SILICON:
BONDING AND STRUCTURE
Annual Survey Covering the Year 1973

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Theoretical-General

Photoelectron spectroscopy has continued to contribute greatly to our understanding of the bonding in organosilicon compounds.

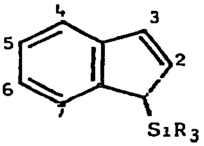
An excellent review on the method and its application through interpretation using MO models has been prepared by Bock and Ramsey.[1] The specific dissection of π and σ interactions for carbon and silicon compounds in this paper is very useful. An example of the application of the technique is the discussion of the bonding in the tetramethyl group IV compounds, Me_4M; M = C, Si, Ge, Sn, or Pb, by Lappert and coworkers. They show that the splitting between the two strictly symmetry determined CH levels, the $1t_1$ and $1e$, drops monotonically from 1.35 eV in neopentane to nearly zero in tetramethylplumbane, consistent with decreasing through space interactions in the $(Me)_4$ tetrahedron. The participation of *d* orbitals is ruled out as this would increase the separation of the levels going down the series.[2]

Hase and Schweig, using CNDO/2 calculations on the $MH_3CH_2CH_2$ cation and anion systems; M = C, Si, Ge; showed that it was impossible to determine the influence of M on conformation on the basis of electronegativity alone. In comparison with carbon, both the silicon and germanium ions had higher occupied and lower energy vacant σ molecular orbitals which were available for hyperconjugative coupling, resulting in anomalous conformations.[3] Pitt has presented a detailed analysis of hyperconjugation and its role in group IV chemistry. The relative roles of hyperconjugation, *p-dπ* bonding, and inductive effects in determining trends in ionization and reduction potentials, electrophilic reactivity, electronic spectra, and charge distribution are considered. Predictions on the importance of σ-π and σ-σ conjugation in organometallic compounds are also presented.[4]

Curtis has reported Extended Hückel calculations on the silaethenes, $H_2C{=}SiH_2$ and $H_2Si{=}SiH_2$. Based on Mulliken population analysis (however, see the Hydride section[96]) the results indicate that the C=Si π bond is exceedingly polar, $H_2C^-{-}SiH_2^+$, and that the energy mismatch of the carbon and silicon *p* orbitals is in large part responsible for the weakness of the π bond. High overlap in the Si=Si π bond suggest that it might be amenable to isolation. The rotation barriers increase in the order Si=C < Si=Si < C=C. In contrast to C_2H_4 in which the triplet state of the 90° twisted molecule is lowest in energy, for twisted H_2CSiH_2 the singlet state is lowest in energy. Inclusion of silicon *d* orbitals strengthen the π bond in SiH_2CH_2 through *p-d* hybrids, but decreases the rotational barrier.[5] The reactions of F_2SiSiF_2 with *cis*- or *trans*-2-butene have been found to be completely stereospecific thermally allowed reactions. Orbital symmetry considerations not involving *d* orbitals for the reactions are consistent with the formulation of an sp^2 or sp^3 hybridized species behaving as a triplet diradical.[6]

The CNDO/2 method has been applied to the conformational analysis of trimethylsilane,[7] and to the analysis of the possible pathways for the Peterson olefination reaction.[8]

The intriguing "fluxional" behavior of the silyl-cyclopentadienes has been investigated. Variable temperature ^1H NMR spectra of 5-(silyl)cyclopentadiene and 5-(silyl)methylcyclopentadiene were analyzed by Hagen and Russo. The results show that prototropic rearrangements proceed much slower than the metallotropic rearrangements. Static low temperature (-50°) isomers become "fluxional" as the temperature is raised.[9] Interestingly, Jutzi and Sauer report that although silyl group and proton migration is observed for *mono-*, *bis-*, and *tris-*(trimethylsilyl)cyclopentadiene, no equilibrium between 2,3,5,5-*tetrakis*(trimethylsilyl)cyclopentadiene on other possible isomers is observed.[10] Rakita and coworkers found for similar rearrangements of indenylsilanes, I



I

which show slow-exchange limiting spectra at room temperature but which equilibrate at elevated temperatures (185°), that the activation energy for the rearrangements is increased slightly by methyl substitution at the 2-position and decreased slightly by methyl substitution at the 4- and 7-positions.[11] For silicon substitution R_3 = Me_2Ph, $MePh_2$, Ph_3, $Me_2(MeO)$, and $Me_2(CH_2Cl)$ the equilibrium distribution of isomers but not the activation parameters are affected, consistent with the rate limiting step being intramolecular hydrogen migration,[12] and Hagen's results for the cyclopentadienes.[9]

The propargylic $MePh(\alpha\text{-naphth})MCH(CH_3)C{\equiv}CH$ and allenic $MePh(\alpha\text{-naphth})MCH{=}C{=}CHCH_3$ compounds; M = Si, Ge, Sn; with two neighboring assymmetric centers exist in two diastereotopic *erythro-* and *threo-*forms which are distinguishable in the ^1H NMR.[13] Another study has further indicated the potential for NMR in configurational studies of optically active silanes.[14]

Infrared[15] and mass spectral[16,17] studies have been reported for organosilicon derivatives of the carboranes. An analysis of the fragmentations and ion yields for the tetramethyl compounds of silicon, germanium and tin in their mass spectra has appeared.[18]

There have been reports of thermodynamic properties of tetraethylsilane,[19] and mixed alkylarylsilanes.[20,21] Mass spectral studies on polyfluorocyclobutylsilanes,[22,23] and a review on the mass spectra of group IV organometallic compounds appeared during 1973.[24]

A review on group vibrational frequencies with excellent tabulations on "normal" ranges for Si-X vibrations was prepared by Goubeau.[25]

Silicon-29 NMR

The use of pulse Fourier transform silicon-29 NMR as a bonding and structure probe increased rapidly during 1973. A survey of papers through mid-1972 and compilation of ^{29}Si chemical shifts was given by Marsmann.[26] The negative nuclear Overhauser enhancement (NOE) problems, which are opposite to those observed for ^{13}C[27] can be nicely overcome by the addition of paramagnetic impurities such as oxygen gas or $Cr(acac)_3$ as relaxation agents.[28] Levy and coworkers have also shown that dipole-dipole interactions between ^{29}Si and directly bonded protons are about 10 times less effective in relaxation processes for ^{29}Si than for ^{13}C-^{1}H interactions.[29] In studies of potential reference compounds for ^{29}Si NMR the intrinsic solvent shifts for the ^{1}H, ^{13}C, and ^{29}Si nuclei in 38 different solvents have been determined.[30] The ^{29}Si chemical shifts for several commonly used reference compounds have been compared (Table 1) to an internal $(EtO)_4Si$ standard.

Table 1. ^{29}Si Chemical Shifts Relative to Internal $(EtO)_4Si$*[31]

Compound		δ ^{29}Si(ppm)
$(Me_3Si)_2O$	[MM]	89.46
Me_4Si	[TMS]	82.59
$(Me_2SiO)_4$	[D_4]	63.05
$Me_3SiO(Me_2SiO)_xSiMe_3$ [$\bar{x} \approx 50$]		60.37
$(MeO)_4Si$		3.37

* Chemical shifts determined ±0.07 ppm, positive shifts to higher frequency, 15% v/v solute and standard in CCl_4. Suggested as a standard reference compound for ^{29}Si NMR because of its low frequency resonance, stability and commercial availability.[31]

The ^{29}Si chemical shifts and NOE effects for a series of linear and cyclic silazanes along with 8 silanes containing the Me_3SiNH-group have been determined and permit structural analysis in a manner analogous to that applied to polyorgano(cyclo)-siloxanes.[32] In a comparative study of the ^1H, ^{29}Si, and ^{119}Sn NMR spectra of methylhalosilanes and stannanes; Me_nMX_{4-n}; M = Si, SN; X = Cl, Br, I; n = 1-3; it was found that the ^1H chemical shifts were governed by the extent of *s* hybridization in the C-H orbitals indicating that it is not necessary to invoke a diamagnetic anisotropy of the Si-X bond to explain the trend observed for the ^1H chemical shifts in the methylhalosilanes. A dependence of ^{29}Si chemical shifts on the electronegativity of the halogen was attributed to significant $p_X \rightarrow d_{Si}$ back donation which increases with increasing electronegativity of the halogen.[33]

In a series of carbon-functional organosilicon compounds, $Me_{3-n}X_nSiCH_2OAc$, the substituent effect on the ^{29}Si chemical shift varied almost linearly with n for both X = OEt and X = OAc. It was also observed that an acetate group separated from silicon by one $-CH_2-$ group increased Si shielding, opposite to what one would predict on the basis of the inductive effect of the acetate group alone.[34] The ^{13}C and ^{29}Si chemical shifts for a series of methyl, phenyl and benzyl substituted silanes $RSiMe_nX_{3-n}$; X = F, Cl, OEt; n = 0-3; were also found to give a linear correlation between the phenyl and benzyl derivatives and also with σ^+ or σ_p constants.[35]

Most disturbing is the observation that the response of ^{29}Si chemical shifts to phenyl substituents in a series of phenyltrimethylsilanes for *meta*- and *para*-Me, MeO, F, Cl, CF_3, NO_2, and H.[36] This indicates that a great deal more work is necessary before correlations of ^{29}Si chemical shifts with electronic or bonding properties will be well understood. See also Silacycles, Ref. 73.

