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Vanadium(III) Tetrahydroborates. Preparation, Reaction Chemistry, and Crystal Structures of $V(BH_4)_3(PMe_3)_2$ and the Oxo Dimer $[V(BH_4)_2(PMe_3)_2]_2O$

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The interaction of $VCl_3(thf)_3$ with $NaBH_4$ in 1,2-dimethoxyethane (dme) gives deep purple solutions from which the only known binary vanadium tetrahydroborate $[Na(dme)][V(BH_4)_4]$ can be crystallized. Solutions of this anion may also be obtained in diethyl ether or tetrahydrofuran from $VOCl_3$, $VCl_4(thf)_2$, or $VCl_3(thf)_3$ and $LiBH_4$, but in these cases the product could not be crystallized. The $[V(BH_4)_4]^-$ anion is eight-coordinate with four bidentate BH_4^- groups based on IR spectroscopy, and it reacts with 2 equiv of PMe_3 to give the neutral tris(tetrahydroborate) derivative $V(BH_4)_3(PMe_3)_2$. This high-spin ($\mu = 2.5\mu_B$) complex is bright green and possesses three bidentate BH_4^- groups as shown by IR spectroscopy and confirmed by an X-ray crystal structure. The vanadium centers in $V(BH_4)_3(PMe_3)_2$ adopt hexagonal-bipyramidal coordination geometries with the phosphine ligands in the axial sites and six hydrogen atoms from the bidentate BH_4^- groups in the equatorial plane: V–P = 2.510 (1) Å, V–H = 1.84 (3) Å, V···B = 2.365 (6) Å, P–V–P = 178.45 (5)°, and B–V–B = 118.9 (2) and 120.6 (1)°. Its structure differs fundamentally from that of the titanium analogue $Ti(BH_4)_3(PMe_3)_2$, and this structural difference may be attributable to a Jahn–Teller effect. Reaction of $V(BH_4)_3(PMe_3)_2$ with the trialkylphosphine $Me_2PCH_2CH_2PMe_2$ (dmpe) or excess PMe_3 leads to reduction to give the vanadium(II) tetrahydroborate complex $V(\eta^1\text{-}BH_4)_2(dmpe)_2$ or $[V(BH_4)H(PMe_3)_2]_2$, respectively. The latter molecule is a paramagnetic vanadium(II) dimer with an edge-shared bioctahedral structure having hydride ligands in the bridging positions. Surprisingly, hydrolysis of $V(BH_4)_3(PMe_3)_2$ does not yield a vanadium hydride but instead gives a divanadium(III) complex possessing a bridging oxygen atom, $[V(BH_4)_2(PMe_3)_2]_2O$. The X-ray crystal structure of this species reveals a pentagonal-bipyramidal geometry about each metal center in which the BH_4^- groups are still bidentate and the two vanadium atoms are joined by a linear oxo bridge: V–O = 1.780 (2) Å, V–O–V = 178.7 (1)°, V–P = 2.530 (1) Å, V–H = 1.97 (3) Å, and V···B = 2.383 (6) Å. This is the first authentic example of a complex containing both tetrahydroborate and oxo ligands. The preparation and characterization of $V(BH_4)_3(thf)_3$ and $[V(BH_4)Cl(thf)_2]_2$ are also reported. All of the molecules described herein are notable since no structurally characterized vanadium complexes containing more than one BH_4^- ligand per metal center have been reported previously.

Introduction

Compounds that contain a direct bond between a transition element and hydrogen play a major role in many stoichiometric and catalytic processes, and the chemistry of catalytically active late-transition-metal hydrides has accordingly been studied extensively.[1-4] By comparison, the chemistry of early-transition-metal hydrides remains largely unexplored.[5] This is surprising in view of the remarkable stoichiometric conversions of alkenes and alkynes to functionalized hydrocarbons[6,7] and of carbon monoxide to methanol[8] that are effected by the group 4 hydrides Cp_2ZrHCl and $(C_5Me_5)_2ZrH_2$.

We have been interested in preparing new hydride derivatives of the early first-row elements, and in the present study focus on approaches to the synthesis of vanadium polyhydrides. Previous workers have shown that the vanadium hydride complex $[CpV(CO)_3H]^-$ is able to transfer hydride stoichiometrically to a wide range of organic halides.[9] Other compounds that contain vanadium–hydrogen bonds have been reported to act as olefin hydrogenation[10,11] or polymerization catalysts.[12]

Tetrahydroborate complexes of the d-block elements often serve as excellent starting materials for the synthesis of transition-metal polyhydrides.[4,5,13] Lewis base abstraction of $BH_3\cdot L$ (eq 1) and

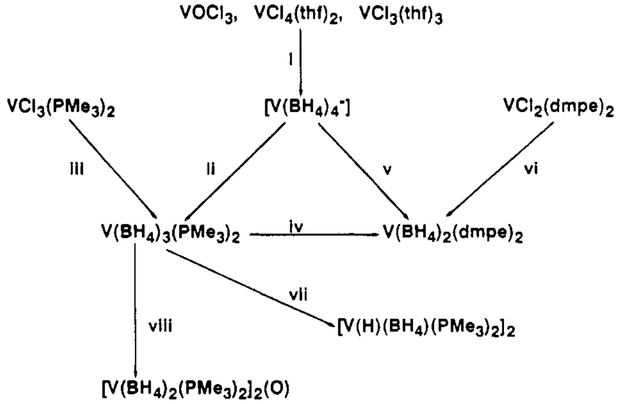
$$M\text{–}BH_4 + L \rightarrow M\text{–}H + BH_3\cdot L \qquad (1)$$

$$M\text{–}BH_4 + 3H_2O \rightarrow M\text{–}H + B(OH)_3 + \tfrac{9}{2}H_2 \qquad (2)$$

hydrolytic cleavage of a BH_4^- ligand (eq 2) are the two principal methods by which hydride ligands may be obtained from BH_4^- groups. Unfortunately, relatively few tetrahydroborate complexes of vanadium are known, and no well-defined complexes with more than one BH_4^- unit per vanadium center have been reported. Among structurally characterized vanadium tetrahydroborates are the cyclopentadienyl complexes $Cp_2V(BH_4)$[14] and $CpV(BH_4)(dmpe)$[10] and the binuclear compounds $V_2(BH_4)_2Cl_2(dppm)_2$[15] and $V_2(BH_4)_2Cl_2(dmpm)_2$.[16] In addition, the complexes $[PPN][CpV(CO)_2(BH_4)]$,[9] "$V(BH_4)_3$",[17] and $[Na(dme)_3][V(BH_4)_4]$[18,19] have been described, although the latter two compounds are incompletely characterized.

