# SILICON HYDRIDES AND THEIR DERIVATIVES

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## I. Introduction

The chemist who wishes to learn about the hydrides of silicon, the silanes, is fortunate in that a number of excellent reviews have appeared in the last decade. Two books, by Stone (*253*) and Ebsworth (*113*), were published in 1962 and 1963, respectively, and between them cover many aspects of the topic. An earlier review by MacDiarmid (*197*) deals specifically with silicon hydrides, while more specialized treatments of preparative techniques have been provided by MacDiarmid (*199*) for halogen and pseudohalogen derivatives of silicon hydrides, and by Aylett (*22*) for silicon-nitrogen compounds, some of which contain Si—H bonds. Other useful recent sources include a general review of silicon-nitrogen chemistry (*271*), a survey of silicon-nitrogen polymers (*23*), and the proceedings of a meeting on organosilicon chemistry (in which hydrogen sometimes masqueraded as an organo group) in Prague (*79*). Principles of silicon chemistry are well expounded in Eaborn's book (*112*) and, finally, Parts B and C of Gmelin's treatise on silicon give a complete coverage of the literature up to the mid-1950's (*154*).

In view of this, it is certainly neither desirable nor possible to attempt to summarize here all aspects of silicon hydride chemistry. The treatment will be illustrative and not comprehensive, will concentrate on that recent work most interesting to the author, and will try to stimulate curiosity and dissatisfaction by pointing out some of the unsolved problems. Such a partial account will succeed most if it conveys that elusive thing—the feel of silane chemistry.

## II. General Aspects of the Behavior of Silane Derivatives

### A. HANDLING

Any discussion must necessarily begin by mentioning two not altogether unrelated points: the contribution of Alfred Stock, and the electronic configuration of silicon. As early as 1903, Stock published a paper on the technique of working with liquefied gases. In the following years he developed the high vacuum techniques that made it possible to study reactive volatile compounds, and also quantitative methods for determining the properties of extremely small amounts of such substances. A series of papers on silicon hydrides appeared between 1916 and 1926, and in these Stock enumerated most of the important modes of behavior of these substances; he later reviewed the field more generally (*247*). It is salutary for us to note how much was achieved without the use of infrared, ultraviolet, n.m.r. and mass spectrometers, without chromatographic methods, and without the interpretative background of quantum mechanics.

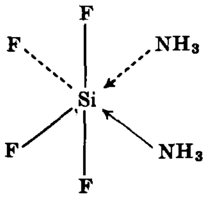
Today most preparative work on silanes and their derivatives is carried out in apparatus similar in principle to Stock's, although improvements in high vacuum taps and greases have made it normally unnecessary to use mercury ventils as valves. Indeed, in some investigations the presence of mercury cannot be allowed (mercury reacts with iodosilanes and seems to catalyze the decomposition of some other derivatives), and special arrangements must then be made for measurements of pressure (e.g., *20*).

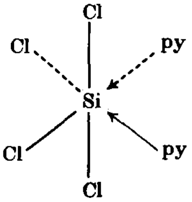
Glove boxes are commonly used in the handling of less volatile derivatives, but it should be emphasized that extreme care is needed, both in desiccation and in removal of oxygen, if quantitative results are to be obtained. Technically, it seems perfectly feasible to construct a "hydride room," filled with ultra-dry nitrogen or argon. Workers would wear nonporous protective clothing with closed-circuit breathing equipment. If the atmosphere in such a small room contained only 1 ppm of water vapor, however, this would be sufficient to hydrolyze roughly a millimole of iodosilane.

## B. BONDING CONSIDERATIONS

The extremely high reactivity of many silicon hydride derivatives, which necessitates the care in handling outlined above, can of course be related to silicon's electronic configuration. It is natural to compare silicon with carbon, and there is the obvious difference that, energetically above the highest filled levels in the valence state of silicon ($1s^2 2s^2 2p^6 3s^1 3p_x{}^1 3p_y{}^1 3p_z{}^1$), there lie five vacant $3d$ orbitals. Carbon in its valence state ($1s^2 2s^1 2p_x{}^1 2p_y{}^1 2p_z{}^1$) has $3s$ as the corresponding next available level. It is usually tacitly assumed that the energy separation $3p \rightarrow 3d$ is so much less for silicon than is the corresponding $2p \rightarrow 3s$ separation for carbon that the first gap is readily bridged while the second is not. Although this may be true when the atoms are combined in molecules, it is not obvious from the energy level separations for the free atoms (cf. *103*, *204*).

It is generally accepted that two different effects may be related to the availability of $d$ orbitals on silicon; in both cases carbon is unable to act analogously. First, silicon may increase its coordination number in various complexes to [5] or [6]. This has long been known: such compounds as $SiF_4 \cdot 2NH_3$ and $SiCl_4 \cdot 2C_5H_5N$ are readily formed from their components at room temperature. Their probable structures are (*56*, *69*):



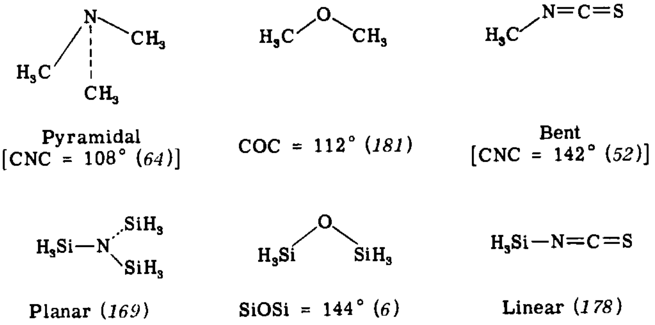


In the case of other adducts (e.g., $SiH_3X \cdot NMe_3$), which are apparently five-coordinate, the position is not completely clear; this will be considered later (Section IV,C). Initial coordination by attacking nucleophiles such as $OH^-$ and $NH_2^-$ has often been postulated as an important step in reactions of substituted silanes, and Eaborn (*112*) has discussed how coordination of this kind may lower the activation energy of the process. We shall refer to such cases as involving an intermolecular use of *d* orbitals; it is accompanied by an increase in the number of $\sigma$-bonds formed by silicon.

Second, *d* orbitals may be involved in $\pi$-overlap with suitable filled orbitals on neighboring ligands. This effect, which is most marked with electronegative atoms or groups, has been increasingly invoked since two important papers, by Jaffé (*176*) and Craig *et al.* (*94*), showed theoretically that it was likely to be significant. Evidence for its occurrence has been reviewed by Stone and Seyferth (*254*) and more recently by Ebsworth (*113*); the most important facts fall under the following headings.

### 1. *Change in Shape*

Some of the more striking differences from carbon are shown in Fig. 1. A more detailed discussion of changes of this type will be given later, but in general all can be rationalized in terms of optimum $\pi$-overlap. The structure alters in such a way that the lone-pair orbital(s) on nitrogen or oxygen develops increased *p* character, and thereby can overlap more effectively with silicon's *d* orbitals. The *s* character of the $\sigma$-bonds to silicon will at the same time increase. This change in shape can be demonstrated by various physical methods; in practice, vibrational and microwave spectroscopy and electron diffraction techniques have been mostly used.



Pyramidal [CNC = 108° (*64*)]

COC = 112° (*181*)

Bent [CNC = 142° (*52*)]

Planar (*169*)

SiOSi = 144° (*6*)

Linear (*178*)

FIG. 1. Structures of corresponding methyl and silyl derivatives.

### 2. *Change in Reactivity*

Amines and ethers behave as typical electron-pair $\sigma$-donors or Lewis bases. The corresponding silyl compounds interact either weakly or not at all with a range of Lewis acids. While a fuller discussion will be given later (Sections V,A,2 and VI,B), the data in Table I are typical. Amines are usually stronger bases than ethers, and the diminution of base strength is more noticeable in the case of silylamines.

TABLE I

COMPARISON OF LEWIS BASE STRENGTHS OF CARBON AND SILICON ANALOGS

| Base | Acid | Adduct combining ratio (base:acid) | Ref. |
|---|---|---|---|
| $(CH_3)_3N$ | $BMe_3$ | 1:1 strong | *(66)* |
| $(SiH_3)_3N$ | $BMe_3$ | (no reaction) | *(257)* |
| $CH_2(NMe_2)_2$ | $BH_3$ | 1:2 strong | *(36)* |
| $SiH_2(NMe_2)_2$ | $BH_3$ | 1:2 weak | |
| $(CH_3)_2O$ | $SiH_3I$ | 1:1 rather weak | *(21)* |
| $(SiH_3)_2O$ | $SiH_3I$ | (no reaction) | *(19)* |

Not only is the electron-donor ability of nitrogen (or oxygen) in such compounds reduced, but the electron-acceptor ability of the attached silicon is simultaneously reduced also. Thus, although silyl halides react very readily with trimethylamine to yield solid adducts, there is no similar reaction between $(SiH_3)_3N$, $(SiH_3)_2NN(SiH_3)_2$, or $(SiH_3)_2O$ and trimethylamine.[1] These facts may be rationalized in the following rather naive way, taking trisilylamine, $(SiH_3)_3N$, as an example. If electron donation by nitrogen is to occur, electron density must be withdrawn from silicon's *d* orbitals, and a change in stereochemistry about nitrogen to an approximately tetrahedral arrangement must take place. The $\pi$-bonding between nitrogen and silicon is reduced, and evidently the gain in energy by complex formation is not sufficient to compensate for this. Also, involvement of silicon's *d* orbitals in $\pi$-bonding to nitrogen makes them less ready to accept electrons from outside, leading to a reduction in Lewis acid strength.

These changes in reactivity have in the main been demonstrated by means of phase studies, measurements of vapor pressures of mixtures, and heats of mixing. Infrared studies based on hydrogen-bonded interactions have also proved helpful. Kinetic studies are not usually feasible

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[1] Slow reaction of a different kind does occur (see Sections V,A,4 and VI,B).

with silicon hydride derivatives, as reactions are extremely rapid, there is a considerable body of such information for organosilicon derivatives, however, which has been interpreted in terms of $p_\pi$-$d_\pi$ interaction (see Eaborn, *112*).

### 3. *Change in Bond Length*

Such evidence is always difficult to interpret, since it is not possible to switch $\pi$-bonding on and off in a particular bond; one must take a bond, with whatever multiple bond character that it possesses, as one finds it. However, the facts in Table II may be significant. The differences are so large, even after generous allowance has been made for electronegativity differences by some relationship such as the Schomaker-Stevenson equation, that it is hard to see how they can be interpreted except in terms of multiple bonding.

TABLE II

BOND LENGTHS IN SILICON COMPOUNDS

| Bond | Sum of covalent radii (Å) | "Corrected" sum[a] (Å) | Experimental bond length (Å) | Compound | Ref. |
|---|---|---|---|---|---|
| Si—N | 1.87 | 1.76 | 1.73 | $(SiH_3)_3N$ | (*169*) |
| | | | 1.71 | $SiH_3NCS$ | (*178*) |
| Si—O | 1.83 | 1.68 | 1.63 | $(Me_3Si)_2O$ | (*278*) |
| | | | | $(SiH_3)_2O$ | (*6*) |
| Si—F | 1.81 | 1.61 | 1.54 | $SiF_4$ | (*65*) |
| | | | 1.59 | $SiH_3F$ | (*45*) |

[a] By Schomaker-Stevenson equation (see text).

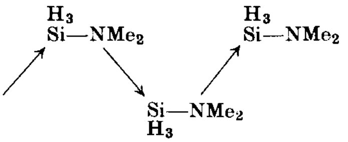
These three effects can thus be regarded as manifestations of $p_\pi$-$d_\pi$ dative $\pi$-bonding, and we shall refer to this as intramolecular use of *d* orbitals. A few points may be noted at this stage. First, because several *d* orbitals are available around the $\sigma$-bond axis, no marked energy barrier to rotation will be expected; the situation is somewhat similar to that in the C≡C triple bond. Second, there is no evidence that dative $\pi$-bonding can occur in the absence of a $\sigma$-bond between the same two atoms; "$\pi$-only" interactions seem unlikely for steric reasons. Third, there is no theoretical reason why silicon should not be involved in dative $d_\pi$-$d_\pi$ interactions, and indeed these were foreshadowed by Jaffé (*176*) and Craig *et al.* (*94*). It is only very recently, however, that they have been invoked in compounds containing a silicon-transition metal bond (see

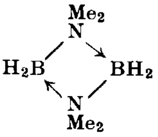
Section VIII,B). Finally, evidence from a number of complex-forming and structural studies suggests that dative $\pi$-bonding decreases in importance in the following orders:

$$N > O > F; \quad N > P; \quad O > S; \quad F > Cl > Br > I$$

Particularly in trifluorosilyl derivatives $\sigma$-inductive effects are decisive, and such compounds generally behave as strong Lewis acids.

In any particular silane derivative, especially one in which silicon is linked to nitrogen or oxygen, there will be competition between inter- and intramolecular use of silicon's *d* orbitals. When a molecule is distant from its neighbors, in the gas phase for example, dative $\pi$-bonding will be important. In condensed phases, however, the molecules may tend to interact via intermolecular dative $\sigma$-bonding. Thus *N*,*N*-dimethylaminosilane, $Me_2NSiH_3$, seems to be considerably associated in the solid phase (*257*). The infrared spectrum of the crystalline compound shows strong absorption around 500 $cm^{-1}$, which is attributed to Si—N---Si bridging (*70*)[2]. It is known that *N*,*N*-dimethylaminoborane, $Me_2NBH_2$, can exist as a dimer even in the gas phase because of similar intermolecular dative $\sigma$-bonding (*68*):





On the other hand, neither $Me_3SiNMe_2$ nor $Me_2BNMe_2$ shows evidence of intermolecular association, presumably because of steric repulsions. It has also been suggested that $SiH_3NCS$ (*196*) and $SiH_3N_3$ (*121*) may be associated in the liquid phase; in the first case, this would probably be associated with nonlinearity of the heavy atoms (see Section IV,B).

Silicon is distinguished from carbon not merely by possession of *d* orbitals. Other differences significant in its hydride chemistry are its larger size (1.17 Å as against 0.77 Å) and its lesser electronegativity. The first has the effect of reducing steric repulsions, especially between hydrogens of silyl groups as compared with those of methyl groups. The exact value of silicon's electronegativity is still a matter of some dispute (e.g., see Allred and Rochow, *5*; Drago, *106*). It is quite certainly less than that of carbon—Pauling's scale gives values based on thermochemical data of 1.8 for Si and 2.5 for C—and this is doubtless a reflection of the

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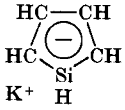
[2] X-Ray studies have now shown that solid $Me_2NSiH_3$ consists of cyclic pentameric units, with nitrogen atoms at the vertices of a regular pentagon, and planar $SiH_3$ groups at the mid-points of, and perpendicular to, the sides of the pentagon (*227a*).

increased efficiency of shielding of silicon's nuclear charge by its filled electron orbitals. The polarity of the $Si^{\delta+}$—$H^{\delta-}$ and $Si^{\delta+}$—$P^{\delta-}$ bonds, for example, is therefore different from that of the corresponding $C^{\delta-}$—$H^{\delta+}$ and $C^{\delta-}$—$P^{\delta+}$ bonds. Two estimates of the actual Si—H bond dipole are 1.25 D (*80*) and 1.6 D (*46*). Both these values seem high, but are consistent with the high observed intensities of infrared absorption associated with Si—H bonds.

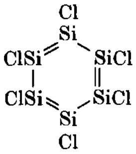
It is significant that silicon does not seem able to form multiple bonds of the $p_\pi$-$p_\pi$ type. The three compounds (I–III) have all been reported in recent years (*148*, *60*, *264*, respectively), but (I) was found to be its

$Me_2Si{=}CHSiMe_3$

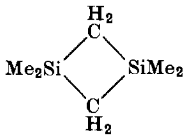
(I)



(II)



(III)



(IV)

isomer (IV) (*152*), the evidence for (II) has been re-examined (*59*), and (III) has not been confirmed. Although hydrides of empirical composition $SiH_2$, SiH, etc., may be made (e.g., *226*, *235*), these are undoubtedly polymeric and contain four-coordinate silicon. It is not clear why $p_\pi$-$p_\pi$ links are so reluctant to form; perhaps silicon is too large for effective sideways overlap of orbitals or, expressing the same idea in different terms, repulsions between nonbonding electrons on silicon and the neighbor atom are too severe. It should be noted that there is some evidence for the formation of $(H_2Si{=}CH_2)^+$ in a mass spectrometer (*182*); it could be argued that the positive charge has the effect of reducing electron-electron repulsions and hence the internuclear Si—C distance, making $\pi$-overlap feasible. (Orbital contraction effects may also be important—see later in this section.)