Alkenyl- and Alkynylsilanes

The photoelectron spectra of divinyldimethylmethane and tetravinylmethane along with the PE spectra of the analogous silicon compounds have been assigned by Schweig and coworkers[37]

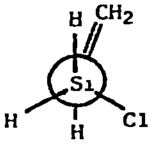
Table 2. PE Data (eV) for Divinyl- and Tetravinyl M Compounds[37]

	Vi_2MMe_2			Vi_4M	
	C	Si		C	Si
b_1	9.55	9.8	e?	9.52	9.7
			a_2	9.67	9.9
a_2	9.95	10.0	e?	10.06	10.1
			b_1	10.40	10.35

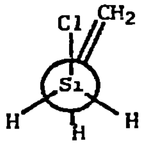
on the basis of MINDO/2 calculations. The a_2 MO of the divinyl compounds is split into b_1 and a_2 MO's of the tetravinyl compounds by spiroconjugation through the central atom. The b_1 level in the divinyl compounds becomes e levels in the tetravinyl compounds which are split by Jahn-Teller distortion. The splitting between the a_2 and b_1 levels in the divinyl compounds, a result of hyperconjugative through conjugation, is less for Si (0.2 eV) than for carbon (0.4 eV).[37]

In the area of hyperconjugative interaction in allylsilanes Ponec and Chvalovsky have found from charge transfer spectra that the electron accepting effect of the β-silicon atom decreased in the order $SiCl_3 > SiH_3 > Si(OEt)_3 > SiMe_3$, consistent with CNDO/2 calculations.[38] Extended Hückel calculations for a series of allyltrimethylmetal compounds, (M = C, Si, Ge, Sn, Pb) in which *d* orbitals were excluded from the basis set indicated that lowest energy conformation for the compounds had an angle between the M-C bond and the allyl π orbitals of about 20° and favored σ-π conjugation. Protonation of the terminal carbon increased the σ-π interactions and produced extensive perturbation of the C-C π bond.[39] However, in analysis and assignment of the infrared and Raman spectra of tetraallylsilane and stannane, no coupling of different allyl groups or perturbations of the methylene vibrations were observed, leading the authors to conclude that no evidence is found from the vibrational frequencies for any interactions between the "*d* orbitals" of the central atom and the allyl π electrons.[40]

Infrared and Raman data for vinylchlorosilane in the crystalline, liquid and gaseous state indicate that the *trans-gauche* conformation, II, exists in the crystalline state, while a dynamic equilibrium between II and III exists in the liquid and gaseous states. The energy difference between the rotomers is 0.25 kcal/mole and at 250°K the mole fraction of III is 0.46.[41]



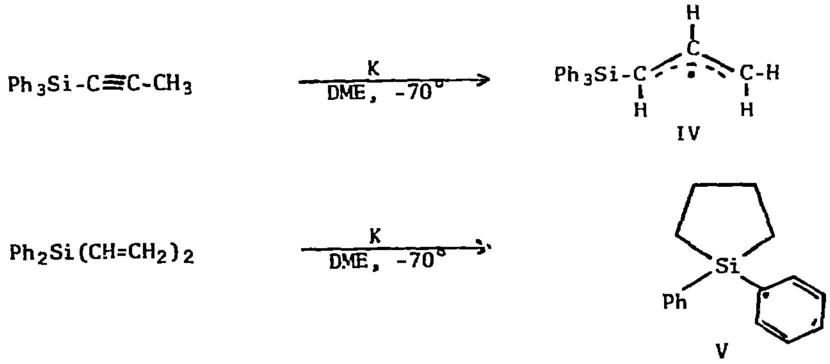
II



III

The NMR spectrum of 1,3-bis(trimethylsilyl)propene is somewhat anomalous in that the vinyl proton *cis* to the trimethylsilyl group has a higher chemical shift (τ = 3.98 ppm) than the proton *cis* to the trimethylsilylmethyl group (τ = 4.63 ppm).[42] This is in opposition to the photoelectron results[43] which indicate a stronger hyperconjugative interaction for the trimethylsilylmethyl group. It is suggested that in this compound the donor effect of the trimethylsilyl group is more important than its acceptor role and that the different chemical shifts are due to the magnetic anisotropy of the Si-C bond.[42]

Eisch and Smith have reported the rather interesting phenomenon that, while triphenylmethylsilane and triphenylcyclopropylsilane could be reduced with potassium in dimethoxyethane at -70° to give parent radical anions detectable by ESR, under similar conditions the radical anions of triphenyl(1-propynyl)silane and diphenyl(divinylsilane) could not be observed. Instead the triphenylsilylallyl radical, IV, and 1,1-diphenylsilacyclopentane radical anion, V, were observed.



On the basis of the results it was concluded that the electron affinities of groups attached to silicon decrease in the order -C≡C-R and CH=CHR > phenyl > methyl > cyclopropyl, and that the cyclopropyl group has no olefin-like conjugating ability with silicon.[44] In a subsequent study, the stability of the radical anions of triphenylvinyl metal compounds, which decreased in the order Si > Ge > Sn was ascribed to better *d*-*p*π bonding in triphenylvinylsilane radical anion.[45]

The acidity of a series of group IV substituted acetylenes, R-C≡CH; R = Me_3C, Me_3Si, Et_3Sn, Et_3Ge, *i*-Bu-S, Bu, and Ph; was studied by equilibrium transmetallation and the results correlated with the various groups.[46] The integrated absorption coefficient of the carbon-carbon triple bond and the acetylenic C-H vibration for a series of acetylenes $R_3M{-}C{\equiv}CH$; M = C, Si, Ge, Sn, Pb; R = Me, Ph; were found to vary linearly with the acetylenic proton chemical shift. However, no simple relation between the ^{13}C chemical shifts of the acetylenic carbons and the infrared data was found.[47] Mass spectra have been described in detail for 11 $R_2R^1SiR^2$ compounds; R = Cl, Me, H, F; R^1 = Me, Cl, F; R^2 = 2,2-difluorocyclopropyl or 3,3-difluoroallyl.[48]

Arylsilanes

The assignment of the first band in the photoelectron spectrum of phenylsilane indicates a slight stabilization of the *a*" orbital (antisymmetric π) compared with toluene (9.43 *vs* 9.35 eV) but a large stabilization of the *a*' orbital (symmetric π) (9.18 *vs* 8.80 eV). Substitution of hydrogens on silicon by methyl groups ha little effect on the π levels. However, inclusion of *d* functions i the CNDO/2 calculations is required to correctly predict the relati orbital energies.[49] In contrast, a series of group IV substituted aromatic nitrosyl radicals, [*para*-(Me_3X)-C_6H_4-N(*t*-Bu)$O^{\bullet}$], studied b NMR and ESR including ^{117}Sn, ^{119}Sn, and ^{207}Pb satellites, showed hyperfine coupling constants linearly related to the *covalent radiu* of X. It was also shown that the data of Kruzic and Kochi for the $Me_3X{-}CH_2^{\bullet}$ system,[51] *followed the same relationship with* covalent radius of X, indicating the spin transfer mechanism is the same for both series of molecules. While a simple hyperconjugative mechanism for spin transfer is not adequate to explain the results, the same spin transfer mechanism for both series, with and without an intervening aromatic ring, suggests that the π system and *d* orbitals are not involved in the spin transfer.[50]

