SILICON:

BONDING AND STRUCTURE

Annual Survey covering the Year 1974

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Contents:

Introduction and Overview

This survey covers the major journals for the year 1974, and volumes 80, no. 20 through 82, no. 20 of Chemical Abstracts. For the Russian literature and for those publications which are not generally available, the Chemical Abstracts reference is given in addition to the original citation. The patent literature and dissertations are not reported. Studies with a primary emphasis on synthesis and reactivity or on reaction mechanisms were excluded with the exception of those which, in the author's opinion, had special bearing on bonding problems.

To no one's surprise, the discussion of $p-d\pi$ $vs.$ σ and σ^* effects in the interaction of silicon with unsaturated systems continued with vigor in 1974. While it is clear that interaction of silicon's σ and σ^* orbitals with π systems can no longer be ignored, the question of the relative importance of d orbital interactions and hyperconjugative electron release or withdrawal by silicon remains open. It seems that an experimental resolution of these problems may lie close at hand in the approach to spectral analysis put forth by M.B. Robin in "Higher Excited States of Polyatomic Molecules" (Academic Press, New York, 1974). We highly recommend this book to those interested in bonding in organosilicon compounds.

Another message which comes through clearly in the 1974 literature is the extreme sensitivity to internal parameterization shown by the semiempirical molecular orbital methods. One must be wary of bonding conclusions based on these calculations.

Theoretical-General

The energies of the s, p, and d valence states for the atoms Si, Al, and Mg and some of their positive and negative ions were

calculated from available spectroscopic data. The results for Si are summarized in Table 1.[1]

Table 1. Valence states for Silicon[1]

Species

Si $\quad s^2p^2(^3P)0.00$; $s^2p^2(V_2)0.21$; $s^2p^2(V_0)1.16$; $sp^3(V_4)8.36$;
$\quad sp^3(V_2)9.33$; $s^2d^2(V_2)15.1$, 14.0; $s^2d^2(V_0)15.5$, 14.2;
$\quad sd^3(V_2)26.9$, 21.2

$Si^+ \quad s^2p(V_1)8.18$; $s^2d(V_1)17.99$; $sp^2(V_3)16.04$; $sp^2(V_1)17.09$;
$\quad sd^2(V_3)30.6$, 29.0; $sd^2(V_1)31.2$, 29.3; $p^3(V_3)24.83$; $p^3(V_1)25.90$

$Si^{2+} \quad s^2(V_0)24.49$; $sp(V_2)31.98$; $sd(V_2)41.56$; $p^2(^3P)40.59$;
$\quad p^2(V_2)40.82$; $p^2(V_0)41.95$; $d^2(V_2)59.9$, 57.6; $d^2(V_0)60.6$, 58.1

$Si^{3+} \quad s(V_1)57.95$; $p(V_1)66.83$; $d(V_1)77.83$

$Si^{4+} \quad (V_0)103.08$

Perry and Jolly have determined the core bonding energies for the series of compounds MH_4, $(MH_3)_2O$; MH_3X, and MX_4; M = C, Si, Ge; X = Me, F, Cl, Br; by gas phase X-ray photoelectron spectroscopy.[2] They have developed a procedure for calculating atomic charges using an electronegativity equalization procedure, which gives good agreement with the experimental core binding energies.[3] Their detailed analysis of the X-ray photoelectron spectra of SiH_4, SiH_3Me, $SiMe_4$, SiH_3Cl, and SiF_4 could be rationalized without assuming substantial participation of silicon d orbitals in the bonding.[4]

Auger-electron spectroscopy has been applied to measure absolute values of inner-shell ionization cross sections for Si, P, S, Cl, Ti, Br, and Sn.[5] Transition probabilities for the $np(n + 1)s \rightarrow np^2$ transition have been calculated using relativistic SCF wave functions and give reasonable agreement with

experimental values.[6] New theoretical transition probabilities
for the Si^+, $3s^2 3p^1 - 3p^3 3d^0$ isoelectronic sequence have been
reported.[7] Spin orbit coupling for the $2p$ level in Si, P, S,
and Cl, detected by X-ray photoelectron spectroscopy, may be
predicted using the Sommerfield formula with a screening constant
of 3.40.[8]

Ab initio SCF-MO calculations on silyl-substituted alkanes,
alkyl radicals, and carbonium ions show that the carbonium ion
is destabilized by an α-silyl group but is stabilized by a
β-silyl group. Little effect of the silyl group is observed for
the radicals or alkanes. A non-classical bridged structure for
$H_3SiCH_2CH_2^+$, I, has an energy about 0.5 eV lower than a classical
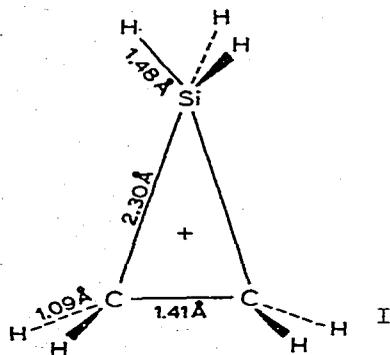
open structure.[9] (See also Ref. 111 and 139)

A study by Ebsworth of the photoelectron spectra of com-
pounds containing the MH_3 group; M = C, Si, Ge; and MH_nX_{4-n} type
compounds indicates that the effect of the silicon d orbitals is
"rather unnoteworthy" in the bonding.[10] A review of X-ray dif-
fraction molecular structures of C, Si, Ge, Sn, and Pb compounds
has appeared.[11] The ^{29}Si chemical shifts of $Me_{4-n}SiX_n$; X = F,
Cl, Br, I, H, OMe, OEt, OPh, OAc, $OC(O)CF_3$, $OSiMe_3$, NMe_2, N_3, Ph,
C_6F_5, Vi, and CH_2Cl; have been interpreted in terms of relative
paramagnetic screening constants; and show that the silicon

chemical shifts depend primarily on the σ-charge of the Si- or C- atom, and that $p-d\pi$ interactions with the Si- atom are of minor importance.[12]

In a theoretical study of the silicon-carbon double bond, Damrauer and Williams have applied unreparameterized CNDO/2 calculations,[13] to $H_2Si=CH_2$, $F_2Si=CH_2$, $H_2Si=CF_2$, and $F_2Si=CF_2$. The results again show the polarity of the silaethene bond, and indicate that d orbital effects are important and increase as the number of electronegative substituents on the Si=C grouping increase.[14] (See, however Ref. 21)

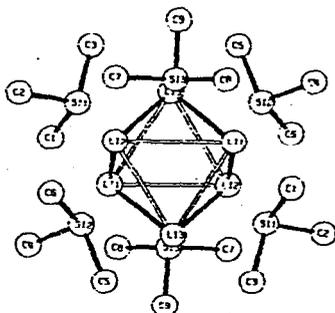The first crystal structure of the interesting aggregate, $(LiSiMe_3)_6$, has been reported, Figure 1.

Figure 1. Structure of the $(LiSiMe_3)_6$ hexamer.[15] (Reproduced by permission of the American Chemical Society)

The lithiums are arranged in a chair-form six-membered ring of approximate D_{3d} symmetry with each face occupied by an electron deficient bridging trimethylsilyl group.[15] In studies of the enthalpies of interaction for BuLi and Me_3SiCH_2Li hexamers with THF, 2-MeTHF, and 2,5-Me_2THF; Quirk and Kester find evidence that the coordination of the furans to the hexameric species may lead directly to solvated tetramers.[16]

Acylsilanes

The first vertical ionization potentials for acetyl-
trimethylsilane and acetyltrimethylgermane have been found to be
8.6 and 8.5 eV, respectively, by photoelectron spectroscopy.
Based on the broad photoelectron band width and modified CNDO/2
calculations, the large bathochromic shift observed in the ultra-
violet spectra of these compounds compared to their carbon
analogs is attributed to strong mixing between the localized
oxygen lone pair and the M-C bond.[17] Other workers have applied
the CNDO method with spectroscopic parameterization to these
systems in an investigation of the $S_o \rightarrow S_{n\pi^*}$ and $S_o \rightarrow T_{n\pi^*}$
transitions,[18] and the infrared spectra.[19] Chemically induced
dynamic nuclear polarization studies of the photolysis of
acylsilanes in CCl_4 solution show that the only polarized products
were acetylchloride (emission), and trichloroacetone (absorption).
The silyl chlorides formed were not polarized, consistent with
a mechanism which involves an initial complex of singlet
acylsilane with carbon tetrachloride.[20]

Alkynyl- and Alkenylsilanes

A study of the photoelectron spectra of mono- and disubsti-
tuted silyl- and methylacetylenes by Bock, Ensslin, and Becker
shows that the observed π splittings can be rationalized by a
hyperconjugation model, without explicit consideration of d
orbitals. Moreover, a series of calculations show that the CNDO/2
method with the usual parameterization,[13] tend to overemphasize
p-$d\pi$ backbonding.[21] A paper by MacLean and Sacher, which contains
a good summary of earlier work in the field of silylacetylene
compounds, reports studies of ionization and appearance potentials,
^{1}H NMR chemical shifts and vibrational stretching frequencies for

$Me_3CC\equiv CH$, $Me_3SnC\equiv CH$, and $Me_nM(C\equiv CH)_{4-n}$; M = Si, Ge; n = 0-3. The ionization potential data are rationalized in terms of changes in hybridization (and therefore electronegativity) of the groups attached to the central atom, but trends in the infrared and NMR data were not explained.[22] The CNDO/2 approximation has been applied to explain apparently anomalous variations in the bond lengths in silyl- and trimethylsilylacetylene and cyanide and their analogous carbon compounds.[23] The considerations in this paper might resolve the unexplained anomalies in the preceding paper.

The esr spectra of the radical anions of $PhC\equiv CMMe_3$; M = Si, Ge, and C; generated by reduction with various alkali metals in THF at low temperature were assigned using deuteration of the phenyl ring, which had a π^* (SYM) type spin distribution. All but the Ge derivative were stable at -90°, but dimerized at higher temperatures.[24] The following paper reports the esr spectra of $(Me_3XC\equiv C-C\equiv CXMe_3)^{\overline{\cdot}}M^+$; X = C, Si; M = Li, Na, K, Rb, Cs; which indicated that electron delocalization to the Me groups occurred only for the Si radical anion by $p-d\pi$ interaction. While the carbon radical dimerized at -40°, the silicon radical was stable at room temperature even on exposure to air.[25]

Analysis of the ultraviolet spectral characteristics of molecules containing the Ph-M or Ph-C≡C-M group; M = C, Si, Ge, Sn, Pb; using a Pariser-Parr Pople type calculation has been performed. The sensitivity of various bands to vacant-orbital contribution and hyperconjugative electron release is discussed.[26] Calculations for the infrared bands of $HC\equiv CSiMe_2OR$; R = Me, Et, Pr, Bu, $n-C_5H_{11}$, and Ph; have been reported and correlated with Taft σ constants.[27]

Two groups have reported *ab initio* SCFMO calculations on the effects of silyl substituents on ethylene. Horn and Murrell made calculations on ethylene, vinylsilane and allylsilane, and found that inclusion of d orbitals in the basis set gives a better interpretation of the photoelectron spectra than their exclusion.[28] Zeeck found that, for vinylsilane and propene, the spectral perturbation produced by silicon substitution can be explained by differences in hyperconjugation between the silyl group or methyl group and the rest of the molecule, but that the inclusion of silicon d-functions gives a quantitatively more accurate description.[29] Both groups agree that $d-p\pi^*$ interactions are significant.

