

Transition Metal Hydroborate Complexes: Structures, Syntheses, and Use as Chemical Vapor Deposition Precursors

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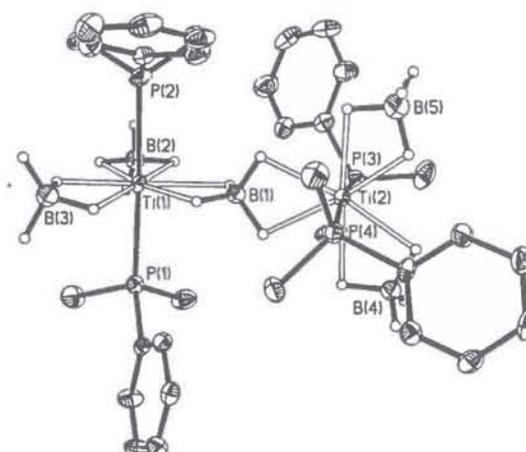
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Transition metal complexes containing hydroborate groups, especially the tetrahydroborate anion BH_4^- , are of interest owing to their catalytic properties, their utility as CVD precursors, and their usefulness as starting materials for other inorganic species. For example, the catalyst $\text{Zr}(\text{BH}_4)_4/\text{SiO}_2$ shows very high activity for the copolymerization of ethylene with propene and 1-hexene,¹ and $\text{Co}(\text{H})(\text{BH}_4)(\text{P}(\text{C}_6\text{H}_{11})_3)_2$ catalyzes the hydrogenation of 1-hexene at room temperature.² Electrically conductive thin films of group 4 transition metal diborides have been deposited using volatile molecular complexes such as $\text{Ti}(\text{BH}_4)_3(\text{dme})$.³ The present research was undertaken to improve our understanding of the nature of transition metal hydroborate complexes, and to develop new CVD methodology for the deposition of transition metal boride phases.

Treatment of $\text{Ti}(\text{BH}_4)_3(\text{Et}_2\text{O})_2$ with $\text{P}(\text{Et}_3)$ or with $\text{P}(\text{Me}_2\text{Ph})$ affords the adducts $\text{Ti}(\text{BH}_4)_3(\text{P}(\text{Et}_3))_2$ and $\text{Ti}(\text{BH}_4)_3(\text{P}(\text{Me}_2\text{Ph}))_2$, which were first prepared in 1988.⁴ A reinvestigation shows that these two complexes adopt distorted trigonal bipyramidal structures; the phosphine ligands occupy the axial sites, two of the BH_4 groups are bidentate, and one is tridentate. In a previous crystallographic study of the $\text{P}(\text{Me}_3)$ analogue, it appeared as if two "side-on" BH_4 groups were present;⁴ this result is now attributed to disorder of a bidentate and a tridentate BH_4 group across a crystallographic mirror plane. In the preparation of the $\text{P}(\text{Me}_2\text{Ph})$ complex, a minor product is formed: the titanium(II) species $[\text{Li}(\text{Et}_2\text{O})_2][\text{Ti}_2(\text{BH}_4)_5(\text{P}(\text{Me}_2\text{Ph}))_4]$. In this complex (Figure 1), one BH_4 group bridges between two Ti centers; each of the latter has a regular trigonal bipyramidal environment consisting of two axial phosphine ligands and three bidentate BH_4 groups. The different local environments seen for the d^1 titanium(III) and the d^2 titanium(II) complexes is attributed to a Jahn-Teller effect.^{5,6}

Figure 1. Structure of the anion in $[\text{Li}(\text{Et}_2\text{O})_2][\text{Ti}_2(\text{BH}_4)_5(\text{P}(\text{Me}_2\text{Ph}))_4]$

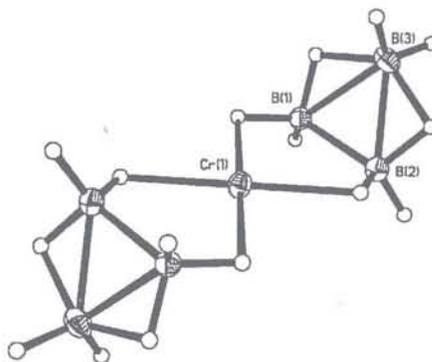


The octahydrotriborate anion, B_3H_8^- , is the third member of the hydroborate series (following BH_4^- and B_2H_7^-). The potassium,⁷ rubidium,⁷ cesium,^{7,8} thallium,⁹ and tetralkylammonium^{8,10} salts of B_3H_8^- have been described, but they are expensive and inconvenient to prepare on a large scale. The sodium salt NaB_3H_8 would be ideal, but to

date no large-scale synthesis of this salt (free of Lewis bases) has been described.^{8,11-15} An efficient, economical, and reliable method for preparing 20 g batches of solvent-free NaB_3H_8 has been developed. This route uses Brown's method¹⁶ to generate diborane 'on demand', which is then immediately passed into a flask containing sodium amalgam and diethyl ether at atmospheric pressure. The Na/Hg reduction of B_2H_6 to NaB_3H_8 is based on Hough's modification¹³ of Stock's original preparative method.¹¹

