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Vanadocene-Mediated Ionization of Water in the Aqua Species $[H_2O{\cdot}B(C_6F_5)_3]$: Structural Characterization of the Hydride and Hydroxide Complexes $[Cp_2V(\mu\text{-}H)B(C_6F_5)_3]$ and $[Cp_2V(\mu\text{-}OH)B(C_6F_5)_3]$

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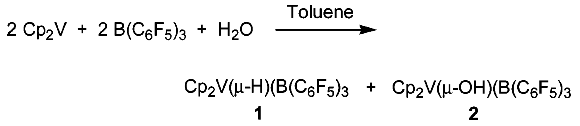
*Summary: The reaction of Cp_2V with $B(C_6F_5)_3$ in the presence of water leads to the hydride complex $[Cp_2V(\mu\text{-}H)B(C_6F_5)_3]$ (**1**) and the hydroxide complex $[Cp_2V(\mu\text{-}OH)B(C_6F_5)_3]$ (**2**), both of which have been characterized by X-ray structure determinations. Both complexes are derived from the ionization of water in the presence of $B(C_6F_5)_3$.*

Various aspects of the chemistry and applications of $B(C_6F_5)_3$ have been recently reviewed.[1,2] Though $B(C_6F_5)_3$ is well-known as an activator for homogeneous group 4 transition-metal-catalyzed olefin polymerization,[3] it displays versatile chemistry and unique reactivity. It is highly reactive with water, and its aqua complex $H_2O{\cdot}B(C_6F_5)_3$ is known to behave as a strong Brønsted acid.[4] Indeed, adventitious water has given access to the hydroxyborate complexes $[M][O(H)B(C_6F_5)_3]$ (M = Ti, Zr).[5] The identification of the hydroxyborate anions $[HOB(C_6F_5)_3]^-$, $[(F_5C_6)_3B(\mu\text{-}OH)B(C_6F_5)_3]^-$, and $[(F_5C_6)_3B(H_3O_2)B(C_6F_5)_3]^-$, which are derived from the reaction of $B(C_6F_5)_3$ with water, suggests the presence of an acidic-proton-containing countercation.[6] Several reactions reported recently in the literature indirectly support the presence of such a cation; treatment of $[MCp_2]$ (M = Cr, Fe, Co) with $H_2O{\cdot}B(C_6F_5)_3$ resulted in metal oxidation with H_2 elimination.[7] The hydride species $[M(\mu\text{-}H)B(C_6F_5)_3]$ (M = Ti, Zr, Nb) has been suggested to be the key intermediate. In some cases the intermediate has been observed by NMR spectroscopy,[8] but it has never been isolated and studied. Here we report the first isolation of this hydride species in a vanadocene system.

Addition of Cp_2V in toluene to a solution of hydrated borane[9] gives a blue-purple solution and, after 1 day, yellow-orange and blue crystals (Scheme 1). After hand separation, both compounds were unambiguously characterized by an X-ray structure analysis. Figures 1 and 2 give ORTEP views of the molecular structures of **1** and **2**, respectively.

Scheme 1



$$2\,Cp_2V + 2\,B(C_6F_5)_3 + H_2O \xrightarrow{\text{Toluene}} \underset{\mathbf{1}}{Cp_2V(\mu\text{-}H)(B(C_6F_5)_3} + \underset{\mathbf{2}}{Cp_2V(\mu\text{-}OH)(B(C_6F_5)_3}$$

