Table I. HREELS Frequencies of Chemisorbed CH_3Br and H_3

	CH_3			
C_s symmetry	photochemical from CH_3Br[a]	thermal from CH_3I[b]		CH_3Br[b]
$\nu(CH_2)$	2950	2925		
$\nu(CH)$	2770[c]	2775	$\nu_s(CH_3)$	3015
$\delta(CH_2)$	1410	1425	$\delta_a(CH_3)$	1420
$\omega(CH_2)$	1180	1165	$\delta_s(CH_3)$	1285
$\tau(CH_2)$	NO[d]	NO		
$\rho(CH_2)$	NO	NO	$\rho(CH_3)$	945
$\delta(CH)$	820	790		
$\rho(CH)$	NO	NO		
$\nu(PtC)$	495	520		
			$\nu(C\text{-}Br)$	565
			$\nu(Pt\text{-}Br)$	NO

[a] This work. [b] Reference 15. [c] Resolved only in off-specular geometry. [d] NO = not observed.

and part of the first monolayer. The UV light, generated from a focused 100 W Hg arc lamp, passed through a neutral density filter and then a quartz window at the vacuum chamber wall. The incident angle was approximately 30 deg off the sample normal. In our experiments, the temperature reached during irradiation never exceeded 135 K and the radiant power on the sample was between 0.30 and 0.35 W. High-resolution electron energy loss spectroscopy (HREELS) was used to measure the vibrational spectra of adsorbed species and was taken with a primary beam energy of 7.0 eV and an elastic peak full width at half maximum of 95 cm^{-1}.

To take HREELS of the species formed and retained during irradiation, we irradiated a submonolayer of CH_3Br for 90 min, flashed the sample to 220 K, and then cooled the sample to 100 K to take the spectrum. As indicated by several experiments where TPD was done before and after HREELS, flashing to 220 K removes all the molecular methyl bromide that remains after photolysis.

Figure 1 (upper panel) shows the HREELS of monolayer CH_3Br after photolysis and flashing to 220 K. Except for the band at 2060 cm^{-1}, which is due to background CO, all other bands (2950, 1410, 1180, 820, and 495 cm^{-1}) can be attributed to CH_3 groups adsorbed on Pt(111).[15] The band assignments are listed in Table I with comparisons to CH_3Br on Pt(111) and to CH_3 generated from the thermal decomposition of CH_3I on Pt(111).[15] Assignments of the latter bands were confirmed with use of CD_3I.[15] Because the intensities are relatively weak and long data accumulation times are required, we did not systematically vary the irradition time.

The symmetric C–H stretches of methyl halides are above 3000 cm^{-1} regardless of coverage, while that of the adsorbed methyl group is below 3000 cm^{-1} (2925 cm^{-1} for CH_3 derived from CH_3I[15]). The C–H stretching frequency (2950 cm^{-1}) shown in Figure 1 is also below 3000 cm^{-1}, supporting the assignment as $CH_3(a)$. The fact that there is no band at 560 cm^{-1} attributable to C–Br stretching also indicates C–Br bond cleavage during photolysis. While it is not well-resolved in the specular direction, there does appear to be a "soft" C–H stretching mode in the 2775–2790-cm^{-1} region, as in CH_3I decomposition on Pt(111)[15] and in activated decomposition of CH_4 on Ni(111).[17] The Br-metal stretching frequency probably lies within the tail of the elastic peak. Thus, we conclude that methyl groups accumulate on the surface during photolysis.

Comparing the specular (Figure 1, upper panel) and off-specular (lower panel) HREELS, we conclude that all the observed modes are dipole allowed. Applying the HREELS dipole selection rule, this methyl group has symmetry less than C_{3v}, probably C_s,[15] as indicated in Table I.