Force field calculations of the normal vibrations show that the force constant of the Si-C bond in vinylsilane, $(4.9-5.2) \times 10^6$ cm^{-2}, is larger than that for methylsilane. Values of the force constant for the C=C bond agree with experiment, but it is concluded that values obtained from vibrational spectroscopy cannot give direct confirmation of $p-d\pi$ bonding in unsaturated organosilanes.[30] The infrared spectra of $H_2C=CH-SiMe_nX_{3-n}$; $n = 1, 2$; $X = F$ or Cl; and laser Raman spectra have been determined and assigned. They indicate the presence of rotamers, explaining the anomalous dipole moments for the molecules.[31] The vibrational spectra of the trihalosilyl-1- or 2-butenes obtained by hydrosilylation have been analyzed with respect to the characteristic out-of-plane =CH deformation frequencies, and have been used to derive rules for semiquantitative infrared analysis of mixtures of alkenylhalosilanes.[32]

From a study of the ^{13}C chemical shifts of trialkylsilyl-, trialkylgermyl-, and trialkylstannyl-substituted ketenes, it

was found that the shielding effects of the heteroatom increased

in the order: Si < Ge < Sn, which was interpreted in terms of re-

hybridization to a polar structure.[33] NQR frequencies for ^{35}Cl

in RSiR'Cl$_2$ compounds; R,R' = allyl, Cl; Ph, allyl; Ph, vinyl;

vinyl, allyl; Me, vinyl; were determined and the correlation of

the sum of the Hammett substituent constants indicated that only

the inductive effect of the double bond was transmitted through

silicon to the Cl atoms. Similar results were obtained for anal-

ogous C or Ge compounds.[34] The configuration of *endo*-3-(trimethyl-

silyl)bicyclo[2.2.1]hept-5-ene (<u>sic</u>), II, was assigned unambigu-

ously using 250 and 300 M Hz NMR spectroscopy and INDOR experi-
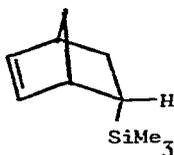
II

ments.[35] Heat capacities and thermodynamic functions for

vinyldimethylphenylsilane have been reported.[36]

    Ionization potentials from photoelectron spectra of the

cyclopentadiene derivatives; RC$_5$H$_5$; R = 1-Me, 2-Me, and 5-SiH$_3$;

correlated well with orbital energies calculated by *ab initio*

methods. Calculated energies indicated the stability orders

2-Me > 1-Me > 5-Me, and 5-SiH$_3$ > 2-SiH$_3$ > 1-SiH$_3$. The Si-C

bonding orbital in the 5-SiH$_3$ derivative was heavily involved

with the π system, and a high overlap integral existed between

the Si and the remote ring C atoms, suggesting a reason for the

fluxional behavior of the silyl compounds.[37] In the charge

transfer spectra of a series of substituted silacyclopentenes

and cyclopentenylsilanes, the changes in ν_{CT} with TCNE as the

acceptor were greater for the cyclopentenyl derivatives in which the Si-C bond was in a conformation suitable for interaction with the π system. The acceptor properties of silicon were explained by the interaction of the Σ^*_π Si-C or Si-X bonds without involving d orbitals. The acceptor strength of the Si-X$_3$group; X = F > Cl > H > Me; agreed with this explanation.[38]

Larrabee has prepared a very informative review on fluxional organosilicon molecules and the application of orbital symmetry considerations to the molecular rearrangements observed.[39] The ground state geometry of cyclopentadienylsilane and transition state geometry for the silyl group migration have been calculated by the CNDO/2 method.[40] A potential curve close to the reaction coordinate for the [1,2] rearrangement was obtained. The calculation demonstrates that the symmetry forbidden [1,3] or across the ring rearrangements cannot be related to the potential curve experimentally known for the reaction.[41]

Mass spectral fragmentation of the cyclopentadienyl compounds C_5H_5-SiMe$_2$R; R = Me, MeO, Cl; C_5H_5GeMe$_3$; C_5H_5SnMe$_3$; C_5H_5SnEt$_2$Cl, $(C_5H_5)_2$SnEt$_2$ and $(C_5H_5)_4$Sn occurred primarily by rupture of the C_5H_5-M bond.[42]

The infrared and Raman spectra of the tetracyclopropyl derivatives of Si, Ge, and Sn, were recorded and assigned on the basis of D_{2d} symmetry, which is only strictly realized for the tin compound. The assignments are in agreement with the dipole moments, 1.8, 3.4, and 2.0 D, respectively.[43] The infrared and Raman spectra of cyclopropyl silanes of the type III, IV, and V, $R_2 = H_2$, HMe, F$_2$

R ───△───SiMe$_3$ R ───△─── Si(OMe)$_3$ R ───△───SiMeF$_2$
  R   R   R
    III   IV   V
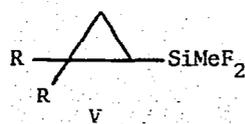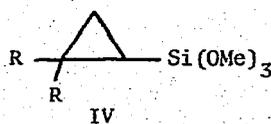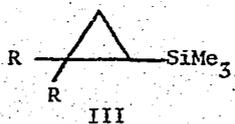
were determined and correlated with structure.[44] Conjugation
in these types of compounds was investigated using the infrared
data, ultraviolet spectra and iodine charge transfer complexes.[45]

Arylsilanes

The photoelectron spectra for the compounds Me_3MPh and
Me_3MCH_2Ph; M = C, Si, Ge, Sn; and MINDO/3[46] calculations for the
M = C or Si compounds have been reported.[47] Treatment by first
order perturbation theory indicates that the inductive and hyper-
conjugative effects of the Me_3M group in the benzyl compounds
are about equal. For the phenyl derivatives the results shown in
Table 2 were obtained.

Table 2. Partition of the effects of an Me_3M substituent on the
HOMO of benzene.[47]

| M | Contributions to $\delta E_{\pi 1}$ (eV) | | |
	Inductive	Hyperconjugative	$p-d\pi$
Si	0.78	0.51	-1.09
Ge	0.64	0.38	-0.82
Sn	0.48	0.34	-0.51

Unfortunately, the possibility of interaction between the σ^*
orbitals and the benzene π system was not considered.[47]

In studies of the charge transfer spectra of phenyl and
benzyl silanes and their carbon analogs, Ponec and Chvalovsky
showed that the results could be interpreted by interaction of
Σ^* orbitals of the CH_2-Si or Si-X bonds without assuming the
participation of silicon d orbitals, using a simple semiempirical

model of hyperconjugation.[48] Schweig, Weidner, and Manuel showed that the destabilization of the π MO's in allyl and benzyl Group IVA derivatives could be quantitatively predicted on the basis of a hyperconjugative model.[49] This paper drew some comments from Pitt.[50]

The analysis of both ground and singlet excited states for phenylsilane and phenylchlorosilane using Pariser-Parr Pople calculations showed that the Si-C bond order in the chloro compound was lower by a factor of 1.5 and that the negative charge on silicon in the chloro compound was higher by a factor of almost 4. Of the two interactions of Si with the phenyl ring, σ, π and $p-d\pi$, the latter was significantly predominant.[51] The infrared spectra of $PhSiMe_3$; $PhCH_2MMe_3$, M = Si, Ge, Sn; $PhCH_2CH_2SiMe_3$; $PhCH_2SiMe_2Cl$ and $PhCH_2SiCl_3$ have been analyzed in terms of mixing in the ground and excited states.[52] Another report analyzes the infrared spectra of 48 silylbenzene derivatives in terms of the effects of conjugation.[53] Substituent effects on the NMR and vibrational spectra of $p-R-C_6H_4MHMe_2$ and $p-R-C_6H_4MH_3$ compounds; R = MeO, Me, H, Cl, Br; M = Si or C; were explained invoking a larger electronic effect transmission by silicon compared to carbon using vacant d orbitals on silicon.[54]

Detailed studies on the phosphorescent state of the tetraphenyl Group IV compounds, C, Si, Ge, Pb, and Sn shows that the internal heavy atom effect arises through both electronic and vibronic interactions while the external heavy atom effect is largely through electronic interactions, that translationally equivalent interactions control triplet energy transfer, and that the magnitude of the spin dipolar interactions and the inter-ring interactions are comparable, about 0.1 cm^{-1}.[55] X-ray diffraction

data and quantum chemical calculations have been combined to determine the lattice energy and conformation of tetraphenylsilane.

Energy level diagrams for effects of the $SiMe_3$, CH_2SiMe_3, $SiMe_2SiMe_3$, and alkyl substituents on β-substituted styrenes have been constructed from ionization energies (mass spectral), infrared and ultraviolet spectra and polarographic reduction potentials. Typical electron release by the trimethylsilylmethyl group and withdrawal by the trimethylsilyl group are observed.[57]

Silicon-29 chemical shifts for a series of aryl silanes, $Ar-SiX_3$ have been reported.[58] As was noted in a communication last year,[59] for a given silicon substituent, X, linear correlations with Hammett σ constants are obtained. However, increasing electron donation by *meta* and *para* substituents on phenyl give upfield shifts for X = H or Me, but downfield shifts for X = F, Cl, or OEt. Two groups have proposed theoretical interpretations of the phenomenon, both based on the electronegativity of silicon's substituents. It appears that an additive, but *non linear* relationship exists between $\delta^{29}Si$ and the summed electronegativity of the groups bonded to silicon.[58,60] Substituent effects on the silicon resonance are not uniform, and chemical shift assignments based on analogies even to closely related silanes can lead to error. Any interpretation of silicon chemical shift data based on a $p-d\pi$ mechanism must be made with extreme caution.[58]

Carbon-13 chemical shifts for three series of Group IV aromatics; $p-X-C_6H_4-YMe_3$, where Y = C, Si, and Ge correlate with substituent parameters σ_I and σ_R^o. The slopes of the Y-Me correlations suggest roughly equal transmitting abilities for carbon and silicon, in contrast to Ref. 54.[61] For the X = NMe_2 compound,

the shifts of the C-4, and C-2,6 carbons vary Si > Ge > C in agreement with atomic charge values from published CNDO/2 calculations,[62] which indicate that while silicon exerts an electron releasing effect through the σ-framework, there is net π withdrawal at C-4 and C-2,6 relative to Y = C.[61] The ^{13}C NMR spectra of p-R-C_6H_4MCl$_3$; R = H, Me; M = Sn or Si; have been reported and analyzed.[63] The ^{13}C NMR spectra of a series of benzyl silanes in which the C-Si bond was constrained to varying degrees from the nodal plane of the aromatic system indicated the suppression of the electron donating effect of the CH$_2$Si group when optimum alignment of the C-Si σ bond and the π system was prevented.[64]

