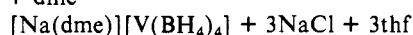
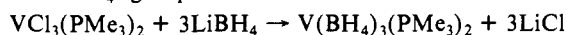


Interaction of $\text{VCl}_3(\text{thf})_3$ with excess NaBH_4 in 1,2-dimethoxyethane (dme) gives a purple solution,⁹ from which the first binary tetrahydroborate of vanadium, $[\text{Na}(\text{dme})][\text{V}(\text{BH}_4)_4]$, **1**,¹⁰ may be obtained after crystallization from diethyl ether (see Scheme I). The infrared spectrum of **1** is consistent with an eight-co-

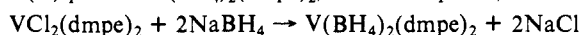


ordinate geometry in which the vanadium center is surrounded by four bidentate BH_4^- groups. Treatment of $[\text{V}(\text{BH}_4)_4^-]$ solutions with PMe_3 , or more conveniently, interaction of $\text{VCl}_3(\text{PMe}_3)_2$ with LiBH_4 , yields the neutral tris(tetrahydroborate), $\text{V}(\text{BH}_4)_3(\text{PMe}_3)_2$, **2**.¹¹ This bright green paramagnetic complex ($\mu_{\text{eff}} = 2.5 \mu_{\text{B}}$) possesses three strong IR bands in a pattern characteristic of bidentate BH_4^- groups.



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 d¹ titanium analogue $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$,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 d¹ ion but orbitally nondegenerate for a d² ion.

Treatment of $\text{V}(\text{BH}_4)_3(\text{PMe}_3)_2$ with excess 1,2-bis(dimethylphosphino)ethane (dmpe), gives $\text{dmpe} \cdot \text{BH}_3$ and a purple vanadium(II) product $\text{V}(\text{BH}_4)_2(\text{dmpe})_2$, **3**.¹⁴ This species, which may



also be prepared from $\text{VCl}_2(\text{dmpe})_2$ and NaBH_4 in tetrahydrofuran, is paramagnetic ($\mu_{\text{eff}} = 3.6 \mu_{\text{B}}$) 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 $\text{Cu}(\eta^1\text{-BH}_4)(\text{PMePh}_2)_3$ and 161.7° for $\text{FeH}(\eta^1\text{-BH}_4)(\text{dmpe})_2$.¹⁻⁴ The structure of **3** again differs from that of its titanium analogue, $\text{Ti}(\text{BH}_4)_2(\text{dmpe})_2$, 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 d³ species to adopt octahedral coordination environments. Interestingly, despite the $\eta^1\text{-BH}_4$ coordination, **3** does not react with Lewis bases such as PMe_3 and excess dmpe.

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($\eta^1\text{-BH}_4$) 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) $\text{Ti}(\text{BH}_4)_3(\text{dme})$.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 $\text{V}(\text{BH}_4)_3(\text{PMe}_3)_2$ and $\text{V}(\text{BH}_4)_2(\text{dmpe})_2$ (4 pages); tables of observed and calculated structure factors for $\text{V}(\text{BH}_4)_3(\text{PMe}_3)_2$ and $\text{V}(\text{BH}_4)_2(\text{dmpe})_2$ (11 pages). Ordering information is given on any current masthead page.

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(17) Hessen, B.; Van Bolhuis, F.; Teuben, J. H. *J. Am. Chem. Soc.* 1988, 110, 295-296.

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

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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 $\text{Os}_3(\text{CO})_{12}$.³ Here we present evidence that in solution the $\text{Cr}(\text{CO})_5$ unit freely rotates in both isomers of the

(1) For example: (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 1083. (b) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chichester, England, 1980; p 211.

(2) (a) Delley, B.; Manning, M. C.; Ellis, D. E.; Berkowitz, J.; Trogler, W. C. *Inorg. Chem.* 1982, 21, 2247 and references therein. (b) Lauher, J. W. *J. Am. Chem. Soc.* 1982, 100, 5305. See, also: Porterfield, W. W. *Inorganic Chemistry*; Addison-Wesley: Reading, MA, 1984; p 551.

