Synthesis of hydroborate compounds as potential chemical vapor deposition precursors and their use for the growth of magnesium diboride thin films

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Metal diborides (MB_2) possess outstanding properties for thin film applications in microelectronics and hard coatings: transition metal diborides such as TiB_2, ZrB_2, and HfB_2 have melting points often exceeding 3000 ºC, electrical resistivities as low as 15 μΩ-cm, and hardnesses approaching 30 GPa.[1-3] In addition, they are chemically robust. Some metal borides are attractive as potential replacements for TiN as electrically conductive diffusion barriers in integrated circuits, preventing the interdiffusion of copper and silicon in interconnects.[4-6] Moreover, magnesium diboride (MgB_2), which becomes superconducting below ca. 40 K,[7] is potentially useful for the fabrication of superconductor-based integrated circuits.

For many transition metal boride phases, it is not possible to use single source CVD precursors to grow films because no precursor of stoichiometry MB_xH_y exists. Volatile $M(BH_4)_n$ complexes of d-block transition metals are rare because the BH_4^- ligand is sterically small and strongly reducing, and in fact only $Ti(BH_4)_3$, $Zr(BH_4)_4$, and $Hf(BH_4)_4$ are known.[8,9] By employing the sterically more demanding hydroborate ligand $B_3H_8^-$, the highly volatile chromium(II) complex of $Cr(B_3H_8)_2$[10] has been prepared. However, although the $B_3H_8^-$ group is sterically larger than the BH_4^- ligand, so far only chromium has been shown to form a highly volatile $M(B_3H_8)_x$ species suitable as a CVD precursor. For MgB_2, no low-temperature CVD methods have been described, largely due to the absence of suitable precursors. Although magnesium complexes of tetrahydroborate (BH_4^-),[11,12] octahydrotriborate ($B_3H_8^-$),[13-15] and nonahydrohexaborate ($B_6H_9^-$) groups[16] have been described, all are nonvolatile.

In an effort to explore the chemistry of transition metal complexes of the $B_3H_8^-$ ligand, the new heteroleptic compounds $Cp*V(B_3H_8)_2$, $Cp*Cr(B_3H_8)_2$, and $Cp*_2Co_2(B_6H_{14})$ have been synthesized by treating the pentamethylcyclopentadienyl complexes $[Cp*VCl_2]_3$, $[Cp*CrCl_2]_2$, and $[Cp*CoCl]_2$ with NaB_3H_8. $Cp*V(B_3H_8)_2$ and $Cp*Cr(B_3H_8)_2$ have the same ligand sets but different molecular structures: the vanadium compound contains two bidentate B_3H_8 ligands whereas the chromium compound has one bidentate B_3H_8 ligand and one B_3H_8 ligand bound in an unprecedented fashion via two *geminal* hydrogen atoms. The different binding modes of the $B_3H_8^-$ group in these compounds are consequences of the number of available empty valence orbitals on the metal centers. The dinuclear complex $Cp*_2Co_2(B_6H_{14})$ can be viewed as a "bi-borallyl" complex or as an eight-vertex *hypho* cluster.
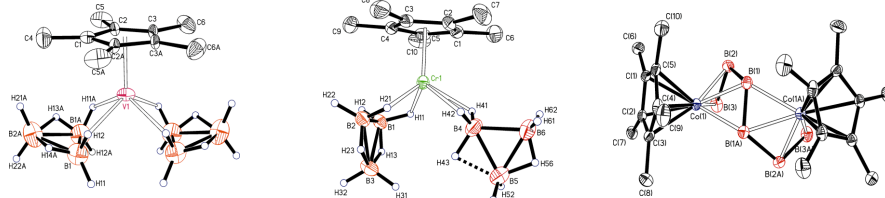

Figure 1. Molecular structures of $Cp*V(B_3H_8)_2$, $Cp*Cr(B_3H_8)_2$, and $Cp*_2Co_2(B_6H_{14})$.

