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Charge Transfers and Polarizations in Bonds to Silicon. Organosilanes and the $S_N2(Si)$ Reaction of $SiH_4 + F^-$. An ab Initio Study

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Abstract: The charge transfers in the bonds between silicon and common nonmetals (X = H, C, O, and F) are reported in terms of Streitwieser and Collin's integrated projection populations (IPP), Reed, Weinhold, and Weinstock's natural populations (NP), and Mulliken populations (MP). The IPP integrated populations are calibrated by several comparisons with populations integrated by the Bader method (IBP) to which they approximate. The integrated populations indicate large charge transfers (0.65–0.92 e) that result in bond moments oriented in the fashion (+)Si–X(−) and emphasize the importance of ionic contributions to common bonds involving silicon. As an example system, the reaction of SiH_4 and F^- to form the ion complex SiH_4F^- is analyzed with emphasis on an ionic model. Two trigonal bipyramid minima (apical (1) and equatorial (2) fluorine) were optimized at the 3-21+G* level. The $S_N2(Si)$ reaction to give SiH_3F and H^- through the intermediate ion complex, 1, is examined with IPP analysis and energy calculations up to the MP2/6-31+G**//HF/3-21+G* level. The stability of pentacoordinate silicon with respect to carbon is discussed in terms of the bond charge distributions.

The formation and cleavage of bonds to silicon have become increasingly important in synthetic organic chemistry.[1] This developing use of silicon reactions has been matched by an increasing interest in the nature of bonds to silicon. Of especial interest is the recent suggestion from structural studies that Si~F bonds are highly ionic and that (p–d)π bonding plays no important role.[2] A number of theoretical studies are now available for silicon compounds but these have mostly focused on structure and energy relationships rather than the nature of the bonding.[3–9] Bonds

to silicon have generally been considered to be rather polar;[10] since silicon is relatively electropositive, its bonds to substituents other than metals are polarized in the fashion (+)Si–X(−). Theoretical electron density analysis can provide a more accurate picture of such polarization and, indeed, a few recent studies of integrated electron density functions have shown that the Si–H bond is much more polar than had been thought.[11–13] As a complement to these

(1) For some sample reviews, see: (a) Negishi, E.-I. *Organometallics in Organic Synthesis*; Wiley: New York, 1980. (b) Paquette, L. A. *Science* 1982, 217, 793–800. (c) Chvalovsky, V.; Bellama, J. M. *Carbon-Functional Organosilicon Compounds*; Plenum: New York, 1984.

(2) Rempfer, B.; Oberhammer, H.; Auner, N. *J. Am. Chem. Soc.* 1986, 108, 3893–7. This conclusion was also applied to Si–O bonds by ab initio calculations: Oberhammer, H.; Boggs, J. E. *J. Am. Chem. Soc.* 1980, 102, 7241–4; but for a contrary view, see: Janes, N.; Oldfield, E. *J. Am. Chem. Soc.* 1986, 108, 5743–53.

(3) (a) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1986, 108, 260. (b) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1986, 108, 270.

(4) (a) Sheldon, J. C.; Hayes, R. N.; Bowie, J. H. *J. Am. Chem. Soc.* 1984, 106, 7711. (b) Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* 1981, 34, 519.

(5) (a) Gordon, M. S.; Davis, L. P.; Burggraf, L. W.; Damrauer, R. *J. Am. Chem. Soc.* 1986, 108, 7889. (b) Davis, L. P.; Burggraf, L. W.; Gordon, M. S.; Baldridge, K. K. *J. Am. Chem. Soc.* 1985, 107, 4415.

(6) Keil, F.; Ahlrichs, R. *J. Am. Chem. Soc.* 1976, 98, 4787.

(7) Baybutt, P. *Mol. Phys.* 1975, 29, 389.

(8) Vitkovskaya, N. M.; Mantsivoda, V. B.; Moskovskaya, T. E.; Voronkov, M. G. *Int. J. Quantum Chem.* 1980, 17, 299.

(9) (a) Kuznesof, P. M. *Inorg. Chim. Acta* 1975, 15, L13. (b) Bunnell, J.; Crafford, B. C.; Ford, T. A. *J. Mol. Struct.* 1980, 61, 383. (c) Komornicki, A. *J. Am. Chem. Soc.* 1984, 106, 3114. (d) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* 1981, 46, 998.

(10) Altshuller, A. P.; Rosenblum, L. *J. Am. Chem. Soc.* 1954, 77, 272.

studies the first part of this ab initio study concentrates on the charge distribution in some simple silanes.

The polar nature of bonds to silicon is also important in characterizing the reactions of silanes. For example, the strength of highly polar silicon bonds is exploited synthetically in the removal of silyl protecting groups by fluoride anion and in the elimination reactions of β-silylated alcohols.[1] To complete this study, a simple reaction system is examined to see how the reactivity of silanes can be understood by the charge distributions of the bonds. Using ab initio methods, we studied the energy surface of the ion complex, SiH_4F^-, with respect to fluoride attack on the silicon of SiH_4. MNDO and high-level ab initio calculations on this and related systems have been published recently and can be compared as regards energy and geometry.[4,5] The addition product is the intermediate in the $S_N2(Si)$ reaction of silane with fluoride to give fluorosilane and hydride. The $S_N2(Si)$ process has been compared often to the analogous carbon-centered process because one goes through a pentacoordinate intermediate (silicon) and the other through a pentacoordinate transition state (carbon).[6-8,14-18] Consequently, the SiH_4F^- system allows the study of the differences in behavior of silicon and carbon centers in the S_N2 process with an analysis based on the charge distributions of the bonds.