The ^{13}C-H coupling constants for a series of $para$ substituted phenyltrimethylsilanes were measured in methylene chloride and carbontetrachloride solutions, and indicated that the solvent effect is too large to allow any straightforward conclusion on ring-substituent interaction.[65] On the other hand, the ^{1}H NMR and other spectra of phenylvinylsilane, phenylallylsilane, diphenylsilane, phenylsilane, and allylbenzene were investigated, and applied to the study of interactions between the π electrons and d orbitals on silicon. Concentration dependence of the chemical shifts suggested the possibility of intermolecular interactions in the organosilanes.[66] Long range F-H couplings for silanes of the type $(C_6F_5)_n$SiMe$_{4-n}$; N = 1, 2, 3; and C_6F_5-(SiMe$_2$)$_2$R; R = CH$_3$ or C_6F_5; between the silylmethyl protons and the ring fluorines have been observed and analyzed.[67] The time dependence of the NOE enhancement for triethoxymethylsilane and diphenyldichlorosilane was used to measure the spin lattice relaxation time for the ^{29}Si nucleus in cases where the NOE enhancement is -1.0.[68]

Sipe and West have reported studies on an extensive series of trimethylsilyl-substituted benzene radical anions. The ESR results were used to derive a general set of Hückel MO parameters treating the trimethylsilyl substituent as a heteroatom, and a semiempirical relation between the π density on silicon *and* on the adjacent carbon atom to the Si-Me proton coupling constants.[6] In the following paper they analyze the ESR spectra for a series of trimethylsilyl-substituted toluenes, xylenes, mesitylene and *tert*-butylbenzene, and trimethylgermyl-*tert*-butylbenzene, in terms of substituent perturbations which stabilize or destabilize the lowest unoccupied MO's of benzene. In all the compounds studied the organo-metal substituent dominated the ordering of the MO energy levels by accepting electron density more effectively that the alkyl substituents release it.[70]

Radical anions of the type $Ph_nX^{\bar{\cdot}}$, where X = P, Si or As have been obtained by electrochemical reduction. The ESR spectra indicate that the X atoms of the bridges are *not* "Isolating bridges",[71] as had been suggested by earlier work involving metal reduction.[72]

The excited state interactions in trimethylsilyl-substituted *N,N*-dimethylanilines suggest that both the symmetric and anti-symmetric π* levels are affected by π interaction with the trimethylsilyl substituent. The magnitude of the effects are proportional to the π density at the point of substitution.[73]

ESR studies and MO calculations on trimethylsilyl and *tert*-butyl- substituted naphthalenes indicated significant p-$d\pi$ conjugation in the silicon compounds.[74] In contrast, the ionization potentials of several α-naphthyl, β-naphthyl, and phenyl derivatives, Ar-X; X = $Me_3SiSiMe_2$-, Me_3SiCH_2, MeO, and CH_3;

determined from charge transfer spectra were analyzed using first order perturbation theory. It is shown that the silicon $3p$ orbital is only 1/3 as effective as the C or O $2p$ orbital in overlap with the π system. The considerable σ-π interaction seen in the disilyl derivatives is attributed to the higher energy of the Si-Si σ bond.[75] The charge transfer spectra of 21 naphthalene derivatives including 11 siloxy and silyl derivatives demonstrated that the inductive effect and $p-d\pi$ interaction between silicon and oxygen was greater than that of silicon with the aromatic ring.[76]

In a set of studies on the electron impact induced fragmentation of substituted phenylsilanes, Dube and Chvalovsky found that, to a first approximation, the fragmentation patterns may be explained by the effect of the substituents on charge distribution in the molecular ion, and thus on the activation energies of fragmentation.[77,78] An isotope effect observed in the formation of $(M-1)^+$ and the presence of intense $(M-2)^+$ and $(M-3)^+$ peaks in the mass spectra of deuterated phenylsilanes indicated that the benzene ring had opened to form a chain, and the silatropylium ion was not formed.[79] A study of the fragmentation and rearrangement processes in the mass spectra of fluoroaromatic heterocyclic Group IV derivatives has appeared.[80]

The vapor pressures and enthalpies of vaporization for *m*-, and *o*- chlorophenyltrichlrosilane have been reported.[81] Another report gives the saturated vapor pressures of β-silyl derivatives of *m*-carborane.[82] The heat capacity of *o*-(trichlorosilylbiphenyl) in the 12 to 300 °K range shows a *trans → cis* transition at 289.5 °K accompanied by a 13.8 kcal/mole heat effect. The infrared spectra of mono- and disubstituted *m*-carboranesilanes

and siloxanes with silicon functionality have been reported.[84]

Silacycles

The vapor pressures, enthalpies and entropies of vaporization for 1,1-dimethylsilacyclobutane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane have been reported.[85]

The microwave spectrum of 1,1-difluoro-1-silacyclopent-3-ene shows that the five-membered ring is planar and the molecule has C_{2v} symmetry. The ring puckering vibration has a frequency of 38 ± 7 cm^{-1} and is nearly harmonic. The data indicate that the ring is not nearly as squashed (due to d-π interactions) as had originally been believed.[86] The infrared, ultraviolet and NMR data for the silacyclopentadiene derivatives; VI; R,R' = Me, H; Ph, H; Me, Me; and VII showed that the silicon atom interacts
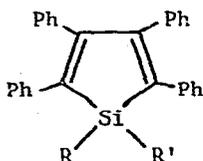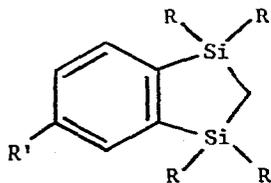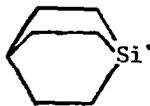

VI   VII
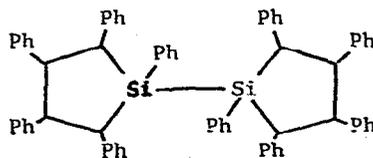
with the π system of the ring *via* "its vacant d orbitals" but that the phenyl groups on silicon are not appreciably conjugated with the silacyclopentadiene ring.[87] The mass spectral fragmen-


VIII   IX

tation pattern of the 1,3-disilaindanes; VIII; R = H, Cl, F, Me; R' = H, Me; involved predominantly loss of R or SiR_2.[88]

Sakurai and co-workers have generated the bridgehead silyl radical, 1-silabicyclo [2.2.2] octyl radical, IX. The β-, γ-, and δ-H coupling constants were 1.53, 0.37, and 0.37 G, respectively. The small β-hydrogen couplings were ascribed to the pyramidal structure of the bridgehead radical site.[89] Mass spectral studies of 1-sila-2,4-cyclohexadiene and its 1,1-dimethyl and 1,1-dichloro- derivatives have been reported.[90] Using force field methods, Ouellette has calculated structures and steric energies for silacyclohexane; 1-, 2-, 3-, and 4-methylsila-cyclohexane; 3-, and 4-*tert*-butylsilacyclohexane; 4-methyl-1-*tert*-butylsilacyclohexane. For the silyl-substituents, an axial conformation is preferred due to a larger negative nonbonded energy term.[91]

X-ray analysis of the structure of 1,1,2,2-tetramethyl-1,2-disilaacenaphthene, X, showed that the C1-C2 and C7-C8 bond
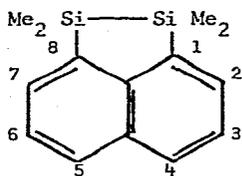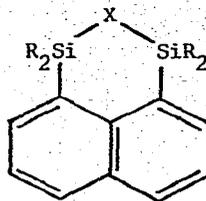

X

lengths increased, and the C2-C3, C3-C4, C5-C6, and C6-C7 bond lengths decreased relative to the corresponding bond lengths in acenaphthene.[92] The mass spectra of XI; R = H, Cl, F, Me, OMe; and XII; R,X = Cl, CH_2; Me, CH_2; Cl, O; have been reported.[93]
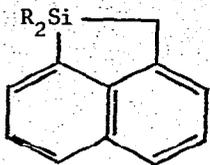
XI   XII

Perhaps one of the most significant reports to appear during 1974 is the work of Ponec, Chvalovský, Cernysev, Scepinov and Krasnova, dealing with the charge transfer spectra of 9-sila-fluroenes, XIII, and some of their carbon analogs.[94] The fluorene system is a good model system in that the highest occupied MO's differ in symmetry, such that the orbital of b_1 symmetry may interact with a silicon $p\pi$ orbital, or the d orbital in the plane perpendicular to the molecule passing through silicon. The two A_2 MO's can only interact with silicon d orbitals. These workers find that only the b_1 MO is affected changing silicon's substituents for XIII; R = R' = H, F, Cl, Me, Ph, OEt; M = Si. The variations are consistent with a hyperconjugative model employing only the silicon Σ_π^* antibonding orbital.[94] In a related study
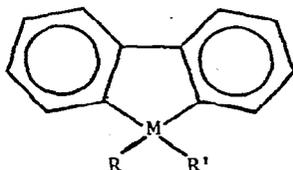


