Stone and co-workers have pointed out that the $^{13}C$ NMR spectra of $(OC)_5M[Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_2]$ (M = Cr, Mo, 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 $M(CO)_5$ 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 $Os(CO)_3$ unit in $Os_6(CO)_{18}$ (in solution at 100 °C) are equivalent but not equivalent to the carbonyls of the other chemically different $Os(CO)_3$ units[18] 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 $Os_3(CO)_{10}[P(OMe)_3]_2$ 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.

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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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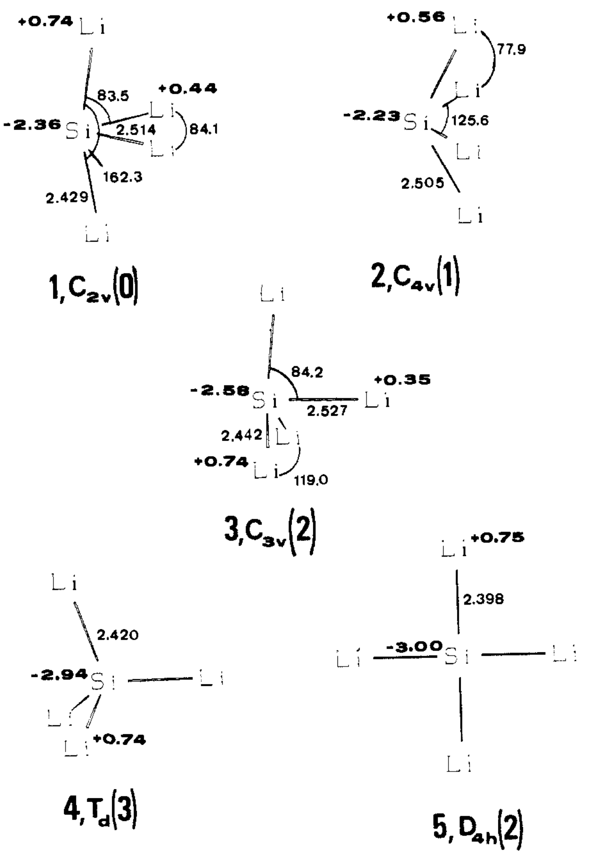
Although $SiLi_4$ is comprised of only two main group elements, its structure is unprecedented. Simple eight valence electron $AX_4$ molecules not only are expected to prefer tetrahedral geometries but also to possess configurational stability.[2] If the A–X bonds are covalent, $sp^3$ hybridization is strongly favored. If the A–X bonds are ionic, e.g., as in $A^{4-}(X^+)_4$, an electrostatic point charge model also dictates a tetrahedral geometry.[3] The interactions 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 Hoff[5] geometries, none of these are as simple as $SiLi_4$.[8]

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(*).

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[†] 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.

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

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(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 $Si_7Li_{12}$ 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).

**Table II.** Absolute Energies of $SiLi_4$ Isomers (–au)

| species | point group | 3-21G//3-21G | ZPE[a] | 3-21G(*)//3-21G(*) | ZPE[a] | 6-31G*//3-21G* HF/ | 6-31G*//3-21G* MP2/ |
|---|---|---|---|---|---|---|---|
| $SiLi_4$ **1** | $C_{2v}$ | 316.991 66 (0) | 3.49 | 317.041 46 (0) | 3.56 | 318.670 89 | 318.826 34 |
| **2** | $C_{4v}$ | 316.985 63 (1) | 3.39 | 317.035 54 | | 318.665 98 | 318.821 02 |
| **3** | $C_{3v}$ inv | 316.989 19 (0) | 3.14 | 317.038 15 (2) | 3.11 | 318.667 96 | 318.821 08 |
| **4** | $T_d$ | 316.988 18 (3) | 2.88 | 317.035 55[b] (3) | 2.86 | 318.665 23 | 318.815 87 |
| **5** | $D_{4h}$ | 316.980 18[b] (2) | 3.35 | 317.028 16[b] | | 318.657 59 | 318.809 20 |
| triplets | $C_{2v}$ | 316.964 21 | | | | | |
| (UHF) | $D_{4h}$ | | | 317.015 04 | | | |
| $SiLi_3$, $1\pi$ | $D_{3h}$ UHF | 309.576 33[b] (0) | 2.04 | 309.624 83[b] | | 311.206 88 | 311.315 76 |
| Li | | 7.381 51 | | 7.381 51 | | 7.431 37 | 7.431 37 |

[a] Zero-point energies in kcal/mol (unscaled). [b] *The Carnegie-Mellon Quantum Chemistry Archive*; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds., 3rd ed.; Carnegie-Mellon University: 1983. [c] Frequencies in $cm^{-1}$ 107.5 ($b_1$), 110.5 ($a_1$), 160.3 ($a_1$), 200.0 ($b_1$), 204.7 ($a_2$), 390.1 ($a_1$), 400.8 ($b_2$), 421.0 ($a_1$), and 492.0 ($b_1$).

