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Low-Valent Silicon

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I. Introduction

Except for SiX_3^- anions and silicides, low-valent silicon compounds exhibiting coordination numbers of 1 to 3 are not stable for long at room temperature. Consequently the structural chemistry of those compounds, which is the subject of this article, has to be based upon investigations at high or low temperature, or upon rapid spectroscopic techniques adapted to the short lifetimes of the species investigated. The reluctance of Si to form compounds analogous to HC≡CH or H_2CO is due to its inability to stabilize the coordination numbers 1, 2 or 3 by $p\pi p\pi$ bonds, polymeric structures being preferred. On the other hand SiF_2 is thermally more stable than the analogous carbene CF_2.

The structural and thermodynamic properties of the short-lived silicon compounds are of considerable interest because these species play an important role in reactions at high temperature and in stellar space. The structural properties of unstable molecules in their ground and excited states are quite often known more precisely from microwave, IR and particularly high-resolution electronic spectra than those of stable compounds. Thus low-valent Si compounds are of great importance for the understanding of bonding in silicon chemistry1, 2). Furthermore they offer tests for theoretical calculations based upon the properties of silicon atoms in different states. Some of the atomic energy levels of

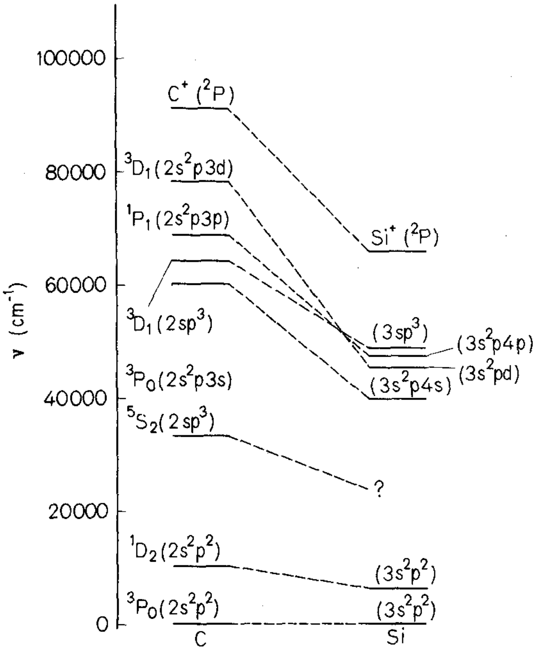


Fig. 1. Atomic energy levels of C and Si (Approximate AO representation in parentheses)

the Si atom are reproduced in Fig. 1 and compared with equivalent states of the carbon atom. The low energy of the s^2pd state of Si should be noted. Calculations however suggest that the contribution from $3d$ orbitals plays only a minor role in the bonding of low valent silicon.

Nomenclature

The energy and structure parameters listed in the tables of this review belong in general to the ν=0 vibrational state; their notation is r_0 for the interatomic distance, T_0 for the 0–0 excitation energy. Vibrational frequencies ν'' are those of the lower (usually ground) state while ν' is the notation for the upper electronic states. Equilibrium parameters refering to the potential minimum and only available for diatomics are indexed by e (r_e, ω_e, x_e). ω_e, x_e and ν_v are connected by the equation

$$\nu_v = \omega_e(\nu + 1/2) - \omega_e x_e(\nu + 1/2)^2 + \text{higher terms}$$

II. Monovalent Silicon

Compounds of monovalent silicon are predominantly diatomic molecules, though exceptions such as SiNH and SiCC are known. Due to the formation of $p\pi p\pi$ bonds, the structural parameters of these molecules or radicals are much closer to those of the carbon analogues than is observed in "stable" Si derivatives.

A) General Considerations

The theory of the electronic spectra of diatomic molecules has been treated comprehensively by Herzberg[3)]. The electronic properties of diatomic molecules belonging either to the point group $C_{\infty v}$ or $D_{\infty h}$ (Si_2) are commonly represented by MO schemes (Fig. 2). In order to obtain a consistent notation,

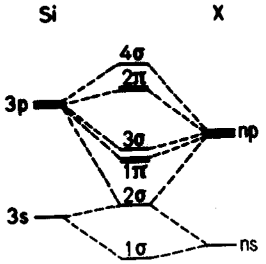


Fig. 2. MO scheme of diatomic SiX compounds

the core electrons have been excluded from the numbering of the MO's. The positions of the 1π and 3σ orbitals, and hence the bonding properties of the MO's, depend mainly on the relative energy levels of the atomic orbitals involved. Bond orders may be evaluated from the MO schemes. As may be deduced from the SiX force constants and distances listed in Table 1, a slight increase in bond order is observed in going from monovalent to tetravalent silicon. A similar behaviour is observed in carbon compounds. It may be attributed to increasing *s* character in the bonds of the tetracoordinated species.

Table 1. Ground-state force constants and distances for SiH, SiF and SiCl compounds

	SiX Force Constants (mdyn/Å)			SiX Distance (Å)		
	X = H	F	Cl	H	F	Cl
SiX	2.39	4.90	2.63	1.531[4]	1.601[5]	2.058[6]
SiX_2	2.34[7]	5.02[8]	2.39[9]	1.5163[10]	1.591[11]	–
SiX_3	2.212[7]	5.49[12]	2.63[13]	–	–	–
SiX_4	2.77[14]	6.33[14]	3.03[14]	1.48[14]	1.55[1]	2.01[1]
SiX_6^{2-}	–	2.94[14]	–	–	1.71[1]	–

B) SiH

Diatomic hydrogen compounds have been studied extensively because of their simplicity in respect of the experimental and theoretical viewpoints.

The electronic spectrum of the SiH radical was first investigated by Jackson[15] and Rochester[16]. Subsequently Douglas[17], Verma[18] and Herzberg *et al.*[4] extended the analysis of the electronic states. The presence of SiH in the solar photosphere has been firmly established[19].

Table 2. Molecular properties of the *X*, *A* and *B* states of SiH and SiD[4]

State		T_0 (cm^{-1})	r_0 (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	f_e (mdyn/Å)
$X\,^2\Pi$	SiH	0	1.531	2041.80	35.51	2.39
	SiD	0	1.528	1469.32	18.23	
$A\,^2\Delta$	SiH	24193.04	1.543	1858.90	99.18	1.98
	SiD	24235.66	1.537	1328.08	48.11	
$B\,^2\Sigma^+$	SiH	30842.23	–	–	–	
	SiD	30907.33	1.558			

The SiH and SiD absorption spectra are obtained from flash discharges in a mixture of SiH_4 or SiD_4 with H_2 or D_2 in a ratio of 1:50 at a partial pressure of $SiH_4(SiD_4)$ of about 1 mm Hg[4)]. Instead of SiH_4 (SiD_4), $C_6H_5SiH_3$ ($C_6D_5SiD_3$) may be used[18)]. The observed electronic states are shown in Fig. 3.

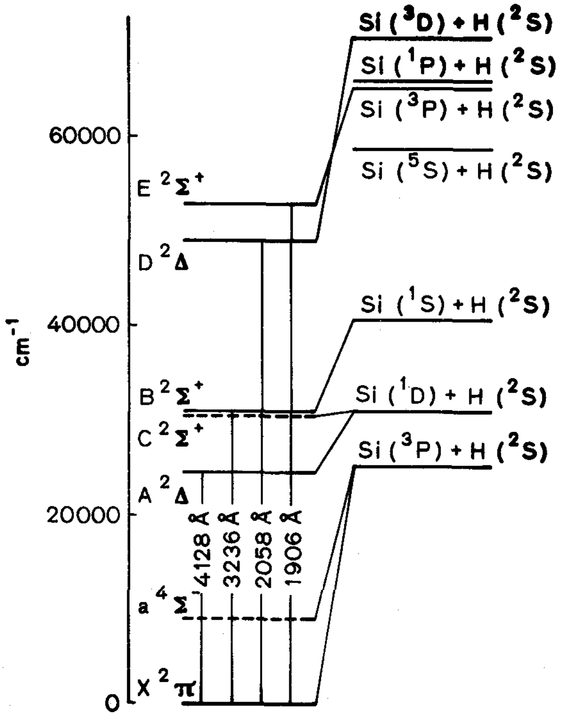


Fig. 3. Electronic states of SiH and their correlation to those of the separated atoms (from Ref.[4)])

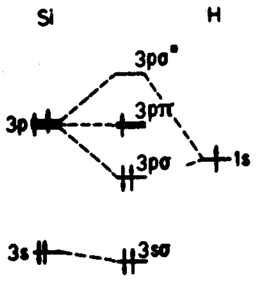


Fig. 4. MO scheme for SiH

The electronic configurations of the three lower states (X, A, B) are similar to those of the CH radical. The A and B states are obtained upon exciting an electron from the bonding $3p\sigma$ orbital to the $3p\pi$ orbital (Fig. 4). As may be seen from Table 2, a slight decrease of the SiH bond order results.

The dissociation energy $D_0\,[\mathrm{SiH} \rightarrow \mathrm{Si}(^3\mathrm{P}) + \mathrm{H}(^2\mathrm{S})]$ has been determined as 3.06 eV (70.6 kcal/Mol)[18].

The electronic states of SiH have been subject to theoretical calculations. Jordan[20] has used a semi-empirical method which was found to show the best agreement with the experimental data when a small percentage of d character was assumed to be involved, the d orbitals being somewhat contracted by polarization. Combined SCF and CI calculations by Wirsam[21], however, fit the observed data without use of d orbitals. These calculations differ mainly in the prediction of the $a^4\Sigma^-$ state ($3s\sigma^2\,3p\sigma\,3p\pi^2$) which has not as yet been observed. The dipole moment of SiH has been calculated by Cade[22] to be $\mu_{\mathrm{SiH}} = 0.302$ D ($\mu_{\mathrm{CH}} = 1.570$ D) with the positive charge on the hydrogen.

Attempts to isolate the SiH radical at low temperature in an Ar matrix by vacuum UV photolysis of SiH_4 and various deuterosilanes provided data for Si_2, SiH_2 and SiH_3, but were not conclusive for the identification of SiH[7].

C) SiH^+

The $A^1\Pi$–$X^1\Sigma^+$ transition of the SiH^+ molecular ion has been observed in the emission spectrum of a hollow cathode discharge through helium containing a trace of SiH_4[23]. Subsequent to this identification the absorption pattern of SiH^+ has also been detected in the solar photosphere[24]. The ionization of SiH ($I_{\mathrm{SiH}} = 8.01 \pm 0.08$ eV) does not substantially alter the SiH bond strength (see Table 3). This is consistent with the electron configuration $3s\sigma^2\,3p\sigma^2$ ($^1\Sigma^+$) for the SiH^+ ground state. The upper $A^1\Pi$ state must have a very flat potential curve; the dissociation energy $D_0[\mathrm{SiH}^+ \rightarrow \mathrm{Si}^+(^2\mathrm{P}) + \mathrm{H}(^2\mathrm{S})] = 25800 \pm 600\ \mathrm{cm}^{-1}$ (3.2 eV) is only slightly greater than T_0.

Table 3. Molecular properties of SiH^+ [23]

State	T_0 (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	f_e (mdyn/Å)
$X\,^1\Sigma^+$	0	1.499	2157.10	34.21	2.66
$A\,^1\Pi$	25025.25	1.971	468.60	39.22	0.13
SiH ($X\,^2\Pi$)[6]		1.520	2041.80	35.51	2.39

D) Si_2

Mass spectrometric studies reveal that silicon vapour produced by heating elementary silicon to 2300 K consists mainly of silicon atoms, but there is also a considerable amount of Si_2, Si_3 and of higher aggregates present[25].

The absorption and emission spectra obtained by flash discharge in an SiH_4 :He=1:50 gas mixture or by similar methods were analysed for bands which could be attributed to Si_2[26-29]. The observed levels are involved in triplet-triplet transitions of the type $^3\Sigma^-_u$–$X^3\Sigma^-_g$ and $^3\Pi_g$–$D^3\Pi_u$ (Fig. 5). Symmetry-forbidden transitions have not so far been detected. Thus information concerning singlet systems is not available. Furthermore an absorption attributed to the $D^3\Pi_u$–$X^3\Sigma^-_g$ transition was observed in a matrix investigation[7], but the excitation energy of about 35000 cm^{-1} is in contradiction to the expectation of a low-lying $D^3\Pi_u$ state. Some molecular constants of the low-lying states of Si_2 are given in Table 4.

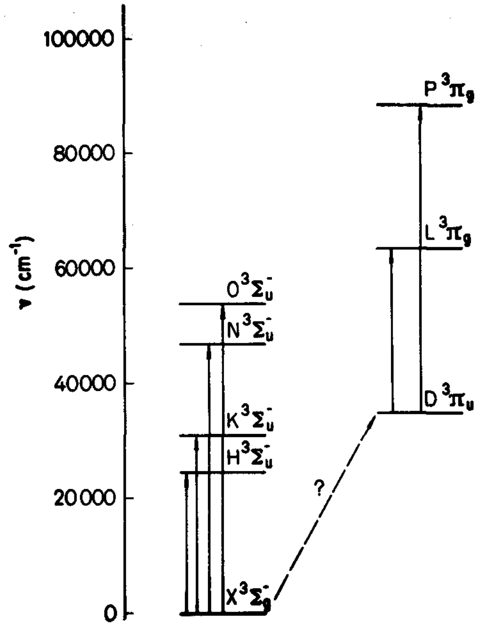


Fig. 5. Electronic states of Si_2

Table 4. Molecular constants of low-lying states of Si_2[28, 29]

State	T_0 (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	f_e (mdyn/Å)
$X\,^3\Sigma^-_g$	0	2.246	510.98	2.02	2.16
$H\,^3\Sigma^-_u$	24311.15	2.654	275.30	1.99	0.63
$K\,^3\Sigma^-_u$	30768.77	2.349	462.6	5.95	1.77
$D\,^3\Pi_u$	(~35000 ?)	2.155	547.94	2.43	2.48

The ground states of C_2 and Si_2 are quite different. This is the consequence of a rearrangement of the molecular orbitals compared in Fig. 6. The lowest triplet states of C_2, $a^3\Pi_u$ and $b^3\Sigma_g^-$ which derive from excitation of π_u electrons to the σ_g orbital are only 716 cm^{-1} and 6437 cm^{-1} above the $^1\Sigma^+_g$ ground state[30]. The $a^3\Pi_u$ state probably corresponds to $D^3\Pi_u$ of Si_2. For this species the lowest allowed transition $H^3\Sigma^-_u$–$X^3\Sigma^-_g$ involves the participation of the strongly antibonding π_g orbital which leads to a considerable decrease of the bond order.

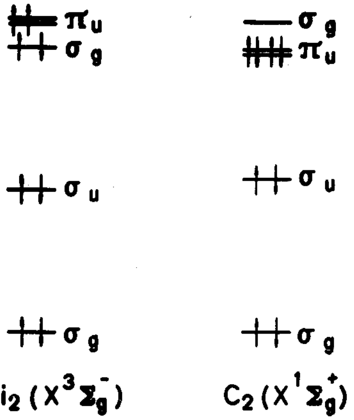


Fig. 6. MO representation of Si_2 and C_2 in their electronic ground states

E) Si-C Compounds

It would be of great interest to have some information available on monomeric SiC on account of its intermediate position between C_2 and Si_2. Unfortunately no spectra of SiC have been reported so far. It was shown by mass spectrometry that the vaporization products of silicon carbide consist mainly of silicon atoms, SiC_2 (9%), Si_2C (8%), Si_2 (0,2%) but have only traces of SiC and heavier binary molecules [31].

The molecule SiC_2 is known to occur in some N-type stars. Its absorption bands in the blue-green region were listed by McKellar [32] and identified by Kleman [33] who observed these bands in emission when heating silicon in a graphite tube. Weltner und McLeod [34] isolated vapours of heated silicon carbide in neon and argon matrices at 4 K and investigated the species Si_3, SiC_2, Si_2C and Si_2C_3 by their absorption, emission and infrared spectra. All these molecules are probably linear. It is suggested that, as with the well-known C_3 molecule, their ground states result from a $\sigma_g{}^2\sigma_u{}^2\pi_u{}^4 - {}^1\Sigma_g^+$ electron configuration.

A vibrational analysis of the asymmetric SiCC molecule afforded the following data for the $X^1\Sigma^+$ ground state and the first excited $A^1\pi$ state:

	$X^1\Sigma^+$	$A^1\Pi$
ν_1 (Si–C)	853 cm^{-1}	1015 cm^{-1}
ν_2 (∡ SiCC)	300 cm^{-1}	230 cm^{-1}
ν_3 (C–C)	1742 cm^{-1}	1461 cm^{-1}

Assuming $f_{12} = 0$, the following force constants have been calculated from these frequencies:

$$f(\mathrm{SiC}) = 7.44 \text{ mdyn/Å}$$
$$f(\mathrm{CC}) = 7.98 \text{ mdyn/Å}$$

This may be compared with $f_{CC} = 10.34$ mdyn/Å for C_3 and 3.1 mdyn/Å for a Si–C single bond.

The Si_2C species probably has a centre of symmetry. A strong absorption in both neon and argon matrices near 5300 Å which is likely to originate from $a^1\Pi_u - X^1\Sigma_g^+$ transition like that of C_3 and SiC_2 has been assigned to this molecule.

Absorption bands with at least two progressions of 393 cm^{-1} and 1997 cm^{-1} between 6500 Å and 5350 Å together with infrared spectra provide evidence of Si_2C_3. Based upon the observed stretching frequencies, an asymmetric SiSiCCC structure is suggested.

F) SiN and HNSi

The spectrum of SiN was first obtained by Jevons [35] and analysed by Mulliken [36], Jenkins and de Laszlo [37], the assignment being established by means of ^{29}Si and ^{30}Si isotope shifts. Recently the ^{15}N isotopic data have also been reported [38].

The SiN spectrum is generated by admission of traces of $SiCl_4$ into the microwave excited nitrogen afterglow. The ground state and the observed excited states are of $^2\Sigma^+$ symmetry. The electron configuration of the $X^2\Sigma^+$ ground state is $1\sigma^2 2\sigma^2 1\pi^4 3\sigma$, the first excited $B^2\Sigma^+$ state may be described as $1\sigma^2 2\sigma 1\pi^4 3\sigma^2$ (Fig. 2). Some molecular constants are collected in Table 5.

Table 5. Molecular constants of SiN[37]

State	T_0 (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	f_e (mdyn/Å)
$X\,^2\Sigma^+$	0	1.572	1151.68	6.56	7.29
$B\,^2\Sigma^+$	24236.47[38]	1.580	1031.01	16.74	5.84
$^2\Sigma^+$	50253.02[39]	1.590			

The data for the second excited $^2\Sigma^+$ state were obtained from a band system near 3840 Å attributed erroneously to SiO$^+$ 40) but which is probably due to a $^2\Sigma^+$–$B^2\Sigma^+$ transition of SiN 39).

A further unstable compound containing a multiple Si–N bond has been studied in a matrix by Ogilvie *et al.* 41). Upon photolysis of H_3SiNNN and D_3SiNNN in an argon matrix, new IR bands appear which were shown to be due to HNSi (DNSi). The force constants given in Table 6 fit best with the observed isotopic shifts. The SiN stretching force constant is of the magnitude of f_e in the SiN radical, which corresponds to a bond order of between 2 and 3.

Table 6. Vibrational parameters of SiNH/SiND and CNH/CND41b)

	HNSi obs.	DNSi obs.	DNSi calc.	HNC obs.	DNC obs.	DNC calc.
ν NH(ND) (cm^{-1})	3583	2669	2670.0	3620	2769	2746.7
ν SiN(CN) (cm^{-1})	1198	1166	1164.4	2029	1940	1949.8
ν bend (cm^{-1})	523	395	399.1	477	374	374.6
f NH(ND) (mdyn/Å)	7.732			7.831		
f SiN(CN) (mdyn/Å)	8.305			16.390		
f bend (mdyn/Å)	0.088			0.111		
r NH(ND) (Å)	(1.00)[1]			(1.00)		
r SiN(CN) (Å)	(1.54)			(1.14)		
∢ HNSi(C)	(180°)			(180°)		

[1] Assumed parameters in brackets.

G) SiO and SiO$^+$

Much work has been done on SiO, particularly in consideration of its applications in industry.

The gaseous SiO monomer is generated by reduction of SiO_2 with elementary silicon or other reducing compounds at high temperature. On rapid cooling,

Table 7. Vibrational frequencies, force constants and structural parameters of matrix-isolated $(SiO)_n$ compounds42b)

	$^{28}Si^{16}O$	$^{28}Si_2{}^{16}O_2$ (D_{2h})	Si_3O_3 (D_{3h})
ν (cm^{-1})	1223.9	804.7 (B_{2u}) 766.3 (B_{3u}) 79 42c) (B_{1u})	972.6 (E') 631.5 (E') (74 ?)
f_{SiO} (mdyn/Å)	8.985	3.55	3.73
∢ OSiO	–	87°	100°
∢ SiOSi	–	93°	140°
r_{SiO} (Å)	–	1.71	1.70

the metastable SiO condenses to a brown polymer $(SiO)_n$. The monomer and cyclic oligomers have been isolated in Ar and N_2 matrices [42]. The infrared spectra indicate four-membered Si_2O_2 and six-membered Si_3O_3 rings. From the observed IR frequencies, including ^{29}Si, ^{30}Si and ^{18}O isotopic shifts, the molecular parameters listed in Table 7 have been elucidated.

Co-condensation of SiO with organic compounds shows that SiO behaves chemically like other silylenes such as SiF_2 [43].

The electronic ground state of SiO may be described by the MO configuration $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 - {}^1\Sigma^+$. Exciting an 3σ electron to the antibonding 2π orbital results in the $a^3\Pi_r$ and $A^1\Pi$ states, whereas the configuration ... $1\pi^3 3\sigma^2 2\pi$ corresponds to ${}^{1,3}\Sigma^+$, ${}^{1,3}\Sigma$ and ${}^{1,3}\Delta$ terms. Ab initio calculations by Heil and Schaefer [44] including corrections based upon the adaption of calculated values to experimental data for CO predict the following sequence of states:

$$X^1\Sigma^+, a^3\Pi(36000\ \text{cm}^{-1}), a'^3\Sigma^+(38000\ \text{cm}^{-1}), {}^3\Delta(42000\ \text{cm}^{-1}),$$
$$e^3\Sigma^-(43500\ \text{cm}^{-1}), I^1\Sigma^-(45000\ \text{cm}^{-1}), A^1\Pi(45400\ \text{cm}^{-1}), {}^1\Delta(45700\ \text{cm}^{-1}).$$

The allowed $A^1\Pi$–$X^1\Sigma^+$ transition has been known for a long time [45]. Higher upper states (denoted as E, F, G, H) have been observed by Barrow and Rowlinson [46]. The symmetry of these states (some of which are likely to belong to the low-lying Rydberg states of SiO) has not been established. The $e^3\Sigma^-$, $I^1\Sigma^-$ and two other states of $^1\Pi$ or $^1\Delta$ symmetry have been discovered by analysing the perturbations of the rotational levels of the $A^1\Pi$ state [47]. Furthermore, some transitions have been observed from the $a^3\Pi_r$ state, the energy of which is unknown relative to the ground state: $^3\Sigma - a^3\Pi_r$ [48], $^3\Pi_i$–$a^3\Pi_r$ and $^3\Sigma^+ - a^3\Pi_r$ [49].

The molecular parameters of these states are summarized in Table 8.

Table 8. Molecular parameters of SiO[45–49]

State	T_0 (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	f_e (mdyn/Å)
$X\,^1\Sigma^+$	0	1.509732[53]	1241.4	5.92	9.242
$A\,^1\Pi$	42640.4	1.620	852.7	6.44	4.360
$^1\Pi$ or $^1\Delta$	$\leqslant 42800$	< 1.79	~ 660		
$I\,^1\Sigma^-$	$\leqslant 43300$	< 1.79	~ 680		
$^1\Pi$ or $^1\Delta$	$\leqslant 44700$				
E	52579.9		675	4.2	2.73
$F\,(^1\Sigma^+?)$	68497.2		1116.5	7.2	7.476
G	72011		831.6	5.7	4.147
H	76391		1138.3	9.3	7.770
$a\,^3\Pi_r$	a	1.562			
$^3\Sigma$	$a + 23569.7$	1.556			
$^3\Pi_i$	$a + 25616.3$	1.702	481.6	3.4	1.391
$^3\Sigma^+$	$\sim(a + 34000)$	–			
$e\,^3\Sigma^-$	$\leqslant 43068$	< 1.79	$\geqslant 684$	~ 4	

The dissociation energy $D_0[SiO(X^1\Sigma^+) \rightarrow Si(^3P) + O(^3P)]$ has been determined by thermodynamic 50), spectroscopic 46) and mass spectrometric methods 51) with a mean value of 8.1 ± 0.3 eV (187 kcal/mol).

The dipole moments of SiO in various vibrational levels of the electronic ground state have been evaluated from microwave studies of molecular beams 52):

v	μ_{SiO} [D]
0	3.0982
1	3.1178
2	3.1372
3	3.1574

The ionization of SiO leads to SiO^+ in a $^2\Sigma^+$ state. There has been some confusion about this cation because some bands attributed to it have been shown to belong to SiN 39, 40). Recently a $B^2\Sigma^+ - X^2\Sigma^+$ transition of SiO^+ has been reported (Table 9) 54).

Table 9. Molecular parameters of SiO^+ 54)

State	T_0 (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	f_e (mdyn/Å)	D_0 (eV)
$X\,^2\Sigma^+$	0	1.647	976.1	5.57	5.71	5.24
$B\,^2\Sigma^+$	30500.1	1.788	634.9	4.45	2.42	2.77

H) SiS, SiSe and SiTe

The ground and excited states of the heavier analogues of SiO have also been investigated 3). Besides the $X^1\Sigma^+$ ground states two excited states are known,

Table 10. Molecular parameters of SiS, SiSe and SiTe3)

State		T_0 (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	f_e (mdyn/Å)	D_0 (eV)
SiS	$X\,^1\Sigma^+$	0	1.929314157)	749.65	2.58	4.941	6.6
	$D\,^1\Pi$	34910.1	2.06	512.0	2.38	2.305	
	$E\,^1\Sigma^+$ 55)	41743.5	2.25	406.8	1.40	1.455	
SiSe	$X\,^1\Sigma^+$	0	2.05832658)	580.0	1.78	4.095	5.8
	$D\,^1\Pi$	32360.2		399.8	1.93	1.946	
	E	38370.3		308.8	1.95	1.160	
SiTe	$X\,^1\Sigma^+$	0		481.2	1.30	3.131	5.5
	$D\,^1\Pi$	28590.4		338.6	1.70	1.550	
	E	33871		242	(3.63)	0.792	

Table 11. Dipole moments of $M^{IV}M^{VI}$ compounds[59)]

	M^{IV}=C	Si	Ge
M^{VI}=O	-0.11[1)]	3.10	3.28
S	-1.96[1)]	1.73	2.00
Se		1.1	1.65
Te			1.06

[1)] The negative sign in CO and CS indicates a negative charge on the carbon atom.

the first of which has π symmetry ($D^1\Pi$) and corresponds to the $A^1\Pi$ state of CO and SiO, whereas the second, denoted as E, proved to have $^1\Sigma^+$ symmetry only for SiS [55)] (Table 10). From perturbations of the D–X system of SiS the $e^3\Sigma^-$, $I^1\Sigma^-$ and a further state ($^1\Pi$ or $^1\Delta$) have been derived [56)]. A comparison of the electronic states of the SiM^{VI} molecules with corresponding states of isoelectronic molecules is given in Fig. 7. The values in brackets indicate the $\omega_e/\omega_e(X)$ rates. There is no state of CO corresponding to the $E^1\Sigma^+$ state of SiS and the other molecules, probably due to the configuration $1\sigma^2 2\sigma^2 1\pi^3 3\sigma^2 2\pi$.

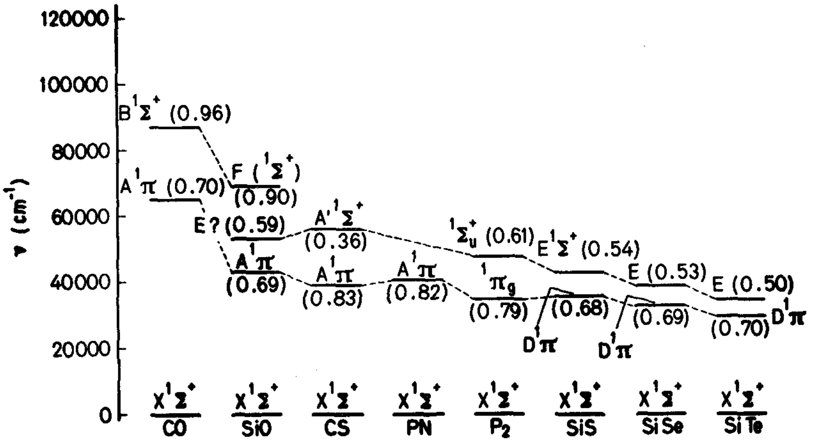


Fig. 7. Low-lying corresponding electronic states of SiO, SiS, SiSe, SiTe and other isoelectronic molecules. The values in parentheses indicate the rate $\omega_e/\omega_e(X)$

The SiM^{VI} molecules have also been investigated by microwave studies which reveal exact distances [53, 57, 58)] and dipole moments [59)] (Table 11).

I) SiF

The spectrum of SiF has been observed in a high-frequency discharge in flowing gaseous SiF_4 [60)] and in a discharge from a hollow cathode consisting of a mixture of Si and $BaSiF_6$ [61)].

A MO treatment of SiF 62) predicts the sequence $1\sigma 2\sigma 1\pi 3\sigma 2\pi$, the 1σ orbital having $2s$(F) character. The upper orbitals 3σ and 2π are mainly localized at the silicon atom. The ground state of SiF is therefore . . . $1\pi^4 3\sigma^2 2\pi - X^2\Pi_r$; molecular constants of the ground and excited states are summarized in Table 12 5, 60, 61, 63).

Table 12. Molecular parameters of SiF5) 60) 61) 63)

State	T_0 (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	f_e (mdyn/Å)
$X\,^2\Pi_r$	0	1.601	857.2	4.7	4.900
$A\,^2\Sigma^+$	22787.5	1.605	718.6	10.2	3.443
$B\,^2\Sigma^+$	34638.3	1.541	1011.2	4.8	6.818
$C\,^2\Delta$	39537.5	1.571	892.4	7.0	5.310
$C'\,^2\Pi$	42052.0	1.529	1031.8	4.5	7.100
$D\,^2\Sigma^+$	47491.4	1.54	1003.2	5.6	6.711
$D'\,^2\Pi$	46700.1	1.534	1032.9	5.3	7.114
G	52020		1020		
$H\,^2\Sigma^+$	52179		1030		
$a\,^4\Sigma^-$	29808.4	r_0 = 1.605			

The observed states may be divided into two groups:

a) non-Rydberg states with $\omega_e < 1000$ cm^{-1} and
b) Rydberg states with $\omega_e \geqslant 1000$ cm^{-1}.