XIII

of silafluorenes; XIII; R = H; R' = H, Me, Ph, Cl; and Ph_2SiHR' compounds; the intensities of the Si-H bonds in the infrared showed a larger degree of π interaction in the fluorene derivatives of silicon.[95]
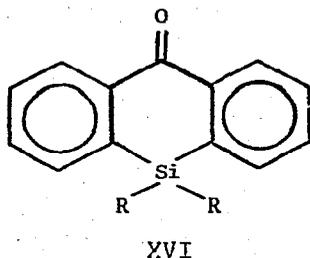
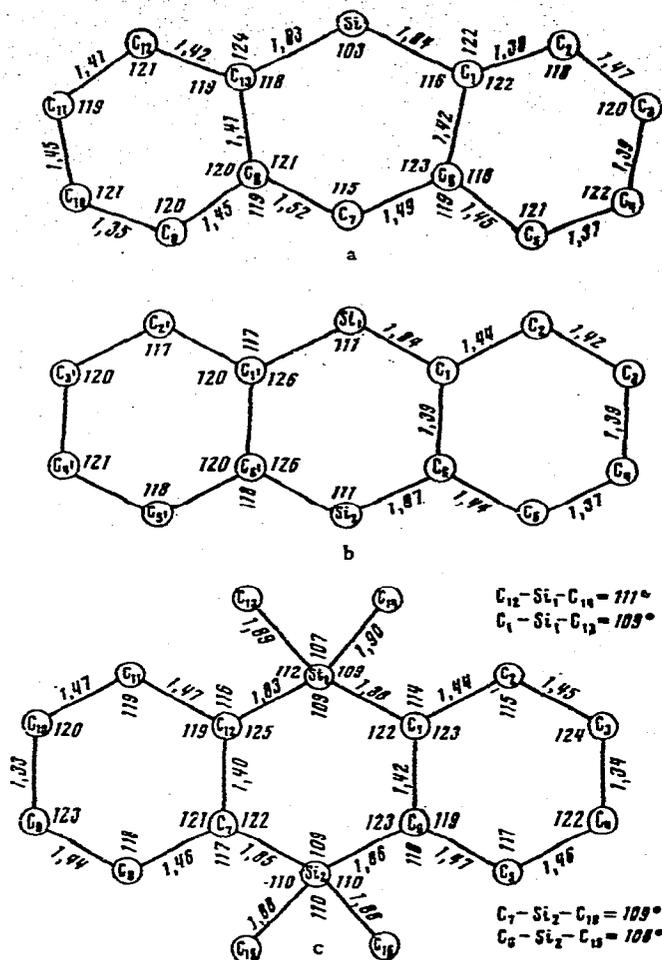The equilibrium acidity of 9,10-dihydro-9,9-dimethyl-10-

phenyl-9-silaanthracene has been determined with cesium

cyclohexylamide in cyclohexylamine. The pK is 27.4, only 0.6

pK units higher than the carbon analog, suggesting that aromatic

through conjugation is not important in this system.[96] In

contrast, comparison of the ESR spectra of the silaanthracenes,

XIV, and XV; R = Me, H with the spectrum of o-bis-(trimethylsilyl)-

benzene, and o-trimethylsilyltoluene anion radicals indicated

that the unpaired electron in the heterocycles was not localized

in one ring.[97]

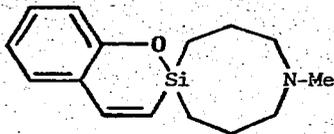XIV   XV
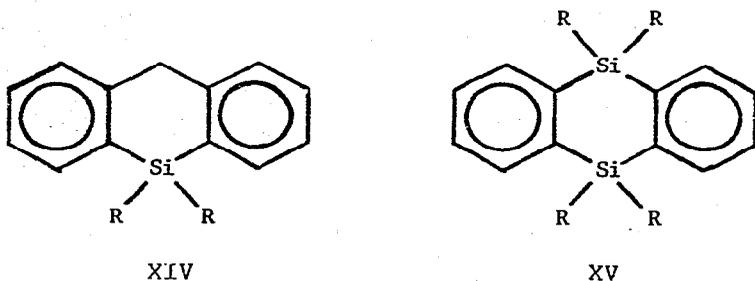
The structures of 9-sila-, 9,10-disila-, and 9,9,10,10-

tetramehtyl-9,10-disiladihydroanthracene have been determined by

X-ray diffraction. The structural details are shown in Figure 2.[98]

The crystal structure of 9,9,10,10-tetraphenyl-9,10-

disiladihydroanthracene has also been reported.[99] The half wave

potentials of the first polarographic waves for the silylanthracene

XVI

Figure 2. The bond lengths (Å) and bond angles for the molecules reported in Ref. 98. Reprinted with permission of the Plenum Publishing Corporation.

ketones, XVI; R = Me, Et, and Ph; were reported as -1.57, -1.53, and -1.46 V, respectively.[100]

The crystal structure of 1-sila-5-methyl-5-azacyclooctanespiro-[2']silachromene, XVII, has been reported along with bond lengths and angles.[101]

XVII

Fritz has reviewed the synthesis of carbosilanes, and their structures.[102] He has also summarized the structures of the 20 compounds which have been isolated from the pyrolysis of tetramethylsilanes. Besides the compounds having a carborundane framework (Si-C six-membered rings in the chair conformation), compounds were found for the first time which are built up ex- clusively of six-membered rings in the boat conformation (sil- ascaphanes). Both boat and chair form rings are found in an isomeric compound of $Si_7C_{16}H_{36}$.[103] The crystal structure of tetramethyloctasiladodecascaphan, $C_{17}H_{36}Si_8$, has been determined. The molecular structure is shown in Figure 3, in which the shaded atoms are silicons.[104]
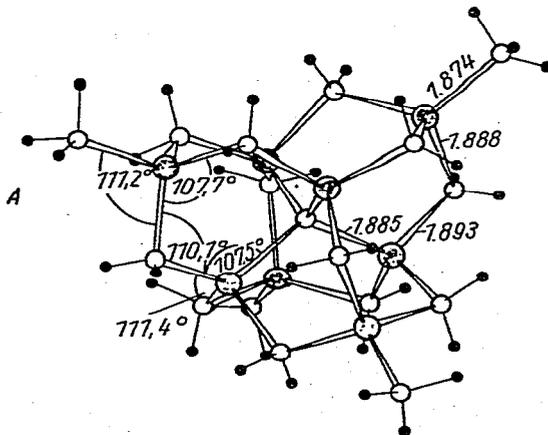

Figure 3. The octasila-dodecascaphan molecule showing bond
distances (Å), and angles.[104] Reproduced with the
permission of J.A. Barth, Leipzig.

The conformations of the tetrasilabicyclononanes; XVIII;
R = Cl or Me, R' = H, Me or Cl; and the pentasilabicyclononanes;
XIX; R, R' = H or Cl; have been determined by NMR spectra. The
XVIII compounds were present in a twofold boat conformation.
In XIX; R = R' = H and R = Cl, R' = H; a change in conformation
is observed, while in XIX; R = R' = Cl; a rigid chair conformation
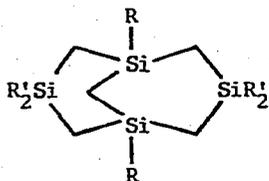
XVIII
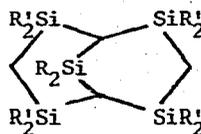
XIX
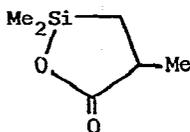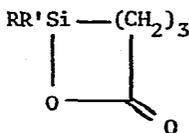
is found for both rings.[105]
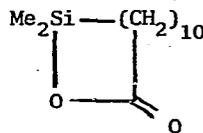
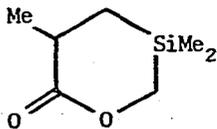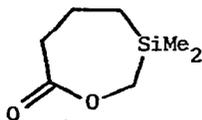Mass spectral studies of the 1-silalactones, XX, XXI, and XXII,[106]
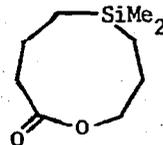
XX

XXI

XXII

and the 2-, and 4-silalactones, XXIII, XXIV, and XXV, and their

XXIII

XXIV

XXV

fragmentation patterns have been reported.[107]

Polysilanes

An extensive review (696 references) of the properties and preparations of silicon-silicon linkages in inorganic and organic silicon compounds has been prepared by Hengge.[108]

Sakurai and his group continue their contributions to the area of polysilane chemistry and bonding with the report of the ESR spectrum of the 1,1,2,2-tetramethyldisilanyl radical, generated by proton abstraction from tetramethyldisilane. The spectrum was consistent with a configuration in which the β Si-H bond is eclipsed with the p orbital on the silyl radical site.[109] Other studies show that the charge transfer energies for the TCNE complexes of hexamethyldisilane, 1,1,2,2-tetramethyl-1,2-disila-cheloheptane, -cyclohexane, and -cyclopentane correlate linearly with the enthalpies of activation for the oxidation of the respective disilanes with m-chloroperbenzoic acid.[110]

Model studies for the computation of the H/D kinetic isotope effect in the displacement reaction of H atoms with disilane:

$$H\cdot \quad + \quad SiH_3SiH_3 \qquad\qquad SiH_4 \quad + \quad \cdot SiH_3$$

suggest that the displacement of silyl radicals proceeds *via* a bridged activated complex rather than a linear intermediate.[111] (See, also Ref. 9)   A rate equation for the pyrolysis of disilane has been derived.[112]   The enthalpies and entropies of sublimation of tetraphenylsilane and hexaphenyldisilane have been determined, and the average bond dissociation energies for the Si-C and Si-Si bonds calculated.   The average value for $D(Si-Si)$ is 88 ± 7 kcal/mole.[113]

West has reviewed the work of his and other groups on the aromatic properties of cyclopolysilanes.   Some very intriguing, hitherto unpublished, findings are reported.[114]   In the first

application of the Woodward-Hoffmann rules to the photochemistry of organopolysilanes, Ramsey has shown that the results of photolysis in polysilanes support the assignment of the low energy electronic transition(s) in these species to a $\sigma \rightarrow \sigma^*$ excitation.[115]

In the ^{1}H and ^{19}F NMR spectra of the halopolysilanes; $X(SiMe_2)_nX$; n = 3,4, and 6; $Me(SiMe_2)_6X$; n = 2, 3, 4, and 6; X = F, Cl, I, and Me; and $XMe_2Si(CH_2)_4SiMe_2X'$; X, X' = Me, Me; Me, Cl; Cl, Cl; the chemical shift of the Me protons of the $SiMe_2X$ group moves to higher field as the chain length increased. Along with other results, the observations are consistent with increased donations from the halogens to vacant orbitals of the polysilane as the chain length increases, and to transmission effects through the chain.[116]

Two groups have reported the formation and studies of the NMR spectra of polysilane anions in 1974. Feher reported the formation of KSi_2H_5, $KSiH(SiH_3)_2$, $KSi(SiH_3)_3$, and $KSi(SiH_3)_2Si_2H_5$ by the reaction of $KSiH_3$ with disilane or trisilane in DME. The species were characterized by NMR spectra and derivatization.[117] Bürger and Marsmann described the ^{29}Si and PMR spectra for $H_3SiSiH_2^-$, $(H_3Si)_2SiH^-$, and $(H_3Si)_3^-$ in HMPA.[118] In a subsequent publication, the infrared and Raman spectra of the polysilane anions, $(SiH_3)_nSiH_{3-n}^-$, and their deuterated analogs were analyzed. The results suggest that the negative charge is mainly localized on the trivalent silicon atom, and that the lone pair acts repulsively rather than strengthening the Si-Si bond through p-$d\pi$ effects.[119]

The Raman spectra of the isomeric tri-, tetra-, penta-, and hexasilanes and n-heptasilanes have been obtained.[120] The infrared and Raman spectra of hexachloroethane, trichloromethyltrichloro-

silane, and hexachlorodisilane have been assigned and correlated.[12]