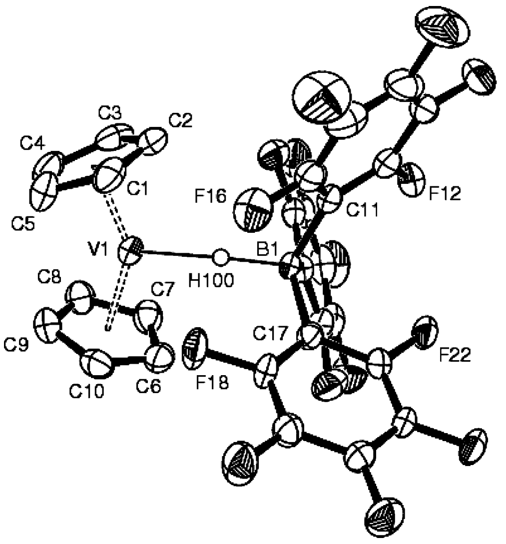


Figure 1. Ortep drawing of the molecular structure of **1** showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity. Selected parameters (bond lengths in Å and angles in deg): V1−H100 = 1.87(2), B1−H1= 1.34(2); V1−H100−B1 = 152.8, Cp1−V1−Cp2 = 142.8 (Cp1 and Cp2 are the centroids of the C1−C5 and C6−C10 Cp ligands, respectively).

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[6] (a) In presence of the "metal base" $[Ir(Cp)(C_8H_{12})]$, a salt containing the hydride ligand on iridium, $[Ir(Cp)(C_8H_{12})H][(F_5C_6)_3B(\mu\text{-}OH)B(C_6F_5)_3]$, was isolated.[4b] (b) Danopoulos, A. A.; Galsworthy, J. R.; Green, M. L. H.; Cafferkey, S.; Doerrer, L. H.; Hursthouse, M. B. *Chem. Commun.* **1998**, 2529−2530. (c) Di Saverio, A.; Focante, F.; Camurati, I.; Resconi, L.; Beringhelli, T.; d'Alfonso, G.; Donghi, D.; Maggioni, D.; Mercandelli, P.; Sironi, A. *Inorg. Chem.* **2005**, *44*, 5030−5041.

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[9] Prepared by the addition 2 equiv of $B(C_6F_5)_3$ with 1 equiv of H_2O or from isolated $H_2O{\cdot}B(C_6F_5)_3)$ (1 equiv) with $B(C_6F_5)_3$ (1 equiv).

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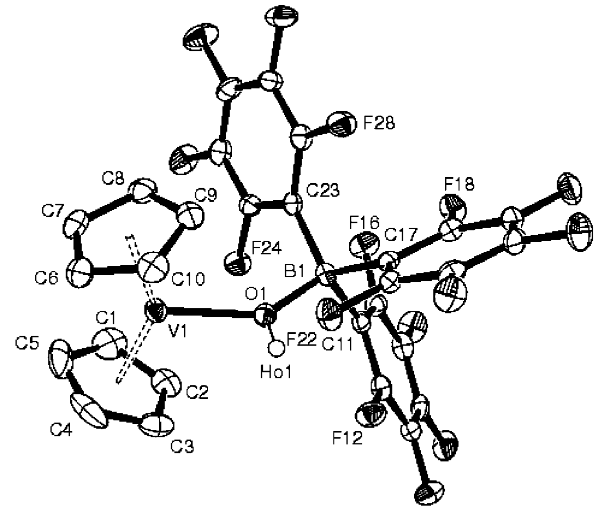
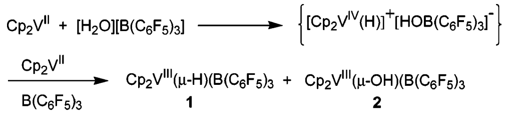


Figure 2. Ortep drawing of the molecular structure of **2** showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity. Selected parameters (bond lengths in Å and angles in deg): V1−O1 = 2.0875(14), B1−O1 = 1.518(3), O1−Ho1 = 0.75(2); V1−O1−B1 = 142.57(13), Cp1−V1−Cp2 = 141.7 (Cp1 and Cp2 are the centroids of the C1−C5 and C6−C10 Cp ligands, respectively).