In conclusion, these results show that the photolysis of submonolayer amounts of methyl bromide, adsorbed on Pt(111), leads to adsorbed methyl groups. These have a C_s symmetry and are the precursor to the methane observed in post-irradiation TPD. Methane formation involves background H_2 chemisorption and some methyl decomposition.[12]

Acknowledgment. This work was supported in part by the National Science Foundation Materials Research Group Program (DMR 8418086).

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(17) Lee, M. B.; Yang, Q. Y.; Tang, S. L.; Ceyer, S. T. *J. Chem. Phys.* **1986**, *85*, 1693.

Observation of a Transition-Metal–Enol Complex and Stereoselective Keto–Enol Tautomerization in Transition-Metal–Acyl Compounds

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Interest in the properties and reactivity of transition metal–acyl complexes stems from the central role that metal–acyl species play in catalytic reactions of industrial importance[1] and from recent advances in the use of metal–acyl complexes as stoichiometric reagents for organic synthesis.[2] The chemistry of organic carbonyl compounds is often influenced by keto–enol tautomerization processes;[3] yet, such a phenomenon has not previously been observed for a transition metal–acyl compound. Here we report the formation of a transition metal–enol complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCHCOH})Re(CO)_4$, **1-Re**, and observation of kinetic, stereoselective tautomerization in the acyl-bridged compounds $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCH_2CO)M}(CO)_4$, [M = Re, **2-Re**; M = Mn, **2-Mn**].

We recently reported the synthesis of the novel acyl-bridged bimetallic complexes **2-Re** and **2-Mn** from reaction of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(COCH_2Li)$ and $M(CO)_5(OSO_2CF_3)$ [M = Mn, Re].[4] The ^1H NMR spectrum of **2-Re** in $CDCl_3$ exhibits doublets at δ 2.48 and 3.13 (J_{HH} = 20.7 Hz) assigned to the diastereotopic methylene hydrogens.[5] We have now observed that THF-d_8 solutions of **2-Re** give rise to three additional distinct resonances in the ^1H NMR spectrum, which we attribute to formation of transition metal–enol complex **1-Re**; singlets at δ 6.28 (1 H), 8.91 (1 H), and 1.73 (15 H) are assigned to the vinyl, hydroxyl, and $\eta^5\text{-}C_5Me_5$ hydrogens, respectively.[6] The intensity

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(1) (a) Casey, C. P. *J. Chem. Educ.* **1986**, *63*, 188. (b) Henrici-Olive, G.; Olive, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136. (c) Hermann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (d) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (e) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (f) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; Chapter 5. (g) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 8, p 19. (h) Tkatchenko, I. *Ibid.* p 101.

(2) (a) Burkhardt, E. R.; Doney, J. J.; Stack, J. G.; Heathcock, C. H.; Bergman, R. G. *J. Mol. Catal.* **1987**, *41*, 41 and references therein. (b) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328 and references therein. (c) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Walker, J. C. *Tetrahedron* **1986**, *42*, 5123 and references therein. (d) Brinkman, K.; Helquist, P. *Tetrahedron Lett.* **1985**, *26*, 2845.

(3) (a) Forsen, S.; Nilsson, M. In *The Chemistry of the Carbonyl Group, II*; Patai, S., Ed.; Wiley Interscience: New York, 1970. (b) Zimmerman, H. E. *Acc. Chem. Res.* **1987**, *20*, 263 and references therein. (c) Nadler, E. B.; Rappoport, Z.; Arad, D.; Apeloig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7873 and references therein. (d) Hine, J.; Miles, D. E.; Zeigler, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 4374. (e) Hine, J. *Acc. Chem. Res.* **1978**, *11*, 1. (f) Capon, B.; Siddhanta, A. K.; Zucco, C. *J. Org. Chem.* **1985**, *50*, 3580.

(4) O'Connor, J. M.; Uhrhammer, R.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1987.

(5) Additional resonances for **2-Re** are observed in the ^1H NMR spectrum ($CDCl_3$) δ 1.75 (s, 15 H), 7.30 and 7.43 (m, 15 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 289.8 (d, J_{CP} = 7.4 Hz), 275.6, 194.9, 191.6, 191.4, 190.9, 133.3 (br), 130.9, 128.8, 128.7, 103.6, 95.7, 9.9.