Hengge and Dieter have prepared and characterized heterocyclic polysilanes of the type, XXVI; X = $BNMe_2$, NMe, NEt, and O; and

$$Ph_2Si - SiPh_2$$
$$Ph_2Si \diagup \diagdown SiPh_2$$
$$X$$
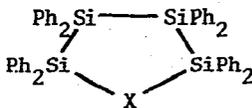
XXVI

characterized them by NMR, ultraviolet, far infrared, and Raman spectra. No evidence for electron delocalization through the heteroatom was found.[122]

The infrared and NMR spectra of derivatives of $Mn(CO)_5$, $Mn(CO)_4PPh$, and π-$Cp(CO)_2Fe$ containing the polysilyl ligands, $(Me_3Si)_nMe_{3-n}Si$; n = 1 - 3; have been discussed in terms of the σ donor and π acceptor properties of the silyl ligands.[123] An X-ray and Kβ study of π interactions, including several polysilanes has appeared.[124]

Alkylsilanes-Hydrides

The united atom theory has been applied to radicals and anions of the type R_3M and R_3M^-; M = C, Si, Ge, Sn; R = H, Me, F, and Cl; and used to predict the relative σ donating ability and π basicity of the various ligands.[125] Unrestricted Hartree-Fock-CNDO/2 calculations for the Me, CH_2F, SiH_3, SiH_2F, $SiHF_2$, SiF_3 and PH_3^+ radicals gave equilibrium geometries by the minimization of total energies and spin densities. The agreement obtained with experiment showed that the CNDO/2 method is suitable for qualitative predictions of the geometries of silicon and phosphorus containing radicals.[126] A calculation of the internal rotational barriers for $MeSiH_3$, MeSH, $MePH_2$, and H_2SiSiH_2 using

three different parameterizations of the CNDO/2 basis functions indicated that Santry's recent reparameterization[127] was most reliable for geometries and barriers, but none of the parameterizations gave very good agreement with dipole moments.[128]

The addition silylene, $:SiH_2$, generated by the pyrolysis of disilane, to *trans*-2-*trans*-4-hexadiene produces equal amounts of *cis*- and *trans*-2,5-dimethyl-1-silacylcopent-3-ene, thus ruling out a concerted 1,4-cycloaddition, and suggesting that the triplet form of silylene is reacting.[129] Silylene produced by the nuclear recoil technique, $^{31}SiH_2$ adds to 1,3-butadiene to give silacyclopent-3-ene.[130] Studies using nitric oxide as a scavenger demonstrate that the reacting silylene is present as 80% triplet and 20% singlet, while studies using neon as a moderator prove that the ground electronic state for silylene is a singlet.[131]

The attack of trimethylsilyl radicals on acetonitrile, *tert*-butylethylene, and 1,2-di-*tert*-butylenthylene produces exceptionally stable radicals of the type $(Me_3Si)_2CHC^{\cdot}RR'$; R = R' = Me_3Si or Me_3C; and R = Me_3Si, R' = Me_3C. The ESR spectra of these radicals consists of one principal line at g = 2.0024, flanked by appropriate ^{13}C and/or ^{29}Si satellites. Coupling with the lone β-hydrogen is never resolved, apparently because it is locked in the nodal plane of the radical by steric effects.[132] The rate of addition of the trimethylsilyl radical to ethylene has been studied by flash photolysis, ESR techniques. The rate constant at 20° is 1.7×10^5 $M^{-1}sec^{-1}$, and the activation energy is 2.5 ± 0.2 kcal/mole.[133]

The kinematics of hydride-ion and hydrogen-atom transfer reactions in monosilane,[134] and methylsilane,[135] have been studied using tandem mass spectrometry. A detailed analysis of the

isotopic distribution of the $SiCX_4^+$ product from the reactions of $SiH_2^+ + CD_4$ and $SiD_2^+ + CH_4$ shows that the product distribution is non-random and that X_2 elimination from the silicon atom is favored by more than an order of magnitude over elimination from any other site.[136] The Arrhenius parameters and kinetic isotope effects for the reactions of hydrogen atoms with silane have been determined.[137] An ESR study of the reaction of atomic deuterium with silane has been reported.[138]

Mayer and Lampe have studied the reactions of Si^+, SiH^+, SiH_2^+, and SiH_3^+ with ethylene and the reactions of $C_2H_2^+$, $C_2H_3^+$, and $C_2H_4^+$ with silane using tandem and high pressure mass spectrometry. A persistent intermediate $SiC_2H_7^+$ of unusual stability is observed which is assigned a cyclic three-membered ring structure.[139] (See also Refs. 9 and 111). Similar studies of the silanonium ions with acetylene were reported.[140] In studies of the ion-molecule reactions of tetramethylsilane, the major reaction path was found to addition of Me_3Si^+ to Me_4Si followed by loss of CH_4.[141] Deuteration experiments showing the $[M-1]^+$ ion formed in mass spectra studies of R_3SiH compounds; R = Me, Et, Pr, Bu, and Ph; Pr_2SiEtH; and Ph_2SiMeH; was a siliconium ion. Rearrangements of the fragment ions was also described.[142]

Other physical studies in silanes and alkylsilanes are summarized in Table 3.

Table 3. Physical Studies on Silanes and Alkylsilanes, 1974.

Species	Techniques	Comments	References
SiH_n; n = 1-4	Semiempirical MO calcns.	d orbital's important	143
SiH_4, CH_4, H_2S, H_2O	SCF-MO, one center	agreed with "all electron" results	144

Table 3 Continued

Species	Techniques	Comments	References
MH_4; M = C, Si, Ge, Sn, Pb	Rel. & non-Rel. Hartree-Fock	orbital energies & spin-orbit coup. good	145
"	Pseudopotential MO's	good bond lengths & force constants	146
BD_4^-, CD_4, SiD_4, ND_4^+, AlD_4^-, PD_4^+	Bond orbital analysis	Deuteron quadrupole coupling	147
SiH_4	Ground state rotational constants		148
SiH_4	Rotational Spectrum	R branch	149
CH_4, SiH_4, CH_3CH_3	H atom interaction energies		150
F atoms + MH_4 M = C, Si, Ge	infrared chemiluminescence		151
SiH_3^-, GeH_3^-	electron photodetachment	electron affinties	152
SiH_5^+	ion-cyclotron resonance	structural models for silanium ion	153
SiH_4	cold neutron scattering	rotational diffusion model	154
Si_2H_x	pulse radiolysis	absorption spectrum	155
$MeSiH_3$, $MeGeH_3$	^1H and ^2H NMR in liquid crystals	quadrupole coupling constants	156
$MeSiD_3$	"	"	157
$MeSiH_3$, $MeSiD_3$, CD_3SiH_3, CD_3SiD_3	Microwave	rotational barriers, equil. geometry	158
Et_2SiH_2, Et_2SiHD, Et_2SiD_2	Urey-Bradley force field	vibrational anallysis, rotational barriers	159

Table 3 Continued

Species	Techniques	Comments	References
Me_4; M = C, Si, Ge, Sn	Gas phase infrared	Coriolis constants evaluated	160
Organosilanes	Polemic Si-H vibrations	Inadequacies in current theories	161
Triorgano-silanes	NMR	spin-lattice & spin-spin relaxation times	162
Germylsilanes	Spectra, Stat. Thermodynamics	Calculated thermo. properties	163
Silane	Second Virial coefficient	300-550 °K	164
Silane, *etc.*	Work Function	Hydrocarbon Mixt.	165
Organosilanes	Self-diffusion studies		166

Halosilanes

Two reports of the photoelectron spectrum of SiF_2 appeared in 1974. These studies are complicated by the difficulty in completely removing the SiF_4 precursor, and thus, difference spectra must be obtained. The spectrum obtained by Fehlner and Turner,[167] is slightly less well resolved than that reported by Westwood.[168] A comparison of the two reports is given in Table 4.

Spectroscopic evidence for the formation of dichlorosilylene during the pyrolysis of hexachlorodisilane has been obtained.[169] Third order Rayleigh-Schroedinger perturbation theory has been applied to Koopmans' Theorem to evaluate the vertical ionization potentials of HCl, H_2S, H_3P, H_4Si, H_3SiF and H_3CCl, giving excellent agreement between theory and experiment.[170]

Table 4.   Vertical Ionization Potentials for SiF_2 (eV)

Fehlner & Turner (167)		Westwood (168)		
Band	Assignment[a]	Band		Assignment[a]
11.08	$4a_1$	11.18	0.04	$4a_1$
		15.5	0.1	$3b_2$
15.57	$1a_2$, $3b_2$	15.8	0.1	$1a_2$
		16.8	0.1	$3a_1$
17.08	$1b_1$, $3a_1$	17.06	0.05	$1b_1$
		17.8	0.15?	$2b_2$

[a] Valence shell orbitals, C_{2v} symmetry.

Ab initio LCAO-SCF-MO computations of the wave functions of chlorosilane were carried out using a moderately sized uncontrolled Gaussian basis set, with and without an appropriate manifold of d orbitals being allowed to the silicon and/or chlorine. The interpretation in terms of the contributing AO's leads to the conclusion that, when d character is allowed only to the silicon, the is a transfer of charge from the chlorine but, when it is allowed only to the chlorine, the effect is essentially just a polarization of the chlorine atom.[171]

The NMR spectra of (diisopropylamino)trichlorosilane showed two Me_2CH doublets which coalesced at about -135°, indicating that, at low temperatures, rotation about the *i*-Pr-N bond was restricted.[172] The microwave spectrum of (trifluorosilyl)difluoroborane has been analyzed. The data suggest a significantly longer than expected Si-B bond length and an extremely low rotational barrier for the bond.[173]

The enthalphy, entropy and free energy of dissociation for tetrafluorosilane-amine adducts have been correlated with steric effects.[174] Dumas and Gomel have prepared a review of the molecular interactions between bases and the Group IV halides.[175] Spectroscopic evidence for the formation of adducts between silicon tetrafluoride and aromatic monoamines has been obtained.[176] Trimethylchlorosilane has been found to form a weak 1:2 complex with dimethylformamide in dioxane,[177] and 1:1 charge transfer complexes with triethylamine, pyridine, and quinoline,[178] which are believed to involve d orbitals on silicon. Other physical studies on halosilanes which appeared during 1974 are listed in Table 5.