On the other hand, ^{19}F chemical shifts for a series of *para*-fluoroaromatic silicon compounds p-F-C_6H_4-MPh_2X (M = C or Si) gave the *para* shielding order H > NH_2 > OEt > OH > Cl ≈ N_3 > Br > F for the carbon compounds and NH_2 > H > OH ≈ OEt > Cl ≈ Br > F ≈ N_3 for the silicon compounds. The changes in shielding order were attributed to possible Si-X π interactions.[52] Several studies of dipole moments[53], and ultraviolet spectra of arylsilanes with various substituents[54,55] showed typical behavior which was interpreted in terms of p-$d\pi$ interaction. In nitrations of phenyltrimethylsilane and isomeric fluorophenylsilanes the trimethylsilyl group was found to be a poor *para*-director suggesting that its inductive effect is diminished by back bonding. A detailed NMR analysis of the products is given in the paper.[56] The rates of pyrolysis of 1-phenylethyl acetate and three 1-trimethylsilylphenylethylacetate isomers showed that the trimethylsilyl group activated in all positions in the order *o*- > *m*- > *p*-, suggesting that $SiMe_3$ functioned as an inductive electron donor in all positions.[57] The ^{19}F NMR Spectra for a series of 21 perfluorophenylsilanes, $(C_6F_5)_nSiX_{5-n}$; n = 1-4; X = H, alkyl, halo or amino; $C_6F_5SiMe_2SiMe_3$, and $(C_6F_5SiMe_2)_2$ were analyzed and discussed in relation to the π acceptor action of the Si-X groups and long-range interannular F-F and F-H coupling.[58]

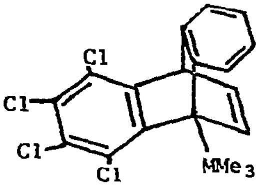
Detailed theoretical calculations using Del Re and Pariser-Parr Pople techniques for a series of phenylfluorosilanes, Ph_nSiF_{4-n} (n = 1-3) have been reported.[59]

A single crystal X-ray structure of tetraphenylsilane indicates that the molecule has S_4 symmetry with an Si-C bond length of 1.863 Å and a mean C-C bond length of 1.389 Å. The C-Si-C bond angle is tetrahedral. In studies of tetraarylsilanes Mislow and coworkers have found the barriers to aryl group rotation in the liquid state for tetra-*ortho*-tolylsilane to be no greater than 16 kcal/mole, too low to allow the isolation of conformational isomers as had been claimed earlier.[61] Similar low temperature NMR studies of triarylsilanes are consistent with a propeller-like conformation in the ground state. The barrier to interconversion of the two enantiomeric propellers by a two-ring flip mechanism is estimated to be 10 to 13 kcal/mole.[62] The ESR spectrum of the radical anion of tetraphenylsilane, formed by electrochemical reduction indicated that the unpaired electron was delocalized over all four phenyl rings.[63]

An infrared study of the symmetric ring stretching band near 1600 cm^{-1} for a series of *meta*- and *para*-substituted benzylsilanes and stannanes confirmed that the Me_3MCH_2- group acts as a resonance donor to the ring with a σ°_R of -0.20 for M = Si and -0.26 for M = Sn.[64]

Values of σ_p constants for some substituted silyl and germyl groups in p-RC_6H_4Me; R = Me_3Si, Me_2HSi, H_3Si, $ClMe_2Si$, Cl_2MeSi, Cl_3Si, FMe_2Si, F_2MeSi, F_3Si, $Me_2(MeO)Si$, $Me(MeO)_2Si$, $(MeO)_3Si$, Br_3Si, $(Me_2N)_3Si$, Me_3Ge, H_3Ge, and Cl_3Ge; have been determined from dipole moments and from ^{13}C-H coupling constants. The values obtained from the two independent methods are in qualitative agreement and correspond with theory better than kinetic values. The results indicate electron back-donation in Si-Cl, Si-F, and Si-O bonds, the effect being most pronounced for Si-OMe groups. GeH_3 has a higher + I effect than SiH_3 and $GeCl_3$ has a higher - I effect than $SiCl_3$.[65]

Suzuki and coworkers have found by variable temperature NMR studies restricted rotation about the C-M bond for compounds of the type VI with the barrier increasing in the order Sn < Ge < Si < C, consistent with the C-M bond length.[66]

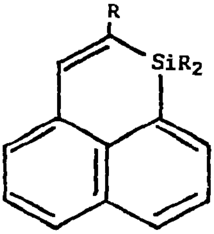


VI

Results consistent with σ-π hyperconjugative interactions have been found for a series of indanyl and indenyl derivatives of silicon and tin by Rakita and coworkers.[67] The ionization potentials determined by mass spectrometry decreased by 0.6 to 0.8 eV when silicon was substituted at the 1-position.[67]

The extent of *p*-*d*π interaction in trimethylsilyl substituted naphthalenes studied by polarography, charge transfer and ultraviolet spectroscopy was greater in the lowest unoccupied molecular orbital. The inductive effect of the substituent was more important for the two highest filled molecular orbitals.[68]

A series of papers dealing with dimethylsilyl and methyl bridged biphenyl units investigated through-conjugation between the biphenyl units. In neither the radical anions nor the triplet states of the molecules was through-conjugation observed on the ESR timescale.[69] An investigation of the ease of reduction and radical anion ESR spectra for a series of silaphenalenes VII has been reported.[70]



VII

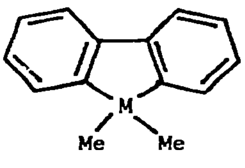
Silacycles

The vertical ionization energies of the uppermost ring orbitals for a series of silacyclobutanes $R_2Si-(CH_2)_3$ have been determined by He(I) PE spectroscopy. Methoxy, hydrogen, and methyl substituents on silicon have about the same effect on the two MO's splitting them by about 0.55 eV. However with increasing chlorine substitution the two MO's begin to converge, the b_1 orbital being destabilized by chlorine substitution but apparently not by methoxy substitution. It is concluded that other effects in addition to the inductive effects of the substitutents must be operating in these systems.[71] (See Group VI, 166)

Table 3. PE Data for Silacyclobutanes[71]

R_2	Ionization energy (EV)		
	a_1	b_1	(C_{2v})
$(MeO)_2$	10.15	10.70	
H_2	10.05	10.60	
Me_2	9.40	10.00	
Me_2-2-Me	9.20	9.65	
MeCl	9.95	10.30	
Cl_2	10.50	10.70	
1,1-diMe-silacyclopentane	9.75	10.10	

In studies of spiroconjugation for fluorenes VIII and IX by



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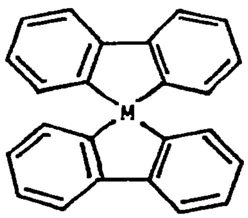


IX

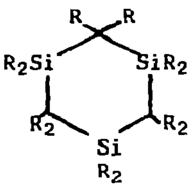
He(I) PE spectroscopy Schweig and coworkers report the following ionization energies.[72]

Table 4. PE Data for Fluorene Derivatives[72]

Compound	1	2	3	4	5	6
VIII, M = C	7.8	8.75	9.75			
VIII, M = Si	7.9	8.80	9.7	10.25		
IX, M = C	7.7	8.0	8.7	9.4	9.9	
IX, M = Si	7.85	8.0	8.85	9.1	9.85	10.25

The ratio of the spiro splitting (0.60) is similar to that observed in tetravinylsilane or tetravinylmethane,[37] and proportional to the square of the $2p_\pi$-AO coefficients (obtained from MINDO/2 calculations) for the atoms next to the spiro atoms.

Proton and ^{29}Si NMR studies of chloro, hydrogen, trimethylsilyl, and methyl derivatives of compounds of the type X, XI, XII



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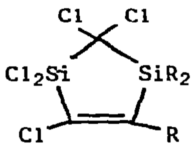

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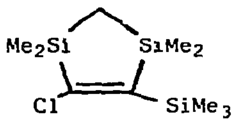
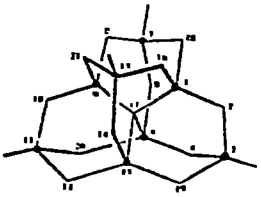


XII

indicate that the polarity of the Si-Cl bond decreases in compounds containing Si-Cl and C-Cl groups with increasing number of CCl_2 groups. In compounds containing Si-H and C-Cl groups, the polarity of the Si-H bond increases with the degree of chlorination of the carbon atoms.[73]

Fritz and coworkers have reported the structures of several new carbosilanes with structures XIII, XIV, XV, XVI determined by PMR, mass spec and crystallographic studies.[74]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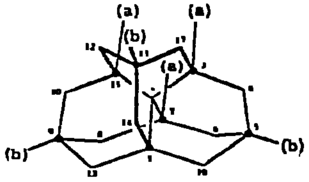
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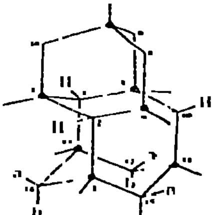
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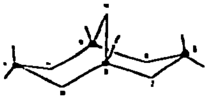
XVI