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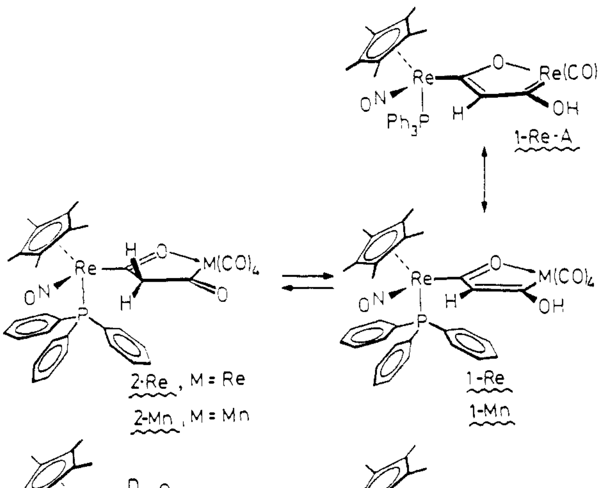
ratio of the ^{1}H NMR resonance at δ 6.28 (**1-Re**) to that at δ 3.00 (**2-Re**) is temperature dependent with $K_{eq}{}^{23\,°C}$ = [**1-Re**]/[**2-Re**] = 0.66. When the THF-d_8 solvent is removed under vacuum and replaced by $CDCl_3$, the ^{1}H NMR spectrum again exhibits resonances due only to **2-Re**. The existence of two species in THF-d_8 solutions is supported by the observation of two singlets in the $^{31}P\{^1H\}$ NMR spectrum at δ 19.36 (**2-Re**) and 22.70 (**1-Re**) in approximately a 2:1 ratio.[7a,b] We rule out an alternative hydroxycarbene formulation, **1-Re-A**, for the dominant ground-state structure of the hydroxy compound on the basis of a δ 225.4 (*C*OH) chemical shift in the $^{13}C\{^1H\}$ NMR spectrum of the isotopically labeled complex, (η^5-C_5Me_5)Re(NO)(PPh_3)(μ-η^1,η^2-$COCH^{13}COH$)Re(^{13}CO)$_4$, **1-Re-^{13}C**.[7a,b] For comparison, the carbene carbon resonance for hydroxycarbene, Re(CO)$_3$(Cl)(=CMe(OH))$_2$, is observed at δ 322.3.[7c]

Addition of D_2O (300 M excess) to a THF-d_8 solution containing an equilibrium mixture of **2-Re** and **1-Re** allows deuterium incorporation into the bridge sites to be monitored by ^{1}H NMR spectroscopy. Three minutes subsequent to D_2O addition, a ^{1}H NMR spectrum of the sample still exhibits resonances for **2-Re** at δ 2.49 (d) and 3.00 (d) as well as a resonance for **1-Re-d_1** at 6.28 (s). The hydroxyl resonance at δ 8.91 is absent, and a new resonance is apparent at δ 2.44 ($\nu_{1/2}$ = 6 Hz) assigned to the methylene hydrogen of **2-Re-d_1**.[8] Rapid ($t_{1/2} \approx$ 3 min) deuterium incorporation into **2-Re** is observed as a decrease in the peak height of the δ 2.49 and 3.00 doublets and as an increase in the 2.44 resonance. Exchange of deuterium into the vinyl site of **1-Re-d_1** (δ 6.28) and the remaining methylene hydrogen site of **2-Re-d_1** (δ 2.44) occurs at a slower rate ($t_{1/2} \approx$ 2 h) to give **2-Re-d_2** and **1-Re-d_2**. Addition of H_2O to an equilibrium mixture of **2-Re-d_2** and **1-Re-d_2** regenerates the protio compounds, **2-Re** and **1-Re**.