The yellow-orange crystals were determined to be the hydride complex $[Cp_2V(\mu\text{-}H)B(C_6F_5)_3]$ (**1**). The data were of sufficiently high quality that we were able to locate a hydrogen atom between the vanadocene moiety and the borane Lewis acid. The V−H distance in **1** (1.87(2) Å) is comparable to those in complexes having an hydrogen atom bridging a vanadium center and a second metal (V, Zn) or a boron atom of a η^1- or η^2-borohydride ligand (V−H = 1.69(4)−1.94(3) Å).[10] The B−H distance in **1** (1.34(2) Å) is longer than that found in the aforementioned η^1- and η^2-BH_4 complexes (1.12 (av) and 1.10 Å, respectively). This B−H bond is also longer than in the anion $[HB(C_6F_5)_3]^-$ (for example, for $[Cp_2V(CO)_2][HB(C_6F_5)_3]$ B−H = 1.14(2) Å[11] and for $[Cp^*{}_2Zr][HB(C_6F_5)_3]$ B−H = 1.06(6) Å[8c]). It is worth noting that the sums of the angles C−B−C around the boron atom are nearly the same in **1** and in the $[HB(C_6F_5)_3]^-$ anion.

A comparative topological analysis was performed using the electron localized function (ELF)[12] in order to get more insight into the V−H−B interaction in **1**. The ELF picture of **1** was compared to those of the free B−H bond in the $[HB(C_6F_5)_3]^-$ anion, free V−H in Cp_2VH, and V−H−V in $Cp_4V_2H_2$. As no crystallographic structure was available for the last two complexes, their structures were calculated at the B3PW91/6-31G* level (see the Supporting Information). According to the ELF analysis of **1**, the H atom interacts with both V and B, as it is involved in a three-center−two-electron bond (defined in the ELF by the trisynaptic basin *V*(V,H,B)). The atomic contribution of V to the population of the trisynaptic basin *V*(V,H,B) is close to but slightly lower for **1** than for $Cp_4V_2H_2$. Similarly, the atomic contribution of the B atom to the population of *V*(V,H,B) is slightly lower for **1** than for the $[HB(C_6F_5)_3]^-$ anion. These findings are in agreement with the structural parameters, which suggest a bridging hydride in **1** with weakened V−H or B−H bonds. In a sense, **1** can be regarded as a vanadium hydride stabilized by a borane before its abstraction by the borane, leading to a salt containing the $[HB(C_6F_5)_3]^-$ anion.[8d,13]

Scheme 2



The blue crystals were structurally characterized as being the expected [hydroxytris(pentafluorophenyl)borato]vanadium(III) complex $[Cp_2V(\mu\text{-}OH)B(C_6F_5)_3]$ (**2**), in which the hydrogen atom of the hydroxide group was also located by the X-ray structure determination. The V−O (2.0875(14) Å) and O−B (1.518(3) Å) distances are those expected for a bridging hydroxide of a zwitterionic complex. In contrast to the case for the analogous titanium complexes $[Cp_2Ti(\mu\text{-}OH)B(C_6F_5)_3]$ and [*rac*-(ebthi)Ti(μ-OH)B(C_6F_5)$_3$], in which a C−F···Ti interaction between the Ti center and an ortho fluorine atom of the borane moiety occurs in the solid-state structure,[5] no such interaction is observed in the vanadium complex **2**.