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The He(I) PE spectra for adamantane, silaadamantane and urotropine have been reported and assigned by Schmidt.[75] Substitution of silicon for carbon results in a reduction of the splitting of the levels and a trend to lower ionization potentials, (see 72 and 37). In a subsequent report[76] the photoelectron spectra of some of the derivatives of 1,3,5,7-tetrasilaadamantane including the tetrafluoro-, tetrachloro-, and tetramethylderivatives indicate the energy levels are dominated by the inductive effect of the substituents. Splitting of levels by silicon *d* orbitals is not observed, emphasizing that *p-dπ* interactions in tetravalent silicon compounds are too weak to be detected by photoelectron spectroscopy.[77]

A complete vibrational analysis of 1,1-difluoro- and 1,1-dichloro-1-silacyclopentane has been performed by Laane and coworkers.[78] Mass spectral studies of silacyclopentanols,[79] and spiro-heptanes, nonanes, and octanes with silicon spiro-atoms[80] have been reported. Electron diffraction structural data for silacyclobutane, 1,1-dichlorosilacyclobutane and 1,1,3,3-tetrachlorodisilacyclobutane are available.[81]

The X-ray crystal structure of octa-chlorohexasila-asterane, $Si_6Cl_6H_8Cl_8$, Figure 1, shows that the Si-atoms have significantly different bond lengths, Si-C = 1.815 Å, Si-Cl = 2.056 Å at the $SiCl_2$ groups but 1.890 Å and 2.025 Å respectively at the SiCl groups. The bond angles at silicon (93°) are larger than those at carbon (87°).[81a]

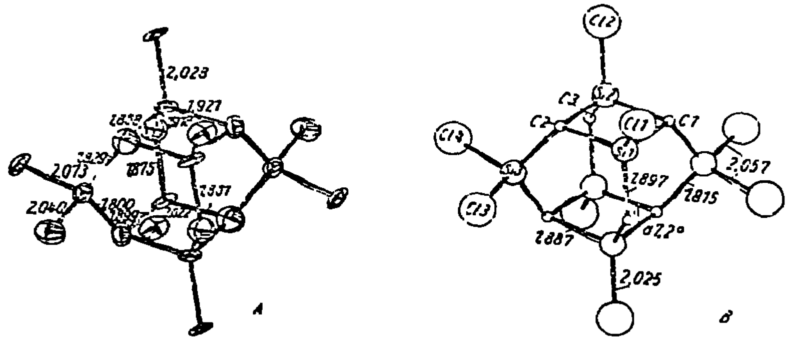


Figure 1. Structure of $Si_6C_6H_8Cl_8$[81a] (Reproduced with the permission Verlag J. A. Barth)

Polysilanes

Traven and West have reported the finding that permethylpolysilanes form weak charge transfer complexes with tetracyanoethylene having band maxima: Si_2, 417; Si_3, 480; Si_4, 520; $Si(Si)_4$, 458; cyclo-Si_6, 507 (two overlapping bands, 477 and 555 nm).[82] These maxima correlate linearly with the first ionization potentials of the compounds determined by photoelectron spectroscopy.[83] Sakurai and coworkers confirmed these results and showed that upon irradiation of the complexes the ESR spectrum of TCNE radical anion may be observed. They also report band maxima for Si_5, 544 nm; and hexamethyldigermane, 435 nm.[84] These reports represent the first examples of charge transfer between σ donors and a π acceptor.

A comparison of the ultraviolet spectra with charge transfer spectra of the TCNE complexes for phenyltrimethylsilane, phenylpentamethyldisilane, phenylheptamethyltrisilane, and their benzyl analogs showed a bathochromic shift of the ^1L_a band with increasing number of silicons but almost no change in the wavelength of the charge transfer band maxima. However, the introduction of a methylene group between phenyl and silicon did result in a destabilization of the HFMO.[85] A study of the charge transfer complexes of *para*-substituted-phenylpentamethyl disilanes with TCNE and Cl, F, Me, MeO, CH_2SiMe_3, or H substituents indicated that the pentamethyldisilyl group has a donor ability comparable with methoxy or trimethylsilylmethyl. A *d* acceptor type of interaction was also observed.[86]

Pentafluorodisilane has been isolated and characterized by infrared, NMR, mass spectral, chemical and thermal stability studies.[87] A kinetic determination of the Si-Si bond dissociation energy in hexamethyl disilane gave a value of 80.5 kcal/mole,[88] substantially higher than the previously accepted value of 67 kcal/mole.[89] From a study of the pure rotational Raman spectra of Si_2H_6 and Si_2D_6, the Si-Si bond length was calculated as 2.327 Å, and the H-Si-H and D-Si-D bond angles as 107.89°.[90] An investigation of the molecular structure of hexachlorodisilane by electron diffraction gave Si-Si and Si-Cl bond lengths of 2.324 and 2.009 Å, respectively, and a Cl-Si-Cl bond angle of 109.7°.[91]

The vibrational spectra of perphenyl, permethoxy, and perchlorotrisilane have been reported and assigned.[92] The physicochemical properties including density, viscosity, surface tension, freezing point, boiling point, heat of vaporization, and vapor pressure constants for trisilane through heptasilane have been determined.[93] In addition to the assignment of Raman spectra, the density, vapor pressure and molecular refraction data for the silanyl iodides, SiH_3I, Si_2H_5I, and Si_2H_7I have been reported.[9]

The very common observance of the $PhSiMe_2^+$ ion in both mass spectral the photochemical studies of organocyclopolysilanes has been pointed out and *p-dπ* stabilization or the formation of the "silatropylium" ion suggested as the reason.[95]

Hydrides

A very significant finding in the area of bonding in organosilicon compounds is that of Bellama, Evans and Huheey, who report that the dipole moment of methylsilane (0.73 D) does not coincide with the bond moment of the $Si \rightarrow C$ bond, but rather is in the direction $H_3C \rightarrow SiH_3$.[96] This is contrary to the results obtained by Mulliken population analysis which predict $H_3C \leftarrow SiH_3$,[96a] and raises an important *caveat* in interpretation of polarities of organosilicon molecules on the basis of Mulliken population analyses. The effect for methylsilane is attributed to the large $Si \rightarrow H$ bond moments.[96] Bond moments and effective charges on hydrogen for 40 triorganosilanes have been reported and vary from 1.59 D and -0.22, respectively, for Pr_3SiH to 0.75 D and -0.11 for $(C_6F_5)_3SiH$.[97]

A study of the effect of hybridization, structure and ^{29}Si-H coupling constants for a series of aryl and alkyl silanes has shown that the experimental bond angles for methylsilanes are accounted for by simple hybridization in terms of directed valency, and that the ^{29}Si-H spin-spin coupling constants correlate with the *s* character of the hydrid orbitals in the same manner for the silanes which has been observed for methanes.[98]

Several reports relating frequencies and integrated intensities of the Si-H stretching mode organosilanes with inductive and *p-dπ* interactions.[99-103] When conjugative effects are absent, ν(Si-H) and the intensity of the Si-H band correlate linearly with the sum of the Taft σ* constants for the silicon substituents, Σσ*.

$$\nu(\text{Si-H}) = 2112 + 23.1\ \Sigma\sigma^* \qquad \sqrt{A} = 0.19\ \Sigma\sigma^* + 1.35$$

Table 5. Physical Measurements on Silicon Hydrides

Compound(s)	Techniques	Comments	References
$MeSiH_3$, $MeGeH_3$, Me_2SiH_2, $EtSiH_3$	normal vibrations	Urey-Bradley	105
$EtMeSiH_2$	infrared, Raman	*trans*-rotomer favored in solid and liquid	106,107
$EtMeSiH_2(D)_2$	microwave	Stark effect, dipole moments	108
Me_2SiH_2	microwave	torsional fine structure analysis	109
Me_2SiH_2, C_3H_8, Me_2S	microwave	rotational barriers	110
$ClCH_2SiMeH_2$	infrared	*trans*-rotomer more polar than *gauche*	111
$BrCH_2SiH_3(D)_3$	microwave	structural parameters reported	112

Table 5 Continued

Compound(s)	Techniques	Comments	References
methylsilanes	tritium recoil	Si-H bond energies	113
$SiH_4(D)_4$	gas infrared & Raman	detailed analysis	114
SiH_4	far infrared	molecular octopole = 3.0×10^{-34} esu/cm^3	115
SiH_4	high resolution infrared	new bands 4200-4500 cm^{-1}	116
SiH_4	tandem mass spec.	proton affinity	117,118
SiH_4	infrared	analysis γ-3 band	119
SiH_4	ion-molecule rxn.	reactions with Si^+	120
SiH_4, GeH_4	MO calc, MSXα method	good I.P.s & transition energies, bad bond lengths and energies	121
CH_4, SiH_4	non empirical MBO calculations	better energies than empirical methods	122
CH_4, SiH_4	Hartree-Fock MO	good core excitation energies	123
SiH_3, SiH_3^+, SiH_3^-	configuration interaction calc.	SiH_3^+ is D_{3h}, SiH_3^- & SiH_3 are C_{3v}	124
$SiH_4 + H^- \rightarrow SiH_5^-$	*ab initio* MO	geometries and energies calculated	125

When calculated values of ν are higher than experimental, *d-pπ* conjugation is important. Similarly, the extent to which the experimental intensity is greater than the calculated intensity may be used as a measure of conjugation effects.[104]

Many studies of structural parameters and rotational barriers in simple alkyl silanes appeared during 1973. These are summarized in Table 5.