The $B^2\Sigma^+$, $D^2\Sigma^+$ and $H^2\Sigma^+$ states seem to belong to the same Rydberg series, involving the excitation of the 2π electron to the $4s$, $5s$ and $6s$ orbitals of Si.

The properties of the first excited $A\,^2\Sigma^+$ state are in accordance with the configuration $1\pi^4 3\sigma^2 4\sigma$, the 4σ orbital having strongly antibonding character. The states $^2\Sigma^+$, $^2\Sigma^-$, $C^2\Delta$ and $a^4\Sigma^-$ result from the configuration $1\pi^4 3\sigma 2\pi^2$. The very small changes in bond distance are in agreement with the prediction of nonbonding or slightly antibonding 3σ and 2π orbitals. The C' and D' states, which have been analysed from C'–A and D'–A transitions 63), are probably due to $1\pi^4 3\sigma^2 \pi$ configurations. Comparison with the heavier homologues GeF, SnF and PbF 63) shows that the properties of the first excited states are quite similar (Table 13).

Table 13. General properties of the $M^{IV}F$ molecules (M^{IV} = Si, Ge, Sn, Pb)63)

State	T_e (eV)	$\omega_e/\omega_e(X)$
$C\,^2\Delta$1)	5.18 ± 0.56	1.03 ± 0.01
$B\,^2\Sigma^+$	4.32 ± 0.19	1.18 ± 0.02
$A\,^2\Sigma^+$	2.69 ± 0.20	0.73 ± 0.11
$X\,^2\Pi_r$	0	1.00

1) Except PbF.

The dissociation energy D_0 has been derived by Johns and Barrow 61) from a linear Birge-Sponer extrapolation as 125 ± 10 kcal/mol, whereas Hastie and Margrave 64) report the value $D^0_{298} = 5.9 \pm 0.1$ eV (136 ± 2 kcal/Mol).

K) SiCl, SiBr and SiI

The spectra of the heavier diatomic silicon halides are usually generated by rf discharge in SiX_4 vapour diluted with nitrogen or a rare gas. The electronic

Table 14. $X\ ^2\Pi$ Ground-state properties of Si-halogen radicals

	A_e (cm^{-1})1)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	r_e (Å)	f_e (mdyn/Å)	D_e (eV)
SiF	161.9	857.2	4.7	1.601	4.90	5.9 64)
SiCl 6)	207.2	535.6	2.2	2.058	2.63	(4.0) 3)
SiBr 66b)	418	424.2	1.5	2.26 2)	2.20	(3.7) 3)
SiI 67c)	(~700)	363.8	1.3	(2.45)	1.79	3.0

1) A is the $\Pi_{3/2}-\Pi_{1/2}$ splitting parameter.

2) r_0 from Ref. 66c).

Table 15. General properties of low-lying electronic states of Si-halogen radicals 65–67)

State	T_e (eV)	$\omega_e/\omega_e(X)$
$C\ ^2\Pi$ 1)	5.15 ± 0.10	1.23 ± 0.03
$B\ ^2\Sigma^+$	4.15 ± 0.15	1.26 ± 0.08
$A\ ^2\Sigma^+$	2.65 ± 0.20	0.70 ± 0.15
$X\ ^2\Pi_r$	0	1.00

1) Except SiI.

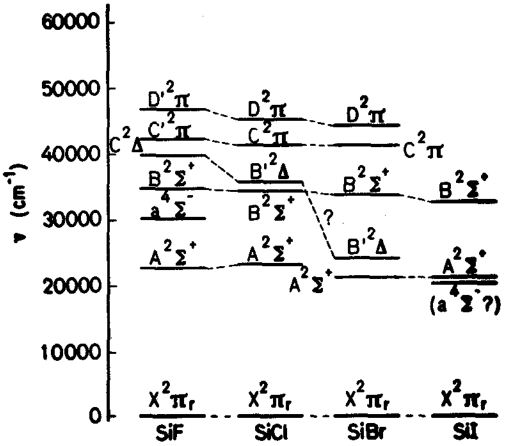


Fig. 8. Corresponding electronic states of SiHal molecules

states of the SiCl [6,65], SiBr [66] and SiI [67] radicals show similar behaviour and are closely related to SiF and the halides of other group IVa elements. Some ground-state properties are collected in Table 14. As can be seen from Fig. 8 and Table 15, the excited states arising from equivalent configurations exhibit nearly identical bonding properties.

L) SiAu

SiAu is the only known diatomic silicon–metal compound[68]. Its emission spectrum in the infrared region is observed upon heating a mixture of silicon and gold to 2500 °C. The band system derives from $^2\Sigma - {}^2\Pi_{3/2}$ and $^2\Sigma - {}^2\Pi_{1/2}$ transitions. The constants are given in Table 16. The electron configuration of the $^2\Pi$ ground state may be described as $s\sigma^2 p\sigma^2 p\pi$, the transition corresponding to the excitation of a $p\sigma$ electron to the $p\pi$ orbital.

Table 16. Molecular parameters of SiAu[68]

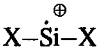
State	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	r_0 (Å)	f_e (mdyn/Å)
$X\ ^2\Pi$	0	390.9	1.35	3.40	2.22
$A\ ^2\Sigma$	13632.4	389.5	2.2	3.45	2.21

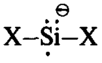
III. Divalent Silicon

Divalent silicon may be present in different types of compounds (A–D). Of these the ions SiX_2^+ (C) and SiX_2^- (D) have been detected in mass spectrometry.

X–Si–X
(A)

X=Si=X
(B)


$X-\overset{\oplus}{\dot{S}i}-X$
(C)


$X-\overset{\ominus}{\dot{\underset{\cdot}{S}}i}-X$
(D)

Of (A – D), only (B) should exhibit a linear structure. It has in fact been confirmed that a molecular beam of SiO_2 generated at 2500 K is not deflected by an electrostatic quadrupole. Consequently SiO_2 must be linear [69].

Silylenes which are homologues of carbenes belong to group (A). The present article will only deal with their molecular properties; their most important chemical properties are discussed in a different review of this volume [70] and treated in the following leading references: SiH_2 [71], $Si(CH_3)_2$ [72], SiF_2 [73], $SiCl_2$ [74], and silylenes as ligands [75]. The silylenes SiH_2, SiF_2, $SiCl_2$, $SiBr_2$, HSiCl, HSiBr and HSiI have so far been studied, and their molecular properties are now discussed in this order.

A) General Considerations

According to the number of valence electrons, Walsh's rules predict bent structures for SiH_2 (6), SiH(Halogen) (12) and $Si(Halogen)_2$ (18 electrons) silylenes.

This prediction is also valid for analogous carbenes, though CH_2 in the X^3B_1 ground state was assumed to be linear until recent investigations[76)] confirmed a ground state bond angle of ca. 140°.

Dependent on the bond angle and the composition, silylenes belong to the following point groups:

	X Si X	H Si X
Linear	$D_{\infty h}$	$C_{\infty v}$
Bent	C_{2v}	C_s

Fig. 9 presents the general qualitative energy levels and molecular orbital notations for SiH_2 ($D_{\infty h}$), SiH_2 (C_{2v}), SiX_2 (C_{2v}) and HSiX (C_s). The notation of Fig. 9 is used throughout. Contributions of X lone pairs have been neglected.

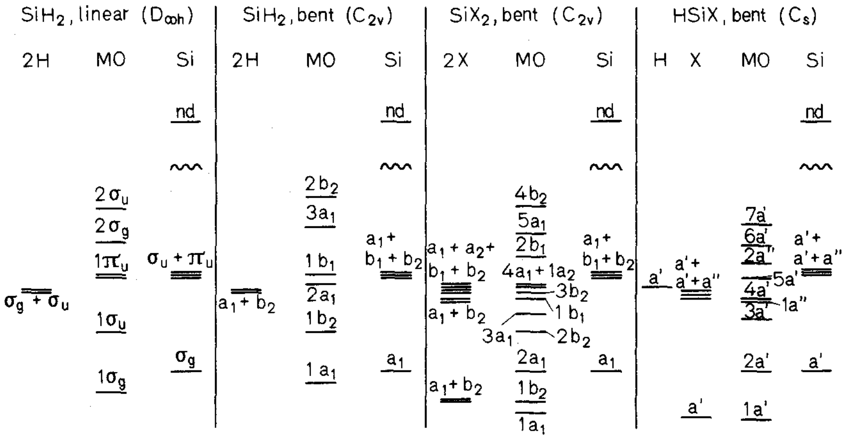


Fig. 9. Qualitative energy levels for linear and bent silylenes

B) :SiH_2

A triplet ground state (analogous to CH_2)

$^3B_1 \ldots (1b_2)^2(3a_1)^1(1b_1)^1$

or singlet state

$^1A_1 \ldots (1b_2)^2(3a_1)^2$

must be considered for SiH_2, but the search for $^3B_1$ or a different excited triplet state has been so far without success. Thus one has to give credence to theoretical calculations which predict a $^1A_1$ ground state and an excited $^3B_1$

Table 17. Molecular parameters of SiH$_2$, SiHD and SiD$_2$. Experimental values according to Ref.[7,76], calculated values from Ref.[20]

State		T_0 (cm^{-1})	∢HSiH(D) (°)	r_0 SiH (Å)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	f_{SiH} (mdyn/Å)	f_{HSiH} (mdyn · Å/rad^2)
$^1A_1$		0	92.08	1.5163		1004			
	SiH$_2$	0	–	–	(2032)	1008	2022	2.34[2]	0.67
	SiHD	0	–	–	–	879	–		
	SiD$_2$	0	–	–	(1412)	729	1468		
	(calc)[1]	0 (B)	93.6						0.56
		0 (C)	95.4						0.60
$^3B_1$	(calc)	17350 (B)	180						0.08
		16180 (C)	137.8						0.15
$^1B_1$		15533	123	1.487	SiH$_2$	860			0.46
					SiHD	740			
					SiD$_2$	610			0.48
	(calc)	21270 (B)	180						0.11
		20460 (C)	146.2						0.11
$^1A_1^{(2)}$	(calc)	29330 (B)	153.9						0.30
		25700 (C)	125.7						0.37

[1] (B): Calculated for cases with totally shielded *d* electrons; (C): partially shielded *d* electrons.

[2] $0 < f_{SiH,\,SiH'} < 0.014$.

triplet state with an excitation energy T_0 of 16180 cm^{-1} [20]. As SiH_2 is usually formed in one of its excited singlet states from which an allowed transition leads to the $^1A_1$ ground state, detection of a triplet state is expected to be difficult.

The available data concern the observation of the $^1A_1 \rightarrow {}^1B_1$ transition of SiH_2 and SiD_2, generated from $C_6H_5SiH_3$ and $C_6H_5SiD_3$ by flash photolysis[10,76], and secondly the infrared spectra of photolysed SiH_4/SiD_4 in an Ar matrix at 4 K providing the vibrational spectra of SiH_2, SiHD and SiD_2 in the electronic ground state[7].

The experimental $^1A_1 \leftrightarrow {}^1B_1$ excitation energy[76] (Table 17) is in line with the calculated value[20]. All molecular parameters available at present of SiH_2, SiHD and SiD_2 and SiD_2 in different electronic states are listed in Table 17.

Experiments prove a greatly widened HSiH angle for the excited $^1B_1$ state. The electronic transition consequently exhibits a pronounced progression with ν_2', the bending frequency of the upper state. The separation of the different ν levels of ν'_2 shows a minimum for ν=5. This suggest for the upper state a potential hump of 3500 cm^{-1} above the 000 level.

C) :SiF_2

SiF_2 is the most thoroughly investigated silylene. It is easily obtained from SiF_4 and Si at 1200 °C. In the gas phase at room temperature it decomposes to 50% within 150 sec, yielding polymeric $(SiF_2)_n$ via the paramagnetic diradical $F_2\dot{Si}\dot{Si}F_2$[73c,77]. The physical properties which are now discussed were obtained from investigations of the electronic and vibrational ground states (IR, MW) and from the analysis of electronic transitions.

These investigations prove a singlet ground state for SiF_2 $X^1A_1 \ldots (3b_2)^2(1a_2)^2(4a_1)^2$, notation of Fig. 9.

Three excited states have been characterized:

$^3B_1 \ldots (3b_2)^2(1a_2)^2(4a_1)(2b_1)$
$^1B_1 \ldots (3b_2)^2(1a_2)^2(4a_1)(2b_1)$ and
$^1B_2 \ldots (3b_2)^2(1a_2)(4a_1)^2(2b_1)$

The molecular parameters of these states are collected in Table 18.

Initially, ground-state geometry and vibrational frequencies were reported erroneously [78]. However, electronic, microwave, gas-phase infrared and matrix infrared spectra reported more recently turned out to be consistent with the ground-state parameters listed in Table 18. ν_1 and ν_3 at ~850 cm^{-1} are perturbed by their close proximity and overlap, but the assignment has been supported by the observation of ^{29}Si and ^{30}Si isotopic shifts. ν_2 has been observed directly [80] and been obtained from the microwave spectrum for the ν=0 and ν=1 levels of ν_2''. Furthermore the electronic transitions $^1A_1 \rightarrow {}^1B_1$ and $^3B_1 \rightarrow {}^1A_1$ exhibit a moderately pronounced progression with $\nu_2'' = 343$ cm^{-1} [81–83].

Table 18. Molecular parameters of SiF_2

State	T_0 (cm^{-1})	∢FSiF (°)	r_0 SiF (Å)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Method	Ref.
$^1A_1$	0			842.8		852.9	Ar matrix	79)
				851.01		864.6		
						861.58	Ne matrix	79)
				855		872	IR, gas phase	8)
				843	343	855	Ar matrix	80)
		100°59′	1.591				MW	11)
		$\mu = 1.23 \pm 0.015$ D						
$^3B_1$	26310				277		$^3B_1 \rightarrow {}^1A_1$	81)
$^1B_1$	44113.9[1])	115°53′	1.601		251		$^1A_1 \rightarrow {}^1B_1$	82)
	44109				~252		$^1A_1 \rightarrow {}^1B_1$	83)
$^1B_2$	62278			~790	~320		$^1A_1 \rightarrow {}^1B_2$, ν_2' and $\nu_2'' = 0$	86)
	62281						$^1B_2 \rightarrow {}^1B_1$	86)

[1]) Extrapolated.

Quadratic and cubic potential constants have been obtained from IR frequencies, isotopic shifts, inertial defects, Coriolis constants and centrifugal distortion, assuming the geometry from microwave data. The quadratic force field is characterized by four symmetry force constants F which are related to the inner force constants by the following equations

$$
\begin{aligned}
F_{11} &= f_r + f_{rr}\\
F_{12} &= \sqrt{2}\, f_{r\alpha}\\
F_{22} &= f_\alpha\\
F_{33} &= f_r - f_{rr}
\end{aligned}
$$

Attempts to determine the force field solely from centrifugal distortion, Coriolis coupling constants and the inertial defect, using no frequency data, were unsuccessful [84]. Consistent force constants are, however, obtained on combining frequency data either with centrifugal distortion constants (case A) or the Coriolis coupling constant $\zeta_{23}(c)$ obtained from the inertial defect $\Delta_{010} - \Delta_{000}$ (case B, Table 19) [8].

Table 19. Force field of SiF_2 [8]

Experimental data	ν_1 855,	ν_2 345,	ν_3 872 (cm^{-1})
	(A) τ_{aaaa}	−1.9807 (MHz)	(B) $\Delta_{010}-\Delta_{000} = 0.3784$
	τ_{bbbb}	−0.0715 (MHz)	(amu · Å^2)
	τ_{aabb}	−0.2613 (MHz)	$[\zeta_{23}^{(c)}]^2 = 0.8164$ [84]
	τ_{abab}	−0.0359 (MHz)	
f_r (mdyn/Å)		5.02	5.01
f_{rr} (mdyn/Å)		0.31	0.30
f_α (mdyn · Å/rad^2)		1.11	1.11
$f_{r\alpha}$ (mdyn/rad)		0.20	0.18
K_{222} −9.5 cm^{-1} from	α_2	−452.23 (MHz) [8]	
	β_2	15.75 (MHz)	
K_{122} 9.9 cm^{-1}	γ_2	22.11 (MHz)	

The excitation energies of the three electronic transitions so far observed differ markedly.

$$
\begin{aligned}
&{}^1A_1 \rightarrow {}^3B_1 \;\; 3801\ \text{Å}\ (26310\ \text{cm}^{-1})\\
&{}^1A_1 \rightarrow {}^1B_1 \;\; 2266\ \text{Å}\ (44110\ \text{cm}^{-1})\\
&{}^1A_1 \rightarrow {}^1B_2 \;\; 1606\ \text{Å}\ (62280\ \text{cm}^{-1})
\end{aligned}
$$

The lowest transition ${}^3B_1 \rightarrow {}^1A_1$ has been observed with low intensity in the near UV in emission of a high-frequency electrodeless discharge of flowing SiF_4 [81]. The spectrum exhibits extended vibrational structure which is recognized to be a progression involving the bending frequencies $\nu_2'' = 343$ cm^{-1} and

$\nu_2' = 277$ cm^{-1} of the lower and upper state. Though the $^1B_1$ and $^3B_1$ states become unexpectedly widely separated, the low intensity (~1/10 of the $^1B_1 \rightarrow {^1A_1}$ transition) and the expected energy level sequence suggest an assignment of the observed transition to $^3B_1 \rightarrow {^1A_1}$.

The transition $^1A_1 \leftrightarrow {^1B_1}$ was first observed in emission and analysed by Johns *et al.* [85] in terms of a vibrational progression involving ν_1'' (937 cm^{-1}) and ν_2'' (427 cm^{-1}). Extension of the spectrum was accompanied by a further erroneous interpretation [78] which was corrected upon observation of the electronic absorption in the gas phase [83] and in a Ne matrix [80].

Making use of the ground-state bending frequency ($\nu_2'' \sim 343$ cm^{-1}) from microwave data, the gas-phase absorption spectrum was analysed in a straightforward manner in terms of a large progression involving ν_2' (252 cm^{-1}; ν=0 to 12) and a weak progression of ν_2'' (ν=0 to 3). This implied in particular a considerable change of the FSiF angle upon electronic excitation [83]. This suggestion and the ν_2' frequency were confirmed by the matrix investigations [80].

More detailed structural information of the $^1B_1$ state was obtained from the rotational analysis of the $^1A_1 \rightarrow {^1B_1}$ transition [82]. The vibrational levels $\nu_1'\nu_2'\nu_3' = 010$, 020, 030 and 040 are separated by ca. 250 cm^{-1}. Their rotational analysis provides the geometry listed in Table 18. The widening of the FSiF angle by 15° is, besides the slightly increased distance, the most prominent structural feature of the $^1B_1$ state.

The $^1A_1 \leftrightarrow {^1B_2}$ transition located in the vacuum UV has been observed in absorption and emission as well[86]. Two similar band systems separated by ~790 cm^{-1} appear in absorption. Each band system shows a splitting with ~26 cm^{-1} which is assigned to the difference $\nu_2''-\nu_2'$, suggesting $\nu_2' = 320$ cm^{-1}. The 790 cm^{-1} splitting may belong to a beginning progression involving ν_1'. The emission spectrum, however, exhibits a progression with ~850 cm^{-1} which is ν_1'', the symmetric stretching frequency of the ground state.

D) :$SiCl_2$:$SiBr_2$ and :SiI_2

The existence of the heavier dihalosilylenes $SiCl_2$, $SiBr_2$ and SiI_2 has been confirmed by the investigation of equilibria in which they are involved[87]; their thermodynamic functions and bonding energies have been tabulated[72c,87].

Direct information on ground-state $SiCl_2$ is available form infrared spectra of matrix-isolated species prepared by vacuum UV photolysis of SiH_2Cl_2 and SiD_2Cl_2[88] or from Si and $SiCl_4$ at ~ 1000 °C[9].

Like SiH_2 and SiF_2, $SiCl_2$ has a $^1A_1$ ground state and according to the emission spectrum[89] two upper states near 29000 cm^{-1}; one of them at 29952 cm^{-1} is obviously $^1B_1$. In 1938 the emission spectrum was interpreted assuming the following vibrational frequencies:

ν_1'' 540 cm^{-1}	ν_1' 445.3 cm^{-1}
ν_2'' 248.2 cm^{-1}	ν_2' 201.1 cm^{-1}

This assignment revealed ν_1' to be strongly anharmonic ($\omega_1'x_1' \sim 20\ \mathrm{cm}^{-1}$) and major inconsistencies for $v = 1 \rightarrow 0$ of ν_1'' and ν_1'.

Bearing in mind the recent matrix IR assignment of $\nu_2'' = 202.2\ \mathrm{cm}^{-1}$, the vibrational structure of the electronic transition observed by Asundi *et al.*[89)] should be re-analysed; a better resolved emission spectrum is also desirable.

Table 20. Molecular parameters of $SiCl_2$ and $SiBr_2$

State	T_0 (cm^{-1})	∢XSiX (°)		ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Method	Ref.
$X\ ^1A_1$	0	(90)	($^{28}Si^{35}Cl_2$)	512.7		502.0	IR, Ar matrix	88)
$[...(1b_1)^2(3b_2)^2(4a_1)^2]$		(105 + 3)	($^{28}Si^{35}Cl_2$)	512.5	202.2	501.4	IR, Ar matrix, site one	9)
				(540.0)	(248.2)		$^1B_1 \rightarrow {}^1A_1$	89)
	28295[a)]							89)
$A\ ^1B_1$ $[...(1b_1)^2(1b_2)^2(4a_1)(2b_1)]$	29952			(445.3)	(201.1)		$^1B_1 \rightarrow {}^1A_1$	89)
$SiBr_2$	0	(109 ± 3)	($^{28}SiBr_2$)	402.6	120[1)]	399.5	IR, Ar matrix	9)

[1)] Estimated.

The vibrational analysis of ground-state $SiCl_2$ affords the frequencies listed in Table 20. Both Milligan and Jacox[88] and Maass, Hauge and Margrave[9] report consistent values, though the latter investigation, which included measurements of $^{35/37}Cl$ and $^{28/29/30}Si$ isotope shifts, gives more details. Further splitting is caused by different sites in the matrix, and the observed frequencies appear to depend on the matrix material itself. Table 21 presents matrix splittings for $^{28}Si^{35}Cl_2$ and isotope splittings for site 1 in an Ar matrix obtained in Ref.[9]. The force field of $SiCl_2$ is quite well determined by the observed isotope shifts; this is also true for the ClSiCl angle. The final force constants are listed in Table 22 and compared with those of SiF_2 from Table 19 and of $SiBr_2$.

Table 21. IR spectra of $SiCl_2$ (cm^{-1})[9] [88]

		ν_1	ν_3
$^{28}Si^{35}Cl_2$	Ar, site 1	512.5	501.4
	site 2	510.0	496.8
	site 3	503.6	486.4
	Ne, site 1	518.7	509.4
	site 2	514.0	505.7
	N_2, site 1	509.9	496.3
	site 2	507.4	491.6
Ar, site 1	$^{28}Si^{35}Cl_2$	512.5	501.4
	$^{28}Si^{35}Cl^{37}Cl$	510.0	497.9
	$^{28}Si^{37}Cl_2$	505.4	496.1
	$^{30}Si^{35}Cl_2$	–	491.0

Table 22. Unscaled ground-state force constants of silicon dihalides

	SiF_2[8]	$SiCl_2$[9] 1)	$SiBr_2$[9] 2, 3)
f_r (mdyn/Å)	5.02	2.39	1.95
f_{rr} (mdyn/Å)	0.31	0.38	0.38
f_α (mdyn · Å/rad^2)	1.11	0.96	0.77
$f_{r\alpha}$ (mdyn/rad)	0.20	0.13	0.02

1) From Ar matrix frequencies, site 1, r SiCl 2.01 Å, ∢ClSiCl 105°.
2) From Ar matrix frequencies, ν_2 = 120 cm^{-1} (assumed).
3) Assumed: r SiBr 2.15 Å, ∢BrSiBr 109°.

No electronic transition of $SiBr_2$ has yet been detected. The Matrix IR spectrum[9] provides precise values for ν_1'' and ν_3'' including ^{29}Si and ^{30}Si isotope shifts; however, ^{79}Br and ^{81}Br features could not be resolved. Compared with those of $SiCl_2$, the force constants and the bond angle of $SiBr_2$ are less well determined by the experimental data.

E) HSiCl, HSiBr and HSiI

Upon flash photolysis of H_3SiCl (D_3SiCl), H_3SiBr and H_3SiI (D_3SiI), systems of absorption bands appear near 20000 cm^{-1}; these are caused by HSiCl (DSiCl), HSiBr and HSiI (DSiI). Simultaneously, emission spectra with similar structure

Table 23. Molecular parameters of HSiCl, HSiBr and HSiI[90, 91]

Species	State	T_0 (cm^{-1})	∢HSiX (°)	r_0 SiH (Å)	r_0 SiX (Å)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})
$HSi^{35}Cl$ $[...(4a')^2(1a'')^2(5a')^2]$	$^1A'$	0	102.8	1.561	2.064		807.56	522.35
	$^1A''$	20717.61	116.1	1.499	2.047	1250 (1756)	567.7	532.6
$[...(4a')^2(1a'')^2(5a')(2a'')]$								
$DSi^{35}Cl$	$^1A''$						411	
$HSi^{79}Br$	$^1A'$	0	102.9	1.561[1]	2.231	1547.8	773.6	408.0
	$^1A''$	19903.05	116.6	1.499[1]	2.208	1270.4 (1784.5)	539.7	412.2
HSiI	$^1A'$	0	102.7	1.561[1]	2.451		727	$\nu_3''-\nu_3' = 14.1$
	$^1A''$	18259.01	116.2	1.499[1]	2.432	1360	485	–
DSiI	$^1A''$						356	

[1] Transferred from HSiCl.

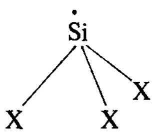
appear at lower energy (6000–4800 Å)[90,91]. The absorption bands exhibit a long progression involving the bending frequency of the upper state ν_2', while the emission spectrum shows a progression with ν_2''. According to $A \gg B$ and $B \cong C$, the rotational structure exhibits a coarse K ($\perp$) structure with narrow J subbands. The surprising observation of subband systems from $\Delta K = 0$ and 2 along with the $\Delta K = 1$ system suggested two different explanations. Firstly a singlet-triplet transition ($^3A'' \leftrightarrow {}^1A'$) has been taken into account, but axis switching caused by the large widening of the HSiX angle upon excitation and allowing $\Delta K = \pm 2$ rotational transitions was favoured by Herzberg and Verma[90]. A thorough analysis of the axis switching effect[92] confirmed the latter alternative. Thus the electronic transition near 20000 cm^{-1} is throughout assigned to $^1A' \leftrightarrow {}^1A''$.

The vibrational analysis of the electronic transitions affords the vibrational frequencies listed in Table 23; force constants have not yet been calculated. The SiH (SiD) stretching frequencies ν_1' are quite uncertain, and the alternative frequencies near 1750 cm^{-1} appear to be more probable by evidence of the SiH shortening upon electronic excitation and by comparison with SiH_2 ($^1A_1$, r_0 1.516$_3$ Å, ν_{SiH} 2030 cm^{-1}). Of course, r_0(SiH) has been determined only for HSiCl/DSiCl, but has been transferred to HSiBr and HSiI.

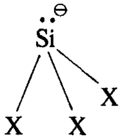
To sum up, all silylenes exhibit a singlet ground state with small bond angles at the Si atom. They may be excited throughout to a (singlet) upper state with a considerably widened angle. Evidence for triplet states is still scarce, though a $^3B_1$ state has been reported for SiF_2.

IV. Trivalent Silicon

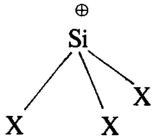
Trivalent silicon has so far been established in species without charge (A) and negative charge (B); cations have not been detected despite great effort directed towards their preparation or even detection as intermediates.



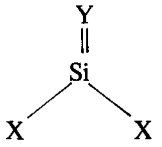
(A)



(B)



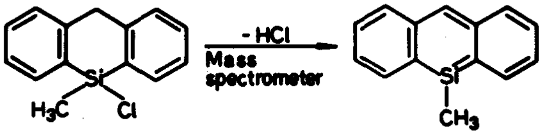
(C)



(D)

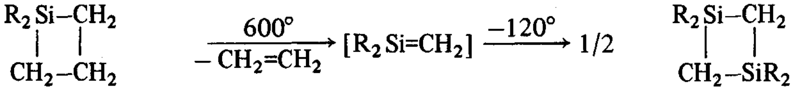
$(CH_3)_3SiOSi(CH_3)_3$ in H_2SO_4, for instance, forms $(CH_3)_3SiOSO_3^-$ [93], while treatment of $(CH_3)_3SiF$ with SbF_5 in SO_2FCl at low temperature yields the five-coordinate complex $(CH_3)_3SiF \cdot SbF_5$, protolytic cleavage being observed above −50 °C [94]. In contrast, carbonium ions are well established under similar conditions.

Type (D) structures with sp^2 hybridized silicon corresponding to CH_2O or $COCl_2$ have not yet been isolated, but are supported by spectroscopic investigations. In the mass spectrum of 9-siladehydroanthracene (I) peaks appear at $m/e = 208$ and $m/2e = 104$; these are attributed to structure II [95].



(I) (II)

Evidence for $R_2Si = CH_2$ (IV) is obtained from the IR spectrum of the pyrolysis products of 1-silacyclobutane (III) at 77 K. An IR absorption at 1407 cm^{-1} which disappears irreversibly at 153 K (formation of V) is attributed to the $Si = CH_2$ group [96].



$$\begin{array}{c} R_2Si{-}CH_2 \\ |\quad\ | \\ CH_2{-}CH_2 \end{array} \xrightarrow[-\,CH_2{=}CH_2]{600^\circ} [R_2Si{=}CH_2] \xrightarrow{-120^\circ} 1/2 \begin{array}{c} R_2Si{-}CH_2 \\ |\quad\ | \\ CH_2{-}SiR_2 \end{array}$$

(III) (IV) (V)

A) General Considerations

Of the type (A) and type (B) species now being discussed, only the anions (B) are stable at room temperature and can be prepared by normal chemical reactions. Structural evidence however is still scarce.

Type (A) species are radicals with one unpaired electron throughout. They may be prepared either by metathesis reactions or by dissociation upon irradiation. Obviously, esr is the most common method for the investigation of silyl radicals. SiH_3, SiF_3 and $SiCl_3$ have been studied by IR matrix technique, too.

The access to silyl radicals is different from that to similar carbon compounds. Hydrogen abstraction is energetically unfavourable, while the pyrolysis which organosilicon compounds undergo differs from that of hydrocarbons due to the inability of silicon to form $p\pi p\pi$ bonds. Pyrolysis of organosilicon compounds proceeds usually via non-chain sequences from which the rate of initial bond rupture into silyl radicals may be obtained [97].