It is well-known that ether solutions of BH_4^- will reduce titanium tetrahalides to give trivalent tetrahydroborate complexes; however, analogous reactions of BH_4^- with vanadium halides are essentially unexplored. We now describe the synthesis and

Scheme I. Reaction Chemistry of Vanadium Tetrahydroborates



[a] Key: (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; (vii) excess PMe_3 in Et_2O; (viii) H_2O and PMe_3 in Et_2O.

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Table I. Crystal Data for $V(BH_4)_3(PMe_3)_2$ and $[V(BH_4)_2(PMe_3)_2]_2O$

	$V(BH_4)_3(PMe_3)_2$	$[V(BH_4)_2(PMe_3)_2]_2O$
T, °C	−50	+25
space group	*Pnma*	$P\bar{1}$
a, Å	10.350 (1)	10.656 (1)
b, Å	11.095 (2)	16.443 (3)
c, Å	14.228 (2)	10.169 (1)
α, deg	90	107.46 (1)
β, deg	90	116.66 (1)
γ, deg	90	85.26 (1)
V, $Å^3$	1634 (1)	1516 (1)
Z	4	2
mol wt	247.63	481.57
ρ_{calcd}, g cm^{-3}	1.007	1.055
λ, Å	0.71073	0.71073
μ_{calcd}, cm^{-1}	7.46	8.05
transmissn coeff	0.815–0.867	0.757–0.873
R_F	0.034	0.034
R_{wF}	0.029	0.039

characterization of new poly(tetrahydroborate) complexes of vanadium via this route. Among these are compounds that contain two, four, six, and eight V–H bonds per metal center.[20]

Results and Discussion

The $[V(BH_4)_4]^-$ Anion. The reaction of VCl_4 with $NaBH_4$ in 1,2-dimethoxyethane (dme) was reported in 1978 to give the trivalent tetrahydroborate complex $[Na(dme)_3][V(BH_4)_4]$.[18,19] However, except for infrared data, no physical measurements or reactivity studies were described. We find that $NaBH_4$ reduction of $VOCl_3$, $VCl_4(thf)_2$, or $VCl_3(thf)_3$ in 1,2-dimethoxyethane (Scheme I) followed by crystallization from diethyl ether gives a product best formulated as the dme *monoadduct* $[Na(dme)][V(BH_4)_4]$ (**1**). This purple species possesses infrared

$$VCl_3(thf)_3 + 4NaBH_4 + dme \rightarrow \underset{\mathbf{1}}{[Na(dme)][V(BH_4)_4]} + 3NaCl + 3thf$$

absorptions at 2462, 2396, and 2069 cm^{-1} that are indicative of bidentate BH_4^- groups; these values are similar to those of 2470, 2410, and 2090 cm^{-1} previously reported for $[Na(dme)_3][V(BH_4)_4]$.[18,19] The structure is accordingly eight-coordinate and a D_{2d} dodecahedral geometry may be inferred. The number of dme molecules reflects the choice of crystallization solvent: the monoadduct is obtained from diethyl ether, while the triadduct is obtained from dme.

Addition of $LiBH_4$ to $VOCl_3$, $VCl_4(thf)_2$, or $VCl_3(thf)_3$ in diethyl ether yields in all cases a purple oily product that is believed to be $[Li(Et_2O)_x][V(BH_4)_4]$ by analogy with the $NaBH_4$ reaction. This material is soluble in ethers and aromatic hydrocarbons, but is insoluble in alkanes. X-Band ESR spectra in frozen toluene at −196 °C show three broad features at 100, 470, and 740 mT.

Attempts have been made to replace or complex the lithium cation of $[Li(Et_2O)_x][V(BH_4)_4]$ in order to obtain a pure crystalline product: addition of tetrahydrofuran, 1,2-dimethoxyethane, or 12-crown-4 yields only oily products, and similar results are obtained upon addition of Bu_4NBr or Ph_4PCl. No reaction is observed to occur upon direct combination of $VCl_3(thf)_3$ and $(PPN)BH_4$ in 1,2-dimethoxyethane, where PPN is the bis(triphenylphosphoranylidene)ammonium cation. Other products formed upon reduction of vanadium halides by tetrahydroborate salts will be discussed below.

Synthesis and Structure of $V(BH_4)_3(PMe_3)_2$. Addition of PMe_3 to diethyl ether solutions of $[V(BH_4)_4]^-$ gives the neutral tris(tetrahydroborate) complex $V(BH_4)_3(PMe_3)_2$ (**2**). This complex can be prepared more conveniently by the interaction of $VCl_3(PMe_3)_2$ with $LiBH_4$ in diethyl ether (Scheme I). In both cases, $V(BH_4)_3(PMe_3)_2$ (**2**) may be isolated as green prisms from pentane.

Table II. Atomic Coordinates for $V(BH_4)_3(PMe_3)_2$

	x/a	*y/b*	*z/c*
V	0.79885 (8)	0.25	0.02438 (5)
P1	0.6133 (1)	0.25	−0.08957 (8)
P2	0.9881 (1)	0.25	0.13440 (9)
C1	0.4549 (6)	0.25	−0.0377 (5)
C2	0.6110 (5)	0.1210 (4)	−0.1668 (3)
C3	0.9428 (7)	0.25	0.2573 (5)
C4	1.0941 (5)	0.1209 (5)	0.1246 (4)
B1	0.9440 (8)	0.25	−0.1042 (5)
B2	0.7241 (5)	0.0665 (4)	0.0890 (3)
H1a	0.387 (4)	0.25	−0.089 (3)
H1b	0.450 (3)	0.183 (2)	−0.003 (2)
H2a	0.598 (3)	0.048 (3)	−0.134 (3)
H2b	0.691 (3)	0.123 (3)	−0.204 (2)
H2c	0.541 (3)	0.126 (3)	−0.205 (2)
H3a	1.016 (4)	0.25	0.291 (3)
H3b	0.898 (3)	0.319 (3)	0.270 (2)
H4a	1.039 (3)	0.050 (3)	0.129 (3)
H4b	1.126 (3)	0.124 (3)	0.064 (2)
H4c	1.157 (3)	0.131 (4)	0.165 (3)
H11	0.912 (4)	0.25	−0.170 (3)
H12	1.047 (5)	0.25	−0.095 (3)
H13	0.898 (3)	0.329 (3)	−0.059 (2)
H21	0.767 (3)	0.021 (3)	0.146 (2)
H22	0.644 (3)	0.030 (4)	0.068 (2)
H23	0.788 (3)	0.083 (3)	0.030 (2)
H24	0.712 (3)	0.158 (3)	0.114 (2)