1-Re-A

2-Re, M = Re

2-Mn, M = Mn

1-Re

1-Mn

2-Re-d_1

1-Re-d_1

2-Re-d_2

1-Re-d_2

Remarkably, the manganese analogue, **2-Mn**, does not enolize to an observable extent by ^{1}H NMR spectroscopy in THF-d_8 ($K_{eq}{}^{23\,°C}$ = [**1-Mn**]/[**2-Mn**] < 0.02).[9,10] Addition of D_2O to THF-d_8 solutions of **2-Mn** also leads to kinetic stereoselective incorporation of deuterium into the methylene sites. The methylene hydrogen doublets observed in the ^{1}H NMR spectrum of **2-Mn** (δ 3.39, 2.81) undergo a slow intensity decrease ($t_{1/2} \approx$ 2.5 h) and a new broad resonance simultaneously grows in at δ 2.77 (**2-Mn-d_1**).[8,10] Exchange of deuterium into the remaining methylene site of **2-Mn-d_1** occurs at a slower rate ($t_{1/2}$ = 36 h) as observed by an intensity decrease in the δ 2.77 resonance. On the basis of an NOE experiment,[11] we tentatively assign the more labile hydrogen (δ 3.13, **2-Re**, and 3.39, **2-Mn**) as the one distal to the PPh_3 ligand when the molecule occupies the conformation with an ~180° ON-Re-C_αO torsion angle.[12]

The stereoselectivity observed for the enolization of **2-Re** and **2-Mn** is largely a consequence of the chiral rhenium center and a favored ON-Re-C_αO torsion angle, which situates the bulky PPh_3 ligand such that it effectively blocks one face of the bridging ligand.[12] We note that in the solid-state structure of **2-Mn** the chelate ring is slightly puckered, which places the methylene hydrogen distal to the PPh_3 ligand in a pseudoaxial position and the hydrogen proximal to the PPh_3 ligand in a pseudoequatorial

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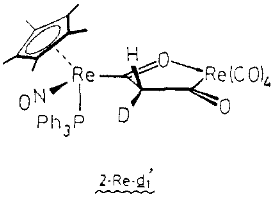
[6] (a) We have never observed only **2-Re** in THF-d_8 solution; even when rigorously dry conditions are employed. The effect of solvent on the equilibrium constant for **1-Re** ⇄ **2-Re** is consistent with enol stabilization by solvent, which can act as a hydrogen-bond acceptor: Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: New York, 1979; Chapter 4. (b) The PPh_3 resonances for **1-Re** are coincident with those for **2-Re** in the ^{1}H NMR spectrum (THF-d_8); resonances assigned to **2-Re**: δ 1.76 (s, 15 H), 2.47 (d, J = 20.5 Hz, 1 H), 3.01 (d, J = 20.5 Hz, 1 H), 7.39, 7.84 (br, 15 H). IR (THF): 3500–3100 (vw, vbr) 2075 (w, sh), 1966 (vs), 1928 (s), 1665 (m), 1631 (w) cm^{-1}.

[7] (a) A 125-MHz $^{13}C\{^1H\}$ NMR spectrum (THF-d_8) of an equilibrium mixture of **2-Re** and **1-Re** exhibited the following resonances: δ 10.0, 10.1, 96.3, 103.4, 104.5, 128.8, 128.9, 129.6, 130.0, 130.4, 131.0, 131.8, 133.2, 134.0 (br), 139.6, 189.7, 191.2, 192.8, 193.0, 193.6, 194.6, 196.4, 225.4, 265.3, and 269.8. The resonances for carbonyl carbons bound to the chiral rhenium atoms are too weak in intensity for a chemical shift to be unambiguously assigned. (b) The $^{13}C\{^1H\}$ NMR resonances attributed to **1-Re** are very similar in chemical shift to those of the trimethylsilyl analogue, (η^5-C_5Me_5)Re(NO)(PPh_3)(COCHCOSiMe$_3$)Re(CO)$_4$,[4] which has resonances in CD_2Cl_2 solution at δ 272.6 (d, J_{PC} = 11.0 Hz), 223.6, 193.9, 193.87, 190.8, 189.3, 145.2, 134.1, 130.6, 128.5 (d, J_{PC} = 10.1 Hz), 103.2, 10.0, 0.9. (c) Darst, K. P.; Lenhert, P. G.; Lukehart, C. M.; Warfield, L. T. *J. Organomet. Chem.* **1980**, *195*, 317.

