

## Transition Metal Hydrides and Allys as Chemical Vapor Deposition Precursors

John E. Gozum

Final Seminar

March 8, 1991

In the last decade there has been increasing interest in the use of titanium diboride,  $TiB_2$ , as a coating prepared by CVD [1-10]. This interest arises from its desirable properties: high hardness, high melting point, moderate strength, resistance to wear and corrosion, and good electrical conductivity [11]. These properties are retained by  $TiB_2$  even at high temperatures, and make it useful for such applications as coatings for metal cutting tools [12], as crucibles and electrodes in metal refining equipment such as aluminum reduction cells [13,14], and potentially as coatings in rocket nozzles, valves, and the nose and leading edge of reusable re-entry vehicles in the aerospace industry [15,16].

Of the various high-temperature synthetic methods [11,17-19], reduction of the metal halide and boron trihalide by hydrogen at  $900^\circ C$ , which was first reported by Moers in 1931 [20], is suitable for the preparation of metal diboride thin films. An alternative vapor phase preparation uses diborane as the source of boron [10].

We have developed alternative CVD precursors that allow the deposition of metal diboride films at lower temperatures. The compound  $Ti(BH_4)_3(dme)$ ,  $dme = 1,2$ -methoxyethane, is one of the few Lewis base adducts of titanium tris(tetrahydroborate) that exhibits appreciable thermal stability and volatility.

Passage of  $Ti(BH_4)_3(dme)$  through an externally-heated Pyrex high-vacuum apparatus at  $200^\circ C$  resulted in deposition of adhesive, mirror-bright thin films on borosilicate glass slides, quartz, aluminum, copper, stainless steel, graphite, and silicon substrates mounted in the hot zone. Auger electron spectroscopy and X-ray photoelectron spectroscopy of the MOCVD deposited  $TiB_2$  films after sputtering of the surface gave signals for titanium and boron, with oxygen and carbon signals near the AES detection limits. The AES profile data indicate a boron-titanium ratio of 2.07 :1 in the film interior. Less than 5% carbon and oxygen were present in the interior of the films.

$Zr(BH_4)_4$  and  $Hf(BH_4)_4$  are readily prepared from  $LiBH_4$  and the metal tetrachloride in diethyl ether [21]. Both compounds have low melting points ( $29^\circ C$ ) and high vapor pressures (15 Torr at  $25^\circ C$ ), which make them ideally suited as CVD precursors. Passage of  $M(BH_4)_4$  through a hot zone at  $250^\circ C$  resulted in deposition of adhesive, mirror-bright thin films on Pyrex glass slides, aluminum, copper, stainless steel, graphite, and silicon substrates.

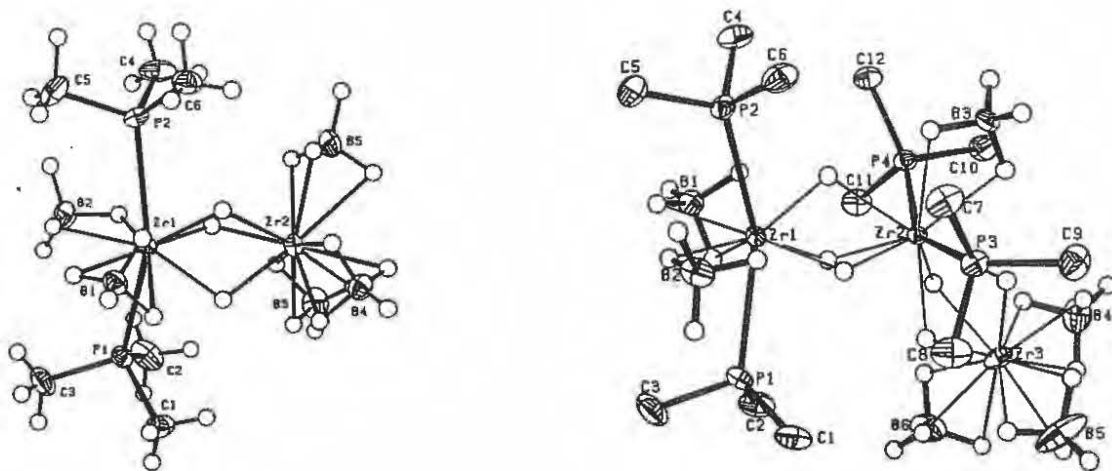
X-ray diffraction studies of the films showed only broad, diffuse scattering in the  $2^\circ$  to  $90^\circ$  ( $2\theta$ ) region. AES spectra show that there is a high oxygen content at the surface of the films which falls to negligible values in the film interiors. XPS data support the AES results. Only peaks due to  $ZrB_2$  and  $HfB_2$  were evident.