Mulliken (*209*, *210*), in an important pair of papers, has suggested that when second-row elements combine with either first- or second-row elements, a small amount of mixing-in of $d$ orbitals may occur. This can then lead to significant strengthening of $\sigma$-bonds and also provide additional bonding $\pi$-overlap. He suggests that Si—Si, Si—X (X = N, O, halogen), and even Si—H bonds, although written as single bonds, may in fact have an effective bond order of more than 1. This description accounts rather neatly not only for the lack of multiple bonds (since, for example, two Si—O "single-plus" bonds will be favored energetically over one Si=O bond), but also for the high observed bond energies of such putative single bonds, shown in Table III.

TABLE III

ENERGIES OF BONDS TO CARBON AND SILICON (IN KCAL MOLE$^{-1}$)

| | H | F | Cl | Br | I | N | O |
|---|---|---|---|---|---|---|---|
| C[a] | 99 | 116 | 78 | 68 | 51 | 73 | 86 |
| Si (experimental)[a] | 76 | 135 | 91 | 74 | 56 | 85[c] | 108 |
| Si (predicted)[b] | (76) | 89 | 60 | 52 | 39 | 56 | 66 |
| $\frac{\text{Si (exptl.)} - \text{Si (predicted)}}{\text{Si (exptl.)}} \times 100$ | 0 | 34 | 34 | 30 | 30 | 34 | 39 |

[a] Cottrell (*86*).
[b] See text.
[c] Estimated.

Let us assume (*pace* Mulliken) that the reduction in bond energy in going from C—H to Si—H represents the normal decrease in the absence of the $d$-mixing and $\pi$-overlap effects referred to above. We then can calculate a set of predicted Si—X single bond energies by decreasing the corresponding C—X bond energies in the same ratio. It can be seen, from the final row of figures in Table III, that the predicted values are consistently 30–40% lower than the observed values, and moreover that the effect is greatest just for those bonds in which the greatest $\pi$-effects have been proposed.

Mulliken based his conclusions on calculations of overlap integrals between, for example, Si $3p\pi$ and Cl $3p\pi$ orbitals, and it is helpful to consider some aspects of overlap at this point. The usual picture of $p_\pi$-$d_\pi$ overlap (Fig. 2) tacitly assumes that the orbitals will be of comparable size, and that overlap will be good. It turns out, however, that, if Slater (hydrogen-like) wave functions are used, the $3d$ orbitals are so diffuse that overlap is rather poor. Two ways out of this difficulty have been suggested. In the first (*91*), it is shown that electronegative ligands can bring about contraction of the $d$ orbitals (by increasing the effective nuclear charge). In the second (*96*), use of a more sophisticated type of self-consistent field (SCF) wave function also results in a less diffuse $d$ orbital. In both cases, $\pi$-overlap will be improved. By a similar argument, $d$-mixing to enable silicon to increase its coordination number above 4 will be possible only if the $d$ orbitals are comparable in size with the valence-shell $s$ and $p$ orbitals. Even a weakly electronegative ligand seems able to bring about $d$-mixing. Silane itself will not react with electron donors, but iodosilane readily does so (see Section IV,C).

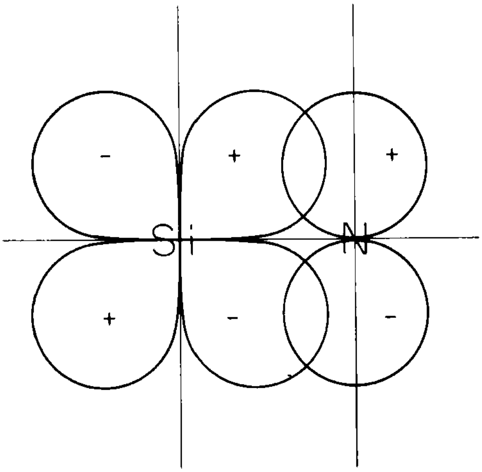


FIG. 2. Diagrammatic representation of $d_\pi$-$p_\pi$ overlap of orbitals.

The qualitative ideas outlined so far have been put on a much firmer basis by some recent calculations of the $\pi$-electron distribution in $(SiH_3)_3N$ by Perkins (*218*). The results of this SCF-MO treatment suggest that the stabilization of the molecule attributable to $\pi$-bonding amounts to about 48 kcal mole$^{-1}$, and that there is appreciable electron delocalization onto the silicon atoms. It had been earlier pointed out by Ebsworth (*114*) that, when a molecule of this kind departs from planarity, the $\pi$-interactions are lessened but by no means vanish; as Randall and Zuckerman (*221*) were quick to point out, this tends to weaken arguments linking the occurrence of $\pi$-bonding with stereochemical changes. Perkins, in taking up this point, stresses that loss of planarity in $(SiH_3)_3N$ results in mixing of $\sigma$ and $\pi$ MO wave functions, and the resulting energy change is hard to estimate.

The simple picture shown in Fig. 2 will be further modified if more than one $\pi$-donating ligand is attached to silicon. In a compound such as $SiH_2(NMe_2)_2$, a number of different $d$ orbitals can be involved, and their orientation with respect to the $\sigma$-framework and also the bond angle will alter in such a way as to optimize the total $\sigma$- and $\pi$-overlap in the $SiN_2$ system. It may not be a sufficiently good approximation in such circumstances to consider $\pi$-overlap separately (cf. *95*). The simple picture will also be modified if the $\pi$-donating orbital has some *s* character (e.g., in $SiH_3NMe_2$, which probably has a nonplanar $SiNC_2$ skeleton) or some *d* character (which is possible in, e.g., Si—P compounds). Detailed calculations of overlap integrals in these more complex situations have not yet been performed; a clue to the results that may be obtained is provided by similar calculations on cyclic P—N systems (*93*), which show that, as the configuration changes, reduction in one type of overlap is often offset by increase in another. This is consistent with the flexibility (i.e., lack of strongly preferred orientation) of Si—O—Si and Si—N—Si chains.

These theories of $\pi$-interaction and *d*-orbital participation can be tested more effectively on derivatives of silane than on any other group of hydrides, because a much wider range of compounds is known. This is the justification for the somewhat extensive treatment given here. It may be noted that $SiH_3$ derivatives seem to manifest both inter- and intramolecular effects more than the corresponding trialkylsilyl derivatives (see Section IV,B). In the first case, this is probably a result mainly of steric effects, but it is not clear why $\pi$-interaction should be lessened. Possibly hyperconjugative effects between alkyl groups and silicon are responsible. Recently, too, it has been reported (*4*) that $SiF_3$ derivatives behave rather like corresponding $SiH_3$ compounds, although the Lewis acid function of the former is more marked.

## C. BOND ENERGIES AND HEATS OF FORMATION

Values of the thermochemical bond energies *E*(Si—H) and *E*(Si—Si) have been discussed by Cottrell (*86*). His preferred values are quoted in Table IV; they will be altered somewhat by a recent change in the accepted value for the heat of sublimation of silicon (see Beezer and Mortimer, *57*). More accurate values for the heats of formation of $SiH_4$, $Si_2H_6$, and $Si_3H_8$ have been obtained by Gunn and Green (*160, 161*); their method is a novel one involving explosive decomposition of the hydride, usually in the presence of stibine. Their value for *E*(Si—H) is very similar to the previous one, but *E*(Si—Si) proves to be appreciably smaller, in both di- and trisilane. Fehér *et al.* (*141, 142*) have also measured the heats of formation of $Si_nH_{2n+2}$ ($n = 1$–$4$) by a direct combustion method, but their values differ radically from those of Gunn and Green, and it seems likely that inherent difficulties of the technique (the heats of combustion to be measured are very small) may be responsible. No thermochemical studies on derivatives of silanes seem to have been reported, although they would be most valuable.

## TABLE IV

### Heats of Formaton of Silanes and Derived Bond Energies

| Compound | $\Delta H_f$ (kcal mole$^{-1}$) | $E$(Si—H) (kcal mole$^{-1}$) | $E$(Si—Si) (kcal mole$^{-1}$) | Ref. |
|---|---|---|---|---|
| $SiH_4$ | +7.3 | 76.5 | — | (*160*) |
| | +7.8 | 72.6 | — | (*229*) |
| | −11.3 | — | — | (*142*) |
| $Si_2H_6$ | +17.1 | 76.5 | 46.4 | (*160*) |
| | +15.1 | 72.6 | 39.7 | (*230*) |
| | −35.8 | — | — | (*142*) |
| $Si_3H_8$ | +25.9 | 76.5 | 46.9 | (*161*) |
| | −54.1 | 72.6 | — | (*142*) |
| *n*-$Si_4H_{10}$ | −70.4 | — | — | |
| | | 76 | 51 | (*86*) |

A number of groups have been active in determining bond-dissociation energies. These have been estimated by mass spectrometry, by measurement of appearance potentials for various ions. The appearance potential is the limiting energy just required to produce a particular ion (with no extra kinetic energy), and is not always easy to establish. Furthermore, the processes by which a certain ion is formed need to be assumed, but are sometimes ambiguous. Steele *et al.* (*243*) first studied silane and several alkylsilanes; from measurements of appearance potentials and a number of assumptions about the processes involved and the ions produced, they were able to deduce that the values of $D(H_3Si—H)$ and $D(H_3Si—SiH_3)$ were 93 and 82 kcal mole$^{-1}$, respectively. In another study, Steele and Stone (*242*) examined disilane itself, and by more direct arguments established a value of 81 kcal mole$^{-1}$ for $D(H_3Si—SiH_3)$. Such large values were surprising; in particular, an earlier estimate of $D(H_3Si—SiH_3)$, based on measurements of the activation energy for the pyrolysis of disilane (*133*), was only 51 kcal mole$^{-1}$.

Similar electron impact experiments and measurements of appearance potentials have been carried out by Saalfield and Svec (*229*, *230*) (who used their results to derive values of the heat of formation of silane and disilane—see Table IV) and by Hess *et al.* (*170*, *171*). Reasonable agreement between the different groups was obtained (see Table V).

Very recently, however, Connor *et al.* (*81*, *82*) have remeasured some of the appearance potentials reported by Hess *et al.* They find appreciably lower values, and combine them with estimates of $D(Me_3Si—SiMe_3)$ to obtain the derived values shown in Table V. The Si—Si bond-dissociation energy was assumed to be equal to the measured activation energy for

TABLE V

BOND-DISSOCIATION ENERGIES (IN THE COMPOUNDS SHOWN)

| D(Si—H) (kcal $mole^{-1}$) | D(Si—C) (kcal $mole^{-1}$) | D(Si—Si) (kcal $mole^{-1}$) | Ref. |
|---|---|---|---|
| 93<br>$H_3Si$—H<br>$Cl_3Si$—H | 65<br>$Me_3C$—$SiH_3$ | 82<br>$H_3Si$—$SiH_3$ | (*243*) |
| | | 81.3<br>$H_3Si$—$SiH_3$ | (*242*) |
| 83<br>$Me_3Si$—H | | 81<br>$Me_3Si$—$SiMe_3$ | (*170*) |
| 88<br>$Me_3Si$—H | 85<br>$Me_3Si$—$CH_3$ | 86<br>$Me_3Si$—$SiMe_3$ | (*171*) |
| 95<br>$H_3Si$—H | | 84<br>$H_3Si$—$SiH_3$ | (*229, 230*) |
| 64–74<br>$Me_3Si$—H | 59–69<br>$Me_3Si$—$CH_3$ | 49,[a] 58[b]<br>$Me_3Si$—$SiMe_3$ | (*81, 82*) |
| 84<br>$Me_3Si$—H | 79<br>$Me_3Si$—$CH_3$ | 69<br>$Me_3Si$—$SiMe_2Et$ | (*100, 101*) |

[a] From molecular flow pyrolysis.
[b] From toluene carrier pyrolysis.

pyrolytic breakdown of hexamethyldisilane, either alone or with an excess of toluene, at about 700°. The fact that trimethylsilane was obtained in the latter case as a major product supports their contention that the primary breakdown produces $SiMe_3\cdot$radicals.

Davidson and Stephenson (*100, 101*) have confirmed the lower value for the appearance potential found by Connor *et al.*, but suggest from their experiments on the pyrolysis of $Me_3SiSiMe_2Et$ that *D*(Si—Si) should be 69 kcal $mole^{-1}$. This leads to higher values generally for *D*($Me_3Si$—X).

The results of such studies, especially the value of *D*(Si—Si), are of great interest in connection with the chemistry of disilane; as will be seen (Section III,B), this compound often reacts via its Si—H bonds

## TABLE VI

INFRARED STRETCHING AND DEFORMATION FREQUENCIES IN SILYL DERIVATIVES

| X *in* $SiH_3X$ | Si—H stretch ($cm^{-1}$) | $SiH_3$ deformation ($cm^{-1}$) | $SiH_3$ rock ($cm^{-1}$) | Ref. |
|---|---|---|---|---|
| H | 2180s, 2183as | — | — | (*187*) |
| F | 2189s, 2210as | 991s, 929as | 730 | (*49*) |
| Cl | 2201s, 2211as | 945s, 952as | 663 | |
| Br | 2200s, 2211as | 930s, 947as | 631 | |
| I | 2192s, 2206as | 903s, 941as | 592 | (*104*) |
| CN | 2205s, 2227as | 920s, 941as | 682 | (*192*) |
| $N_3$ | 2170 | 945 | (690) | (*121*) |
| NCS | 2200s, 2207as | 949s, 950as | 710 | (*129*) |
| NCO | 2300–2200 | 960 | 710 | (*118*) |
| Me | 2169s, 2166as | 943 | (539) | (*48*) |
| OMe | 2150 | 982, 968 | 732 | (*245*) |
| $NMe_2$ | 2160, 2110 | 969s, 921as | 695 | (*70*) |
| $PH_2$ | 2169 | 920, 904 | — | (*193*) |
| $AsH_2$ | — | 890 | — | (*107*) |
| $Co(CO)_4$ | 2160 | 906s, 947as | (600) | (*27*) |
| $Mn(CO)_5$ | 2156, 2136 | 906 | (609) | |

rather than by cleavage of the Si—Si bond. Nevertheless, chemically, the lower estimates of dissociation energies seem more reasonable.

### D. VIBRATIONAL SPECTROSCOPY

Infrared studies at various levels of sophistication have been carried out on a wide range of silicon hydride derivatives. Relevant data are summarized in Table VI ($SiH_3X$ derivatives), Table VII ($SiH_2X_2$ and $SiHX_3$ derivatives), Table VIII [$(SiH_3)_3M$ and $(SiH_3)_2M$ derivatives], and Table IX ($Si_2H_5X$ derivatives). It should be emphasized that, although Si—H stretching vibrations occur in a frequency region that is usually free from interference by other vibrations, severe coupling is possible among modes at lower frequencies. Because of this, terms like $\delta(SiH_3)$ rock are only approximate descriptions of the actual movement of the molecule that is responsible for a particular absorption. Where it is reasonably certain that such coupling is serious, values in the tables have been enclosed in parentheses. All these measurements refer to gas phase spectra, an indication of the volatility of most silane derivatives.