Table 5. Physical Studies on Halosilanes, 1974

Species	Techniques	Comments	References
SiCl	Microwave	Rotational analysis	179
MX_4; M = C, Si, Ge, Sn, Ti; X = Cl, Br, I	Preresonance Raman	Complete quadratic force field for each molecule	180
$SiCl_4$, $GeCl_4$, $SnCl_4$	Gas phase infrared	Band intensities & bond polarities analyzed	181
SiI_4, GeI_4, SnI_4	Raman	analysis	182
SiF_4, solid	Calculation	crystal absorption spectrum	183
$SiCl_4$, $SiCl_4^-$	Mass spec.	ΔH_f° for $SiCl_3(g)$ = -81 kcal/mole	184
MCl_4; M = C, Si, Sn, or Ti	Isothermal liq. vap. equil.	excess free enthalpy calculated	185

Table 5 Continued

Species	Techniques	Comments	Reference
$SiBrH_3$, $SiBrD_3$	Infrared	analysis	186
SiF_3H	Infrared	analysis	187
$SiCl_3H$	Heteronuclear Double Resonance	spin-lattice relaxation times	188
$EtSiCl_3$	Microwave	analysis	189
XCH_2-SiMe_2X'; X = F, Cl, Br, I, Me, Ph, X' = H or F	infrared & Raman	conformational analysis	190
Me_nSiF_{4-n}; n = 1-4	Mass spec.	analysis	191
$SiBr_4$	Heat capacity measurement		192

Group VI Compounds

Conformational analyses of 1,3-dioxa-2-silacyclohexane systems
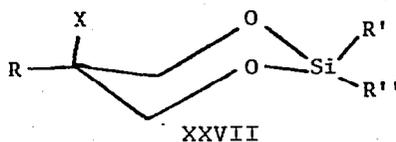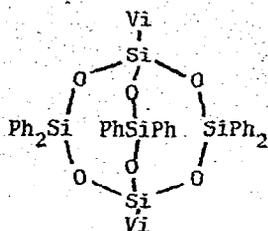

XXVII

XXVII, have appeared. For XXVII; X = H; R, R', R" = H, Me, Me;

Me, Me, Me; Me_3C, Me, Me; H, Me_3C, Me; and Me, Me, Me_3C; studied

by NMR, the chair form is preferred and isomers with an axial

substituent in the 5-position were not detected.[193] On the other

hand, for XXVII; R' = R" = Me; R = H, or Me; X = NO_2 or NH_2; dipole

moment and NMR studies indicated a chair conformation with the

nitro group in the axial position.[194]

The structures of 1-oxa-2,6-disilacyclohexane derivatives, investigated in dipole moment studies, indicated chair configurations, with silicon's substituents *trans* to each other.[195]

The ^{1}H NMR spectra of $RC_6H_4SiMe_2CH_2CH_2X$; R = H, *m*-Me, *p*-Me, *m*-CF$_3$, *m*-Cl, *p*-Cl, *p*-F, *p*-MeO; X = OH; and several analogous compounds where X = Cl indicated that the silanes are a mixture of conformers in which those with the OH group or Cl atom in a synclinal position predominate.[196] The dipole moments of a series of alcohols, $Me_3M(CH_2)_nOH$; M = C, Si, Ge; and n = 1-4; have been reported.[197] The ^{29}Si NMR chemical shifts of a series of compounds $Me_{3-n}SiX_nCH_2Cl$ and $Me_{4-n}SiX_n$; X = Cl, n = 0-3; and X = OEt or AcO, n = 1-3; have been shown not to be a directly additive property of the substituents.[198] (See also References 58 and 60). X-ray photoelectron spectra of the lithium salts of the oxyanions of Si, P, S, Cl, Mn and Cr show that the contribution of the oxygen 2s orbitals to the bonding in the main group compounds increases with increasing atomic number of the central atom. The increase in the *e* $3t_2$-t_1 energy splitting from $SiO_4{}^{4-}$ to $ClO_4{}^-$ is attributed to increased π back bonding between the oxygen 2p and the central atom 3d orbitals, which by implication is least for $SiO_4{}^{4-}$.[199]

The possible use of paramagnetic shift reagents in the ^{1}H NMR spectra of organosilicon compounds containing oxygen or nitrogen has been investigated.[200] A study of the 100 MHz [29]Si nuclear Overhauser effects in 16 methyl and phenyl substituted siloxanes has been reported.[201] The crystal structures of the cyclic siloxanes, XXVIII,[202] XXX,[203] and the silazoxane, XXIX,[204] have been reported.

XXVIII
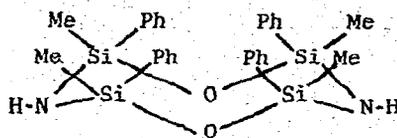
XXIX
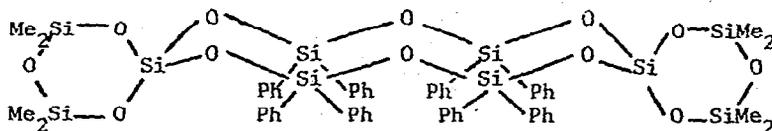
XXX

The molecular structure of [iminobis(ethyleneoxy)]diphenyl-
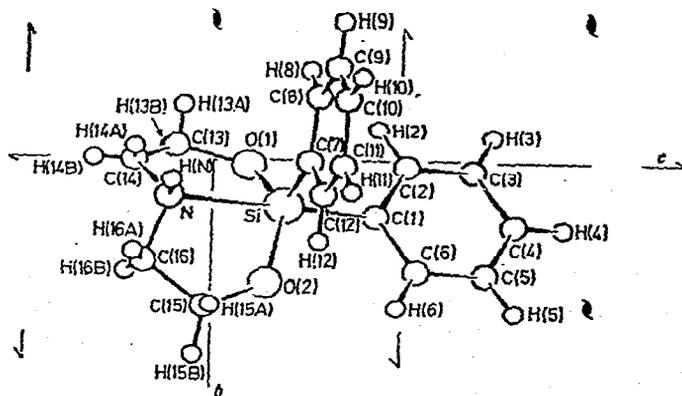silane, Figure 4, determined by X-ray crystallography, shows that

Figure 4. Molecular structure of [iminobis(ethyleneoxy)]diphenyl-
silane.[205] (Reproduced with the permission of the
Chemical Society.)

the silicon has approximately trigonal bipyramidal geometry. The Si-N bond distance is 2.301 Å.[205] In a related study, the crysta and molecular structure of the β form of 1-phenylsilatrane, Figur 5, has been reported.[206] The molecular geometry is similar to
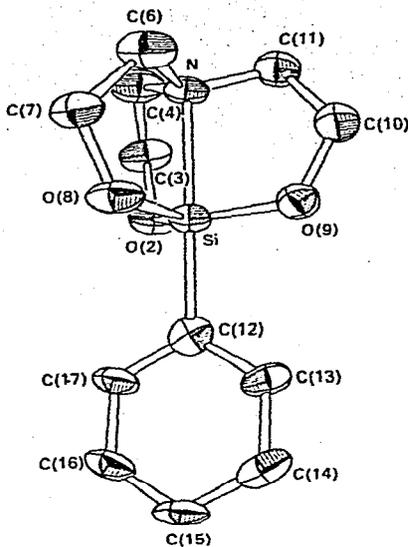

Figure 5. Molecular structure of β-1-phenylsilatrane, hydrogens omitted.[206] (Reproduced with permission of the International Union of Crystallography).

that of the α form, but the Si-N dative bond, 2.156 Å, is 0.037 Å shorter than in the α form.[207] The bonding in the silatranes, substituted at silicon with H, Me, Et, Me_2CH, vinyl, cyclohexyl, and Ph, and in 10 model compounds has been discussed in terms of the X-ray spectra.[208] Conformational energy calculations for 1-methylsilatrane indicate no stable conformer without an inter-action between the silicon and nitrogen.[209] The effect of the length of the methylene chains on the stability and Si-N coordina-tion bonds in silatranes has been examined by quantum mechnical calculations.[210]

The infrared and Raman spectra of deuterated and undeuterated trimethylsiloxyethylenes have been analyzed and show that the enoxysilane exists in two conformers, the major being the *gauche* with silicon eclipsing the ethylene π system, and the minor the

gauche   *s-cis* (planar)
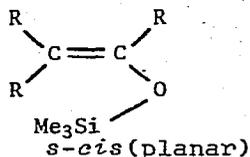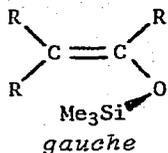
s-cis one.[211] The characteristic vibrations the oxacyclopentanes and cyclopentenes, XXXI and XXXII, X = Si, or Sn have been
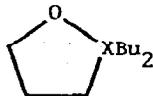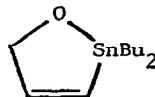
XXXI   XXXII

assigned and correlated with structure.[212] Infrared and Raman spectra for vinyl- and phenylacetoxysilanes,[213] methylacetoxy-silanes,[214] and mono- and dimethacrylate esters of organosilicon compounds,[215] have been reported.

The use of mass spectra to differentiate between isomeric α-, ω-unsaturated diols after derivatization with trimethylchloro-silane has been reported.[216,217] Studies of the fragmentation of trimethylsilyl derivatives of 2,3-dialkyl-1,4-cyclopentanediols,[218] dimethylalkoxysilanes,[219] and methylphenyldisiloxanes,[220] in their mass spectral analyses have appeared.

The acid dissociation constant of triethylsilanol, pK = 13.63 ± 0.07 at 25°, has been determined.[221] The vibrational spectra of some (aminoalkoxy)ethoxysilanes,[222] and some 3-amino-propoxy, and *N*-substituted-2-aminoethoxy silanes showed the absence

of Si-N donor-acceptor bonds but indicated some p-$d\pi$ interactions between oxygen or nitrogen and silicon.[223] The relative basicities of organosiloxanes have been studied by infrared spectroscopy,[224-226] and can be correlated with Taft inductive constants.[226] The equilibrium constant for complexation of SnI_4 and $SnBr_4$ with isopropoxytrimethylsilane has been evaluated with the aid of Mössbauer spectroscopy.[227]

Liquid-liquid phase equilibria for trimethylethoxysilane with some amines,[228] tetraisopropoxysilane-acetone-water,[229] and tetraisopropoxy-amine-water systems have been examined.[230]

Saturated vapor pressure studies for polydiorganosiloxanes containing silacyclohexane, silaacenaphthene, and silacyclopentene substituents have appeared.[231] The excess volumes,[232] and excess enthalpies,[233] of mixtures of *tetrakis*(2-ethylbutoxy)silane with cyclohexane, benzene, and carbon tetrachloride have been determined

The photoelectron spectra of $S(MMe_3)_2$ and $MeSMMe_3$ compounds; M = C, Si, Ge, Sn, and Pb; were obtained and assigned on the basis of semilocalized orbitals and a consideration of symmetry and substituent effects.[234] The molecular structure of tetra-(2-thienyl)silane, Figure 6, was found to have somewhat longer than usual Si-C bonds.[235]

The dipole moments of $PhSMMe_3$, m- and p-$ClC_6H_4SMMe_3$, and $(Me_3M)_2S$ have been measured and analyzed. They indicate a growing electron releasing ability of M in the order C < Si < Ge < Sn < Pb. Charge transfer spectra,[237] and NMR studies of 36 organosilicon derivatives of thiophene have been reported.[238] Another report deals with the infrared spectra of the same compounds.[239]