(3) Johnston, V. J.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* 1987, 109, 8111.

(7) (a) Marks, T. J.; Kinnely, W. J. *J. Am. Chem. Soc.* 1975, 97, 1439-1443. (b) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* 1978, 100, 7902-7915. (c) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* 1984, 23, 4113-4115. (d) Cotton, F. A.; Duraj, S. A.; Falvello, L. R.; Roth, W. J. *Inorg. Chem.* 1985, 24, 4389-4393. (e) Hessen, B.; Teuben, J. H.; Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Organometallics* 1985, 4, 946-948.

(8) " $\text{V}(\text{BH}_4)_3$ " has been claimed, but no data have been reported. Klejnot, O. Dissertation, University of Munich, 1955.

(9) Makhaev, V. D.; Semenenko, K. N. *Bull. Acad. Sci. USSR* 1978, 27, 2520-2521.

(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) Å³, $Z = 4$, $R_F = 3.4\%$, $R_{wF} = 2.9\%$ 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.

(13) Jensen, J. A.; Girolami, G. S. *J. Chem. Soc., Chem. Commun.* 1986, 1160-1162.

(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_3), -19.3 (s, fwhm = 950 Hz, PMe_3). 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) Å³, $Z = 2$, $R_F = 3.2\%$, $R_{wF} = 3.0\%$ on 168 variables and 1629 data with $I > 2.58\sigma(I)$. Non-hydrogen atoms and hydrogen atoms were refined as above.

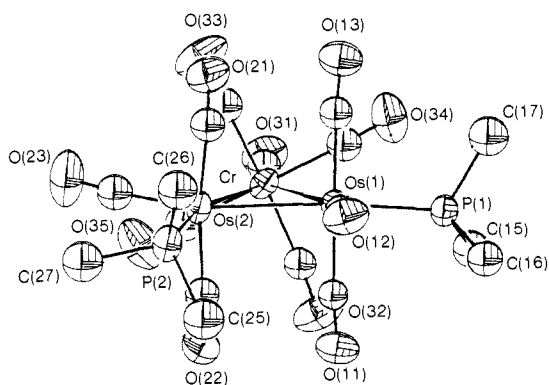


Figure 1. Molecular structure of $(\text{OC})_5\text{Cr}[\text{Os}(\text{CO})_3(\text{PMe}_3)]_2$ (**1**).

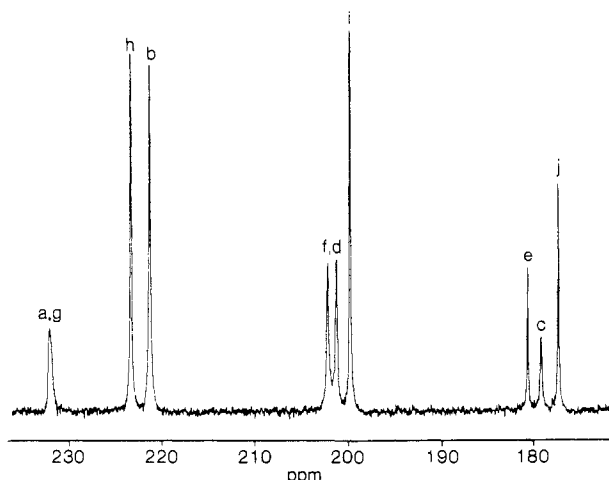


Figure 2. 100.6-MHz ^{13}C NMR spectrum of **1** (^{13}CO -enriched) in $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ solution at -122°C . The assignment of the signals is as shown in the text except that signals labeled d, f, and i refer to the axial carbonyls on the osmium atoms labeled d, f, and i in the text.