A number of correlations have been suggested between particular absorption frequencies in a related class of compounds and various

TABLE VII

INFRARED ABSORPTION FREQUENCIES IN $SiH_2X_2$ AND $SiHX_3$ DERIVATIVES

| X in $SiH_2X_2$ | Si—H stretch ($cm^{-1}$) | $SiH_2$ scissors ($cm^{-1}$) | $SiH_2$ wag ($cm^{-1}$) | $SiH_2$ twist ($cm^{-1}$) | Ref. |
|---|---|---|---|---|---|
| F | 2246s, 2251as | 982 | 903 | 730 | (*87*) |
| Cl | 2200 | 953 | 877 | 710 | (*126, 167, 168, 213*) |
| Br | 2206s, 2232as | 925 | 828 | 688 | (*168*) |
| I | — | 925 | 791 | — | (*126*) |
| Me | 2145 | 961 | (919) | — | (*47, 126*) |
| OMe | 2180 | 933 | — | — | (*244*) |
| $NMe_2$ | 2136 | 953 | (918) | — | (*35*) |

| X in $SiHX_3$ | Si—H stretch ($cm^{-1}$) | Si—H bend ($cm^{-1}$) | Ref. |
|---|---|---|---|
| F | 2315 | — | (*214*) |
| Cl | 2274 | 808 | (*153a*) |
| Me | 2123 | — | (*47*) |
| OMe | 2210 | — | (*244*) |
| $NMe_2$ | 2108 | 811 | (*35*) |

properties of the atom attached to silicon. Thus Kriegsmann (*187*) has suggested that the Si—H stretching vibration increases in frequency as the Pauling electronegativity of the other attached groups increases, and has related this to a reduction in the size of the $Si^{\delta+}$—$H^{\delta-}$ bond dipole. Smith and Angelotti (*239*) correlated Si—H stretching frequencies with a set of additive empirical parameters ($E$ values); these were related, according to Thompson (*259*), to Taft's $\sigma^*$ values of the substituents concerned. It was therefore argued that inductive effects were paramount. While it is true that these trends are followed in a rough and ready way, inspection of the tables will show many instances of anomalies. For example, the values of $\nu$(Si—H) for all the silyl halides are approximately equal, while the values for the compounds $SiH_2X_2$ decrease in the order $X = Br > OMe > Me > NMe_2$, which is certainly not an order of decreasing electronegativity. Only by certain arbitary assumptions concerning the effect of $\pi$-bonding can such difficulties be avoided.

The symmetrical $SiH_3$ deformation frequency has been shown by Jolly (*180*) to increase roughly linearly with increase in electronegativity of the attached group, and Ebsworth *et al.* (*126, 129*) have suggested

## TABLE VIII

### INFRARED ABSORPTION FREQUENCIES IN DI- AND TRISILYL DERIVATIVES

| Compound | Si—H stretch (in cm$^{-1}$) | $SiH_3$ deformation (in cm$^{-1}$) | Ref. |
|---|---|---|---|
| $(SiH_3)_3N$ | 2167, 2140 | 944 | (*225*) |
| $(SiH_3)_3P$ | 2165, 2154 | 939, 885[a] | (*99*) |
| $(SiH_3)_3As$ | 2165, 2092 | 917,[a] 874 | (*11*) |
| $(SiH_3)_3Sb$ | 2160 | 908[a], 853[a] | |
| $(SiH_3)_2O$ | 2183, 2169 | 957 | (*195*) |
| $(SiH_3)_2S$ | 2180 | 956,[a] 907[a] | (*127*) |
| $(SiH_3)_2Se$ | 2185 | 932, 890 | |

[a] Mean of two or more closely similar frequencies.

## TABLE IX

### INFRARED ABSORPTION FREQUENCIES IN DISILANYL COMPOUNDS

| X in $SiH_3SiH_2X$ | Si—H stretch (cm$^{-1}$) | $SiH_3$ and $SiH_2$ deformation and/or rock (cm$^{-1}$) | Ref. |
|---|---|---|---|
| H | 2179, 2153[a] | 934,[a] 909, 844 | (*62, 163*) |
| Cl | 2190 | 942,[a] 883,[a] 807[a] | (*90*) |
| Br | 2190 | 944, 882,[a] 818, 788[a] | (*273*) |
| I | 2200, 2180 | 940,[a] 872,[a] 757[a] | (*272, 274*) |
| $OSi_2H_5$ | 2155 | 937, 853, 808, 755 | |
| $N(Si_2H_5)_2$ | 2150 | 931, 885, 849,[a] 808, 733 | (*274*) |
| $SSi_2H_5$ | 2160 | 940, 878, 794, 764 | |

[a] Mean of two or more closely similar frequencies.

similar correlations for $SiH_2$ "scissors" and "wagging" deformation modes in $SiH_2X_2$ derivatives, and for the $SiH_3$ rocking mode in simple $SiH_3X$ compounds. Again, examples of these trends and exceptions to them may both be found in the tables. They often prove useful in a comparison of several closely similar compounds.

Relatively few Raman studies have been carried out, for obvious reasons; precision Raman spectrometers are not plentiful, and preparative chemists are reluctant to prepare the necessary amounts of samples. For instance, the author needed to carry out seventeen separate preparations of tetrasilylhydrazine in order to produce an acceptably large sample (see Section V,A,5). These limitations are now not so severe, and it seems likely that soon Raman spectra will become semiroutine. It was feared at one time that photolysis of silane derivatives would produce cloudiness and spectra of poor quality, but this has proved to be overpessimistic. By working at low temperatures, good spectra have been obtained in a number of detailed studies; these will be referred to later.

### E. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A considerable amount of proton resonance data has been obtained, largely by Ebsworth and Turner (*123, 124*) and Van Dyke and MacDiarmid (*267*). A fairly complete selection of $\tau$ values and $J(^{29}\text{Si—H})$ coupling constants is assembled in Table X ($SiH_3X$, $SiH_2X_2$, and $SiHX_3$ derivatives) and Table XI ($Si_2H_5X$ derivatives). In almost all cases, the natural abundance of $^{29}Si$ (4.7 %) was sufficient for splitting (due to its nuclear spin of $\frac{1}{2}$) to be observed. Other coupling constants, for example $J(^1\text{H—}^1\text{H})$, have been much less studied. Danyluk (*98*) has shown that the sign of the $^{29}$Si—H coupling constant in $Me_2Si\mathit{H}Cl$ is negative.

Any general discussion of the significance of these values is beset with difficulties and pitfalls. It can be seen at once that the range of $\tau$ values is not very large, and also that there is a general inverse relation between the values of $\tau$ and $J(^{29}\text{Si—H})$. In general, too, the Si—H protons become less shielded as H in $SiH_4$ is replaced by more electronegative groups. In the early halcyon days of such studies (before about 1963), it was widely believed that values of proton chemical shifts were a valid measure of the electron distribution in the molecule. Any deviations from the expected deshielding behavior of electronegative substituents were imputed to $\pi$-bonding effects. Thus the *increase* in proton shielding in passing from $SiH_3F$ to $SiH_2F_2$ to $SiHF_3$ would be rationalized by assuming that $p_\pi$-$d_\pi$ donation increasingly outweighed inductive effects. Similarly, in the series of compounds $C\mathit{H}_3SiH_2X$, it was found that the methyl proton shielding *decreased* in the order $X = H > N > O > F$, an order consistent with the operation of inductive deshielding, but *increased* in the order $X = I < Br < Cl < F$, which might be rationalized in terms of steadily increasing $X \rightarrow Si$ $\pi$-donation.

Unfortunately, however, this kind of interpretation does not seem to be justified. In an important series of papers, Ebsworth and Turner (*123, 124*) and Ebsworth and Frankiss (*115, 116*) analyzed both chemical shift and coupling constant data in detail, and discussed possible mechanisms that could account for the trends observed. They pointed out inter alia that the behavior outlined in the previous paragraph, and attributed to $\pi$-bonding effects, was also observed in the case of corresponding $C\mathit{H}_3CH_2X$ $\beta$-proton chemical shifts, where no *d* orbitals can be invoked.

## TABLE X

N.M.R. DATA FOR $SiH_3X$, $SiH_2X_2$, AND $SiHX_3$ DERIVATIVES

| Compound | $\tau$ (ppm) (±0.01 unless otherwise stated) | $J(^{29}Si—H)$ (c/s) | Ref. |
|---|---|---|---|
| $SiH_4$ | 6.80 | 202.5 ± 0.2 | (*123*, *124*) |
| $SiH_3F$ | 5.24 | 229.0 ± 0.6 | |
| $SiH_2F_2$ | 5.29 ± 0.02 | 282 ± 3 | |
| $SiHF_3$ | 5.49 | 381.7 ± 1.5 | |
| $SiH_3Cl$ | 5.41 | 238.1 ± 0.2 | |
| $SiH_2Cl_2$ | 4.60 | 288.0 ± 0.4 | |
| $SiHCl_3$ | 3.93 | 362.9 ± 0.2 | |
| $SiH_3Br$ | 5.83 | 240.5 ± 0.3 | |
| $SiH_2Br_2$ | 4.83 | 289.0 ± 0.6 | |
| $SiH_3I$ | 6.56 ± 0.03 | 240.1 ± 0.2 | |
| $SiH_2I_2$ | 5.97 | 280.5 ± 0.2 | |
| $SiH_3CN$ | 6.18 | — | |
| $SiH_3NCO$ | 5.58 ± 0.02 | 231.5 ± 0.7 | (*118*) |
| $SiH_3NCS$ | 5.54 | 240 ± 2 | (*123*, *124*) |
| $SiH_3NCSe$ | 5.52 ± 0.02 | 243.2 ± 0.4 | (*119*) |
| $SiH_3N_3$ | 5.51 | 230.3 ± 0.5 | (*121*) |
| $SiH_3Me$ | 6.42 | 194.4 | (*234*) |
| $SiH_2Me_2$ | 6.18 | 190 | |
| $SiHMe_3$ | 6.00 | 190 | |
| $(SiH_3)_3N$ | 5.56 ± 0.02 | 212 ± 2 | (*123*, *124*) |
| $(SiH_3)_2NMe$ | 5.56 ± 0.02 | 212 ± 2 | |
| $SiH_3NMe_2$ | 5.66 ± 0.04 | 208 ± 2 | |
| $(SiH_3N)_2C$ | 5.55 | 225 ± 1 | (*117*) |
| $(SiH_3)_2O$ | 5.39 | 221.5 ± 0.2 | (*123*, *124*) |
| $SiH_3OMe$ | 5.48 | 216.2 | (*267*) |
| $(SiH_3)_2S$ | 5.64 ± 0.02 | 224.0 ± 0.3 | (*123*, *124*) |
| $SiH_3SCF_3$ | 5.58 ± 0.02 | 234 ± 1 | (*105*) |
| $(SiH_3)_2Se$ | 5.88 ± 0.04 | — | (*123*, *124*) |
| $SiH_3SeCF_3$ | 5.70 | — | (*128*) |
| $SiHI_3$ | 5.51 | 325.1 | (*75*) |
| $SiH_2(NMe_2)_2$ | 5.62 | 217.6 ± 0.4 | |
| $SiH(NMe_2)_3$ | 5.87 | 235 ± 1 | |
| $SiH_2(OMe)_2$ | 5.58 | 247.6 ± 0.6 | |
| $SiH(OMe)_3$ | 5.91 | 297.9 [illegible] 0.3 | |
| $SiH_2(OSiH_3)_2$ | 5.46 ($SiH_2$)<br>5.33 ($OSiH_3$) | 256.6 ± 0.3 | |
| $SiH(OSiH_3)_3$ | 5.82 ($SiH$)<br>5.34 ($OSiH_3$) | 316.0 ± 0.5 | |
| $SiH_3PH_2$ | 6.27 | 204 ± 1 | (*108*) |
| $SiH_3AsH_2$ | 6.33 | 203 ± 1 | |

They therefore argued that, until a convincing mechanism of shifts and coupling constants can be put forward that accounts satisfactorily for the observed trends in silicon and carbon compounds, it is premature to single out certain changes and relate them to the presence of *d* orbitals on silicon.

Such considerations are relevant when considering an experiment described as an experimental test of Si—N $\pi$-bonding (*222*). The $^{15}N—H$ spin coupling in $Me_3Si^{15}NHPh$ was compared with that in (a) $^{15}NH_4^+$ and $Ph^{15}NH_2$ (both considered as examples of $sp^3$ hybridization), and (b) $C_5H_5^{15}NH^+$ ($sp^2$ hybridization). It was argued that, if Fermi contact interaction were the dominant coupling mechanism, changes in *s* character in the bond from N to H would be observed as changes in $J(^{15}N—H)$. In the event, the observed coupling was similar to examples (a) and distinctly different from (b). This means either that there is no significant Si—N $\pi$-bonding in $Me_3SiNHPh$ or that $J(^{15}N—H)$ is not an effective measure of such bonding, but it does not seem possible to say more at this stage.

TABLE XI

N.M.R. DATA FOR DISILANYL COMPOUNDS[a]

| | $\tau$ (ppm) | | $J(^{29}Si—H)$ | |
|---|---|---|---|---|
| X in $Si_2H_5X$ | $SiH_3$ | $SiH_2$ | $SiH_3$ | $SiH_2$ |
| H | 6.74 | — | 196.2 | — |
| F | 6.73 | 4.70 | — | 217.0 |
| Cl | 6.59 | 5.14 | 201.4 | 221.2 |
| Br | 6.41 | 5.70 | 202.6 | 225.8 |
| I | 6.14 | 6.61 | 204.6 | 224.4 |
| $OSi_2H_5$ | 6.80 | 4.88 | 194.4 | 214.8 |
| $OSiH_3$ | 6.78[b] | 4.87 | 192.8[b] | 210.6 |
| $N(Si_2H_5)_2$ | 6.72 | 5.16 | — | 205.2 |
| $NMe_2$ | 6.85 | 5.26 | — | 199.8 |

[a] Van Dyke and MacDiarmid (*267*).

[b] Refers to $SiH_3$ of $Si_2H_5$ group.

The disilanyl compounds in Table XI show behavior somewhat similar, as far as the $SiH_2$ protons are concerned, to that of silyl compounds. The same inverse relationship between $\tau$ values and $J(^{29}Si—H)$ values is roughly obeyed, and again there is no simple connection between chemical shift and electronegativity. The difference, $\Delta$, given by $[\tau(SiH_3) - \tau(SiH_2)]$, between chemical shifts of the two different sets of

Si—H protons decreases with decreasing electronegativity of the substituent X; a similar effect is observed in $CH_3CH_2X$ and $CH_3SiH_2X$ compounds (*97*, *116*). It is interesting that, in $SiH_3SiH_2I$, $\Delta$ is negative, i.e., the $SiH_2$ resonance is to high field of the $SiH_3$ resonance. Van Dyke and MacDiarmid (*267*), in an extensive discussion of these and other effects in disilanyl derivatives, suggest that this is compatible with a very low effective electronegativity of iodine in $Si_2H_5I$, which may be related to $\pi$-bonding effects in the Si—I bond. They also suggest that certain observed trends may indicate interactions across the Si—Si bond of a type not found in ethyl compounds. It is tempting to ascribe these to Si—Si $\pi$-interaction of the type suggested by Mulliken (see Section II,B), but in view of the discussion in the earlier part of this section, such suggestions must be viewed with some caution.

Most of the values in Tables X and XI refer to moderately dilute solutions, and it is found generally that dilution shifts are small. In particular, dilution shifts for both proton and $^{19}F$ resonances in the fluorosilanes $SiH_{4-x}F_x$ ($x = 1$–$3$) are almost within the limits of error for the determinations (*124*). This does not support the idea that association of these compounds in the liquid phase is significant (see Section II,G). An exception is found in the case of dimethylaminosilane, $Me_2NSiH_3$, in which the proton dilution shift is considerable. There is other evidence for the association of this compound in condensed phases (see Section V,A).

Apart from studies of $^{19}F$ resonance where appropriate, very few other nuclei in silane derivatives have been studied by this technique. Holzman *et al.* (*174*) examined the $^{29}Si$ resonances of a number of compounds, but found that intrinsically weak absorption and severe quadrupole broadening were limiting factors. The latter effect was particularly troublesome when N, Cl, Br, or I was attached to silicon. It appears that only one study of $^{15}N$ attached to silicon (referred to earlier) and none of $^{17}O$ have been made, although the results would be of great interest.

### F. USE OF OTHER PHYSICAL METHODS

Microwave spectroscopy has been of value in providing precise bond parameters for pseudohalides such as $SiH_3NCS$ and $SiH_3CN$ (see Section IV,B). Estimates of barrier heights to internal rotation have also been obtained; for example, Schwendeman and Jacobs (*236*) quote values (in kcal mole$^{-1}$) of 2.55 for $SiH_3CH_2Cl$ and 1.67 for $SiH_3CH_3$.

