrystalline powders of a paramagnetic compound identified as the Ti(III) η^2-hydridoborate complex **1** (eq 1) were isolated from these reactions in 87% (R = CH_3) and 86% yield (R = CH_2Ph).



Due to its paramagnetism, ^1H, ^{13}C, and ^{11}B NMR spectroscopy for **1** is uninformative; the ^{19}F NMR spectrum, however, exhibits peaks attributable to B-C_6F_5 moieties. A significantly broadened signal centered around −131 ppm is ascribed to the *ortho* fluorine atoms, which are most affected by the paramagnetic center. Sharper resonances at −155.8 and −163.1 ppm

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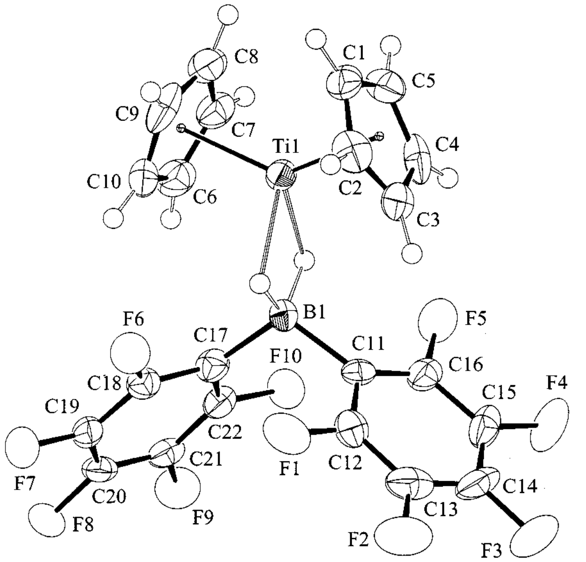
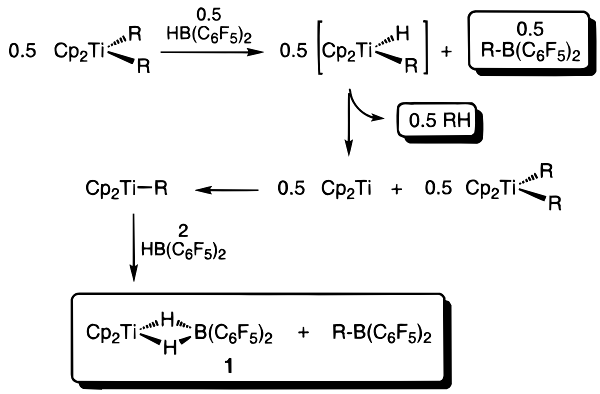


Figure 1. Molecular structure of **1** (one of the two independent molecules). Selected bond distances (Å): Ti(1)−B(1), 2.450(10); Ti(1)−C(1), 2.343(9); Ti(1)−C(20, 2.349(9); Ti(1)−C(3), 2.349(8); Ti(1)−C(4), 2.335(8); Ti(1)−C(5), 2.348(9). Selected bond angle (deg): C(11)−B(1)−C(17), 109.1(7).

are due to the *para* and *meta* fluorines, respectively. IR spectroscopy is consistent with the presence of a η^2-hydridoborate ligand, exhibiting a ν(B−H)$_{sym}$ stretching vibration at 2009 cm^{-1} and the ν(B−H)$_{asym}$ stretch at 2075 cm^{-1}.[7] The EPR spectrum of **1** exhibits a broad singlet with a g-value of 1.974, in good agreement with the values found for other Ti(III) η^2-hydridoborate compounds, including $Cp_2Ti(\eta^2\text{-}H_2BO_2C_6H_4)$ ($g = 1.990$)[3d] and $Cp_2Ti(\eta^2\text{-}BH_4)$ ($g = 2.004$).[8,9] Like with these previous Ti(III) hydridoborates, no hyperfine coupling was observed in the EPR signal for **1**, even at −196 °C in a frozen matrix. This is due primarily to the fact that the SOMO is essentially 3d in character and localized on the titanium center.[10]

The spectroscopic data on **1** were corroborated via an X-ray crystallographic analysis of crystals grown from toluene solution. There are two unique, independent molecules in the unit cell, which differ only in the orientation of the $-C_6F_5$ rings. Figure 1 shows the molecular structure of one of the unique molecules of **1**, along with selected metrical parameters; the values for the other molecule are essentially the same. The hydrogen atoms of the hydridoborate ligand were located on the difference map but not refined; nevertheless, it is clear that the $[H_2B(C_6F_5)_2]^-$ ligand is η^2-coordinated. The metrical parameters, when compared to those found for the parent compound $Cp_2Ti(\eta^2\text{-}BH_4)$,[11] suggest that the dihydridoborate ligand of **1** is less strongly bound to the titanium. For example, the Ti−B distance of 2.450(10) Å is somewhat longer than the 2.37(1) Å found in the BH_4 derivative. In addition to being sterically more bulky, the $[H_2B(C_6F_5)_2]^-$ ligand is expected to be less electron donating by virtue of the higher effective electronegativity of the boron atom conferred by the $-C_6F_5$ substituents.