Calculations

Optimizations and single-point calculations were performed on a VAX 11/750 with either the GAUSSIAN 80[19] or GAUSSIAN 82[20] quantum mechanical program. All structures were fully optimized with the appropriate symmetry constraints as noted. A number of basis sets were employed, but all are based on Pople's 3-21G or 6-31G* basis sets.[21] As needed, diffuse and polarization functions were added to the basis sets.[22] Wave functions were converted to planar projection functions with the program PROJ.[23] Molecular fragments were demarked with a program designed to find relative minima in the projection function, and integration
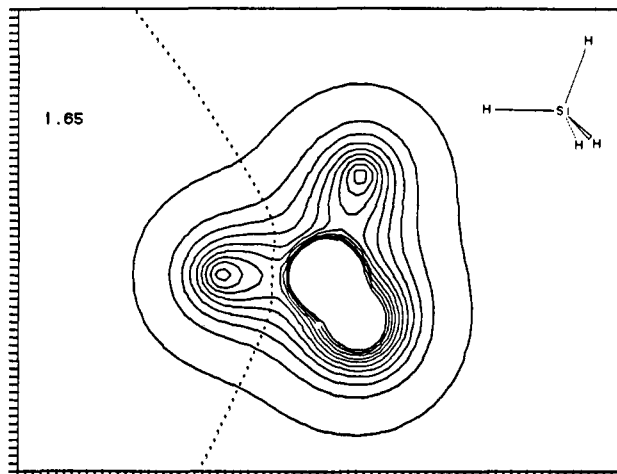

Figure 1. Contour representation of the projection function for silane at the 3-21G* level. Contours from 0.01 to 0.51 with a gradient of 0.05 e au^{-2}. Dotted lines demark regions integrated for IPP analysis.

of the area within the line of demarkation is referred to as the integrated projection population (IPP). Details of this procedure have been presented in previous publications.[24] Natural populations were calculated by using Reed, Weinstock, and Weinhold's supplement to GAUSSIAN 82.[25]

Results and Discussion

Atomic Populations of Substituted Silanes. In order to study charge distributions in bonds to silicon, we examined the atomic populations of several substituted silanes. The atomic population gives a quantification of the charge transfer and an indication of the ionic contribution to the bond. A number of techniques are available for this type of analysis and three were considered: Mulliken populations (MP),[26] Weinstock, Weinhold, and Reed's natural populations (NP),[25] and the integrated projection populations (IPP) regularly employed by this group.[23,24,27] The deficiencies and basis set dependencies of Mulliken populations have been reported in the past, and these populations are only presented for comparison.[28] The natural populations are relatively new and their utility has yet to be fully tested; however, it appears that they are less basis set dependent than Mulliken populations.[22c,25] The NP values are presented here, in part, to provide a further test of their utility.

IPP values are approximations to the populations of Bader's ATOMS (atoms topologically observed in molecules).[29] Bader has shown that such ATOMS defined by the zero-flux surface of electron density have important properties, including the application of the virial theorem.[30] Integrations of the electron density function within the zero-flux boundaries give an atomic

(11) Wiberg, K. B.; Wendoloski, J. J. *J. Phys. Chem.* **1984**, *88*, 586–93.

(12) MacDougall, P. J.; Bader, R. F. W. *Can. J. Chem.* **1986**, *64*, 1496–508.

(13) Bader, R. F. W.; Larouche, A.; Gatti, C.; Carroll, M. T.; MacDougall, P. J.; Wiberg, K. B. *J. Chem. Phys.* **1987**, *87*, 1142–52.

(14) Dewar, M. J. S.; Healy, E. *Organometallics* **1982**, *1*, 1705.

(15) Carrion, F.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 3531.

(16) Bader, R. F. W.; Duke, A. J.; Messer, R. R. *J. Am. Chem. Soc.* **1973**, *95*, 7715–22.

(17) Dedieu, A.; Veillard, A. *J. Am. Chem. Soc.* **1972**, *94*, 6730.

(18) (a) Mitchell, D. J.; Schlegel, H. B.; Shaik, S. S.; Wolfe, S. *Can. J. Chem.* **1985**, *63*, 1642. (b) Kost, D.; Aviram, K. *J. Am. Chem. Soc.* **1986**, *108*, 2006. (c) Ishida, K.; Morokuma, K.; Komornicki, A. *J. Chem. Phys.* **1977**, *66*, 2153. (d) Lowe, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 60. (e) Simons, G.; Talaty, R. *Chem. Phys. Lett.* **1978**, *56*, 554. (f) Dougherty, R. C.; Dalton, J.; Roberts, J. D. *Org. Mass Spectrom.* **1974**, *8*, 77. (g) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7692. (h) Chandrasekhar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 3049. (i) Talaty, E. R.; Woods, J. J.; Simons, G. *Aust. J. Chem.* **1979**, *32*, 2289. (j) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *Can. J. Chem.* **1982**, *60*, 1291. (k) Yamabe, S.; Yamabe, E.; Minato, T. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1881. (1) Serre, J. *Int. J. Quantum Chem.* **1984**, *26*, 593.

(19) Singh, U. C.; Kollman, P. *QCPE* **1982**, *2*, 17.

(20) GAUSSIAN 82, Release A. Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachavi, K.; Whitesides, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon University, 1983.

(21) (a) 3-21G: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (b) 6-31G*: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *62*, 2921. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(22) (a) Diffuse functions: Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. See also: Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363. The following diffuse function exponents were used: H, 0.036; Si, 0.0331; F, 0.1076. (b) Polarization functions: Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. The polarization exponents employed on the 3-21G* basis set are as follows: C, 0.80; O, 0.80; F, 0.80; Si, 0.45. (c) For an excellent summary of these basis sets, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; Section 4.3.

(23) Collins, J. B.; Streitwieser, A., Jr. *J. Comput. Chem.* **1980**, *1*, 81.

(24) McDowell, R. S.; Grier, D. L.; Streitwieser, A., Jr. *J. Comput. Chem.* **1985**, *9*, 165.

(25) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1986**, *108*, 3586. Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 1919. We thank Professor Weinhold and Dr. Reed for providing a copy of their program before its publication.

(26) Mulliken, R. B. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343.

(27) Some recent examples are: Bachrach, S. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 1186–90. McDowell, R. S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5849–55. Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 3946–51. McDowell, R. S.; Streitwieser, A., Jr. *J. Mol. Struct. (Theochem)* **1986**, *138*, 89–95. Kaufmann, Elmar; Schleyer, Paul von Rague; Gronert, Scott; Streitwieser, Andrew, Jr.; Halpern, Mitchell *J. Am. Chem. Soc.* **1987**, *109*, 2553–9. Streitwieser, A., Jr.; Rajca, A.; McDowell, R. S.; Glaser, R. *J. Am. Chem. Soc.* **1987**, *109*, 4184–8. Rajca, A.; Rice, J. E.; Streitwieser, A., Jr.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 4189–92. Streitwieser, A., Jr.; McDowell, R. S.; Glaser, R. *J. Comput. Chem.* **1987**, *8*, 788–93.

(28) (a) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283. (b) Bachrach, S. M.; Streitwieser, A., Jr. *J. Comput. Chem.*, in press.

(29) Bader, R. F. W., personal communication.

