

A New Class of CVD Precursors to Metal Borides: $\text{Cr}(\text{B}_3\text{H}_8)_2$ and Related Octahydrotriborate Complexes

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Molecular complexes that contain only a metal, boron, and hydrogen are of interest because of their utility as CVD precursors to metal diboride phases; an excellent example of this approach is the deposition of ZrB_2 and HfB_2 thin films from the volatile tetrahydroborate complexes $\text{Zr}(\text{BH}_4)_4$ and $\text{Hf}(\text{BH}_4)_4$.^{1–4} Unfortunately, the ability to grow a wide variety of MB_x phases is limited by the scarcity of homoleptic $\text{M}(\text{BH}_4)_n$ complexes.^{5–10} Apart from the alkali metal derivatives (which are nonvolatile), only 10 such compounds are known, of which five are oligomers or polymers in the solid state (those containing Be^{II} ,⁵ Ti^{III} ,⁶ Th^{IV} ,⁷ Pa ,⁸ or U^{IV} ⁹) and five are monomers (those containing Al^{III} ,¹⁰ Zr^{IV} ,¹¹ Hf^{IV} ,¹² Np^{IV} ,^{8,13} or Pu^{IV} ⁸).

The rarity of volatile $\text{M}(\text{BH}_4)_n$ complexes is a consequence of two factors: the BH_4^- group is sterically small and is a strong reductant.¹⁴ The small size means that three or four BH_4 groups are required to saturate the coordination spheres of most transition metals. Because volatile complexes are almost invariably electrically neutral, the metal oxidation state must be +3 or +4. For many transition metals, however, these oxidation states are not stable in the presence of strongly reducing BH_4^- groups.

We now report the synthesis of several new transition metal complexes of the octahydrotriborate ion, B_3H_8^- . Because B_3H_8^- is larger than BH_4^- , it should be better able to saturate sterically the coordination spheres of transition metals in lower oxidation states. Although heteroleptic transition metal complexes containing B_3H_8^- ligands are known,^{15–17} no homoleptic complexes have been reported until now.

Grinding CrCl_3 with excess NaB_3H_8 ¹⁸ at 20 °C produces a volatile purple liquid (**1**) that can be purified by distillation or by extraction with pentane. The product is thermally unstable. We tentatively assign the formula $\text{CrH}(\text{B}_3\text{H}_8)_2$ to **1** on the basis of the following evidence: (i) the boron-to-chromium ratio is ~6:1, and the compound contains no chloride, as judged by hydrolyzing a pentane solution of **1** and analyzing the hydrolysis products; (ii) the EPR spectrum (see below) suggests that **1** contains low-symmetry chromium(III) centers; and (iii) the infrared spectrum of **1** in pentane shows strong terminal B–H bands at 2554 and 2485 cm^{-1} and a strong bridging B–H band at 2005 cm^{-1} that are consistent with the presence of B_3H_8^- groups. No IR band ascribable to a terminal hydride ligand was observed; it is possible that such a band is present but hidden by features due to the pentane solvent. For comparison, $\text{Cr}(\text{BH}_4)\text{H}(\text{dmpe})_2$,¹⁹ $\text{dmpe} = 1,2$ -bis(dimethylphosphino)ethane, exhibits a $\nu(\text{Cr}–\text{H})$ band at 1580 cm^{-1} . Mass spectrometry (field ionization and electron-impact ionization) did not afford useful information.

The X-band EPR spectrum of **1** in a toluene glass at –196 °C (see Supporting Information) reveals three features at ca. 125, 170, and 330 mT; no hyperfine structure is evident. The EPR spectrum is consistent with a d^3 ion possessing a g factor of 2, a zero-field

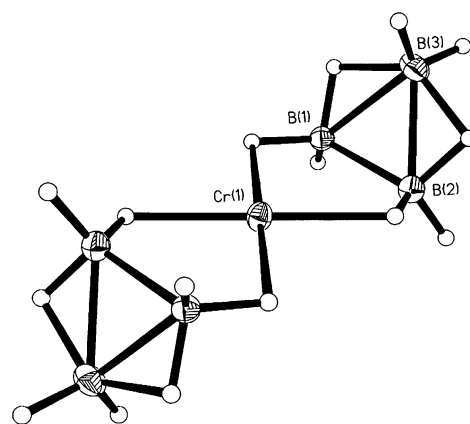


Figure 1. Molecular structure of $\text{Cr}(\text{B}_3\text{H}_8)_2$ (**2**). Ellipsoids are drawn at the 30% probability level, except for hydrogen atoms, which are represented as arbitrarily sized spheres.

splitting $D > 0.4 \text{ cm}^{-1}$, and a symmetry parameter $\lambda \approx 0.15$; the latter is indicative of a rhombic structure.