Very few diffraction studies have been reported in recent years; the electron diffraction experiments on $(SiH_3)_3N$, $(SiH_3)_3P$, $(SiH_3)_3As$, $(SiH_3)_2O$, and $(SiH_3)_2S$ are referred to (Sections V,A,5, V,B,2, and VI,C), but no X-ray or neutron diffraction studies of silicon hydride derivatives have been carried out. The last-named method is of particular interest, because determination of hydrogen positions in solid silyl compounds, for example, could tell us much about the effects of intermolecular interactions on stereochemistry.

Dipole moments are often difficult to interpret, but the zero moment found for $(SiH_3)_3N$ (*269*) in the gas phase gives unequivocal confirmation of the planarity of the $NSi_3$ skeleton. The same authors in 1964 reported a similar study of $(SiH_3)_2O$ and $SiH_3OCH_3$ (*270*). The values found (0.24 and 1.17 D, respectively) were compared with the moment of $(CH_3)_2O$ (1.31 D) and discussed in terms of the bond angles in these compounds (see Section VI,C) and of $p_\pi$-$d_\pi$ bonding between silicon and oxygen. The Si—H bond moment has been mentioned (Section II,B); measurements of the Si—N bond moment (which is small and variable) have been made by Schaarschmidt (*232*), and are consistent with a situation where the $\sigma$-inductive moment is opposed by a moment due to $\pi$-donation in the opposite direction.

Interesting information has recently been deduced by Bell and Walsh (*58*) from the vacuum ultraviolet spectra of silyl compounds. Although little detail could be seen, the spectra of $SiH_3Cl$, $(SiH_3)_2O$, $(SiH_3)_3N$, and $(SiH_3)_2NMe$ were all shifted to shorter wavelengths relative to those of the corresponding methyl compounds. It therefore appears that the silyl compounds possess higher first ionization potentials. Although this would not be expected from the relative electronegativities of silicon and carbon, it may be rationalized in terms of delocalization of lone-pair electron density onto silicon by $d_\pi$-$p_\pi$ interaction.

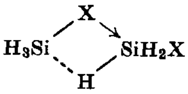
## G. DISPROPORTIONATION

One of the most obvious and annoying features of the behavior of silyl compounds is their readiness to disproportionate. When almost any such compound is allowed to remain in the liquid phase, the following reaction occurs:

$$2SiH_3X \rightarrow SiH_4 + SiH_2X_2 \qquad (1)$$

It may be slow, as in the case of $SiH_3I$ at room temperature, or rapid, as in the case of $SiH_3NMe_2$, $SiH_3OMe$, and $SiH_3F$; of course other modes of decomposition may supervene, as in the case of $SiH_3CN$. Further decomposition may occur, giving rise to $SiHX_3$ and $SiX_4$, if X is not too large. The reaction is generally extremely slow in the gas phase.

MacDiarmid (*197*) suggested that such reactions might involve a bimolecular complex of the type shown. Initial coordination of X to Si would provide a relatively easy reaction path via the four-center intermediate shown; the ability of silicon to increase its coordination above 4, as discussed earlier, will not make it necessary for bond-breaking and bond-making processes to be synchronous (although they may be). The formation of a complex of this kind will clearly be more difficult (a) in the gas phase, and (b) if X is either of low electronegativity or is heavily involved in π-bonding with silicon.



This kind of reaction has been known for almost exactly 100 years; Friedel and Ladenburg (*143*) observed that triethoxysilane gave silane and tetraethoxysilane:

$$4SiH(OEt)_3 \xrightarrow{OEt^-} SiH_4 + 3Si(OEt)_4 \qquad (2)$$

In their case, the reaction had to be catalyzed by a base, ethoxide ion, and it is now known that a wide variety of bases will catalyze the disproportionation of simple silyl compounds. A full discussion of this effect in relation to $(SiH_3)_3N$, $(SiH_3)_2NR$ (R = H, Me, Ph), $Si_2H_5NMe_2$, $(SiH_3)_2O$, and $(SiH_3)_2S$ will be given (Sections V,A,4 and VI,B).

Acid catalysis of reaction (1) is also possible. Stock and Somieski (*249*) found that aluminum chloride greatly accelerated the disproportionation of chlorosilane, and more recently Russell (*228*) in a series of papers has thoroughly discussed the behavior of compounds of the type $Me_3SiR$ (R = H, Et, Ph). A wide variety of conditions, solvents, and Lewis acids was employed, and it was concluded that aluminum halides were among the most effective catalysts, and that mechanisms involving siliconium ions or organometallic intermediates were unlikely. The most probable reaction intermediate was a complex involving two molecules of the substituted silane and one $AlX_3$ molecule. The formation of this complex could be assisted by the presence of a weakly donating solvent (e.g., benzene) or by small amounts of a basic co-catalyst (e.g., trimethylamine or water).

Free radical initiators may also speed disproportionation. Nelson *et al.* (*212*) found that diphenylsilane (which is reasonably stable thermally alone) could be attacked rapidly by ultraviolet radiation or by organic peroxides at 130°. They postulated a mechanism in which a silyl radical, formed either by Si—H cleavage or by a hydrogen abstraction process, rapidly abstracted hydrogen or phenyl from another molecule of $Ph_2SiH_2$:

$$R_2 \rightarrow 2R\cdot \ (initiator) \tag{3}$$

$$R\cdot + HSiHPh_2 \rightarrow RH + \cdot SiHPh_2 \tag{4}$$

$$\cdot SiHPh_2 + PhSiH_2Ph \rightarrow SiHPh_3 + \cdot SiH_2Ph \tag{5}$$

It may be noted that silyl radicals are extremely elusive, and have not so far been detected by methods appropriate for methyl radicals. As will be discussed (Section III,C), they appear to remove hydrogen extremely rapidly from various substrates.

Only by $\gamma$-irradiation of $SiH_4$ in an inert matrix at 4°K were Morehouse *et al.* (*205*) able to demonstrate the presence of trapped $SiH_3$ radicals by e.s.r. spectroscopy. It appears that, unlike $CH_3$, the $SiH_3$ radical is pyramidal.

The three types of disproportionation catalyst referred to above are paralleled by the three types of catalyst that have been used to promote the addition of Si—H to multiple bonds. These are bases (*61*), metal salts (e.g., *50, 112*), and free radical initiators (e.g., *237*). The situation is often complicated by the fact that reaction seems to proceed simultaneously by more than one mechanism.

## III. The Silanes, $Si_nH_{2n+2}$

### A. PREPARATION AND SEPARATION

The classical method for the preparation of large quantities of silanes is by the action of dilute hydrochloric acid on magnesium silicide. In this way Stock and Somieski (*248*) prepared and characterized $Si_nH_{2n+2}$ ($n = 1$–4), and obtained a less volatile mixture of presumed isomers of $Si_5H_{12}$ and $Si_6H_{14}$, which they were unable to separate. This method still represents a good way of making large quantities of the higher silanes;

TABLE XII

THE SILANES, $Si_nH_{2n+2}$

| Compound | M.P. | B.P. | $d$ (gm/ml) | $\Delta H_{vap}$ (cal mole$^{-1}$) | $\Delta S_{vap}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|
| $SiH_4$ | −185° | −111.9° | 0.68 (−185°) | 2982 | 18.4 | (*154, 280*) |
| $Si_2H_6$ | −132° | −14° | 0.69 (−25°) | 5200 | 20.1 | (*154*) |
| $Si_3H_8$ | −114.8° | 53° | 0.74 (0°) | 6783 | 20.8 | (*154, 161*) |
| $Si_4H_{10}$ | − 84° | 108° | 0.79 (0°) | 8260 | 21.7 | (*154, 208*) |

Fehér *et al.* (*139*) used an adaptation of it to prepare more than 300 ml of a liquid mixture of higher silanes. In the following paper (*140*), the same authors describe their most ingenious set of techniques for handling such reactive compounds. Special hypodermic syringes with protected needles are used to transfer the liquid silanes from one nitrogen-filled vessel to another via soft rubber septum caps that act as self-sealing closures. Attachments to the vacuum system that are sealed in the same way allow transfer of silanes to and from the usual fractionation line and storage vessels. Courage appears to be a prerequisite for such procedures.

Other metal silicides are known to contain varied arrangements of chains and rings of silicon atoms (*276*), and it seems likely that their hydrolysis would yield a rather different distribution of silanes from that afforded by $Mg_2Si$. In a preliminary note, Borer and Phillips (*63*) described the separation of twenty-one components derived from $Mg_2Si$ and phosphoric acid; they used a vapor phase chromatography (v.p.c.) column containing silicone fluid on Celite, and showed that the products ranged up to $Si_8H_{18}$, and included a number of isomers of the higher members. Fehér and Strack (*138*) reported a similar separation, using a column filled with squalane on kieselguhr.

In a further report, Timms and Phillips (*262*) described the preparation of a mixture of silanes from silicon monoxide and 10 % hydrofluoric acid. The products were again separated by v.p.c., and the distribution was shown to be rather different from that obtained before:

| | Relative amounts ($Si_3H_8$ = 100) | | | | |
|---|---|---|---|---|---|
| Source of silanes | $Si_3H_8$ | $n$-$Si_4H_{10}$ | $i$-$Si_4H_{10}$ | $n$-$Si_5H_{12}$ | $i$-$Si_5H_{12}$ |
| $Mg_2Si$ | 100 | 36 | 2.5 | 12 | 4.5 |
| SiO | 100 | 43 | 5.5 | 20 | 8 |

A most useful method for the production of higher silanes is that employing a silent discharge of the ozonizer type. Spanier and MacDiarmid (*240*) first used this to make $Si_2H_6$, $Si_3H_8$, and crude $Si_4H_{10}$ from silane. Gokhale and Jolly (*155*) and Gokhale *et al.* (*158*) used a similar method to prepare $n$- and $i$-$Si_4H_{10}$, which were separated by gas chromatography. Evidence for silanes up to $Si_8H_{18}$ was obtained. Finally, in a recent paper, Andrews and Phillips (*14*) describe in detail the separation of a mixture of silanes, germanes, and silicon-germanium hydrides, prepared by the action of a silent discharge on a mixture of $SiH_4$, $Si_2H_6$, and $GeH_4$. Besides the mixed hydrides (discussed in Section VIII,A) they were able to identify *neo*-$Si_5H_{12}$, $n$-$Si_6H_{14}$, $n$-$Si_7H_{16}$, and branched-chain $Si_6$ and $Si_7$ hydrides. Identification was based partly on a consideration of column retention times and partly on the behavior of the silane when passed into a 5-Å molecular sieve. Only straight-chain hydrides were removed.

Reduction of tetrachlorosilane by lithium aluminum hydride in ether remains the most favored way of making monosilane in the laboratory. Disilane (*62*) and trisilane (*260*) can be made similarly in quite good yields from the corresponding chlorosilane in a high-boiling ether. Commercial interest in monosilane (for the production of transistor-grade silicon by its pyrolysis) has led to a search for cheaper large-scale methods. Silica and lithium aluminum hydride give a 7 % yield of silane when heated to 200° (*275*), while the high-pressure hydrogenation of a mixture of silica, aluminum, and aluminum chloride at moderate temperatures (*175*) produces yields up to 76 %.

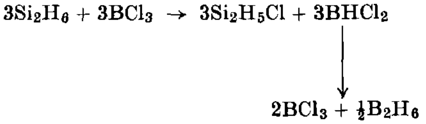
Like molecular sieves, the formation of clathrate compounds can be an effective way of differentiating between straight-chain and branched isomers. In an interesting paper by Müller and Meier (*208*), it is reported that both urea and thiourea form clathrate compounds with $n$-$Si_nH_{2n+2}$ when $n$ is $\geqslant 3$. These derivatives become more stable toward oxidation and hydrolysis as $n$ increases; the $Si_5H_{12}$-urea complex is stable in air at room temperature.

## B. REACTIVITY

One of the few recent reports concerning the chemical properties of silane itself comes from Hagenmuller and Pouchard (*165*). They give a detailed description of the reaction of sodium and sodium hydride with silane under various conditions. Those reactions that lead to the production of $NaSiH_3$ are dealt with later (Section VIII,A), but it was also shown that sodium in liquid ammonia reacts with silane to give sodium amide and $Si(NH)_2$ (a polymer). At 350°, a sodium film reacts with silane to form sodium hydride and NaSi.

A new, detailed study of the pyrolysis of silane has been reported by Purnell and Walsh (*220*). They show that an initial reaction accompanied by no overall pressure change yields hydrogen, disilane, and a trace of trisilane as the volatile products; its activation energy is 56 kcal $mole^{-1}$. Later, when 10–20 % of the silane has decomposed, the pressure rises and the activation energy falls to 51 kcal $mole^{-1}$. The authors suggest that initially the formation of $SiH_2$ radicals derived from the unimolecular reaction, $SiH_4 \rightarrow SiH_2 + H_2$, may be an important step. In the later stages, loss of hydrogen from solid (polymeric) silicon hydrides may be the rate-determining process.

Even now, very little is known of the reactivity of disilane and the higher silanes. It seems fairly clear, however, that reaction often involves Si—H rather than Si—Si bonds, and that it proceeds more readily than with silane itself. When $BCl_3$ is mixed with silane there is no immediate reaction, although diborane may be produced by heating (*131*) or by introducing methyl radicals (*233*). Disilane and $BCl_3$ react together readily, however, to give diborane and disilanyl chloride (*265*):



$$\begin{tikzcd} 3Si_2H_6 + 3BCl_3 \arrow[r] & 3Si_2H_5Cl + 3BHCl_2 \arrow[d] \\ & 2BCl_3 + \tfrac{1}{2}B_2H_6 \end{tikzcd} \quad (6)$$

$PCl_3$ behaves similarly, giving disilanyl chloride and phosphine (*38*), but $BF_3$ and $PF_3$ do not react with disilane under these conditions. The very mild conditions under which reaction (6) proceeds make it possible that other chloro derivatives of higher silanes may be prepared in this way.

Analogously, $BBr_3$ reacts with $Si_2H_6$ to give not only $Si_2H_5Br$ but also *sym-* and *unsym*-dibromodisilane and the more symmetrical tri- and tetrabromodisilanes (*110*). Heated silver halides have also been used by Hollandsworth *et al.* (*173*) to halogenate disilane.

It is interesting that disilane, like hexahalodisilanes and many silyl derivatives, will undergo base-catalyzed disproportionation (cf. Section II,G). Morrison and Ring (*206*) have shown that hydride ions and even lithium chloride are effective catalysts in diglyme solution; they suggest that a silene intermediate may be involved.

Studies of vibrational spectra of the higher silanes have now become feasible; Spanier and MacDiarmid (*240*) reported the infrared spectrum of trisilane, while Fehér and Fischer (*137*) published infrared and Raman spectra of trisilane and *n*- and *i*-tetrasilane.

## C. PHOTOLYSIS

In 1936 Emeléus and Stewart studied the photolysis of silane, and found that, in the presence of mercury, hydrogen and a solid of composition $(SiH_{0.91-0.48})_x$ were produced (*134*). This reaction has recently been re-examined with important results (*215*). Silane at 1-cm pressure and 25°, with a drop of mercury present, was irradiated with ultraviolet light (2537 Å) from a helical source of high intensity. After 5 seconds, the products were led into a mass spectrometer and found to be hydrogen (3.8 %), $Si_2H_6$ (1.7 %), and $Si_3H_8$ (0.2 %) together with traces of $Si_4H_{10}$ and $Si_5H_{12}$. Simultaneously a film of solid was formed on the walls of the tube; with longer irradiation a stationary state was reached. If the tube was then emptied of volatile products, filled with hydrogen, and re-irradiated, the film was removed and a mixture of volatile silanes was produced. The system seems to involve a number of radical chain processes; it is suggested that the primary steps are:

$$SiH_4 + Hg(^3P_1) \rightarrow SiH_2 + H_2 + Hg(^1S_0) \quad (7)$$

$$\rightarrow SiH_3 + H + Hg(^1S_0) \quad (8)$$

When an equimolar mixture of $SiH_4$ and $SiD_4$ was irradiated, the resulting hydrogen consisted approximately of $H_2$ (40%), HD (40%), and $D_2$ (20%). Addition of ethylene (up to 10% molar) hardly altered the yield of hydrogen or its isotopic distribution. This surprising result implies that silane is much more efficient as a radical scavenger than ethylene. This conclusion has been confirmed by extensive studies of the photolysis of $SiD_4$ and the methylsilanes by Nay *et al.* (*211*). In the same laboratory, Yarwood *et al.* (*279*) estimated that the radical-quenching cross section of silane is about 400 times that of methane. Furthermore, Kerr *et al.* (*184, 185*) measured the rate of hydrogen abstraction by methyl radicals from $SiHCl_3$, etc., at various temperatures. They infer that the rapid quenching results from a high *A* factor in the Arrhenius equation rather than from an especially small activation energy.

