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Reexamination of the Evidence for Silicon–Silicon Multiply Bonded Intermediates. Possible Existence of [F$_2$Si=SiF$_2$]?

Sir:

For more than 50 years, the chemical literature has seen periodic resurgences of the question, "Can and/or does silicon form multiple bonds with silicon, carbon, oxygen, nitrogen, sulfur, etc.?" The answer has never been unequivocally, "No", but even today there has not been a single substantiated report of the preparation and properties of a polyatomic molecule containing such a multiple bond. We are apparently at the height of another resurgence of interest in this question, and it is time to recall attention to the alternate explanations for most of the synthetic processes for which a multiple bond is sometimes invoked as a transient intermediate species and to cite pertinent data for the most conveniently studied divalent silicon species, the SiF$_2$ molecule.[1]

After reviewing reports postulating the existence of multiply bonded silicon intermediates with respect to silicon–nitrogen,[2,3] silicon–carbon,[4,5] and silicon–oxygen[6,7] linkages, we noted a number of similarities between these systems and previous work carried out in our laboratory involving SiF$_2$ which could be used to argue for the existence of >Si=Si< bonds. It is our purpose in this communication to bring out several points of prima facie evidence for the formation of diamagnetic or paramagnetic Si$_2$F$_4$ species from monomeric SiF$_2$ while at the same time pointing out plausible mechanisms for the reactions of these unique species; also, we shall enumerate several properties of SiF$_2$ which should be considered in the elucidation of its chemistry.

While many reactions of SiF$_2$ have been reported,[8] one reaction system which serves to illustrate the chemistry of this reactive carbene analogue with unsaturated organic molecules is that of SiF$_2$ with acetylene.[9] A proposed mechanism for the acetylene–SiF$_2$ reaction (modified from our original report[9]) is given in Scheme I. The major feature of the reaction mechanism is the formation of a free-radical species, [·(-SiF$_2$-)·]$_n$, directly from the singlet SiF$_2$ monomer, with the possibility of an F$_2$Si=SiF$_2$ intermediate species of transient existence. In such reactions, we always found at least two adjacent silicon atoms in the products (Table I) which would be in line with such intermediates.

Alternately, there is some experimental and theoretical evidence that can be used to support a diamagnetic, doubly bonded species such as Si$_2$F$_4$ in such reactions. This is given in the following sections.

(1) SiF$_2$, when first produced from the Si–SiF$_4$ reactant pair at 1200 °C, is diamagnetic. There is no mass spectrometric indication of (SiF$_2$)$_n$ polymer in the gas phase, but this could be fragmented on electron impact. Electron spin resonance studies performed by Hopkins et al.[10] have indicated the lack of any appreciable amount of paramagnetic species in the noncondensed gas-phase state. No signal could be detected when a gaseous SiF$_2$–SiF$_4$ mixture was passed through the ESR spectrometer cavity. Similarly, the argon matrix isolated SiF$_2$ yielded no signal in very dilute concentrations (such a low matrix concentration would simulate a pseudo-gas-phase environment); however, in more concentrated condensed matrix solutions, the SiF$_2$ molecules interact with one another and yield a strong ESR spectrum. Clearly, free-radical formation

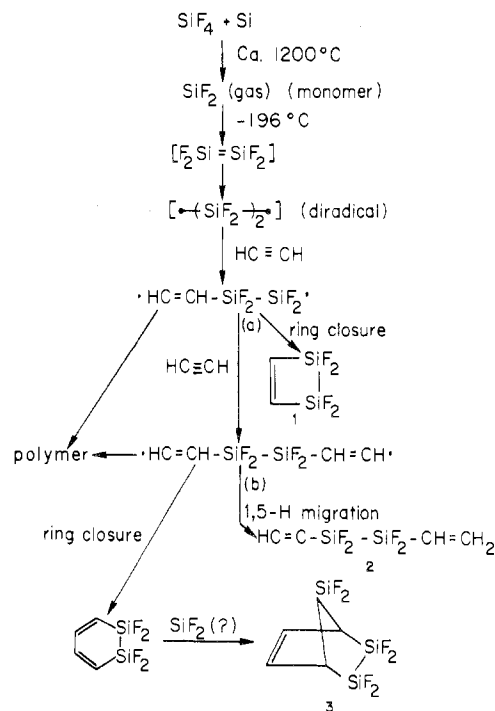**Scheme I.** Proposed Mechanism of the Reaction of SiF$_2$ with Acetylene