Halosilanes

The photoelectron spectra of the fluorosilanes, SiF_3X (X = H, Cl, Br, Me), have been reported, assigned and compared with other PE data.

Table 6. Ionization Potentials (eV ± 0.02 eV) for Fluorosilanes[126]

	SiH_3X	SiF_3X	CH_3X	CF_3X
Cl *pπ* lone pair	11.61	13.44	11.28	13.08
M-Cl σ	13.4	15.33	14.4	15.15
Br *pπ* lone pair	10.96	12.46	10.53	12.12
M-Br σ	12.85	14.55	13.5	14.26
	Si_2H_6	Si_2Cl_6	Si_2F_6	
Si-Si σ	10.60	10.79	13.20	

Although some aspects of the perturbations can be rationalized by invoking *p-dπ* interactions, the spectra show no compelling evidence for such. Vibrational band comparisons suggest no interaction peculiar to the silicon compounds.[126] The NQR ^{35}Cl, ^{79}Br and ^{80}Br frequencies were measured for a series of organometallic compounds of germanium and tin. A comparison of these data with earlier data for silicon and carbon compounds indicates that π bond character exists only in the Si-Cl bond and to a lesser degree in the Ge-Cl bond. The ionic character of the metal-halogen bond in all the series decreases with increasing halogen substitution.[127,128]

A linear correlation has been noted between the average values of ^{35}C NQR frequencies and the Si-Cl symmetric stretching frequency in $SiCl_4$, $(Cl_3Si)_2O$, $(Cl_3Si)_2NH$, and Cl_3SiF. Because Si_2Cl_6 deviated from the correlation, a new assignment of the vibrational bands at 492 and 352 cm^{-1} to the symmetric SiCl stretch and the symmetric deformation vibration, respectively was proposed.[129]

The radicals $\cdot SiCl_3$, $\cdot GeCl_3$, and $\cdot SnMe_nCl_{3-n}$ ($n = 0-3$), prepared in either an adamantane matrix or in the self-matrix, have been studied in ESR spectroscopy. Comparison with other available data indicates that the radicals $\cdot MMe_3$, $\cdot MH_3$, and $\cdot MCl_3$ are strongly bent for M = Si, Ge, and Sn, but the carbon radicals are nearly planar. The *g* values increase from carbon to tin in the methyl series but decrease in the chloro series. This indicates that ligand spin-orbit coupling from *p-dπ* bonding involving chlorine is important in the chloro radicals.[130]

The analysis of torsional barriers from the infrared spectra of chloromethyl-, dichloromethyl-, methylchloro-, and methyldichlorosilane shows lower rotational barriers for the chlorosilyl compounds than for the chloromethyl compounds. It is suggested that secondary overlap between C-Cl bonds and Si-H bonds is more effective than secondary overlap between Si-Cl bonds and C-H bonds resulting in the higher barriers for the chloromethyl compounds.[131] In CNDO calculations applied to methyltrifluorosilane the staggered conformation was found to be most stable and non-bonded Si...H interactions important in the definition of the potential curve for rotation.[132]

A large number of papers dealing with physical properties of halosilanes appeared during 1973. While not all the compounds are organosilanes, the results are potentially useful to organosilicon chemists and are summarized in Table 7.

Table 7. Physical Measurements on Halosilanes

Compound(s)	Study	Comments	References
SiF_4(g)	Electron Diffraction	rSi-F (1.552 Å)	133
SiF_4	Electron Diffraction	rSiF = 1.555 Å	134
SiF_2	Excited vibrational states microwave	rSiF = 1.5901 Å <FSiF = 100°46'	135
SiF_2	*ab initio* calculations	ground state	136
SiF_2	*ab initio* calculations	electronic spectrum	137
SiF_4, CF_4	Dissociative electron capture	heat of formation SiF_3(g)	138
SiF_3(g)	Emission spectrum		139
$HSiF_3$	Excited vibrational states microwave	rSiH = 1.4468 Å; rSiF = 1.5624 Å <HSiF = 110.64°	140
MXH_3; MHX_3 M = C, Si, Ge; X = F, Cl, Br	Bond lengths *vs* electronegativity	linear correlation	141
$SiCl_nF_{4-n}$ n = 0-4	Raman spectra	Assignments, Urey-Bradley Field Calulation	142
MH_2X_2	Urey-Bradley force constants	M = C, SiGe	143

Table 7 Continued

Compound(s)	Study	Comments	References
MX_4 X = F, Cl, Br, I	Vapor phase Raman	Assignments: M = C, Si, Ge, Sn, Ti, Zr	144
MHX_3 X = F, Cl, Br, I	Coriolis constants	Theoretical calculation M = C, Si	145
MX_4 X = Br, Cl	Raman spectra	M = C, Si, Ge, Sn	146
$SiCl_4$	Raman spectra	Dilution studies	147
MF_4	Vibrational analysis	Green's function M = C, Si, Ge	148
$SiFCl_2Br$ and $SiFClBr_2$	Vibrational spectra ^{19}F NMR		149
F_3SiPH_2	Electron diffraction	rSi-P = 2.207 Å is short	150
SiF_5^-, $SiF_5NH_3^-$ SiF_5HNEt^-	^{19}F NMR	Intermolecular exchange study	151
$SiCl_3X{\cdot}NMe_3$	Raman and IR	X = H, F, Br, I	152
$MX_4{\cdot}(PMe_3)_2$ M = Si, Ge, Sn X = Cl, Br	Vibrational spectra	Assignment of M-P modes	153
$MeSiCl_3$	Microwave spectra		154
Methylhalosilanes	Thermodynamic	Enthalpy of Formation 29 compounds	155
$MeSiCl_3$	Thermodynamic functions	Calculation from IR	156
Cl_3SiOMe	Raman and IR		

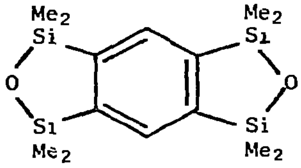
Group VI Compounds

Bock, Mollere, Becker and Fritz have assigned and correlated the photoelectron spectra of dimethyl ether, methoxysilane and disiloxane on the basis of CNDO/2-SCF-MO calculations.[158] A relatively small change in conformation from doubly eclipsed in dimethyl ether and methoxy silane to singly eclipsed in disiloxane results in an inversion of two molecular orbitals energy, the $3b_2$ crossing above the $4a_1$ level, giving an assignment of the spectra different from previous reports.[159]

The widening of the central M-O-M bond angle is not a function of *d* orbital involvement. The molecular orbital, $3b_2$, which experiences a large stabilization on widening the angle, has the wrong symmetry for π interaction, and the $4a_1$ orbital, which has the correct symmetry for π interactions, is destabilized as the bond angle increases. The patterns are found to be just those predicted by simple Walsh diagrams.[160] Substitution of silicon for carbon is found to result in a general inductive destabilization which is, to some extent countermanded by electron delocalization in the higher molecular orbitals by *d* orbital interaction.[158] For the corresponding sulfides the same workers found the orbital sequence ($2b_1$, $4a_1$, $3b_2$) was independent of conformation. The large inductive effect upon silicon substitution for carbon and *d* orbital stabilization observed were consistent with the findings for the oxygen systems.[161]