Silyl radicals may react with organic substrates, for example, according to the following sequence [98].

$$^tBuOO^tBu \xrightarrow{h\nu} 2\ ^tBuO\cdot$$

$$^tBuO\cdot + Et_3SiH \rightarrow {}^tBuOH + Et_3Si\cdot$$

$$Et_3Si\cdot + RBr \rightarrow R\cdot + Et_3SiBr$$

$$Et_3Si\cdot + R_2'CO \rightarrow R_2'\dot{C}OSiEt_3$$

All structural information discussed now favours pyramidal silyl radicals. The XSiX angle appears to be nearly tetrahedral or larger, evidence being obtained from esr hyperfine splitting. Table 24 presents the symmetry and selection rules for vibrational spectra for silyl radicals of different composition and different geometry.

Table 24. Symmetry and selection rules for silyl radicals

	Point group	Planar			Point group	Bent		
SiX_3	D_{3h}	A_2' (Ra p, IR –)	ν_1	ν_s SiX_3	C_{3v}	A_1 (Ra p, IR a)	ν_1	ν_s SiX_3
		A_2'' (Ra –, IR a)	ν_2	γ SiX_3		A_1	ν_2	δ_s SiX_3
		E' (Ra dp, IR a)	$\nu_{3,4}$	ν_e SiX_3		E (Ra dp, IR a)	$\nu_{3,4}$	ν_e SiX_3
		E'	$\nu_{5,6}$	δ_e SiX_3		E	$\nu_{5,6}$	δ_e SiX_3
SiX_2Y	C_{2v}	A_1 (Ra p, IR a)	ν_1[1]	ν_s SiX_2	C_s	A' (Ra p, IR a)	ν_1	ν_s SiX_2
		A_1	ν_3	ν SiY		A'	ν_3	ν SiY
		A_1	ν_5	δ_s SiX_2		A'	ν_5	δ SiX_2
		B_1 (Ra dp, IR a)	ν_2	γ SiX_2Y		A'	ν_2	δ $YSiX_2$ (γ)
		B_2 (Ra dp, IR a)	ν_4	ν_{as} SiX_2		A'' (Ra dp, IR a)	ν_4	ν_{as} SiX_2
		B_2	ν_6	δ XSiY		A''	ν_6	δ $YSiX_2$ (ρ)

[1]) The notation correlates SiX_3 with SiX_2Y vibrations.

B) $\cdot SiH_3$

Vacuum UV photolysis of SiH_4 in an Ar matrix at 4 or 14 K yields the reactive species SiH, SiH_2 and SiH_3. The analysis of the matrix IR spectra is complicated by the presence of several species along with the starting material SiH_4, and substitution by deuterium is of only modest value.

The appearance of two bending modes in the infrared gives support to the pyramidal structure deduced from esr. Several alternative assignments are discussed by Milligan and Jacox [7] who point out that Fermi resonance of $2\nu_2$ and ν_1 or $\nu_{3,4}$ is favoured.

	obs. (cm^{-1})	calc. (cm^{-1})	Scaled force constants (mdyn/Å)	
ν_1	1999	1985	f_{SiH}	2.212
ν_2	996	996	$f_{SiH/SiH'}$	0.052
$\nu_{3,4}$	1955	1955	f_{HSiH}	0.348
$\nu_{5,6}$	926	925	$f_{HSiH/HSiH'}$	0.160

The SiH_3 radical has been studied in solution [99,100] and in a Kr [101] and Xe matrix [102] by esr technique. While the solution of SiH_3 was prepared by UV irradiation of ${}^tBuOO{}^tBu$ in SiH_4 (method A), the matrix-trapped SiH_3 radicals were obtained from 2% SiH_4 in Kr and Xe at 4.2 K by means of a ${}^{60}Co$ γ-ray source. The observed g factors and isotopic nuclear coupling constants are listed in Table 25. The Xe matrix smeared the proton hyperfine structure out, and the isotopic ${}^{29}Si$ nuclear coupling differs from that observed for the Kr matrix.

The value of the isotopic ${}^{29}Si$ coupling is diagnostic for the s character of the unpaired electron and hence dependent on hybridization and interbond angles. Assuming $a\ {}^{29}Si = 1206$ G for a pure s electron, one obtains for the bonding orbitals an s character of 0.26 from $a^{29}Si = 266$ G; this corresponds to an HSiH bond angle of 110.6° [101]. The angle for SiH_3 in Xe is similarly calculated to be 113.5° [102].

C) Alkylsilyl Radicals

Organosilyl radicals may also be studied by esr technique. The results obtained are listed in Table 25.

Substitution of one H by CH_3 hardly changes $a^{29}Si$. The introduction of $(CH_3)_3Si$ groups, however, causes a considerable decrease of $a^{29}Si$ and increase of a CH_3. Both effects are commonly interpreted as indicating an angle widening, suggesting even a planar structure for $\cdot Si[Si(CH_3)_3]_3$ [105]. One should keep in mind that $a^{29}Si$ of $\cdot Si(CH_3)_3$ drops from 172.5 to 129 G on replacing a $Si(CH_3)_4$ matrix ($\mu = 0$ D) by $(CH_3)_3SiCl$ ($\mu = 1.87$ D) [106].

Table 25. ESR spectra of $\cdot SiH_3$ and $\cdot SiR_3$ radicals

Radical	Temp. (K)	Conditions	g Factor	Isotropic hyperfine splitting (G)	Ref.
$\cdot SiH_3$	4.2	2% in Kr	$g_{\parallel}$ 2.003 $g_{\perp}$ 2.007	$a^{29}Si$ 266, ^{a}SiH 8.1 ± 0.5	101)
	4.2	2% in Xe	g_{as} 2.003 ± 0.001	$a^{29}Si$ 190	102)
	~203	neat + $^{t}Bu00^{t}Bu$ (A)	2.0032	^{a}SiH 7.84	99)
	120	30 Vol% in ethane		^{a}SiH 7.96	100)
$\cdot SiH_2CH_3$	152	(A)		^{a}SiH 11.82, $^{a}CH_3$ 7.98	100)
	~203	(A)	2.0031	^{a}SiH 12.11, $^{a}CH_3$ 8.21	99)
	77	solid	2.0032 ± 0.0005	$a^{29}Si$ 181, ^{a}SiH 11.8, $^{a}CH_3$ 8.0	103)
$\cdot SiH(CH_3)_2$	150	(A)		$a^{29}Si$ 183.05, ^{a}SiH 16.99, $^{a}CH_3$ 7.19	100)
	~203	(A)	2.0031	^{a}SiH 17.29, $^{a}CH_3$ 7.30	99)
$\cdot SiH(CH_3)Si(CH_3)_3$	~203	(A)	2.0037	^{a}SiH 16.30, $^{a}CH_3$ 8.15, $^{a}Si(CH_3)_3$ 0.30	99)
$\cdot Si(CH_3)_3$	77	$Si(CH_3)_4$ matrix		$a^{29}Si$ 172.5, $^{a}CH_3$ 6.32	106)
	77	$ClSi(CH_3)_3$ matrix		$a^{29}Si$ 129, $^{a}CH_3$ 6.2	106)
	153	(A)		$a^{29}Si$ 181.14, $^{a}CH_3$ 6.28	100)
	~203	(A)	2.0031	$a^{29}Si$ 183, $^{a}CH_3$ 6.34	99)
	77	solid	g_{av} 2.0029 ± 0.0005 $g_{\parallel}$ 2.0019, $g_{\perp}$ 2.0034	$a^{29}Si$ 181, $^{a}CH_3$ 6.3 $a_{\parallel}{}^{29}Si$ 233 ± 3, $^{a}{\perp}{}^{29}Si$ 155 ± 3	103)
$\cdot Si(C_2H_5)_3$	183	(A)		$^{a}CH_2$ 5.69, $^{a}CH_3$ 0.16	100)
	~203	(A)	2.0030	$^{a}CH_2$ 5.73	99)
$\cdot Si(C_6H_5)_3$	298	single crystal	2.0036	$a^{29}Si$ 79.6	104)
$\cdot Si(CH_3)_2Si(CH_3)_3$	~203	(A)	2.0036	$a^{29}Si$ 137, $^{a}CH_3$ 8.21, $^{a}Si(CH_3)_3$ 0.47	99)
$\cdot Si(CH_3)_2CH_2Si(CH_3)_3$	~203	(A)	2.0030	$^{a}CH_2$ 5.56, $^{a}Si(CH_3)_2$ 6.43	99)
$\cdot Si[Si(CH_3)_3]_3$	~203	(A)	2.0050	$^{a}CH_3$ 0.44, $a^{29}Si$ 65	99, 105)
$\cdot Si(CH_3)[Si(CH_3)_3]_2$	~203	(A)	2.0045	$a^{29}Si$ 71, $^{a}SiCH_3$ 9.36, $^{a}Si(CH_3)_3$ 0.47	105)

D) ·SiF_3 and ·SiF_nH_{3-n}

·SiF_3 has been studied both by IR spectroscopy 12) and esr 107). Vacuum UV photolysis of $HSiF_3$ at 14 K in Ar, N_2 or CO matrices yields predominantly SiF_3 radicals, the vibrational frequencies of which are reproduced by Table 26. Additionally ^{29}Si and ^{30}Si satellites have been observed of ν_1 in a N_2, of ν_3 in an Ar matrix, respectively. From the splitting, the FSiF angle is calculated to be 110±2°. The scaled force constants are listed in Table 26.

Table 26. Observed and calculated vibrational frequencies of ·SiF_3 (cm^{-1}). Force field assuming an angle of 71° between the SiF bonds and the threefold axis (≙ ∢FSiF 110°)12)

	Observed			Calculated		
	^{28}Si	^{29}Si	^{30}Si	^{28}Si	^{29}Si	^{30}Si
$\nu_{5,6}$	290			290	289.4	288.8
ν_2	406			406	403.0	400.2
$2\nu_2$	807			(812)		
ν_1	832	828.5	825	832	828.4	825.1
$\nu_{3,4}$	954	946	939	954	945.7	937.9
f_{SiF}		5.49 (mdyn/Å)				
$f_{SiF/SiF'}$		0.30 (mdyn/Å)				
f_{FSiF}		0.45 (mdyn/Å)				
$f_{FSiF/FSiF'}$		0.17 (mdyn/Å)				

The SiF_3 radicals obtained from radiolysis of $HSiF_3$ in SF_6 at 77 K have been investigated by esr; the results are presented in Table 27. The large value of the isotropic ^{29}Si hyperfine splitting indicates a strongly pyramidal structure, probably due to the polarity of the SiF bond.

Mono and difluorosilyl radicals exhibit similar properties with gradually changing parameters (Table 27). *a* H decreases rapidly from ·$SiHF_2$ (89.9 G) to ·SiH_3 (8 G), while the *g* factor hardly varies. All data so far obtained are consistent with pyramidal structures for mono and difluorosilyl radicals.

Table 27. ESR spectra of fluorosilyl radicals107)

Radical	Temp. (K)	Conditions	*g* Factor	Isotropic hyperfine splitting (G)
·$^{28}SiF_3$	96	3–4% in SF_6	2.00028	^aF (+)136.64
·$^{29}SiF_3$	96	matrix, natural abundance	2.00033	^aF (+)136.64, ^{a29}Si −498.03
·$SiHF_2$	96	3–4% in SF_6 matrix	2.0013	^aF 77.8, ^aH 89.9
·SiH_2F	96	3–4% in SF_6 matrix	2.0024	^aF 55.2, ^aH 34.6
·$Si(CH_3)_2F$	127	20% in $^tBuOO^tBu$ + cyclopropane	2.0022	^aF 65.2, $^aCH_3$ 4.53

E) $\cdot SiCl_3$ and $\cdot SiCl_n(CH_3)_{3-n}$

The $\cdot SiCl_3$ radical has been studied in Ar and N_2 matrices at 14 K by IR spectroscopy [13)] and in matrices of $SiCl_4$ at 180 K and CH_3SiCl_3 at 190 K by esr [106)].

At 14 K the IR matrix spectrum of vacuum UV photolysed $HSiCl_3$ exhibits above 225 cm^{-1} two band systems at ~470 and ~580 cm^{-1} showing extensive isotopic splitting which are attributed to the SiCl stretching modes ν_1 and $\nu_{3,4}$ of the $SiCl_3$ radical. The presence of 4.68% ^{29}Si, 3.05% ^{30}Si and 24.5% ^{37}Cl along with ^{28}Si and ^{35}Cl is responsible for the total of 12 different $SiCl_3$ molecules, the abundance of which is given in Table 28.

Table 28. Observed and calculated frequencies (cm^{-1}) for $\cdot SiCl_3$ species in Ar matrices. Stretching force constants assuming an angle of 72 (± 5)° between the SiCl bond and the threefold axis[13)]

Abundance of species (%)	$^{35}Cl_3$	$^{35}Cl_2{}^{37}Cl$	$^{35}Cl^{37}Cl_2$	$^{37}Cl_3$
^{28}Si	39.4	38.6	12.6	1.38
^{29}Si	2.00	1.96	0.64	0.07
^{30}Si	1.31	1.28	0.42	0.05
Symmetry	C_{3v}	C_s	C_s	C_{3v}

	obs.	calc.	Species
ν_1	470.2	470.2	$^{28}Si^{35}Cl_3$
	....	467.3	$^{29}Si^{35}Cl_3$
	467.8	466.9	$^{28}Si^{35}Cl_2{}^{37}Cl$
	....	464.6	$^{30}Si^{35}Cl_3$
	464.8	463.8	$^{28}Si^{35}Cl^{37}Cl_2$
	462.0	460.7	$^{28}Si^{37}Cl_3$
$\nu_{3,4}$	582.0	582.0	$^{28}Si^{35}Cl_3$
ν_4		582.0	$^{28}Si^{35}Cl_2{}^{37}Cl$
ν_3		580.1	$^{28}Si^{35}Cl^{37}Cl_2$
ν_3	578.5	578.2	$^{28}Si^{35}Cl_2{}^{37}Cl$
$\nu_{3,4}$	577.0	576.1	$^{28}Si^{37}Cl_3$
ν_4		576.1	$^{28}Si^{35}Cl^{37}Cl_2$
$\nu_{3,4}$		575.1	$^{29}Si^{35}Cl_3$
$\nu_{3,4}$	570.0	568.6	$^{30}Si^{35}Cl_3$

f_{SiCl}	2.63	(mdyn/Å)
$f_{SiCl/SiCl'}$	0.26	(mdyn/Å)
f_{ClSiCl}	0.25	(mdyn/Å)
$f_{ClSiCl/ClSiCl'}$	0.016	(mdyn/Å)

Assuming pyramidal structure, 6 of them belong to point group C_{3v} and the others to C_s. The isotopic pattern observed accounts for both the stoichiometry and a ClSiCl angle of 111±5°. The observed and calculated vibrational frequencies are listed in Table 28. The two bending modes ν_2 and $\nu_{5,6}$ have not been observed owing to instrumental cut-off at 225 cm^{-1}. Consequently, bending and stretching force constants are not very certain.

Esr spectra of $SiCl_3$ have been obtained upon γ irradiation of $SiCl_4$ and of CH_3SiCl_3. Though γ irradiation of methyl chlorosilanes causes predominantly the rupture of CH bonds, silyl radicals from SiC and SiCl cleavage could be detected unequivocally. $\cdot SiCl_3$, $\cdot SiCl_2(CH_3)$, $\cdot SiCl(CH_3)_2$ and $\cdot Si(CH_3)_3$ reveal strong matrix effects which depend on the dipole moment of the matrix molecule. The esr parameters are tabulated in Table 29. Consistent g factors of 2.0035±0.0010 have been measured.

Table 29. ESR spectra of chlorosilyl radicals[106)]

Radical	Temp. (K)	Matrix	μ of Matrix (D)	Isotropic hyperfine splitting (G)
$\cdot SiCl_3$	180	$SiCl_4$	0	$a^{29}Si$ 440, $a^{35}Cl$ 13.4
	190	CH_3SiCl_3	1.87	$a^{29}Si$ 416, $a^{35}Cl$ 12.4
$\cdot SiCl_2CH_3$	190	CH_3SiCl_3	1.87	$a^{29}Si$ 308, $a^{35}Cl$ 11.4
	185	$(CH_3)_2SiCl_2$	2.28	$a^{29}Si$ 295, $a^{35}Cl$ 10.5
$\cdot SiCl(CH_3)_2$	185	$(CH_3)_2SiCl_2$	2.28	$a^{29}Si$ 215, $a CH_3$ 5.2
	185	$(CH_3)_3SiCl$	2.09	$a^{29}Si$ 229[1)], $a CH_3$ 5.2

[1)] Ref.[103)] gives $a^{29}Si$ 290 ± 3 G, g 2.003 ± 0.001.

The large value of $a^{29}Si$ is likely to indicate nearly sp^3 hybridized Si in $SiCl_3$. Furthermore, it calls in question the suggestion of non-planar structures for $\cdot SiH_3$ and $\cdot Si(CH_3)_3$ [106)].

F) Silyl Anions

Few structural data are available on type (B) silyl anions. The SiH_3^- anion may be prepared from SiH_4 and the alkali metals in the solvents $CH_3OCH_2CH_2OCH_3$ or $OP[N(CH_3)_2]_3$. While the vibrational spectrum of SiH_3^- has not yet been obtained, the ^1H nmr in $CH_3OCH_2CH_2OCH_3$ solutions has been reported [108)].

τ ^1H 9.12 ppm [$(CH_3)_4Si = 10$]

J $^1H^{29}Si$ 77 Hz

An x-ray powder investigation [109)] of $KSiH_3$, $RbSiH_3$ and $CsSiH_3$ confirmed that all salts are isomorphous, crystallizing fcc in the NaCl lattice. The lattice parameters are as follows

$KSiH_3$	a	7.23 Å
$RbSiH_3$	a	7.52 Å
$CsSiH_3$	a	7.86 Å

Using Pauling ionic radii for the cations, the effective radius of the SiH_3^- is calculated to be 2.26±0.04 Å. By means of broad-line ^1H nmr 109) it was established that the SiH_3 groups rotate round the threefold axis above −75 °C; rotation of the C_3 axis does not occur. The intra-molecular distance $d_{H..H}$ was estimated from the second moment of the rigid SiH_3 groups at −100 °C to be 2.17±0.05 Å. Assuming $d_{SiH} = 1.48$ Å, an HSiH angle of 94±4° is calculated, which is consistent with the predominantly *p* character of the bonding electrons of the Si atom.

Under certain conditions $HSiCl_3$ and tertiary amines form saltlike compounds of the composition $R_3NH^+SiCl_3^-$. The chemistry of the $SiCl_3^-$ anion, which is isoelectronic with PCl_3, has been studied extensively 110); however, no structural data for $SiCl_3^-$ have been reported.

V. Silicides

While the properties of monomeric species have been reported in the preceding chapters, some structural aspects of silicides will now be discussed. In the context of low-valent silicon, the discussion is restricted to ionic silicides $M_p^{m+}Si_n^{m-}$ in which Si_n^{m-} may be regarded as a separate species. The influence of the cations M_p^{m+} should, however, not be neglected. In general the SiSi bond length of silicides is larger than in silicon (2.35 Å), due to localization of negative charge on the Si_n^{m-} anion. According to the formal charge of the Si atoms, silicides exhibit structures similar to those of isoelectronic elements. Thus the coordination number towards Si atoms drops from four in the lattice of the $Si^{\pm 0}$ element to zero in the case of isolated Si^{4-} anions (*e. g.* Mg_2Si).
Silicides of the composition M^ISi have structural properties like those of P and As (*e. g.* cordination number 3). While NaSi 111), KSi, RbSi, CsSi 112) and $BaSi_2$ 113) are composed of Si_4^{4-} tetrahedra analogous to P_4, $CaSi_2$ exhibits puckered hexagonal layers corresponding to the lattice of $(As)_\infty$. $SrSi_2$, however, forms a three-dimensional network with three-coordinated Si which is not analogous to any group-V structure 113).

The SiSi distance in the regular tetrahedra has been determined to be 2.43 – 2.46 Å, while 2.41 Å and SiSiSi bond angles of 104.8° and 113.0° have been reported for $CaSi_2$ and $SrSi_2$, respectively. A slightly shorter SiSi distance of 2.36 Å has been observed in $Ca_{0.5}Sr_{0.5}Si_2$, forming hexagonal layers, too 114). The F_2 mode of the tetrahedra active in the IR has been observed in alkali silicides at 345±15 cm^{-1}, from which an SiSi stretching force constant of 1.0±0.1 mdyn/Å has been deduced 115).

Silicides of the compositon M_2^ISi with formally two negative charges on the Si atom may show similarities to group-VI elements. CaSi, SrSi and BaSi form Si^{2-} chains 116) with bond lengthening to 2.47 Å (CaSi) and 2.52 Å (SrSi, BaSi) due to increased charge density. Bond shortening caused by decreasing charge has been reported for Si_n chains in ternary Ca-Li-Si phases 117). Unexpectedly short distances of 2.29 and 2.34 Å have been obtained in Ba_3Si_4, where distorted Si_4^{6-} tetrahedra contain both divalent and trivalent Si atoms 118).

Furthermore Si_2^{4-} analogous to O_2 has been detected in Li_2Si[119] and ternary $ThCr_2Si_2$ type silicides such as $SrAg_2Si_2$[120]. The relatively short SiSi distances of 2.37 and 2.33 Å may indicate some degree of covalent MSi bonding or even π contributions in the SiSi bond.

Halogenlike units Si_2^{6-} have been shown to exist along with isolated Si^{4-} ions for Li_7Si_2[121] and $M_5^{II}Si_3$ (M^{II} = Ca, Sr, Ba)[122]. The SiSi distance of 2.38 Å in Li_7Si_2 again argues to some extent against the formation of a free Si_2^{6-} ion.

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VI. References

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Organometallic Synthesis of Carbosilanes

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A. Introduction

It is not the purpose of this article to give a complete summary of all investigations carried out on the synthesis of the Si-C bond, but simply to review the synthesis of compounds having a molecular framework of alternating silicon and carbon linkages (carbosilanes) and formed mainly by the pyrolysis of $Si(me_3)_4$ and the methylchlorosilanes. The primary purpose of this synthetic work was to investigate this new class of compounds in order to determine their structures and chemical properties. Although considerable progress has been made in the controlled synthesis of carbosilanes, by far the greatest number have as yet been prepared only by pyrolytic methods¹⁾.

1. Historical Development of the Synthesis of Si-C Bonds

The historical development of the chemistry of organosilicon compounds is closely related to organometallic chemistry. In Bansen's laboratory about the middle of the nineteenth century, Frankland was investigating the reactions of C_2H_5I with Zn to withdraw the iodine from the C_2H_5I and form free C_2H_5 radicals. The product formed was diethyl zinc. It was soon discovered that an ethyl group could be transferred to other elements from this compound if the reaction were favored by the formation of a salt.

The discovery of the first organosilicon compound dates back to Friedel and Crafts$^{2-4)}$:

$$2\,Zn(C_2H_5)_2 + SiCl_4 = 2\,ZnCl_2 + Si(C_2H_5)_4 \qquad (1)$$

In about 1885 Polis used a reaction similar to the Wurtz reaction for the synthesis of the Si-C bond:

$$SiCl_4 + 4\,RCl + 8\,Na = SiR_4 + 8\,NaCl \qquad (2)$$

The close relationship between organosilicon chemistry and organometallic chemistry is confirmed by a reaction formulated by Ladenburg in 1874:

$$Hg(C_6H_5)_2 + SiCl_4 = C_6H_5SiCl_3 + C_6H_5HgCl$$

The discovery of the Grignard reagents initiated a new period in the chemistry of organosilicon compounds. The outstanding contribution of Kipping and Bygden was to have carried out systematic investigations on the synthesis and properties of organosilicon compounds:

$$2\,C_2H_5MgCl + SiCl_4 = (C_2H_5)_2SiCl_2 + 2\,MgCl_2 \qquad (3)$$

This reaction made numerous silicon compounds available and even today is still of great importance. Kipping expected to find an analogy between silicon and carbon compounds, but his later papers reveal his disappointment in the lack of versatility and limited reactivity of silicon compounds. Kipping was rather pessimistic about the further development of organosilicon chemistry, being so much influenced by ideas of carbon chemistry that he underestimated the importance of the formation of the siloxanes from the silicon halides, as now evidenced in the industrial applications of organosilicon compounds.

The development of organo-alkali-compounds, especially organolithium compounds, led to attempts to form Si-C bonds:

$$RMe + X{-}Si\leqslant \; = R{-}Si\leqslant + MeX \qquad (4)$$

The reactions of silicon halides with organomagnesium or organolithium compounds for the synthesis of organosilicon compounds are oversimplified in Eqs. (3) and (4). If several reactive groups are attached to the silicon atom, as in $C_2H_5SiCl_3$, the reaction cannot be controlled so as to yield a particular substitution product, since all possible substitutions will occur simultaneously. All that can be done is to favor the yield of the desired compound by manipulation of reaction conditions.

The reaction shown in Eq. (4) (X=halogen, OR; Me=MgCl, Li, Na) was used to synthesize linear fully methylated carbosilanes (me = CH_3). By the reaction

$$me_3Si{-}CH_2Me + Cl{-}Sime_2{-}CH_2Cl \longrightarrow me_3Si{-}CH_2{-}Sime_2{-}CH_2Cl + MeCl$$

it was possible to obtain the following compounds (5):

$$me_3Si{-}CH_2{-}Sime_3$$
$$me_3Si{-}CH_2{-}Sime_2{-}CH_2{-}Sime_3$$
$$me_3Si{-}CH_2{-}Sime_2{-}CH_2{-}Sime_2{-}CH_2{-}Sime_3$$

Side reactions are virtually excluded as the number of functional groups is limited. The reaction is applicable only to the preparation of unbranched chains.

The reaction of $SiHCl_3$ with $me_3Si{-}CH_2MgBr$ leads already to the formation of $me_3Si{-}CH_2{-}SiHCl_2$, $[me_3Si{-}CH_2]_2$ SiHCl and $[me_3Si{-}CH_2]_3SiH$[6].

A controlled synthesis of cyclic carbosilanes and complicated linear compounds requires molecules with reactive groups at both the Si and C atoms which can be used to synthesize carbosilanes with several Si atoms carrying functional groups in particular positions[1]. Difficulties also occurred during the synthesis of the corresponding silicon compounds, such as the need to avoid side reactions of the functional groups while carrying out the condensation to form the Si–C–Si linkages. Example: the treatment of equimolar amounts of

me_3SiCH_2Li with
$Cl_2Sime(CH_2Cl)$

should lead to the formation of the compound

$$me_3Si{-}CH_2{-}SiClme(CH_2Cl)$$

(functional groups at the Si and C atoms), however, quite a large amount of $[me_3SiCH_2]_2$ Sime(CH_2Cl) forms as a by-product[7].

2. The Si-phenyl Group as a Protective Group

These difficulties in the synthesis of Si-functional carbosilanes were resolved by applying the Si-phenyl group as a protective group once the mechanism of the cleavage of the Si-phenyl group by hydrogen halides was known[8]. The reaction proceeds as follows:

$$\geqslant Si{-}C_6H_5 + HBr \longrightarrow \geqslant SiBr + C_6H_5$$
$$\geqslant Si{-}C_6H_5 + Br_2 \longrightarrow \geqslant SiBr + C_6H_5Br$$

As indicated by the example in Table 1, the reaction takes place at –78 °C without any bromination of the Si–H group and is strongly influenced by the groups attached to the same Si atom. Increasing the number of electronegative substituents at the Si atom inhibits the cleavage of the Si-phenyl group. Thus, no cleavage follows the action of HBr on $(C_6H_5)SiCl_3$ at –78 °C.

Table 1. Reactions of Phenylsilanes with HBr at –78 °C

	Remarks	Relative electro-negativity
1. $C_6H_5Sime_3 + HBr = C_6H_6 + (CH_3)_3SiBr$	Vigorous reaction	5.0
2. $(C_6H_5)_2SiH_2 + HBr = C_6H_6 + C_6H_5SiH_2Br$	Vigorous reaction	5.9
3. $C_6H_5SiH_3 + HBr = C_6H_6 + SiH_3Br$	Quantitatively in 2 h	6.3
4. $C_6H_5SiH_2I + HBr = C_6H_6$ + Si halides	Quantitatively in 7 d	6.7
5. $C_6H_5SiH_2Br + HBr = C_6H_6 + SiH_2Br_2$	63% yield in 6 d	7.0
6. $C_6H_5SiH_2Cl + HBr = C_6H_6$ + Si halides	20% yield in 3 d	7.2
7. $(C_6H_5)_2SiCl_2 + HBr$ = no reaction	After 7 d	7.7
8. $C_6H_5SiCl_3 + HBr$ = no reaction	After 7 d	9.0

This use of the different reactivity of the $Si{-}C_6H_5$ groups in $(C_6H_5)_2SiH_2$ and $C_6H_5SiH_2Br$ allows preparation of either $C_6H_5SiH_2Br$ or SiH_2Br_2. These examples suggested it was possible to attach a Si-functional group at a certain Si atom in a carbosilane chain with several Si-phenyl groups by cleavage of a Si-phenyl group with respect to the substituents. It is thus possible to insert a Si-functional group at the most favorable stage in the reaction sequence.

Compounds such as C_6H_5 meSi–CH_2Li (me = CH_3) and $(C_6H_5)_2$meSi–CH_2Li are of decisive importance for the synthesis of Si-functional carbosilanes. However, $C_6H_5me_2SiCH_2Cl$ does not react with lithium metal to form the desired compound.

3. Preparation of $me_2C_6H_5Si–CH_2Li$

For the preparation of $me_2C_6H_5Si–CH_2Li$, which is important for further synthesis, use of compound $me_2C_6H_5SiCH_2MgCl$ was tried in accordance with Eq. (5).

$$2\ me_2C_6H_5SiCH_2MgCl + HgCl_2 = [me_2C_6H_5SiCH_2]_2Hg + 2\ MgCl \qquad (5)$$

This gives the mercury compound which then forms the lithium compound by reaction with lithium metal[7]:

$$[me_2C_6H_5SiCH_2]_2Hg + 2\ Li = 2\ me_2C_6H_5SiCH_2Li + Hg. \qquad (6)$$

Diethylether was used as the solvent. An excess of lithium was employed and the reaction mixture was stirred under nitrogen. After 40 h, 50%, and after 110 h, 86% of the starting compound had reacted. An orange-red solution of $me_2C_6H_5SiCH_2Li$ was obtained. This tedions method is no longer used, since it was found that, unlike $C_6H_5meSiCH_2Cl$, the compound $C_6H_5me_2SiCH_2Br$ reacts easily with lithium to form $C_6H_5me_2CH_2Li$ in 90% yield[9]. The bromine compound can readily be obtained by the reaction of $C_6H_5me_2SiCH_2MgCl$ with bromine. The application of the Si–C_6H_5 group was a protective group and the more convenient preparation of the lithium compound $C_6H_5me_2CH_2Li$ are two decisive steps facilitating further synthesis.