(30) The method has been summarized in recent papers: Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63. Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9–15.

population that we refer to as the "integrated Bader population" or IBP. These populations are based on a physical observable, the electron density function, are precisely defined, and have been used recently in a number of studies of electronic structure.[11-13,31] IPP values are derived from a partitioning of the projection function (integration of the molecular density from $-\infty$ to $+\infty$ along a single axis to give a planar representation) rather than the three-dimensional wave function. This approximation of the Bader technique leads to demarkation lines that represent vertical curtains rather than the curved demarkation surfaces defined by Bader. The resulting differences between IPP and IBP can be significant when the demarkation surfaces involve regions of high electron density as in a carbonyl group[28b] but they are less important where the density is low along the line of demarkation as in the present bonds to silicon. In particular, a comparison of several IPP values with the corresponding IBP integrations shows sufficient agreement for the present interpretations of silicon compounds. The projected integrations are faster to compute and can therefore be useful especially for such qualitative interpretations. Moreover, the projected densities lend themselves well to graphical representation.[31h]

The integrated populations will be discussed in the text; the values for the other population methods are reported and will be discussed at the end of the population section. For all of the substituted silanes, 3-21G basis sets with polarization functions on silicon and all first-row centers (3-21G*) were used for the optimizations and wave functions.

Silane. A contour plot of the projection function for silane is given in Figure 1 along with the line of demarkation. It is important to note that the line passes through a region of relatively low density and a well-defined valley of minimum density is present between the silicon and hydrogen. These features are observed in all of the bonds to silicon and are important in determining the reliability of the population analysis. The projection demarkation method cannot be applied to most C-H bonds because the electron density at the critical point (point of lowest density on the bond path between the nuclei)[30] is too high; the value of the electron density ρ at the critical point of a C-H bond is 0.268 au compared to 0.119 au for a Si-H bond.[13] The IPP value for the hydrogens in silane is 1.65 au (Table II), giving a formal charge of −0.65 per hydrogen. For comparison, the IBP is 1.765 at 3-21G(*) (d functions on Si only)[32] and 1.721 at 6-31G**.[11] An analysis[33] of the difference caused by the vertical curtain demarkation surface of IPP compared to the curved surface of IBP points out that IPP will underestimate the population of the more electronegative atom and will tend to give charge-transfer values that are smaller than the IBP values. This generalization is borne out by the Si-H results; nevertheless, it is clear even by the IPP value that the Si-H bond is highly polarized toward hydrogen and contains a significant ionic contribution. Although highly polar, the bond is still not an "ionic bond" since the electron density at the bond critical point is significantly greater than the values of about 0.05 au typical of more ionic bonds as in lithium compounds. This result of hydride-like character persists in other compounds. Bader and Messer[35] found IBP hydrogen values for

(31) Some recent examples are: (a) Bader, R. F. W.; Wiberg, K. B.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985. (b) Ibid. **1987**, *109*, 1001. (c) Bader, R. F. W. *Can. J. Chem.* **1986**, *64*, 1036-45. (d) Tang, T. H.; Bader, R. F. W.; MacDougall, P. J. *Inorg. Chem.* **1985**, *24*, 2047-53. (e) Bachrach, S. M. *J. Am. Chem. Soc.* **1986**, *108*, 6406. (f) Ritchie, J. R.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909. (g) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935. (h) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 1872. (i) Siggel, M. R. F.; Streitwieser, A.; Thomas, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 8022.

(32) We thank Andrzej Rajca and Peng Wang for these calculations using Bader's program (Biegler-Koenig, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317). We are indebted to Professor Bader for a copy of his program.

(33) Glaser, R. *J. Comput. Chem.* **1989**, *10*, 118.

(34) For a discussion of the use of such electron densities at the bond critical point as a necessary but not sufficient condition for covalency, see: Streitwieser, A., Jr.; Grier, D. L.; Kohler, B. A. B.; Vorpagel, E. R.; Schriver, G. W. *Electron Distributions and the Chemical Bond*; Coppens, P., Hall, M., Eds.; Plenum: New York, 1982.

(35) Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1974**, *52*, 2268.

Table I. Geometries Used for Substituted Silanes (3-21G*)[a]

compd	symmetry	bond length, Å		angle, deg	
SiH$_4$	T_d	Si-H	1.475[c]		
SiH$_3$CH$_3$[b]	C_{3v}	Si-H	1.478	H-Si-C	110.6
		C-H	1.089	H-C-Si	111.1
		Si-C	1.888		
SiH$_2$CH$_2$	C_{2v}	Si-H	1.467	H-Si-C	122.9
		C-H	1.079	H-C-Si	122.5
		Si-C	1.694		
SiH$_3$F	C_{3v}	Si-H	1.471	H-Si-F	109.6
		Si-F	1.568		
SiH$_3$OCH$_3$[b]	C_s	Si-H	1.461 (1.471)	H-Si-O	107.7 (111.9)
		C-H	1.091 (1.088)	H-C-O	112.5 (109.1)
		Si-O	1.633	Si-O-C	127.4
		C-O	1.412		
SiH$_3^+$	D_{3h}	Si-H	1.452		
SiH$_3^-$	C_{3v}	Si-H	1.535	H-Si-H	96.4

[a] Diffuse functions added to hydrogens and silicon in SiH$_3^-$. [b] Optimized in staggered conformation. The first value refers to the unique hydrogen. We thank S. M. Bachrach for the calculation on SiH$_3$OCH$_3$. [c] Optimized at 6-31G*; see: Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. Other summaries of geometries may be found in ref 22c, Chapter 6, and in: Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M. B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, Paul v. R. *J. Am. Chem. Soc.* **1986**, *108*, 260-9.