In a series of structural studies on hexaalkyldisiloxanes and trialkylalkoxy- or aryloxysilanes, R_3SiOX, with R = Me, Et, Pr; X = SiR'_3 (R' = Me, Et, Pr) or Me, *t*-Bu, Ph, *p*-Cl-C_6H_4, the M-O-M bond angles were determined by dipolemetry.[162] An analysis of the factors which influence the bond angle led to the conclusions that *p*-*d* or *p*-*p* π conjugation with the oxygen lone pair resulted in an increase in the oxygen valence angle and that steric factors also tended to open the Si-O-X angle.[163] (Compare with the PE results discussed above.) A study of the molecular optical anisotropies of the Me_3CO- and R_3SiO- groups R = Me, Et, Pr, determined by a depolarized Rayleigh diffusion method indicated a lack of conjugation between the two *p-dπ* bonds of the Si-O-Si system.[164]

The crystal and molecular structure of the benzo-bis-oxadisilole, XVII, has been reported. The oxadisilole rings have approximately C_{2v} symmetry and bond length of C-C, 1.411 Å, Si-C, 1.882 Å, and Si-O, 1.647 Å were determined.[165]



XVII

The ^1H NMR chemical shifts of 5 disilapentanes, $CH_2(CH_2SiMeRR')_2$, R, R' = Cl or Me, compared with oxadisilacyclohexanes and other literature values showed that the oxygen functionality has a considerably lower influence on the chemical shifts of the SiMe groups than chlorine, consistent with inductive effects along with better *2p-3d* interactions for the Si-O compounds than *3p-3d* interactions for the chlorine compounds.[166] (Compare with silacycles, Ref. 71.) The vibrational spectra of hexamethylcyclotrisiloxane and hexamethylcyclotrisilazane have been more completely assigned using infrared and Raman data.[167]

The relative basicities of the oxygen atom in $Me_3Si(CH_2)_n$-$OSiMe_3$ n = 1-4 was shown by infrared spectroscopy to be equivalent to that of $Me_3C(CH_2)_4OSiMe_3$, suggesting that for n $\geq$ 2, O → Si coordination interaction is significant. The dipole moments and basicities of the cyclic $O-(CH_2)_4SiMe_{2-n}(OEt)_n$,

$n = 0-2$, were higher than $(EtO)_nMe_{3-n}SiR$, R = Me, Et, Bu; $n = 1.3.$[168] However, for the symmetric bis(trimethylsilylalkyl)-ethers, $[Me_3Si(CH_2)_n]_2O$, infrared and NMR studies indicated that O → Si coordination was insignificant for $n > 2$.[169] In a further study of the "alpha effect" in organosilicon compounds Chvalovsky and coworkers found that the valence vibrational frequency $\upsilon(D-O-X)$ for $R_3Si(CH_2)_nOX$; X = H, $SiMe_2L$, Ac, $(CH_2)_mSiMe_3$ ($m = 1-4$); L = Et, Ph; were considerably lower when $n = 1$ than for the carbon analogs. The effect, not observed when $n > 2$, was attributed to some type of interaction of the σ system of the C-O bond with the silicon *d* orbitals.[170] The basicity of a series of 39 ethoxy silanes and disiloxanes have been determined by measuring the infrared shifts of the OH group in phenol on complex formation, and correlated with Taft substituent constants.[171] Intramolecular hydrogen bonds in compounds of the type $PhMe_2Si-(CH_2)_n-OH$, $n = 1,2$ and Ph_3SiCH_2OH, studies by infrared techniques were found to be weaker than in the carbon analogs. The increasing separation of the OH group from the aromatic system and the inductive effect on silicon substitution are more important than *p-d*π interactions with the aromatic ring.[172]

The infrared bands for Si-H and Si-F for a series of 32 aryloxysilanes with H, F, alkyl, Ph, and/or p-RC_6H_4O; R = H, Cl, NH_2, Me, or NO_2; were measured and discussed in terms of bonding interactions.[173] The infrared spectra for a series of chloromethyl and acetoxymethyl substituted silanes, $ClCH_2Si(OEt)_nMe_{3-n}$, $ClCH_2Si(Ac)_nMe_{3-n}$, $AcCH_2Si(OEt)_nMe_{3-n}$, and $AcCH_2Si(Ac)_nMe_{3-n}$ have been reported.[174]

An examination of the carbonyl stretching frequency for a group of α-metalloid ketones, R_3MCOR' and $(R_3M)_2C{=}O$; M = C, Si, Ge, Sn; R = Me, Ph; R' = Me, Ph; using a corrected $\upsilon^*(CO)$ which excludes effects extraneous to the CO bond such as molecular geometry and potential energy contributions from internal coordinates other than the CO bond indicates that C, Ge, and Sn, affect the CO bond strength to the same degree while α-silicon weakens the CO bond. The results were interpreted in terms of *d*-π electron withdrawal from the ground state.[175]

It has been observed that the dithioacids of the type $RCS_2MR'_3$ RCS_2MMe_3; R = Ph, *p*Me-C_6H_4, *p*-Cl-C_6H_4, *i*-Pr, and α-naphth; M = Si, Ge, Sn; have similar properties in the infrared and ultraviolet regions of the spectrum similar to the acylsilanes and germanes. The π→π* band shifts to the blue and the π→π* transition to the red in the order of increasing atomic number of M.[176]

The ^1H NMR spectra and infrared spectra of trialkylsilyl esters of aroylphosphonic acids have been determined but do not correlate with LCAO molecular orbital calculations.[177] Similar properties to those discussed above for the alkoxy silanes and the "alpha" effect of silicon have been observed in the dipole moments and ultraviolet spectra of sulfur containing organosilicon compounds, $[R_3Si(CH_2)_nSCH_2]_2$, $R_3Si(CH_2)_nSCH{=}CH_2$, and $R_3Si(CH_2)_nSH$; n = 1-3; R = Me, Et.[178] NMR, infrared and Raman data for a series of seleno, $Me_{4-n}M\ (SeMe)_n$; M = Se, Ge, Sn; n = 1-4 has appeared.[179]

The gas and liquid phase infrared and Raman spectra of $Me_3SiOH(D)$ have been determined and assigned.[180]

The infrared and Raman frequencies and intensities of $R_3SiO(CH_2)_2NHSiR'_3$; R = R' = Me; R = Et, R' = Me; R = R' = Et; $Me_2Si(OCH_2CH_2NHSiMe_3)_2$; $Me_3SiO(CH_2)_3NHSiMe_3$; $Me_3SiOCH(Me)CH_2NHSiMe_3$ and $(Me_3SiOCH_2)_2C(Me)NHSiMe_3$ have been reported and analyzed.[181] Studies on the related silatranes and germatranes have included crystal structures,[182] and ultraviolet spectra.[183]

Mass spectral studies of phenylphenoxy- and phenylcresoxysilanes,[184] trimethylsilyl derivatives of long chain alcohols, C_9 to C_{12},[185] and trimethylphenoxy silanes[186] have appeared. The properties of the tetraethoxysilane-iodine charge transfer complex have been determined.[187]

Group V Compounds

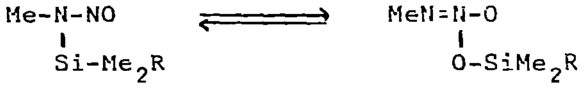
The role of $p \rightarrow d\pi$ bonding between silicon and nitrogen has been investigated using stereochemistry, dipole moments and low energy photoelectron spectra comparisons with molecular orbital calculations for SiH_3NCO, SiH_3N_3, and $(SiH_3)_3N$. *Ab initio* calculations predict the correct geometry for the pseudohalides whether or not *d* orbital functions are included, but trisilylamine is only correctly predicted to be planar when *d* orbitals are included. The agreement with experimental dipole moments and low energy PE data is only good when *d* orbitals are included in the calculations, except for silylazide, in which inclusion of orbitals does not improve the fit with PE data.[188] This is interesting in that silylazide is the only bent silicon compound treated in the paper. The cyrstal structure of triphenylsilylazide shows that this molecule is also bent with an Si-N-N angle of 120.5° and that the Si-N bond length (1.74 ± 0.02 Å) agrees with the sum of the silicon and nitrogen single bond radii.[189]

Quantum calculations for *ortho*-, *meta*-, and *para*-, phenylene diamine and the N,N'-bis(trimethylsilyl) analogs using a Del Re approximation for the σ-system, a modified Pariser Parr Pople method for the π system and only partial overlap of the *p* and *d* orbitals gave good agreement with experiment for singlet energy transitions and oscillator strengths.[190]