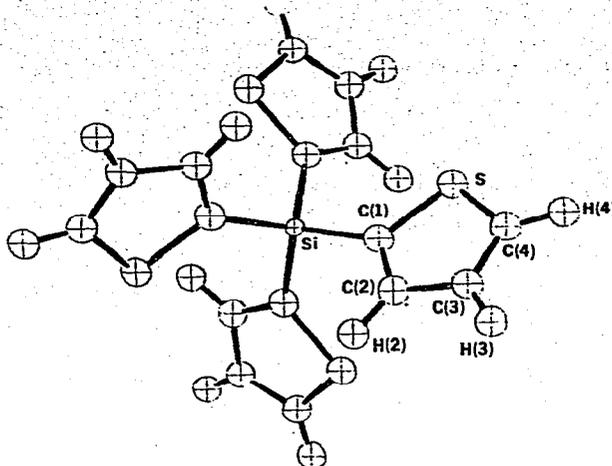The mass spectra of $Me_3Si(CH_2)_nX$; X = SO_2Me or SMe; n = 2 or

Figure 6. Molecular structure of tetra-(2-thienyl)silane. Only one ring is labeled for clarity.[235] (Reproduced with the permission of the International Union of Crystallography)

3 indicate a strong interaction between silicon and the sulfide or sulfone functional group.[240] Comparison of the ionization energies (mass spectral) of $PhSMMe_3$ and MMe_4 compounds is taken as evidence for $p-d\pi$ bonding in the sulfur compounds.[241]

Group V Compounds

The molecular structure of trimethylsilylcyanide, determined by electron diffraction gave bond lengths of: Si-C(N), 1.844 Å; C-N, 1.170 Å; Si-C(Me), 1.871 Å; C-H, 1.111 Å; and bond angles C(Me)-Si-C(N), 107.0 ± 1.5° and Si-C-H, 110.4 ± 1.5°. The authors make the point that the $p-d\pi$ effects often discussed in the literature really represent a summary description for a number of effects.[242] The electronic structures and energies for silylsyanide, silylisocyanide, and *bis*(silylcyanide) have been obtained for minimum energy geometries using CNDO calculations.[243] CNDO/2 calculations have also been performed for the isocyanates,

CF_3NCO, H_3SiNCO and PF_2NCO and give minimum energy geometries in agreement with spectroscopic data. Interestingly, only for CF_3NCO and SiH_3NCO, does the isocyanate group appear to be non-linear.[244]

An electron diffraction study of silylazide, and $(SiH_3)_2NCN$ has shown that SiH_3N_3 has a nonlinear SiN_3 skeleton with an Si-N-N angle of $123.8 \pm 1.0°$. The molecule $(SiH_3)_2NCN$ is a carbodiimide with the SiNCNSi unit probably linear. It is suggested that the wider Si-pseudohalogen bond angles are mainly a function of steric interactions and Si-X bond lengths, rather than p-$d\pi$ interactions.[245]

The crystal and molecular structure of *bis*(trimethylsilyl)-diimide, $Me_3Si-N=N-SiMe_3$, Figure 7, determined at -130° has been
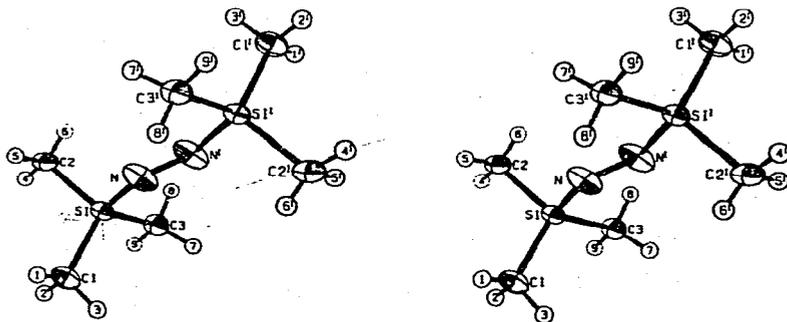

Figure 7. Stereoscopic representation of a *bis*(trimethylsily)-diimide molecule.[246] (Reproduced with the permission of the International Union of Crystallography.)

reported. The molecule has a very short N-N bond, 1.17 Å, and an unusually long Si-N bond, 1.181 Å. The Si-N-N bond angle in the crystal is 120°.[246] Organosilyl iminamino radicals of the

type $Ph_2C=N-\overset{\cdot}{N}-SiR_2R'$; R, R' = Me, Me; Ph, H; Ph, Ph; and Et, Et; have been studied by ESR spectroscopy. The radicals are σ radicals, with a C-N-N bond angle much less than 180°.[247]

The crystal structure of *tris*(methyldiphenylsilylmethyl)-amine, Figure 8, shows that the geometry at nitrogen is pyramidal
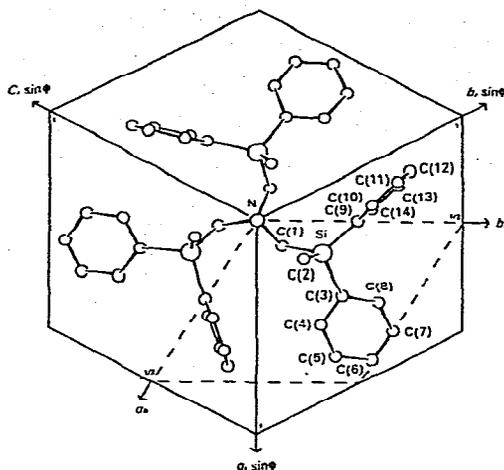

Figure 8. Structure of *tris*(methyldiphenylsilylmethyl)amine.[248]
(Reproduced with permission of the International Union
of Crystallography)

with a C-N-C bond angle of 111.5°.

The Si-C sp^2 and sp^3 bond lengths are 1.875 and 1.873 Å, respectively.[248] The nitrogen isotope effect in the Raman spectrum of trisilylamine indicates that in the gas phase the molecule has planar trigonal geometry. In the liquid and solid phases there are distortions of this geometry.[249]

The crystal structure of *bis*(dioxane) potassium *bis*(trimethyl-silyl)amide shows an essentially ionic structure. The very short Si-N bond, 1.64 Å, is considered to be consistent with delocaliza-tion of the negative charge on nitrogen through $p-d\pi$ interactions.[250] (Compare with the results in Ref. 119)

A preliminary report of ESR studies on radicals of the type [(Me$_3$Si)$_2$CH]$_3$M· and [(Me$_3$Si)$_2$N]$_3$M·; M = Si, Ge, Sn; produced by photolysis has appeared. The radicals' half-lives range from about 10 minutes to 1 year, and well defined splittings are observed in their spectra.[251] Unusually stable radicals are also produced by the addition of trimethylsilyl radical or the diethylphosphonyl radical to di-*tert*-butylimine or *tert*-butylnitril The radicals are "locked" sterically into a conformation which should allow maximum hyperconjugative interaction between the Si-N bond and the unpaired electron, yet the extent of hyperconjugation is only about half that found in the related *t*-Bu$_2$ĊCH$_2$F radicals.[252]

Infrared and NMR studies of a series of *bis*(trimethylsilyl) amides, XXXIII or XXXIV; R = H, Me, Et, *i*-Pr, *t*-Bu, and CF$_3$, show that all the molecules except R = H have the imidate structure, XXXIV. The free energies of activation for the intramolecular
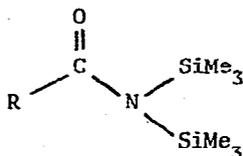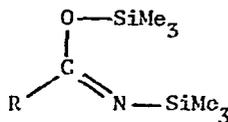
XXXIII   XXXIV

rearrangement of trimethylsilyl groups range from 15.0 to 22.1 kcal/mole and are related to the steric and electronic properties of the substituent at the carbonyl carbon.[253]

The first quantitative measurement of the basicity of a silyl amine, 1-diethylamino-3,5,7-trimethyl-13,5,7-tetrasilaadamant has been reported. The pK_B, 8.32, showed that the silylamine was a substantially weaker base than anlogous carbon amines. The results are consistent with either *p-d*π bonding or the adjacent

charge rule.[254]   The basicity of a series of silylmethylamines;

Me_3SiCH_2NHR; R = H, Pr, i-Pr, Bu, i-Bu, cyclohexyl, benzyl, or

CH_2SiMe_3; and RMe_2SiCH_2NHBu; R = Me, Bu, m- or p-MeC_6H_4, Ph, m-

or p-ClC_6H_4, or m-FC_6H_4 was investigated by infrared spectroscopy.

In the former series, no basicity increasing effect due to the

trimethylsilylmethyl group was observed, while, in the latter

series the basicity correlated with Taft σ* inductive constants.[255]

   The ^{14}N chemical shifts for 39 silylamines and ^{14}N and ^{11}B

chemical shift data for 19 silylaminoboranes have been reported

and related to Si-N p-$d\pi$ bonding.[256]   The potential barrier to

rotation of the C-N bond in $(ClSiMe_2CH_2)_2NCOCl$ was determined by

NMR to be 8.9 ± 1.3 kcal/mole.[257]   Studies of the ^1H and ^{13}C NMR

spectra of the fluxional molecules XXXV and XXXVI; R = Me, Et,

OEt; and the trimethylgermyl derivative were interpreted by

assuming that the organometal group migrates by intermolecular
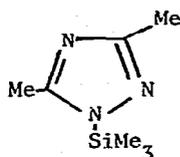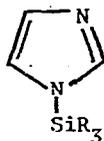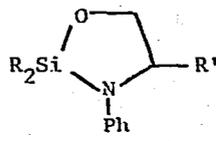
| XXXV | XXXVI | XXXVII |

exchange.[258]   The mass spectra of the sila-substituted oxazolines,

XXXVII; R = Ph; R' = H, Me or Et; showed definite evidence for

migration of a phenyl group from nitrogen to silicon.[259]   The

mass spectra of the trimethylsilyl derivatives of a series of

alkyl- and aminoalkyl-phosphonates,[260] and silylated pyrazoles,[261]

have been reported and analyzed.

   The nature of the bond in the pyridine-chlorotrimethylsilane

has been investigated.[262]   The high resolution ^{13}C NMR spectra of

N-trimethylsilyl-3,5-dimethylpyrazole has been studied.[263]   The

pK_a's of 16 trialkylsilylalkyl piperidines have been correlated with Taft σ constants.[264] The dipole moment of hexamethylcyclo-trisilazane,[265] and the heat capacity and thermodynamic functions of N-β-trimethylsilylethyl ethyleneimine have been determined.[266]

The photoelectron spectra of the simplest phosphorus ylide, $Me_3P=CH_2$, and several C-silyl-substituted derivatives have been reported. Experimental values for the P=Cπ ionization and CNDO/2 calculations show that silyl stabilization is not a consequence of a π energy lowering, but of a decrease of the MO coefficient at the ylidic, quasi-anionic carbon atom.[267] The ^{31}P and ^{13}C chemical shifts and $^{31}P-^{13}C$ and $^{31}P-^{29}Si$ coupling constants for a series of 10 N-trimethylsilyltriorganophosphine imines were explained by a mechanism of intramolecular coordination of the β-Me group to phosphorus using d orbitals.[268]

The substituent effects on the ^1H and ^{31}P NMR spectra were determined for PH_3 and 24 compounds of the type $(Me_xSiH_{3-x})_nPR_{3-n}$; x = 0-3, n = 1-3; R = H or Me.[269] Vibrational spectra and analyses for $(Me_3C)_nP-(MMe_3)_{3-n}$; M = Si, Ge, Sn; n = 0, 1, or 2;[270] $(CF_3)_2-X-MMe_3$; with X = P or As; M = Si or Ge;[271] and triorganosily derivatives of phosphorus acids,[272] have appeared.