4. Metal-halogen Exchange Reactions of $C_6H_5meSi–CH_2Li$

$C_6H_5me_2Si–CH_2Li$ reacts at –10 °C with $Clme_2SiCH_2Br$ to form several compounds which are listed in Table 2.

Table 2. Reaction Products of $(C_6H_5)me_2Si–CH_2Li$ with $Clme_2Si–CH_2Br$ (me = CH_3)

$C_6H_5me_2Si–CH_2Li$	+	$Clme_2Si–CH_2Br$	
2		*3*	
$C_6H_5(me_2Si–CH_2)_2Br$		$C_6H_5me_2Si–CH_2Br$	*1*
4		$Cl(me_2Si–CH_2)_2Br$	*5*
		$C_6H_5(me_2Si–CH_2)_3Br$	*6*

The starting material *2* did not contain any $C_6H_5me_2Si{-}CH_2Br$ *1*. Compound *4* was the expected product. After completing the reaction of *2* with *3*, compounds *1*, *5* and *6* (*6* at 10–15% yield) were found besides *4*, and in the residue 20% of compounds with $Si{-}CH_2{-}CH_2{-}Si$ linkages.

The amount of *1* can be increased by carrying out the reaction at a lower temperature; on cooling to −78 °C compounds *1*, *4* and *5* are obtained in the ratio 2 : 2 : 1, whereas *6* is no longer observed. With cooling, fast stirring, and slow addition of the reagent the yields of *1* are even higher.

The formation of this compound involves the following reaction:

$$C_6H_5me_2Si{-}CH_2Li + Clme_2Si{-}CH_2Br \longrightarrow C_6H_5(me_2Si{-}CH_2)_2Br + LiCl \quad (7)$$

and a lithium— halogen exchange

$$C_6H_5me_2Si{-}CH_2Li + Clme_2Si{-}CH_2Br \longrightarrow C_6H_5me_2Si{-}CH_2Br + \underset{7}{Clme_2Si{-}CH_2Li}. \quad (8)$$

Then compound *7* gives

$$Clme_2Si{-}CH_2Li + Clme_2Si{-}CH_2Br \longrightarrow Cl(me_2Si{-}CH_2)_2Br + LiCl; \quad (9)$$

$(me_2Si{-}CH_2)_3$ which might be formed from *7* by elimination of LiCl, was not obtained. At −10 °C reaction of *5* gives

$$C_6H_5me_2Si{-}CH_2Li + Cl(me_2Si{-}CH_2)_2Br \longrightarrow C_6H_5(me_2Si{-}CH_2)_3Br + LiCl \quad (10)$$

The formation of compound *6* is not observed in the reaction at −78 °C.

No metal-halogen exchange occurs between $C_6H_5me_2Si{-}CH_2Li$ and $Cl(me_2Si{-}CH_2)_2Br$ *5*, so it is not applicable for the formation of higher Li compounds and their use for syntheses (Eq. (11)).

$$\underset{2}{C_6H_5me_2Si{-}CH_2Li} + \underset{5}{Cl(me_2Si{-}CH_2)_2Br} \longrightarrow C_6H_5me_2Si{-}CH_2Br + Cl(me_2Si{-}CH_2)_2Li \quad (11)$$

Compounds *2* and *5* follow exclusively the reaction route in Eq. (6). Compounds *4* and *6*, which were formed by metal-halogen exchange following the scheme in Table 2, were isolated and their structures determined by pmr and mass spectrometry. $C_6H_5me_2Si{-}CH_2Br$ *1*, which was recovered in the reaction along with compound *5*, could be identified in the mixture by pmr and mass spectrometry. Further proof was that compound *5* in that mixture reacted with a stoichiometric amount of $C_6H_5me_2Si{-}CH_2Li$ to yield $C_6H_5(me_2Si{-}CH_2)_3Br$ (9).

B. Cyclic Carbosilanes

I. Monocyclic Compounds

The synthesis of linear compounds with SiBr and CH_2Br groups, respectively, attached to the beginning and end of the chain and the succeeding cyclization forms a general route to monocyclic carbosilanes.

1. The Linear Compounds $C_6H_5(me_2Si{-}CH_2)_nBr$ and $Br(me_2Si{-}CH_2)_nBr$

The next step was the synthesis of carbosilanes of the general formula $Br(me_2Si{-}CH_2)_nBr$. To obtain these chains, carbosilanes like $C_6H_5(me_2Si{-}CH_2)_nBr$ containing the SiC_6H_5-protective group were required. One route to these compounds[9] is:

$$C_6H_5(me_2Si{-}CH_2)_{n-x}Li + Br(me_2Si{-}CH_2)_xBr \longrightarrow C_6H_5(me_2Si{-}CH_2)_nBr + LiBr \qquad (13)$$

The ether solution of the lithium compound was dropped into the bromosilane (cooled by an ice/NaCl cooling mixture) after an excess of Li resulting from the preparation of the Li compound had been removed. The reaction occurs instantaneously.

It is desirable to use starting miaterials with short Si–C chains, to avoid loss of substances by side reactions (Wurtz's reaction). The reactions are shown below:

$$C_6H_5me_2Si{-}CH_2Li + Cl(me_2Si{-}CH_2)_2Br \longrightarrow C_6H_5(me_2Si{-}CH_2)_3Br + LiCl \qquad (14)$$

$$C_6H_5me_2Si{-}CH_2Li + Br(me_2Si{-}CH_2)_2Br \longrightarrow C_6H_5(me_2Si{-}CH_2)_3Br + LiBr \qquad (15)$$

$$C_6H_5(me_2Si{-}CH_2)_2Li + Br(me_2Si{-}CH_2)_2Br \longrightarrow C_6H_5(me_2Si{-}CH_2)_4Br + LiBr \qquad (16)$$

$$C_6H_5(me_2Si{-}CH_2)_2Li + Br(me_2Si{-}CH_2)_3Br \longrightarrow C_6H_5(me_2Si{-}CH_2)_5Br + LiBr \qquad (17)$$

$$C_6H_5(me_2Si{-}CH_2)_3Li + Br(me_2Si{-}CH_2)_3Br \longrightarrow C_6H_5(me_2Si{-}CH_2)_6Br + LiBr \qquad (18)$$

Yields range from 60–80%. None of these reactions gives any evidence of the metal-halogen exchange which was observed in the synthesis of the compound *4* listed in Table 2.

Carbosilanes with Si- and C-functional groups that can be used for cyclization are obtained by the reaction of phenyl compounds with bromine:

$$C_6H_5(me_2Si{-}CH_2)_nBr + Br_2 \longrightarrow Br(me_2Si{-}CH_2)_nBr + C_6H_5Br. \qquad (19)$$

These compounds can be purified by vacuum distillation. They form oils, rather than crystalline compounds, and easily undergo hydrolysis, depending on content of SiBr groups. A slight decomposition is observed by distilling longer chains ($n = 4, 5, 6$).

Table 3 lists reactions for the synthesis of C_6H_5 $(me_2Si{-}CH_2)_nBr$ ($n = 3 - 6$); Table 4 lists reactions for the synthesis of $Br(me_2Si{-}CH_2)_nBr$ ($n = 2 - 6$)9).

Table 3. Reactions for the Synthesis of $C_6H_5(me_2Si{-}CH_2)_nBr$; $n = 3 - 6$

Starting materials (moles)1)	Products	Yield	b.p. °C/Torr
$C_6H_5me_2SiCH_2Li$(30 g = 0.13 Mol) +$Cl(me_2SiCH_2)_2Br$(24.5 g = 0.095 Mol)	$C_6H_5(me_2SiCH_2)_3Br$	26.2 g – 74.4%	$119/10^{-2}$
$C_6H_5me_2SiCH_2Li$(48.1 g = 0.21 Mol) +$Br(me_2SiCH_2)_2Br$(58.6 g = 0.193 Mol)	$C_6H_5(me_2SiCH_2)_3Br$	62.5 g – 86.7%	$119/10^{-2}$
$C_6H_5(me_2SiCH_2)_2Li$(11.8 g = 0.0392 Mol) +$Br(me_2SiCH_2)_2Br$(8.8 g = 0.029 Mol)	$C_6H_5(me_2SiCH_2)_4Br$	10 g – 77.5%	$131/10^{-1}$
$C_6H_5(me_2SiCH_2)_2Li$(11.8 g = 0.0392 Mol) +$Br(me_2SiCH_2)_3Br$(11.4 g = 0.0304 Mol)	$C_6H_5(me_2SiCH_2)_5Br$	12.9 g – 82.2%	$154/10^{-1}$
$C_6H_5(me_2SiCH_2)_3Li$(26.3 g = 0.0705 Mol) +$Br(me_2SiCH_2)_3Br$(25.0 g = 0.0665 Mol)	$C_6H_5(me_2SiCH_2)_6Br$	–	2)

1) Data on Li compounds refer to the bromine compounds used for preparation of Li compounds.
2) The raw material was cleaved with Br_2 without determining the yield.

Table 4

Starting material	Product	Yield	b.p. °C/Torr
$C_6H_5(me_2SiCH_2)_2Br$ (11.8 g = 39.2 m Mol)	$Br(me_2SiCH_2)_2Br$	8.8 g – 73.9%	$48/10^{-2}$
$C_6H_5(me_2SiCH_2)_3Br$ (22.3 g = 59.8 m Mol)	$Br(me_2SiCH_2)_3Br$	17.2 g – 76.5%	$68–72/10^{-2}$
$C_6H_5(me_2SiCH_2)_4Br$ (9.4 g = 21.1 m Mol)	$Br(me_2SiCH_2)_4Br$	6.8 g – 71.8%	$110/10^{-2}$
$C_6H_5(me_2SiCH_2)_5Br$ (12.3 g = 23.8 m Mol)	$Br(me_2SiCH_2)_5Br$	10.6 g – 85.6%	$135/10^{-2}$
$C_6H_5(me_2SiCH_2)_6Br$	$Br(me_2SiCH_2)_6Br$	21.1 g – 53.6%1)	$151/10^{-2}$

1) The yield refers to the amount of $C_6H_5(me_2Si–CH_2)_3Br$ applied.

The pure phenyl compounds (without solvent) are cleaved by elemental bromine to obtain the bromine compounds (addition of Br_2 in 5–10% excess with ice-cooling). The end of the reaction is indicated when bromine is no longer decolored. The mixture is stirred at room temperature for 12 h; an excess of Br_2 is evaporated and the mixture distilled under vacuum. The by-product C_2H_5Br is separated first.

2. Cyclizations of $(me_2Si–CH_2)_n$

The starting compounds $Br(me_2Si–CH_2)_nBr$ ($n = 3, 4, 5, 6$) were dissolved in ether and after the Li suspension was added, reaction occurred to yield the cyclic carbosilanes9):

$$Br(me_2Si–CH_2)_nBr + 2\ Li \longrightarrow (me_2Si–CH_2)_n + LiBr. \qquad (20)$$

The six-membered ring was obtained in good yields by the reaction of $Br(me_2Si–CH_2)Cl$. When $Br(me_2Si–CH_2)_3Br$ reacts with Li, yields are even higher (95%). The compound $(me_2Si–CH_2)_n$ ($n = 4, 5, 6$) was prepared in 30–40% yields. After separation of LiCl the isolation of the cristalline eight membered ring is quite straightforward as it can be purified easily by sublimation and crystallization. $(me_2Si–CH_2)_5$ and $(me_2Si–CH_2)_6$ form oils so they can be purified only by distillation. A slight tendency to cristallization can be observed with $(me_2Si–CH_2)_5$ at low temperatures, when crystal nuclei are present.

The reactions for the synthesis of $(me_2Si–CH_2)_n$ are listed in Table 5.

Table 5. Reactions for the Synthesis of $(\mathrm{me_2Si{-}CH_2})_n$

Starting material	Lithium	Ether in ml	Product	Yields	b.p. °C/Torr
$\mathrm{Br(me_2Si{-}CH_2)_3Br}$ (3,8 g = 10 m Mol)	0,21 g 30 m Mol	30	$\mathrm{(me_2Si{-}CH_2)_3}$	2.05 g 95%	1)
$\mathrm{Br(me_2Si{-}CH_2)_4Br}$ (6,5 g = 14,6 m Mol)	0,305 g 44 m Mol	30	$\mathrm{(me_2Si{-}CH_2)_4}$	1,56 g 37.4%	Fp. 81
$\mathrm{Br(me_2Si{-}CH_2)_5Br}$ (10,2 g = 19,6 m Mol)	0,42 60,5 m Mol	50	$\mathrm{(me_2Si{-}CH_2)_5}$	2.9 g 41.1%	$86/10^{-2}$
$\mathrm{Br(me_2Si{-}CH_2)_6Br}$ (9,6 g = 16,3 m Mol)	0,35 g 50 m Mol	30	$\mathrm{(me_2Si{-}CH_2)_6}$	1.7 g 24.1%	$108/10^{-2}$

1) Separated by fractionated condensation from the ether Boiling points in Tables 3–5 were measured during the distillation.

The compound $\mathrm{Br(me_2Si{-}CH_2)_nBr}$ was dissolved in ether and dropped slowly while stirring into a suspension of lithium (in 50% excess). The beginning of the reaction is indicated by precipitation of LiCl and brightening of Li metal. The reaction proceeds more slowly with increasing n ($n \approx 4 - 6$). A reaction time of 48–96 h was required for the amounts used.

The ether is directly evaporated under vacuum without separation of the excess Li and LiBr precipitate. The six-membered ring $\mathrm{(me_2Si{-}CH_2)_3}$ is partly evaporated with the ether from which it has to be recovered. In the other cases the cyclic compounds can be distilled from the crude product.

1,1,3,3-Tetramethyl-1,3-disilacyclobutane is similary obtained in good yields by reaction of $\mathrm{me_2SiBr{-}CH_2{-}Sime_2{-}CHCl}$ with Mg or Li (10). The last step of this synthesis is similar to an earlier synthetic route (11) where the cyclization is effected with $\mathrm{me_2SiF{-}CH_2{-}Sime_2{-}CH_2Cl}$ prepared from

$$\mathrm{me_3Si{-}O{-}Sime_2{-}CH_2{-}Sime_2{-}CH_2{-}SiCl}$$

by cleavage with $\mathrm{BF_3}$. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane is obtained by the reaction of $\mathrm{me_2SiCl{-}CH_2Cl}$ with Mg (12) (13) (14).

The eight-membered ring can also be synthesized by the reaction of $\mathrm{me_2Si(CH_2Cl)}$ with sodium (7). The reaction starts immediately after the ether solution of $\mathrm{(CH_3)_2C_6H_5SiCH_2Li}$ is added to $\mathrm{Cl_2Si(CH_3)_2}$; the reaction can be observed quantitatively by the change in color (from red to colorless) as in a titration. The LiCl is separated and the

$$\mathrm{[me_2C_6H_5SiCH_2]_2Sime_2}$$

distilled and reacted with stoichiometric amounts of $\mathrm{Br_2}$ to form $\mathrm{[me_2BrSiCH_2]_2Sime_2}$. The synthesis of the eight-membered ring $\mathrm{[Sime_2{-}CH_2)_4}$ occurs by the reaction of a mixture containing molar amounts of

$me_2BrSi{-}CH_2{-}Sime_2{-}CH_2{-}Sime_2Br$ and $me_2Si(CH_2Cl)_2$

with molten sodium in boiling toluene. The reaction starts immediately and a light-blue precipitate is formed. At 90–100 °C long colorless needles of $[Sime_2{-}CH_2]_4$ sublime from the reaction mixture. They readily dissolve in nonpolar organic solvents.

II. Bicyclic Carbosilanes

Bicyclic carbosilanes are more difficult to synthesize than compounds of the $(me_2Si{-}CH_2)_n$ type, partly owing to differences in the reactivity of the functional intermediates caused by effects of the substituents. So far synthesis of the 1,3,5,7-tetrasila-bicyclo-[3.3.1]nonane system and of the 1,3,5,7,9-pentasiladecaline system has been reported (16).

1. Synthesis of 1,3,5,7,7-Hexamethyl-1,3,5,7-tetrasila-bicyclo-[3.3.1]nonane *8*

Initially the synthesis of compound *8* was attempted similar to that of $(me_2Si{-}CH_2)_4$ 7). However, the synthesis failed owing to the low reactivity of the CH_2Cl group in $me(CH_2Cl)Si\ ({-}CH_2{-}SimeC_6H_5)_2$, which failed to react with either Mg or Li. Synthesis of *8* was effected by the route in Table 6, the $Si{-}C_6H_5$ group beeing used as a protective group attached to the intermediates, which can, if necessary be cleaved by Br_2 to form the functional SiBr group.

a) $me(CH_2Cl)_2Si{-}CH_2{-}Si(C_6H_5)_2me$ 9 reacts:

$$\begin{aligned} &meSi(CH_2Cl) + LiCH_2Si(C_6H_5)_2me \longrightarrow \\ &me(CH_2Cl)_2Si{-}CH_2{-}Si(C_6H_5)_2me + LiCl \end{aligned} \qquad (21)$$

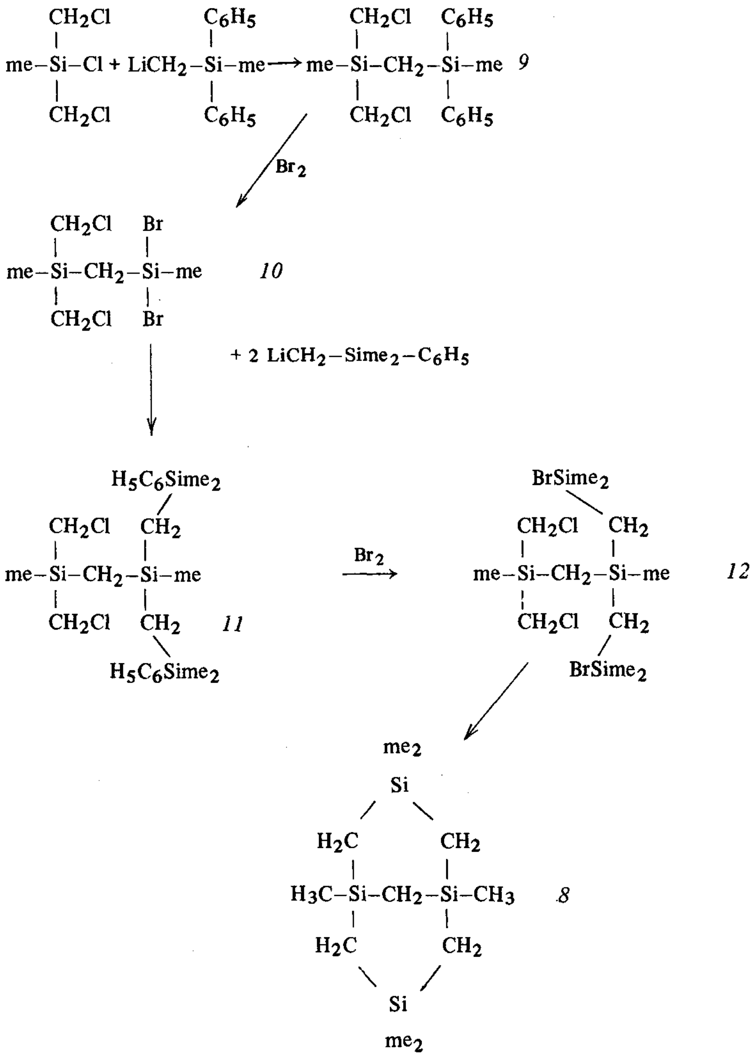
The reaction is carried out in diethylether with ice-cooling. It occurs immediately on adding the Li compound. Pure compound *9* is obtained in 47% yield.

b) $me(CH_2Cl)_2Si{-}CH_2{-}SiBr_2me$ 10 is synthesized by cleavage of the phenyl groups with Br_2:

$$\begin{aligned} &me(CH_2Cl)_2Si{-}CH_2{-}Si(C_6H_5)_2me + 2\ Br_2 \longrightarrow \\ &me(CH_2Cl)_2Si{-}CH_2{-}SiBr_2me + 2\ C_6H_5Br. \end{aligned} \qquad (22)$$

A nmr study revealed that the compound $me(CH_2Cl)_2{-}Si{-}CH_2{-}SiBr(C_6H_5)me$ is formed before the second phenyl group is cleaved.

Table 6. Synthetic route used for 1,3,3,5,7,7-Hexamethyl-1,3,5,7-tetrasila-bicyclo-[3.3.1]-nonane *8*



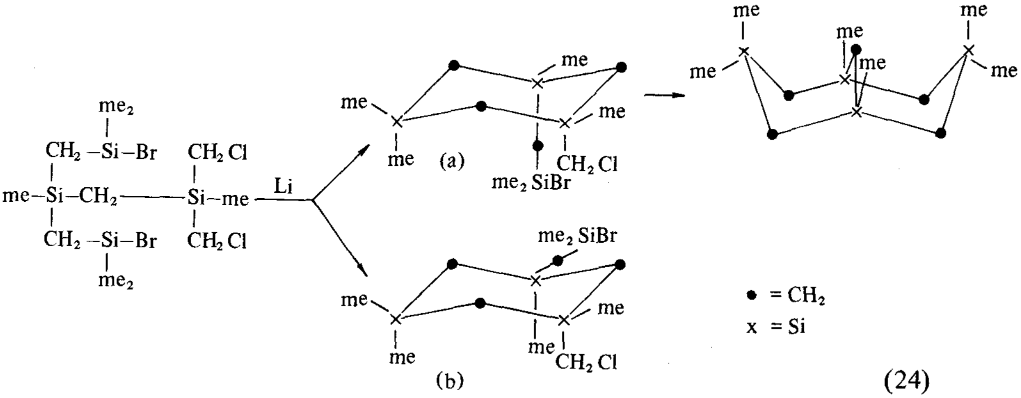
c) me(CH$_2$Cl)$_2$Si–CH$_2$–Sime[CH$_2$–Sime$_2$(C$_6$H$_5$)]$_2$ 11 is obtained by the reaction of *10* with $LiCH_2{-}Sime_2C_6H_5$:

$$me(CH_2Cl)_2Si{-}CH_2{-}SiBr_2me + 2\,LiCH_2{-}Sime_2C_6H_5 \longrightarrow \mathit{11} \qquad (23)$$

$LiCH_2{-}Sime_2C_6H_5$ is easily prepared from $me_2(C_6H_5)Si{-}CH_2Br$ with lithium[9]. In the reaction indicated (23), the compounds $me_3Si(C_6H_5)$ and $[me_2(C_6H_5)SiCH_2]_3$ are obtained as by-products. $me_3SiC_6H_5$ is formed by reduction of the lithium compound with ether, while $me_2(C_6H_5)SiCH_2Br$ gives $(me_2C_6H_5SiCH_2)_2$ by a Wurtz synthesis. Both compounds can be separated form the reaction product by distillation. By column chromatography with active carbon the higher molecular weight compounds can be removed, and fairly pure compound *11* is obtained.

d) $me(CH_2Cl)_2Si{-}CH_2{-}Sime(CH_2{-}Sime_2Br)_2$ 12 is easily prepared by cleavage of a Si-phenyl group in *11*. The C_6H_5Br which is formed can be distilled off, leaving *12*. No further purification by distillation or crystallization could be achieved as this compound decomposes when heated, and does not show any tendency to crystallize. Identification was by determining the molecular weight, by elemental analysis, and from the pmr spectrum. The pmr peaks of compound *11* show a shift to lower field due to the attachment of the electronegative bromine[15].

e) Cyclization to tetrasilanonane 8: the bicyclic compound can be formed from *12* only by a double cyclization reaction. The first step will yield a six-membered ring containing the functional groups which are able to undergo a second cyclization.



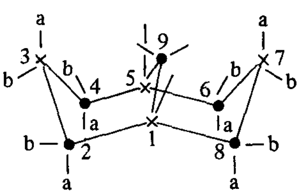
(24)

It is evident that formation of the second ring is possible only when the SiBr and CH_2Cl groups occupy an axial position after the first cyclization step. However, compounds of the 1,3,5-trisilacyclohexane system containing both axial and equatorial CH_2Sime_2Br and CH_2Cl groups will be formed, so that the yields of the bicyclic system are expected to be rather low.

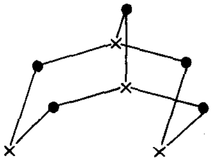
The synthesis yielded a mixture of products. Compound *8* was distilled off and purified by gas chromatography. The structure was determined by elemental analysis, mass spectrometry and by a study of the pmr spectrum[15].

It is apparent from examination of a model that structure *8a* will not exist for steric reasons. The methyl groups at the Si atoms 3 and 7 interfere with each other, precluding an arrangement of both six-membered rings in a chair configuration. Only in compounds where the silicon atoms 3 and 4 are linked by a CH_2 group, as occurs in the pyrochemically formed 1,3,7,7-tetrasilaadamantanes, does that configuration exist (1)[17]. The structures *8* and *8b* are sterically stable.

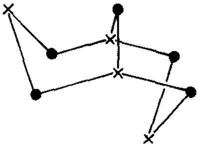
The nmr spectrum shows the presence of structure *8* with both six-membered rings in the boat form.



8



8a



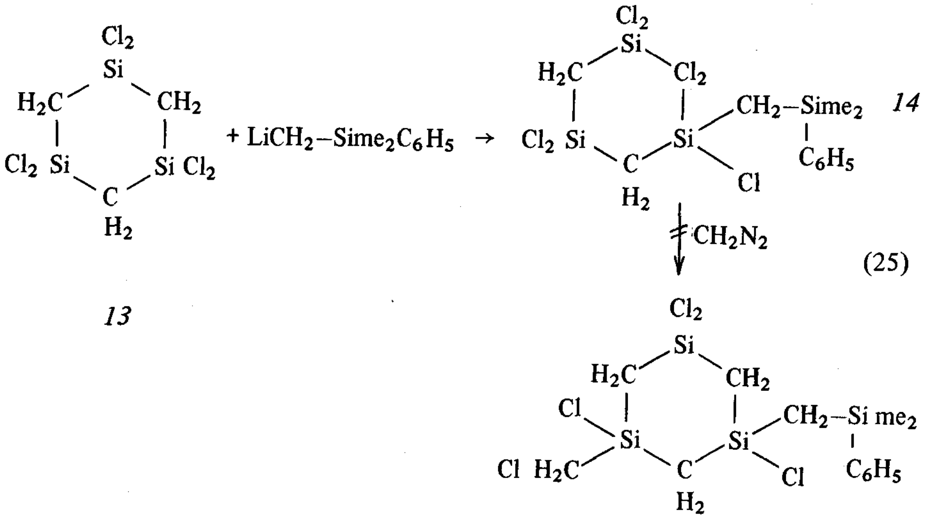
8b

In the nmr spectrum, three peaks are observed with a relative intensity of 1 : 1 : 1, due to the CH_3 groups 1 and 5, 3a and 7a, 3b and 7b in *8*. A further splitting would be expected if structure *8b* were present; however, it is not observed. More information can bo obtained by investigating the CH_2 signals. The same chemical shift is expected for the four CH_2 signals of the carbon atoms 2, 4, 6 and 8, while a different shift is expected for the bridging CH_2 group 9. In the four CH_2 groups each of the two protons are different (a, b) and an AB spectrum would be expected, whereas in the CH_2 group 9, the environment is equivalent for both H atoms, and therefore they show the same shift, which is consistent with the spectrum obtained: AB spectrum $\tau_A = 10.239$, $\tau_B = 10.348$, $J_{AB} = 13.9$ Hz, for the bridging CH_2 group 9 $\tau = 10.334$; relative intensities: of the CH_2 protons 4 : 1; of the CH_3 protons 3 : 3 : 3. The signals are broadened due to long-range coupling.

If structure *8b* were present, there would be more peaks for the $Si{-}CH_2{-}Si$ as well as $Si{-}CH_3$ groups.

2. Synthesis of 1,3,5,7-Tetrasila-bicyclo-[3.3.1]nonanes Containing Si-functional Groups

Further investigations on the synthesis of ring system *8* started from the 1,3,5-trisila-cyclohexane derivatives. A reaction sequence is proposed in Eq. (25). The insertion of a CH_2 group into the Si–Cl bond is essential. In the case of $SiCl_4$, it is obtained by reaction with CH_2N_2 (18). This reaction does not occur with $(Cl_2Si{-}CH_2)_3$ and reaction (25) yielded only compound *14*–

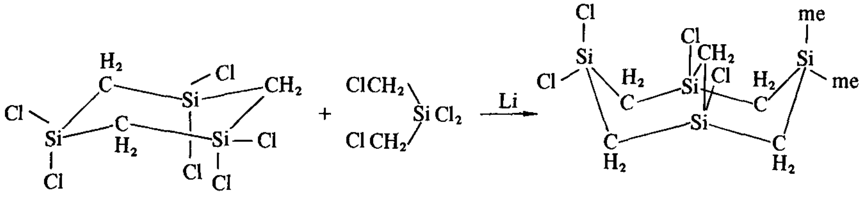

13

14

(25)

a) Reaction of $(Cl_2Si-CH_2)_3$ 13 and its Derivatives with $(CH_2Cl)_2Sime_2$

The synthesis of the bicyclic system *8* containing Si-functional groups was attempted following reaction (26); the desired bicyclic compound *15* was isolated in 6% yield from the products of the reaction of *13* with $(CH_2Cl)_2Sime_2$


13

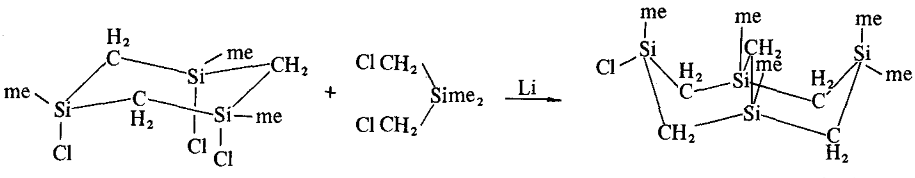
15

(26)

The formula was confirmed by elemental analysis and mass spectrometry. The 60 MHz pmr spectrum shows three peaks (87; 53; 18 Hz) with the relative intensity 2 : 4 : 10. This ratio indicates that the signals of two CH_3 and two CH_2 groups coincide.

Neither yields nor reaction rates were improved even with butyl ether as solvent. Derivatives of $(CH_2Cl)_2Sime_2$ were tried, as the reactivity of the CH_2Cl groups is strongly dependent on the substitution of the Si atom; for instance $(CH_2Cl)_2SimeC_6H_5$ does not react with Li even after a long time, so it cannot be used in a reaction with *13*. No reaction occurs with $(CH_2I)_2Sime(C_6H_5)$ and *13* to form the bicyclic system *15*, and application of $me_2Si(CH_2Cl)(CH_2Br)$ was similary unsuccessful.