Volatile magnesium complexes of the $B_3H_8^-$ group, $Mg(B_3H_8)_2$, $Mg(B_3H_8)_2(Et_2O)_2$ and $Mg(B_3H_8)_2(Me_2O)_2$ were also synthesized; these molecules are the first crystallographically characterized magnesium-B_3H_8 compounds.
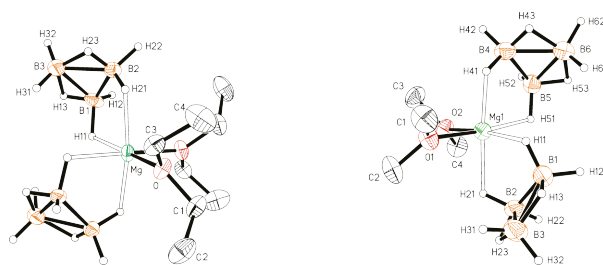

Figure 2. Molecular structures of $Mg(B_3H_8)_2(Et_2O)_2$ and $Mg(B_3H_8)_2(Me_2O)_2$.

An entirely new class of highly volatile transition metal complexes has been discovered that contain the *N,N*-dimethyldiboranamide ligand:, $M(H_3BNMe_2BH_3)_2$, where M is Ti, Cr, Mn, or Mo. Several aspects of this system are notable: (1) The $[H_3BNMe_2BH_3^-]$ ligand chelates to the metal center by means of four B-H-M bridges. (2) Two diboranamide ligands are sufficient to saturate the coordination spheres of the divalent metal centers, making all the complexes highly volatile. (3) The titanium, chromium, and molybdenum complexes exhibit square-planar geometries whereas the manganese complex adopts a distorted tetrahedral geometry. This difference in molecular geometry is electronic in origin.
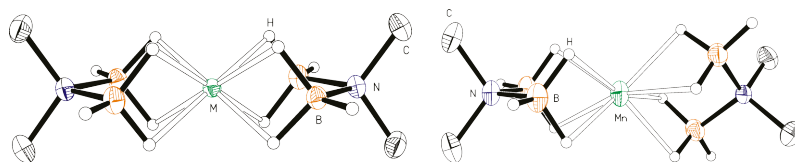

Figure 3. Molecular structures of $M(H_3BNMe_2BH_3)_2$, (M=Ti, Cr, or Mo) and $Mn(H_3BNMe_2BH_3)_2$

The magnesium diboranamide complex $Mg(H_3BNMe_2BH_3)_2$, its adducts with ethers, and the mixed ligand complex $Cp*Mg(H_3BNMe_2BH_3)(thf)$ have also been prepared. Significantly, the binary complex $Mg(H_3BNMe_2BH_3)_2$ has a vapor pressure of 800 mTorr at 25 °C, which makes it the most volatile magnesium complex known.

The first low-temperature chemical vapor deposition of doped MgB_2 phases has been achieved by passing the precursor $Mg(H_3BNMe_2BH_3)_2$ over a surface in the presence of a catalyst that accelerates the rate of the CVD growth reaction. When the catalyst is a titanium compound, the films have the stoichiometry $Mg_{0.8}Ti_{0.2}B_2$ owing to substitution of Ti atoms into the Mg sites of the film. Although the metal substitution renders the films non-superconducting above 4K, the results clearly point the way to the development of technologically-attractive CVD processes to grow superconducting MgB_2 thin films at temperatures below 400 °C. We believe that the idea of catalyzing CVD reactions constitutes a fascinating new direction for CVD research.
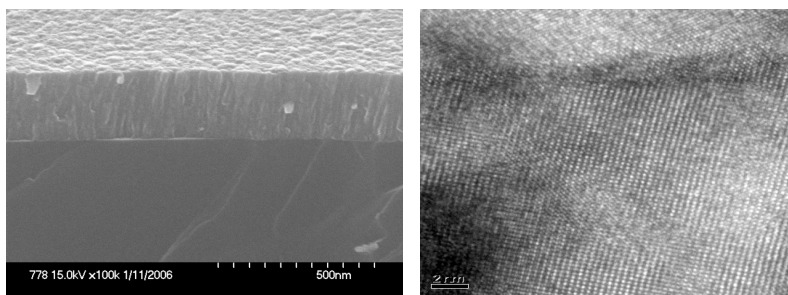
Figure 3. Fracture cross-sectional SEM image(left) and TEM image of $Mg_{0.8}Ti_{0.2}B_2$

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