position.[4] Thus, a stereoelectronic effect may also be involved in this stereoselective enolization process.[13] The factors that influence the metal-dependent keto–enol equilibria as well as the further reactivity of transition metal–enol compounds are currently under investigation.

Acknowledgment. Partial support from the Universitywide Energy Research Group at the University of California and helpful discussions with Professor Charles Perrin are gratefully acknowledged. We thank Dr. John M. Wright for the 500-MHz NOE and 125-MHz ^{13}C NMR data.

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Vanadium Tetrahydroborates: Preparation and Characterization of $V(\eta^2\text{-}BH_4)_3(PMe_3)_2$ and the Unusual Unidentate BH_4^- Complex $V(\eta^1\text{-}BH_4)_2(dmpe)_2$

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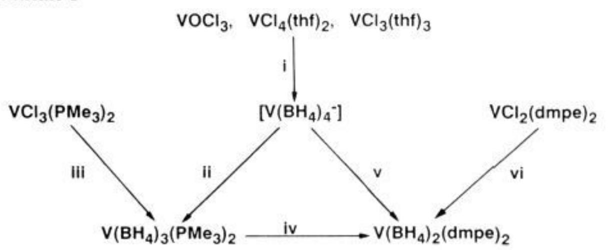
Received February 22, 1988

Unidentate tetrahydroborate ligands were the most recently discovered of the three major BH_4^- bonding modes and still remain the least well-understood, compared with bidentate and tridentate geometries. Few examples are known: of these, only $Cu(\eta^1\text{-}BH_4)(PMePh_2)_3$,[1] $Cu(\eta^1\text{-}BH_4)[(PPh_2CH_2)_3CMe]$,[2] $FeH(\eta^1\text{-}BH_4)(dmpe)_2$,[3] and $Hf_2[N(SiMe_2CH_2PMe_2)_2]_2H_3(BH_4)_3$[4] have been characterized structurally, while other examples have been formulated on spectroscopic grounds.[5] All of these complexes contain at most one unidentate BH_4^- group, and all but one are 18-electron species. We now describe the synthesis and properties of several interesting vanadium tetrahydroborates; among them are compounds that contain six and eight V–H bonds, and a 15-electron complex that contains two unidentate BH_4^- groups.

Scheme I[a]



[a] (i) $LiBH_4$ in Et_2O or $NaBH_4$ in dme; (ii) PMe_3 in Et_2O; (iii) $LiBH_4$ in Et_2O; (iv) dmpe in Et_2O; (v) dmpe in Et_2O; (vi) $NaBH_4$ in thf.