If silanes are photolyzed in the presence of other substances, it may be possible to isolate silyl derivatives from the products. Thus, mixtures of $SiH_4$ with $GeH_4$ or MeI have been shown to yield $SiH_3GeH_3$ or $MeSiH_3$ in the presence of mercury vapor (*153*). The extension of such experiments to systems containing $Si_2H_6$ is an obvious step.

## IV. Halogen and Pseudohalogen Derivatives of Silanes

### A. HALIDES

From a preparative point of view, the recent development of routes to halosilanes that do not involve silane itself is of considerable importance. Both Fritz and Kummer (*149–151*) and Aylett and Ellis (*28*) have described preparations based on the cleavage of phenylsilanes, of which the following are typical:

$$Ph_2SiH_2 + 2HCl \rightarrow SiH_2Cl_2 + 2PhH \quad (9)$$

$$ClC_6H_4SiH_3 + HI \rightarrow SiH_3I + PhCl \quad (10)$$

The phenylsilanes are readily made from the corresponding Si—Cl compounds by reduction with lithium aluminum hydride; the chlorination of the phenyl ring in Eq. (10) is an important preliminary step, as otherwise the product mixture of iodosilane and benzene is very hard to separate completely.

Another important development has been the preparation of the monohalogen derivatives of disilane (Table XIII). First, $Si_2H_5I$ was prepared by treating disilane with hydrogen iodide and aluminum iodide for $2\frac{1}{2}$ hours at room temperature (*272*). Similar preparations of the chloride and bromide were accomplished later (*2*). The bromide and chloride were also prepared, in that order, by allowing $Si_2H_5I$ vapor to steam over an appropriate heavy metal salt (*90*, *273*). For example:

TABLE XIII

DISILANYL HALIDES

| Compound | M.P. | B.P. | $d$ (gm/ml) | $\Delta H_{vap}$ (cal mole$^{-1}$) | $\Delta S_{vap}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|
| $Si_2H_5Cl$ | −112° | 40° | — | 7000 | 22.4 | (*90*) |
| $Si_2H_5Br$ | — | 69° | — | 7590 | 22.1 | (*273*) |
| $Si_2H_5I$ | −86° | 103° | 1.764 (0°) | 8087 | 21.5 | (*272*) |

$$Si_2H_5I + AgBr \rightarrow Si_2H_5Br + AgI \qquad (11)$$

Disilanyl fluoride was made by the cleavage of $(Si_2H_5)_3N$ with $BF_3$ (*1*) (see Section V,A,3). The disilanyl halides were then employed in the preparation of such derivatives as $(Si_2H_5)_3N$ and $(Si_2H_5)_2M$ ($M = O, S$) (as discussed in Sections V,A,1 and VI,A).

Many examples of reactions such as Eq. (11) are known; MacDiarmid (*197*) has proposed that a conversion series for silyl compounds can be set up such that, if A and B are two members of the series, and A comes before B, the silyl derivative of A will react with the silver salt of B to give the silyl derivative of B. An augmented form of this series (which is only approximately followed) is:

$$\mathrm{Co(CO)_4} \longrightarrow \mathrm{I} \longrightarrow \mathrm{Se} \longrightarrow \mathrm{S} \longrightarrow \left.\begin{matrix}\mathrm{Br}\\ \mathrm{NCSe}\\ \mathrm{SCF_3}\end{matrix}\right\} \longrightarrow \left.\begin{matrix}\mathrm{Cl}\\ \mathrm{CN}\end{matrix}\right\} \longrightarrow \mathrm{CN_2} \longrightarrow \mathrm{NCS}$$

$$\longrightarrow \mathrm{NCO} \longrightarrow \mathrm{O} \longrightarrow \mathrm{F}$$

So far as the Group VI and VII elements are concerned, this is approximately an order of increasing electronegativity.

## B. PSEUDOHALIDES

The silyl pseudohalides, almost all of which have been made via a conversion reaction (Section IV,A), are shown in Table XIV. In their pre-

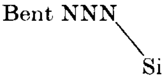
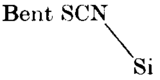
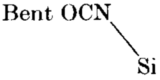
TABLE XIV

Pseudohalide Derivatives of Silane

| Compound | M.P. | B.P. | *d* (gm/ml) | $\Delta H_{\text{vap}}$ (cal mole$^{-1}$) | $\Delta S_{\text{vap}}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|
| $SiH_3CN$ | +32° | 49.6° | — | 7169 | 22.2 | (*196*) |
| $SiH_3N_3$ | −82° | 26° | — | 6680 | 22.3 | (*121*) |
| $SiH_3NCO$ | −89° | 18° | — | 6540 | 22.5 | (*118*) |
| $SiH_3NCS$ | −52° | 84° | 1.05 (20°) | 8923 | 25.0 | (*196*) |
| $SiH_3NCSe$ | −15° | 111° | — | 10,800 | 28 | (*119*) |
| $(SiH_3N)_2C$ | −75° | 85° | — | 8100 | 22.6 | (*117*) |

TABLE XV

Structural Studies on Pseudohalogen Derivatives

| Compound | Shape | Remarks | Method | Ref. |
|---|---|---|---|---|
| $SiH_3CN$ | Linear SiCN | *n*-Cyanide | IR<br>Microwave | (*192*)<br>(*207, 238*) |
| $SiH_3N_3$ |  Bent NNN<br>Si | — | IR<br>Microwave | (*121*)<br>(*130*) |
| $SiH_3NCS$ | Linear SiNCS | Si-N, 1.71 Å | Microwave<br>IR/Raman | (*177, 178*)<br>(*129*) |
| $SiH_3NCO$ | Linear SiNCO (probably) | — | Microwave<br>IR | (*130*)<br>(*118*) |
| $(SiH_3N)_2C$ | Linear SiNCNSi | Di-imide | IR/Raman | (*120*) |
| $SiMe_3NCS$ |  Bent SCN<br>Si | Si-N, 1.78 Å | ED | (*186*) |
| $SiMe_3NCO$ |  Bent OCN<br>Si | — | ED | |

paration it is usually helpful and sometimes essential to dilute the halosilane vapor with nitrogen when passing it over the metal salt. An exception is silyl azide—this was made by cleavage of a silylamine (Eq. 12) in dibutyl ether (*121*):

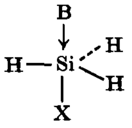
$$4HN_3 + (SiH_3)_3N \rightarrow 3SiH_3N_3 + NH_4N_3 \qquad (12)$$

Structural studies on these compounds have attracted considerable attention; results are collected in Table XV. We may note that while silyl azide [like methyl azide (*194*)] is bent, silyl isocyanate and silyl isothiocyanate [unlike their methyl analogs (*52*, *136*)] have a linear skeleton. This can be thought of as a change in hybridization from $sp^2$ to $sp$ at the nitrogen atom in $SiH_3NCX$; the amount of energy for this process (which is not known accurately) must be provided as a result of increased $p_\pi$-$d_\pi$ overlap between nitrogen and silicon. Linnett (*190*) has discussed these compounds in terms of the number of possible valence bond canonical forms that can be written for them. A restriction is imposed on the formal charges that may be placed on various atoms: nitrogen is limited to the range $+1$ to $-\frac{1}{2}$, while oxygen and sulfur may be in the range $+1$ to $-1$. Silicon is allowed to form more than four electron-pair bonds, while carbon of course is not. He finds that there are four allowed linear forms for $H_3SiNCX$ ($X = O, S$) but none for $H_3SiN_3$. All but one of the forms for $H_3CNCX$ and all for $H_3CN_3$ are bent. Linnett emphasizes that the difference between —NCX and —NNN is basically due to the lower nuclear charge of nitrogen as compared to oxygen, and nitrogen's unwillingness to accept a large excess negative charge.

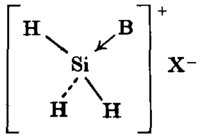
It can also be seen that the trimethylsilyl derivatives, $Me_3SiNCX$, show less evidence of $\pi$-bonding than the hydride derivatives, $SiH_3NCX$. They are bent, not linear, and the Si—N distances are larger.

## C. ADDUCTS

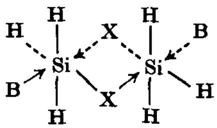
Halosilanes have been known for many years to form adducts with tertiary amines (*41*, *132*), and it is interesting to consider various structural possibilities for such compounds. A 1:1 adduct, $SiH_3X \cdot B$ (B = base), may be molecular and five-coordinate (V), ionic and four-coordinate (VI), halogen-bridged and six-coordinate (VII), or some more complex combination of these possibilities. A 1:2 adduct, $SiH_3X \cdot 2B$, may most simply be molecular and six-coordinate (in *cis* and *trans* forms)



(V)



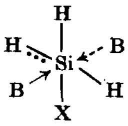
(VI)



(VII)

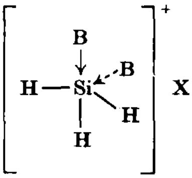
(VIII), or ionic and five-coordinate (with various isomers) (IX). Similar possibilities for silicon tetrahalides have been discussed by Beattie (*53*).

Aylett and Sinclair (*39*) and Campbell-Ferguson and Ebsworth (*73, 74, 74a*) have recently provided a good deal of fresh information concerning these adducts. Pyridine and various 2-substituted pyridines reacted readily with iodosilane to form adducts $SiH_3I \cdot 2B$. No 1 : 1 adducts could be made. The pyridine compound dissolved in an excess of pyridine or in acetonitrile to give conducting solutions, in which it behaved as a weak or a strong electrolyte, respectively. When the adduct $SiH_3I \cdot 2coll$ (coll = collidine = 2,4,6-trimethylpyridine) reacted with trimethylamine, the substituted pyridine was displaced and, in the absence of solvent, $SiH_3I \cdot NMe_3$ was formed. When acetonitrile was present, a 1:2 adduct $SiH_3I \cdot 2NMe_3$ was formed. Both the 1 : 1 and 1 : 2 adducts gave conducting solutions in acetonitrile, while the 1 : 2 adduct gave a sublimate of the 1 : 1 adduct on gentle heating. α,α′-Bipyridyl and iodosilane gave a 1 : 1 adduct that behaved similarly to $SiH_3I \cdot 2py$.



[6] *trans*

(VIII)



[5] axial-equatorial

(IX)

With no solvent, trimethylamine formed a 1 : 1 adduct with $SiH_3X$ (X = Cl, Br, I) and the extent of dissociation on heating increased from the iodide to the chloride (*38*). Thus the iodide forms the strongest adduct. When the 1 : 1 adduct with iodosilane was dissolved in acetonitrile, and the solvent subsequently removed, Campbell-Ferguson and Ebsworth noted that $SiH_3I \cdot 2NMe_3$ remained behind. They also reported inter alia that the infrared spectra of the solid adducts $SiH_3X \cdot 2py$ (X = Br, I) were closely similar in the region down to 250 $cm^{-1}$, implying that similar groupings were present in each.

All this evidence is consistent with the idea that the adducts can be formulated as $(Me_3NSiH_3)^+I^-$ and $(B_2SiH_3)^+I^-$, where $B = NMe_3$, pyridine, etc., and $B_2$ = bipyridyl. In solution it seems probable that the mono- and bistrimethylamine cations exist in equilibrium. The true nature of the solids can be established only by diffraction experiments, however; a small amount of $Si^{\delta+}$—$I^{\delta-}$ charge separation in a structure still essentially that of a five- or six-coordinate molecular adduct might give rise to the behavior observed. In particular, ionization in donor solvents would be anticipated, and the Si—X infrared stretching frequencies could be shifted to such low values that they were not observed, particularly in the case of iodides.

The difficulties inherent in the use of infrared spectroscopy to establish adducts' structures are revealed in a salutary study by Beattie and Parrett (*54*). A simple valence force field (SVFF) calculation on the adduct $SiH_3I \cdot NMe_3$ showed that there are three vibrational frequencies, covering a range of more than 700 $cm^{-1}$, to which the Si—N stretch contributes. This mixing makes it hazardous or impossible to assign absorption bands to vibrations of particular bonds or groups.

The adduct $SiH_3I \cdot$bipyridyl mentioned above deserves comment. Recently the analogous compound $Ph_3SiI \cdot$bipyridyl was prepared by Corey and West (*84*), who refer to it as containing the siliconium ion $(bipy \cdot SiPh_3)^+$, with five-coordinate silicon. While this ion may indeed be present in solution (and perhaps in the solid), the name "siliconium ion" seems unfortunate; as Beattie and Webster (*55*) point out, ions of this kind are usually thought of as derivatives of quaternary $N^+$, and by analogy $H_3\overset{+}{C} \leftarrow NMe_3$ is certainly not a conventional representation of the tetramethylammonium ion.

The ditertiary amine $CH_2(NMe_2)_2$ forms a 1:2 adduct with excess iodosilane, while an equimolar amount of iodosilane produces a 1:1 complex that may be chelate (*36*). The corresponding amine with no bridging methylene group, namely, tetramethylhydrazine, $Me_2NNMe_2$, gives only a 1:1 adduct with iodosilane under the same conditions (*18*).

The interaction of much weaker bases, such as ethers and thioethers, with iodosilane has also been investigated by Aylett (*21*). It is found that the order of donor ability is:

$$(CH_2)_4O > (CH_3)_2O > (CH_3)_2S; \qquad (CH_2)_4O \gg (CH_2)_4S$$

Secondary reactions such as disproportionation of iodosilane and ether cleavage occur readily even at low temperatures, but it is clear that $SiH_3I$, unlike $BH_3$, uniformly adopts so-called Class (a) behavior (*3*) and forms stronger complexes with oxygen than with sulfur. A similar conclusion can be drawn from earlier results (*41*), which show that toward iodosilane the order of donor strength of Group V donors is $NMe_3 > PMe_3 > AsMe_3$.

It will be seen that iodosilanes have received the most attention; however, it appears that bromosilanes show a similar tendency to yield ionic adducts, while fluorosilanes may produce molecular complexes. The behavior of chlorosilanes is not yet certain, but Campbell-Ferguson and Ebsworth (*74a*) have made the interesting suggestion that adducts of

$SiH_3Cl$ and $SiH_2Cl_2$ may contain chlorine-bridged polymeric cations. When formation of halide ions and halogen bridging are both impossible, as in the case of the liquid adduct $CHF_2CF_2SiH_3 \cdot NMe_3$, a simple molecular species is formed (*83*).

## V. Silane Derivatives with Group V Elements

### A. SILICON-NITROGEN COMPOUNDS

### 1. *Preparation*

A wide range of silicon hydride derivatives containing Si—N bonds has now been prepared (Table XVI), and it is possible to make a number of interesting comparisons between them. While their boiling points are not particularly remarkable (apart from being rather low for compounds of such high molecular weight), melting points are uniformly very low, with one striking exception. This is dimethylaminosilane, already referred to (Section II,B) as a compound that seems to be associated in the solid phase.