Table III. Important Bond Lengths (Å) and Angles (deg) for $V(BH_4)_3(PMe_3)_2$

	Bond Lengths		
V–P1	2.513 (1)	P2–C3	1.810 (7)
V–P2	2.507 (1)	P2–C4	1.810 (5)
V···B1	2.367 (8)	B1–H11	1.00 (5)
V···B2	2.364 (5)	B1–H12	1.07 (5)
V–H13	1.80 (3)	B1–H13	1.19 (3)
V–H23	1.86 (3)	B2–H21	1.06 (3)
V–H24	1.86 (3)	B2–H22	0.97 (4)
P1–C1	1.799 (6)	B2–H23	1.08 (3)
P1–C2	1.805 (5)	B2–H24	1.09 (3)
	Bond Angles		
P1–V–P2	178.45 (5)	V–H23–B2	104 (2)
B1–V–B2	120.6 (1)	V–H24–B2	104 (2)
B2–V–B2′	118.9 (2)	V–B1–H11	121 (3)
P1–V–B1	89.2 (2)	V–B1–H12	122 (3)
P1–V–B2	90.1 (1)	V–B2–H21	125 (2)
P2–V–B1	89.2 (2)	V–B2–H22	121 (2)
P2–V–B2	90.7 (1)	H13–B1–H13′	95 (2)
H13–V–H13′	59 (1)	H23–B2–H24	100 (2)
H23–V–H24	53 (1)	H11–B1–H12	116 (4)
H13–V–H23	65 (1)	H21–B2–H22	114 (3)
H24–V–H24′	66 (1)	H11–B1–H13	112 (2)
V–P1–C1	115.6 (2)	H12–B1–H13	109 (2)
V–P1–C2	113.8 (2)	H21–B1–H23	115 (2)
V–P2–C3	113.6 (2)	H21–B2–H24	104 (2)
V–P2–C4	115.2 (2)	H22–B2–H23	111 (3)
V–H13–B1′	103 (2)	H22–B2–H24	113 (3)

$$VCl_3(PMe_3)_2 + 3LiBH_4 \rightarrow \underset{\mathbf{2}}{V(BH_4)_3(PMe_3)_2} + 3LiCl$$

Compound **2** is paramagnetic ($\mu_{eff} = 2.5\mu_B$), and its ^1H NMR spectrum shows a single broad resonance at δ −12.4 due to the PMe_3 protons. No resonances due to the tetrahydroborate groups were observed, evidently due to the proximity of these protons to the paramagnetic vanadium center. The infrared spectrum of **2** reveals three strong bands at 2431, 2385, and 2087 cm^{-1}, which indicate a bidentate ligation mode for the BH_4^- groups. The complex is ESR silent.

Single crystals of $V(BH_4)_3(PMe_3)_2$ were obtained by cooling saturated pentane solutions to −20 °C. Crystal data are given

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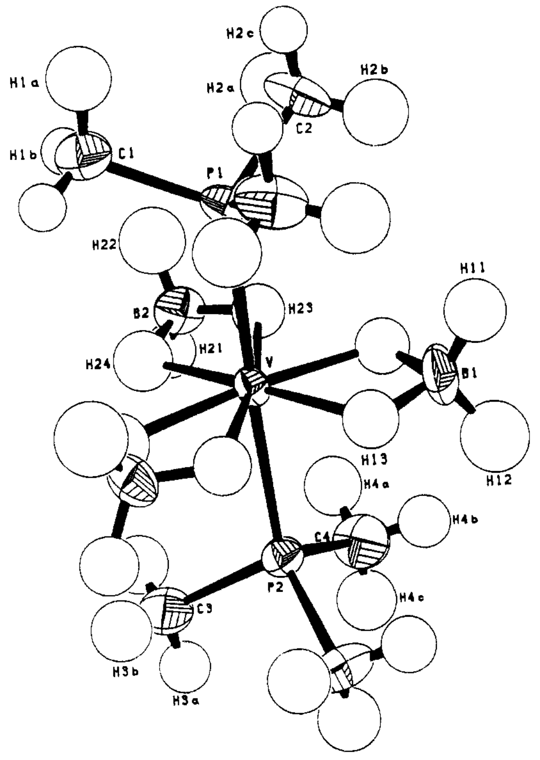


Figure 1. Molecular structure of $V(BH_4)_3(PMe_3)_2$ (**2**).

in Table I, while final atomic coordinates and important bond distances and angles are given in Tables II and III. The structural analysis reveals that although molecules of **2** lie on a crystallographic mirror plane, overall the geometry is a hexagonal bipyramid with nearly ideal D_{3h} symmetry (Figure 1). The two phosphine ligands occupy the axial positions of the bipyramid, with the P–V–P angle being very nearly linear at 178.45 (5)°. The average V–P distance of 2.510 (1) Å in **2** is comparable to those of 2.536 (2) and 2.508 (1) Å in the vanadium(III) complexes of $VCl_3(PMePh_2)_2$[21] and $CpVCl_2(PMe_3)_2$,[22] respectively. The methyl substituents on the phosphorus atom are oriented in a staggered fashion with respect to the three equatorial BH_4^- groups, evidently in order to minimize steric repulsions.

The three V···B vectors form angles of 120.6 (1) and 118.9 (2)° and confirm the regularity of the D_{3h} geometry. All of the hydrogen atoms contained in the molecule were readily apparent in the difference maps, and their positions were refined with independent isotropic thermal coefficients. The bidentate coordination of the BH_4^- ligands is thus confirmed; the V···B contacts of 2.365 (5) Å are also expected for bidentate BH_4^- groups, based on ionic radii.[23] The six bridging hydrogen atoms constitute the equatorial girdle of the hexagonal bipyramid, with the H_b–V–H_b angles involving a *single* BH_4^- group of 55 (1)° being only slightly smaller than the H_b–V–H_b angles *between* BH_4^- groups of 65 (1)°. In all of the BH_4^- ligands, the hydrogen atoms are somewhat displaced from ideal tetrahedral locations: the B–H_b distances of 1.14 (3) Å are slightly longer than the B–H_t contacts of 1.03 (3) Å, and the interior H_b–B–H_b angles of 97 (2)° are slightly smaller than the remaining angles at boron, which average 111 (2)°. Both of these effects, the lengthening of the B–H_b bonds and the closing of the H_b–B–H_b angle, have been noted in other bidentate BH_4^- complexes and are indicative of strong bonding with the metal center.[24]

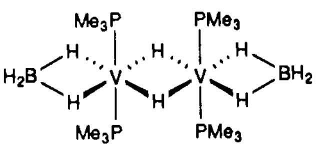
The structure of **2** differs fundamentally from that of the d^1 titanium analogue $Ti(BH_4)_3(PMe_3)_2$, in which the symmetry is lowered to C_s and two of the tetrahydroborate groups adopt unusual "side-on" bonding geometries.[25] The structural differences between the titanium and vanadium species may arise from a Jahn–Teller distortion: in D_{3h} symmetry, the lowest energy d orbitals, d_{xz} and d_{yz}, are of E symmetry and yield an orbitally degenerate (Jahn–Teller-susceptible) ground state for a d^1 ion, but an orbitally *nondegenerate* ground state for a d^2 ion.