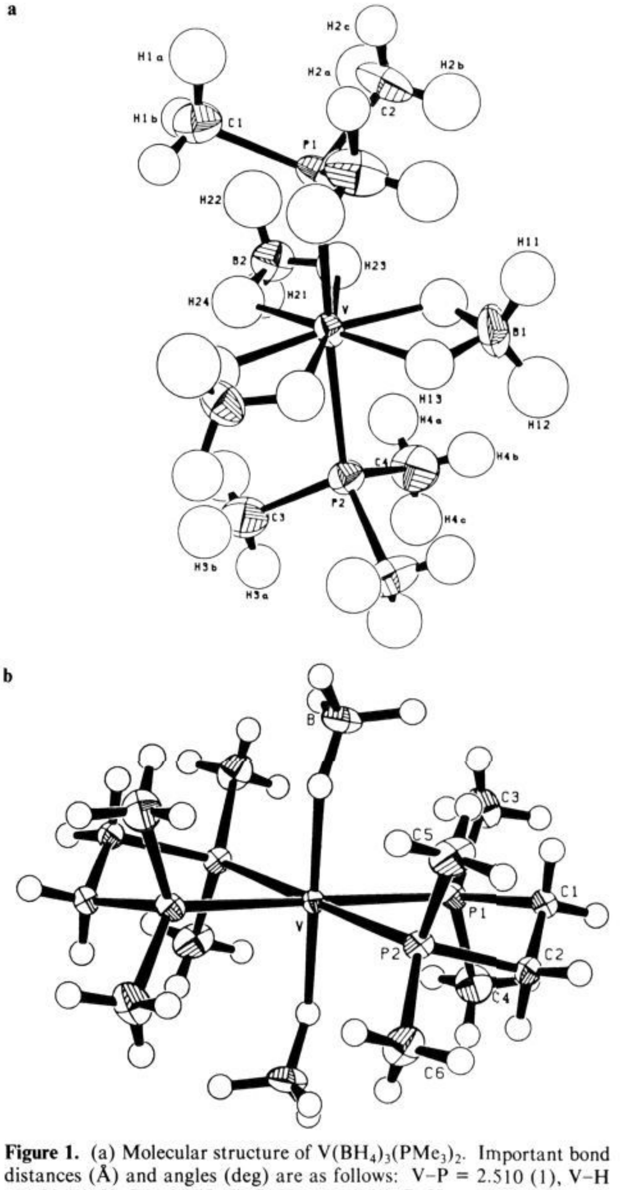


Figure 1. (a) Molecular structure of $V(BH_4)_3(PMe_3)_2$. Important bond distances (Å) and angles (deg) are as follows: V–P = 2.510 (1), V–H = 1.83 (3), V···B = 2.365 (5), B–H_b = 1.14 (3), B–H_t = 1.03 (3), P–V–P = 178.45 (5), B–V–B = 118.9 (2), 120.6 (1). (b) Molecular structure of $V(BH_4)_2(dmpe)_2$. Important bond distances (Å) and angles (deg) are as follows: V–P = 2.503 (1), V–H = 1.88 (3), V···B = 2.833 (4), B–H_b = 1.12 (3), B–H_t = 1.03 (4), V–H–B = 140 (1).

Tetrahydroborates of the group 5 elements are rare,[6] and, for the first-row metal vanadium, the only well-characterized examples known contain at most one BH_4^- group per metal center.[7,8]

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Interaction of $VCl_3(thf)_3$ with excess $NaBH_4$ in 1,2-dimethoxyethane (dme) gives a purple solution,[9] from which the first binary tetrahydroborate of vanadium, $[Na(dme)][V(BH_4)_4]$, **1**,[10] may be obtained after crystallization from diethyl ether (see Scheme I). The infrared spectrum of **1** is consistent with an eight-coordinate geometry in which the vanadium center is surrounded by four bidentate BH_4^- groups. Treatment of $[V(BH_4)_4^-]$ solutions with PMe_3, or more conveniently, interaction of $VCl_3(PMe_3)_2$ with $LiBH_4$, yields the neutral tris(tetrahydroborate), $V(BH_4)_3(PMe_3)_2$, **2**.[11] This bright green paramagnetic complex ($\mu_{eff} = 2.5\ \mu_B$) possesses three strong IR bands in a pattern characteristic of bidentate BH_4^- groups.

$$VCl_3(thf)_3 + 4NaBH_4 + dme \rightarrow [Na(dme)][V(BH_4)_4] + 3NaCl + 3thf$$

$$VCl_3(PMe_3)_2 + 3LiBH_4 \rightarrow V(BH_4)_3(PMe_3)_2 + 3LiCl$$

The X-ray crystal structure of **2** (Figure 1a)[12] reveals a nearly ideal D_{3h} hexagonal bipyramid with three bidentate BH_4^- groups in the equatorial plane and two PMe_3 ligands occupying the axial sites. The V–P distance of 2.510 (1) Å is comparable with those of other vanadium phosphine complexes, while the V–H and V···B distances of 1.83 (3) Å and 2.365 (5) Å, respectively, are similar to those in other vanadium BH_4^- complexes.[7] This structure differs fundamentally from that of the d^1 titanium analogue $Ti(BH_4)_3(PMe_3)_2$,[13] in which the symmetry is lowered to C_s and two of the tetrahydroborate groups adopt unusual "side-on" bonding geometries. The structural differences between the titanium and vanadium species may arise from a Jahn–Teller distortion: in D_{3h} symmetry, the electronic configuration is orbitally degenerate (Jahn–Teller susceptible) for a d^1 ion but orbitally *nondegenerate* for a d^2 ion.

Treatment of $V(BH_4)_3(PMe_3)_2$ with excess 1,2-bis(dimethylphosphino)ethane (dmpe), gives $dmpe{\cdot}BH_3$ and a purple vanadium(II) product $V(BH_4)_2(dmpe)_2$, **3**.[14] This species, which may also be prepared from $VCl_2(dmpe)_2$ and $NaBH_4$ in tetrahydrofuran, is paramagnetic ($\mu_{eff} = 3.6\mu_B$) and possesses two strong broad ν_{BH} IR bands of equal intensity and an intense absorption at 1060 cm^{-1} that has been attributed to unidentate BH_4^- coordination.[1a] The X-ray crystal structure (Figure 1b)[15] reveals that *both* tetrahydroborate groups are indeed *unidentate*. The vanadium center adopts a trans octahedral geometry with V–P = 2.503 (1) Å, V–H = 1.88 (3) Å, and V···B = 2.833 (4) Å. The V–H distance is comparable to that in **2**, but the long V···B distance clearly establishes the η^1 bonding mode. The V–H–B angle of 140 (1)° is intermediate between those of 121.7 (4)° for $Cu(\eta^1\text{-}BH_4)(PMePh_2)_3$ and 161.7° for $FeH(\eta^1\text{-}BH_4)(dmpe)_2$.[1–4] The structure of **3** again differs from that of its titanium analogue, $Ti(BH_4)_2(dmpe)_2$, which possesses an eight-coordinate geometry with bidentate BH_4^- ligands.[16] The difference may be attributed to the smaller size of vanadium and to the preference of d^3 species to adopt octahedral coordination environments. Interestingly, despite the η^1-BH_4 coordination, **3** does *not* react with Lewis bases such as PMe_3 and excess dmpe.