Table II. Atomic Populations in Substituted Silanes[a]

compd	atom or group	MP[b]	NP[c]	IPP[d]
SiH$_4$	Si	13.48	13.12	11.40
	H	1.13	1.22	1.65
SiH$_3$CH$_3$	Si	13.29	12.85	11.34
	CH$_3$	9.28	9.43	9.68
	H (SiH$_3$)	1.14	1.24	1.66
SiH$_2$CH$_2$	Si	13.47	12.93	11.54
	CH$_2$	8.32	8.64	9.04
	H (SiH$_2$)	1.10	1.22	1.71
SiH$_3$F	Si	13.00	12.50	10.98
	F	9.48	9.61	9.92
	H	1.17	1.29	1.70
SiH$_3$OCH$_3$	Si	13.08	12.56	11.08
	CH$_3$O	17.40	17.59	17.85
	H (SiH$_3$)[e]	1.16	1.27	1.69
SiH$_3^+$	Si	13.05	12.44	11.25
	H	0.98	1.18	1.58
SiH$_3^-$	Si	13.97	14.16	12.90
	H	1.34	1.28	1.70

[a] Wave functions and geometries obtained at levels given in Table I. [b] Mulliken population analysis; see ref 26. [c] Natural population analysis; see ref 25. [d] Integrated projection population analysis; see ref 23 and 24. [e] Values for hydrogen in C_s plane are given.

the diatomic SiH molecule as an anion, a neutral, and a cation of 1.91, 1.80, and 1.67 au (electrons), respectively. Although SiH is quite different from SiH$_4$, the hydrogen populations found are of comparably high magnitude in both systems. A similar result was found for SiH$_2$ with its IBP hydrogen charge of −0.754.[12]

The polarization of the Si-H bond is consistent with electronegativity differences and experimental bond moments, but the extent of the polarization may not have been fully appreciated. The predicted ionic character should lead to some hydride-like properties for silanes, and indeed, there is experimental evidence for silanes acting as hydride donors. Silanes may be used in solution to reduce various trityl halides to the corresponding triphenylmethanes[36] and in both solution and gas phase to reduce alkyl cations.[37-39] Furthermore, olefins may be hydrosilylated by various silanes with an appropriate metal catalyst.[40]

(36) Corey, J. Y.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 2430.

(37) Carey, F. A.; Hsu, C.-L. W. *J. Organomet. Chem.* **1969**, *19*, 29.

(38) Chojnowski, J.; Wilczek, L.; Fortniak, W. *J. Organomet. Chem.* **1977**, *135*, 13.

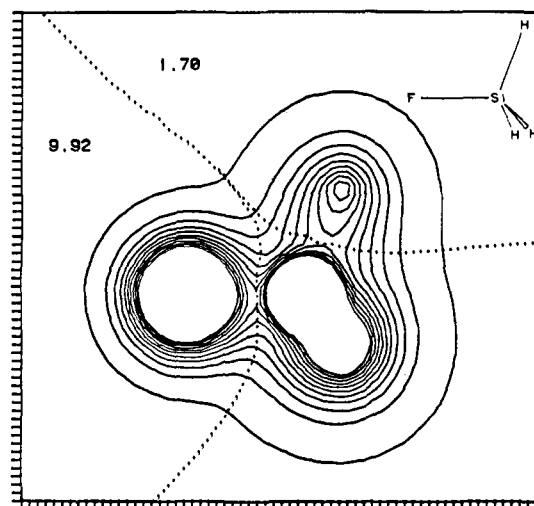(39) Goodloe, G. W.; Lampe, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 6028.
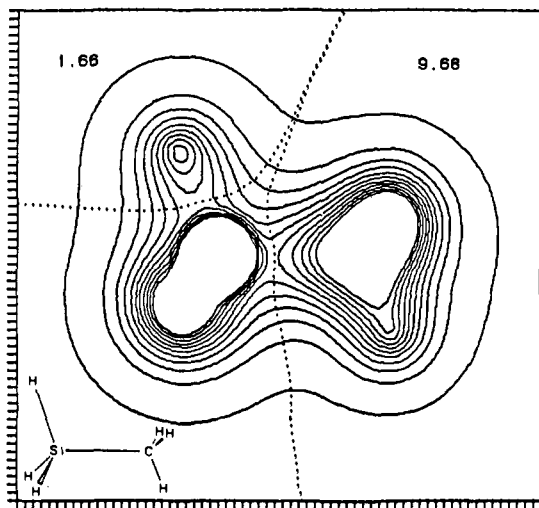
Figure 2. Contour representation of the projection function for methylsilane at the 3-21G* level. Contours from 0.01 to 0.51 with a gradient of 0.05 e au^{-2}. Dotted lines demark regions integrated for IPP analysis.

Figure 3. Contour representation of the projection function for fluorosilane at the 3-21G* level. Contours from 0.01 to 0.51 with a gradient of 0.05 e au^{-2}. Dotted lines demark regions integrated for IPP analysis.

Methylsilane. This compound is another example of silicon bound to a moderately electronegative element, carbon. It is also of interest because several years ago there was some controversy over the direction of experimental dipole moment of 0.73 D.[41] The calculations of Liskow and Schaefer show that the dipole is arranged $(-)H_3Si-CH_3(+)$, but this seems superficially inconsistent with the expected polarity of the Si–C bond.[42,43] In Table II, the IPP value of 9.65 for the CH_3 fragment of methylsilane implies that there is considerable charge transfer and that the bond moment is aligned $(+)Si-C(-)$. The charge on the methyl fragment is comparable to that of the hydrogens. Thus, the local dipole at silicon is relatively small since it is made up of four comparable bond dipoles arranged approximately tetrahedrally. *The key to understanding the net molecular dipole moment is recognition of the higher polarizability of a methyl group compared to hydrogen.* That is, the methyl group is polarized $Si(-)CH_3(+)$ induced by the positive silicon. It is the sum of this induced local dipole and the small local dipole at silicon that results in the observed total moment and the resultant direction of this moment.

The contour map for methylsilane (Figure 2) dramatically points out the differences in Si–H and C–H bonds. For the Si–H bond, the projection function shows a well-defined minimum along the bond axis, whereas for the C–H bond the hydrogen is literally engulfed in the carbon density and the minimum is hardly distinct. For this reason, we cannot partition the density in C–H bonds. Nonetheless, the figure clearly shows that the Si–H hydrogens have a "hydride" character that is completely absent in the C–H bonds. This conclusion is confirmed by the IBP values for the two types of hydrogen in methylsilane (6-31G*):[32] 1.737 for H(Si) and 0.994 for H(C). The hydrogen attached to silicon is essentially like that in silane whereas the methyl hydrogen is slightly positive and distinctly more positive than hydrogen in methane (IBP = 1.065 au) or ethane (IBP = 1.082 au).[11] The polarization of the methyl group is further emphasized by the IBP charge on the carbon, −0.761.