Geometry optimizations and frequency calculations on a number of $SiLi_4$ structures (**1–5**; Scheme I) were carried by using the GAUSSIAN 82 program[7] with the 3-21G and 3-21G(*) basis sets. Geometries at the latter level are given in Scheme I, where the number of imaginary frequencies for each stationary point is given in parentheses. The single point MP2/6-31G*//3-21G(*) energies were corrected for zero-point energy differences to yield the "final" relative energies in Table I.[9] As seen from this table, the relative energies are rather insensitive to the level of theory, except that the $T_d$ and $D_{4h}$ structures are even less favored at the correlated MP2 level. Nevertheless, the entire $SiLi_4$ potential energy surface (PES) lies within an energy bound of only 12 kcal/mol. The triplet PES was not examined as extensively, as this is indicated to be of higher energy (even at the SCF level) than the singlet. At UMP2/6-31G*//3-21G(*) + ZPE, **1** is bound by 48.2 kcal/mol relative to Li and $SiLi_3$ ($D_{3h}$) and by 64 kcal/mol relative to $Li_2$ and $SiLi_2$ (linear triplet).

*Remarkably*, *$SiLi_4$ is not tetrahedral*; the $T_d$ structure **4** has *three* degenerate imaginary frequencies (46i $cm^{-1}$ at 3-21G(*)). At 3-21G(*), **1** ($C_{2v}$) is the only minimum located on the PES. The axial and equatorial lithiums in **1** can interchange through a $C_{4v}$ transition structure, **2**, which is only 3.2 kcal/mol higher in energy. The potential energy surface around **3**, lying 2.9 kcal/mol above **1**, is quite flat. Hence by involving **2** and structures closely related to **3**, all the lithiums in $SiLi_4$ can change places in all possible configurations with activation energies of only a few kcal/mol. This is the first eight valence electron $AX_4$ molecule predicted to be fluxional.

Unusual chemical bonding in $SiLi_4$ is responsible for this behavior. The natural charges (by natural population analysis[10]) on Si, more negative than –2 in all forms of $SiLi_4$, reveal that the bonds are partially ionic. In addition, natural bond orbital (NBO) analysis[11] indicates the presence of a high occupancy (1.90–1.93e) Si lone pair of 90% s-character in structures **1–3**. These essentially doubly occupied Si 3s orbitals are inactive[12] with respect to Si–Li covalent bonding, which involves only the Si 3p orbitals. This is consistent with the greater radial extension of 3p than 3s orbitals.[13] By contrast, 2s and 2p orbitals have similar radial extensions,[13] and a tetrahedral geometry is favored for $CLi_4$.[14] NBO analysis of the $C_{2v}$ form indicates two two-center-two-electron $Si–Li_{eq}$ bonds and a three-center-two-electron $Li_{ax}–Si–Li_{ax}$ bond. These three bonds delocalize strongly into the low-lying, low-occupancy 2s (and 2p) orbitals of other lithium atoms, leading to attractive Li–Li interactions[15] and the inward bending of the Li–Si–Li bond angles with respect to an ideal trigonal bipyramid (see Scheme I); this inward bending is greater than in the superficially analogous ten valence electron $C_{2v}$ species $SF_4$ and $SeF_4$.[2b,c]

The electronic structure of $SiLi_4$ will be discussed in more detail subsequently.

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(9) The RHF/3-21G(*) wave functions for all structures of $SiLi_4$ except **4** ($T_d$) were found to be unstable with respect to UHF (suggestion of a referee). Relaxation of the RHF/3-21G(*) wave function for **1** resulted in an energy decrease of 6.1 kcal/mol and strong spin contamination ($S^2$ = 0.93). However, when electron correlation is included (MP4SDTQ), the RHF reference state leads to an energy 10.0 kcal/mol *lower* than the UHF "state" (9.7 kcal/mol lower at MP2), due to the very strong spin polarization of the UHF function. Furthermore, UHF/3-21G(*) optimization does not lead to qualitative changes in the relative energies [in kcal/mol: 0.0 (**1**), 1.9 (**2**), 1.2 (**3**), 10.4 (**4**); **5** ($D_{4h}$) optimizes to **2**($C_{4v}$)] or in the geometries (the bond lengths are about 0.1 Å longer, but the Li–Si–Li angles are reduced; this gives a smaller **1**–**3** energy difference). MCSCF calculations (Prof. R. Janoschek, personal communication) show only two configurations to be important and **2** to be 3.5 kcal/mol higher in energy than **1**.

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(12) This is reminiscent of the "inert s-pair effect" see, e.g.: Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper & Row: New York, 1978; p 723. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 327.

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(15) The attractive/repulsive nature of the interactions was judged by bond orders based on NPA/NLMO analysis (ref 10 and 11). The Mulliken overlap populations led in all cases to the same conclusions.

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## Synthesis of Naphthalene-Bridged Porphyrin Dimers and Their Orientation-Dependent Exciton Coupling

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The recent X-ray analysis of a bacterial photosynthetic reaction center from Rhodopseudomonas viridis dramatically shows the critical arrangement of six interacting tetrapyrroles at the active site.[1] Since these results strongly suggest the importance of the interchromophore distance and orientation in the efficient charge separation, development of porphyrin aggregates having systematically changing geometries is highly desirable.

We now report the synthesis of naphthalene-bridged dimeric porphyrins (NDP) and the remarkable splitting of the Soret band, which depends on the spatial arrangement of the two porphyrin rings. Two porphyrin rings in NDP are rigidly held in a certain geometry by the combined steric restrictions of the naphthalene spacer and the flanking ethyl groups. Consequently, the naphthalene bridge remains perpendicular to the mean porphyrin plane,

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