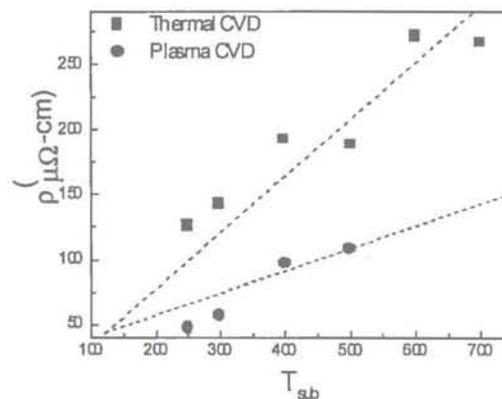
Treatment of CrCl_3 with NaB_3H_8 affords a thermally unstable purple liquid tentatively identified as the chromium(III) hydride $\text{CrH}(\text{B}_3\text{H}_8)_2$. This species decomposes over several hours at room temperature to the blue, volatile chromium(II) complex $\text{Cr}(\text{B}_3\text{H}_8)_2$. The two bidentate B_3H_8 groups describe a square-planar coordination geometry about the Cr center; along each of the two axial directions, there is a weak intermolecular $\text{Cr}\cdots\text{H}$ contact with a B-H group of a neighboring molecule. The Lewis base adducts $\text{Cr}(\text{B}_3\text{H}_8)_2\text{L}_2$ ($\text{L} = \text{Et}_2\text{O}$, thf, PMe_3) have also been isolated and structurally characterized; like the parent complex, all are high-spin. The adducts adopt tetragonally-elongated octahedral structures. Treatment of VCl_3 with NaB_3H_8 , followed by addition of dry O_2 , affords the oxo-bridged vanadium(III) complex $[\text{V}(\text{B}_3\text{H}_8)_2(\text{Et}_2\text{O})]_2\text{O}$, which also has been structurally characterized.

Figure 2. Crystal structure of $(\text{B}_3\text{H}_8)_2$.



Passage of $\text{Zr}(\text{BH}_4)_4$ or $\text{Hf}(\text{BH}_4)_4$ over heated silicon or glass substrates with a coincident flux of remotely-generated H atoms results in the formation of adhesive, mirror-bright films. Film thickness of greater than 0.3 μm thickness can be grown in 1 hour ($\sim 60\text{\AA}/\text{min}$). These films are smooth and featureless, do not oxidize in air or water, and have electrical resistivities as low as $45\ \mu\Omega\text{-cm}$.

Figure 3 Resistivity of films grown from $\text{Zr}(\text{BH}_4)_4$ as a function of deposition method and substrate temperature.



The films are free of carbon and have low concentrations of oxygen (~4 at. %) Films grown on glass at 150 °C with 6 sccm H₂ activated at 90 Watts microwave power have a formula of ZrB_{1.8}O_{0.1}. In contrast, films grown under purely thermal conditions or by other plasma-assisted methods have boron-to-metal ratios near 1:3 and oxidize readily in air.^{3,17-20} In situ studies support the hypothesis that the remote plasma is responsible for removing boron-containing species from the film.

References

1. Panchenko, V. N.; Zakharov, V. A.; Echevskaya, L. G.; Nesterov, G. A. *Vysokomol. Soedin., Ser. A Ser. B* **1994**, *36*, 5-9.
2. Nakajima, M.; Moriyama, H.; Kobayashi, A.; Saito, T.; Sasaki, Y. *J. Chem. Soc., Chem. Commun.* **1975**, *3*, 80-81.
3. Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643-1644.
4. Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977-4982.
5. Jensen, J. A.; Girolami, G. S. *Inorg. Chem.* **1989**, *28*, 2114-2119.
6. Volatron, F.; Duran, M.; Lledos, A.; Jean, Y. *Inorg. Chem.* **1993**, *32*, 951-954.
7. Hill, T. G.; Godfroid, R. A.; White, J. P.; Shore, S. G. *Inorg. Chem.* **1991**, *30*, 2952-2954.
8. Ryschkewitsch, G. E.; Nainon, K. C.; Dewkett, W. J.; Grace, M.; Beall, H. *Inorg. Synth.* **1974**, *15*, 111-118.
9. Amberger, E.; Gut, E. *Chem. Ber.* **1968**, *101*, 1200.
10. Graybill, B. M.; Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 2669-2670.
11. Stock, A. *Hydrides of Boron and Silicon*, Cornell University Press, Ithaca, N.Y., 1933, pp. 58, 138.
12. Hough, W. V.; Edwards, L. J.; McElroy, A. D. *J. Am. Chem. Soc.* **1956**, *78*, 689.
13. Hough, W. V.; Edwards, L. J.; McElroy, A. D. *J. Am. Chem. Soc.* **1958**, *80*, 1828-1829.
14. Down, J. L.; Lewis, J.; Moore, B.; Wilkinson, G. *J. Chem. Soc., London* **1959**, 3767-3773.
15. Titov, L. V.; Levicheva, M. D.; Rosolovskii, V. Ya. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1980**, *25*, 1625-1627.
16. Kanth, J. V. B.; Brown, H. C. *Inorg. Chem.* **2000**, *39*, 1795-1802.

17. Wayda, A. L.; Schneemeyer, L. F.; Opila, R. L. *Appl. Phys. Lett.* **1988**, *53*, 361-363.
18. Rice, G. W.; Woodin, R. L. *J. Am. Ceram. Soc.* **1988**, *71*, C181-C183.
19. Feichtner, J. D.; Veligdan, J. T. *U.S. Patent* **1987**, 4,668,538.
20. Reich, S.; Suhr, H.; Hanko, K.; Szepes, L. *Adv. Mater.* **1992**, *4*, 650-653.