[8] (a) Isotope chemical shift effects resulting from substitution of a deuterium atom for a methylene hydrogen atom generally lead to an upfield shift of ~0.01 to 0.02 ppm in the ^{1}H NMR spectrum: Batiz-Hernandez, H.; Bernheim, R. A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1967**, *3*, 63. (b) For isotope shifts of 0.03 ppm, see: Barras, C. A.; Roulet, R.; Carrupt, P.-A.; Berchier, F.; Vogel, P. *Helv. Chim. Acta* **1984**, *67*, 886. Golding, B. T.; Ioannou, P. V.; Sellers, P. *J. Inorg. Chim. Acta* **1981**, *56*, 95. Sakaguchi, U.; Morito, K.; Yoneda, H. *J. Am. Chem. Soc.* **1979**, *101*, 2767. (c) The ^{1}H NMR isotope chemical shifts observed for **2-Re-d_1** (0.05 ppm) and **2-Mn-d_1** (0.04 ppm) are larger than expected and may not represent the intrinsic isotope shift value. Consistent with our assignment of the δ 2.44 resonance to **2-Re-d_1** is the observed 6-Hz bandwidth expected for $J_{HD} \approx$ 3 Hz. In addition, when H_2O is added to a CD_2Cl_2 solution containing **2-Re-d_2**, a broad resonance is observed at δ 3.03; shifted 0.04 ppm to higher field from the 3.07 doublet of **2-Re** in CD_2Cl_2. We therefore assign the δ 3.03 resonance to **2-Re-d_1′**.



2-Re-d_1′

[9] (a) Although the factors which influence K_{eq} in this system are not yet completely clear, we do note that rhenium is more electronegative than manganese[9b] and in simple organic keto–enol systems K_{eq} typically increases with increased electron withdrawal by α-substituents.[3c] It is also expected that coordination of the acyl oxygen to a more electronegative metal will shift the equilibrium toward the enol form. (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; p 93.

[10] For **2-Mn**: ^{1}H NMR (THF-d_8) δ 1.97 (s, 15 H), 2.81 (d, J_{HH} = 20 Hz, 1 H), 3.36 (d, J_{HH} = 20 Hz, 1 H), 7.4 (m, 15 H).[4]

[11] For **2-Re**, at 500 MHz ($CDCl_3$), saturation of the ^{1}H NMR resonance at δ 7.30 (m, 6 H, PPh_3) results in a 4.6% increase in the δ 2.48 doublet and a barely perceptible decrease in the downfield δ 3.13 doublet. Saturation of the δ 1.76 (15 H, C_5Me_5) resonance results in a barely perceptible decrease in the upfield doublet (2.48) and a 1.3% increase in the downfield doublet (3.13). It was not possible to selectively saturate resonances at δ 2.48 and 3.13 due to the width of the signals (J_{HH} = 20.7 Hz).

[12] For an excellent discussion on ON–Re–C_αO torsion angles and asymmetric induction in (η^5-C_5H_5)Re(NO)(PPh_3)(R) complexes, see: Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688 and references therein.

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.