TABLE XVI

SILICON HYDRIDE DERIVATIVES WITH NITROGEN

| Compound | M.P. | B.P. | *d* (gm/ml) | $\Delta H_{vap}$ (cal mole$^{-1}$) | $\Delta S_{vap}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|
| $(SiH_3)_2NH$ | −132° | 36° | — | 5560 | 18.0 | (*33*) |
| $(SiH_3)_3N$ | −106° | 52° | 0.895/−106° | — | — | (*250*) |
| $(SiH_3)_2NMe$ | −124° | 32° | — | 6770 | 22.2 | (*132*) |
| $(SiH_3)_2NEt$ | −127° | 66° | — | — | — | |
| $(SiH_3)_2NPh$ | −69° | 189° | 0.801/22° | 8320 | 18.0 | (*32*) |
| $SiH_3NMe_2$ | + 2.2° | 19° | 0.700/20° | 6340 | 21.8 | (*29, 257*) |
| $SiH_3NEt_2$ | −149° | 78° | 0.751/20° | 7410 | 21.2 | (*29*) |
| $SiH_3NC_4H_8$ | −46° | 81° | 0.810/20° | 8860 | 25.0 | (*30*) |
| $SiH_3NC_5H_{10}$ | −109° | 104° | 0.775/20° | 7780 | 20.6 | |
| $SiH_2(NMe_2)_2$ | −104° | 93° | 0.788/20° | 7710 | 21.1 | (*35*) |
| $SiH(NMe_2)_3$ | −90° | 142° | 0.850/20° | 9830 | 23.7 | |
| $(Si_2H_5)_3N$ | −97° | 176° | 0.873/0° | 10,660 | 23.7 | (*274*) |
| $Si_2H_5NMe_2$ | <−134° | 66° | — | 8470 | 25.0 | (*1*) |
| $(SiH_3)_2NN(SiH_3)_2$ | −24° | 109° | 0.83/0° | 8190 | 21.4 | (*17*) |

The heat of association of $SiH_3NMe_2$ has been semiquantitatively assessed by Sujishi and Witz (*257*) and more recently by Aylett and

Emsley (*29*), using the following argument. The latter pair of workers measured both the heats of sublimation, $\Delta H_1$, and of vaporization, $\Delta H_2$, of the compound. It was then assumed that the heat of fusion of the hypothetical unassociated solid, $\Delta H_3$, was similar to that of trimethylamine. The last quantity is in any case rather small (1.5 kcal $\text{mole}^{-1}$) so an error of up to 25 % will not be serious. The heat of association of solid $SiH_3NMe_2$ is now given by $\Delta H_1 - \Delta H_2 - \Delta H_3$, which turns out to be about 4.8 kcal $\text{mole}^{-1}$. This is comparable with the strength of hydrogen-bonding interactions in ice.

Methods of making these compounds have been discussed in detail (*22*). A halosilane is usually allowed to react under the mildest possible conditions with the corresponding N—H compound, either in the gas phase or in dilute solution at low temperature. Typical examples of such reactions are:

$$4NH_3 + 3SiH_3I \rightarrow (SiH_3)_3N + 3NH_4I \qquad (13)$$

$$3N_2H_4 + 4SiH_3I \rightarrow (SiH_3)_2NN(SiH_3)_2 + 2N_2H_6I_2 \qquad (14)$$

If the reacting base is a strong one (toward protons) and not too hindered sterically, an excess of base will result in a drastic lowering of yields because of base-catalyzed disproportionation, to be discussed later. If, on the other hand, the N-Si product is a fairly strong base, an excess of halosilane will also be harmful, since adducts such as $SiH_3NR_2 \cdot SiH_3I$ may be formed.

Because of the harmful effect of an excess of base, the amine exchange reaction that is so useful in organosilicon chemistry is of limited applicability. One interesting example of its use, however, is in the preparation of disilylamine, $(SiH_3)_2NH$, which cannot be prepared from ammonia and a halosilane, but is made in the following way (*33*):

$$2Ph_2NSiH_3 + NH_3 \rightarrow 2Ph_2NH + (SiH_3)_2NH \qquad (15)$$

A deficit of ammonia is used; diphenylamine is such a weak base that it does not catalyze the decomposition of the product.

The existence of disilylamine is important, because it was postulated by Stock and Somieski (*250*) as an intermediate in the preparation of trisilylamine by reaction (13) in a stepwise process. It has now been shown to react with iodosilane to give a high yield of trisilylamine,

$$4(SiH_3)_2NH + SiH_3I \rightarrow 3(SiH_3)_3N + NH_4I \qquad (16)$$

which shows that the last step in Stock's process is feasible. It has not yet proved possible to isolate $SiH_3NH_2$, however.

### 2. *Base Strength*

The reduction in base strength of Si-N compounds as compared with corresponding C-N compounds has already been commented on (Section II,B). Table XVII records a selection of published information on adducts (or the lack of them) between simple silicon hydride amines and various Lewis acids. It will be seen that a compound containing three silyl groups attached to one nitrogen atom is a weaker base than one with two silyl groups attached to nitrogen, which in turn is weaker than a compound with only one silyl group on nitrogen. This is consistent with the picture of N → Si $p_\pi$-$d_\pi$ donation already developed; this donation is more extensive when more silyl groups interact with a particular nitrogen atom. Furthermore, when more than one nitrogen atom is attached to a single silicon atom, the resulting compounds are stronger bases. In the series $SiH_{4-x}(NMe_2)_x$, the order of base strength with respect to borane has been shown by Aylett and Peterson (*36*) to be:

TABLE XVII

REACTIONS OF SILICON-NITROGEN COMPOUNDS WITH LEWIS ACIDS

| Acid | Base | Complex (base:acid) | Ref. |
|---|---|---|---|
| $BH_3$ | $(SiH_3)_3N$ | (none)/−80° | (*67*) |
| | $(SiH_3)_2NMe$ | 1:1/−80° | (*256*) |
| | $SiH_3NMe_2$ | 1:1/−80° | |
| | $SiH_2(NMe_2)_2$ | 1:2/−84° | (*36*) |
| | $SiH(NMe_2)_3$ | 1:2/−135° | |
| | $Si(NMe_2)_4$ | 1:1/−135° | |
| $BMe_3$ | $(SiH_3)_3N$ | (none) | (*67*) |
| | $(SiH_3)_2NH$ | (interacts below −100°) | (*33*) |
| | $(SiH_3)_2NMe$ | (none) | (*257*) |
| | $SiH_3NR_2$ | 1:1/−80° | (*29, 257*) |
| | $SiH_2(NMe_2)_2$ | 1:1/−84° | (*36*) |
| | $SiH(NMe_2)_3$ | (none) | |
| | $SiH_3NC_5H_{10}$ | 1:1/−96° | (*30*) |
| $SiH_3I$ | $(SiH_3)_3N$ | (none) | (*19*) |
| | $(SiH_3)_2NMe$ | (none) | |
| | $(SiH_3)_2NN(SiH_3)_2$ | (none) | (*17*) |
| | $SiH_3NR_2$ | 1:1/−78° | (*29*) |
| | $SiH_3NC_5H_{10}$ | 1:1/−46° | (*30*) |
| HCl | $SiH_3NMe_2$ | 1:2/−96° | (*29*) |
| | $SiH_3NEt_2$ | 1:3/−96° | |
| | $SiH_3NC_5H_{10}$ | 1:2/−88° | (*30*) |

$$SiH_4 \ll SiH_3NMe_2 < SiH_2(NMe_2)_2 \sim SiH(NMe_2)_3 > Si(NMe_2)_4$$

It will be noted that steric effects become predominant with the later members of the series; if a smaller reference acid could be used, it might be possible to demonstrate a continuous rise in base strength. Unfortunately, $H^+$ cleaves the Si—N bond in most such compounds (e.g., *35*).

When warmed to room temperature, most of the adducts in Table XVII become fully dissociated. Some, however, may undergo further reaction, as follows (*30*):

$$SiH_3NC_5H_{10}\cdot 2HCl \rightarrow SiH_3Cl + C_5H_{10}NH_2Cl \qquad (17)$$

### 3. *Cleavage Reactions*

Boron halides have been shown to react in a similar fashion to Eq. (17) to produce silyl halides from Si-N compounds (*67*, *257*, *258*):

$$\begin{tikzcd} (SiH_3)_3N + BF_3 \arrow[r] & (SiH_3)_2NBF_2 + SiH_3F \arrow[d] \\ & \frac{1}{3}(SiH_3NBF)_3 + SiH_3F \end{tikzcd} \qquad (18)$$

$$\begin{tikzcd} (SiH_3)_2NMe + BCl_3 \arrow[r] & (SiH_3)NMeBCl_2 + SiH_3Cl \arrow[d] \\ & \frac{1}{3}(MeNBCl)_3 + SiH_3Cl \end{tikzcd} \qquad (19)$$

Disilanyl-nitrogen compounds also undergo similar cleavage with no breaking of the Si—Si bond (*1*):

$$(Si_2H_5)_3N + BF_3 \rightarrow Si_2H_5F + (Si_2H_5)_2NBF_2 \qquad (20)$$

Probably other nonmetallic halides will be found to react in analogous ways; with organosilicon-nitrogen compounds they are known to do so (e.g., *102*). A related reaction occurs when $(SiH_3)_3N$ is mixed with methanol or ROH (R = MeCO, HCO, $CF_3CO$); $SiH_3OMe$ or silyl esters are formed, respectively (*122*).

### 4. *Disproportionation; Polymers*

The action of bases on silyl-nitrogen compounds has been investigated in some detail. Stock and Somieski (*250*) noted that excess ammonia reacted with trisilylamine to produce silane, and the outlines of base-catalyzed disproportionation have been presented (Section II,G). In an extensive study, Wells and Schaeffer (*277*) have shown how trisilylamine in the liquid phase reacts with a variety of bases to give silane:

$$\begin{tikzcd} (SiH_3)_3N \arrow[r, "base"] & \frac{1}{x}[(SiH_3)NSiH_2]_x + SiH_4 \arrow[d] \\ & \frac{1}{x}(NSiH)_x + SiH_4 \end{tikzcd} \qquad (21)$$

The initial product shown was normally polymeric, but small amounts of a cyclic compound with $x = 3$ were also isolated. The species $(NSiH)_x$ is of course highly cross-linked. Suitable bases included $NH_3$, $MeNH_2$, LiH in ether, and $NMe_3$; the last gave only slow reaction. By deuteration of either the trisilylamine or the added base, the authors were able to show that no base protons were incorporated in the silane produced, e.g.:

$$(SiD_3)_3N \xrightarrow{NH_3} SiD_4 + \text{polymer} \tag{22}$$

$$(SiH_3)_3N \xrightarrow{ND_3} SiH_4 + \text{polymer} \tag{23}$$

Kinetic studies at low temperatures showed that the activation energy for the process was about 4 kcal $\text{mole}^{-1}$, which is not much more than the value expected for a diffusion-controlled reaction. In general, the results were consistent with the ready formation of a bimolecular complex as reaction intermediate, although other possibilities could not be entirely eliminated.

It is interesting that the relatively stable compound $Si_2H_5NMe_2$ undergoes disproportionation to give disilane and unsymmetrical $SiH_3SiH(NMe_2)_2$. No silane and very little hydrogen appear to be produced in this reaction, so that presumably only one reaction path is important. Abedini and MacDiarmid (*1*) discuss this reaction in terms of nucleophilic attack by nitrogen, which preferentially occurs at a silicon atom already linked to nitrogen. This implies that $\sigma$-abstraction from this silicon outweighs $\pi$-donation to it.

Aylett (*17*) noted that tetrasilylhydrazine did not react rapidly with $NMe_3$, and there was no evidence of complex formation. It was therefore inferred that $\pi$-bonding had greatly decreased the readiness of the $SiH_3$ group to form extra dative $\sigma$-bonds as compared with, say, iodosilane.

The base-catalyzed disproportionation of disilazanes has been reported recently by Aylett and Hakim (*31*). The authors studied the action of various bases on the compounds $(SiH_3)_2NR$ (R = Me, Ph) and found that, with any given base, the N-methyl compound reacted much more rapidly than the N-phenyl:

$$(SiH_3)_2NR \xrightarrow{\text{base}} \frac{1}{x}(SiH_2NR)_x + SiH_4 \tag{24}$$

The order of catalyst efficiency for both compounds was $NH_3 > NH_2Me > C_5H_5N \sim PhNH_2 > NMe_3 > (CH_2)_4O$. It can be seen that for the nitrogen donors this order is based more on steric requirements than on proton affinity. Ammonia and methylamine reacted exceedingly rapidly in the initial stages, even below room temperature; the rate fell off markedly later, presumably because of the increasing viscosity of the system. It has since been found that disilylamine is even more susceptible to this kind of attack (*33*).

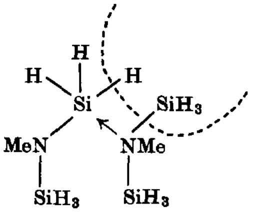
The polymers of composition $(\mathrm{SiH_2NR})_x$ that are formed in reaction (24) have been prepared by a number of other routes (*22*, *23*, *34*, *43*):

$$\mathrm{SiH_2I_2} + 3\mathrm{RNH_2} \longrightarrow \frac{1}{x}(\mathrm{SiH_2NR})_x + 2\mathrm{RNH_3I} \qquad (25)$$

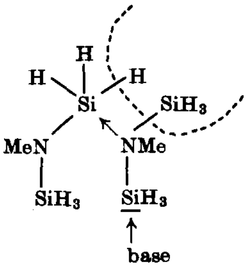
$$\mathrm{SiH_2(NMe_2)_2} + \mathrm{MeNH_2} \longrightarrow \frac{1}{x}(\mathrm{SiH_2NMe})_x + 2\mathrm{Me_2NH} \qquad (26)$$

$$\begin{tikzcd} (n+1)(\mathrm{SiH_3})_2\mathrm{NR} \arrow[r, "\text{(a) }350^\circ\text{–}450^\circ", "\text{(b) UV}"'] & \mathrm{SiH_3NR(SiH_2NR)}_n\mathrm{SiH_3} + n\mathrm{SiH_4} \arrow[d] \\ & \frac{n+1}{x}(\mathrm{SiH_2NR})_x + \mathrm{SiH_4} \end{tikzcd} \qquad (27)$$

The first is a straightforward condensation reaction, the second is an amine exchange process, while the third, involving pyrolysis or photolysis in the gas phase, is noteworthy in that oligomers with $n = 1$–$3$ have been isolated in the case of the N-methyl derivative (*37*). No cyclic products of low molecular weight have ever been detected. The polymers possess considerable thermal and hydrolytic stability; for example, a sample prepared according to Eq. (25) suffered 3.5 % weight loss after 12 hours at 400°, and dissolved only slowly in hot concentrated aqueous alkali. This stability may be thought of as arising from both electronic and steric factors; $\pi$-delocalization (cf. *92*) along the polymer chain could logically confer resistance toward nucleophilic attack by decreasing silicon's electron-acceptor ability, while coiling of the polymer chains effectively shields silicon atoms from the outside world.



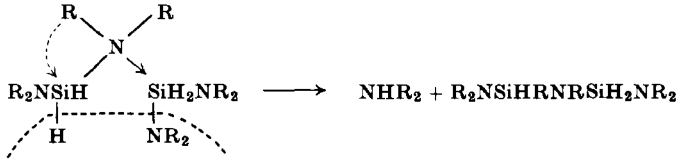
(X)



(XI)

In accord with the previous discussion of disproportionation, the reaction intermediate for reaction (27) is probably a bimolecular complex (X). This can lose silane, as shown, in the first stage of an oligomerization reaction. Such a complex will be weak since, as was mentioned (Section V,A,2), the base strength of disilazanes is low (and their electron-acceptor power is also weak). The base strength will be enhanced, however, by electron donation from an added Lewis base (XI) because here the underlined silicon atom, in accepting σ-donated electrons, will π-bond less strongly to the central nitrogen atom. The nitrogen is thus enabled to donate electrons more effectively to another disilazane molecule. This is another manifestation of the intermolecular-intramolecular competition referred to (Section II,B).