Silaethylene. In silaethylene, the effects of hybridization on the polarizations and charge transfers can be observed. Of particular interest is the extent of polarization in the π bond of silaethylene. The IPP value for the CH_2 group is 9.04, giving a formal charge of −1.04. This value is of somewhat lower magnitude than that given by IBP analysis, −1.28, but both values are large and indicate a highly polar carbon–silicon double bond. Comparing this IPP result to the IPP formal charge on the methyl group of methylsilane, −0.68, it is evident that the double bond results in larger total charge transfer to carbon. This charge transfer can be dissected into π and σ contributions by integration of the same region using only the π density. The carbon π IPP of 1.38 indicates that there is a π transfer of 0.38 e and consequently, a σ charge transfer of 0.66 e; the charge transfer is not the same for the two bonds and occurs preferentially within the σ framework. The σ charge transfer is about the same as in methylsilane. Note that the effect of hybridization on the hydrogen populations is minimal; the sp^2-bonded hydrogens in silaethylene have only slightly large IPP values than the sp^3-bonded hydrogens in methylsilane.

Fluoro- and Methoxysilanes. On the basis of the charge transfers in the Si–C and Si–H bonds, bonds between silicon and highly electronegative elements should be largely ionic. In fluorosilane, the IPP value for the fluorine is 9.92, indicating that there is a transfer of nearly a full charge; consequently, the fluorine is best described as fluoride anion and the most important resonance form is $H_3Si^+F^-$. It would appear that the combination of the short Si–F distance (1.57 Å) and large charge transfer (0.92 e) is responsible for the unusual strength of the Si–F bond. The effect of the fluorine on the IPP's of the hydrogens on silicon is small; the IPP value of 1.69 is slightly larger than that found in SiH_4 and H_3Si-CH_3. Since the hydrogens do not counter the polarization of the Si–F bond, the silicon in fluorosilane carries a larger positive charge (+3.02) than in any of the previous compounds. The high ionic character of the silicon–fluorine bond is evident in the relatively low contour levels along the Si–F bond axis in Figure 3.

The results are similar when methoxysilane is considered; however, the methoxy group is less electronegative than fluorine, so there is less charge transfer. Nevertheless, a strong polarization of the Si–O bond leads to an IPP value for the methoxy group of 17.85 (a formal charge of −0.85). This large charge transfer indicates that, as with the Si–F bond, the ionic component of the Si–O bond plays a dominating role. These conclusions agree with those of Oberhammer et al.[2]

Other Si–H Bonds. Two extreme cases may be considered: SiH_3^+ and SiH_3^-. These ions fundamentally represent silanes with strongly electron-withdrawing and electron-donating substituents, respectively. In the silyl anion, the IPP value of 1.70 for the hydrogens is similar to that found in SiH_4 and other silanes; consequently, the deprotonation of silane leads to only a modest increase in the polarization of the other Si–H bonds. The electronegativity of the silicon in SiH_3^+ is enhanced by the empty p orbital; hence, the IPP value for the hydrogens in the silyl cation

(40) For example, see: Kuncova, G.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2085.

(41) Lide, D. R.; Cole, D. K. *Phys. Rev.* **1950**, *80*, 911.

(42) Liskow, D. H.; Schaefer, H. F. *J. Am. Chem. Soc.* **1972**, *94*, 6641.

(43) The 3-21G* structure is similar to Schaefer's double-ζ structure. At 3-21G*, C–Si = 1.89 Å and Si–H = 1.48 Å. At double ζ, C–Si = 1.87 Å and Si–H = 1.49 Å.

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(1.58) is less than those in the other silanes, but only by about 0.07 e. Thus, in going from the anion to the cation, the IPP values for the hydrogens of the SiH_3 structure change by only 0.12. This result clearly points out the relative unimportance of other substituents to the charge transfers of the Si–H bonds.

The IPP study of substituted silanes yields several other interesting results. For all of the substituents considered (H, C, O, and F), the bonds are highly polarized in the fashion (+)Si–X(–), leading to charge transfers from 0.65 to 0.92 e. With the more electronegative substituents the bonds are dominated by ionic interactions, but even with moderately electronegative substituents the bonds contain significant ionic contributions. Apparently, silicon 3s and 3p orbitals are not electronegative enough to compete with the orbitals on the substituents so that strong polarizations leading to large charge transfers are observed. This result would certainly imply that the higher energy silicon 3d orbitals are unimportant in bonding and are only necessary calculationally as polarization functions.[2] Finally, it is evident in reviewing these integrated hydrogen population values that these hydrogens are substantially hydride-like and that this character is not appreciably affected by other substituents on silicon.

Basis Set Populations. The natural and Mulliken populations for the substituted silanes are also given in Table II. It is evident that the NP values for the hydrogens parallel the IPP values, but the extent of charge transfer is much less. In silane, the NP value is only 1.22 compared to 1.65 from the IPP method. This difference can be understood in terms of the NP and IPP definitions of atomic populations. The NP method relies on a partitioning based on atomic orbitals centered on individual nuclei. As a result, the density is assigned to the atom whose functions best describe it. In the IBP and IPP analyses, the density within a specific region of space near an atom is assigned to that atom. The region is determined by a surface of relative minimum density around the atom. The important difference is that the NP analysis uses a basis set partitioning and the topological analyses use spatial partitioning. The silicon valence functions have small exponents so they are relatively diffuse;[44] hence, these functions may describe not only density on silicon and in the Si–H bonding region but also density around the hydrogen nucleus. The difference in the hydrogen populations from the two methods is the result of density that is physically close to the hydrogens but is partially described by diffuse functions centered on silicon; consequently, the NP analysis assigns such density to silicon whereas the IBP and IPP methods assign it to the hydrogens. This effect is seen to some extent with all of the substituents on silicon.

The Mulliken values also indicate less charge transfer than the IPP method. The MP values for the hydrogens (about 1.2 e) are slightly less than NP values and tend to vary more with the substituents. The importance of these MP values is additionally limited because they are basis set dependent, especially when ionic interactions are present.

There is another important difference in the fundamental meaning of "atomic charge" as given by the two types of procedure. In the NP method as a typical example of Hilbert space partitioning, the electron density is assigned to functions that are centrosymmetric except for orthogonality effects.[45] The resulting atomic charges are centered close to the nuclei. On the other hand, the actual electron density functions around nuclei in molecules are generally anisotropic and generate high local atomic polarizations.[13,46] Thus, the different approaches give fundamentally different types of "atomic charges" whose relative value in chemical interpretation depends on their use. As pointed out elsewhere,[28b] for estimation of the electrostatic potential away from the molecule

Table III. Geometries and IPP's of SiH_4F^- Trigonal Bipyramids[a]

	1[b]	2[c]
Si–F, Å	1.750	1.693
S–H$_e$, Å	1.506	1.526
SiH$_a$, Å	1.600	1.561
F–Si–H$_e$, deg	89.6	125.6
F–Si–H$_a$, deg	180.0	85.9
IPP Values		
F	10.01	9.98
Si	11.26	11.20
H$_e$	1.69	1.74
H$_a$	1.66	1.67

[a] At the 3-21+G* level. Compare ref 52. [b] Apical fluorine with C_{3v} symmetry. [c] Equatorial fluorine with C_{2v} symmetry.

from the "charges" alone, populations of the NP and MP type may be suitable, but for applications close to the atoms, as in considerations of bonding, the integrated populations may well be more appropriate, particularly when due consideration is given to the local polarizations.