When samples of **1** are kept at room temperature, the purple liquid converts within 3 h into blue needles of $\text{Cr}(\text{B}_3\text{H}_8)_2$ (**2**), which can be isolated by sublimation at 35 °C and 20 mTorr. (Hydrogen can be detected among the decomposition products, but it is difficult to establish whether it is formed by thermolysis or adventitious hydrolysis.) The IR spectrum of **2** features strong bands at 2541, 2482, and 2406 cm^{-1} due to terminal B–H stretches, and strong bands at 2131 and 2081 cm^{-1} due to bridging B–H stretches. The pattern of bands is similar to those seen for bidentate B_3H_8^- ligands in other complexes.¹⁶ The magnetic moment of 4.8 μ_B measured in solution indicates that the chromium(II) center is high-spin.

The molecular structure of **2** is illustrated in Figure 1. The chromium atom is coordinated to two bidentate B_3H_8^- groups in a square-planar geometry. The Cr–H distances of 1.86(4) and 1.88(5) Å and the Cr···B distances of 2.423(3) Å are similar to those of 1.78(6) and 2.433(3) Å, respectively, seen in $[(\text{CO})_4\text{Cr}(\text{B}_3\text{H}_8)]^-$.¹⁷ Along the axial directions of the square plane, there are two intermolecular Cr···H contacts of 2.30(5) Å, each of which involves a terminal B–H group of a neighboring molecule. These intermolecular Cr···H interactions are long and presumably weak, in view of the fact that **2** sublimates readily at 35 °C.

Bis(octahydrotriborate)beryllium(II) is the only other example of a MB_xH_y complex that does not contain BH_4^- ligands.^{20,21} Compound **2** is the first molecular MB_xH_y complex of a transition metal to be discovered since $\text{Ti}(\text{BH}_4)_3$, $\text{Zr}(\text{BH}_4)_4$, and $\text{Hf}(\text{BH}_4)_4$ were reported by Hoekstra and Katz in 1949.⁷

Interaction of CrCl_3 with excess NaB_3H_8 in diethyl ether at 0 °C affords the chromium(II) complex $\text{Cr}(\text{B}_3\text{H}_8)_2(\text{Et}_2\text{O})_2$ (**3**), which reacts readily with tetrahydrofuran or trimethylphosphine to afford the Lewis base substitution products $\text{Cr}(\text{B}_3\text{H}_8)_2(\text{thf})_2$ (**4**) and

Cr(B₃H₈)₂(PMe₃)₂ (**5**). The molecular structures of **3–5** have been determined by X-ray diffraction (see Supporting Information). The ether ligands in six-coordinate **3** and **4** occupy axial, mutually trans sites; the equatorial B₃H₈ ligands are bound to the metal in a symmetrical fashion (i.e., the Cr–H_b and Cr···B distances are all nearly identical) with Cr···B distances of 2.57–2.60 Å that are ~0.15 Å longer than those in four-coordinate **2**. In contrast, the PMe₃ ligands in **5** occupy equatorial, mutually cis positions. Each of the B₃H₈ groups spans an equatorial and axial site of the square plane and is bound unsymmetrically owing to Jahn–Teller effects: there is one short Cr···B distance of ~2.53 Å (equatorial; trans to PMe₃) and one long distance of ~2.64 Å (axial; cis to PMe₃). The Cr–H distances are similarly unequal at 1.87(2) vs 2.10(2) Å. The preference of the PMe₃ ligands in **5** to occupy equatorial positions suggests that the relative bond strength to the Cr center varies as PMe₃ > B₃H₈[−] > thf ~ Et₂O.

The transition metal borides are hard, refractory, and electrically conductive materials of interest as hard coatings and as barriers in ULSI circuits.^{22,23} Passage of **2** over substrates heated to >200 °C affords silvery metallic mirrors of highly pure CrB₂ (details to be described elsewhere).²⁴ The successful use of Cr(B₃H₈)₂ to grow CrB₂ thin films suggests that other metal borides for which no suitable CVD precursor currently exists may be accessible through the use of molecules containing the octahydrotriborate ligand.^{25,26}

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Supporting Information Available: Figures of the EPR spectrum of **1** and the molecular structures of **3–5** and experimental and characterization details for **1–5**. X-ray structural data for **2–5** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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