Table I. Products of the Reaction of SiF$_2$ with Acetylene and Alkyne Derivatives[a]

Reactant	Products(s)	Structure
HC≡CH	C$_2$H$_4$Si$_2$F$_4$	
	C$_4$H$_4$Si$_2$F$_4$	H$_2$C=CHSiF$_2$SiF$_2$C≡C–H
	C$_4$H$_4$Si$_3$F$_6$	
HC≡CCH$_3$	C$_6$H$_8$Si$_2$F$_4$	
HC≡CC-(CH$_3$)$_2$CH$_3$	C$_{12}$H$_{20}$Si$_2$-F$_4$[b]	(a) (b)

[a] Data are taken from ref 9 and also from Liu et al., *Can. J. Chem.*, **50**, 459 (1972). [b] The product consists of isomers a and b.

occurred only after condensation at low temperatures and not in the gas phase.

(2) Infrared matrix-isolation studies[8] of SiF$_2$ in dilute and

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in concentrated solutions show the simple features of a triatomic molecule and a complex spectrum typical of that expected for the (–SiF$_2$–) polymer, respectively. In dilute systems, one either has monomer or dimer since the activation energy for polymerization to form [·(–SiF$_2$–)·]$_n$. paramagnetic radicals is very low. Perfluoropolysilanes up to Si$_{14}$F$_{30}$ have been prepared by this approach.

(3) SiF$_2$ does not undergo appreciable gas-phase reaction,[8] in agreement with the proposed solid-state free-radical mechanism illustrated in Scheme I, since free radicals do not exist in a gas-phase situation (in agreement with the ESR studies described above).

(4) When SiF$_2$ polymerizes on a cold surface in the absence of a reactive trapping reagent, perfluoropolysilanes are formed as shown by mass spectral studies[11] and Raman spectroscopy[12] which indicates a backbone of Si–Si single bonds. This observed reaction completely parallels the polymerization of the hypothetical unsaturated species (CH$_3$)$_2$Si=CH$_2$ which has been reported.[13]

Several other features of SiF$_2$ chemistry should also be pointed out. Microwave studies[14] have shown the Si–F bond in SiF$_2$ to be longer than might be expected, e.g., 1.59 Å in SiF$_2$ as compared to 1.54 Å in SiF$_4$. Recent theoretical work[15] utilizing the CNDO/2 molecular orbital treatment suggests that elongation of the Si–F bond could be expected in multiply bonded silicon systems such as F$_2$Si=CF$_2$. Although the calculated Si–F bond distances (1.85 Å) seem abnormally high to us, the conclusions provide support for the existence of an intermediate such as [F$_2$Si=SiF$_2$]. Along this same line, Curtis[16] (via Hoffmann's EHMO theoretical approach) has predicted that silicon–silicon double bonds should be more stable than the silicon–carbon double bonds which are now being claimed in the literature.

We should also mention that the average bond dissociation energy in SiF$_2$ is higher than that of any other group 4 element for either MF$_2$ and MF$_4$ species.[17] Coupled with the longer Si–F bond length mentioned above, this would indicate that the hybridization of the silicon atomic orbitals is decidedly different from that of SiF$_4$, and this suggests some double-bond character for the Si–F bond as postulated by Pauling long ago.

Multiple bonds involving silicon clearly are present in various diatomic gaseous molecules like Si$_2$, SiC, SiO, SiS, SiN, etc. but not in their condensed phase analogues. There is also a report of a matrix-isolation spectrum[18] for the F$_2$Si=O molecule; logical structures for mass spectral fragmentation species like Si$_2$F$_4^+$ and SiC$_2^+$ could require multiple bonds for the silicon atoms.

Infrared data also provide evidence for the existence of Si=C bonds in the solid-state products formed by silicon difluoride interaction with organic trapping agents. An ab initio calculation predicted[19] the stretching vibration in H$_2$Si=CH$_2$ to be 1490 cm^{-1} while Barton et al.[20] have tentatively assigned a $\nu_{Si=C}$ value of 1407 cm^{-1}: such bands appear in the infrared spectrum of the C$_6$F$_5$SiF$_3$ complex[21] prepared in our laboratory, thus giving some credence to the double-bond character of silicon–carbon linkages in such compounds. The infrared spectrum of this compound also contains an absorption band at 1317 cm^{-1}, almost identical with the 1315-cm^{-1} value assigned to the coordinated Si=C bond by Sakurai and co-workers.[22]