Reactions of Silanes: The SiH_4F^- System. The polar nature of bonds to silicon affects the reactivities of silanes in important ways. In particular, there are some instructive comparisons with alkanes. For example, silicon readily forms stable pentacoordinate species,[47,48] but there are few examples of stable pentacoordinate carbon structures. In fact, the parent pentacoordinate silane, SiH_5^-, has been observed recently in gas-phase experiments and was found to be a potent hydride donor.[49] Theoretical studies show SiH_5^- to be more stable than $SiH_4 + H^-$.[50] We use the reaction of silane with fluoride anion to model the $S_N2(Si)$ process and to study the stability of pentacoordinate silicon.[51] Analogous reactions with other anions in the gas phase give addition products (SiH_4X^-); however, deprotonation to give SiH_3^- is a competing process with basic nucleophiles.[50] The deprotonation reaction of SiH_4 with F^- was studied calculationally, but the correlation corrections required to adequately describe the H–F interactions were beyond our present means. The same product is obtained by reaction of fluorosilane with hydride ion; this reaction has recently been studied computationally by Deiters and Holmes, who have shown that axial attack is more facile than edge or equatorial attack.[52]

The reaction surface of SiH_4F^- requires more extensive basis sets to fully account for the anionic character. Since all of the centers (Si, F, H) may potentially carry some negative charge, the basis sets used include a set of diffuse sp functions on silicon and fluorine and diffuse s functions on the hydrogens. The resulting basis sets are designated by a "+" in the basis set name but note that because of the diffuse functions on H, these are augmented compared to the normal "+" basis sets.[22] Optimizations and single-point calculations were performed with the following basis sets: 3-21+G(*), 3-21+G*, 6-31+G*, and 6-31+-G**. The 3-21+G* refers to 3-21+G with polarization functions on first- and second-row centers (Si and F) with the first-row exponents taken from 6-31G*. Correlation was considered in some cases by using the Møller–Plesset second-order corrections (MP2) as supplied by GAUSSIAN 82.[53] Throughout the text the results

(44) The radial maximum of an s function (maximize the expression χ^2 $(4\pi r^2)$) occurs at $1/2^{1/2}\alpha$ (α is the Gaussian exponent). At 3-21G, the outer valence function for silicon has a maximum at 2.31 Å and carbon at 0.84 Å; see: Streitwieser, A., Jr.; Grier, D. L.; Kohler, B. A. B.; Vorpagel, E. R.; Schriver, G. W. *Electron Distributions and the Chemical Bond*; Coppens, P., Hall, M., Eds.; Plenum: New York, 1982.

(45) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. See: Weinhold, F.; Carpenter, J. E. *J. Mol. Struct. (Theochem)* **1988**, *165*, 189.

(46) Slee, T.; Larouche, A.; Bader, R. F. W. *J. Phys. Chem.*, submitted.

(47) Bird, P.; Harrod, J. F.; Than, K. A. *J. Am. Chem. Soc.* **1974**, *96*, 1222.

(48) For some examples, see: (a) Marat, R. K.; Janzen, A. F. *Can. J. Chem.* **1977**, *55*, 3846. (b) Marat, R. K.; Janzen, A. F. *Can. J. Chem.* **1977**, *55*, 1167. (c) Ault, B. S. *Inorg. Chem.* **1979**, *18*, 3339. (d) Stevenson, W. H., III; Wilson, S.; Martin, J. C.; Farnham, W. B. *J. Am. Chem. Soc.* **1985**, *107*, 6340–52. (e) Martin, J. C.; Stevenson, W. H., III. *Phosphorus Sulfur* **1983**, *18*, 81–4. (f) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490–4.

(49) Hajdasz, D. J.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 3139.

(50) (a) Brandemark, U.; Siegbahn, P. E. M. *Theor. Chim. Acta* **1984**, *66*, 233–243. (b) Reed, A. E.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1987**, *133*, 553–61.

(51) For recent reviews of displacement mechanisms on silicon, see: Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231–320; *Adv. Organomet. Chem.* **1982**, *20*, 265–312.

(52) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1686, 1692.

from the highest calculational level are discussed.

Two pentacoordinate structures for the SiH_4F^- anion were found on the surface: a C_{3v} trigonal bipyramid with apical fluorine (1)

1   **2**
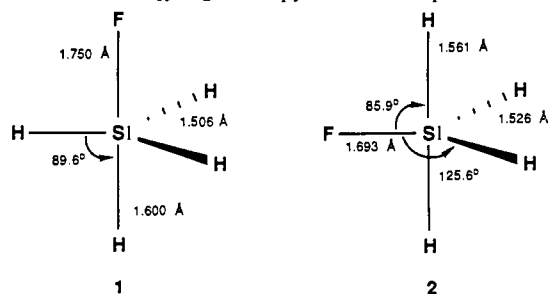
and a higher energy (by 8 kcal mol^{-1}) C_{2v} trigonal bipyramid with equatorial fluorine (2) (Table III). Both structures were determined to be true minima by using analytical frequencies. A C_{4v} tetragonal pyramid with apical fluorine was also considered, but it is significantly higher in energy than the trigonal bipyramids (about 10–15 kcal mol^{-1}) and on relaxation to C_{2v} symmetry constraints, it reverts to the trigonal bipyramid, **2**. Both trigonal bipyramids have been examined previously, and our geometries are comparable to those derived from higher level calculations.[5,52,54]