During the CVD of the metal diborides, some of the  $BH_4^-$  ligands fragment to give  $B_2H_6$ , while others fragment more completely to give interstitial boron atoms. This means there are at least two possible reaction pathways that each  $BH_4^-$  ligand may follow. One possible route is the elimination of 2 equivalents of  $H_2$  leaving behind a metal-boron fragment. This route does not change the metal to boron ratio. The other mechanistic route involves the loss of  $BH_3$  as a first step leaving a metal-hydride unit which can subsequently reductively eliminate  $1/2 H_2$ . This second route changes the metal to boron ratio.

In order to trap some of the hydride species that may be formed from the CVD of  $\text{Zr}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BH}_4)_4$ , the precursors were thermolyzed in the presence of small alkyl phosphines. The result of this work is the isolation and characterization of several new zirconium and hafnium polyhydrides which are models of the intermediates that may be present in the CVD of  $\text{ZrB}_2$  and  $\text{HfB}_2$  from  $\text{Zr}(\text{BH}_4)_4$  and  $\text{Hf}(\text{BH}_4)_4$ .

Treatment of the zirconium and hafnium tetrahydroborate complexes  $\text{M}(\text{BH}_4)_4$  with trimethylphosphine yields crystals of the new polyhydride complexes  $\text{Zr}_2\text{H}_3(\text{BH}_4)_5(\text{PMe}_3)_2$  and  $\text{Hf}_2\text{H}_3(\text{BH}_4)_5(\text{PMe}_3)_2$  [23]. These  $d^0$  complexes exhibit triplets ( $J_{\text{PH}} \sim 13$  Hz) for the hydride ligands in the  $^1\text{H}$  NMR spectra at  $\delta$  3.96 (Zr) and  $\delta$  8.53 (Hf). The  $^1\text{H}$ ,  $^{11}\text{B}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra show that there is only one phosphine environment but two  $\text{BH}_4^-$  environments in a 2:3 ratio. Single crystal X-ray diffraction studies of the two complexes in each case reveal a distinctly asymmetric dinuclear structure bridged by three hydrogen atoms. One metal center is ligated by three terminal tridentate  $\text{BH}_4^-$  groups, while the other is ligated by the two phosphines, and by one tridentate and one bidentate  $\text{BH}_4^-$  group.