In the gas-phase pyrolysis of bis- and tris-dialkylaminosilanes (*35*) and of dialkylaminosilanes (*29*, *30*), the major products derive from disproportionation processes. The presence of small amounts of dialkylamines, however, suggests that an alternative orientation of the bimolecular complex (X) and simultaneous alkyl migration (XII) may be significant:

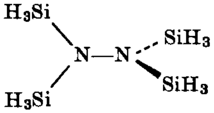


$$R_2NSiH \quad SiH_2NR_2 \longrightarrow NHR_2 + R_2NSiHRNRSiH_2NR_2 \qquad (27a)$$

(XII)

### 5. *Structures*

Structural studies on simple derivatives have yielded important results. Hedberg (*169*) showed by electron diffraction techniques that $(SiH_3)_3N$ has a planar skeleton of heavy atoms. Three complete studies of the vibrational spectra of the same molecule (*125*, *188*, *225*) confirmed this result, and it was suggested that deformation from this planar arrangement was energetically quite easy; this leads to band broadening. Infrared and Raman spectra of $(SiH_3)_2NMe$ (*71*) and infrared spectra of $SiH_3NMe_2$ (*70*), together with their silyl-deuterated analogs, have also been reported. While it seems likely that the skeletal structure of $(SiH_3)_2NMe$ is almost planar and that of $SiH_3NMe_2$ is distinctly nonplanar (and the observed absorptions were assigned on these bases), no definite information concerning molecular shapes could be deduced. In the case of tetrasilylhydrazine, an infrared and Raman investigation suggested strongly that the molecule has a skeleton of $D_{2d}$ symmetry (*42*):



Two planar $NSi_2$ units are connected at right angles. The adoption of this structure, rather than the all-planar $D_{2h}$ arrangement, suggests that electron $\pi$-donation from N to Si is not sufficient to lessen appreciably the strong repulsions between essentially filled N $2p\pi$ orbitals. In $N_2O_4$, which is planar, it is reasonable to suppose that there is considerable removal of electron density from the N—N region.

## B. Silicon-Phosphorus, Silicon-Arsenic, and Silicon-Antimony Compounds

### 1. *Preparation and Properties of Silicon-Phosphorus Compounds*

Much less is known about these compounds (listed in Table XVIII) than about the corresponding Si-N derivatives, probably because they are more difficult to prepare. The field has recently been reviewed by Fritz (*146*).

TABLE XVIII

Silicon Hydride Derivatives with Phosphorus, Arsenic, and Antimony

| Compound | M.P. | B.P. | $d$ (gm/ml) | $\Delta H_{\text{vap}}$ (cal mole$^{-1}$) | $\Delta S_{\text{vap}}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|
| $SiH_3PH_2$ | <−135° | 13° | — | — | — | (*144, 145*) |
| $(SiH_3)_3P$ | — | 114° | — | 8697 | 22.5 | (*11*) |
| $SiH_3PEt_2$ | — | 53°/79 mm | — | — | — | (*146*) |
| $SiH_2(PEt_2)_2$ | — | 110°/13 mm | — | — | — | |
| $SiH_3PI_2$ | <−2° | 190° | 2.9/20° | 9300 | 20.5 | (*41*) |
| $(SiH_3)_3As$ | — | 120° | 1.201/20° | 9798 | 24.9 | (*11*) |
| $(SiH_3)_3Sb$ | — | 255° | — | (7638) | — | |

In 1953 Fritz reported that, when a mixture of silane and phosphine was heated at 450°–500°, silylphosphine, $SiH_3PH_2$, was formed in rather low yield (*144*). In subsequent publications, it was shown that $SiH_3PH_2$

reacted with a wide variety of protic reagents to give phosphine (*145*, *147*). At about the same time, Aylett *et al.* (*41*) studied the reaction of iodosilane with white phosphorus in the temperature range 20°–100°. A mixture of products resulted, from which $SiH_3PI_2$ could be isolated. It seemed probable that trisilylphosphine, $(SiH_3)_3P$, was also formed, but it appeared to form a 1 : 1 adduct with iodosilane rather readily, and was not obtained in a pure state. The basic nature of Si-P compounds has also been demonstrated recently by the isolation of the liquid molecular adduct $SiH_3PH_2 \cdot BH_3$ (*111*).

Trisilylphosphine was first obtained by Amberger and Boeters (*9*, *11*) by the reaction of bromosilane with $KPH_2$ in dimethyl ether solution at low temperatures (yields of up to 55 % were reported):

$$3SiH_3Br + 3KPH_2 \xrightarrow{-100^\circ} (SiH_3)_3P + 2PH_3 + 2KBr \qquad (28)$$

It seems likely that $SiH_3PH_2$ is first formed and this, under the experimental conditions, then undergoes metal-hydrogen exchange with $KPH_2$ to form $KPHSiH_3$. This reacts further with bromosilane to give $(SiH_3)_2PH$, and the process is repeated, yielding $(SiH_3)_3P$. Disproportionation does not seem to be excluded, however (*13*).

A discharge method has proved useful for making Si-P compounds. When a mixture of silane and phosphine was passed through an ozonizer-type discharge at −78°, $SiH_3PH_2$, $(SiH_3)_2PH$, and $Si_2H_5PH_2$ but not $(SiH_3)_3P$ were formed (*107*, *156*). In subsequent experiments, $SiH_4/SiH_3PH_2$ and $Si_2H_6/PH_3$ mixtures were subjected to a discharge; isomeric $(SiH_3)_2PH$ and $Si_2H_5PH_2$, respectively, were obtained in this way, each essentially uncontaminated by the other (*157*). A number of physical properties of these compounds, including infrared and n.m.r. spectra, were reported.

Aylett and Sinclair (*38*) have found that adducts of substituted pyridines and iodosilane react directly with phosphine in a suitable solvent to give trisilylphosphine:

$$3SiH_3I \cdot 2\ \text{hexpy} + PH_3 \xrightarrow[-40^\circ]{NBu_3} (SiH_3)_3P + 3\ \text{hexpy} \cdot HI \qquad (29)$$

where hexpy is 2-*n*-hexylpyridine. This method has the advantage that it avoids the preparation of a metal derivative of phosphine.

### 2. *Structures of Silicon-Phosphorus Compounds*

From a study of the infrared and Raman spectra of $(SiH_3)_3P$ and its deuterated analog, the very interesting structural conclusion was drawn that the $PSi_3$ skeleton is planar or nearly so (*99*). On the other hand, trigermylphosphine, $(GeH_3)_3P$, appears from similar evidence to be nonplanar (*87*). Steric effects in the two molecules must be virtually the same, and the stereochemical difference was taken to imply that $p_\pi$-$d_\pi$ donation from phosphorus to silicon is more pronounced than that from phosphorus to germanium.

An electron diffraction study, however, has now shown that $(SiH_3)_3P$ (also its arsenic analog) is definitely pyramidal, with a SiPSi bond angle of about 95° (*51*); its stereochemistry therefore affords no positive (or negative) evidence for $\pi$-bonding. It is interesting that the infrared/Raman selection rules are insensitive to such a large deviation from planarity. Presumably, as in the case of $(SiH_3)_2O$, the potential energy function for $(SiH_3)_3P$ shows only a low barrier to inversion (see Section VI,C).

The infrared spectrum of silylphosphine has been reported (*193*). The molecule appears to be of low symmetry, and the observed absorption bands have been assigned in a similar way to those of $CH_3PH_2$.

### 3. *Silicon-Arsenic and Silicon-Antimony Compounds*

Trisilyl-arsine and -stibine have been made by Amberger and Boeters (*9–11*) via the reaction of bromosilane with $KAsH_2$ and $Li_3Sb$, respectively:

$$3KAsH_2 + 3SiH_3Br \xrightarrow[-100^\circ]{Me_2O} (SiH_3)_3As + 2AsH_3 + 3KBr \qquad (30)$$

$$Li_3Sb + 3SiH_3Br \xrightarrow[-78^\circ]{Me_2O} (SiH_3)_3Sb + 3LiBr \qquad (31)$$

The discharge method has also been used to make $SiH_3AsH_2$ and two $Si_2AsH_7$ isomers, which were identified mass spectrometrically (*107*). Little is known about their chemistry, but it seems that in at least one case the Si—H bond may be broken before the Si—As bond; $SiH_3AsH_2$ reacts with $BBr_3$ at low temperatures to give first $SiH_2BrAsH_2$, which then reacts further with Si—As cleavage (*109*):

$$SiH_3AsH_2 + BBr_3 \xrightarrow{-80^\circ} SiH_2BrAsH_2 + BHBr_2 \qquad (32)$$

$$SiH_2BrAsH_2 + BBr_3 \xrightarrow{-23^\circ} SiH_2Br_2 + \frac{1}{x}(AsH_2BBr_2)_x \qquad (33)$$

## VI. Silane Derivatives with Group VI Elements

### A. PREPARATION

Such derivatives (tabulated in Table XIX) have been prepared almost always by means of the reaction between a halosilane and a silver or mercury salt, e.g. (*135*):

$$2SiH_3I + HgS \rightarrow (SiH_3)_2S + HgI_2 \quad (34)$$

or by hydrolysis, e.g. (*272*):

$$2Si_2H_5I + H_2O \rightarrow (Si_2H_5)_2O + 2HI \quad (35)$$

TABLE XIX

SILICON HYDRIDE DERIVATIVES WITH GROUP VI ELEMENTS

| Compound | M.P. | B.P. | $d$ (gm/ml) | $\Delta H_{vap}$ (cal mole$^{-1}$) | $\Delta S_{vap}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|
| $(SiH_3)_2O$ | −144° | −15° | 0.881/-80° | 5630 | 21.8 | (*251, 252*) |
| $SiH_3OSi_2H_5$ | — | 43° | — | 7500 | 23.8 | (*266*) |
| $(Si_2H_5)_2O$ | −112° | 95° | 0.876/0° | 8700 | 23.6 | (*90*) |
| $SiH_3OMe$ | −98° | −21° | — | 6040 | 23.9 | (*244*) |
| $SiH_2(OMe)_2$ | −100° | 33° | — | 7528 | 24.8 | (*245*) |
| $SiH(OMe)_3$ | −115° | 81° | — | 8782 | 24.8 | |
| $(SiH_3)_2S$ | −70° | 59° | 0.929/10° | 7740 | 23.3 | (*135*) |
| $(Si_2H_5)_2S$ | −70° | 144° | 0.950/0° | 11,380 | 27.3 | (*274*) |
| $SiH_3SH$ | −134° | 14° | — | 6200 | 21.9 | (*135*) |
| $SiH_3SMe$ | −117° | 46.8° | — | 7340 | 22.9 | (*246*) |
| $SiH_3SCF_3$ | −127° | 14° | — | 6150 | 21.4 | (*105*) |
| $(SiH_3)_2Se$ | −68° | 85° | 1.36/20° | 8220 | 22.9 | (*135*) |
| $SiH_3SeCF_3$ | −126° | 35° | — | 6700 | 22 | (*128*) |

Mixed compounds present more difficulty. Thus $Si_2H_5OSiH_3$ was made (*266*) in 18% yield by the cohydrolysis of $Si_2H_5Br$ and $SiH_5I$.

$$SiH_3I + Si_2H_5Br \xrightarrow{H_2O} Si_2H_5OSiH_3 + 2HX \quad [+ (SiH_3)_2O, (Si_2H_5)_2O] \quad (36)$$

or by equilibration of $(SiH_3)_2O/(Si_2H_5)_2O$ mixtures at 0° for long periods (32% yield). Methoxysilanes were made from silane and methanol in the presence of copper (for derivatives with more than one methoxy group) or by the following reaction (*244, 245*):

$$SiH_3I \cdot NMe_3 + MeOH \rightarrow MeOSiH_3 + NMe_3HI \quad (37)$$

## B. CHEMICAL BEHAVIOR

The areas of interest in the chemistry of these compounds are similar to those of Group V derivatives and will be dealt with only in outline. Reported information is in any case sparser, and the interpretation of it follows the same lines. All those compounds that contain only one Group

VI atom are weak or negligible electron donors. Thus $(SiH_3)_2O$ does not interact with diborane (*255*) nor does $SiH_3OMe$ (*245*). Also, $(SiH_3)_2S$ does not appear to form 'onium-type adducts with either iodosilane or iodomethane (*135*). Lewis acids such as boron and aluminum halides cause cleavage of the Si—O bond (e.g., *189*, *217*):

$$(SiH_3)_2O + BCl_3 \xrightarrow[\text{fast}]{-80^\circ} SiH_3Cl + SiH_3OBCl_2 \qquad (38)$$

$$SiH_3OBCl_2 \xrightarrow[\text{slow}]{-80^\circ} 3SiH_3Cl + BCl_3 + B_2O_3 \qquad (39)$$

It is interesting that $(Si_2H_5)_2O$ reacts more readily than $(SiH_3)_2O$ with $BCl_3$, and also that $Si_2H_5OSiH_3$ is cleaved preferentially at the $Si_2H_5$—O bond (*266*). These authors discuss this effect in terms of effective electron withdrawal from the α-silicon atom of the disilanyl group by means of possible $d_\pi$-$d_\pi$ interactions across the Si—Si bond.

Base-catalyzed disproportionation has been observed with both $(SiH_3)_2O$ and $(SiH_3)_2S$. Early work by Stock *et al.* (*251*, *252*) suggested that $(SiH_3)_2O$ readily lost silane to give polymeric $(SiH_2O)_x$, which was termed prosiloxane. This reaction has been recently re-examined by Campbell-Ferguson (*72*), who finds that $(SiH_3)_2O$ in the presence of various bases (e.g., water, acetonitrile, trimethylamine) or dihalosilanes and water yield $(SiH_2O)_4$ and higher oligomers. MacDiarmid (*200*) has also reported that $(SiH_3)_2O$ in the presence of bases gives $SiH_2(OSiH_3)_2$ and $SiH(OSiH_3)_3$. It is possible that different reaction conditions lead to different products. Ammonia or trimethylamine also brings about the disproportionation of $(SiH_3)_2S$; in this case, silane and an adduct of approximate composition $(SiH_2S \cdot base)_x$ are formed (*198*).

## C. STRUCTURES

Structural studies have been confined to $(SiH_3)_2O$ and $(SiH_3)_2S$. Recent electron diffraction studies of high precision by the Oslo school have resolved the uncertainties that existed, particularly in relation to the first compound's structure; disiloxane has a bond angle (SiOSi) of 144°, while the corresponding angle in disilyl sulfide is 97° (*6*, *7*). Infrared and Raman studies of $(SiH_3)_2S$ had strongly suggested a bond angle of about 100° (*127*, *191*), but results on disiloxane were more conflicting. Early work by Lord *et al.* (*195*) had suggested that the skeleton was linear (or sufficiently close to linear so that the selection rules for $D_{3d}$ symmetry were still obeyed). Later studies (*15*, *16*, *202*, *203*, *261*) seemed more consistent with a bent molecule, although it was not possible to estimate the bond angle with precision.

It is interesting to compare the forms of the potential energy function for various molecules as the bond angles change. The well-known double

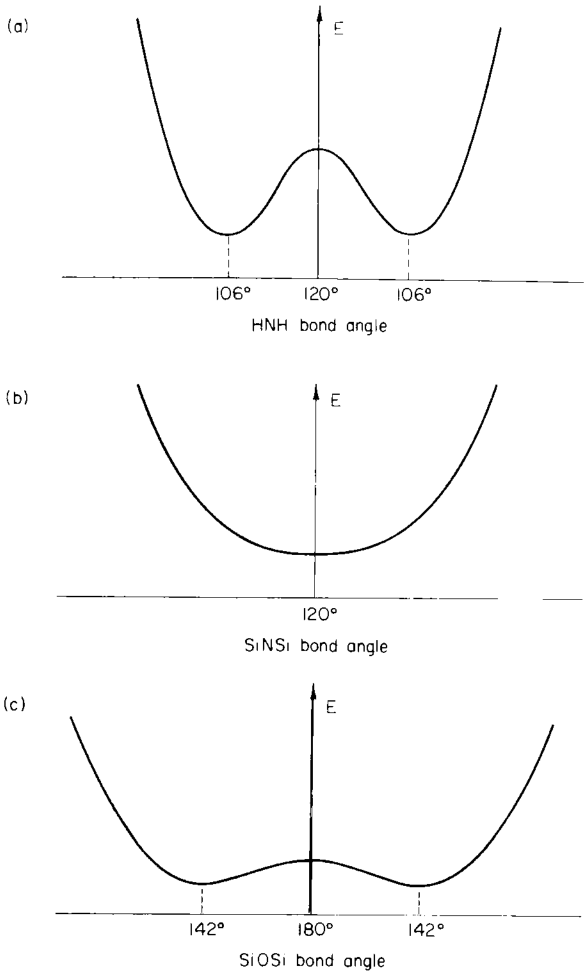


FIG. 3. Schematic potential energy functions for: (a) ammonia, (b) $(SiH_3)_3N$, and (c) $(SiH_3)_2O$.

minimum curve for ammonia (Fig. 3a) represents a common situation in pyramidal molecules; the height of the potential barrier to inversion, about 6 kcal mole$^{-1}$, is a measure of the $sp^3 \rightarrow sp^2$ rehybridization energy. Trisilylamine can probably be represented by a curve with a shallow minimum (Fig. 3b), implying fairly easy out-of-plane bending. Disiloxane occupies an intermediate position (Fig. 3c); the curve has a shallow double minimum, and one analysis of the infrared data (*15*) suggests that the height of the potential barrier may be about 450 cal mole$^{-1}$. This leads to very easy bending of the molecule, even at low temperatures. Trisilylphosphine is expected to have a curve that is a flatter version of Fig. 3a.