In solution, $V(BH_4)_3(PMe_3)_2$ is a reactive species and will polymerize ethylene at room temperature and 150 psi. Analysis of the reaction solvent by GC showed that no short-chain oligomeric hydrocarbons were present. The vanadium complex could not be recovered from the reaction residue.

Reactions of $V(BH_4)_3(PMe_3)_2$ with Phosphines. Transition-metal hydrides are often obtained upon Lewis base abstraction of BH_3 from transition-metal tetrahydroborates.[26–29] For example, addition of PMe_3 to $Ta(BH_4)H_2(PMe_3)_4$ under H_2 has been shown to give the tantalum polyhydride $TaH_5(PMe_3)_4$;[26] similar reactions of group 4 tetrahydroborate complexes are also known.[27–30] By contrast, addition of an excess (>3 equiv) of 1,2-bis(dimethylphosphino)ethane, dmpe, to a cold diethyl ether solution of $V(BH_4)_3(PMe_3)_2$ gives the vanadium(II) tetrahydroborate complex $V(BH_4)_2(dmpe)_2$, which has been described elsewhere.[24] This compound can be prepared more conveniently from $VCl_2(dmpe)_2$ and $NaBH_4$.

Addition of excess PMe_3 to $V(BH_4)_3(PMe_3)_2$ causes a similar reduction of the vanadium center, and a purple crystalline product may be obtained from pentane. Microanalytical and spectroscopic data suggest that this complex is best formulated as the vanadium(II) hydride dimer $[V(BH_4)H(PMe_3)_2]_2$ (**3**). The tetrahydroborate groups are bidentate as judged by the ν_{BH} IR bands at 2363, 2338, and 2104 cm^{-1}, although the frequency difference between the average ν_{B-H}(terminal) and average ν_{B-H}(bridging) absorptions of 246 cm^{-1} is small compared with the 321-cm^{-1} separation in $V(BH_4)_3(PMe_3)_2$. A small frequency separation has previously been noted in the divalent titanium(II) complex $Ti(\eta^2\text{-}BH_4)_2(dmpe)_2$ and is indicative of a weak M–BH_4 interaction.[24] Complex **3** is paramagnetic, and the lowering of the magnetic moment to 2.9 μ_B per vanadium from the spin-only value of 3.87 μ_B expected for vanadium(II) is consistent with the presence of an antiferromagnetically coupled dimer. The absence of ν_{V-H} hydride bands in the IR spectrum indicates that the hydride ligands bridge between the two vanadium centers. Overall, the spectroscopic data for **3** point to an edge-shared bioctahedral structure analogous to $[V(BH_4)Cl(dppm)]_2$[15] and $[V(BH_4)Cl(dmpm)]_2$,[16] with hydride in place of chloride:

$$2V(BH_4)_3(PMe_3)_2 + 2PMe_3 \rightarrow \underset{\mathbf{3}}{[V(BH_4)H(PMe_3)_2]_2} + 2PMe_3{\cdot}BH_3 + H_2$$



Presumably, the central V_2H_2 unit is similar to that in the recently described cyclopentadienyl complex $Cp_2V_2H_2(dmpe)_2$.[11,31]

Reaction of $V(BH_4)_3(PMe_3)_2$ with Water. Hydrolysis of transition-metal tetrahydroborates (or tetrahydroaluminates) leads

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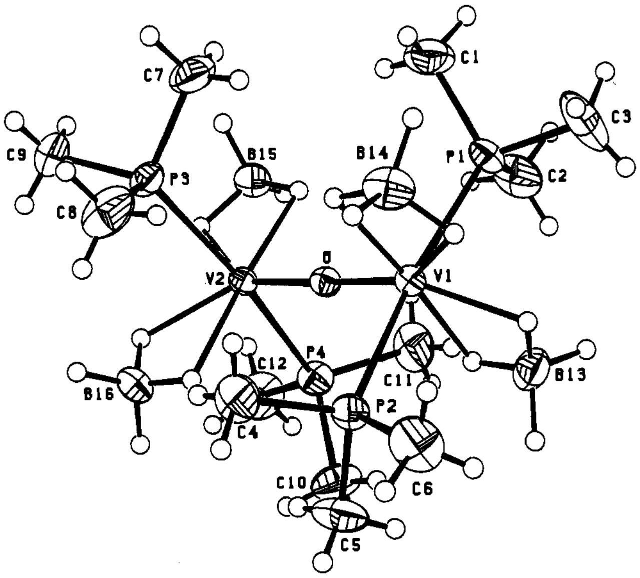

Figure 2. Molecular structure of $[V(BH_4)_2(PMe_3)_2]_2O$ (**4**).

in many cases to the formation of polyhydride complexes; the only other common preparative method for metal polyhydrides is direct hydrogenation or hydrogenolysis.[4,5,13] For example, Cp_2NbH_3 was originally prepared by treatment of $NbCl_5$ with NaCp and $NaBH_4$, followed by hydrolytic workup of the probable intermediate $Cp_2Nb(BH_4)$.[32,33] In view of the rarity of polyhydride derivatives of the group 5 elements (only two[34,35] are known for vanadium), a study of the hydrolysis products of $V(BH_4)_3(PMe_3)_2$ is of interest.