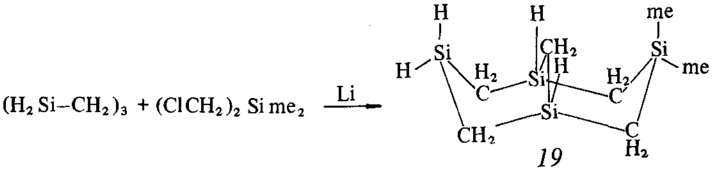
However, in a reaction similar to (26), the bicyclic system shown in reaction (27) is formed and the 1,3,3,5,7-pentamethyl-7-monochloro-1,3,5,7-tetrasila-bicyclo-[3.3.1]-nonane is obtained.



16 17 (27)

$(meClSi{-}CH_2)_3$ *16* is prepared by the chlorination of $[me(H_5C_2OSi{-}CH_2]_3$ with PCl_3, the latter being formed by reaction of $(H_5C_2O)_2SiCH_2Cl$ with Mg (19). However, satisfactory yields were not obtained in the synthesis by reaction (27).

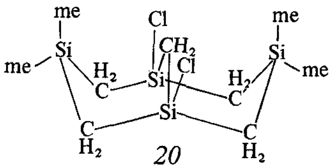
The preparation of the Si–H derivative of the bicyclic system is similary carried out with $(H_2Si{-}CH_2)_3$ and $me_2Si(CH_2Cl)_2$ as in reaction (28a), but again only small yields of the bicyclic compound were obtained.



19 (28a)

b) Remarks on the Methylation of the SiCl-Containing 2,3,5,7-Tetrasila-bicyclo[3.3.1]nonanes

Reaction (26) produces 1,3,3,5-tetrachloro-7,7-dimethyl-1,3,5,7-tetrasila-bicyclo-[3.3.1]nonane with four SiCl groups. A complete methylation would lead to compound *8*. On carrying out that reaction it is observed that methylation does not go to completion, even if a 50% excess of Li is applied and the mixture is stirred for two days in boiling ether, though, 1,3,5,7-tetrasila-bicyclo-[3.3.1]nonane containing two SiCl groups is obtained, presumably compound *20*. As with 1,3,5,7-tetrasilaadamantane, methylation with meMgCl does not occur because of steric hindrance.

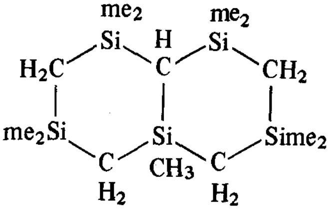


20

Compound *17* formed in accordance with reaction (27) reacted easily with meMgCl to form compound *8*, as expected.

3. Synthesis of Cis- and Trans-Pentasiladecaline *21*

It is obvious from the reported results that the greatest difficulty lies in the synthesis of the CH(Si≡)$_3$ group in compound *21*.



21

1,1,3,3,5,5-Hexamethyl-1,3,5-trisila-6-methylene-cyclohexane *20* cannot be used as a starting material in the synthesis of a Pentasila-decaline system, since hydrosilylation does not lead to the 1,1,1-trisilylethane. Since all the conditions for the synthesis of a silicon-functional carbosilane chain are known, the preparation of compound *21* should be possible following successful cyclization to the CH(Si≡)$_3$ group. Reactions of Si-halide groups with methylhalides (CCl_4, CBr_4, $CHCl_3$, $CHBr_3$) are therefore considered. The formation of HC(Sime$_3$)$_3$ in 10–15% yields from $HCCl_3$, ClSime$_3$ and Li is reported by Merker and Scott[21]. Better yields of compound *22* were sought by varying the reaction conditions with a view to cyclization of suitable Si-functional carbosilanes to compound *21*. The reactivity of several methyl halides was investigated[22].

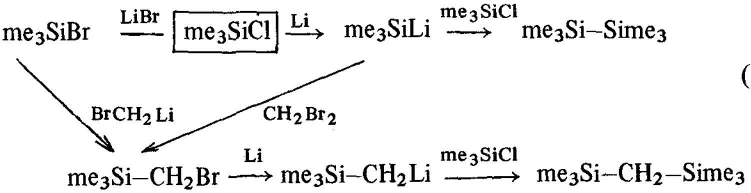
a) Reaction of Dihalo-methanes with me$_3$SiCl and Li(Mg)

Dibromoalkanes form stable Li compounds only with the Br atoms separated by at least 4 C atoms[23]. Only low yields of me$_3$Si–CH$_2$–Sime$_3$ were obtained by the reaction of me$_3$SiCl with Li and CH_2Br_2[23] or CH_2Cl_2[22]. By varying the reaction conditions, me$_3$SiCl was reacted with Li(Mg) and CH_2Br_2, CH_2I_2, CH_2BrCl[22].

The yields of the different compounds were determined by integration of the nmr spectra of the unseparated reaction product.

The best yields of me$_3$SiCH$_2$Br are obtained when using powdered Li, low temperature, diethylether as solvent, and an excess of CH_2Br_2. The most favorable conditions for the formation of me$_3$Si–CH$_2$–Sime$_3$ occur when CH_2I_2 in THF is applied at low temperature with an excess of Li. me$_3$SiCH$_2$I is not observed, possibly owing to its high reactivity with Li. CH_2BrCl gave no better results, i. e. me$_3$SiCH$_2$Cl is not formed in reasonable yields; me$_3$Si–O–Sime$_3$ is formed as a by-product in all reactions, possibly due to a reaction with ether.

The reaction of Si-halide compounds with methyl dihalides is suitable for the preparation of C–Si bonds with the insertion of special halogen-CH_2 groups; however the preparative value is rather limited because of low yields. Eq. (28b) accounts for the formation of all the observed compounds[21–23].



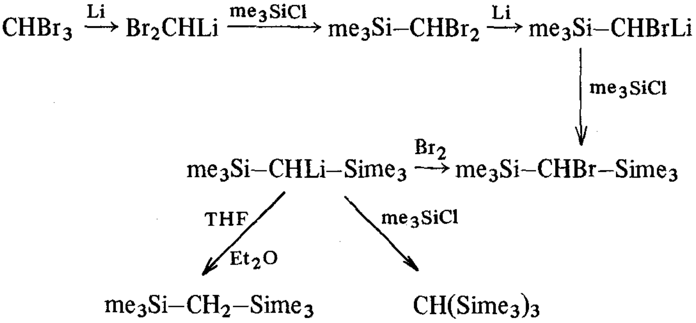
(28b)

An inhibitory tendency is initially observed with the reactions of CH_2Br_2, after which they are vigorous and exothermic, when the SiCl compound is not present in excess. When the excess of the SiCl-compound is twofold ore more, the reaction sometimes does not occur at all or occurs with uncontrollable vigor after several days. After completion of the reaction, the Li particles show a white metal appearance.

b) Reaction of Trihalo-methanes with me_3SiCl and Li(Mg)

The reactivity of trihalomethanes might be expected to be lower, as the number of substituent groups is increased, but this is not borne out empirically. Compound $HC(Sime_3)_3$ is obtained in surprisingly high yields when the reaction is carried out in THF at low temperature and with stoichiometric amounts of the reactants. The products depended mainly on reaction conditions. CH_3Cl reacts quite easily whereas CH_2BrCl shows little tendency to react. Better yields are obtained with lithium than with magnesium. Lu must be used as a fine powder to effect a fast and selective reaction.

A halogen exchange to form me_3SiBr as well as coupling reactions to form $me_3Si–Sime_3$ are expected in this reaction. Formation of $me_3Si–CH_2–Sime_3$ is difficult to explain as it involves hydrogenation of a C–Br group. The H atom presumably originates from THF or diethylether. The formation of the silylmethane compounds may occure by the following reaction sequence:



(29)

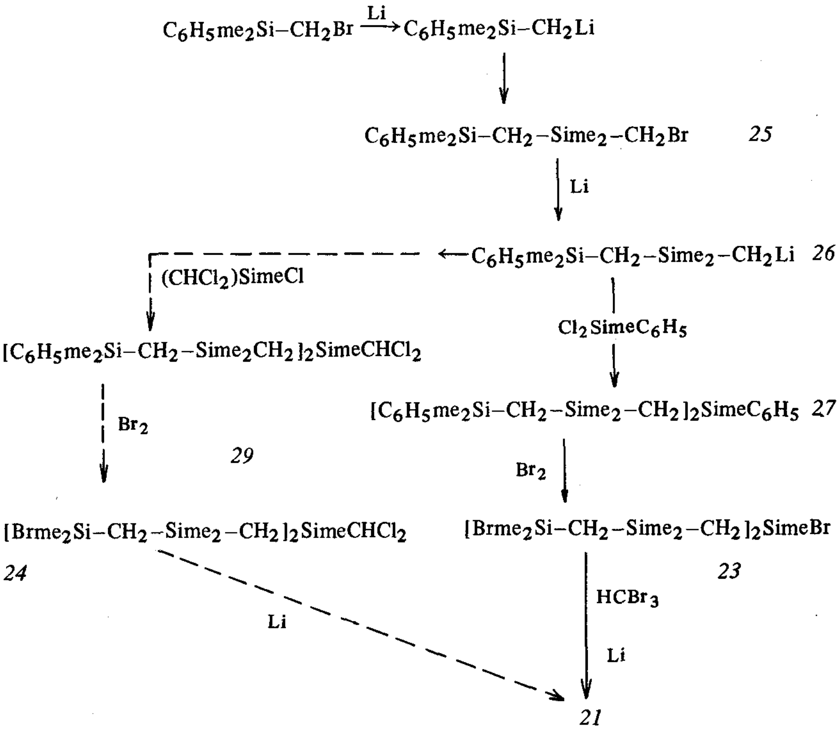
At low temperature these compounds can be coupled with halogen-Si compounds[24–26]. Similar reactions occur e. g. when $me_3Si–CBr_3$ is used for further reaction with $me_2CH–MgCl$ or $me(CH_2)_3Li$[23–25]. The same reactions may occur when Mg or Li metal is used instead of $me_2CH–MgCl$ or $me(CH_2)_3Li$. The carbenoid intermediates which are formed in this process seem to be so stable that they can be formed under temperature conditions up to # –65 °C and then enter into further reactions[22].

Under the conditions used the intermediates cannot be isolated nor detected by nmr spectroscopy. However, by using special techniques these polyhalogenated metallomethanes can be obtained at low temperature, *e. g.* CBr_3MgCl[24–26].

4. Synthesis of Cis- and Trans-Pentasiladecaline

There is an evident potential for the synthesis of the $HC(–Si\equiv)_3$group by following the procedures in Chapter B. Carbosilane chains with Si-functional

Table 7. Synthetic route to compound *21*



-------- Reaction does not yield this compound groups have to be prepared in order to synthesize compound *21*. The reaction sequence is given in Table 7. Compound *23* has to undergo repeated cyclization with $CHBr_3$ and Li whereas the first step is already effected in compound *24* so only reaction with Li is required. However, it has so far not been possible to prepare compound *24*.

a) Synthesis of the Starting Material

The synthesis of $C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH_2Br$ *25* and its reaction with Li to form the Li compound $C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH_2Li$ *26* was illustrated in the preceding chapters. Compound *26* dissolves easily in ether to give an orange-red solution and can be readily identified by the Li–CH_2 group (τ = 12.01) in the nmr spectrum. Coupling of compound *26* with $Cl_2SimeC_6H_5$ proceeds to compound *27* with good yields.

$$2\ C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH_2Li + Cl_2SimeC_6H_5 \longrightarrow \qquad (30)$$
$$[C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH_2]_2SimeC_6H_5 \quad 27$$

Compound *27* (m. w. = 562) cannot be distilled under vacuum as it decomposes. However, it is obtained quite pure from reaction (30). The structure of *27* has been determined by chemical reactions; cleavage of the phenyl group with Br_2 and subsequent hydrogenation with $LiAlH_4$ leads to compounds *23* and *28*.

$$27 + 3\ Br_2 \longrightarrow [BrSime_2{-}CH_2{-}Sime_2{-}CH_2]_2SiBrme\ 23 + 3\ C_6H_5Br \qquad (31)$$
$$\big\downarrow{\scriptstyle LiAlH_4}$$
$$[HSime_2{-}CH_2{-}Sime_2{-}CH_2]_2SimeH \quad 28$$

Characteristic shifts are observed in the nmr spectrum on changing the substituents in compound *27*. There is good evidence for the structure from the observed splitting of the doublet in compound *28* due to the HSi groups adjacent to the CH_3Si- and -$SiCH_2Si$-groups[22)].

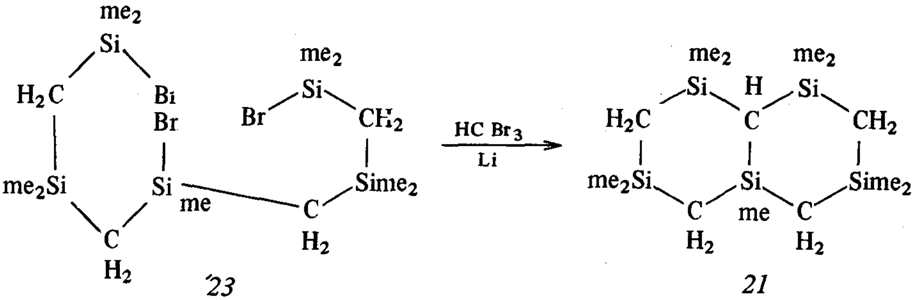
Synthesis of compound *29* by reaction of the compound *26* with $Cl_2SimeCHCl_2$ was attempted. The reaction yielded $[C_6H_5me_2Si]_2CH_2$ *30* and $[C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH_2]_2Sime(CH_2Cl)$ *31*, whereas compound *29* was not formed at all judging from the absence of the $Cl_2HC{-}Si$ signal at τ = 4 in the nmr spectrum. Similar reactions lead to the formation of compounds *30* and *31*:

$$\begin{tikzcd}
C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH_2Li + Cl_2Sime{-}CHCl_2 \arrow[r] \arrow[dd, "Cl_2Sime(CH_2Cl)"'] & \begin{array}{l} C_6H_5me_2Si{-}CH_2{-}Sime \\ \quad + Cl_2Sime(Cl_2CLi) \end{array} \arrow[d, dash, "30"] \\
Cl_2Sime(CH_2Cl) & {} \arrow[l, "(C_2H_5)_2O"'] \\
{[C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH_2]_2Sime(CH_2Cl)} &
\end{tikzcd}$$

31

b) Cyclization of Compound 23 to Compound 21

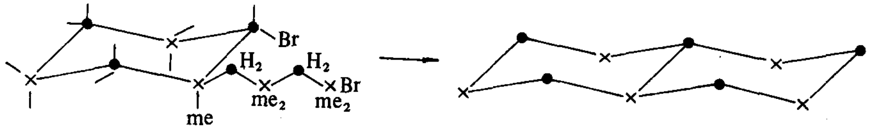
By application of the optimal conditions described in Section 3, the cyclization of *23* can be accomplished.



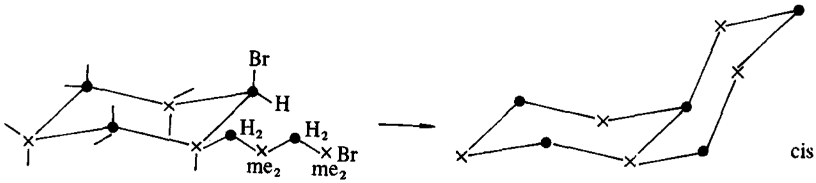
23 *21*

(33)

Thermodynamic considerations during the formation of the six-membered rings indicate that only one of the rings is initially formed, resulting in a new Si–CHBr–Si bridging group. Depending on whether the Br atom is equatorial or axial, the second cyclization step will lead to a trans- or cis-1,1,3,3,5,7,7,9,9-nonamethyl-1,3,5,7,9-penta-sila-decaline.



trans *21*



cis *21*

x = Si

• = C

In THF the reaction is very fast. After removal of the solvent and separation of LiBr,a light-brown viscous product remains. At 90–95 °C (under vacuum) a colorless fraction can be distilled off (16% yield). Further separation of this fraction can be achieved by preparative gas chromatography (200 °C; 5% phenylsilicone oil O S 26.14 P/E on Sterchamol; 6 m column, ϕ 10 mm, 200 ml/min helium). After an elution period of more than 3 hrs, only two fractions were obtained, the first containing most of the product. The nmr spectrum (proton nmr at 60 and 100 MHz indicated that the cis- and trans trans 1,3,5,7,9-pentasiladecalines are present in the reaction product. This is confirmed by a C 13 nmr spectrum (90 MHz). In the following investigations, the separation of cis- and trans siladecalines will be reported and the nmr spectra discussed.

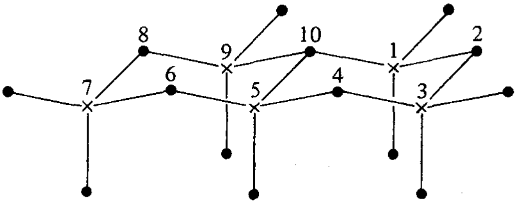
c) Isolation and Identification of the Cis- and Trans-Nonamethyl-1,3,5,7,9-pentasiladecaline

Complete separation of the cis and trans compounds was accomplished by fractional crystallization: 8 g of the mixture was dissolved in pentane and submitted to a crossed fractional crystallization. The solution was always cooled very slowly to –50 °C or –70 °C. At this temperature, the crystals were separated by filtration under cooling. 1.3 g of crystals and 3.4 g of mother liquor were obtained.

With carbon decalines, the cis configuration is at a higher energy level than the trans configuration. A similar behavior can be expected for the Si-methylated 1,3,5,7,9-pentasiladecalines so the smaller amount (1.3 g) is associated with the higher-energy cis compound, whereas the 3.4 g represent the lower-energy trans compound. The synthesis should produce the trans compound in higher yields since it is energetically favored. Study of the nmr spectrum gives the same result. Meltung points were determined as 64–64.5 °C for the cis compound *21* and 29–30 °C for the trans compound *21*. The cis compound *21* has an angular configuration which is much nearer a sphere than the trans compound *21* which shows an almost planar arrangement of the two six-membered rings. Consequently, the melting point of the trans compound *21* is more than 30 °C below that of the cis configuration.

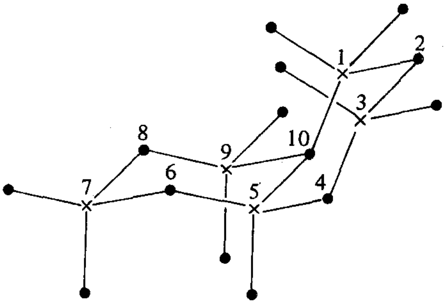
A further proof for the structure can be given by a comparison of the nmr spectra of the cis- and trans siladecalines with the cis- and trans-carbon decalines$^{22)}$. Only the bridging CH_2 groups are considered here: in this area the pmr spectrum of cis-1,3,3,5,7,7,9,9-nonamethyl-1,3,5,7,9-pentasiladecaline shows a good correlation with that of ciscarbon decaline; Similiar results are found for the trans compounds. The Si-29 nmr spectra also support the postulated structures$^{22)}$.

In the trans compound the Si atoms 1 and 9 and the Si atoms 3 and 7 are equivalent, whereas the Si atom 5 is different. Thus, three signals are expected; they appear at –18.12 ppm, –20.04 ppm and –20.35 ppm [measured against octamethylcyclotetrasiloxane in a 90 MHz spectrometer at 17.87 MHz; broadline decoupling].



trans *21*

x = Si
• = C

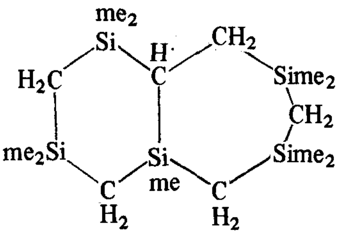


cis *21*

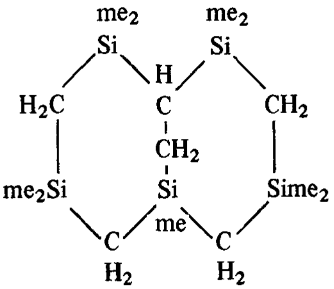
In this compound, all Si atoms possess a different chemical environment, so 5 peaks are expected in a Si-29 nmr spectrum. Peaks are observed at −18.62 ppm, −19.80 ppm and −20.68 ppm. Due to very similar chemical shifts, two peaks are coincident with others. The mass-spectrometric study confirm the formula $Si_5C_{14}H_{36}$ of the two isomers (calculated molecular weight 344.166335; measured 344.16669; difference 1 ppm). The compounds are of high thermal stability. After a sample had been heated to 550 °C in a sealed nmr tube for 3 h, very little decomposition had occurred, as indicated by a weak yellow color, increase in viscosity and evolution of a gas. However, no changes were apparent in the nmr spectra.

d) Synthesis of another Bicyclic Carbosilane, Compound 32

In the reaction of compound *3* with $HCBr_3$ and Li, another bicyclic carbosilane (compound *32* is formed; this was isolated by gas chromatography in 1,5% yield. In the nmr spectrum, peaks are observed in 3 regions (for$(\equiv Si)_2CH{-}CH_2Si\equiv$, $CH_3Si\equiv$ and $CH_2(-Si-)_2$). The resonance line of the $CH(Si\equiv)_3$ group, seen in the spectrum of the isomeric cis- and trans-nonamethyl-1,3,5,7,9-pentasiladecalines, is not observed. A high resolution run shows that numerous peaks are superimposed on that poorly defined peak, indicating a lack of symmetry in the molecule. Form the mass spectrum, the general formula $Si_5C_{15}H_{30}$ was obtained. All data are consistent with the formula of compound *32*, which is less rigid than formula *32a*.

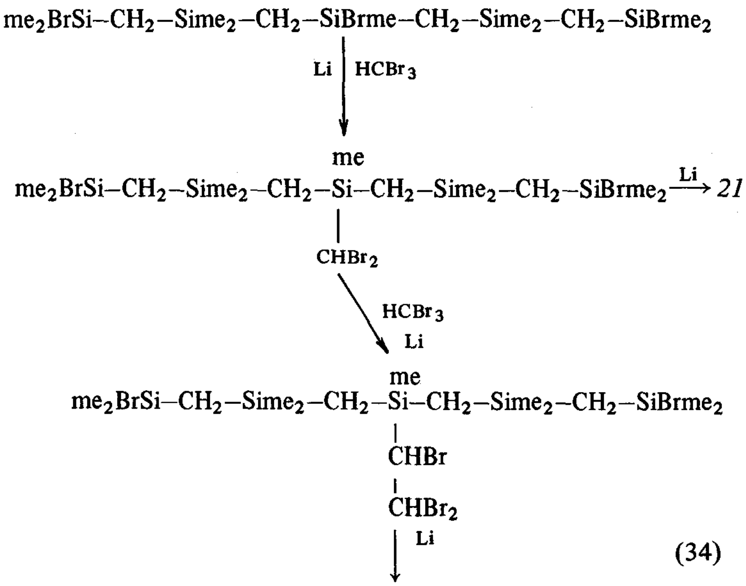


32



32a

The formation of *32* with a six-membered and a seven-membered ring can be illustrated by the following reaction sequence, in which cyclization of compound *23* occurs:



$$me_2BrSi{-}CH_2{-}Sime_2{-}CH_2{-}SiBrme{-}CH_2{-}Sime_2{-}CH_2{-}SiBrme_2$$

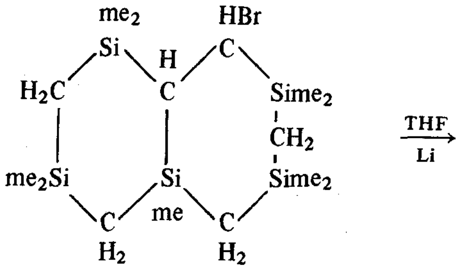
$$\Big\downarrow \text{Li} \mid HCBr_3$$

$$me_2BrSi{-}CH_2{-}Sime_2{-}CH_2{-}\underset{\substack{|\\ CHBr_2}}{\overset{me}{Si}}{-}CH_2{-}Sime_2{-}CH_2{-}SiBrme_2 \xrightarrow{\text{Li}} 21$$

$$\searrow HCBr_3,\ \text{Li}$$

$$me_2BrSi{-}CH_2{-}Sime_2{-}CH_2{-}\underset{\substack{|\\ CHBr\\ |\\ CHBr_2}}{\overset{me}{Si}}{-}CH_2{-}Sime_2{-}CH_2{-}SiBrme_2$$

$$\Big\downarrow \text{Li} \qquad (34)$$



32

As previously mentioned, the last step in this sequence is hydrogenation of the intermediate compound containing a LiCH group by THF. A melting point of 37–39 °C was determined for compound *32*. However, it has to be borne in mind that a mixture of cis and trans configuration may be present; separation has not yet been tried.

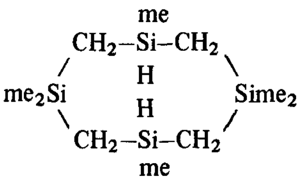
5. Synthesis and Reactions of Si-functional 1,3,5,7-Tetrasilacyclooctanes

The synthesis of the Si-methylated 1,3,5,7,9,11-hexa-sila-perhydrophenaline was not achieved by starting with meA_2SiX (me = CH_3; A = CH_2Cl, CH_2Br, H, C_6H_5, $CH_2{-}Sime_2C_6H_5$; X = Cl, Br)[28]. Synthesis of suitable Si-functional carbosilanes precussors for bi- and tricyclic compounds was planned, utilizing experience with synthesis of linear carbosilanes[28] with Si-functional groups.

The following compounds were available for use in the cyclization reaction:

$meH_2Si{-}CH_2{-}Sime_2{-}CH_2{-}SiHme{-}CH_2{-}Sime_2{-}CH_2Br$ *33*
$meBrHSi{-}CH_2{-}Sime_2{-}CH_2{-}SiHme{-}CH_2{-}Sime_2{-}CH_2Br$ *34*
$meBr_2Si{-}CH_2{-}Sime_2{-}CH_2{-}SiBrme{-}CH_2{-}Sime_2{-}CH_2Br$ *35*

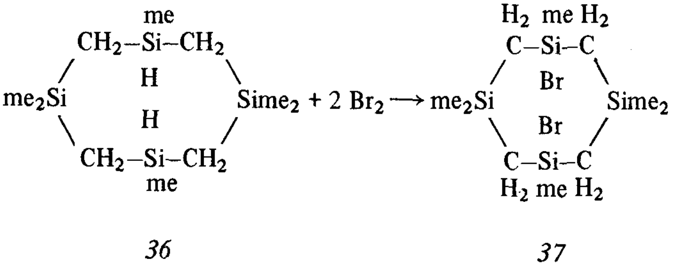
The compounds *33* and *34* react with Li to form compound *36*, whereas no reaction occurs with *35* even when heated under diethylether reflux.



36

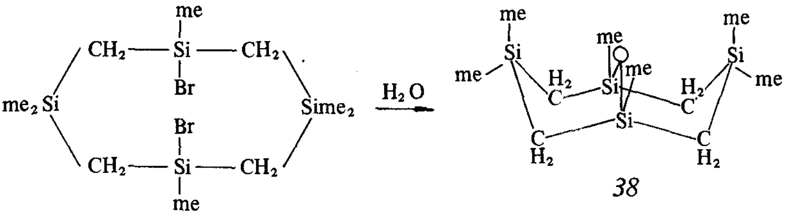
Compound *36* is isolated by distillation. A mass-spectrometric investigation confirms the formula $Si_4C_{10}H_{28}$; calculated M.W. for CH_3: 245.103333; measured 245.103167 (diff. 0.7 ppm).

The nmr spectrum agrees with structure *36*. The Si-H groups in this compound can be transformed by Br_2 (in pentane) to give compound *37*, of which white crystals precipitate even at room temperature; crystallization is complete at –80 °C. (m.p. 119–122 °C)



(35)

The mass spectrum confirms the formula $Si_4C_{10}H_{24}Br$. Further reactions give proof for the structure of *37*. Compound *38* is formed by hydrolysis of *37*, reaction (36)



(36)

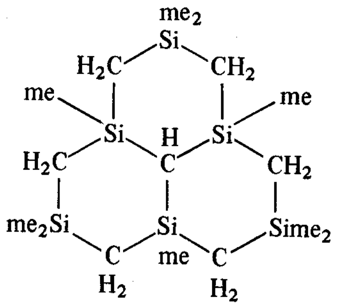
Compound *38* is isolated as a pure substance, m.p. 37–39 °C. A mass-spectrometric investigation confirms the formula $Si_4C_{10}H_{24}O$; calc. M.W. for the fragment CH_3:259,082598; meas. 259,083646. Besides the structure illustrated here, another configuration of compound *38* could be considered in which one six-membered ring is in the chair form and the other in the boat form. However, transmutation have not yet been observed. A structure with both rings in the chair form can be excluded for steric reasons.

We had intended to synthesize 1,3,3,5,7,7-hexamethyl-1,3,5,7-tetrasila-bicyclo[3.3.1]-nonane by reacting *37* with CH_2Br_2 and lithium (15), but we obtained a siloxane *38* instead. As the reaction was carried out with exclusion of air and moisture, the formation of compound *38* cannot be attributed to hydrolysis. Its formation is due to an ether cleavage and a subsequent reaction.

III. Tricyclic Carbosilanes

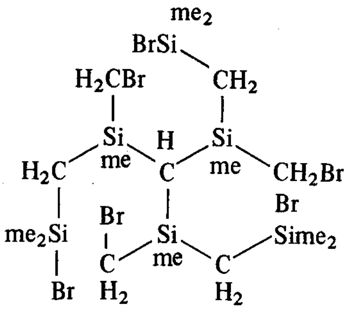
1. Synthesis of Cis,Trans- and Trans,Trans-Hexasila-perhydrophenaline *39*

In addition to efforts in the synthesis of the bicyclic carbosilanes, attempts have been made to prepare a Si-methylated 1,3,5,7,9,11-hexasila-perhydrophenaline *39*



39

Preparation of compound *39* was first attempted by use of compounds of the (α) type.

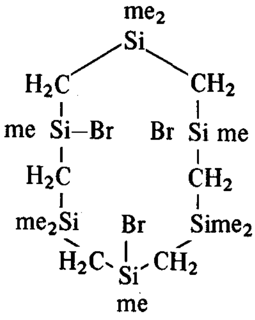


(α)

Treatment of substances having the general formula me(A)$_2$SiX [X = Cl, Br; A = CH_2Cl; CH_2Br; H; C_6H_5; CH_2–Sime$_2$$C_6H_5$] with $HCBr_3$ or HCl_3 and Li did not give compounds of the HC[Si(A$_2$)me]$_3$ type. As there is inadequate knowledge of procedure for the reactions of me(CH_2Cl)$_2$SiBr *40*, me(CH_2Br)$_2$SiBr *41*, meH_2SiBr *42*, me(C_6H_5)$_2$SiBr *43* and (C_6H_5)me$_2$Si–CH_2–SiBrme(CH_2Cl) *44* with $CHBr_3$ and Li to trisilylmethanes, that route was not pursued.