## VII. Silicon-Metal Derivatives

### A. NONTRANSITION METAL DERIVATIVES

Although various unsuccessful earlier attempts had been made to prepare silyl Grignard reagents and silyl-mercury compounds, the first silyl-metal compound to be isolated was potassium silyl, $KSiH_3$. Ring and Ritter (*223*) prepared it either by the long reaction of silane or disilane with potassium metal in glyme (1,2-dimethoxyethane) at −78°, or by the reaction of potassium hydride with disilane in glyme at room temperature:

$$K + SiH_4 \rightarrow KSiH_3 + \tfrac{1}{2}H_2 \qquad (40)$$

$$KH + Si_2H_6 \rightarrow KSiH_3 + SiH_4 \qquad (41)$$

Potassium silyl proved to be remarkably stable thermally (up to 240°), but, while it reacted with chloromethane to give a quantitative yield of methylsilane, its behavior with other halides was disappointing. Thus with $SiBr_4$ no higher silanes were produced, but quantities of monosilane. With $SiD_3Br$, extensive rearrangement occurred to give mixtures of all possible deuterated silanes and disilanes. Probably the use of glyme as a solvent in these reactions was harmful.

Recently, however, Amberger (*8*) reported that $KSiH_3$ reacts smoothly with a variety of halides in the absence of solvent to give some very interesting new compounds, e.g.:

$$KSiH_3 + Me_2AsCl \rightarrow SiH_3AsMe_2 + KCl \qquad (42)$$

Also Hagenmuller and Pouchard (*165*) have described the preparation of sodium silyl from silane and sodium in glyme at −30°; formidable precautions were taken in handling the large quantities of silane required. Sodium silyl apparently reacts with $AlCl_3$ to give unstable aluminum trisilyl, $Al(SiH_3)_3$. In a further publication, Ring *et al.* (*224*) have presented evidence for the formation of $KSi_2H_5$ and $KSi_3H_7$ by the reaction of $KSiH_3$ with disilane.

The earlier difficulties associated with the use of $KSiH_3$ in glyme have been partly overcome by Kennedy *et al.* (*183*). They find that, if the volatile products are allowed to escape rapidly, coupling reactions produce reasonable yields of $Si_2H_6$ (from $SiH_3Br$) and $Si_3H_8$ (from $Si_2H_5Br$). Their observation that lithium halides in glyme cause rapid disproportionation of $Si_2H_6$, producing $SiH_4$ and a solid Si-H polymer, is probably significant in this connection (cf. Section III,B). A different approach is to replace glyme by another donor solvent: Cradock *et al.* (*88*) find that hexamethylphosphoramide, $(Me_2N)_3PO$, is very suitable both as a medium for the preparation of $MSiH_3$ (M = Li, Na, K) and for its further reaction with MeI, EtBr, and $MeOCH_2Cl$. The corresponding silyl derivatives were isolated in fair to high yields, especially from the potassium compound. (For the recent use of $KSiH_3$ to prepare Si-Ge and Si-B compounds, see Section VIII,A and B.)

Würtz reactions can conveniently be considered at this point. Craig and MacDiarmid (*89*) successfully coupled iodosilane and methyliodosilane with liquid sodium amalgam to give reasonable yields of disilane and 1,2-dimethyldisilane, respectively. Less encouraging, however, was an attempted coupling of diiodomethane and iodosilane with sodium-potassium alloy in diglyme [bis(2-methoxyethyl) ether], which led to the formation of dimethylsilane (*19*)! Similar difficulties arose in the reaction of dibromosilane and potassium germyl, $KGeH_3$, in dimethyl ether, which gave germane as the only volatile product (*11*).

## B. Transition Metal Derivatives

The first silicon-transition metal compound to be prepared was $(\pi\text{-}C_5H_5)Fe(CO)_2SiMe_3$ (*219*); it was made by the following reaction:

$$Me_3SiCl + (\pi\text{-}C_5H_5)Fe(CO)_2Na \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2SiMe_3 + NaCl \qquad (43)$$

The compound proved to be thermally but not oxidatively stable. Some years later, Gorsich reported that $Ph_3SiMn(CO)_5$ could be made similarly from $Ph_3SiCl$ and $NaMn(CO)_5$ (*159*).[3]

The first detailed study of organosilicon-transition metal compounds, however, was reported by Chalk and Harrod (*76–78*, *166*). As part of an investigation into the catalysis of addition of Si-H compounds to olefins, it was found that the following reactions occurred quite readily:

$$R_3SiH + (Ph_3P)_2Ir(CO)Cl \rightarrow (Ph_3P)_2Ir(CO)Cl(SiR_3)H \qquad (44)$$

$$2R_3SiH + Co_2(CO)_8 \rightarrow R_3SiCo(CO)_4 + H_2 \qquad (45)$$

The addition reaction (44) could be reversed on heating. Only rather electronegative substituents were successful in Eq. (44): $R_3$ was $Cl_3$, $EtCl_2$, $PhCl_2$, or $(OEt)_3$, but not alkyl or aryl. In Eq. (45), however, R may be an alkyl, aryl, or alkoxy group or chlorine. Furthermore, MacDiarmid and his co-workers (*44*, *164*) have shown that $Me_3SiCo(CO)_4$, $MeSiH_2Co(CO)_4$, and $F_3SiCo(CO)_4$ may be prepared analogously.

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[3] Jetz *et al.* (*179*) have recently made authentic $Ph_3SiMn(CO)_5$ by another route, and find it to be different from Gorsich's product.

Independent studies by Aylett and Campbell (*24–27*, *40*) have led to the preparation of the first unsubstituted silyl metal carbonyls (Table XX). These compounds were all made by the reaction of the appropriate iodosilane with sodium cobalt or manganese carbonyl in ether at low temperatures, e.g.:

TABLE XX

TRANSITION METAL DERIVATIVES OF SILICON HYDRIDES

| Compound | M.P. | B.P. | $d$ (gm/ml) | $\Delta H_{vap}$ (cal mole$^{-1}$) | $\Delta S_{vap}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|
| $SiH_3Co(CO)_4$ | −53.5° | 112° | 1.27/20° | 8080 | 21.0 | (*24*) |
| $SiH_3Mn(CO)_5$ | +25.5° | 134° | — | 9450 | 23.3 | (*26*) |
| $SiH_2[Co(CO)_4]_2$ | ~15° | 170° | — | 9250 | 20.8 | (*25*) |
| $(SiH_3)_2Fe(CO)_4$ | 52° | 145° | — | 10,470 | 23.3 | (*40*) |

$$2NaCo(CO)_4 + SiH_2I_2 \xrightarrow[-40^\circ]{Me_2O} SiH_2[Co(CO)_4]_2 + 2NaI \qquad (46)$$

$$NaMn(CO)_5 + SiH_3I \xrightarrow[-30^\circ]{Et_2O} SiH_3Mn(CO)_5 + NaI \qquad (47)$$

In comparison with the corresponding alkyl metal carbonyls, these new derivatives are remarkably stable thermally. While $CH_3Co(CO)_4$ is reported to decompose above −30° (*172*), $SiH_3Co(CO)_4$ can still be recovered in 30 % yield after 30 minutes at 100°. The other products are hydrogen, carbon monoxide, cobalt carbonyl hydride, and a dark solid residue containing Co—Si bonds.

Silyl cobalt carbonyl reacts readily with protic reagents in the following way:

$$SiH_3Co(CO)_4 + HX \rightarrow SiH_3X + HCo(CO)_4 \qquad (48)$$

where X = Cl, OH, $NH_2$. The initial product reacts further in the case of water and ammonia attack to give $(SiH_3)_2O$ and $(SiH_3)_3N$, respectively.

Further experiments on the cleavage of the Si—Co bond in $Me_3SiCo(CO)_4$ by Baay and MacDiarmid (*44*) have shown that it is broken at room temperature by water, methanol, $Me_2AsCl$ [to give $Me_2AsCo(CO)_3$], and $GeF_4$ [to give $F_3GeCo(CO)_4$].

The equilibrium (49) lies well to the left at room temperature,

$$2SiH_3Co(CO)_4 + HgI_2 \rightleftharpoons 2SiH_3I + Hg[Co(CO)_4]_2 \qquad (49)$$

and hence $Co(CO)_4$ lies to the left of I in the conversion series (Section IV,A), and appears to be effectively less electronegative. Also, in so far as correlations can legitimately be drawn between infrared absorption frequencies and electronegativity, it will be seen from Tables VI and VII that $Co(CO)_4$ appears to be about as electronegative as iodine.

Trimethylamine and pyridine both form adducts of composition $SiH_3Co(CO)_4 \cdot 2$base with no displacement of carbon monoxide, and $\alpha,\alpha'$-bipyridyl gives a similar 1:1 product. The three most likely possibilities for the structures of these adducts are (a) a molecular compound of six-coordinate silicon, (b) an ionic compound, $(SiH_3 \cdot 2\text{base})^+Co(CO)_4^-$, and (c) a situation intermediate between (a) and (b). An analogous problem has been discussed (Section IV,C). This time, however, we have a built-in probe that can help us to assess the degree of negative charge on the anion, namely, the carbonyl stretching frequency of the adduct. It is generally accepted that, as the negative charge on the metal atom in a carbonyl compound increases, the extent of $\pi$-donation outward to the carbonyl ligands also increases. Since this $\pi$-electron density must be accommodated in $\pi^*$ antibonding orbitals of the ligands, the C—O bond is weakened and the carbonyl stretching frequency decreases (see, e.g., Cotton and Wilkinson, *85*). In $SiH_3Co(CO)_4$ itself, the mean $\nu$(CO) frequency is 2052 cm.$^{-1}$, while that of fully ionized $Co(CO)_4^-$ in solution is 1883 cm$^{-1}$. The corresponding values for the trimethylamine, pyridine, and bipyridyl complexes as mulls are 1870, 1882, and 1860 cm$^{-1}$, respectively, from which it can be seen that all the complexes have appreciable ionic character, and approximate very closely to type (b) above.

Silyl manganese pentacarbonyl (*26*) behaves somewhat similarly to the cobalt analog, but is generally less reactive, particularly with respect to cleavage of the Si—metal bond. Thus HCl at 75° causes substitution of H by Cl to yield $SiH_{3-x}Cl_xMn(CO)_5$ ($x = 1$–$3$). Its adducts with tertiary amines are weaker, but the same kind of infrared evidence as before suggests that they are essentially ionic in nature, viz. $(SiH_3 \cdot 2B)^+Mn(CO)_5^-$. On the other hand, the product of the reaction of an excess of $NMe_3$ with $(SiH_3)_2Fe(CO)_4$, which can probably be represented as $(SiH_3 \cdot NMe_3)_2Fe(CO)_4$ (*40*), has much less ionic character.

One notable feature of the chemistry of alkyl metal carbonyls is the ease with which they undergo carbonyl insertion reactions, e.g.:

$$MeCo(CO)_4 + CO \rightarrow MeCOCo(CO)_4 \quad (50)$$

$$MeMn(CO)_5 + PPh_3 \rightarrow MeCOMn(CO)_4(PPh_3) \quad (51)$$

Numerous attempts to bring about similar reactions with silyl metal carbonyls have been unsuccessful. Triphenylphosphine displaces CO from silyl cobalt carbonyl in a substitution reaction, giving $SiH_3Co(CO)_3(PPh)_3$, while direct carbonylation fails, even at high pressures. These facts, together with the considerable thermal stability of these compounds, are consistent with the presence of $d_\pi$-$d_\pi$ interaction between silicon and the metal; carbonyl insertion, by breaking this bond, would be an energetically unfavorable step.

Further evidence regarding $d_\pi$-$d_\pi$ interactions comes from infrared data. Detailed studies of the $\nu$(CO) region for $R_3SiCo(CO)_4$ species [including $RSiH_2Co(CO)_4$] (*164*) and $Ph_3SiMn(CO)_5$ (*179*) indicate that they approximate closely to $C_{3v}$ and $C_{4v}$ symmetry, respectively. A force constant analysis suggests in both cases that the silyl group is competing with the carbonyl group *trans* to it for the electrons in the metal's filled $d_\pi$ orbitals.

## VIII. Other Miscellaneous Derivatives

### A. SILICON-GERMANIUM HYDRIDES

The hydrolysis of mixtures of metal silicides and germanides and also the action of a silent discharge on silane/germane mixtures have led to the production of complex mixtures of silicon-germanium hydrides. Higher silanes and germanes are of course produced simultaneously. Spanier and MacDiarmid (*241*) reported the preparation of $SiH_3GeH_3$ by the second route, while the Oxford group have shown how by the ingenious use of gas chromatography it is possible to separate and identify a wide range of mixed hydrides ranging up to mixed $(Si, Ge)_6H_{14}$ species (*14*, *262*, *263*). Varma and Cox (*268*) have also described the preparation of $SiH_3GeH_3$ from $KSiH_3$ and chlorogermane.

Mass spectrometry was used by Royen and Rocktäschel (*227*) to show the presence of $SiH_3GeH_3$, $Si_2GeH_8$, and $SiGe_2H_8$ among the hydrolysis products of a mixed calcium silicide-germanide. Recently, too, measurements of the appearance potential (*231*) and heat of formation (*162*) of $SiH_3GeH_3$ have been reported. Values of its bond-dissociation energy and thermochemical bond energy were inferred to be 100 and 42.5 kcal mole$^{-1}$, respectively. This very large difference is as yet unexplained, and should be compared with the present uncertainty regarding the Si—Si bond energy, previously discussed (Section II,C).

As might be expected, the chemistry of $SiH_3GeH_3$ shows close resemblances to that of $Si_2H_6$. Mackay *et al.* (*201*) have reported that it does not react under mild conditions with HCl or $BF_3$, but yields HCl with $AlCl_3$.

### B. SILICON-BORON HYDRIDES

Various earlier attempts to make mixed unsubstituted boron-silicon hydrides (e.g., *216*, *263*), using such methods as the hydrolysis of boridesilicide mixtures, were unsuccessful. There was some evidence that rapid disproportionation of the presumed products had occurred.

It has now been found by Amberger and Römer (*12*) that $KSiH_3$ will react with a variety of chloroboron compounds to yield Si-B derivatives such as $SiH_3B(NMe_2)_2$ and $SiH_3BBu(NMe_2)$. The adduct $BH_2Cl \cdot NEt_3$ gave rise to another adduct $SiH_3BH_2 \cdot NEt_3$; attempts to remove the amine led to decomposition. No compounds of the type $SiH_3BX_2$ (X = Cl, alkyl) or with more than one silyl group attached to boron could be isolated.

## IX. Conclusion

Silicon hydride derivatives have many attractive features. They are usually volatile, and can therefore be conveniently handled in a high vacuum system; they are often small molecules, and thus are well suited to examination by various physical techniques; and they provide a convenient and varied set of systems in which theories of $\pi$-bonding and *d*-orbital use can be tested.

For these reasons, and because they offer a challenge to manipulative ingenuity and theoretical description, it seems very probable that these compounds will be much more widely studied in the next decade. Doubtless the second most abundant element holds plenty of surprises in store.

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