Treatment of **2** with water in the presence of trimethylphosphine results in a color change from green to red-purple. Crystallization from diethyl ether results in the isolation of purple needles of the *oxo* complex $[V(BH_4)_2(PMe_3)_2]_2(\mu\text{-}O)$ (**4**). The compound is

$$2V(BH_4)_3(PMe_3)_2 + H_2O + 2PMe_3 \rightarrow \underset{\mathbf{4}}{[V(BH_4)_2(PMe_3)_2]_2(\mu\text{-}O)} + 2H_3B{\cdot}PMe_3 + H_2$$

very soluble in diethyl ether and toluene. The infrared spectrum of **4** displays doublets at 2400 and 2359 cm^{-1} and a strong band at 2106 cm^{-1} indicative of a bidentate ligation mode for the tetrahydroborate groups. The ^1H NMR spectrum of $[V(BH_4)_2(PMe_3)_2]_2(\mu\text{-}O)$ shows a single broad (fwhm = 830 Hz) resonance due to the PMe_3 protons at δ −16.2 ppm, and as before the tetrahydroborate signal could not be located. Examples of metal complexes containing both BH_4^- and oxo ligands are essentially nonexistent; the compounds $Cp_2MoO(BH_4)_2$ and $Cp_2WO(BH_4)_2$ have been claimed.[36]

X-ray Structure of $[V(BH_4)_2(PMe_3)_2]_2(\mu\text{-}O)$. Suitable crystals of the μ-oxo dimer **4** were grown from diethyl ether, and its molecular structure is shown in Figure 2. Crystal data are given in Table I, final atomic coordinates are given in Table IV, and selected bond distances and angles are presented in Table V. Each vanadium center is formally trivalent and 7-coordinate, with the coordination geometry around each metal best described as a pentagonal bipyramid with the PMe_3 ligands in the apical positions. The average V–P distance of 2.530 (1) Å closely resembles those in $V(BH_4)_3(PMe_3)_2$ and other vanadium(III) alkylphosphine complexes (see above).

The V–H_b distances range from 1.91 (3) to 2.05 (3) Å and average 1.97 (3) Å. This average value is slightly longer than the average V–H_b distance of 1.89 (3) Å observed in $V(BH_4)_3(PMe_3)_2$ (**2**), but the difference is only of marginal significance statistically. The V⋯B distances fall within the narrow range 2.372–2.392 (6) Å (average value = 2.383 (6) Å) and are consistent with those of other structurally characterized vanadium tetrahydroborate complexes.

Table IV. Atomic Coordinates for $[V(BH_4)_2(PMe_3)_2]_2O$

	x/a	*y/b*	*z/c*
V1	0.24689 (6)	0.24977 (4)	−0.21310 (6)
V2	0.25460 (6)	0.25249 (4)	0.14184 (6)
P1	0.3467 (1)	0.10400 (7)	−0.2570 (1)
P2	0.1467 (1)	0.39486 (7)	−0.2110 (1)
P3	0.0083 (1)	0.18441 (7)	0.0168 (1)
P4	0.5009 (1)	0.32092 (7)	0.3067 (1)
O	0.2526 (2)	0.2518 (2)	−0.0346 (3)
C1	0.2532 (6)	0.0158 (3)	−0.2618 (7)
C2	0.5200 (5)	0.0963 (3)	−0.1115 (6)
C3	0.3631 (7)	0.0664 (4)	−0.4319 (6)
C4	−0.0190 (5)	0.4062 (3)	−0.2005 (6)
C5	0.2505 (6)	0.4854 (3)	−0.0544 (6)
C6	0.1108 (6)	0.4262 (3)	−0.3803 (6)
C7	−0.0220 (5)	0.0802 (3)	−0.1226 (5)
C8	−0.1329 (5)	0.2417 (4)	−0.0919 (7)
C9	−0.0469 (5)	0.1663 (3)	0.1507 (6)
C10	0.5242 (5)	0.4270 (3)	0.2971 (6)
C11	0.6374 (4)	0.2660 (4)	0.2633 (6)
C12	0.5641 (5)	0.3357 (4)	0.5110 (5)
B13	0.4484 (6)	0.3086 (4)	−0.2036 (8)
B14	0.0364 (7)	0.1892 (4)	−0.4367 (7)
B15	0.3405 (6)	0.1296 (3)	0.2279 (6)
B16	0.1723 (6)	0.3759 (4)	0.2692 (7)
H13a	0.347 (3)	0.274 (2)	−0.319 (3)
H13b	0.432 (3)	0.305 (2)	−0.106 (3)
H13c	0.537 (4)	0.275 (3)	−0.209 (4)
H13d	0.459 (3)	0.379 (3)	−0.191 (4)
H14a	0.128 (3)	0.220 (2)	−0.447 (3)
H14b	0.052 (3)	0.197 (2)	−0.310 (4)
H14c	0.026 (4)	0.121 (3)	−0.501 (4)
H14d	−0.056 (4)	0.231 (3)	−0.480 (4)
H15a	0.301 (3)	0.188 (2)	0.293 (3)
H15b	0.334 (3)	0.142 (2)	0.121 (3)
H15c	0.266 (3)	0.078 (3)	0.194 (4)
H15d	0.449 (3)	0.127 (2)	0.301 (4)
H16a	0.215 (3)	0.321 (2)	0.314 (3)
H16b	0.182 (3)	0.366 (2)	0.159 (3)
H16c	0.066 (3)	0.378 (2)	0.251 (3)
H16d	0.242 (3)	0.430 (2)	0.353 (3)

Table V. Important Bond Lengths (Å) and Angles (deg) for $[V(BH_4)_2(PMe_3)_2]_2O$

	Bond Lengths		
V1–P1	2.537 (1)	V1–H13a	1.95 (3)
V1–P2	2.530 (1)	V1–H13b	1.91 (3)
V2–P3	2.529 (1)	V1–H14a	2.05 (3)
V2–P4	2.525 (1)	V1–H14b	2.00 (3)
V1⋯B13	2.379 (6)	V2–H15a	1.99 (3)
V1⋯B14	2.372 (6)	V2–H15b	1.93 (3)
V2⋯B15	2.392 (6)	V2–H16a	1.98 (3)
V2⋯B16	2.389 (6)	V2–H16b	1.95 (3)
V1–O	1.779 (2)	B–H_b	1.15 (4)[a]
V2–O	1.782 (2)	B–H_t	1.09 (4)[a]
	Bond Angles		
P1–V1–P2	170.48 (4)	P4–V2–B16	88.2 (1)
P3–V2–P4	170.85 (4)	H13a–V1–H13b	57 (1)
B13–V1–B14	126.8 (2)	H14a–V1–H14b	60 (1)
B15–V2–B16	126.5 (2)	H15a–V2–H15b	57 (1)
P1–V1–B13	88.5 (2)	H16a–V2–H16b	55 (1)
P1–V1–B14	87.7 (2)	V–H_b–B	96 (2)[a]
P2–V1–B13	87.1 (2)	V⋯B–H_t	121 (2)[a]
P2–V1–B14	88.3 (2)	H_b–B–H_b	110 (2)[a]
P3–V2–B15	88.3 (1)	H_b–B–H_t	107 (2)[a]
P3–V2–B16	87.5 (1)	H_t–B–H_t	118 (2)[a]
P4–V2–B15	87.7 (1)		

[a] Average. H_b = bridging hydrogen, H_t = terminal hydrogen.