Reaction of (me$_3$Si)$_3$CH with concentrated H_2SO_4 and subsequent cleavage with anhydrous NH_4Cl did not lead to satisfactory yields of (Clme$_2$Si)$_3$CH or of (Cl_2meSi)$_3$CH.

Synthesis of *39* (in Table 8) was finally accomplished by preparing the cyclic carbosilane *45* and reacting it with $CHBr_3$ and Li.



45

a) Synthesis of Linear Carbosilanes with Functional Groups

α) Synthesis of functional carbosilane chains with two Si atoms. Synthesis starts with preparation of $meCl_2Si{-}CH_2Cl$ *46*, which is obtained by photochlorination of me_2SiCl_2. The reaction of *46* with an excess of C_6H_5MgBr at 60–80 °C gives $(C_6H_5)_2meSi{-}CH_2Cl$ *47*, which forms the Grignard reagent $(C_6H_5)_2meSiCH_2MgCl$ *48* on treatment with Mg in ether. However, the reaction does not proceed to $(C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2Cl$ *51* with $me_2ClSi{-}CH_2Cl$. In order to obtain compound *51*, the lithium compound has to be prepared, because it is more reactive than the Grignard reagent. The Li compound cannot be obtained by direct reaction of the CH_2Cl groups of *47* with Li metal. However, it may be obtained by using the mercury compound.

$$\begin{aligned}&2(C_6H_5)_2meSi{-}CH_2MgCl + HgCl_2 \longrightarrow [(C_6H_5)_2meSi{-}CH_2]_2Hg + MgCl_2\\&\xrightarrow{2\ Li} 2\ (C_6H_5)_2meSi{-}CH_2Li + Hg. \qquad (37)\end{aligned}$$

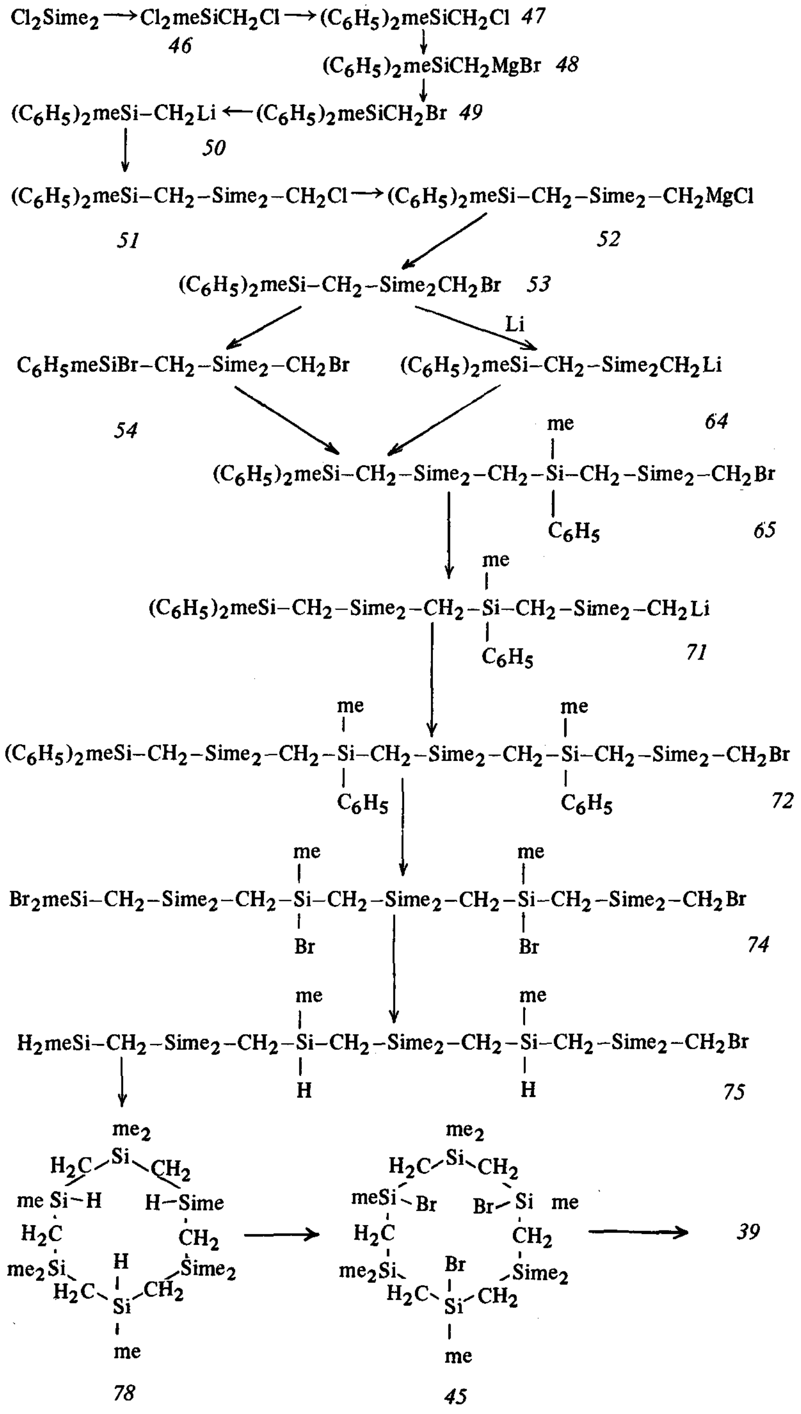
This unsatisfactory route can be avoided by use of the reactions indicated in the following equations:

$$(C_6H_5)_2meSi{-}CH_2MgCl + Br_2 \longrightarrow (C_6H_5)_2meSi{-}CH_2Br + MgClBr \quad (38)$$

$$(C_6H_5)_2meSi{-}CH_2Br + Li \longrightarrow (C_6H_5)_2meSi{-}CH_2Li + LiBr \quad (39)$$

Compound *48* is dissolved in ether at –20 °C, and an equivalent amount of Br_2 (dissolved in pentane) is added. Reaction readily occurs. If temperature is controlled, side reactions such as bromination of the ether or cleavage of the Si-phenyl group can be excluded almost completely. After hydrolysis, compound *49* can be distilled off. Reaction (39) is easily achieved with Li powdered.

Table 8. Synthetic route to *39*



Treatment of the Li compound *50* with $\mathrm{Clme_2Si{-}CH_2Br}$ does not lead to the desired brominated derivative of compound *51*, but a metal – halogen exchange occurs. However, the reaction of *50* with $\mathrm{Clme_2SiCH_2Cl}$ gives compound *51* by reaction (41).

$$\begin{tikzcd}[column sep=small]
\mathrm{(C_6H_5)_2meSi{-}CH_2Li + Clme_2Si{-}CH_2Br \longrightarrow} & \\
\mathrm{(C_6H_5)_2meSi{-}CH_2Br\ +} & \mathrm{Clme_2Si{-}CH_2Li} \arrow[d, "\mathrm{Clme_2Si{-}CH_2Br}"] \\
 & \mathrm{Clme_2Si{-}CH_2{-}Sime_2{-}CH_2Br}
\end{tikzcd} \tag{40}$$

55

$$\mathrm{(C_6H_5)_2meSi{-}CH_2Li + Clme_2Si{-}CH_2Cl \longrightarrow (C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2Cl} \tag{41}$$

51

$\mathrm{Clme_2Si{-}CH_2Cl}$ itself is easily obtained by a strongly exothermic rearrangement of the Si–H compound with $\mathrm{AlCl_3}$.

$$\mathrm{Clme_2Si{-}CH_2Cl \xrightarrow{1/4\ LiAlH_4} Hme_2Si{-}CHCl_2 \xrightarrow{AlCl_3} Clme_2Si{-}CH_2Cl} \tag{42}$$

Further steps follow this synthetic route:

$$\begin{tikzcd}
\mathrm{(C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2Cl} \arrow[r, "\mathrm{Mg}"] & \mathrm{(C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2MgCl} \arrow[d, "\mathrm{Br_2}"] \\
 & \mathrm{(C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2Br}
\end{tikzcd} \tag{43}$$

53

This reaction is followed by cleavage of the phenyl group with $\mathrm{Br_2}$; in a careful procedure at 20 °C only one phenyl group is cleaved. Hydrogenation with $\mathrm{LiAlH_4}$ follows.

$$\begin{tikzcd}
\mathrm{[C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2Br} \arrow[r, "\mathrm{Br_2}"] & \mathrm{C_6H_5meBrSi{-}CH_2{-}Sime_2{-}CH_2Br}\ \mathit{54} \arrow[d, "\mathrm{LiAlH_4}"] \\
 & \mathrm{C_6H_5meHSi{-}CH_2{-}Sime_2{-}CH_2Br}
\end{tikzcd} \tag{44}$$

56

The compounds *54* and *56* readily react with $\mathrm{Br_2}$ to give compounds *57* and *58*:

$$\mathrm{C_6H_5meBrSi{-}CH_2{-}Sime_2{-}CH_2Br + Br_2} \xrightarrow[80\,^{\circ}\mathrm{C}]{\mathrm{CCl_4}}$$

$$\mathrm{meBr_2Si{-}CH_2{-}Sime_2{-}CH_2Br + C_6H_5Br} \qquad (45)$$

$$\mathrm{C_6H_5meHSi{-}CH_2{-}Sime_2{-}CH_2Br + Br_2} \xrightarrow{\mathrm{CCl_4}}$$

$$\mathrm{meBr_2Si{-}CH_2{-}Sime_2{-}CH_2Br + C_6H_6} \qquad (46)$$

To complete reaction (45), a period of 10 h in boiling $\mathrm{CCl_4}$ is required, whereas the reaction (46) is rapidly completed even at 0 °C. The compounds resulting from these reactions are identified by nmr spectroscopy[28)].

As discussed above, the reactions of phenyl-free compounds with $\mathrm{SiCH_2Br}$ and SiH containing compounds and Li were used to form the $\mathrm{{-}Si{-}CH_2{-}Si{-}}$ groups. A similar reaction of $\mathrm{C_6H_5meHSi{-}CH_2{-}Sime_2{-}CH_2Br}$ did not lead to the cyclic di- and trimer compounds. The compounds

$\mathrm{C_6H_5meHSi{-}CH_2{-}Sime_3}$ *58* and

$\mathrm{C_6H_5meHSi{-}CH_2{-}Sime_2{-}CH_2{-}Sime(C_6H_5){-}CH_2{-}Sime_3}$ *59*

were obtained. These react with $\mathrm{Br_2}$ to form

$\mathrm{meBr_2Si{-}CH_2{-}Sime_3}$ *60* and

$\mathrm{meBr_2Si{-}CH_2{-}Sime_2{-}CH_2{-}SimeBr{-}CH_2{-}Sime_3}$ *61*.

Hydrogenation with $\mathrm{LiAlH_4}$ leads to

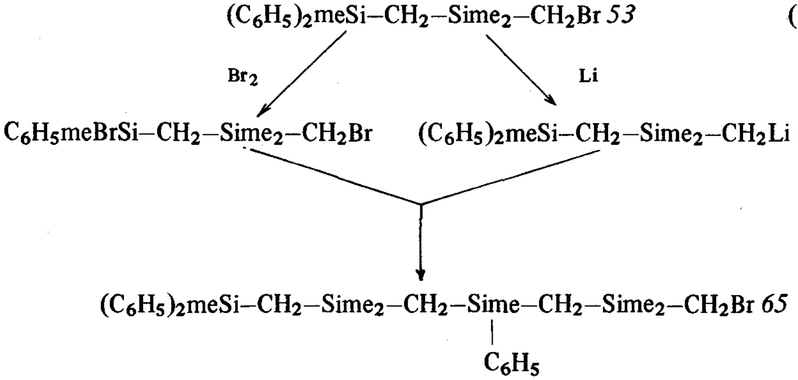
$\mathrm{meH_2Si{-}CH_2{-}Sime_3}$ *62* and

$\mathrm{me_2H_2Si{-}CH_2{-}Sime_2{-}CH_2{-}SimeH{-}CH_2{-}Sime_3}$ *63*.

Cyclization is prevented by the steric hindrance of the phenyl groups. A $\mathrm{LiCH_2{-}Si}$ group is involved in the formation of the compounds isolated. This group reacts with the SiH group only to a small extent, but preferentially forms a $\mathrm{H_3C{-}Si}$ group by a reaction with ether.

β) Synthesis of Si-functional carbosilanes with four Si atoms. Since it was not possible to obtain cyclic Si-functional carbosilanes by cyclopolymerization of $\mathrm{C_6H_5meHSi{-}CH_2{-}Sime_2{-}CH_2Br}$ *56*, attempts have been made to synthesize the corresponding linear derivatives and to convert them to cyclic compounds.

Compound *53* is suitable for the preparation of chains with four Si atoms. It can easily be obtained in high yields and reacts to form compound *65*.



(47)

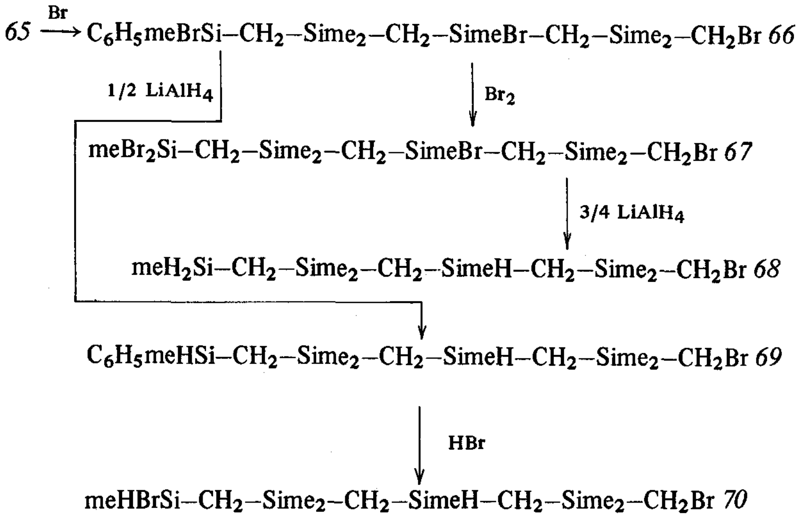
$(C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2Br$ *53*

$\xrightarrow{Br_2}$ $C_6H_5meBrSi{-}CH_2{-}Sime_2{-}CH_2Br$

$\xrightarrow{Li}$ $(C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2Li$ *64*

$$(C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2{-}\underset{\displaystyle C_6H_5}{\underset{|}{Sime}}{-}CH_2{-}Sime_2{-}CH_2Br$$ *65*

After hydrolysis, separation of LiBr, and distilling off the solvent and volatile by-products, compound *65* remains in the residue. In the nmr spectrum of *65* two clearly separated peaks are found for the me_2Si groups. These are due to hindrance of free rotation around the molecular axis caused by the phenyl groups. A complete correlation of all peaks in the nmr spectrum is very difficult. Derivatives were found useful in the determination of the structures, changing the substituents produces a definite chemical shift in the nmr spectra.



65 $\xrightarrow{Br}$ $C_6H_5meBrSi{-}CH_2{-}Sime_2{-}CH_2{-}SimeBr{-}CH_2{-}Sime_2{-}CH_2Br$ *66*

$\xrightarrow{Br_2}$ $meBr_2Si{-}CH_2{-}Sime_2{-}CH_2{-}SimeBr{-}CH_2{-}Sime_2{-}CH_2Br$ *67*

$\xrightarrow{3/4\ LiAlH_4}$ $meH_2Si{-}CH_2{-}Sime_2{-}CH_2{-}SimeH{-}CH_2{-}Sime_2{-}CH_2Br$ *68*

66 + *68*, $1/2\ LiAlH_4$ $\rightarrow$ $C_6H_5meHSi{-}CH_2{-}Sime_2{-}CH_2{-}SimeH{-}CH_2{-}Sime_2{-}CH_2Br$ *69*

$\xrightarrow{HBr}$ $meHBrSi{-}CH_2{-}Sime_2{-}CH_2{-}SimeH{-}CH_2{-}Sime_2{-}CH_2Br$ *70*

Free rotation around the molecular axis is prevented in the left part of the molecule in compound *66*, whereas free rotation occurs in the right part. This is confirmed by the presence in the nmr spectrum of two peaks of the me_2Si group adjacent to the phenyl group, whereas the me_2Si group adjacent to the $BrCH_2Si$ group is represented by an absorption line of doubled intensity. There is free rotation in all other compounds, and the nmr spectra can easily be interpreted.

A phenylation of compound *66* to yield.

$C_6H_5BrmeSi{-}CH_2{-}Sime_2{-}CH_2{-}SimeC_6H_5{-}CH_2{-}Sime_2{-}CH_2Br$ is not successful. The phenylation occurs unspecifically at both BrSi groups.

γ) Synthesis of Si-functional carbosilane chains with six Si atoms. The synthesis of the desired carbosilane *72* starts with compound *65*:

$$\begin{tikzcd}
(C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2{-}Sime(C_6H_5){-}CH_2{-}Sime_2{-}CH_2Br \; 65 \arrow[d, "Li"] \\
(C_6H_5)_2meSi{-}CH_2{-}Sime_2{-}CH_2{-}Sime(C_6H_5){-}CH_2{-}Sime_2{-}CH_2Li \; 71 \arrow[d, "C_6H_5meBrSi{-}CH_2{-}Sime_2{-}CH_2Br"] \\
(C_6H_5)_2meSi{-}CH_2{-}[Sime_2{-}CH_2{-}Sime(C_6H_5){-}CH_2]_2{-}Sime_2{-}CH_2Br \; 72
\end{tikzcd}$$

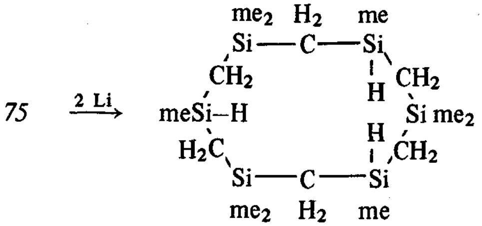
The nmr spectrum of compound *72* shows steric hindrance due to the phenyl group. The spectrum shows therefore six signals of identical intensity for the three me_2Si groups. Identification of meSi groups and $BrCH_2Si$ groups is easily achieved, but formation of derivatives is necessary in order to determine the total structure by nmr-spectroscopy.

$$\begin{tikzcd}
72 \arrow[r, "3\,Br_2"] & C_6H_5meBrSi{-}CH_2[Sime_2{-}CH_2{-}SimeBr{-}CH_2]_2Sime_2{-}CH_2Br \; 73 \arrow[d, "Br_2"] \arrow[ddd, bend right, "LiAlH_4"'] \\
 & meBr_2Si{-}CH_2[Sime_2{-}CH_2{-}SimeBr{-}CH_2]_2Sime_2{-}CH_2Br \; 74 \arrow[d, "LiAlH_4"] \\
 & meH_2Si{-}CH_2[Sime_2{-}CH_2{-}SimeH{-}CH_2]_2Sime_2{-}CH_2Br \; 75 \\
 & C_6H_5meHSi{-}CH_2[Sime_2{-}CH_2{-}SimeH{-}CH_2]_2Sime_2{-}CH_2Br \; 76 \arrow[d, "HBr"] \\
 & meBrHSi{-}CH_2[Sime_2{-}CH_2{-}SimeH{-}CH_2]_2Sime_2{-}CH_2Br \; 77
\end{tikzcd}$$

As free rotation does not occur in the left part of the molecule *73*, two signals arise for the adjacent me_2Si group in the nmr spectrum, whereas the two other me_2Si groups give one signal of double intensity. Compound *75* can be distilled under vacuum without decomposition and is obtained in high purity. By bromination in pentane it forms the pure compound *74*. A controlled phenylation of *73* with C_6H_5MgBr is not possible.

b) Cyclization of $me_2HSi{-}CH_2[Sime_2{-}CH_2{-}SimeH{-}CH_2]_2Sime_2{-}CH_2Br$ *75*

Using our experience in the cyclization of linear carbosilanes having four Si atoms[29)], we carried out reactions (48a).



78 (48a)

After activation of Li with a small amount of CH_3I, the reaction occurs exothermically with slow precipitation of LiH.

Compound *79* is obtained in higher yields than compound *78* (as a hydrogenation product of *75*.

$meH_2Si{-}CH_2[Sime_2{-}CH_2{-}SimeH{-}CH_2]_2Sime_3$ *79*

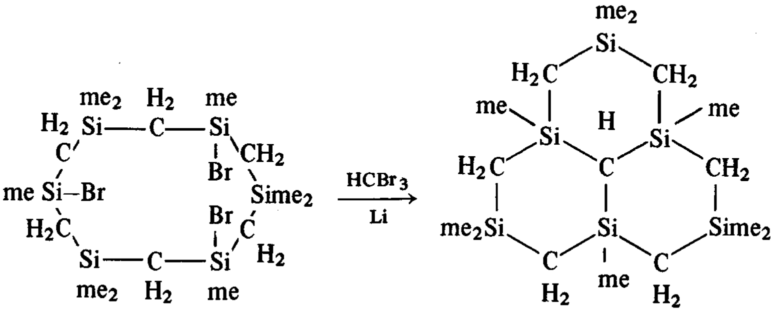
Compounds *78* and *79* can be distilled under vacuum from the reaction mixture. The different chemical properties of the brominated compounds are used for their isolation. By reaction of the mixture of *78* and *79*, compound *45* is formed from *78*, whereas *79* is converted to *80*.

$meBr_2Si{-}CH_2[Sime_2{-}CH_2{-}SimeBr{-}CH_2]_2Sime_3$ *80*

The cyclic compound *45* is only slightly soluble in pentane, while the linear compound does not show any tendency to crystallize. By hydrogenation with $LiAlH_4$, the two Si–H substituted compounds *78* and *79* are produced in good purity and high yields. The Si-brominated 12-membered ring *45* crystallized in fine needles of m.p. 91–93 °C. This is 30 °C below the analogous Si–Br-substituted 8-membered ring *45*. This behavior can be explained in terms of increasing the ring size of *45* which resembles a double chain. Three signals with a relative intensity of 18 : 9 : 12 are expected in the nmr spectrum. However, more unexplained peaks are found. By integration of peaks to groups of peaks, results agree with the postulated values. nmr spectra at 60 and 90 MHz prove that no couplings are present as the shifts have different values. The mass spectrum confirms the general formula.

c) Ring-partition by $CHBr_3$ and Li to Si-methylated 1,3,5,7,9,11-Hexasila-perhydro-phenaline

In the synthesis of the 12-membered ring *45*, 2000 g of $(C_6H_5)_2meSi-CH_2Cl$ was used, and 6.5 g of the Si–Br-substituted ring *45* was obtained. Splitting the 12-membered ring into three combined rings represents the last step in that sequence, which is postulated to occur by reaction with $CHBr_3$ and Li.



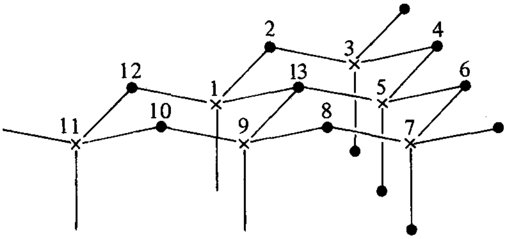
(48b)

39

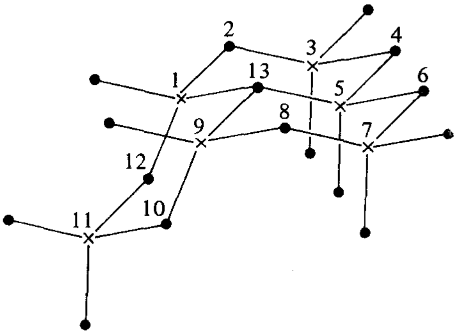
Side reactions (intermolecular condensation forming polymers) have to be considered, since the starting material contains three functional groups. However, they can be minimized by dilution; when the reaction was completed, the solvent was distilled off, and a colorless fraction was obtained by vacuum distillation between 110°–120 °C. White crystals appear in that fraction after some days, but no further separation is achieved by crystallization. Yields were 55%.

d) Isolation of Cis,Trans- and Trans,Trans-Hexasila-perhydrophenaline

In the nmr spectrum of the crystal fraction, two peaks are observed in the $HC(-Si\equiv)_3$ region, which might arise from the two expected isomers of compound *39*. Separation was carried out by gas chromatography (column: 5% silicone resin SG 52(PE) on kieselguhr; 250 °C, 4 m column, ϕ 20 mm, 300 ml/min; helium, 0.2 g was injected per column). A partial separation into two main peaks by cutting off certain regions was observed. The two isomers *39a* and *39b* were separated. Their spectra both show 3 regions of peaks; one for $CH(-Si-)_3$, one for $-Si-CH_2-Si$ and one for the CH_3Si group. The integration correlates with the structure. Many fewer peaks are observed in the CH_3Si region for the trans, trans compound than for the cis, trans compound, due to a high symmetry in the trans, trans molecule.



trans,trans *39b*



cis,trans *39a*

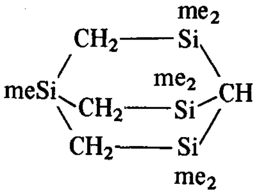
x Si

• C

For the trans,trans compound three signals with identical intensities are expected in the CH_3Si region, whereas in the cis,trans compound six signals should be found with the relative intensity 3 : 3 : 3 : 6 : 6 : 6. All these peaks are observed, confirming the structures of the isomers. Another determination was given by the Si-29-nmr spectrum (with broadline decoupling). The Si atoms 1,5,9 are equivalent, as are also the Si atoms 3,7,11, in the trans,trans compound *39b* and therefore one expects two signals, which are observed indeed at −18.30 ppm and −20.20 ppm (measured in octamethylcyclotetrasiloxane at 17,87 MHz). The cis,trans compound has a plane of symmetry (passing through the atoms 5,13,11 in the sheet plane) which creates two pairs of equivalent (3,7 and 1,9) Si atoms. The Si atoms 5 and 11 differ from these, so four peaks at 20.12 ppm, −18.73 ppm, −19.30 ppm and 20.35 ppm result in the nmr spectrum. Mass spectrometry gives the formula $Si_6C_{16}H_{40}$; cal. M.W. 400.174562; meas. 400.174178, diff. 0.9 ppm. At room temperature, the cis,trans isomer is crystalline, while the trans,trans isomer is a liquid[28].

2. Synthesis of Tetrasila-bicyclo-[2.2.2]-octane *81*

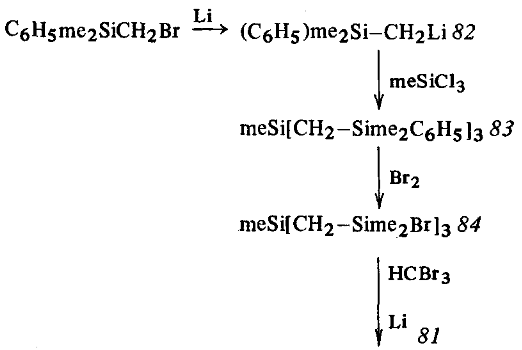
The synthesis of the Si-methylated 1,3,5,7,9,11-hexasila-perhydrophenaline was accomplished by ring partition of the 1,5,9-trihydro-1,3,5,7,9,11-hexasila cyclododecane with $CHBr_3$ and Li[28], whereas the Si-methylated 1,3,5,7,9-pentasila-decaline was obtained by cyclization of the linear $[Brme_2Si{-}CH_2{-}Sime_2{-}CH_2]_2SimeBr$ with $HCBr_3$ and Li[22]. In a similar way, the synthesis of the Si-methylated 1,3,5,8-tetrasila-bicyclo[2.2.2]octane *81* was obtained. This is the first carbosilane representative of that conformation (Barrelan)[31].



81

The synthesis of *81* is accomplished comparatively easily. The synthetic route is shown in Table 9:

Table 9. Synthetic route to compound *81*



$$C_6H_5me_2SiCH_2Br \xrightarrow{Li} (C_6H_5)me_2Si{-}CH_2Li\ \mathit{82}$$

$$\downarrow meSiCl_3$$

$$meSi[CH_2{-}Sime_2C_6H_5]_3\ \mathit{83}$$

$$\downarrow Br_2$$

$$meSi[CH_2{-}Sime_2Br]_3\ \mathit{84}$$

$$\downarrow HCBr_3,\ Li$$

$$\mathit{81}$$

The Li compound *82* is obtained in good yield[9]. It is directly reacted with me$SiCl_3$ to give compound *83*, which is not sufficiently volatile to be distilled off. The nmr spectrum of *83* shows a multiplet in the C_6H_5Si region, two signals in the CH_3Si and a multiplet in the $-Si-CH_2-Si$-region. The two peaks in the CH_3Si region appear with a relative intensity of 9 : 12, which is due to hindered rotation at the $-Si-CH_2-Si$-axis. Therefore the two phenyl groups adjacent to the methyl groups are no longer equivalent and result in two nmr-signals at 9 : 9 intensity. The nmr signal of the remaining $Si-CH_3$ group happens to superimpose on one of the two signals, giving an intensity of 9 : 12 for the $Si-CH_3$ groups. Cleavage of the Si-phenyl group in *83* leads to *84*. The nmr spectrum of *84* shows the three expected signals with a relative intensity of 8 : 3 : 6. The structure of *84* is confirmed by forming meSi[CH_2–SimeH]$_3$ *85* with $LiAlH_4$. This compound gives a nmr spectrum with doublets for the neighbouring $(CH_3)_2Si$ and $Si-CH_2-Si$ groups, a singlet for the CH_3Si and a nonet for the HSi group.

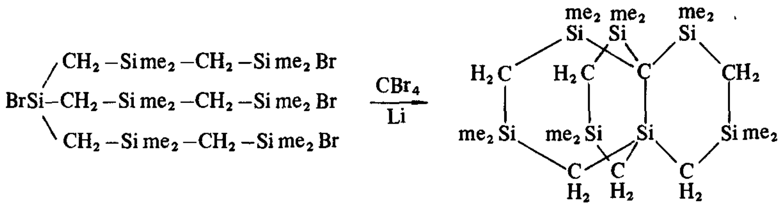
The following double cyclization of *84* with $CHBr_3$ and Li in THF at 0 °C occurs rapidly, and compound *81* is obtained in a 25% yields. Compound *81* can be distilled off (b.p. 125 °C/10 Torr) and crystallizes at room temperature. A better purification is accomplished by gas chromatography (5% silicon resin SE 52. Perkin Elmer on kieselguhr, 4 m column, ϕ 20 mm 160 °C, 300 ml He/min.), m.p. 55–56 °C.