In summary, there are plausible mechanistic and theoretical arguments which can be offered and an increasing volume of indirect experimental evidence for the existence of multiple bonds involving silicon in terms of stable polyatomic species like X$_2$Si=SiX$_2$, X$_2$Si=CX$_2$, or X$_2$Si=O which would necessitate the formation of π bonds. Nevertheless, we also wish to call attention to the absolute evidence for the existence of paramagnetic, diradical species like [·(–SiF$_2$–)·]$_n$ and the

Table II. Insertion Reactions of SiF$_2$ with Various Compounds[a]

| Reactant	A–B bond type	Product(s)
H$_2$O	O–H	HSiF$_2$OH
		HF$_2$SiOSiF$_2$H
H$_2$S	S–H	HSiF$_2$SH
		HSiF$_2$SiF$_2$SH
		Si$_2$F$_5$H
		SiF$_2$HSSH }minor products
		Si$_2$F$_4$HSSH
CF$_3$I	C–I	CF$_3$SiF$_2$I
		CF$_3$SiF$_2$SiF$_2$I
		SiF$_3$SiF$_2$I
		SiF$_3$SiF$_2$SiF$_2$I }lesser products
		SiF$_2$ISiF$_2$I
		SiF$_2$ISiF$_2$SiF$_2$I
C$_6$H$_5$F	C–F	C$_6$H$_5$SiF$_3$
C$_6$F$_6$	C–F	C$_6$F$_5$(SiF$_3$)
		C$_6$F$_4$(SiF$_3$)$_2$ (o, m, p)
		C$_6$F$_3$(SiF$_3$)$_3$
C$_2$F$_x$H$_{4-x}$	C–F	C$_2$(SiF$_3$)$_x$H$_{4-x}$ (for x = 1–4)
GeH$_4$[b]	Ge–H	GeH$_3$SiF$_2$H
		GeH$_3$SiF$_2$SiF$_2$H
		GeH$_3$Si$_3$F$_6$H

[a] Data are taken from ref 8 and other references cited therein.
[b] D. Solan and P. L. Timms, *Inorg. Chem.,* 7, 2157 (1968).

established chemistry of the products of interaction between such diradicals and various unsaturated organic molecules. Furthermore, there are several examples of cyclic polymers of F$_2$Si=O, including the four-membered ring
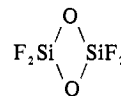
and the six-membered ring
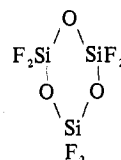
etc., that have been detected by mass spectral studies and by infrared/NMR procedures.[18a] There also are SiF$_2$ reactions which seem to proceed through the diamagnetic monomer to form a three-membered metastable ring, followed by a rearrangement step, which essentially results in SiF$_2$ insertion into an A–B bond (see Table II). Obviously, divalent silicon species are interesting, reactive entities which fully exploit the possible alternatives for chemical reactions.

Registry No. Si$_2$F$_4$, 62107-71-5; SiF$_2$, 13966-66-0.

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A Graph-Theoretical Interpretation of Stereochemically Nonrigid Coordination Structures

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Sir:

In 1956 Günthard and Primas[1] demonstrated the connection between graph theory and MO theory in the Hückel treatment of conjugated systems. Subsequently Schmidtke[2,3] showed that similar graph-theoretical methods could also be used for the LCAO treatment of directed valency in ML_n complexes. This communication shows how an extension of Schmidtke's methods can immediately provide information on the stereochemical nonrigidity of certain ML_n structures. Such information is not accessible from the standard treatment[4] of directed valency based solely on the hybridization of atomic orbitals.

Schmidtke has shown[2,3] that the usual secular equation $|H - ES| = 0$ can be converted to the equation $|A - \rho I| = 0$ where A is the adjacency matrix[5–9] of the graph representing the nearest-neighbor interactions, ρ corresponds to the usual Hückel numbers for the energy eigenvalues by the relationship $E = (\alpha + \rho\beta)/(1 + \rho S)$, and I is the unit matrix. For ML_n complexes we therefore consider first the ligands L and introduce a graph representing nearest-neighbor repulsive interactions. The spectrum of this graph,[5–9] which corresponds to the ρ values in the solution of $|A - \rho I| = 0$, is now used to determine the resulting energy levels of the set L_n of the n interacting ligands L.