The V–O distance of 1.780 (2) Å is similar to that of 1.769 (5) Å reported for the closely related vanadium(III) dimer

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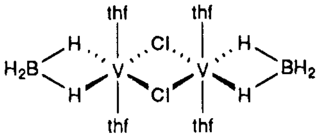
[VCl_2(thf)$_3$]$_2$(μ-O).[37] In the present complex, the V–O–V angle is nearly linear at 178.7 (1)° and the P–V–O angle is 94.67 (8)°. The atoms V1–P1–P2–O and V2–P3–P4–O define two planes with a dihedral angle of 90.5°.

Reactions of VCl_3(thf)$_3$ with $NaBH_4$ in Tetrahydrofuran. Treatment of $VOCl_3$, VCl_4(thf)$_2$, or VCl_3(thf)$_3$ with $NaBH_4$ in dme leads to the sodium salt [Na(dme)][V(BH_4)$_4$] as described above. In other attempts to prepare vanadium tetrahydroborates via similar routes, we have found that the products formed upon reduction of vanadium halides by tetrahydroborate salts are not only dependent upon the alkali-metal cation (see above) but are also dependent upon the solvent used and the reaction duration. Addition of a tetrahydrofuran solution of $NaBH_4$ to VCl_3(thf)$_3$ causes the initially red solution to turn green after 3 days of reaction. Filtration, concentration, and cooling of this solution yields green crystals of a thermally unstable complex, which is assigned the stoichiometry V(BH_4)$_3$(thf)$_3$ based on microanalytical data. The IR bands at 2365, 2180, and 2090 cm^{-1} indicate that the BH_4^- ligands are bidentate. However, if this reaction is continued for longer than 3 days, a dark red solution develops. After 10 days, dark purple prisms of the vanadium(II) complex [V(BH_4)Cl(thf)$_2$]$_2$ can be obtained. The infrared spectrum of this vanadium(II) species contains B–H stretching bands at 2444, 2386, and 2066 cm^{-1} and is consistent with the presence of bidentate BH_4^- ligands. The spectroscopic data suggest that [V(BH_4)Cl(thf)$_2$]$_2$ is a chloride-bridged dimer with an edge-shared bioctahedral structure analogous to that proposed above for [V(BH_4)H(PMe_3)$_2$]$_2$ (3).



Conclusions

The compounds described above considerably extend the class of vanadium poly(tetrahydroborate) complexes. Both mononuclear and binuclear molecules have been prepared, and the number of metal–hydrogen bonds per vanadium center in these species ranges from two to eight. The molecule V(BH_4)$_3$(PMe_3)$_2$ adopts a regular hexagonal-bipyramidal structure that differs significantly from that of the previously described titanium analogue Ti(BH_4)$_3$(PMe_3)$_2$, which has C_s symmetry and two "side-on" BH_4^- groups.[25] The structural difference is proposed to be electronic in origin and probably results from the different susceptibilities of d^1 and d^2 molecules of D_{3h} symmetry toward Jahn–Teller distortions.

Despite the existence of niobium and tantalum polyhydrides such as NbH_5(PMe_3)$_4$, NbH_5(dmpe)$_2$, and TaH_5(dmpe)$_2$,[38-40] polyhydrides of vanadium are still elusive. We have described the preparation of the bridging hydride [V(BH_4)H(PMe_3)$_2$]$_2$ but have found that vanadium poly(tetrahydroborates) are generally not suited as starting materials for the preparation of vanadium polyhydrides. Instead, Lewis base abstraction of L·BH_3 from a vanadium(III) tetrahydroborate is usually followed by loss of the remaining hydride (presumably as H_2) and reduction of the metal center to vanadium(II), whereas hydrolysis gives oxo species such as the divanadium(III) complex [V(BH_4)$_2$(PMe_3)$_2$]$_2$(μ-O). Nevertheless, vanadium poly(tetrahydroborate) complexes are interesting in their own right. Efforts are currently directed toward the synthesis of a volatile representative of this class; in analogy with the chemistry of Ti(BH_4)$_3$(dme),[41] such a compound may serve as a starting material for the chemical vapor deposition of vanadium borides.

Experimental Section

All operations were carried out in vacuum or under argon using standard techniques. Solvents were distilled from sodium (toluene) or sodium-benzophenone (pentane, diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane) under nitrogen immediately before use. Trimethylphosphine,[42] VCl_3(thf)$_3$,[43] and VCl_4(thf)$_2$[44] were prepared via literature routes, $LiBH_4$ (Strem) and $NaBH_4$ (Alfa) were used without purification, and $VOCl_3$ (Alfa) was distilled before use. Ethylene (Airco) was purified by sequential passage through H_2SO_4, KOH pellets, BTS catalyst (BASF), and 4A molecular sieves (Linde). Ethylene polymerization studies were carried out as described previously.[25]

Microanalyses were performed by Josef Nemeth and Thomas McCarthy of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B or Perkin-Elmer 1750 FTIR instrument on samples as Nujol mulls. ^{1}H NMR data were obtained on a Varian EM-390 instrument at 90 MHz, or on a General Electric QE-300 instrument at 300 MHz. Chemical shifts are uncorrected for the paramagnetic shift of the solvent and are reported in δ units (positive shifts to high frequency) relative to TMS. Magnetic moments were determined in toluene by a modification of Evans' method.[45] Melting points were determined in closed capillaries under argon.

(1,2-Dimethoxyethane)sodium Tetrakis(tetrahydroborato)vanadate(III). To a cold (−78 °C) flask containing VCl_3(thf)$_3$ (0.97 g, 2.6 mmol) and $NaBH_4$ (0.88 g, 23.3 mmol) was added 1,2-dimethoxyethane (70 mL). A purple solution formed immediately, and the solution was stirred for 0.5 h at −78 °C and then for 22 h at room temperature. During this time, the color progressed through brown, dark blue, and purple stages and a white precipitate formed. The precipitate was allowed to settle, the solution was filtered, and the solvent was removed under vacuum. The residue was extracted with diethyl ether (150 mL), and the extract was filtered, concentrated to ca. 120 mL, and cooled to −20 °C to yield a purple powder. Further material could be isolated by concentration and cooling of the supernatant. Yield: 0.27 g (45%). Mp: 51–52 °C. Anal. Calcd for $C_4H_{26}B_4NaO_2V$: C, 21.5; H, 11.7; V, 22.8. Found: C, 22.2; H, 10.8; V, 21.4. IR (Nujol, cm^{-1}): 2462 m, 2396 m, 2296 w, 2214 w, 2069 m, 1959 w, 1279 m, br, 1240 w, 1188 w, 1110 s, 1084 w, 1040 s, 1000 m, 857 m, 819 w, 723 w, 440 m.