The nmr spectrum of *81* in CCl_4 as the solvent shows only three signals in the CH_3Si-, $-Si-CH_2-Si$- and $(-Si)_3CH$ region with relative intensities of 21 : 6 : 1. However, two signals having an intensity of 18 : 3 should result for the CH_3Si region. These two peaks coincide in CCl_4 solution, whereas the signals occur with the expected intensities in C_6H_6. Mass spectrometry confirms the formula $Si_4C_{11}H_{28}$; cal. 272.126809, meas. 273.126483.

3. Synthesis of Heptasila-[4.4.4]-propellane

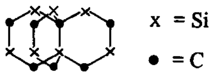
The same synthetic route could be used for the synthesis of 3,3,5,5,7,7,9,9,12,-12,14,14-dodecamethyl-1,3,5,7,9,12,14-heptasila-[4.4.4]-propellane.

The final step in this synthesis is:



The synthesis is based on the preparation of BrSi(CH_2–Sime$_2$–CH_2–Sime$_2$Br)$_3$ which had not previously been synthesized but was thought to be obtainable with present knowledge.

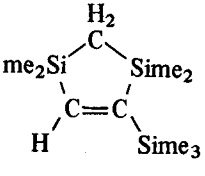
$$\begin{aligned}
&C_6H_5Sime_2{-}CH_2Li\\
&\big\downarrow \; Clme_2Si{-}CH_2Br\\
&C_6H_5Sime_2{-}CH_2{-}Sime_2{-}CH_2Br\\
&\big\downarrow \; Li\\
&C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH_2Li\\
&\big\downarrow \; C_6H_5SiCl_3\\
&C_6H_5Si(CH_2{-}Sime_2{-}CH_2{-}Sime_2C_6H_5)_3\\
&\big\downarrow \; Br_2\\
&BrSi(CH_2{-}Sime_2{-}CH_2{-}Sime_2Br)_3\\
&\big\downarrow \; CCl_4 \mid 8\,Li
\end{aligned}$$



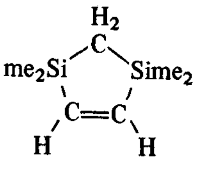
The Si propallane is obtained in low yield (5%, m.p. 203–204 °C). Its structure was confirmed by the nmr and mass spectrometric investigations[32]. The resonances in the nmr spectrum are well defined and it can be concluded that the six-membered rings are present in the chair form.

C. Synthesis of 1,3-Disilacyclopentenes and Related Compounds

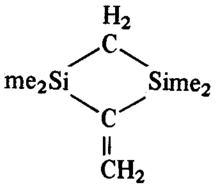
The investigations in the synthesis of this class of carbosilanes also arose from problems in determining the structures of compounds such as *86* *87* and *88* obtained by the pyrolysis of $Sime_4$[33, 34].



86



87



88

I. The Synthesis of 1,3-Disilacyclopentanes

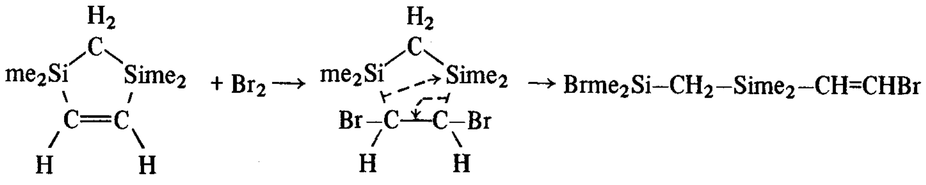
Firstly, some reactions which did not lead to compound *87* are mentioned.

α) The reaction of $Brme_2Si-CH_2-Sime_2Br$ with 1,2-dibromethylene and Mg in diethylether and THF did not yield compound *87*, and *88* was not obtained from $Brme_2Si-CH_2-Sime_2Br$. No reaction was observed with 1,1-dichloroethylene, and the reaction of 1,2-dibromoethylene in THF gave acetylene and $MgBr_2$.

β) $Brme_2Si-CH_2-Sime_2-C\equiv CH$ *132* forms

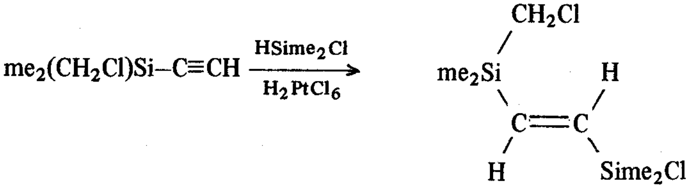
$$Brme_2Si-CH_2-Sime_2-CH{=}CHBr \quad \textit{119}$$

with HBr [by-products: $Brme_2Si-CH_2-Sime_2Br$ and $Brme_2Si-CH_2-Sime_2-CH_2-CHBr_2$ *122*; *119* does not react to a cyclic compound, and is identical with a rearrangement product formed by β-elimination of the brominated product of *87*, compound *102*:



87 *102* *119*

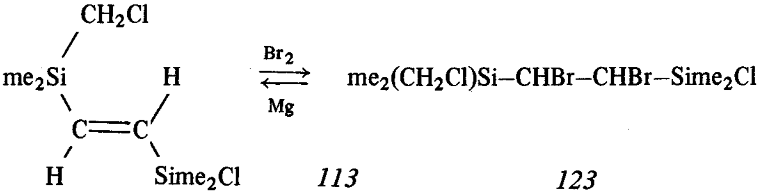
γ) The formation of the trans compound by addition of SiH groups to acetylene in the presence of H_2PtCl_6 is well known[36]. Accordingly, the addition of $HSime_2Cl$ to *133* gives the trans compound *113*.



$$me_2(CH_2Cl)Si-C\equiv CH \xrightarrow[H_2PtCl_6]{HSime_2Cl} \qquad (50)$$

133 *113*

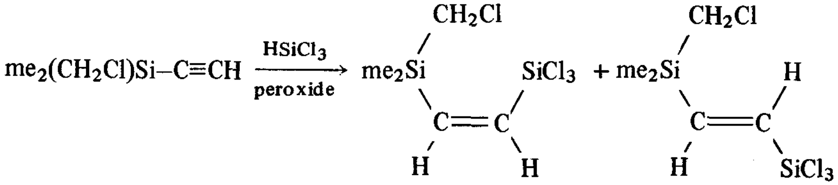
It was intended to achieve a free rotation in the molecule formed from *113* by addition of Br_2, followed by a cyclization step with Mg and subsequent removal of bromine to yield a double bond in the ring system. Though Br_2 is added to *113* [reaction (51)], this route is not successful since the trans compound *115* is regenerated from *123* with Mg, and no cyclization occurs.



$$\underset{Mg}{\overset{Br_2}{\rightleftarrows}} me_2(CH_2Cl)Si-CHBr-CHBr-Sime_2Cl \qquad (51)$$

113 *123*

σ) The addition of $HSiCl_3$ to an acetylene group in reaction (52) gives the cis and trans compounds in a 4 : 1 ratio, though no cyclization can be accomplished as the reactivity of the CH_2Cl group with either Mg or Li is not sufficiently high.



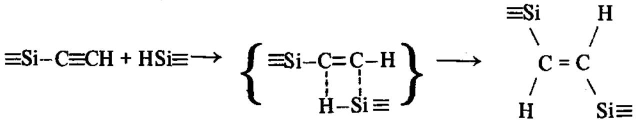
133 *110* 4 : 1 *111*

(52)

The distinction between the cis and trans compounds was made by nmr measurements (determination of the coupling constants in the AB spectra of the vinyl groups). The low reactivity of the CH_2Cl group must be due to the influence of the C=C double bond, since the saturated compound $me_2(CH_2Cl)Si{-}CH_2{-}CH_2{-}SiCl_3$ *135* reacts with Mg to give the cyclic compound *91*.

For further experiments the CH_2Br group was used, as it shows much more reactivity. In contrast to reaction (52), however, the addition of $HSiCl_3$ to $me_2(CH_2Br)SiC \equiv CH$ *134* in presence of benzoylperoxide leads only to the trans$-me_2(CH_2Br)Si{-}CH{=}CH{-}SiCl_3$ *112*. The identity of *112* formed in this reaction was confirmed by comparison with the pmr spectra of compound *112* synthesized with H_2PtCl_6[35].

These attempts to synthesize five-membered ring system failed due to the low reactivity of the CH_2Cl group or the formation of unsuitable isomeric trans compounds. The addition of the SiH group to a C≡CH group occurs as a "cis" addition when catalysts of group-VIII elements are present[37]; a trans olefine subsequently formed:

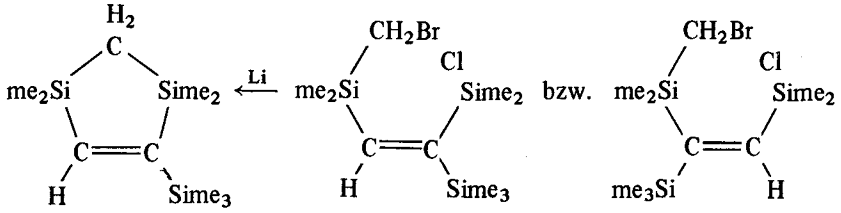


(53)

A suitable starting material for the cyclization should be obtained by applying an acetylene group with an attached Si-functional group, when addition of a HSi group occurs in the correct steric position, i.e. in cis position. Reaction (54) shows the synthetic route leading to the five-membered ring *86*.

$$\begin{tikzcd}
me_2(CH_2Br)Si{-}C{\equiv}CH \arrow[r, "C_2H_5MgBr"] & me_2(CH_2Br)Si{-}C{\equiv}C{-}MgBr + C_2H_6 \arrow[d, "me_2SiCl_2"] \\
& me_2(CH_2Br)Si{-}C{\equiv}C{-}Sime_2Cl\ \mathit{126} \arrow[d, "HSime_3"] \\
& {}
\end{tikzcd}$$

(54)

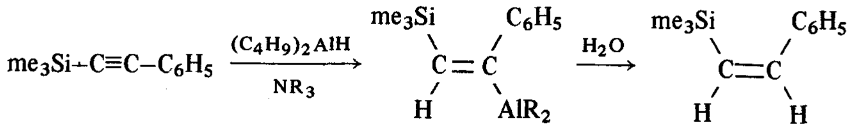


86 116

The cyclization in ether is effected by using Li; Mg does not react. The high reactivity of the CH_2Br group adjacent to a double bond towards Li is also observed in the formation of the four-membered ring *88*. The structure of *86* is determined by nmr and mass spectra. In the nmr spectrum, 5 peaks (−20.5 Hz; 4.0 Hz; 6.0 Hz; 10.0 Hz and 451 Hz) are observed with the relative intensities 2 : 9 : 6 : 6 : 1. The coupling constant (J Si–29-C-H) of the bridging CH_2 groups at −20.5 Hz is 6.6 Hz; this confirms the ring size[1]. The signal of the vinylic protons at 451 Hz has two pairs of satellites with the coupling constants $J_1 = 13.6$ Hz and $J_2 = 22.9$ Hz (rel. intensity 2 : 1). Thus, at least three different ^{29}Si atoms are coupling with the vinyl-proton. In the more intensive pair of satellites (J_1), the coupling of the cis and geminal Si^{29} presumably superimpose. The trans ^{29}Si atom causes the less intensive satellite coupling with a higher coupling constant (J_2). The molecular peak for $Si_3C_{10}H_{24}$ in the mass spectrum is found to be 228.11846322 (cal. 228.118581, diff. 0.6 ppm). An absorption line appears at 1480 cm^{-1} (C = C valence vibration in the Raman spectrum. This line was not observed in the ir spectrum.

To obtain compound *87* from *86*, the $Sime_3$ group should be replaced by hydrogen. In view of the reaction of *87* with HBr or Br_2 cleavage of *86* by HBr to form *87* was not expected to occur[34]. This was confirmed experimentally[39].

The synthesis of *86* in reaction (54) implies that preparation of *87* requires a reagent which adds to the acetylenic compound *126* and then can be substituted with formation of a CH group. It is known from the pure carbon acetylenes that R_2AlH adds to the C≡C bond and that cis-olefines are formed after hydrolysis. This reaction was tried using trimethylsilylphenyl acetylene[40].

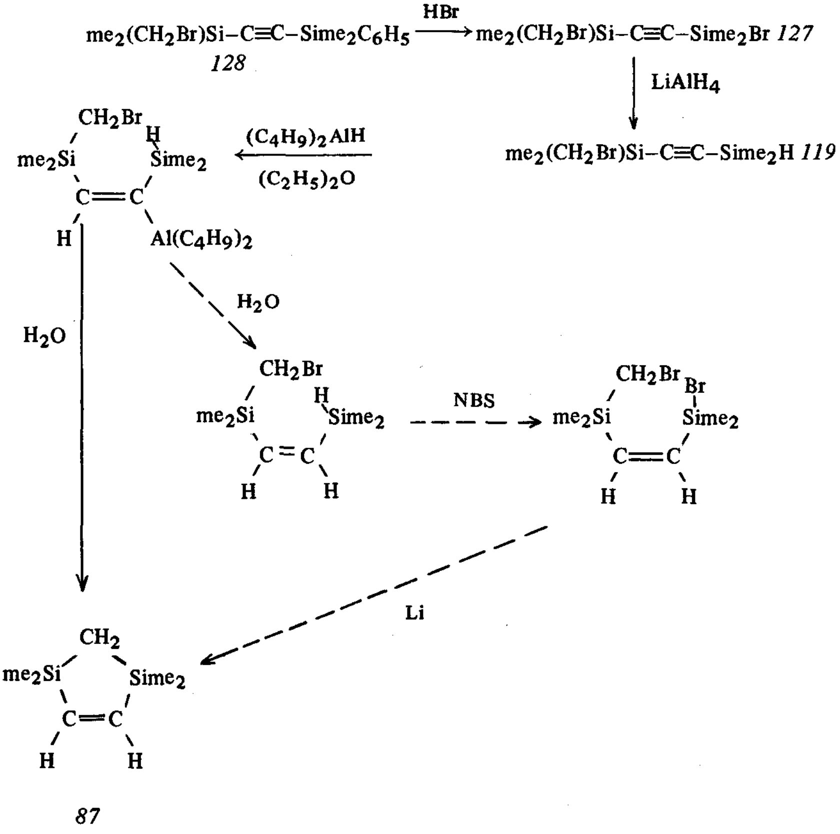


(55)

The application of this procedure to such disilylacetylenes as $me_2(CH_2Br)Si-C\equiv C-Sime_2H$ leads to a suitable starting compound for the synthesis of the five-membered ring *87*, diethylether being used instead of a tertiary amine.

The Si group can be converted into the SiBr group by N-bromsuccinimide[41)] without attacking the C = C double bond. A SiBr-functional group can be thereby obtained for cyclization. The synthetic route is given in Table 10.

Table 10



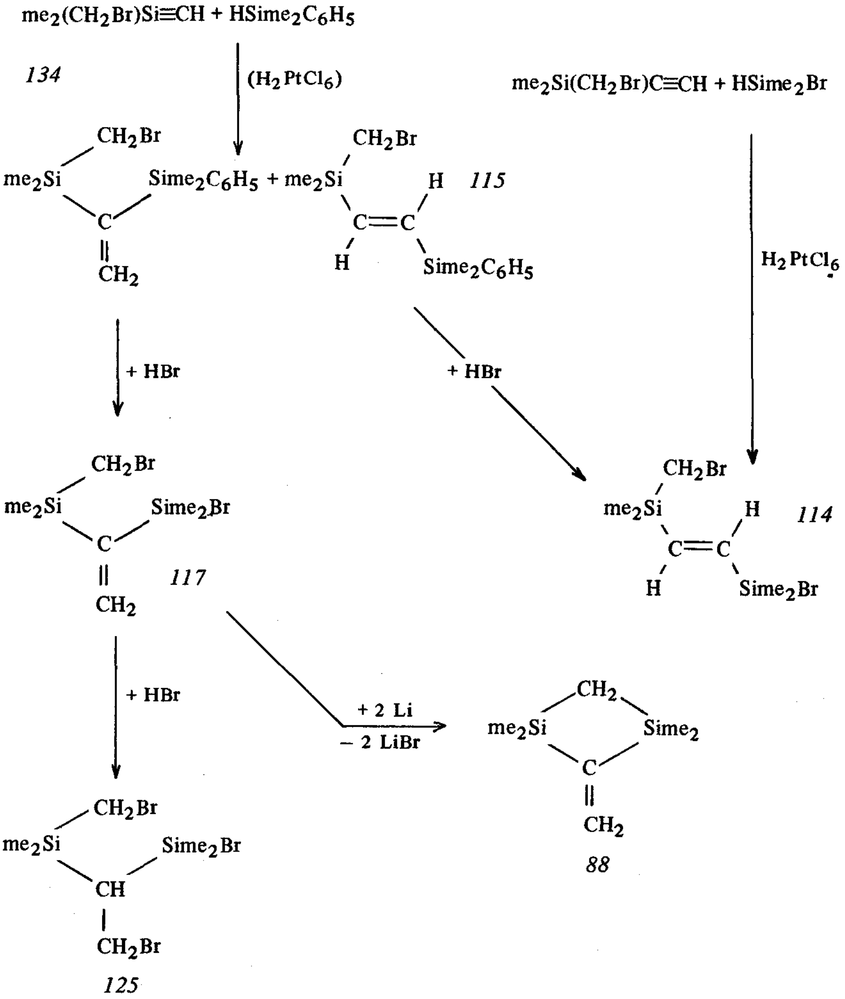
1,1,3,3-Tetramethyl-1,3-disilacyclopentane *89* was obtained by the hydrolysis of the Al compound. Addition of R_2AlH to the acetylenic group must therefore lead to the cis-olefine compound besides other products. Only compound *89* conform the five-membered ring; *87* was obtained in about 40% yield.

II. Synthesis of 1,1,3,3-Tetramethyl-1,3-disila-2(methylene)-cyclobutane

The synthesis of the four-membered ring *88* results from the addition of $C_6H_5me_2SiH$ to $me_2(CH_2Br)Si–C≡CH$, as the 1,1-disilylethylene-derivative

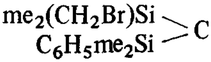
118 is also formed besides the 1,2-disilylethylene-derivative *115*. In both compounds the Si-phenyl groups can be transformed into the SiBr group with little addition to the C=C bond provided the reaction is carried out with due care (−78 °C). Addition occur to same extent addition with the 1,1 compound *118*. A Cyclization occurs with the 1,1 compound *117* in contrast to the 1,2 compound *114*. Table 11 shows the synthetic route and contains the reactions of the two possible addition products used for identification.

Table 11. Synthetic route for 1,1,3,3-Tetramethyl-1,3-disila-2(methylene)-cyclobutane



1. Addition of $C_6H_5me_2SiH$ to $me_2(CH_2Br)Si{-}C{\equiv}CH$

The addition of $C_6H_5me_2SiH$ in presence of $H_2PtCl_6 \cdot 6\,H_2O$ should give trans-$me_2(CH_2Br)Si{-}CH = CHSime_2C_6H_5$ in high purity (analogous to reaction 50). However, the nmr spectrum shows two different groups of signals in the region of the vinyl protons, a doublet at 406.5 Hz and a singlet at 383.5 Hz, indicating that two different addition products were formed. The formation of cis-$me_2(CH_2Br)Si{-}CH = CH{-}Sime_2C_6H_5$ can be excluded when H_2PtCl_6 is used. Besides trans-$me_2(CH_2Br)Si{-}CH{=}CH{-}Sime_2C_6H_5$ (30),

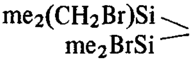


$\left.\begin{matrix} me_2(CH_2Br)Si \\ C_6H_5me_2Si \end{matrix}\right\rangle C = CH_2$ *118* was also formed (see Table 11).

The yields were determined as *118* : 57%, *115* : 43% by integration of the vinyl proton resonance in the nmr spectrum.

2. Reaction of the Addition Products with HBr

The formation of the compounds *118* and *115* ought to be confirmed by a reaction with HBr, and trans-$me_2(CH_2Br)Si{-}CH{=}CH{-}Sime_2Br$ *114* and



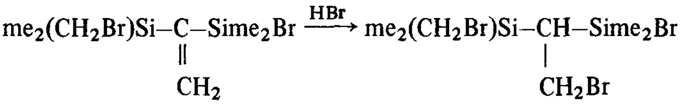
$\left.\begin{matrix} me_2(CH_2Br)Si \\ me_2BrSi \end{matrix}\right\rangle C = CH_2$ *117* should be prepared.

Besides the cleavage of the Si-phenylgroup, addition of HBr to the double bond is expected (reactions 56 and 57).

trans-$me_2(CH_2Br)Si{-}CH{=}CH{-}Sime_2Br$ *114*

$$\Big\downarrow \text{HBr}$$

$me_2(CH_2Br)Si{-}CH_2{-}CHBr{-}Sime_2Br$ or $me_2(CH_2Br)Si{-}CHBr{-}CH_2{-}Sime_2Br$ (56)



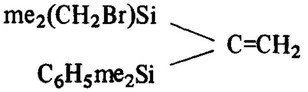
$$\underset{\underset{CH_2}{\|}}{me_2(CH_2Br)Si{-}C{-}Sime_2Br} \xrightarrow{HBr} \underset{\underset{CH_2Br}{|}}{me_2(CH_2Br)Si{-}CH{-}Sime_2Br} \qquad (57)$$

117 *125*

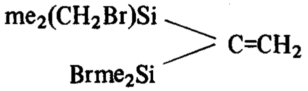
Rreactions were therefore carried out with 1 mol HBr under mild conditions. AX_2 spectra for the $-CH_2{-}CHBr$ and $=CH{-}CH_2Br$ groups should result from the addition products, as the chemical shift of the CHBr protons must be much higher than that of the C*H*protons. In the addition products resulting from reaction (50) the doublet is expected to appear at higher field and the triplet at lower field. In the case of compound *125* the resonance of the doublet and triplet are changed.

The reaction with HBr was carried out in a bomb tube at −78 °C without solvent. In the nmr-spectrum of the reaction products with 1 ml HBr the doublet in the phenylmoiety resulting from the starting material had disappeared.

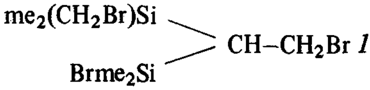
A new single peak resonance appearing almost the same frequency (404.5 Hz) is due to the vinyl protons of *114*. The pure substance was synthesized by addition of $Brme_2SiH$ to $me_2Si(CH_2Br)C{\equiv}CH$ in presence of H_2PtCl_6, and the AB spectrum was found at 386 Hz. It is superimposed on a singlet which was observed in the starting material. Besides that a triplet is found at 75.5 Hz (high-field) and a doublet at 220 Hz (low-field) with identical coupling constants (J = 6.2 Hz) attributable to the $=CH{-}CH_2Br$ group. It can therefore be concluded that in the starting compound spectrum the singlet at 383.5 Hz is assignable to



In the reaction with 1 mol HBr the phenyl group was cleaved to a large extent, forming



which partly reacts with HBr (by reaction 57) and leaving a corresponding amount of starting material *118* unreacted. However, cleavage of the Si-phenyl group has gone to completion with the trans compound *115*. It cannot be decided from the nmr spectrum whether or not the addition of HBr to the double bond has already occured. It differs very much from the cis compound in which the addition of HBr to the double bond is greatly preferred to the cleavage of the phenyl group. The reaction with 2 moles HBr was carried out under identical conditions and confirmed the results. The starting materials have undergone complete cleavage of the phenyl group. The C=C double bonds have undergone HBr addition to a very high degree.



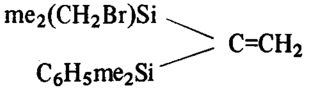
125

was obtained as a main product. It cannot be definitely stated whether the addition of HBr to form the trans compound has occured according the reaction (56).

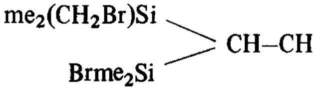
3. Cyclization to 1,1,3,3-Tetramethyl-1,3-disila-2(methylene)-cyclobutane

In the reaction of the addition products of $me_2(CH_2Br)Si{-}C{\equiv}CH$ and $HSime_2C_6H_5$ (see Table 11) with 1 mol HBr at −78 °C, benzene and a mixture of the compounds below are obtained:

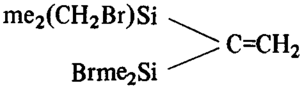
trans-$me_2(CH_2Br)Si{-}CH{=}CH{-}Sime_2Br$ *114*



118

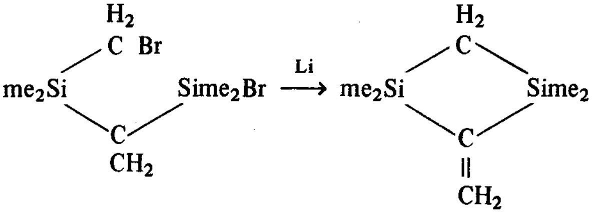


125



117

Because of the synthesis of the four-membered ring having an exocyclic vinyl group *88*, the compound *117* is of special interest:



88

(58)

This compound was used for the cyclization because of the reactivity of the CH_2Br group towards Li.

In this reaction two Si compounds are obtained which are more volatile than the starting material. The nmr resonances at –25 Hz, 4.0 Hz and 39 Hz are assigned to $Si_2C_7H_{18}$ (1,1,3,3-tetra-methyl-1,3-disilacyclopentane *89*, which can also be synthesized in a different procedure (see Section 4). The signal intensities at 1.5 Hz, 12 Hz and 370 Hz are in a 2 : 12 : 2 ratio and represent the three different proton groups of the four-membered ring *88*. The coupling constants of the Si-29 atoms and bridging CH_2 protons cannot be clearly observed as the satellite on the left-hand side of the resonance line is superimposed upon the Si-methyl resonance of the saturated five-membered ring, so bearing in mind this restriction, the coupling constant is given as J = 6.1 Hz. It confirms the ring size of the synthesized molecule. The Si-29 satellites of the vinyl protons at 370 Hz (2 signals with identical intensity) on both sides of the main line (intensive middle line of AB spectrum) are part of an ABX spectrum. According to the integrated nmr spectrum the reaction mixture comprises 65% of the four-membered ring *88* and 35% of the saturated five-membered ring *89*. The mass spectrum confirms the presence of the molecules $Si_2C_7H_{16}$ *88* and $Si_2C_7H_{18}$ *89*. (Exact mass determination: $Si_2C_7H_{16}$: meas. 156.07893757, calc. 156.0790954, difference 0.2 ppm; $Si_2C_7H_{18}$: meas. 158.0937409, calc. 156.094704, difference 0.6 ppm.) The line at 1620 cm^{-1}

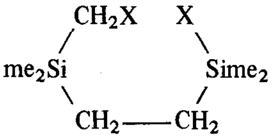
in the ir spectrum can be assigned to the C=C valence vibration of the exocyclic double bond.

It was not possible to separate the mixture by gas chromatography as the four-membered ring *88* decomposes during that procedure. This agrees with the results of investigations on the stability of cyclic carbosilanes. No specifications can so far be given for the formation of 1,1,3,3-tetramethyl-1,3-disilacyclopentane *89*.

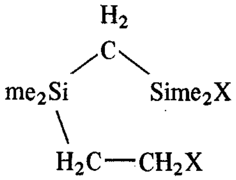
III. Synthesis of 1,3-Disilacyclopentanes

1. 1,1,3,3-Tetramethyl-1,3-disilacyclopentane *89*

Not very much had so far been reported on the 1,3-disilacyclopentanes. Small amounts of 1.1.3.3-tetramethyl-1,3-disilacyclopentane were found in the products of the pyrolysis of tetramethylsilane[33)] and trimethylsilane[42)]. Furthermore, 1,1,3,3-tetramethyl (or tetraphenyl-)-2-methyl-1,3-disilacyclopentane is obtained in low yields by the reaction of $HR_2SiCH = CH_2$ ($R = CH_3$ and C_6H_5) at platinum contacts[43)]. According to the results of the synthesis of the 1,3-disila-pentanes *86* and *87* two cyclization reactions are expected to be suitable for the synthesis of 1,1,3,3-tetramethyl-1,3-disilacyclopentane a and b



(a)



(b)

Both reactions require the removal of the halogen atom by Li or Mg. Compound

$$me_2(CH_2X)Si{-}CH_2{-}CH_2{-}Sime_2Br \ (X = Cl, Br)$$

is needed for route (a), compound

$$Brme_2Si{-}CH_2{-}Sime_2{-}CH_2{-}CH_2Br \ \mathit{121} \text{ for route (b).}$$

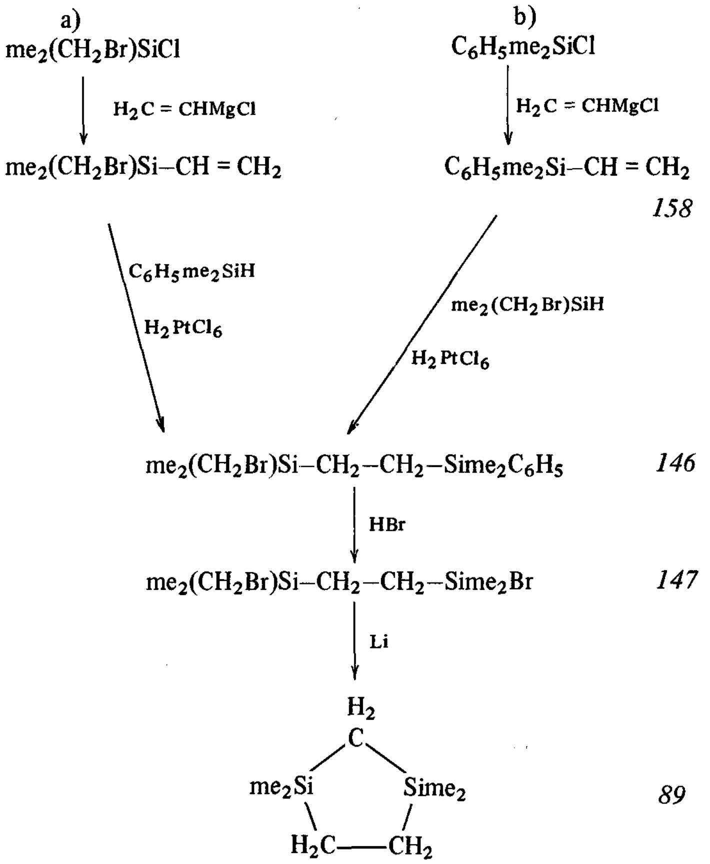
The synthetic route (b) first seemed to be easier, as

$$C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH = CH_2 \ \mathit{120}$$

is readily obtained from $Clme_2SiCH{=}CH_2$ and $C_6H_5me_2SiCH_2Li$. The cleavage of the phenyl groups and the addition to the double bond occur simultaneously upon treatment with HBr at −78 °C, so compound *121* is found with benzene and $Brme_2Si{-}CH_2{-}Sime_2Br$ (by β elimination) in the reaction mixture. *121* reacts with Li in ether (not with Mg) undergoing cyclization, though, this route is less suitable for the synthesis of *89* due to side reactions.

The synthesis was eventually carried out by route (a).