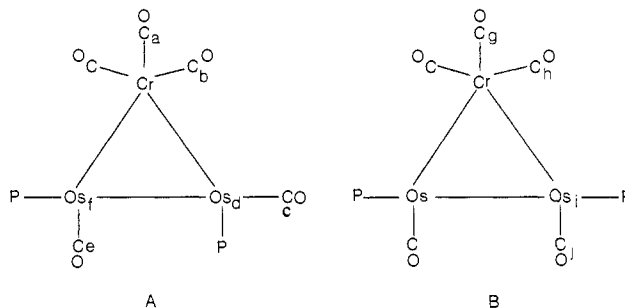
trinuclear cluster $(\text{OC})_5\text{Cr}[\text{Os}(\text{CO})_3(\text{PMe}_3)]_2$. This suggests that the only bond between the chromium atom and the two osmium atoms is a centrally directed, three-center two-electron bond.

The cluster $(\text{OC})_5\text{Cr}[\text{Os}(\text{CO})_3(\text{PMe}_3)]_2$ (**1**) was isolated as deep red, air-stable crystals from the UV irradiation of $(\text{Me}_3\text{P})(\text{OC})_4\text{OsCr}(\text{CO})_5$ in C_6F_6 .⁵ The structure⁶ of **1** (Figure 1) consists of a triangular CrOs_2 unit with Cr–Os vectors of 3.024 (2) Å (Os(1)–Cr) and 2.996 (2) Å (Os(2)–Cr) and an Os–Os bond of length 2.838 (1) Å. There do not appear to be any Cr–Os bond lengths reported in the literature. The Cr–Os lengths in **1** are, however, slightly longer than 2.979 (1) Å, the length of the dative Os–Cr bond in $(\text{Me}_3\text{P})(\text{OC})_4\text{OsCr}(\text{CO})_5$.⁷ Dative metal–metal bonds are usually longer than comparable covalent metal–metal bonds.⁸

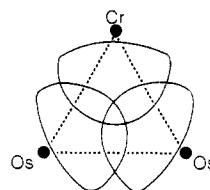
The carbonyls of $\text{M}(\text{CO})_4$ units in trinuclear clusters usually occupy sites that are either essentially perpendicular (axial) or

parallel (equatorial) to the M_3 plane.⁹ However, and as can be seen from Figure 1, the radial carbonyls of the $\text{Cr}(\text{CO})_5$ group are considerably rotated from this arrangement, e.g., the dihedral angle between the Os(1)–Os(2)–Cr and CO(31)–Cr–CO(34) planes is $25.5(2)^\circ$. This staggered arrangement is more typical of bimetallic $(\text{L})(\text{OC})_4\text{MM}'(\text{CO})_4(\text{L})$ complexes where there is free rotation about the metal–metal single bond.^{4,10}

The ^{13}C NMR spectrum of **1** (^{13}CO -enriched) in $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ at -122°C (Figure 2) is consistent with the presence of roughly equal concentrations of two isomers, A and B as shown (Me and axial CO groups have been omitted). The assignment



shown is straightforward based on the characteristic region the resonances of carbonyls of a given type occur,¹¹ the intensities, and the mode of collapse of the signals at higher temperature (when a given mechanism is assumed). As can be seen, even at -122°C the four radial carbonyls of the $\text{Cr}(\text{CO})_5$ unit in each isomer are equivalent but not equivalent to the fifth (axial¹²) carbonyl. For A, this equivalence cannot be due to the radial carbonyls adopting positions an equal distance above and below the CrOs_2 plane because the osmium atoms are chemically different (Figure 1). Accidental degeneracy can also be confidently ruled out; for trinuclear clusters, there is usually a large chemical shift difference between carbonyls located in the metal plane and those perpendicular to the plane.¹¹ Furthermore, we have observed similar equivalence of carbonyls in compounds related to **1** including $(\text{OC})_5\text{W}[\text{Os}(\text{CO})_3(\text{PMe}_3)]_2$ and $(\text{MeO})_3\text{P}(\text{OC})_4\text{W}[\text{Os}(\text{CO})_3(\text{PMe}_3)]_2$.¹³ We believe the simplest explanation for this observation is that the $\text{Cr}(\text{CO})_5$ unit in each isomer of **1** freely rotates in much the same way as in binuclear complexes with unbridged, single metal–metal bonds. This implies that the bond between the chromium atom and the two osmium atoms is a single, three-center two-electron bond directed to the middle of the metal triangle as shown.¹⁴ A similar bonding scheme has been proposed