In Situ Preparation of (Diethyl ether)lithium Tetrakis(tetrahydroborato)vanadate(III). To $VOCl_3$ (1.0 mL, 10.6 mmol) in diethyl ether (100 mL) was added dropwise a solution of $LiBH_4$ (1.92 g, 88.1 mmol) in diethyl ether (150 mL). The initially dark red $VOCl_3$ solution was observed to proceed through aqua, blue, black, and finally violet stages as the tetrahydroborate solution was added. After the addition was complete, the solution was stirred for an additional 2 h, cooled to −78 °C, and then filtered. Removal of the solvent gave a purple oil. The compound decomposes thermally over several hours at room temperature under argon, and reproducible elemental analyses were not obtained. EPR (PhMe, 25 °C): broad resonance at 355 mT. EPR (PhMe, −196 °C): three broad features at 100, 470, and 740 mT.

Tris(tetrahydroborato)bis(trimethylphosphine)vanadium(III), V(BH_4)$_3$(PMe_3)$_2$. Method A. To a solution of VCl_3(thf)$_3$ (2.25 g, 6.0 mmol) in tetrahydrofuran (90 mL) was added PMe_3 (1.3 mL, 12.8 mmol). The solution was stirred for 3 h and the solvent was removed under vacuum to give VCl_3(PMe_3)$_2$.[22] The purple residue was extracted with diethyl ether (65 mL) and the solution was cooled to −78 °C. A cold (−78 °C) solution of $LiBH_4$ (0.67 g, 30.8 mmol) in diethyl ether (50 mL) was added via cannula. The solution was stirred for 30 min at −78 °C and then for 6 h at 0 °C. The dark green solution was filtered into a cold (0 °C) flask and the solvent removed under vacuum. The green residue was extracted with cold (0 °C) pentane (300 mL), and the filtered extract was concentrated to ca. 200 mL and cooled to −20 °C. Green prisms of the complex were isolated, and several further crops of crystals were obtained by concentration and cooling of the supernatant. Yield: 0.69 g (46%). Mp: 94 °C dec. Anal. Calcd for $C_6H_{30}B_3P_2V$: C, 29.1; H, 12.2; V, 20.6. Found: C, 28.6; H, 12.3; V, 20.3. ^{1}H NMR (C_6D_6, 25 °C): δ −12.42 (s, fwhm = 300 Hz, PMe_3). Magnetic moment (PhMe, 25 °C): 2.5 μ_B. IR (Nujol, cm^{-1}): 2431 s, 2385 s, 2353 sh, 2227 sh, 2218 w, 2087 s, 1951 w, 1418 m, 1366 m, br, 1304 w, 1288 m, 1236 m, br, 1116 s, 973 sh, 948 s, 846 w, 739 m, 671 w, 422 m.

Method B. A solution of [Li(Et_2O)$_x$][V(BH_4)$_4$], prepared as described above from $VOCl_3$ (1.0 mL) and $LiBH_4$ (1.92 g) in diethyl ether (250 mL), was filtered into a receiving flask cooled to −78 °C. Trimethyl-

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phosphine (3.2 mL, 32 mmol) was added, causing the violet solution to turn bright green. The solution was warmed to 0 °C, the solvent was removed, and the residue was extracted with cold (0 °C) pentane (375 mL). The pentane extract was filtered, concentrated to ca. 340 mL, and cooled to −20 °C. Green crystals of the complex were isolated, and several further crops of crystals were obtained by concentration and cooling of the supernatant. Yield: 0.60 g (23%).

Bis(μ-hydrido)bis(tetrahydroborato)tetrakis(trimethylphosphine)divanadium(II), $[V(BH_4)H(PMe_3)_2]_2$. To $V(BH_4)_3(PMe_3)_2$ (0.33 g, 1.33 mmol) in diethyl ether (80 mL) was added PMe_3 (1.0 mL, 9.9 mmol). The solution was stirred for 3.5 h, by which time a purple color had developed. The solvent was removed, and the residue was extracted with pentane (300 mL). The filtered extracts were concentrated and cooled to −20 °C to yield a lavender solid. Subsequent crops could be obtained by concentration and cooling of the supernatant. Yield: 0.25 g (86%). Mp: 101 °C dec. Anal. Calcd for $C_{12}H_{46}B_2P_4V_2$: C, 32.9; H, 10.6; V, 23.3. Found: C, 34.3; H, 11.0; V, 21.9. Magnetic moment (PhMe, 25 °C): 2.9 μ_B. ^{1}H NMR (C_6D_6, 23 °C): δ −16.2 (s, fwhm = 1060 Hz, P*Me*$_3$). IR (Nujol, cm^{-1}): 2362 s, 2338 s, 2214 m, 2145 sh, 2104 s, 2031 w, 1943 w, 1415 m, 1352 m, 1300 m, 1281 m, 1122 m, 1103 s, 1008 m, 945 s, 842 m, 726 s, 664 m.

(μ-Oxo)tetrakis(tetrahydroborato)tetrakis(trimethylphosphine)divanadium(III), $[V(BH_4)_2(PMe_3)_2]_2(\mu\text{-}O)$. To a cold (−78 °C) solution of $V(BH_4)_3(PMe_3)_2$ (0.21 g, 0.85 mmol) in diethyl ether were added H_2O (0.25 mL of a 1.67 M diethyl ether solution, 0.42 mmol) and PMe_3 (0.2 mL, 2.0 mmol). The solution was stirred for 2.5 h at −78 °C and then for 1.5 h at 0 °C, resulting in a red-purple solution. The solvent was removed and the residue dried under vacuum. The residue was extracted with diethyl ether (50 mL), and the extract was filtered, concentrated to ca. 10 mL, and cooled to −20 °C. Purple needles were isolated from this solution and subsequent crops could be obtained by concentration and cooling of the supernatant. Yield: 0.11 g (79%). Mp: 120 °C dec. Anal. Calcd for $C_{12}H_{52}B_4OP_4V_2$: C, 29.9; H, 10.9; V, 21.2. Found: C, 29.7; H, 10.9; V, 21.1. ^{1}H NMR (C_6D_6, 25° C): δ −16.2 (s, fwhm = 830 Hz, P*Me*$_3$). IR (Nujol, cm^{-1}): 2408 s, 2397 s, 2359 s, 2229 m, 2106 s, 1953 w, 1423 m, 1370 m, br, 1300 m, 1280 m, 1260 w, 1223 m, br, 1171 w, 1120 s, 986 w, 947 s, 845 w, 838 w, 796 w, 738 w, 730 m, 660 w, 408 m, 382 m.

