retention of unsaturated tin in the product is precluded either by conversion to four-coordinate Sn or by hydride bridging to tin. This is a conclusion also evident from our study[21] of the products of reductive elimination of methane from $AlMe_3$ and $ReH_m(PR_3)_n$. Our consistent finding that hydride ligands in heterometallic polyhydride clusters do not rapidly migrate past Cu, Ag, and now Sn centers suggests that hydrogen spillover,[22,23] the migration of hydrogen on a surface, may encounter significant activation barriers.[24]

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported by the Canadian Natural Sciences and Engineering Research Council. We thank Rhenium Alloys, Inc. for material support and Scott Horn for skilled technical assistance.

Supplementary Material Available: Listing of atomic positional and thermal parameters for $SnRe_4H_{12}(PMe_2Ph)_8{\cdot}C_7H_8$ (2 pages). Ordering information is given on any current masthead page.

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Titanium, Zirconium, and Hafnium Tetrahydroborates as "Tailored" CVD Precursors for Metal Diboride Thin Films

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Received October 19, 1987

In the last decade, there has been increasing interest in the use of group 4 diborides, MB_2 (where M = Ti, Zr, Hf), as coatings prepared by chemical vapor deposition (CVD).[1] This interest arises from their desirable properties: high hardness, high melting point, moderate strength, resistance to wear and corrosion, and good electrical conductivity.[2] Such properties are retained even at high temperature and make the diborides, particularly TiB_2, useful for such applications as coatings for metal cutting tools,[3] as crucibles and electrodes in metal-refining equipment such as aluminum reduction cells,[4] and potentially as coatings in rocket nozzles, valves, and the nose and leading edge of reusable re-entry vehicles in the aerospace industry.[5] There are currently four principal methods for preparing group 4 diborides: synthesis from the elements at over 2000 °C, reduction of the metal oxide and boron oxide by carbon at 2000 °C, reduction of the metal oxide by boron carbide and carbon at 2000 °C, and reduction of the metal halide and boron trihalide by hydrogen at 1200 °C; of these methods, only the last is suitable for the preparation of thin films.[1] An earlier publication dealth with the successful use of "tailored" molecular precursors to prepare thin films of TiC at 250 °C;[6] here we describe a remarkable extension of this CVD approach to the preparation of thin films of TiB_2, ZrB_2, and HfB_2 at exceptionally low temperatures (200 °C).

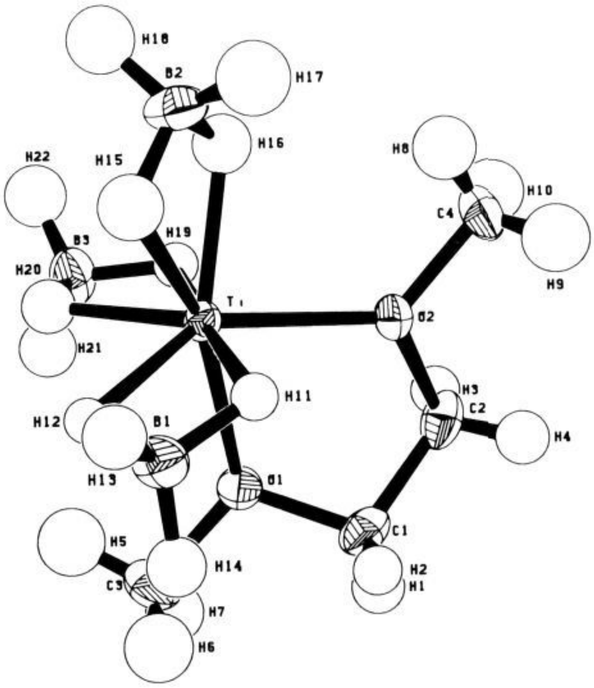

Figure 1. Molecular structure of $Ti(BH_4)_3(dme)$.