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(13) For examples of stereoselective hydrogen–deuterium exchange in organic systems, see: Peiris, S.; Ragauskas, A. J.; Stothers, J. B. *Can. J. Chem.* **1987**, *65*, 789. Keys, L. D., III; Johnston, M. *J. Am. Chem. Soc.* **1985**, *107*, 486. Cheng, A. K.; Ghosh, A. K.; Stothers, J. B. *Can. J. Chem.* **1984**, *62*, 1385. Wu, G. D.; Serianni, A. S.; Barker, R. *J. Org. Chem.* **1983**, *48*, 1750. Gabioud, R.; Vogel, P. *Tetrahedron Lett.* **1983**, *24*, 1983. Guthrie, R. D.; Nicolas, E. C. *J. Am. Chem. Soc.* **1981**, *103*, 4637. Fraser, R. R.; Champagne, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 657 and references therein. Barbarella, G.; Garbesi, A.; Fava, A. *J. Am. Chem. Soc.* **1975**, *97*, 5883 and references therein. King, J. F.; du Manoir, J. R. *Can. J. Chem.* **1973**, *51*, 4082. Hofer, O.; Eliel, E. L. *J. Am. Chem. Soc.* **1973**, *95*, 8045. Eliel, E. L. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 748. Hutchinson, B. J.; Andersen, K. K.; Katritzky, R. *J. Am. Chem. Soc.* **1969**, *91*, 3839. Bullock, E.; Scott, J. M. W.; Golding, P. D. *J. Chem. Soc., Chem. Commun.* **1967**, 168. Nishio, M. *J. Chem. Soc., Chem. Commun.* **1967**, 562. Rauk, A.; Buncel, E.; Moir, R. T.; Wolfe, S. *J. Am. Chem. Soc.* **1965**, *87*, 5498. Fukunaga, M.; Arai, K.; Iwamura, H.; Oki, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 302. Saito, H.; Matsuo, T. *Nippon Kagaku Kaishi* **1979**, *12*, 1720. Also see ref 8b.

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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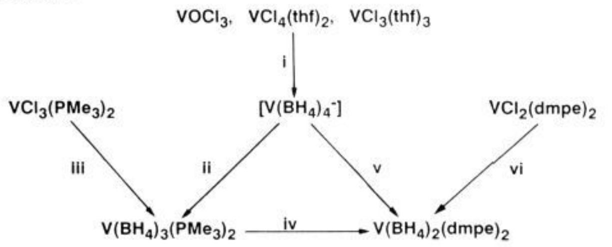
Unidentate tetrahydroborate ligands were the most recently discovered of the three major BH_4^- bonding modes and still remain the least well-understood, compared with bidentate and tridentate geometries. Few examples are known: of these, only $Cu(\eta^1\text{-}BH_4)(PMePh_2)_3$,[1] $Cu(\eta^1\text{-}BH_4)[(PPh_2CH_2)_3CMe]$,[2] $FeH(\eta^1\text{-}BH_4)(dmpe)_2$,[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.