In a study of the ^{15}N-H NMR coupling constants for a series of aminosilanes and related compounds Cowley and Schweiger found that variations in the coupling constants could be explained on the basis of electronic distributions within the σ framework of the molecules without recourse to π bonding interactions.[191] Hetero- and homonuclear double resonance techniques have been applied to the magnitudes and signs of the coupling constants, and the chemical shifts involving ^{1}H, ^{15}N, ^{19}F, ^{29}Si, and ^{31}P in PF_2NH_2, PF_2NHSiH_3, $NH(SiH_3)_2$, and $N(SiH_3)_3$.[192]

The first examples of organosilylhydrazyl radicals, tris(trimethylsilyl)hydrazyl and tris(*tert*-butyldimethylsilyl)hydrazyl, have been generated by electrolytic oxidation of the parent hydrazines, or by photolysis. West and Bichlmeir report that the ESR spectra of these radicals show unusual localization of spin density on one nitrogen and attribute the phenomenon to dative lone-pair delocalization from the disubstituted nitrogen to silicon.[193]

Low temperature ^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR studies of organosilyl nitramines has revealed a new form of tautomerism:



$$\underset{\displaystyle Si\text{-}Me_2R}{Me\text{-}\overset{}{N}\text{-}NO} \rightleftarrows \underset{\displaystyle O\text{-}SiMe_2R}{MeN{=}N\text{-}O}$$

in which the equilibrium constants increase in the order R = H, Me, *i*-Pr, *t*-Bu.[194]

Structure-basicity relationships for a variety of silylamines have been studied using infrared spectra,[195] and competitive titrations techniques[196] and suggest that resonance and hyperconjugative interactions are more important than inductive effects in these systems. Tris(chloro and methylsilyl)amines have been found by differential thermal analysis techniques to have unusually high cyroscopic constants.[197]

Infrared studies of the acidity of the N-H group in a variety of silyl amines and silazanes showed that the acidity increased as the electron accepting ability of the silicon substituents increased.[198,199] Octamethylcyclotetrasilane and hexamethylcyclotrisilazane function as bidentate ligands with titanium(III) and (IV) chlorides and vanadium and chromium halides to give rather unusual complexes in which one nitrogen from the silazane ring is coordinated to each metal in a bridged dimeric complex,[200] Figure 2.

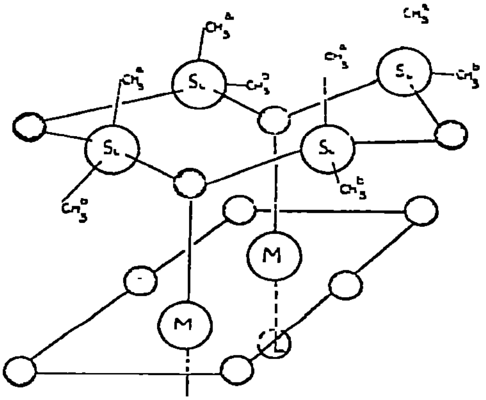


Figure 2. Structure of the cyclotetrasilazane complex with titanium(III) chloride[200] (Reported with permission of the American Chemical Society)

A detailed analysis of the mass spectra of some 1,3-diaza-2-silacyclopentanes and 1,3-diaza-2-silacyclohexanes has appeared.[201]

Transition Metal Compounds - Silicon Complexes

A detailed vibrational assignment for some trihalometalcobalt tetracarbonyls, $X_3MCo(CO)_4$; M = Si, Ge, Sn; X = Cl, Br, I; has been performed.[202]

The infrared spectra of iridium complexes, $Ir(X)Y(SiR_3)CO(PPh_3)_2$; X = H, D; Y = Cl, Br; SiR_3 = $SiCl_3$, $Si(OEt)_3$, $SiCl_2Me$, $SiClMe_2$; show that the phosphine groups, and the X, Co and Y,

SiR_3 pairs are *trans*.[203] Variations in the metal-C stretching frequency in the complexes and in related Pt(II) complexes give the following *trans*-influence series:

$SiF_3 = SiCl_3 < SiCl_2Me < Si(OEt)_3 \ll SiClMe_2$;
$SiCl_3 < SiCl_2H < SiClH_2 < SiH_3 \ll SiMe_3$;
$GeClH_2 \ll GeMe_3$; $SnMe_3 \ll GeMe_3 \approx SiMe_3$
$SnCl_3 \ll SnMe_3 \approx SiCl_3$.

From the analysis of the infrared spectra for the manganese pentacarbonyl derivatives, $Cl_3SiMn(CO)_5$, $Cl_3GeMn(CO)_5$, $Br_3GeMn(CO)_5$, and $I_3SnMn(CO)_5$ the M-Mn force constant was found to decrease in the order Si-Mn > Ge-Mn > Sn-Mn. It was concluded that the π bond character for the M-Mn bonds is approximately equal and that the σ bond character is primarily responsible for the order of the M-Mn bond strengths.[204] However, a study of the trimethylmetal manganese pentacarbonyl compounds, $Me_3MMn(CO)_5$; M = Si, Ge, Sn; by vibrational and electron impact methods showed a decrease in the M-Mn bond strength between Si and Ge.[204a]

A single crystal x-ray structure of the tris[bis(trimethylsilyl)amide] complexes of Scandium and Europium, Figure 3, indicates that the complexes have an unusual pyramidal 3-coordinate

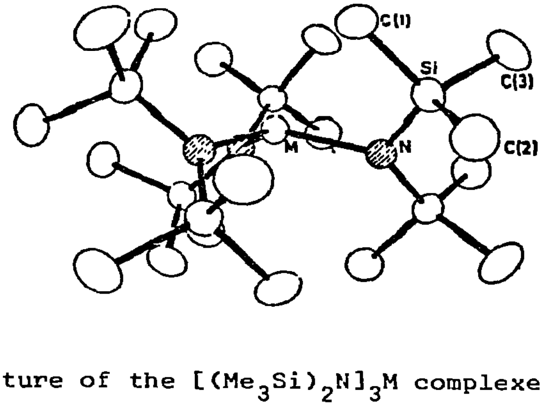


Figure 3. Structure of the $[(Me_3Si)_2N]_3M$ complexes[205] (Reproduced by permission of the Chemical Society)

structure with N-M-N angles of 115.5° and 116.6° for Sc and Eu respectively. The bis(trimethylsilyl)amide groups retain the D_3 configuration found in trisilylamine.[205]

The complexes of copper(II), $Cu(O_2CMPh_3)_2 \cdot nH_2O$, M = Si, Ge, have unusually low magnetic moments compared to M = C, which was attributed to the +I inductive effect of Si and Ge.[206] The crystal structure of tetrakis[trimethylsilylmethylcopper(I)], Figure 4, shows that it contains an unusual square planar arrangement of copper atoms, and the bridging methylene groups also lie approximately in the plane of the copper atoms. It is suggested that the alkyl bridges involve three center, two electron bonds and that copper-copper bonding is relatively unimportant in the compound.[207]

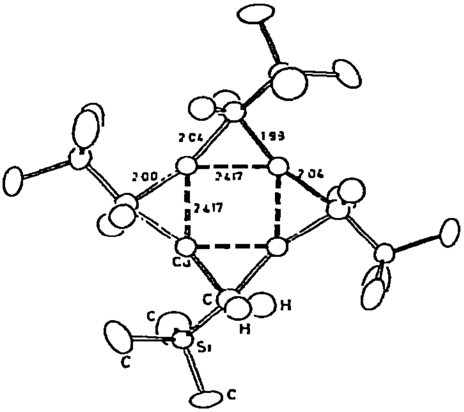
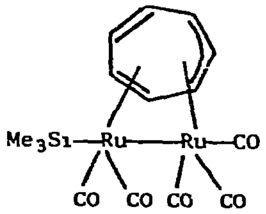


Figure 4. Structure of $[Me_3SiCH_2Cu]_4$[207] (Reproduced with permission of the Chemical Society)

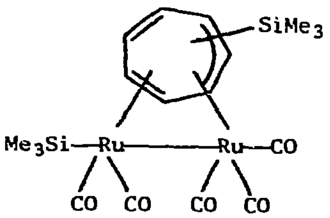
The He(I) photoelectron spectra of the trimethylsilylmethyl compounds, $(Me_3SiCH_2)_4M$; M = Cr, Sn, Pb; $(Me_3CCH_2)_4Cr$ and Me_3SiCH_2Cl were reported and tentatively assigned on the basis of a localized bond model. There appears to be no stabilizing interaction between the chromium *d* electrons and empty silicon *d* orbitals, but that the chromium-carbon bond is stronger for the silicon compound, supporting the argument that the stability of the trimethylsilylmethyl and neopentyl complexes is due to kinetic factors. In trimethylsilylmethylchloride the C-Cl ionization energy (12.24 eV) is 2.2 eV lower than that for the C-Cl bond in methyl chloride, the effect being attributed to a strong interaction between the methylene C-H bonding pairs and the C-Cl bond in Me_3SiCH_2Cl.[208] The vibrational, ^1H NMR, and mass spectra of bis(trimethylsilylmethyl)mercury and trimethylsilylmethylmercuric halides (Cl, Br, I) have been reported and compared. Minimal effects are found due to varying the halogen, and the metal sensitive CH_2 bands in the infrared are observed.[209] The infrared and NMR spectra of the tris(trimethylsilylmethyl)phosphine complexes, $Fe(CO)_3L_2$, $Fe(CO)_4L$, $[Co(CO)_3L_2][Co(CO)_4]$, $[Co(CO)_3L]_2$, and $Ni(CO)_3L$ have been reported and compared.[210] The crystal and molecular structure of bis(trimethylsilylmethyl) bis-(2,2'-bipyridyl)chromium(III) iodide has been reported twice, by the same group.[211,212]

Deuterium labeling of trimethylsilylferrocene shows that the upfield resonance at 4.07δ is due to the 2,5-protons adjacent to the trimethylsilyl group while the 4.30δ resonance is due to the 3,4-protons. The deshielding of the 3,4-positions is attributed to electron withdrawal by the silicon *d*-orbitals.