Transition-metal tetrahydroborates[7] should serve as excellent CVD precursors for metal borides, since they are often appreciably volatile and are known to thermolyze under mild conditions to give hydrogen and variable amounts of diborane. Unfortunately, binary titanium tetrahydroborates are poorly suited for CVD studies since $Ti(BH_4)_4$ is unknown (Ti^{IV} is reduced by BH_4^-) and $Ti(BH_4)_3$[8] is an exceedingly unstable species that decomposes well below room temperature. However, derivatives of $Ti(BH_4)_3$ are known,[9,10] and tris(tetrahydroborato)(1,2-dimethoxyethane)titanium(III) was chosen for CVD studies since it is one of the few Lewis base adducts of titanium tris(tetrahydroborate) that exhibits appreciable thermal stability and volatility. Light blue $Ti(BH_4)_3(dme)$ can be prepared by addition of dme to the thermally unstable adduct $Ti(BH_4)_3(OEt_2)$[10] or, more simply, by direct interaction of $TiCl_4$ with excess $NaBH_4$ in dme followed by crystallization from diethyl ether. $Ti(BH_4)_3(dme)$ is paramagnetic ($\mu_{eff} = 1.8\ \mu_B$), and its IR spectrum shows intense B–H stretches at 2412 cm^{-1} (terminal) and 2114 cm^{-1} (bridging) that are diagnostic of bidentate tetrahydroborate groups. This is confirmed by the X-ray crystal structure of $Ti(BH_4)_3(dme)$ which reveals a distorted trigonal bipyramidal geometry (Figure 1), considering the BH_4^- groups to occupy one site. The dme ligand bridges between an axial and an equatorial position, with Ti–O = 2.110 (1), 2.074 (1) Å. The Ti⋯B contacts are all equal at 2.411 (3)

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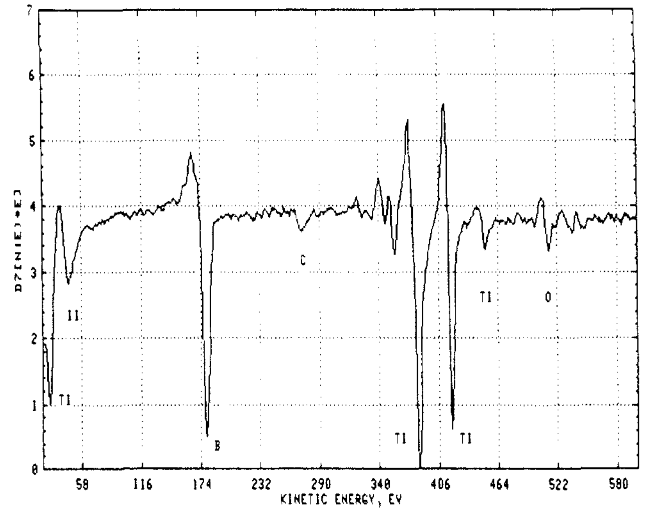

Figure 2. Auger electron spectrum of TiB_2 films prepared at 200 °C from $Ti(BH_4)_3(dme)$ showing the characteristic Ti and B peaks. The surface oxide layer has been removed by sputtering.

Å; this distance is comparable to the 2.40 (1) and 2.37 (1) Å distances observed for the bidentate tetrahydroborate groups in the titanium(III) compounds $Ti(BH_4)_3(PMe_3)_2$[9] and $Cp_2Ti(BH_4)$,[12] respectively. The hydrogen atoms in the structure were all located and independently refined, and the Ti–H_b bond distances of 1.84 (2)–1.93 (2) Å are reasonably consistent with the 1.90 (6) and 1.75 (8) Å distances observed in $Ti(BH_4)_3(PMe_3)_2$ and $Cp_2Ti(BH_4)$. Interestingly, all three tetrahydroborate groups are *tipped* away from the other two BH_4^- ligands due to steric effects, so that the Ti···B–H angles involving the terminal B–H hydrogen atoms fall into two groups: a larger angle averaging 129 (1)° and a smaller angle averaging 117 (2)°. This bonding mode is unprecedented in the literature and represents an intermediate along a reaction coordinate connecting bidentate and tridentate BH_4^- coordination geometries.