In the LCAO treatment of ML_n complexes the energy levels of the set L_n must be matched with the relative energy levels of the bonding atomic orbitals of the central atom M. The n M–L bonds arise from linear combinations of the type $\psi = \phi_L + \phi_M$ where the ϕ_L have the energy levels of the set L_n and the ϕ_M have the energy levels of the atomic orbitals of M. The energies of these bonds are minimized if ϕ_L and ϕ_M have the same energies. For this reason favorable coordination graphs of ML_n structures which represent relatively deep minima of energy hypersurfaces will be those in which the energy levels of the spectra of the graphs from the L_n set match those of the available bonding orbitals of M. Mismatch of the spectra of the L_n graphs with the energy levels of the bonding orbitals of M will lead to a relatively flat energy hypersurface. Such a relatively flat energy hypersurface will have shallow minima and a low activation energy for the interconversion of
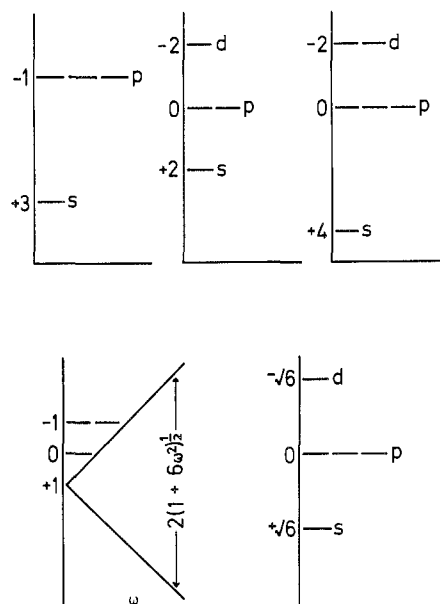
Figure 1. Eigenvalue patterns of the various graphs used to represent coordination structures: (a) the tetrahedron; (b) the square; (c) the octahedron; (d) the trigonal bipyramid, where ω represents the interactions of the apical–equatorial edges relative to the equatorial–equatorial edges; (e) the bipartite graph $K_{2,3}$.

equivalent structures thereby leading to stereochemical nonrigidity.

The coordination numbers of 4 and 6 are known to lead to stereochemically rigid structures. We start by illustrating our method for these structures. The spectrum of the K_4 graph,[9] i.e., that of the tetrahedron (Figure 1a), has one eigenvalue at +3 and three degenerate eigenvalues at –1. These four eigenvalues correspond respectively to the energies of the one s and three p atomic orbitals of M. Thus the tetrahedron will be the stereochemically rigid[10] graph for coordination number 4 in the usual cases where all three p orbitals of M can participate in the M–L bonding. Similarly, the eigenvalues of the C_4 graph,[9] i.e., that of the square (Figure 1b), are +2, 0, 0, and –2 corresponding, respectively, to one s orbital, two p orbitals, and one d orbital of M. The square will thus be the graph for systems where only two of the p orbitals of M are available for bonding to the ligands. The H_3 graph of the octahedron has eigenvalues of +4, 0, 0, 0, –2, and –2 (Figure 1c) corresponding directly to the single s orbital, the three p orbitals, and the two d orbitals of M involved in octahedral bonding. This is consistent with the occurrence of the octahedron as the usual and stereochemically rigid[10] graph for coordination number 6. In all of these four- and six-coordinate systems, the graph for the coordination is thus identical with the coordination polyhedron usually considered.

The situation changes drastically, however, when the coordination number 5 is considered. In order to match the energies of the sp^3d hybrids used in this coordination a five-vertex graph is required having only three distinct eigenvalues, where the lowest and highest eigenvalues are unique and the middle one is triply degenerate; i.e., a 1, 3, 1 eigenvalue pattern is required. The five eigenvalues of the Π_3 graph, i.e. that of the trigonal bipyramid, are $1 \pm (1 - 6\omega^2)^{1/2}$, 0, –1, and –1, where ω is a weighting factor for the equatorial–equatorial and equatorial–axial interactions. As illustrated schematically in Figure 1d, there are no reasonable values of ω giving the desired 1, 3, 1 eigenvalue pattern. Similarly the eigenvalues of the W_4 graph, i.e., that of the square pyramid, are $1 \pm (1 - 4\omega^2)^{1/2}$, 0, 0, and –2, where ω is again a weighting factor for the basal–basal and apical–basal interactions. The desired 1, 3, 1 pattern can be attained for the square pyramid only