A New Class of CVD Precursors to Metal Borides: Cr(B₃H₆)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 ZrB₂ and HfB₂ thin films from the volatile tetrahydroborate complexes Zr(BH₄)₄ and Hf(BH₄)₄. Unfortunately, the ability to grow a wide variety of MBₙ phases is limited by the scarcity of homoleptic M(BH₄)ₙ complexes. 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 Be²⁺, Ti³⁺, Th⁴⁺, Pa, or U⁴⁺) and five are monomers (those containing A¹⁺, Zr⁴⁺, Hf⁴⁺, Np⁴⁺, or Pu⁴⁺).

The rarity of volatile M(BH₄)ₙ complexes is a consequence of two factors: the BH₄⁻ group is sterically small and is a strong reductant. The small size means that three or four BH₄ 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 BH₄⁻ groups.

We now report the synthesis of several new transition metal complexes of the octahydrotriborate ion, B₃H₆⁻. Because B₃H₆ is larger than BH₄, it should be better able to saturate sterically the coordination spheres of transition metals in lower oxidation states. Although heteroleptic transition metal complexes containing B₃H₆ ligands are known, no homoleptic complexes have been reported until now.

Grinding CrCl₃ with excess NaB₃H₈ 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 CrH(B₃H₆)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 hydronizing a pentane solution of 1 and analyzing the hydrosis 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 B₃H₆ 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, Cr(BH₄)H(dmpe)₄, dmpe = 1,2-bis(dimethylphosphino)ethane, exhibits a ν(Cr–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 d⁴ ion possessing a g factor of 2, a zero-field 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 Cr(B₃H₆)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 hydrosis.) 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 B₃H₆ ligands in other complexes. The magnetic moment of 4.8 \( \mu_B \) 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 B₃H₆⁻ 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 [(CO)₆Cr(B₃H₆)]⁺.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 sublimes readily at 35 °C.

Bis(octahydrotriborato)beryllium(II) is the only other example of a MB₆ complex that does not contain BH₄ ligands. Compound 2 is the first molecular MB₆ complex of a transition metal to be discovered since Ti(BH₄)₂, Zr(BH₄)₄, and Hf(BH₄)₄ were reported by Hoekstra and Katz in 1949.7 Interaction of CrCl₃ with excess NaB₃H₈ in diethyl ether at 0 °C affords the chromium(II) complex Cr(B₃H₆)₂(EtO)₂ (3), which reacts readily with tetrahydrofuran or trimethylphosphine to afford the Lewis base substitution products Cr(B₃H₆)₂(thf)₂ (4) and...
Cr(B\(_2\)H\(_6\))(PM\(_3\))\(_2\) (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 B\(_2\)H\(_6\) ligands are bound to the metal in a symmetrical fashion (i.e., the Cr–H 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 PM\(_3\) ligands in 5 occupy equatorial, mutually cis positions. Each of the B\(_2\)H\(_6\) 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 PM\(_3\)) and one long distance of ~2.64 Å (axial; cis to PM\(_3\)). The Cr–H distances are similarly unequal at 1.87(2) vs 2.10(2) Å. The preference of the PM\(_3\) ligands in 5 to occupy equatorial positions suggests that the relative bond strength to the Cr center varies as PM\(_3\) ≈ B\(_2\)H\(_6\) ≫ thf ≈ Et\(_2\)O.

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 CrB\(_2\) (details to be described elsewhere).\(^{24}\) The successful use of Cr(B\(_3\)H\(_8\))\(_2\) to grow CrB\(_2\) 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.

References