A x-ray crystal structure on the compound believed to be the bridged cycloheptatrieneyl complex, XVIII, revealed that the com-



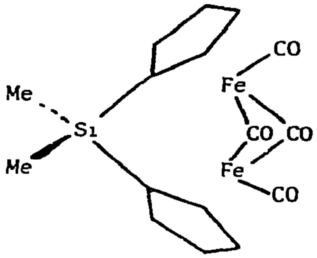
XVIII



XIX

pound was in fact XIX, resulting from a transfer of a trimethylsilyl group from ruthenium to the cycloheptatrieneyl ring.[214]

The crystal structure of the bis(cyclopentadieneyl)dimethylsilane iron carbonyl complex, XX, indicates that the molecule is distorted from perfect C_{2v} symmetry and the environment about silicon is very close to tetrahedral.[215]



XX

From the crystal structure of tetrakis(π-cyclopentadienyl)-di-μ-silylene-dititanium, Figure 5, it is found that the molecule consists of two $(\pi\text{-Cp})_2Ti$ units linked by two SiH_2 bridges with

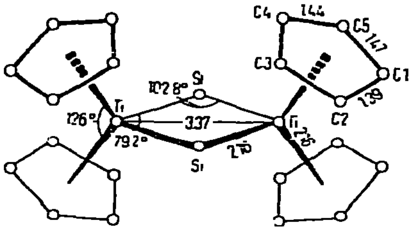


Figure 5. Structure of $[(\pi\text{-Cp})_2TiSiH_2]_2$[216] (Reproduced with permission of Verlag Chemie GmbH)

the Ti-Si-Ti bond angle of 102.8° very close to tetrahedral.[216]

The mass spectra of the silacyclopentadiene complexes of cobalt, (π-Cp)(1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene)-

cobalt and (π-Cp)(1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)cobalt show strong peaks at $M^+ - 15$, indicating existence of silicon analogs of the cobalticenium ion.[217] The stereochemical assignment of (π-Cp)(1-*exo*-hydroxy-1-*endo*-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)cobalt was accomplished through the use of the paramagnetic shift reagent $[Eu(DMP)_3]$.[218]

A study of the ^{195}Pt, ^{31}P, and ^{1}H NMR spectra of the complexes formed by the reaction of silylacetylene and silylperfluoroacetylene with *trans*-$HPt(PEt_3)_2X$; X = Cl, I; indicated simple addition to give *trans*-$YC{\equiv}CSiH_2PEt_3)_2X$; Y = H, CF_3. No interaction between the acetylene and Pt was observed.[219]

The absolute configuration of (+)-*trans*-chlorobis(dimethylphenylphosphine)methyl-(1-naphthyl)phenylsilylplatinum, Figure 6, is established by a crystallographic investigation to be *S*, corresponding with that of (*R*)(+)-(1-naphthyl)phenylmethylsilane from which it is made.[220]

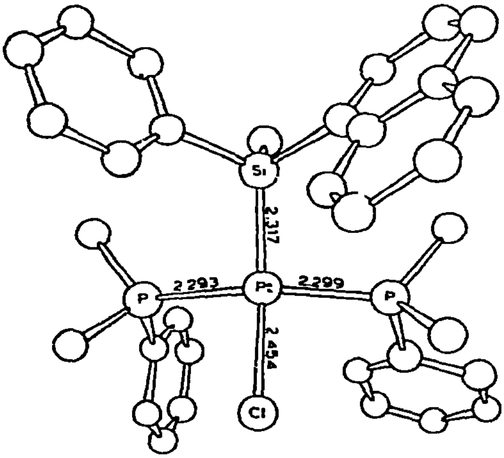


Figure 6. Structure of (+)-*trans*-$[PtCl\{SiMe(1\text{-}C_{10}H_7)Ph\}(PMe_2Ph)_2]$[220]

Two reviews in the area of coordinated silicon compounds appeared during 1973, one dealing with a topological approach to the stereochemistry of four, five, and six-coordinate group IV metals,[221] and one discussing the anomalies in the structural chemistry of silicon.[222]

A new ionic *tris*(2,2'-bipyridine)silicon tetrabromide complex was shown by conductivity, ^{1}H NMR, ultraviolet and infrared studies to have silicon octahedrally coordinated by the three bipyridyl ligands.[223] A study of the luminescence, fluorescence, phosphorescence yields and phosphorescence lifetimes for porphyrin complexes, MX_2R; M = Si, Ge, Sn, Pb; X = F, Cl, Br, I, OH, benzoate; R = etioporphyrin or octaethylporphin; and spin orbit interactions were found not to agree with calculations based on the extended Hückel model for the systems.[224] It has been reported that the vibronic structure of the *Q* band of the silicon phthalocyanine dimer may be satisfactorily explained in terms of vibronic coupling in the dimer between nondegenerate monomer electronic levels.[225]

Radicals

In addition to those reports on organosilicon radicals discussed in the sections on classes of compounds above there have been some which seem more appropriately grouped together in one section. Sakurai has prepared an extensive review on the preparation and properties of free radicals of Si, Ge, Sn, and Pb with major emphasis on silicon.[226] Along with his coworkers, he has also shown that trimethylsilyl sodium is a convenient one electron transfer reagent for the generation of radical anions of aromatic compounds which are remarkably free from interactions with the counter cation.[227,228]

The photolysis of *bis*[*bis*-(trimethylsilyl)methyl]tin(II) with visible light gives the unusually stable *tris*[*bis*-(trimethylsilyl)-

methyl]tin(III) radical. The coupling with the methine protons in the ESR spectrum of 0.21 mT is comparable with the 0.275 mT found for the methyl protons in the trimethyltin(III) radical.[229]

The ease of addition of a series of group IV radicals to carbonyl compounds was found to be $Et_3Si^\cdot > Et_3Ge^\cdot \approx Bu_3Sn^\cdot > Me_3Pb^\cdot$ for a given carbonyl compound, and diketones > oxalates > ketones > trifluoroacetates > formates > acetates for a given group IV radical by ESR spectroscopy. The order is consistent with the greater Si-O bond energy, and the stabilization of the radicals formed. $(Me_3Si)Si^\cdot$ was less reactive than the triethylsilyl radical due to steric factors and enhanced stability from electron delocalization within the radical.[230]

The photolysis of trimethylsilyl-*tert*-butylperoxide in the presence of ethylene, propene, or isobutene gives only homolytic fission of the O-O bond. The ESR spectra of the $Me_3SiO^\cdot$ adducts to the olefins are observed together with those of allylic radicals produced by proton abstraction.[231]

The ESR spectra of $^{28}SiH_3$ and $^{29}SiH_3$ have been calculated by a perturbation treatment of the Zeeman levels. The calculation accounts for the assymmetry in the positions of the ^{29}Si satellite lines from the apparent center of the spectrum, and predicts a difference of 10.75 gauss between the two displacements, a large second order effect which should be readily observable.[232] In the application of the INDO approximation to the calculation of equilibrium geometries and isotropic hyperfine coupling constants for a series of tetraatomic radicals including SiH_3F_{3-n}, n = 0-3, good agreement is obtained in every case except for SiH_3. It appears that the INDO method overemphasizes the pyramidal character of the radical while $^\cdot SiH_3$ is nearly planar, the H-Si-H bond angle = 115 - 117°.[233]

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