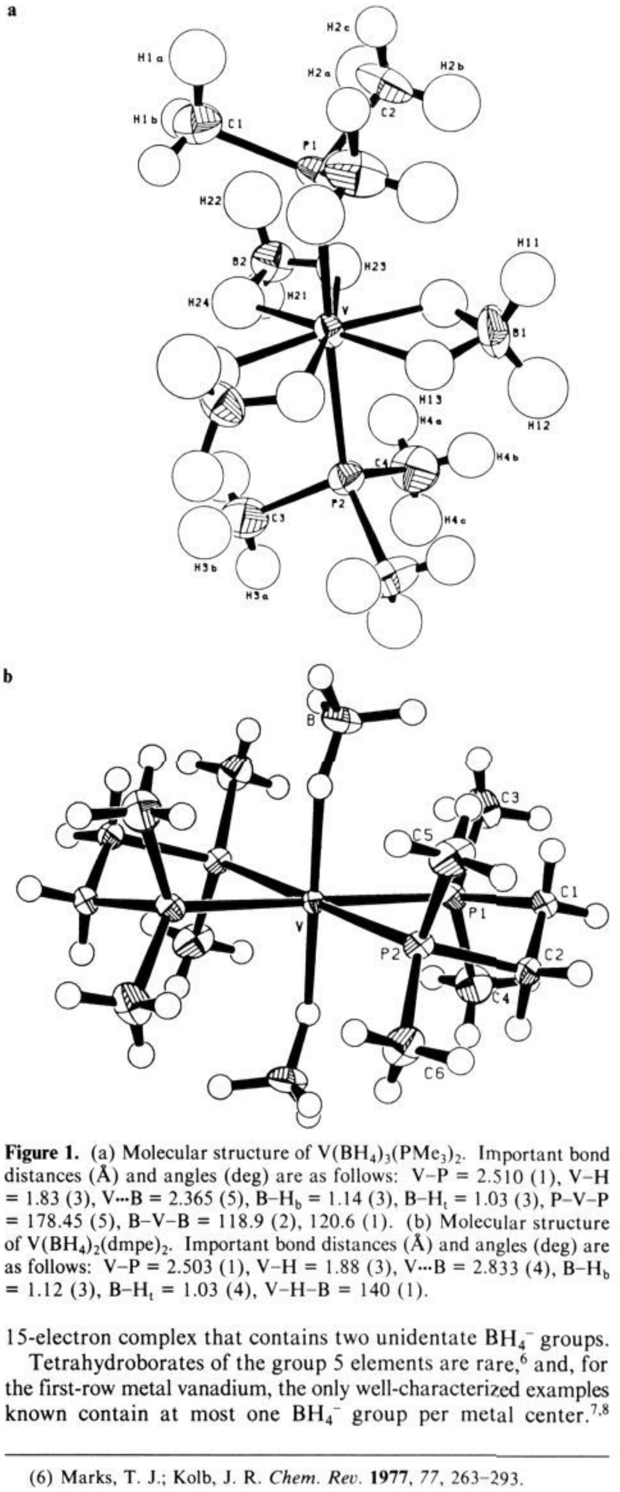


Figure 1. (a) Molecular structure of $V(BH_4)_3(PMe_3)_2$. Important bond distances (Å) and angles (deg) are as follows: V–P = 2.510 (1), V–H = 1.83 (3), V···B = 2.365 (5), $B\text{–}H_b$ = 1.14 (3), $B\text{–}H_t$ = 1.03 (3), P–V–P = 178.45 (5), B–V–B = 118.9 (2), 120.6 (1). (b) Molecular structure 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), $B\text{–}H_b$ = 1.12 (3), $B\text{–}H_t$ = 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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(1) (a) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1980**, *19*, 587–593. (b) Kutal, C.; Grutsch, P.; Atwood, J. L.; Rogers, R. D. *Inorg. Chem.* **1978**, *17*, 3558–3562. (c) Tagusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Shore, S. G.; Schmitkons, T.; Fratini, A. V.; Morse, K. W.; Wei, C.-Y.; Bau, R. *J. Am. Chem. Soc.* **1981**, *103*, 5165–5171.

(2) (a) Dapporto, P.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 2768–2774. (b) Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4096–4098.

(3) (a) Baker, M. V.; Field, L. D. *J. Chem. Soc., Chem. Commun.* **1984**, 996–997. (b) Bau, R.; Yuan, H. S.; Baker, M. V.; Field, L. V. *Inorg. Chim. Acta* **1986**, *114*, L27–L28.

(4) (a) Fryzuk, M. D.; Rettig, S. J.; Westerhaus, A.; Williams, H. D. *Inorg. Chem.* **1985**, *24*, 4316–4325.

(5) (a) Holah, D. G.; Hughes, A. N.; Wright, K. *Can. J. Chem.* **1974**, *52*, 2990–2999. (b) Holah, D. G.; Hughes, A. N.; Hui, B. C. *Can. J. Chem.* **1976**, *54*, 320–328. (c) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1979**, *18*, 531–538. (d) Luetkens, M. L.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1985**, *107*, 3361–3362. (e) Barron, A. R.; Salt, J. E.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1986**, *5*, 1833–1837.

(6) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263–293.

0002-7863/88/1510-4450$01.50/0