The apically substituted trigonal bipyramid, **1**, may be considered as the product of fluoride addition along one of the C_3 axes of silane. A brief survey of this addition path indicates that **1** is formed without activation. The absence of a barrier is consistent with previous calculations[50] and with the experimental result that fluoride adds to tetramethylsilane at near the gas-phase collision rate.[4] In the apical positions, both the fluorine (1.75 Å) and hydrogen (1.60 Å) have significantly longer bonds than found in tetravalent analogues such as SiH_3F (Si–F = 1.57 Å and Si–H = 1.47 Å). In contrast, the equatorial Si–H bonds (1.51 Å) are only slightly longer than normal. In the optimized structure of SiH_5^-, the apical bonds are also longer than the equatorial ones.[6,7,50] Moreover, extension of the apical bonds is consistent with the results on the isoelectronic trigonal-bipyramidal structures of neutral phosphorus compounds.[55] The relative lengths of the apical and equatorial bonds can be explained in two complementary ways. In one, the two apical bonds are presumably formed by a three-center, four-electron bond using a single 3p orbital on silicon to give a bonding and a nonbonding MO. This covalent interaction in the apical bonds should be weaker than that of the three equatorial bonds which employ a set of three sp^2 hybrids on silicon to give three bonding MOs. Alternatively, shorter equatorial bonds are electrostatically preferred in the wholly ionic model of five anions surrounding a central tetracation. The advantage of shortening *three* equatorial compared to only *two* apical bonds clearly dominates such an electrostatic analysis. Consequently, both the ionic and covalent components of the bonds cooperate to yield the long apical bonds in these trigonal bipyramids. The Si–F bond length in **1** is similar to the ones found in the X-ray structure of a salt of SiF_5^-, but analysis of the anion structure is complicated by exceptionally large apparent vibrational motions in the crystal.[47] Finally, the F–Si–H$_e$ angle is nearly 90°; thus, the silicon is hardly displaced from the plane of the equatorial hydrogens. On the basis of this angle, it is apparent that the geometry of this intermediate is approximately midway on the reaction path of $F^- + SiH_4 \Rightarrow FSiH_3 + H^-$.

The C_{2v} trigonal bipyramid with equatorial fluorine, **2**, may be envisioned as the result of pseudorotation of **1** or as F^- attack along one of the C_2 axes of SiH_4. The trigonal-bipyramidal structure of this anion is more distorted than that of **1**. The F_e–Si–H$_{eq}$ angle in **2** is opened to 125.6°, resulting in a nearly
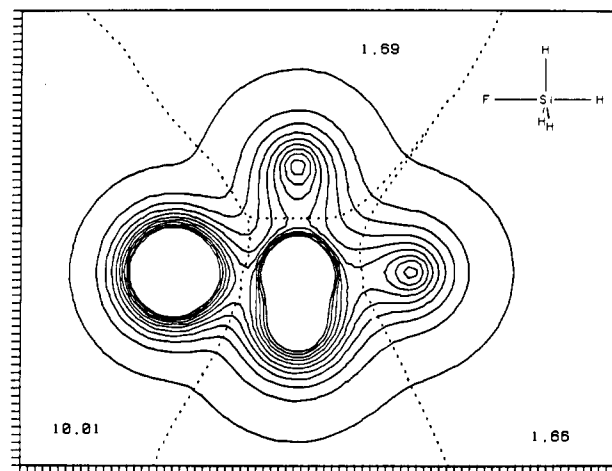

Figure 4. Contour representation of the projection function for SiH_4F^- (1) at the 3-21+G* level. Contours from 0.01 to 0.51 with a gradient of 0.05 e au^{-2}. Dotted lines demark regions integrated for IPP analysis.

Table IV. Relative Energies of SiH_4F^- Isomers[a]

structure	MP2/6-31+G**// HF/3-21+G*	HF/6-31+G**// HF/3-21+G*	HF/3-21+G*// HF/3-21+G*
1	−31.8	−33.4	−38.0
2	−23.6	−25.3	−30.0
$SiH_3F + H^-$	+16.0	+3.1	

[a] Relative to $SiH_4 + F^-$; energies in kcal mol^{-1}. SiH_4 and SiH_3F were optimized at 3-21G*. Compare ref 52.

tetrahedral H$_e$–Si–H$_e$ angle (108.8°). Of course, this angle is nearly 120° in the anion **1**. There is also a slight tilt of the apical hydrogens toward fluorine, leading to an H$_a$–Si–F$_e$ angle of 85.9°. As in **1**, a trend toward shorter equatorial bonds is seen in the relative Si–H bond lengths. In **2**, the bond lengths to the fluorine and the apical hydrogens are shorter than in **1**, but those to the equatorial hydrogens are longer than in **1**. However, a direct comparison of these structures is complicated by the distortion of the trigonal bipyramid in **2**.

The association energies with respect to SiH_4 and F^- were calculated for both anions at several levels (Table IV). These energies appear to be fairly basis set independent because only a 6 kcal mol^{-1} range of values is observed over all of the basis sets. Furthermore, they are consistent with higher level calculations of Davis and Gordon.[5] The apically substituted anion, **1**, is the more stable and has an association energy of −31.8 kcal mol^{-1} at the highest theoretical level (MP2/6-31+G**//HF/3-21+G*). The equatorially substituted anion, **2**, is less stable than **1** by about 8 kcal mol^{-1} in all of the calculations and has an association energy of −23.6 kcal mol^{-1} at the highest level. The apical preference for the more electronegative substituent is consistent with Bent's rule[56] and has also been observed in ab initio calculations on related systems.[4,5,52,55]

The atomic populations for the trigonal-bipyramidal anions are given in Table III. For **1**, the fluorine has an IPP of 10.01; there is a transfer of a full unit of charge, and the Si–F bond is essentially ionic (Figure 4). The hydrogens have populations similar to those found in the tetracoordinate silanes discussed above. The result is that when fluoride ion forms the complex with silane, there is effectively no charge transfer to nor charge redistribution within the SiH_4 fragment. The only change is in the geometry. This result points out the importance of ionic interactions in describing silicon compounds. Obviously all of the bonds in SiH_4F^- are not wholly ionic, but the fluoride addition may be better understood in terms of an ionic rather than a covalent model. Without changes in the silane charge distribution during the fluoride addition, *the silicon acts more as a central cation rearranging its ligands to create a further coordination site than as a covalently*

(53) For a discussion of the effects of Møller–Plesset corrections, see: DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085.

(54) The high-level ab initio calculations by Gordon and Davis[5] were published after we completed our studies using 3-21+G* geometries.

(55) McDowell, R. S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5849. Wang, P.; Zhang, Y.; Glaser, R.; Schleyer, P. v. R.; Streitwieser, A., to be submitted.