According to the stoichiometry of the reaction (Scheme 1) compounds **1** and **2** should be obtained in equimolar amounts. However, only a low yield of **1** is obtained. Varying the experimental (solvent, concentration of reactants) or workup conditions did not improve the yield of isolated **1** significantly, and as a consequence this precluded its full characterization and its reactivity study.[13] Furthermore, meticulously dried aprotic solvent added to a mixture of **1** and **2** immediately emitted fumes and led to partial decomposition of **1** (leaving **2** unchanged, as monitored by IR). The very high sensitivity of **1** toward adventitious water may explain the difficulty we encountered in its isolation and may also explain why such hydride species have remained elusive in other metal systems that have been studied. The magnetic moments measured for **1** and **2** are in agreement with those of vanadium(III) species (μ_{eff} = 2.85 and 2.95 μ_B, respectively).[13] The ν_{OH} infrared frequency of **2** in KBr is observed at 3614 cm^{-1}. The deuterated analogue $[Cp_2V(\mu\text{-}OD)B(C_6F_5)_3]$[14] has a ν_{OD} value of 2666 cm^{-1}. For **1** (which was always contaminated by a small amount of **2**) the medium-broad B−H stretching bands centered at 1904 cm^{-1} are too complex to be assigned but are compatible with a monodentate borohydride species;[15] the B−D stretching band of the deuterated analogue is not observed, due to its superposition with other bands of the complex.

The concomitant formation of a hydride species **1** and a hydroxide species **2**, starting from $[H_2O][B(C_6F_5)_3]$, implies the two-electron reduction of H_2O by Cp_2V. We suggest the reaction to proceed via the overall pathway depicted in Scheme 2, which involves the intermediacy of a V(IV) species ($[Cp_2VH]^+[HOB(C_6F_5)_3]^-$) that further evolves through disproportionation with Cp_2V into the vanadium(III) complexes **1** and **2**.[16]

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(13) The spectroscopic and magnetic studies were conducted at room temperature on a pure crystalline sample obtained after separation by hand of a mixture of large crystals of **1** and **2**. Spectroscopic studies of **1** in THF-d_8 showed the formation of the vanadium(III) EPR-silent salt $[Cp_2V]^+$-$[HB(C_6F_5)_3]^-$: ^1H NMR (400 MHz) 145 (br, Cp), 4.28 ppm (br q, BH, J_{BH} = 80 Hz); ^{11}B NMR −24.5 ppm (d, J_{BH} = 76 Hz); ^{19}F NMR −46.2, −83.9, −85.3 ppm. Complex **2** is EPR-silent. Spectroscopic studies of **1** in THF-d_8: ^1H NMR (400 MHz) 134 ppm (br, Cp) (*H*O unobserved); ^{11}B NMR −3.3 ppm; ^{19}F NMR unresolved. (note: ^{19}F NMR (188.3 MHz), reference CF_3CO_2H; ^{11}B NMR (160.5 MHz), reference $BF_3{\cdot}Et_2O$).

(14) $[Cp_2V(\mu\text{-}OD)B(C_6F_5)_3]$ was obtained from the above reaction scheme using D_2O in place of H_2O.

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We have already reported the formation of a hydride species (at that time wrongly formulated as the salt $[Cp_2V][HB(C_6F_5)_3]$) from the reaction of $[Cp_2VCO]$ with $B(C_6F_5)_3$.[11] We can now see that redox and disproportionation reactions afford four different complexes: **1**, the structurally established, unprecedented, zwitterionic ring-borylated vanadium(III) complexes $CpCp^BV$ and $CpCp^BV(CO)_2$ ($Cp^B = \eta^5$-$C_5H_4B(C_6F_5)_3$), and the ionic vanadium(III) species $[Cp_2V(CO)_2][HB(C_6F_5)_3]$.

In conclusion, the existence of complex **1** is of considerable importance and contributes to a better understanding of ion pairs.[17] It shows for the first time that such a hydride intermediate postulated for early-transition-metal complexes exists, and we have demonstrated that its formation implies a two-electron reduction of water (mediated, in our work, by Cp_2V). Due to the powerful water scavenging ability of $B(C_6F_5)_3$, one may not exclude the possibility that such hydride and hydroxide species can be formed during catalytic olefin polymerization processes involving metallocenes and $B(C_6F_5)_3$ cocatalyst in the presence of traces of water.[1] We are currently working to answer this point.

Acknowledgment. We are grateful to the CNRS for financial support.

Supporting Information Available: CIF files giving crystal data for complexes **1** and **2** and tables giving computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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