for the linkage of the $\text{M}(\text{CO})_5$ groups to the Ni_3 triangle in the pentanuclear cluster anions, $[\text{Ni}_3\text{M}_2(\text{CO})_{16}]^{2-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$).¹⁵ It is also consistent with molecular orbital calculations for the square–pyramidal $\text{Cr}(\text{CO})_5$ fragment that indicate it has only one low–energy acceptor orbital of a_1 symmetry.¹⁶

(4) Prepared in a similar manner to $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$; Einstein, F. W. B.; Jones, T.; Pomeroy, R. K.; Rushman, P. *J. Am. Chem. Soc.* **1984**, *106*, 2707.

(5) Isolated yield: 31% (after chromatography). IR $\nu(\text{CO})$ (hexane) 2074 (w), 2003 (s), 1991 (vs), 1955 (w), 1939 (m), 1920 (w), 1887 (w, br) cm^{-1} ; MS, m/e 892 (M^+); ^{13}C NMR ($\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$, 4/1, -122°C) δ 232.0, 223.3, 221.2, 202.1, 201.2, 199.7, 180.7, 179.2, 177.4. anal. calcd for $\text{C}_{17}\text{H}_{18}\text{CrOs}_2\text{O}_{11}\text{P}_2$: C, 22.87; H, 2.03. Found: C, 23.09; H, 2.04.

(6) X-ray diffraction data for $(\text{OC})_5\text{Cr}[\text{Os}(\text{CO})_3(\text{PMe}_3)]_2$; $M_r = 892.4$; triclinic; space group $P\bar{1}$; $a = 9.331(1)$ Å, $b = 12.013(1)$ Å, $c = 12.357(1)$ Å, $\alpha = 87.35(1)^\circ$, $\beta = 85.94(1)^\circ$, $\gamma = 68.81(1)^\circ$, $V = 1287.9$ Å³, $Z = 2$, $D_c = 2.302$ g cm^{-3} (an analytical absorption correction was applied); diffractometer, Enraf-Nonius CAD4F; radiation, Mo $K\alpha$, graphite monochromator ($\lambda(K\alpha_1) = 0.70930$ Å); scan range = $0^\circ \leq 2\theta \leq 50^\circ$; reflections = 3660 with $I_0 \geq 2.5\sigma I_0$; (number of variables = 213) $R_f = 0.0406$, $R_w = 0.0501$.

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(10) For example: (a) Churchill, M. R.; Amoh, K. N.; Wasserman, H. *J. Inorg. Chem.* **1981**, *20*, 1609. (b) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1985**, *4*, 914. (c) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2277.

(11) (a) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437. (b) Mann, B. E.; Taylor, B. F. *¹³C NMR Data for Organometallic Compounds*; Academic: New York, 1981; references therein.

(12) We have chosen to label the unique carbonyl of the $\text{Cr}(\text{CO})_5$ an axial carbonyl even though it lies in the equatorial plane of the cluster.

(13) Davis, H. B.; Pomeroy, R. K., unpublished results.

(14) Adapted from Porterfield's text.²

(15) Ruff, J. K.; White, R. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 2159.

(16) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

Stone and co-workers have pointed out that the ^{13}C NMR spectra of $(\text{OC})_5\text{M}[\text{Rh}_2(\mu\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) are consistent with free rotation of the dirhodium fragment about an axis through the metal atom M and perpendicular to the Rh-Rh vector.¹⁷ This is, of course, equivalent to considering the rotation as that of the $\text{M}(\text{CO})_5$ unit about the Rh_2 moiety. That metal atoms and their associated ligands may freely rotate in cluster compounds may have general implications. For example, the observation that the carbonyls of each $\text{Os}(\text{CO})_3$ unit in $\text{Os}_6(\text{CO})_{18}$ (in solution at 100 °C) are equivalent but not equivalent to the carbonyls of the other chemically different $\text{Os}(\text{CO})_3$ units¹⁸ may be rationalized in this way.