Transition Metal Compounds

The photoelectron spectra for compounds of the type MR_4 and $M'R'_4$; M = Ti, Zr, Hf; M' = M, Ge, Sn; R = Me_3CCH_2 or Me_3SiCH_2 have been assigned in terms of a localized bond model assuming a tetrahedral framework. The HOMO, in the range 8-9 eV, was as-signed to σ M-C or σ M'-C ionizations, and small inductive ef-fects for the trimethylsilylmethyl groups was observed.[273]

The crystal structure of $[Me_3SiNTiCl_2]_n$, Figure 9, shows
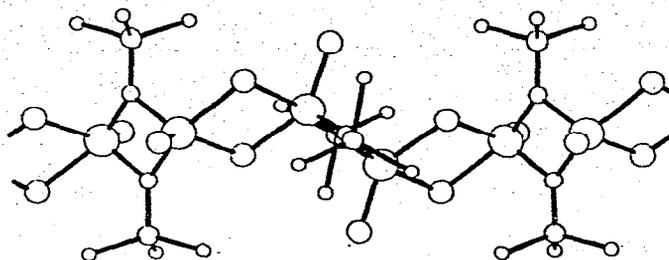
Figure 9. The ordered chain of $[Me_3SiNTiCl_2]_n$. The circles are, in order of decreasing size, Ti, Cl, Si, N, and C.[274] (Reproduced with the permission of The Chemical Society)

that the catenated compound has both bridging trimethylsilylamino groups and chlorine atoms.[274] The vibrational spectra of N-tri-methylsily-*tris*(trimethylsiloxy)vanadium(V) imine, $(Me_3SiO)_3V=N-SiMe_3$, suggest a vanadium-nitrogen triple bond and a nearly linear V-N-Si arrangement, perhaps due to delocalization of the nitrogen lone pair to both vanadium and silicon.[275]

The infrared spectra for a series of compounds, $X_3M-Mn(CO)_5$; M = Si, Ge, Sn; X = Cl, Br, and I; were interpreted in terms of the interaction between the M-Mnσ orbitals and the π* orbitals of the four equatorial carbonyls.[276] For a related series of mole-cules; X = Me or H; the π interaction between the Group IV metal and manganese was weaker than that for the halogens.[277] Analysis of the force fields for a series of cobalt carbonyls, $X_3M-Co(CO)_4$; M = Si, Ge, Sn; X = H, D, F, Sl, Br, and I; led to an interpretation indicating that metal-ligand backbonding is the most important contributor to the trends observed.[278] The infrared and proton NMR spectra of derivatives of $-Mn(CO)_5$, $-Mn(CO)_4PPH_3$, and $\pi-Cp(CO)_2Fe-$, containing the polysilyl ligands $(Me_3Si)_nMe_{3-n}Si-$,

n = 1-3, have been analyzed in terms of force constants and discussed in terms of the σ-donor and π-acceptor properties of the polysilyl ligands.[279]

The Mössbauer spectrum and mass spectral studies on the silylene-irontetracarbonyl complex, $[(CO)_4FeSiCl_2]_3$, suggest that, in the gas phase, the monomeric silylene complex exists, and leads to the proposal of two isomeric forms for the trimer, Figure 10.[280] The Mössbauer spectrum of the trigonal planar
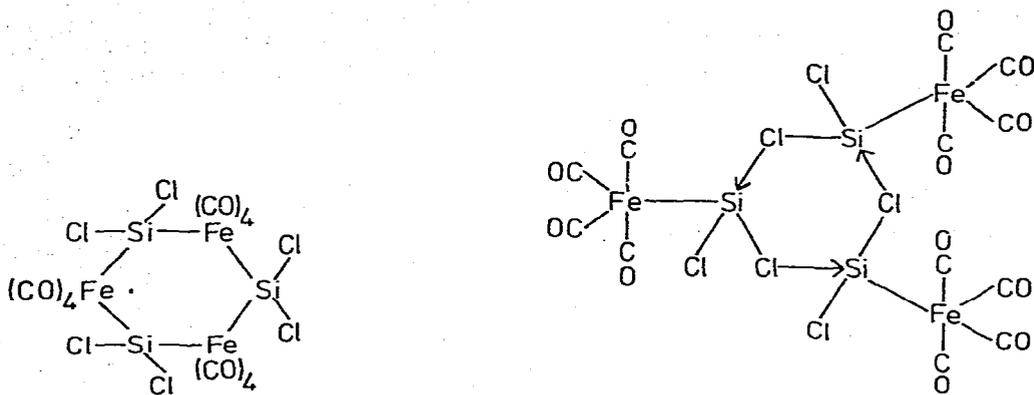
Figure 10. Posible structures for $[(CO)_4FeSiCl_2]_3$.[280]

high spin ferric compound, $Fe[N(SiMe_3)_2]_3$, shows a very high temperature dependant quadrupole splitting, and at low temperatures, a novel type of magnetic hyperfine spectrum.[281]

While transition metal-silicon σ bonds have traditionally been considered to be stronger than the corresponding metal-carbon σ bond, kinetic evidence has been presented which indicates that the Fe-C and Fe-Si bonds in η-Cp(CO)$_2$FeSiMe$_{2-n}$Cl$_n$CH$_2$Cl, and analogous carbon compounds may be of comparable strength.[282] The molecular structure of (π-cyclopentadienyl)-[*trans*-diphenyl-*bis*(trimethylsilyl)cyclobutadiene]-cobalt, determined by X-ray crystallographic methods, Figure 11, shows that the C$_4$ ring is
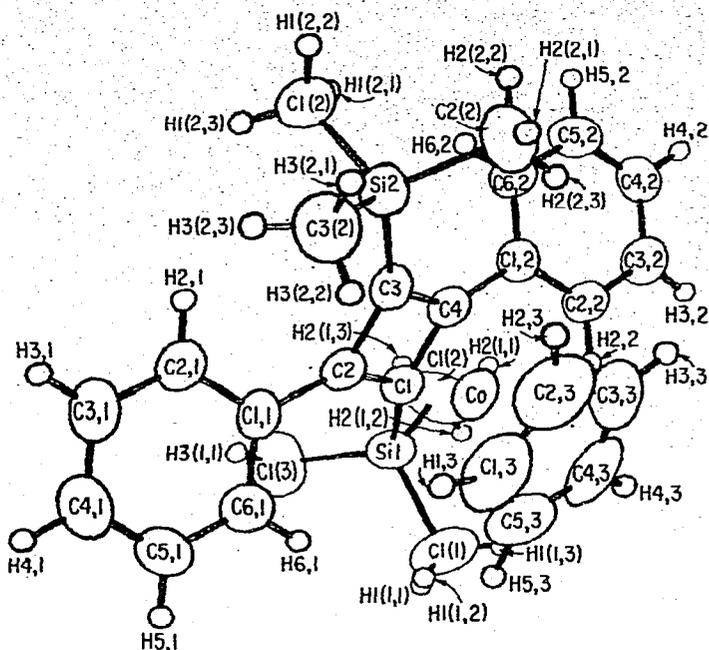
Figure 11. Molecular structure of $(\pi\text{-}C_5H_5)\text{-}Ph_2(Me_3Si)_2C_4Co.$[283]
(Reproduced with permission of Gordon and Breach, Ltd.

planar and all four C-C distances are the same length, 1.467 Å,
but the two angles at the carbons bonded to phenyl are about 88°
while the two angles at the carbons bonded to silicon are about
92°.[283] The infrared spectra of cobalt compounds, $R_3MCo(CO)_4$;
R = Me; M = Si, Ge, Sn; and R = Et, M = Ge; indicated that the
equatorial carbonyl substituents were displaced towards the Group
IV substituent only for the silicon compound.[284] Crystal
structures of the complexes XXXVII, M = Ni, X = NEt, and M = Co,
X = O have been reported.[285] The crystal structure of *trans*-
chlorobis(dimethylphenylphosphine)(trimethylsilyl) platinum(II)
indicates the presence of discrete square-planar molecules.[286]
The crystal structures of the ruthenium complexes, XXXIX,[287] and
XL,[288] Figures 12 and 13 have been determined. Evidence has been
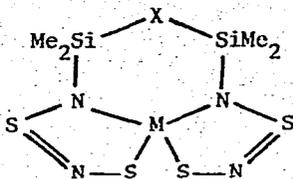
XXXVIII
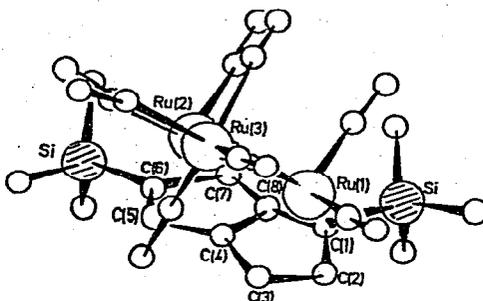
Figure 12. Structure of $Ru_3(CO)_8[C_8H_4(SiMe_3)_2]$, XXXIX.[287] (Re-
produced with the permission of the Chemical Society)

presented which shows that while XXXIX is not fluxional, the
analogous symmetrically substituted complex formed by reaction
of 1,4,6-*tris*(trimethylsilyl)cycloocta-2,4,7-triene is.[287]
In addition to the structure of XL, evidence is presented which
suggests that the migration of the trimethylsilyl group to the
cycloheptadienyl ring from ruthenium is intramolecular.[288]

Acknowledgement
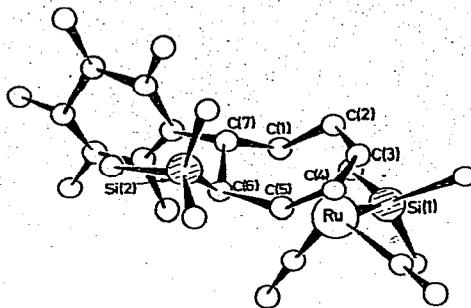
Figure 13. Structure of Ru(SiMe$_3$)(CO)$_2$C$_7$H$_7$(C$_6$F$_5$)(SiMe$_3$), XL.[288]

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