$$VCl_2(dmpe)_2 + 2NaBH_4 \rightarrow V(BH_4)_2(dmpe)_2 + 2NaCl$$

These vanadium complexes are of interest as molecules that contain V–H bonds;[17] further, **3** is notable as the first example of a crystallographically characterized bis(η^1-BH_4) complex. Vanadium tetrahydroborates may also prove useful as molecular precursors for ceramic thin films, as shown by the formation of TiB_2 by thermolysis of the titanium tris(tetrahydroborate) $Ti(BH_4)_3(dme)$.[18] Further studies along these directions are in progress.

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 particularly acknowledge Dr. Scott Wilson and Charlotte Stern of the University of Illinois X-ray Crystallographic Laboratory for performing the X-ray crystal structure determination. G.S.G. is the recipient of an A. P. Sloan Foundation Fellowship (1988–1990).

Supplementary Material Available: Tables of atomic coordinates and complete lists of bond distances and angles for $V(BH_4)_3(PMe_3)_2$ and $V(BH_4)_2(dmpe)_2$ (4 pages); tables of observed and calculated structure factors for $V(BH_4)_3(PMe_3)_2$ and $V(BH_4)_2(dmpe)_2$ (11 pages). Ordering information is given on any current masthead page.

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(10) IR (Nujol, cm^{-1}) 2462 s, 2396 s, 2296 m, 2214 m, 2069 s, 1959 m. Anal. Calcd: C, 21.5; H, 11.7; V, 22.8. Found: C, 22.2; H, 10.7; V, 21.4.

(11) IR (Nujol, cm^{-1}) 2431 s, 2385 s, 2227 w, 2218 w, 2087 s, 1951 w; ^1H NMR (C_6D_6, 25 °C) δ −12.4 (s, fwhm = 300 Hz, PMe_3). Anal. Calcd: C, 29.1; H, 12.2; V, 20.6. Found: C, 28.6; H, 12.3; V, 20.3.

(12) Space group (−50 °C) *Pnma*, with $a = 10.350$ (1) Å, $b = 11.095$ (2) Å, $c = 14.228$ (2) Å, $V = 1634$ (1) Å^3, $Z = 4$, $R_F = 3.4\%$, $R_{wF} = 2.9\%$ on 128 variables and 959 data with $I > 2.58\sigma(I)$. Atoms V, P1, P2, C1, C3, B1, H1a, H3a, H11, and H12 were constrained to the crystallographic mirror plane at $y = 0.25$, all non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were located in the difference Fourier maps and refined with independent isotropic thermal parameters.

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(14) IR (Nujol, cm^{-1}) 2341 sh, 2312 vs b, 2110 sh, 2095 vs b; ^1H NMR (C_6D_6, 25 °C) δ −8.6 (s, fwhm = 500 Hz, PCH_2), −19.3 (s, fwhm = 950 Hz, PMe_2). Anal. Calcd: C, 37.8; H, 10.6; V, 13.4. Found: C, 37.8; H, 10.4; V, 13.5.

(15) Space group (−75 °C) $P2_1/n$, with $a = 8.469$ (2) Å, $b = 13.735$ (4) Å, $c = 9.666$ (7) Å, $\beta = 96.14$ (3)°; $V = 1118$ (2) Å^3, $Z = 2$, $R_F = 3.2\%$, $R_{wF} = 3.0\%$ on 168 variables and 1629 data with $I > 2.58\sigma(I)$. Non-hydrogen atoms and hydrogen atoms were refined as above.

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Evidence for Centrally Directed Bonds in Trinuclear Metal Cluster Compounds: The Apparent Free Rotation of the $Cr(CO)_5$ Unit in $(OC)_5Cr[Os(CO)_3(PMe_3)]_2$

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Received January 25, 1988

Metal–metal bonds in trinuclear clusters are usually regarded as two-center two-electron bonds.[1] There are, however, studies that indicate that the metal–metal bonding in these compounds should be described in terms of a centrally directed, three-center two-electron molecular orbital, along with edge-bridging molecular orbitals.[2] We have recently reported observations consistent with the latter view for $Os_3(CO)_{12}$.[3] Here we present evidence that in solution the $Cr(CO)_5$ unit freely rotates in both isomers of the

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