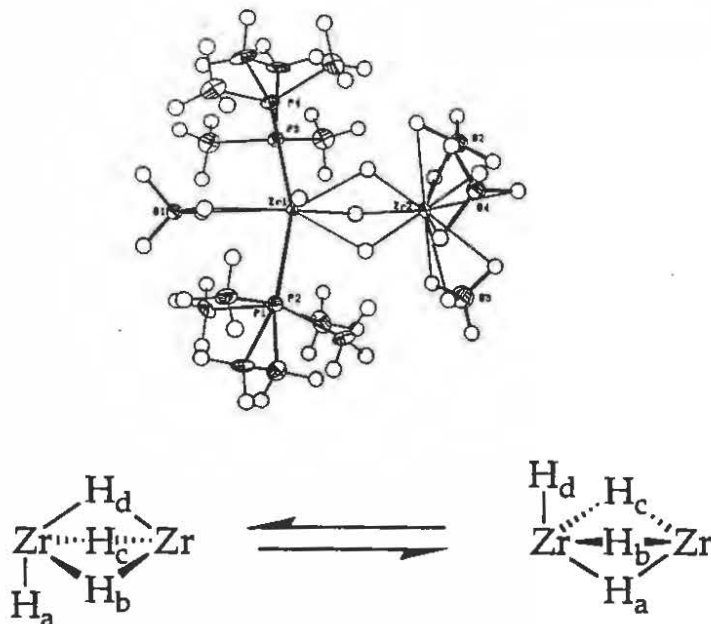
Treatment of  $\text{Zr}(\text{BH}_4)_4$  or  $\text{Hf}(\text{BH}_4)_4$  with trimethylphosphine for extended reaction times has given two new polyhydrides of stoichiometry  $\text{M}_3\text{H}_6(\text{BH}_4)_6(\text{PMe}_3)_4$  where M is Zr or Hf [24]. The variable temperature  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{11}\text{B}$  NMR data suggest that these trinuclear compounds contain a non-cyclic  $\text{M}(\mu\text{-H})_3\text{M}(\mu\text{-H})_3\text{M}$  backbone with the phosphine and tetrahydroborate ligands distributed in 2:2:0 and 2:1:3 ratios among the three metal centers. This suggestion has been confirmed by the single crystal X-ray structure of  $\text{Zr}_3\text{H}_6(\text{BH}_4)_6(\text{PMe}_3)_4$ . The metal-metal vectors are each bridged by three hydride ligands; the average Zr-H-Zr angle is  $108(2)^\circ$ , and the Zr-Zr-Zr angle is  $124.12(1)^\circ$ . This is the first example of a trinuclear group 4 polyhydride that does not contain cyclopentadienyl ligands.



Treatment of the  $\text{M}(\text{BH}_4)_4$  complexes with the bidentate phosphine 1,2-bis(dimethylphosphino)ethane gives mononuclear hydrides of stoichiometry  $\text{MH}(\text{BH}_4)_3(\text{dmpe})_2$  or  $\text{MH}_2(\text{BH}_4)_2(\text{dmpe})_2$  depending on the conditions [23]. The monohydride complexes  $\text{MH}(\text{BH}_4)_3(\text{dmpe})_2$  contain both bidentate and tridentate  $\text{BH}_4^-$  groups as judged by IR spectroscopy. The  $^1\text{H}$  NMR spectra show a triplet for the terminal hydride groups at  $\delta$  6.08,  $J_{\text{PH}} = 56$  Hz for  $\text{M} = \text{Zr}$  and at  $\delta$  10.99,  $J_{\text{PH}} = 45$  Hz for  $\text{M} = \text{Hf}$ . The  $^1\text{H}$  NMR spectra also show that there are two  $\text{PMe}_2$  environments, while the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra show that there is a single  $\text{BH}_4^-$  and a single phosphorus environment. These data are consistent with a pseudo-octahedral structure in which the three mutually fac  $\text{BH}_4^-$  groups are exchanging with each other. The  $\text{BH}_4^-$  groups in the dihydride complexes  $\text{MH}_2(\text{BH}_4)_2(\text{dmpe})_2$  are bidentate by IR

spectroscopy. The  $^1\text{H}$  NMR spectra show that there is one hydride environment and one  $\text{BH}_4^-$  environment, but that the two ends of each dmpe ligand are inequivalent. The terminal hydride resonances at  $\delta$  3.38 (Zr) and  $\delta$  6.65 (Hf) are complex multiplets arising from the X part of  $\text{XX'AA'BB'}$  spin systems. Simulation of the resonances suggests that the coupling constant between the two hydride ligands may be unusually large at ca. 30 Hz. The possibility that nuclear exchange processes are responsible for this large coupling constant was ruled out based on deuteration studies. Interestingly, these  $\text{MH}_2(\text{BH}_4)_2(\text{dmpe})_2$  molecules are non-fluxional at room temperature despite the high coordination numbers (8 or 10, depending on how the  $\text{BH}_4^-$  groups are counted). Variable-temperature NMR spectroscopy shows that the molecules undergo an intramolecular fluxional process with an activation energy of 15.6 kcal $^{-1}$ ; this value is unusually high for a molecule with such a high coordination number.