Tris(tetrahydroborato)tris(tetrahydrofuran)vanadium(III), $V(BH_4)_3(thf)_3$. To $VCl_3(thf)_3$ (0.78 g, 2.1 mmol) was added a slurry of $NaBH_4$ (0.56 g, 14.8 mmol) in tetrahydrofuran (60 mL). Immediately a pale purple solution formed, which after 10 h was deep red and after 24 h turned orange-red. The solution was stirred for 72 h at room temperature, filtered, concentrated to ca. 9 mL, and cooled to −78 °C. A crop of green crystals was isolated and subsequent crops were obtained by concentration and cooling of the supernatant. Yield: 0.25 g (38%). Mp: 140 °C dec. Anal. Calcd for $C_{12}H_{36}B_3O_3V$: C, 46.2; H, 11.6; V, 16.3. Found: C, 47.2; H, 11.0; V, 15.0. ^{1}H NMR (C_6D_6, 25°C): δ 20.40 (s, fwhm = 790 Hz, α-*CH*$_2$), 4.28 (s, fwhm = 130 Hz, β-*CH*$_2$). IR (Nujol, cm^{-1}): 2365 s, 2220 sh, 2180 s, 2090 s, 2020 m, 1342 m, 1297 w, 1248 m, br, 1172 w, 1135 s, 1068 m, 1023 s, 920 m, 869 s, 681 m.

Dichlorobis(tetrahydroborato)tetrakis(tetrahydrofuran)divanadium(II), $[V(BH_4)Cl(thf)_2]_2$. Solid $VCl_3(thf)_3$ (3.94 g, 10.5 mmol) was combined with $NaBH_4$ (1.88 g, 49.7 mmol), and tetrahydrofuran (100 mL) was added. After being stirred for 10 days, the purple solution was filtered and concentrated to ca. 15 mL. Toluene (30 mL) was added, and the solution was cooled to −20 °C. Purple prisms of the complex were isolated, and several further crops of the crystals were obtained by concentration and cooling of the supernatant. Yield: 1.55 g (60%). Mp: 100 °C dec. Anal. Calcd for $C_{16}H_{40}B_2Cl_2O_4V_2$: C, 39.2; H, 8.2; Cl, 14.4; V, 20.8. Found: C, 38.4; H, 8.3; Cl, 14.6; V, 20.6. $\mu_{eff} = 2.5\ \mu_B$. X-band ESR (77 K, 2:1 toluene/THF): $g_{eff} = 4.320$, $g_{eff} = 2.009$, $A(^{51}V) = 0.0078$ cm^{-1}. IR (Nujol, cm^{-1}): 2444 s, 2386 s, 2205 w, 2066 s, 1959 m, 1343 m, 1290 s, br, 1169 w, br, 1107 s, 1024 s, 997 sh, 957 w, 920 m, 877 s, 689 w, 446 m, br.

Crystallographic Studies.[46] Single crystals of $V(BH_4)_3(PMe_3)_2$ grown from pentane were sealed in thin-walled glass capillaries under argon. [Single crystals of $[V(BH_4)_2(PMe_3)_2]_2O$ grown from diethyl ether were treated similarly. Subsequent comments in brackets refer to this compound.] Preliminary photographs yielded rough cell dimensions, and a suitable crystal was transferred to the diffractometer. Standard peak search and automatic indexing procedures, followed by least-squares refinement using 25 reflections yielded the cell dimension given in Table I.

Data were collected in one quadrant [two quadrants] of reciprocal space ($+h,+k,\pm l$) [$\pm h,+k,\pm l$]. Systematic absences for $0kl$, $k + l \neq 2n$, and $hk0$, $h \neq 2n$, were consistent with space groups $Pnma$ and $Pn2_1a$. [The unit cell of $[V(BH_4)_2(PMe_3)_2]_2O$ was triclinic.] The average values of the normalized structure factors suggested the centric choice $Pnma$ [$P\bar{1}$], which was confirmed by successful refinement of the proposed model. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied. Systematically absent reflections were eliminated and symmetry equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by using direct methods and Patterson and weighted difference Fourier methods. [Average values for $hk0$ normalized structure factors scaled on the basis of parity groups were hypercentric; $hk0$, $h + k = 2n$, dominated phase relations among strong reflections and $h + k \neq 2n$ reflections dominated relationships among weak reflections. After these groups were rescaled, the structure was solved by direct methods (MULTAN); correct positions for the vanadium and phosphorus atoms were deduced from an E map. A weighted difference Fourier synthesis gave positions of the remaining non-hydrogen atoms.] The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.30/(\sigma(F_o)^2 + (\mathrm{p}F_o)^2)$ [$w = 1.20/(\sigma(F_o)^2 + (pF_o)^2)$]. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. Atoms V, P1, P2, C1, C3, B1, H1a, H3a, H11, and H12 were constrained to the crystallographic mirror plane at $y = 0.25$. In the final cycle of least squares, all nonhydrogen atoms were independently refined with anisotropic thermal coefficients, while the hydrogen atoms (which were located in the Fourier difference maps) were independently refined with isotropic thermal parameters. [For $[V(BH_4)_2(PMe_3)_2]_2O$ a group isotropic thermal parameter was varied for the methyl hydrogen atoms, which were located in the difference Fourier maps and fixed in "idealized" positions with C–H = 0.95 Å. Positions of the hydrogen atoms of the tetrahydroborate groups were located in the difference maps and independently refined with isotropic thermal coefficients.] Successful convergence was indicated by the maxium shift/error of 0.023 [0.038] in the last cycle. Final refinement parameters are given in Table I. The final difference Fourier map had no significant features. There were no apparent systematic errors among the final observed and calculated structure factors. Refinement of the proposed model in the acentric space group $Pn2_1a$ did not significantly change the model or improve the fit of the data; the acentric choice was rejected on the basis of a Hamilton R factor ratio test.

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Supplementary Material Available: Tables S1–S6, giving full crystallographic details, methyl hydrogen atom positions, anisotropic thermal parameters, and complete bond distances and angles for $V(BH_4)_3(PMe_3)_2$ (**2**) and $[V(BH_4)_2(PMe_3)_2]_2(\mu\text{-}O)$ (**4**) (7 pages); listings of final observed and calculated structure factors for **2** and **4** (17 pages). Ordering information is given on any current masthead page.

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[46] For a full description of the crystallographic procedure, see ref 25.