When the temperature of the solution of **1** is raised above -122 °C there is immediate collapse of some of the NMR signals of A (but not B). The pattern of the coalescence of these signals is consistent with a partial equatorial merry-go-round CO exchange.¹⁹ Above -20 °C all the signals assigned to B collapse. This is consistent with terminal-bridge CO exchange in those two carbonyl-containing planes that are perpendicular to the CrOs_2 plane and do not contain a phosphine ligand. The latter exchange was observed in $\text{Os}_3(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2$ which also exists in solution as isomers analogous to A and B.^{11a} The exchange processes in **1** will be discussed in detail in a future publication.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and Simon Fraser University for financial support.

Supplementary Material Available: Tables of atomic coordinates, temperature factors, and bond lengths and angles for **1** (4 pages). Ordering information is given on any current masthead page.

(17) Barr, R. D.; Green, M.; Marsden, K.; Stone, F. G. A.; Woodward, P. J. *Chem. Soc., Dalton Trans.* 1983, 507. See, also: Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1983, 759.

(18) Eady, C. R.; Jackson, W. G.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Chem. Commun.* 1975, 958.

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The Nontetrahedral Structure and Fluxional Character of SiLi_4 . A Violation of Both van't Hoff and Electrostatic Bonding Principles^{†,1}

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Although SiLi_4 is comprised of only two main group elements, its structure is unprecedented. Simple eight valence electron AX_4 molecules not only are expected to prefer tetrahedral geometries but also to possess configurational stability.² If the A-X bonds are covalent, sp^3 hybridization is strongly favored. If the A-X bonds are ionic, e.g., as in $\text{A}^+(\text{X}^-)_4$, an electrostatic point charge model also dictates a tetrahedral geometry.³ The interactions

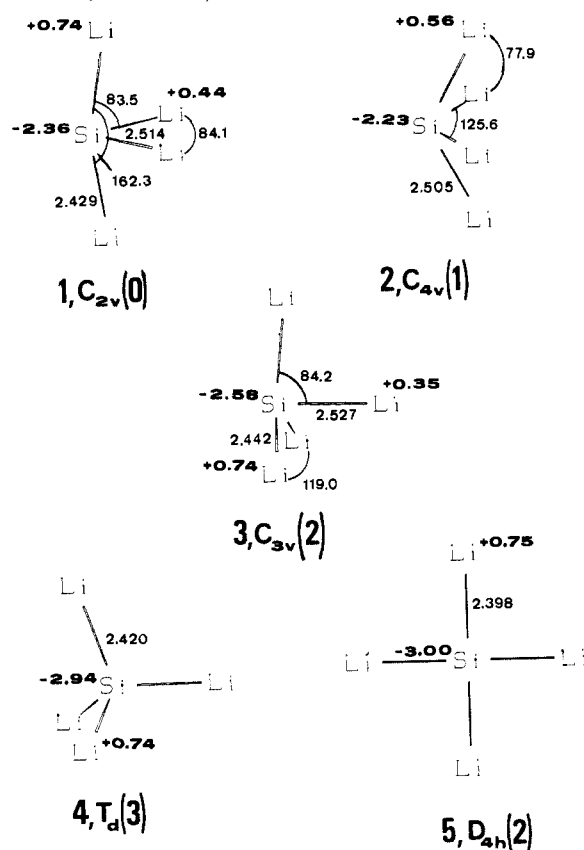
[†] This paper is dedicated to Professor Kurt Mislow on the occasion of his 65th birthday.

(1) Presented at the World Association of Theoretical Organic Chemistry (WATOC) Congress, Budapest, Hungary, August 1987.

(2) For discussions and leading references, see: (a) Pauling, L. *The Nature of the Chemical Bond*; Cornell: 1st ed.; 1938; 2nd ed.; 1948. (b) Gimarc, B. M. *Molecular Structure and Bonding*; Academic Press: New York, 1979; pp 50f, 59f. (c) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 148f, 295f. (d) Gillespie, R. J.; Nyholm, R. S., *Q. Rev. Chem. Soc.* 1957, 11, 339.