Low-temperature (200 °C) and low-pressure (10^{-4} Torr) chemical vapor deposition of $Ti(BH_4)_3(dme)$ was achieved by using a Pyrex high-vacuum apparatus containing an externally heated reaction zone. The precursor sublimes readily without decomposition at 25 °C in vacuum, and passage through the apparatus resulted in the deposition of adhesive thin films of TiB_2 on Pyrex glass slides mounted in the hot zone. X-ray diffraction studies of the silvery metallic films showed only broad diffuse scattering in the 15–40° (2θ) region characteristic of an amorphous solid, while Auger electron spectroscopy (AES) revealed the presence of titanium and boron in a Ti/B ratio of ca. 1:2.07 (Figure 2). AES depth-profile studies indicate a high oxygen content near the surface of the films that falls off to a negligible amount (<2%) in the bulk. This undoubtedly results from surface oxidation of the films upon exposure to air; the oxide overlayer is only ca. 15–20 nm thick. X-ray photoelectron spectroscopy (XPS) results indicated that the Ti $2p_{3/2}$ peak at 454.7 eV and the B 1s peak at 187.1 eV do in fact correspond to a TiB_2 phase.[13] Titanium metal and elemental boron were entirely absent, while negligible oxygen and carbon concentrations were present except at the surface of the films. These results indicate that the dme ligand dissociates intact from $Ti(BH_4)_3(dme)$ during deposition and does not fragment under the experimental conditions. Depth-profile studies showed that there were no significant changes in the relative elemental amounts or shapes of the XPS peaks in the interior of the films. The thickness of the films varies with the deposition time; typically, films of 0.6-μm thickness may be grown from 0.25 g of $Ti(BH_4)_3(dme)$ over 30 h.

Analogous zirconium and hafnium diborides, ZrB_2 and HfB_2, can be prepared by CVD of the binary tetrahydroborates[14] $Zr(BH_4)_4$ and $Hf(BH_4)_4$, respectively, although slightly higher temperatures are required in the deposition zone (250 °C) than for TiB_2. X-ray diffraction studies show these films to be amorphous, and AES confirms the 1:2 metal-to-boron ratio. All of the diboride films can be deposited on a variety of substrates, including glass, copper, aluminum, and steel; adhesion between the substrate and the film is good in all cases.

Diborane is a byproduct of the low-temperature preparation of the metal diboride films, as established by mass spectroscopy.

$$Ti(BH_4)_3(dme) \rightarrow TiB_2 + {}^1/_2B_2H_6 + {}^9/_2H_2 + dme$$

$$M(BH_4)_4 \rightarrow MB_2 + B_2H_6 + 5H_2$$

Since diborane decomposes to higher boron hydrides upon heating,[15] depositions from the metal tetrahydroborate precursors at temperatures above 250 °C give higher boron hydrides (principally B_5H_9 by GC/MS) as byproducts and yield thin films that are boron-rich.[16] Quantitative measurements of the absolute amounts of dihydrogen, diborane, and higher boron hydrides formed are in progress, but at the lower temperatures, the predominance of diborane indicates that the principal thermolytic reactions are as shown. All of these reactions probably proceed via loss of diborane to give metal hydrides that subsequently reductively eliminate H_2; this reaction is similar to the preparation of metal hydrides by addition of Lewis bases to tetrahydroborate complexes.[17]

These results have shown that TiB_2, ZrB_2, and HfB_2 thin films can be obtained by using chemical vapor deposition techniques under remarkably mild conditions—some 1000 °C lower in temperature than previous CVD methods. Further investigations of the electrical and mechanical properties of these films are underway, and we are actively exploring the "tailored" precursor approach to the preparation of thin films of other materials at low temperatures.

Acknowledgment. We thank the National Science Foundation (Grant CHE 85-21757) and the Office of Naval Research under their Young Investigator Award Program for support of this research. We thank Nancy Finnegan and Carol Kozlowski of the University of Illinois Materials Research Laboratory for instruction in Auger and XPS techniques, and we particularly acknowledge Dr. Scott Wilson and Charlotte Stern of the Univeristy of Illinois X-ray Crystallographic Laboratory for performing the X-ray crystal structure determination. We also thank Dr. Andrea Wayda for communicating her results on $Zr(BH_4)_4$ prior to publication (added in proof).

Supplementary Material Available: Tables of atomic coordinates and a complete list of bond distances and angles for $Ti(BH_4)_3(dme)$ (4 pages); listing of final observed and calculated structure factors for $Ti(BH_4)_3(dme)$ (7 pages). Ordering information is given on any current masthead page.

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(11) Crystal data ($T = -50$ °C): monoclinic, space group $P2_1/n$, with $a = 7.573$ (5) Å, $b = 12.261$ (2) Å, $c = 12.337$ (3) Å, $\beta = 97.43$ (4)°, V: 1136 (1) Å^3, $Z = 4$, $R_F = 2.9\%$, $R_{wF} = 3.3\%$ on 179 variables, and 1745 unique data with $I > 2.58\sigma(I)$. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located in the difference maps, and their positions were refined with independent isotropic thermal parameters.

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