Scheme 1



Scheme 1 shows a plausible route for formation of **1**, which also accounts for the observed stoichiometry of the reaction. The first step involves an exchange of alkyl and hydride between titanium and the borane. Similar reactivity between Cp_2TiR_2 derivatives and HB(catecholate) boranes has been observed and involves a σ-bond metathesis mechanism.[3g] In the case of the more Lewis acidic $HB(C_6F_5)_2$, the mechanism likely proceeds stepwise via methide abstraction followed by hydride back-transfer to titanium, as was established for the analogous zirconium chemistry.[5c] Whatever the case may be, reductive elimination of RH from the resulting $Cp_2Ti(H)R$ species is rapid, forming "Cp_2Ti". At this point, the path for $HB(C_6F_5)_2$ diverges from that seen for HB(catecholate) boranes. In the latter systems, the titanocene is trapped by the electron-rich B−H bonds, forming Ti(II) σ-complexes $Cp_2Ti[HB(catecholate)]_2$.[3e−h] In the $HB(C_6F_5)_2$ reaction, this trapping process is slow relative to redox conproportionation between "Cp_2Ti^{II}" and the remaining half an equivalent of $Cp_2Ti^{IV}R_2$[12] to form $Cp_2Ti^{III}R$.[13] The Cp_2TiR species then undergoes abstractive alkyl/hydride exchange with $HB(C_6F_5)_2$ to form the Ti(III) hydride Cp_2TiH and one further equivalent of $RB(C_6F_5)_2$. Cp_2TiH is rapidly trapped with another equivalent of $HB(C_6F_5)_2$ to form the observed product **1**.[14]

Several factors may account for the failure of $HB(C_6F_5)_2$ to trap "Cp_2Ti" in an analogous fashion to that observed for HB(catecholate) boranes. First, the borane is poorly soluble in toluene, and so there is likely a deficit of $HB(C_6F_5)_2$ in solution when "Cp_2Ti" is formed.

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[12] (a) Such Ti(II)/Ti(IV) conproportionation reactions are well precedented.[12b] In this case, the fact that "Cp_2Ti" is not complexed by strong ligands presumably makes this a very facile process. Similar behavior has been observed for Cp_2Zr^{II}/Cp_2ZrR_2.[12c] (b) Bochmann, M. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; 1995; Vol. 4, p 221. (c) Dioumaev, V.; Harrod, J. F. *Organometallics* **1997**, *16*, 1452.

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[14] An alternative pathway for the formation of **1** involves the trapping of the initially formed alkyl hydride $Cp_2Ti(H)R$ by $HB(C_6F_5)_2$. Loss of $R^{\bullet}$ from the product of this process, $Cp_2Ti(R)[\eta^2\text{-}H_2B(C_6F_5)_2]$, would lead directly to **1**. Indeed, when R = CH_2Ph, small amounts (<5%) of $PhCH_2CH_2Ph$ were observed, but even when $R^{\bullet}$ is relatively stable, this constitutes a minor pathway for formation of **1**.

Second, we have shown that, while significant amounts of monomer exist in solution when the borane is fully dissolved, the B−H bond is less polarized than other boranes[4a] and would be a poorer donor than, for example, HB(catecholate) boranes. The high reactivity observed for monomeric $HB(C_6F_5)_2$ largely stems from its high electrophilicity; the lack of σ-complex formation with Cp_2Ti is partially a consequence of its poor abilities as a donor. Finally, steric pressure exacted by the nonplanar $-C_6F_5$ substiuents would probably tend to disfavor the peculiar geometry necessary at boron for maximal overlap of the acceptor orbitals on the borane with the metallocene orbitals in the σ-complex structure.[3e,g]

Experimental Section

General Considerations. General techniques have been described in detail elsewhere.[5c] EPR spectra were obtained on a Bruker EMX spectrometer operating at the X-band and 25 °C. The following compounds were prepared according to literature procedures: $XB(C_6F_5)_2$ (X = H,[4a] D,[4a] CH_3,[5c] CH_2Ph[5c]); Cp_2TiR_2 (R = CH_3,[15] CH_2Ph[16]).