Treatment of the polyhydride complexes  $\text{M}_2\text{H}_3(\text{BH}_4)_5(\text{PMe}_3)_2$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) with 1,2-bis(dimethylphosphino)ethane(dmpe) in pentane has given two new group 4 polyhydrides of stoichiometry  $\text{M}_2\text{H}_4(\text{BH}_4)_4(\text{dmpe})_2$  [24]. The variable temperature  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{11}\text{B}$  NMR data suggest that these dinuclear compounds contain a  $\text{M}(\mu\text{-H})_3\text{M}$  backbone with the phosphine and tetrahydroborate ligands distributed in 2:0 and 1:3 ratios among the two metal centers. A terminal hydride is positioned in between the two bidentate dmpe ligands. This suggestion has been confirmed by the single crystal X-ray structure of  $\text{Zr}_2\text{H}_4(\text{BH}_4)_4(\text{dmpe})_2$ . The metal-metal vector is bridged by three hydride ligands and the average  $\text{Zr-H-Zr}_{\text{ave}}$  angle is  $108(2)^\circ$ . A dynamic process exchanges these hydride environments, and a likely mechanism for this process has been proposed.



## References

1. Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643-1644.
2. Girolami, G. S.; Jensen, J. A.; Gozum, J. E.; Pollina, D. M. *Mat. Res. Soc. Symp. Proc.* **1988**, *121*, 429-438.
3. Girolami, G. S.; Gozum, J. E. *Mat. Res. Soc. Symp. Proc.* **1990**, *168*, 319-329.

4. Pierson, H. O.; Mullendore, A. W. *Thin Solid Films* **1981**, *95*, 99-104.
5. Caputo, A. J.; Lackey, W. J.; Wright, I. G.; Angellini, P. J. *Electrochem. Soc.* **1985**, *132*, 2274-2280.
6. Bouix, J.; Vincent, H.; Boubenhiru, M.; Viala, J. C. *J. Less-Common Met.* **1986**, *117*, 83-89.
7. Takahashi, T.; Kamiya, H. *J. Cryst. Growth* **1974**, *26*, 203-209.
8. Bessman, T. D.; Spear, K. E. *J. Electrochem. Soc.* **1977**, *124*, 786-790.
9. Bessman, T. D.; Spear, K. E. *J. Cryst. Growth* **1975**, *31*, 60-65.
10. Pierson, H. O.; Mullendore, A. W. *Thin Solid Films* **1980**, *72*, 511-516.
11. Matkovich, V. I., ed., *Boron and Refractory Borides*, Springer-Verlag: New York, 1977.
12. Funk, R.; Lux, B.; Schachner, H.; Tannenberger, H. French Patent 2144823 (1973); *Chem. Abstr.* **1973**, *79*, 107206.
13. Meyer, R.; Pastor, H. *Bull. Soc. Franc. Ceramique* **1965**, *66*, 59.
14. Murata, Y.; Miccioli, B. R. *Amer. Ceram. Soc. Bull.* **1971**, *50*, 182-184.
15. Fenter, J. R. *S.A.M.P.L.E. Quart.* **1971**, *2*(4), 1-15.
16. Gangler, J. J. *High Temp., High Pres.* **1971**, *3*, 487-502.
17. Schwarzkopf, P.; Kieffer, R. *Refractory Hard Metals: Borides, Carbides, Nitrides, and Silicides*; Macmillan: New York, 1953.
18. Post, B. *Boron, Metallo-Boron Compounds and Boranes*, Adams, R. D., ed.; Wiley-Interscience: New York, 1964, Ch. 5.
19. Aronsson, B.; Lundstrom, T.; Rundqvist, S. *Borides, Silicides and Phosphides*; Motheun: London, 1965.
20. Moers, K. *Z. Anorg. Allg. Chem.* **1983**, *198*, 243-275.
21. James, B. D.; Smith, B. E. *Synth. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 461-465.
22. Hoekstra, H. R.; Katz, J. J. *J. Am. Chem. Soc.* **1949**, *71*, 2488-2492.
23. Gozum, J. E.; Girolami, G. S. *J. Am. Chem. Soc.* **1991**, in press.
24. Gozum, J. E.; Girolami, G. S., in preparation.