(56) Bent, H. A. *J. Chem. Educ.* **1960**, *37*, 616. Bent, H. A. *J. Chem. Phys.* **1960**, *33*, 1258, 1259, 1260. Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

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bound atom expanding its valency.[54,57]

The situation is similar with the equatorially substituted anion, **2**. The fluorine IPP is 9.98 and the hydrogen IPP's vary from 1.67 to 1.74 for the apical and equatorial hydrogens, respectively; therefore, again in this complex the fluorine is best described as a fluoride ion, and the polarization of the Si–H bonds is little affected with respect to SiH$_4$. In both anions, the equatorial hydrogens have larger IPP's than their apical counterparts, but the differences are small and may not be significant in view of the limitations of the IPP method.

At this point it is appropriate to discuss the S$_N$2(Si) process because the reaction of SiH$_4$ with F$^-$ to give SiH$_3$F and H$^-$ is expected to go through the pentacoordinate intermediate anion **1**.[52] The relative energies of all of the important species on the reaction path are given in Table IV at various calculational levels. The reaction passes through the stable intermediate, **1**, which is 31.8 kcal mol^{-1} below the reactants and finally results in SiH$_3$F and H$^-$ with an overall reaction energy of +16.0 kcal mol^{-1} at the MP2/6-31+G**//HF/3-21+G* level. The overall reaction energy is only +3.1 kcal mol^{-1} at the Hartree–Fock level so the correlation corrections are stabilizing the reactants to a much greater extent than the products. It should be noted that the inclusion of third-order MP corrections has little effect on the reaction energy. The apparent negative activation barrier of the S$_N$2(Si) reaction has been noted in past theoretical studies.[6-8] Of course, the carbon analogue of the reaction has been calculated as going through a pentacoordinate transition state with a corresponding positive activation barrier. Since the carbon analogue of the reaction has been the basis of several theoretical studies,[14-18] there is no need to perform similar calculations in the present work.

The stability of pentacoordinate silicon species has been explained in the past by the ability of silicon to expand its valency octet with 3d orbitals and also by the lesser steric demands (with respect to carbon) of placing five substituents around the larger silicon center.[1,14] In light of the population study presented above, it is unlikely that silicon 3d orbitals would be important when the lower energy valence orbitals (s and p) are so weakly populated. Reed and Schleyer[50b] have also recently concluded that d orbitals are not significantly involved in SiH$_5^-$. The key difference in silicon and carbon pentacoordinate species is evident in their geometries. In **1**, the Si–F and Si–H$_a$ bonds are lengthened with respect to tetravalent analogues, but by <10%. In the carbon analogue transition structure (CH$_4$F$^-$) presented by Keil and Ahlrichs the apical bond lengths are stretched over 35 and 75% with respect to normal C–F and C–H bond lengths, respectively.[6] In the carbon reaction, the transition structure is "late" on the reaction path; hence, the C–H bond length is affected most. However, the long apical bonds are also present in the identity reactions H$^-$ + CH$_4$ and F$^-$ + CH$_3$F, which have C–H and C–F bonds stretched from the normal values of 1.08 and 1.42 Å to 1.73 and 1.80 Å, respectively.[6] Steric effects do not appear to be important in these transition structures because the X$_a$–X$_e$ distance is generally long (for CH$_5^-$, H$_a$–H$_e$ is 2.03 Å as compared to the H–H distance of 1.76 Å found in CH$_4$). As noted by Simons et al.,[18e] the long C–X$_a$ distances indicate that the covalency of these bonds is greatly weakened in the transition state of the carbon-centered S$_N$2 reaction. Carbon is unable to form two strong covalent bonds with a single p orbital; thus, the triple-ion configuration, X$^-$CR$_3^+$X$^-$, is important in the resonance hybrid. Considering again the

identity reactions on carbon (H$^-$ + CH$_4$ and F$^-$ + CH$_3$F), it can be seen that the more ionic C–F bond is less perturbed in the transition state than the C–H$_a$ bond. The C–F bond is stretched by 25% and the C–H$_a$ bond by 65%.[6] Moreover, Bader's integration of the fragments of CH$_3$F$_2^-$ leads to formal charges of +0.73 and −0.86 on the CH$_3$ and F fragments, respectively.[16] The transition state barrier results from breaking the covalent bond to the leaving group to a greater extent than forming the new one to the entering nucleophile.[58] The situation with silicon is similar, except that covalency is not as important. As stated above, the attack of fluoride on silane results in silicon opening a further coordination site without appreciably affecting the other bonds. The favorable ionic interaction with the nucleophile stabilizes the pentacoordinate silicon with little adverse effects to the remaining bonds (the necessary rehybridization is not particularly important to bonds with high ionic character). The important difference is the ability of silicon to accept a more ionic bonding. Carbon is more committed to covalency, but in pentacoordinate structures it is forced to exchange a covalent bond for two more ionic interactions. Energetically this is unfavorable for carbon, and a transition state barrier results.

Conclusions

In this study, integrated population analyses indicate that bonds between silicon and common nonmetals (H, C, O, and F) are extensively polarized in the fashion (+)Si–X(−) to give significant charge transfers (0.65–0.92 e). As a result, bonds between silicon and highly electronegative elements (O and F) are dominated by ionic interactions, and even bonds between silicon and moderately electronegative elements (C and H) have important ionic character. The high polarity of these bonds makes ionic considerations important with silicon compounds. The ionic nature of these bonds allows silicon to expand its coordination sphere to form stable pentacoordinate species whereas carbon, an element that more strongly prefers covalent bonding, forms unstable pentacoordinate species.

The present interpretation differs from most conventional treatments of silicon chemistry in its emphasis on ionic character rather than bond covalency but the results show that an ionic model has many advantages and such models should clearly not be neglected in comparison with covalent models in describing electronic structures and reactivities. In particular, unusual bonding modes (e.g., expansion of valence octets) are unnecessary. Moreover, the amount of ionic character in silicon compounds is relatively independent of the degree of coordination about silicon. Hence, the increased reactivity of the Si–H bond as a hydride-donor reducing agent in pentacoordinate silicon compounds[59] can be simply associated with the negative charge of the reagent; that is, a pentacoordinate Si–H anion leaves a neutral tetracoordinate silicon after donating its H$^-$.

(57) Minimum basis set calculations on SiF$_4$·NH$_3$ and SiF$_4$·2NH$_3$ show the Si–N bond to be essentially ionic: Chehayber, J. M.; Nagy, S. T.; Lin, C. S. *Can. J. Chem.* **1984**, *62*, 27–31.

(58) Streitwieser, A., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 8288.
(59) Boyer, J.; Breliere, C.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1986**, *311*, C39–C43.