Reaction of $Cp_2Ti(CH_3)_2$ with $HB(C_6F_5)_2$. In air, $Cp_2Ti(CH_3)_2$ (0.120 g, 0.58 mmol) was weighed into a 50 mL round-bottomed flask and attached to a frit assembly; the apparatus was thoroughly covered with aluminum foil (to prevent decomposition of $Cp_2Ti(CH_3)_2$) and evacuated. Toluene (ca. 10 mL) was condensed onto the solid at −78 °C, and $HB(C_6F_5)_2$ (0.598 g, 1.73 mmol), dissolved in hot toluene (25 mL), was added via syringe to the $Cp_2Ti(CH_3)_2$ solution. The solution was warmed to room temperature and stirred overnight. The solvent was removed in vacuo, and hexanes (40 mL) were condensed onto the residues. The mixture was filtered and the purple product washed with hexanes (2 × 10 mL). Yield: 0.265 g, 87%. IR (cm^{-1}, KBr): 3120 (w), 2075 (m), 2009 (m), 1645 (m), 1479 (s), 1103 (s), 968 (s), 813 (s). ^{19}F NMR (282.41 MHz, C_6D_6, ppm): −163.1 (br s, 2 F, *m*-C_6F_5), −155.8 (br s, 1 F, *p*-C_6F_5), −131 (v br, 2 F, *o*-C_6F_5). EPR (C_7H_8) $g = 1.976$. Anal. Calcd for $C_{22}H_{12}BF_{10}Ti$: C, 50.33; H, 2.30. Found: C, 49.93; H, 2.09.

Reaction of $Cp_2Ti(CH_2Ph)_2$ with $HB(C_6F_5)_2$. $Cp_2Ti(CH_2Ph)_2$ (0.15 g, 0.42 mmol) was dissolved in toluene (40 mL) and added via cannula to a solution of $HB(C_6F_5)_2$ (0.361 g, 1.04 mmol) in toluene (20 mL) at −78 °C. After warming the reaction to room temperature for 16 h, the solvent was removed in vacuo, and hexanes (40 mL) were condensed onto the residues. The suspension was filtered and the purple product washed with hexanes (2 × 10 mL). Yield: 0.19 g, 86%. NMR data were identical to the product formed from $Cp_2Ti(CH_3)_2$ and $HB(C_6F_5)_2$.

Table 1. Summary of Data Collection and Refinement Details for 1

formula	$C_{22}H_{12}F_{10}BTi$
fw	525.03
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	12.648(3)
b, Å	15.678(3)
c, Å	11.565(3)
α, deg	109.373(19)
β, deg	110.63(2)
γ, deg	90.69(2)
V, $Å^3$	2003.0(10)
Z	4
d_{calc}, mg m^{-3}	1.741
F(000)	1044
μ, cm^{-1}	5.19
T, °C	−103
cryst dimens, mm^3	0.54 × 0.52 × 0.25
rel transmn factors	0.9407−1.0000
scan type	$\omega-2\theta$
2θ (max), deg	50.1
no. of unique reflns	7098
no. of reflns with $I > 3\sigma I$	3601
no. of variables	614
R	0.058
R_w	0.052
gof	2.80
max Δ/σ (final cycle)	0.00
residual density, e/$Å^3$	−0.41−0.44

X-ray Structure Determination of 1. A summary of crystal data and refinement details for all structures is given in Table 1. Crystals of **1** were grown from toluene/hexanes solution at room temperature, covered in paratone oil, mounted on a glass fiber, and immediately placed in a liquid N_2 cold stream on the diffractometer. Measurements were made using a Rigaku AFC6S diffractometer with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) source at −103 °C with the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.1°. The compound crystallizes as two independent molecules in the unit cell. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms attached to boron were located from a difference map; hydrogen atoms were included at geometrically idealized positions and were not refined. All calculations were performed using the TEXAN[17] crystallographic software package of Molecular Structure Corporation.

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Supporting Information Available: An ORTEP diagram of the second independent molecule of **1**, ^1H and ^{11}B NMR spectra along with tables of atomic coordinates, anisotropic displacement parameters, and complete bond distances and angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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