(3) See: (a) Bartell, L. S.; Barshad, Y. *J. Am. Chem. Soc.* 1984, 106, 7700. (b) Bartell, L. S. *Croat. Chim. Acta* 1984, 57, 927. (c) Sachs, L. *J. Chem. Ed.* 1986, 63, 288 and references cited. (d) For references to Bent, H. A.'s "tangent sphere model", see: Schultz, E. I. *Ibid.* 1986, 63, 961.

Scheme I. Optimized HF/3-21G(*) Geometries of SiLi_4 Species^a



^a Number of imaginary frequencies are in parenthesis. The natural atomic charges at HF/6-31G* are also given.

Table I. Relative Energies of SiLi_4 Isomers (kcal/mol)

level	1, C_{2v}	2, C_{4v}	3, C_{3v} inv	4, T_d	5, D_{4h}
3-21G//3-21G	0.0	3.8	1.5	2.2 ^a	7.2
3-21G(*)//3-21G(*)	0.0	3.7	2.1	3.7 ^a	7.3
6-31G*//3-21G(*)	0.0	3.1	1.8	3.6	8.3
MP2/6-31G*//3-21G(*)	0.0	3.3	3.3	6.6	11.4
ZPE	3.5 (3.6) ^c	3.4	3.1 (2.8) ^c	2.9 (2.9) ^c	3.4
MP2/6-31G* + ZPE ^b	0.0	3.2	2.9	6.1	11.3

^a Structures optimized with D_{2d} or C_{3v} (regular) symmetries deviate only slightly in geometry and have essentially the same energy as the T_d forms. ^b ZPE energies scaled by 0.9 (see ref 7). ^c ZPE's at 3-21G(*)

among the hydrogens in methane are known to be repulsive, as is generally the case among ligands in AX_4 systems.⁴ Through ab initio calculations, we have been discovering molecules with rule-breaking structures.⁵⁻⁷ While a number of these have been found to prefer anti van't Hoff⁵ geometries, none of these are as simple as SiLi_4 .⁸

(4) This is shown, e.g., by population analyses of various types. See ref 13 and 15.

(5) Schleyer, P. v. R. *Pure Appl. Chem.* 1983, 55, 355; 1984, 56, 151.

(6) (a) Krogh-Jespersen, K.; Cremer, D.; Poppinger, D.; Pople, J. A.; Schleyer, P. v. R.; Chandrasekhar, J. *J. Am. Chem. Soc.* 1979, 101, 4843. (b) Schleyer, P. v. R.; Clark, T. *J. Chem. Soc., Chem. Commun.* 1987, 1371.

(7) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(8) SiLi_4 has been synthesized by the gas-phase reaction of Li atoms with SiCl_4 (Morrison, J. A.; Lagow, R. *J. Inorg. Chem.* 1977, 16, 2972), but there has been no structural characterization of either the solid or the gas-phase material. Numerous other Si/Li stoichiometries are known experimentally see Wen et al., (Wen, C. J.; Huggins, R. A. *J. Solid State Chem.* 1981, 37, 271) and Dergochev et al. (Dergochev, Yu. M.; Elizarova, T. A.; Grechanaya, N. A. *Russ. J. Inorg. Chem. (Engl. Trans.)* 1982, 27, 1383) for references. For the crystal structure of Si_2Li_2 and discussions, see: von Schnering, H. G.; Nesper, R.; Curda, J.; Tebbe, K.-F. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 1033; *Angew. Chem.* 1980, 92, 1070. Liebman, J. F.; Vinant, J. S. *Angew. Chem. Int. Ed. Engl.* 1982, 21, 632; *Angew. Chem.* 1983, 94, 649. Both SiLi and Si_2Li_2 have been studied in the gas phase (Ihle, H. R.; Wu, C. H.; Miletic, M.; Zmbov, K. F. *Adv. Mass. Spectrosc.* 1978, 7A, 670).