Table 12. Synthetic route for 1,1,3,3-tetramethyl-1,3-disilacyclopentane



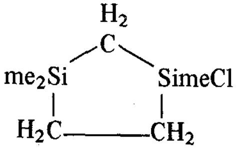
Route a) and b) only differ in the preparation of compound *146*. No side reactions occur in the sequence via compound *158*. 1,1,3,3-tetramethyl-1,3-disila-cyclopentane *89* is obtained in 89% yield. The synthesis of *89* can also be achieved with $me_2(CH_2Cl)SiCH_2{-}CH_2{-}Sime_2Br$ *144* which is prepared as in Table 12 from $me_2(CH_2Cl)SiCH{=}CH_2$. Cyclization of the CH_2Br compound *147* works better with Li, whereas the CH_2Cl compound *114* reacts more easily with Mg. *147* also forms the cyclic compound with Mg (in a slow reaction); in the reaction of the CH_2Cl compound *144* with Li, extensive side reactions are observed.

The structure of *89* is confirmed by elemental analysis, molecular weight determination. nmr and mass spectrometry[39]. The nmr spectrum is consistent with three resonances (at −24.8 Hz; 4.0 Hz; 40.0 Hz) having a relative intensity of 2 : 12 : 4 and due to the three kinds of protons in *89*. The high-field shift is characteristic of the methylene bridging $Si{-}CH_2{-}Si$ group, and the coupling constant value $J_{^{29}Si-CH_2} = 6.75$ Hz is typical of a five-membered ring as was shown in earlier investigations[1].

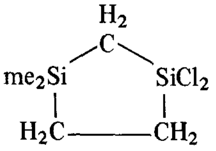
2. Synthesis of Si-functional Derivatives of 1,1,3,3-Tetramethyl-1,3-disilacyclopentane

a) Synthetic Route and Formation of Intermediates

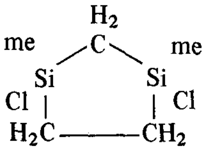
The synthesis of the Si-functional derivatives of *89* can be accomplished in a similar way. All the Si–Cl-containing derivatives of 1,3-disilacyclopentane were obtained[39]:



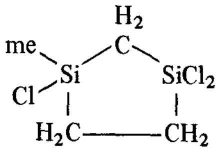
90



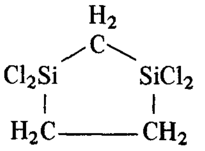
91



92 cis
93 trans

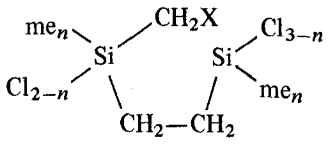


94



95

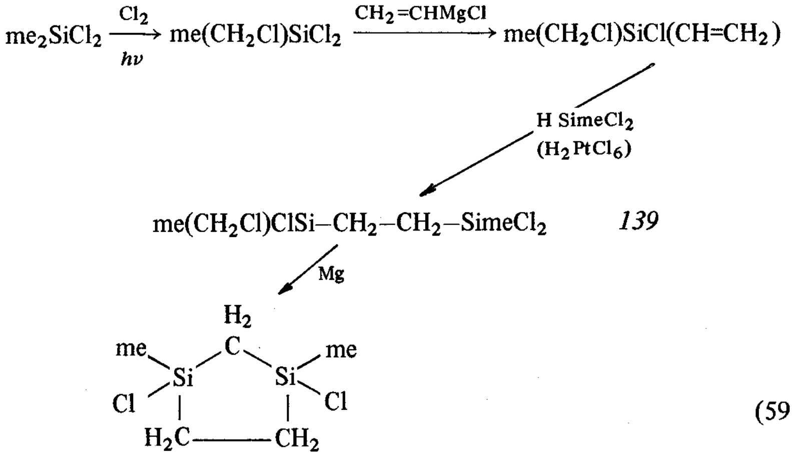
Starting materials of the general formula (c) are needed for the cyclization



(c)

$n = 0, 1, 2$
$X = Cl, Br$

The general synthetic route for compound *92* is shown below.



139

(59)

92 *93*

The halogen methyl-chlorosilanes were prepared by photochlorination or photobromination of methylchlorosilanes. The compounds

$me_2(CH_2Cl)SiCl$, $me(CH_2Cl)SiCl_2$ and
$(CH_2Cl)SiCl_3$

are obtained in high yield by a vapor-phase photochlorination of me_3SiCl, me_2SiCl_2 and $meSiCl_3$. Photobromination of me_3SiCl in the vapore-phase leads to $me_2(CH_2Br)SiCl$; me_2SiCl_2 reacts slowly to $me_2(CH_2Br)SiCl$ whereas no bromination occurs with $meSiCl_3$. Thus, the following compounds were available:

$me_2(CH_2Cl)SiCl$, $me_2(CH_2Br)SiCl$, $me(CH_2Cl)SiCl_2$ and $(CH_2Cl)SiCl_3$.

The halogen methylvinylsilanes are obtainable from these compounds with

$CH_2{=}CHMgCl$, $me_2(CH_2Cl)SiCl$ and
$me_2(CH_2Br)SiCl$ provide
$me_2(CH_2Cl)SiCH{=}CH_2$ *151*
and $me_2(CH_2Br)SiCH{=}CH_2$.

Vinylation of $(CH_2Cl)SiCl_2$ and Cl_3SiCH_2Cl leads to a similar yield of all possible substitution products, even when the reaction is carried out under ice-cooling and a large excess of the chlorosilane is applied. $me(CH_2Cl)SiCl_2$ forms

$$\mathrm{me(CH_2Cl)SiCl(CH{=}CH_2)}\ \mathit{152}\ \text{and}$$
$$\mathrm{me(CH_2Cl)Si(CH{=}CH_2)_2}\ \mathit{153};$$

$(CH_2Cl)SiCl_3$ reacts to $(CH_2Cl)SiCl_2(CH{=}CH_2)$ *154*, $(CH_2Cl)SiCl(CH{=}CH_2)_2$ *155* and $(CH_2Cl)Si(CH{=}CH_2)_3$ *156*. The formation of compound $(CH_2Cl)SiCl_2(CH{=}CH_2)$ predominates in the reaction of Cl_3SiCH_2Cl with $CH_2{=}CHMgCl$ (at −78 °C) (39).

Separation of the reaction mixture by distillation is difficult as these compounds have only slightly different boiling points. Though, the starting materials could be distilled off, concentration not was possible for the respective vinylsilanes, so mixtures were used for further reactions. Identification of the vinylsilanes was effected via the nmr spectrum of the reaction mixture from the characteristic ABC multiplets due to the vinyl groups[39)].

The addition of $HSiCl_3$ or $HSimeCl_3$ to

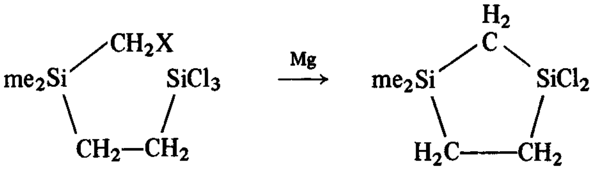
$$\mathrm{me(CH_2Br)SiCH{=}CH_2,\ me_2(CH_2Cl)SiCH{=}CH_2,}$$
$$\mathrm{me(CH_2Cl)Si(CH{=}CH_2)Cl\ and\ (CH_2Cl)Si(CH{=}CH_2)Cl_2}$$

in presence of $H_2PtCl_6 . 6\ H_2O$ leads to Si- and C-functional carbosilanes which give cyclization reactions yielding the five-membered rings *90* to *95*. As the two latter vinylsilanes cannot be separated from other vinyl compounds, addition products are formed and these cannot be used for cyclization. Reaction (60) lists the addition products, which either are obtained pure or can be separated by distillation.

$$\begin{array}{l}
\mathrm{me_2(CH_2Br)SiCH{=}CH_2 + HSiCl_3 \longrightarrow me_2(CH_2Br)SiCH_2CH_2SiCl_3}\ \mathit{145} \longrightarrow \mathit{91}\\
\mathrm{me_2(CH_2Cl)SiCH{=}CH_2 + HSiCl_3 \longrightarrow me_2(CH_2Cl)SiCH_2CH_2SiCl_3}\ \mathit{135} \longrightarrow \mathit{91}\\
\mathrm{me_2(CH_2Cl)SiCH{=}CH_2 + HSimeCl_2 \longrightarrow me_2(CH_2Cl)SiCH_2CH_2SimeCl_2}\ \mathit{136} \longrightarrow \mathit{90}\\
\mathrm{meCl(CH_2Cl)SiCH{=}CH_2 + HSiCl_3 \longrightarrow meCl(CH_2Cl)SiCH_2CH_2SiCl_3}\ \mathit{137} \longrightarrow \mathit{94}\\
\mathrm{me(CH_2Cl)Si(CH{=}CH_2)_2 + 2\ HSiCl_3 \longrightarrow me(CH_2Cl)Si(CH_2CH_2SiCl_3)_2}\ \mathit{138}\\
\mathrm{meCl(CH_2Cl)SiCH{=}CH_2 + HSimeCl_2 \longrightarrow meCl(CH_2Cl)SiCH_2CH_2SimeCl_2}\\
\hfill \mathit{139} \longrightarrow \mathit{92, 93}\\
\mathrm{me(CH_2Cl)Si(CH{=}CH_2)_2 + 2\ HSimeCl_2 \longrightarrow me(CH_2Cl)Si(CH_2CH_2SimeCl_2)_2}\ \mathit{140}\\
\mathrm{Cl_2(CH_2Cl)SiCH{=}CH_2 + HSiCl_3 \longrightarrow Cl_2(CH_2Cl)Si{-}CH_2{-}CH_2{-}SiCl_3}\ \mathit{141} \longrightarrow \mathit{95}\\
\mathrm{Cl(CH_2Cl)Si(CH{=}CH_2)_2 + 2\ HSiCl_3 \longrightarrow Cl(CH_2Cl)Si(CH_2{-}CH_2{-}SiCl_3)_2}\ \mathit{142}
\end{array} \qquad (60)$$

These products are identified by their nmr spectra[39)]. For most of these compounds characteristic A_2B_2 spectra are obtained for the $SiCH_2{-}CH_2{-}Si$ protons. For the compound $meCl(CH_2Cl)Si{-}CH_2{-}CH_2SimeCl_2$ *139*, only a broad singlet is found.

The compounds *135–137, 139, 141* and *145* listed under (60) react easily with Mg to form five-membered rings. In contrast to *147*, the compound $me_2(CH_2Br)Si{-}CH_2{-}CH_2{-}SiCl_3$ does not react with Li but only with Mg:



(X = Cl, Br) (61)

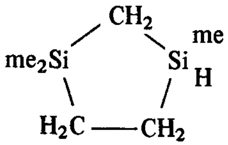
91

No particular difference in the reactivity of the CH_2Cl and CH_2Br groups is apparent here. In contrast to reaction (61), no cyclization occurs with cis-$me_2Si(CH_2Cl)CH{=}CH{-}SiCl_3$ with either Li or Mg.

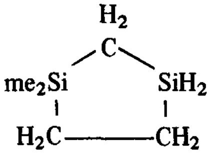
92/93 is found in a cis and trans conformation, as expected (distinguished by the nmr spectrum). The trans conformation *93* is obtained in higher yield.

b) Hydrogenation of the SiCl-containing 1,3-Disilacyclopentanes (SiH-containing Derivatives)

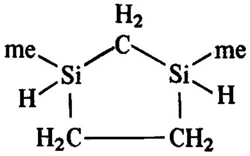
Hydrogenation of SiCl groups in carbosilanes can be accomplished by $LiAlH_4$ to form SiH groups without any changes in the molecular framework[44]. The reduction is carried out with an excess of $LiAlH_4$ in ether under ice-cooling. No cleavage is observed in this procedure and the compounds *96* to *101* are obtained[39].



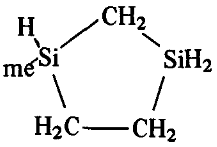
96



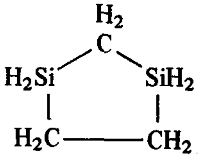
97



98 cis
99 trans



100



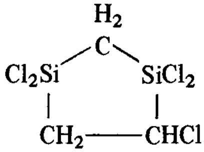
101

The work-up of the reaction mixtures is carried out by fractional condensation without prior acidic hydrolysis. Difficulties occur only in separation of the ether from compound *100*. The hydrogenated ring compounds can be separated by gas chromatography on Sterchamol/Silicon oil, *e.g.* Compound *97* which was separated from a mixture with $me_2(CH_2Cl)Si{-}CH_2{-}CH_2{-}CH_2{-}SiCl_3$.

The nmr spectra of 1,3-disilacyclopentanes show higher bond orders. In all cases, the structures were confirmed by their characteristic spectra$^{39)}$.

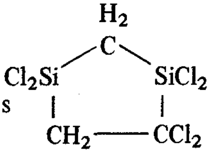
c) Synthesis of CCl-containing Derivatives of 1,1,3,3-Tetrachloro-1,3-disilacyclopentane and 1,1,3,3-Tetrachloro-1,3-disilacyclopentene

Since the reactions of 1,1,3,3-tetramethyl-1,3-disilacyclopentene *87* with Br_2 and HBr (34) and the rearrangement of the addition product *102* involving β-elimination were studied, there has been special interest in the synthesis of stable C-chlorinated derivatives of 1,3-disilacyclopentane in order to obtain derivatives of 1,3-disila-cyclopentene by substitution for Cl at the C atom. Synthesis of C-chlorinated derivatives of 1,3-disila cyclopentane was also desirable in view of the reactions of $(Cl_2Si{-}CCl_2)_3$ with $CH_3MgCl^{45)}$. Chlorination of 1,1,3,3-tetrachloro-1,3-disilacyclopentane *95* was first investigated: this compound can be obtained in 80% yield from $Cl_2(CH_2Cl)Si{-}CH_2{-}CH_2{-}SiCl_3$ with Mg and does not have methyl groups attached to the S atoms, which can thus form additional by-products on chlorination. On chlorination of *95*, 17 different C-chlorinated compounds could be formed. Reaction of *95* with SO_2Cl_2 (in presence of dibenzoylperoxide) leads to



103

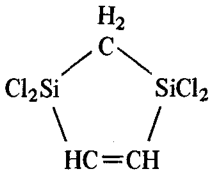
as a main product besides



104

and other chlorinated compounds.

103 and *104* are thermally stable compounds and can be distilled without decomposition, whereas the corresponding $Si{-}CH_3$ compounds (reaction of *87*



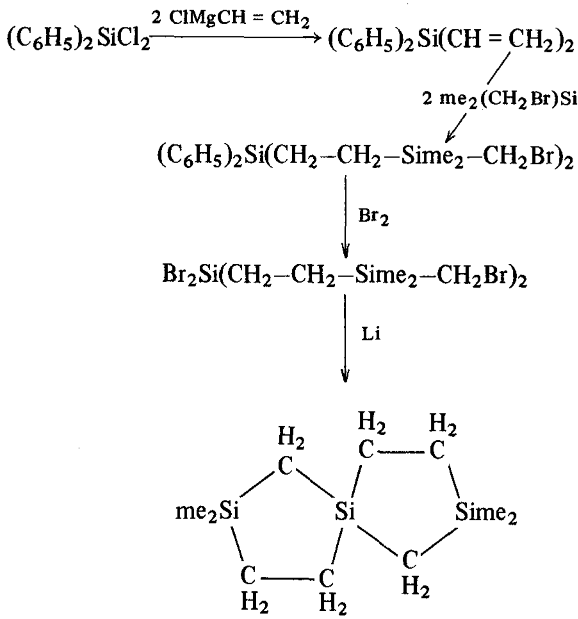
105

with HBr or Br_2) undergo rearrangement and cleavage of the ring. HCl is removed from *103* by N-methylpyrrolidine and compound *105* is formed without side reactions. A synthetic route is thus afforded for SiCl-containing 1,3-disilacyclopentenes. Compound *104*, which could not be separated, forms 1,1,3,3,4-pentachloro-1,3-disilapentene.

105 is methylated by CH_3MgI to 1,1,3,3-tetramethyl-1,3-disilacyclopentene *87*, confirming the structure of *105*[39].

IV. Synthesis of a Spiro-carbosilane

The addition of $me_2(CH_2Br)SiH$ to $C_6H_5me_2Si{-}CH{=}CH_2$ yielding $C_6H_5me_2Si{-}CH_2{-}Sime_2(CH_2Br)$ *146* formed an important step in the synthesis of 1,1,3,3-tetramethyl-1,3-disilacyclopentane. By using $(C_6H_5)_2Si(CH{=}CH_2)_2$ *159* as a starting material, the synthesis of the spirane *106* is accomplished in a double cyclization reaction, reaction (61a):



$$(C_6H_5)_2SiCl_2 \xrightarrow{2\ ClMgCH=CH_2} (C_6H_5)_2Si(CH=CH_2)_2$$ *159*

$2\ me_2(CH_2Br)SiH$

$$(C_6H_5)_2Si(CH_2{-}CH_2{-}Sime_2{-}CH_2Br)_2$$ *148*

Br_2

$$Br_2Si(CH_2{-}CH_2{-}Sime_2{-}CH_2Br)_2$$ *150*

Li

(61a)

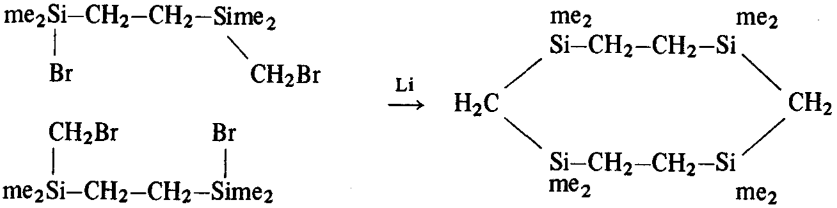
106

$(C_6H_5)_2SiCl_2$ reacts with 2 moles of $ClMgCH{=}CH_2$ to give $(C_6H_5)_2Si(CH{=}CH_2)_2$ *159* in high yield. The addition of $me_2(CH_2Br)SiH$ to the C=C group of *159* occurs in the presence of $H_2PtCl_6 \cdot 6\ H_2O$. The formation of the $Si{-}CH_2{-}CH_2{-}Si$ group can be inferred from a symmetric A_2B_2 multiplet in the Si-methyl region in the nmr spectrum[39]. Compound *148* is separated by distillation from unidentified by-products and determined by its nmr spectrum.

Successive cleavage of the phenyl groups in *148* occurs with Br_2. In CCl_4 solution, the cleavage of one phenyl group is favored. Bromine has to be applied in the absence of a solvent to cleave the second phenyl group. The cyclization step to the spirane *106* occurs without difficulty with Li in ether. The structure of *106* is confirmed by the nmr and mass spectrum. The nmr spectrum indicates resonances at −22.3 Hz, 4.1 Hz and 39.7 Hz (relative intensity 4 : 12 : 8) assigned to the three different kind of protons. The value of the coupling constant is $J_{^{29}\text{Si}-\text{CH}_2} = 6.6$ Hz for the ^{29}Si satellites of the $Si{-}CH_2$ protons.

V. Synthesis of Ten-Membered Rings with Four Si Atoms

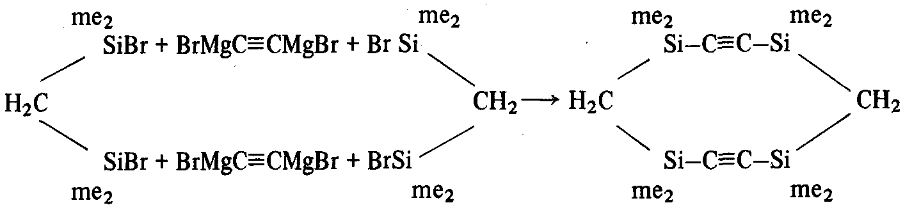
The synthesis of the five-membered ring 1,1,3,3-tetramethyl-1,3-disilacyclopentane was achieved by cyclization of $me_2(CH_2Br)Si{-}CH_2{-}Sime_2{-}Br$ with Li. In this procedure, intermolecular condensation reactions with removal of LiBr and compounds of higher molecular weight are formed. Heating under vacuum causes white crystals to sublime (m.p. 138–139 °C); these were identified as compound *107* formed by reaction (61b):



107 (61b)

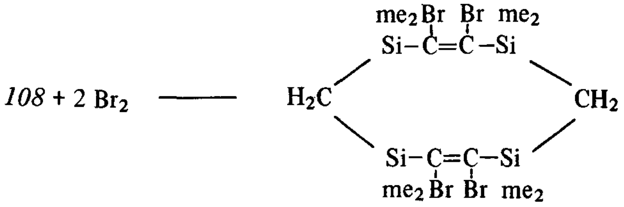
The structure of *107* was determined by analysis, molecular weight determination, nmr and mass spectrometric investigations. In the nmr spectrum three signals at −14.3 Hz, −1.5 Hz, 26.2 Hz occur with the relative intensity 2 : 12 : 4; ring-CH_2 coupling constant.

$J_{^{29}\text{Si}-\text{CH}_2} = 8.7$ Hz. The mass spectrum confirms the formula $Si_4C_{14}H_{36}$. The ten-membered ring is a crystalline compound which sublimes under vacuum. In this procedure *101* was formed in 22% yield, whereas the five-membered ring *89* is obtained in 89% yield[39]. A ten-membered ring with two acetylene-groups is formed in reaction (62)



108 (62)

Br_2 is added to *108* forming the tetrabromo compound *109*



109

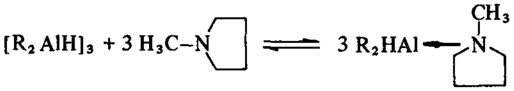
Further addition of Br_2 to the double bond is not observed. The compounds were isolated and their structures determined by nmr and mass spectrometry[35].

D. Influence of Lewis Bases on the Formation of 1,3-Disilacyclopentenes from Disilylethynes and R_2AlH

In the synthesis of carbosilanes the most difficult step is often the cyclization reaction. To obtain disilylethynes bearing substituents which are suitable for cyclization reactions, the addition to the C≡C bond must occur in the cis position. E.g. $me_2(CH_2Br)Si{-}CH{=}CH{-}SiClme_2(Sime_3)$ was obtained by cis-addition of $HSime_3$ to $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiClme_2$. Reaction with Li led to 1,1,3,3-tetramethyl-1,3-disila-4-trimethylsilylpentene[35]. In the alkyl- and arylethyne series cis-addition of alanes and boranes is well known. Subsequent hydrolytic cleavage leads to cis-olefins bearing no heteroatoms[40, 47]. It was found that the reaction products of the addition of diisobutylalane to monosilylethynes depend on whether Lewis bases are present during the reaction[48]. The cis-compound is formed when NR_3 is present and the trans compound when NR_3 is absent. It was known that with the disilylethynes, the reaction of $me_2(CH_2Br)Si{-}C{\equiv}C{-}Sime_3$ *119* with diisobutylalane in ether produces compound *87* in 40% yield after hydrolysis, whereas *87* is not formed at all when diethylaniline is present[35]. The influence of Lewis bases on the reaction of $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2$ *119* with R_2AlH was investigated owing to its great importance for the cyclization reactions in which $Si{-}CH_2{-}Si$ groups are formed[49].

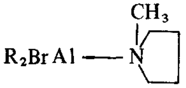
1. Reaction of $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2$ *119* with R_2AlH (R = Isobutyl) and N-Methylpyrrolidine

N-Methyl-pyrrolidine and diisobutylalane form a 1 : 1 donor-acceptor complex *50*.



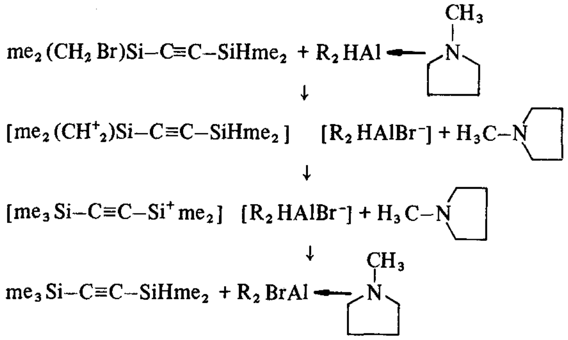
$$[R_2AlH]_3 + 3\,H_3C{-}N\!\!\bigcirc \rightleftharpoons 3\,R_2HAl \leftarrow N(CH_3)\!\!\bigcirc \qquad (63)$$

A pentane solution of the Al-complex *160* was dropped into the disilylethyne compound *119* in pentane to give a molar ratio 2 : 1 after 1 h (reaction temperature 45 °C). After 48 h, the CH_2Br nmr signal of the starting material was no longer detectable. Evolution of gas did not occur. After hydrolysis (0 °C, 4 *N* H_2SO_4), extraction with pentane, and distillation, $me_3Si{-}C{\equiv}C{-}SiHme_2$ *162* was obtained in 95% yield. This indicates that addition of R_2AlH or its amino complex to the triple bond of *119* did not occur. The resonances which arise during the reaction are assigned to *165*.



165

The reaction sequence (64) resembles a rearrangement reported by Kumada[51)]



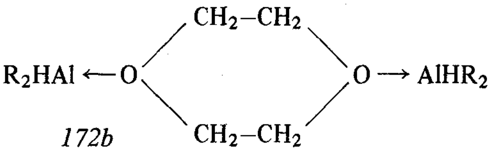
(64)

2. Reaction of $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2$ *119* with weak Lewis Bases

As weak Lewis bases, diethylether and dioxane form 1 : 1 *172a* and 2 : 1 complexes respectively *172b*.

$R_2HAl \leftarrow O(C_2H_5)_2$;

172a

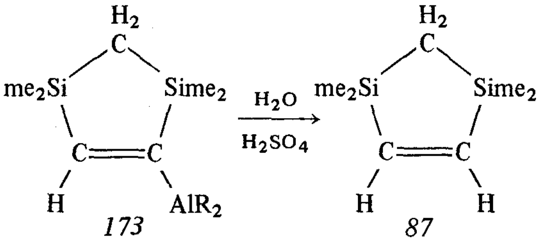


172b

These donor-acceptor complexes represent equilibrium states dependent on the basicity of the donor. The reactions of *119* with R_2AlH are similar in diethylether and dioxane.

At 40 °C, a double molar amount of the complex *172* (in pentane) is added to the disilylethyne *119*. Vigorous gas evolution is observed which decreases toward the end of the reaction (1.25 mmol H_2, 0.25 mmol isobutane, small amounts of me_2SiH_2).

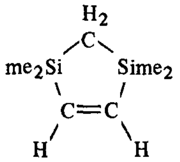
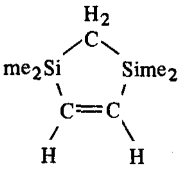
In the nmr spectrum of the reaction mixture a fast, then a slow decrease in the intensity of the CH_2Br resonance of *119* was observed. Several new lines with a low intensity appeared in the region of $\tau = 2.25$, at $\tau = 10.44$ and $\tau = 10.50$ Hz, and disappeared after hydrolysis. They are assigned to compound *173* which is the addition compound of the Lewis bases. It was not possible to isolate this compound either by distillation, sublimation or crystallization. Compound *87* is formed by hydrolysis.



173 *87* (65)

The compounds are listed in Table 13.

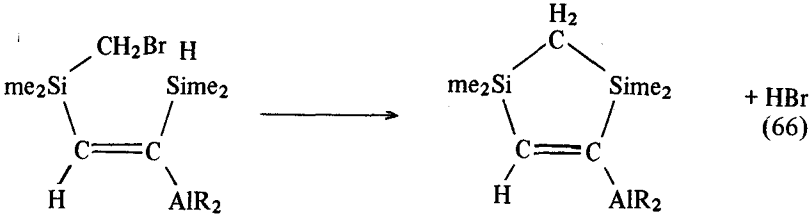
Table 13. Reaction of $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2$ *119* with R_2AlH (R = isobutyl) in presence of Lewis bases of different base strengths and with pentane as solvent

Compounds formed following hydrolysis	with:	N-Methyl-pyrrolidine		Dioxane		Diethyl-ether		Pentane	
	Reaction temp. °C	45		45	0	45		45	0
		% of the compounds in the reaction mixture							
	*87*	–		40	5	40		1	2
	*89*	–		2	–	2		10	10
$me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2$ *119*		1		20	30	20		–	–
$me_3Si{-}C{\equiv}C{-}SiHme_2$ *162*		95		15	30	15		–	–
trans-$me_2(CH_2Br)Si{-}CH{=}CH{-}SiHme_2$ *166*		–		5	2	2		–	–
trans-$me_3Si{-}CH{=}CH{-}SiHme_2$ *167*		–		10	10	10		–	–
cis-$me_3Si{-}CH{=}CH{-}SiHme_2$ *168*		–		5	2	5		–	–
$me_2(CH_2Br)Si{-}CH_2{-}CH_2{-}SiHme_2$ *169*		–		–	–	–		–	–
$me_3Si{-}CH_2{-}CH_2{-}SiHme_2$ *170*		–		5	10	5		–	–
$me_3Si{-}CH_2{-}CH_2{-}Sime_2{-}C_4H_9$ *171*		–		2	–	2		60	70

Those compounds not clearly identifiable by nmr spectroscopy, were synthesized for comparison. On lowering the reaction temperature to 0 °C, the undesirable hydrogenation of the CH_2Br group of *119* becomes dominant and the cyclic compound *87* is obtained in only 5% yield. From the number and nature of the compounds formed it can be concluded (see Table 13) that several parallel reactions occur.

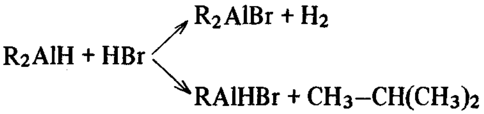
The reaction sequences are illustrated here:

a) addition of R_2AlH to *119* in cis and trans position
b) cyclization of the cis compound following by reaction (66)



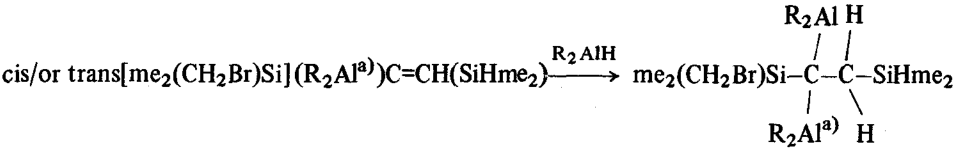
(66)

The gas evolution observed is due to the formation of HBr which occurs in the molar ratio in which compound *87* is obtained:



$$R_2AlH + HBr \begin{cases} \nearrow R_2AlBr + H_2 \\ \searrow RAlHBr + CH_3{-}CH(CH_3)_2 \end{cases} \qquad (67)$$

c) addition of R_2AlH to disilylethynes:



$$\text{cis/or trans}[me_2(CH_2Br)Si](R_2Al^{a)})C{=}CH(SiHme_2) \xrightarrow{R_2AlH} me_2(CH_2Br)Si{-}\overset{\overset{R_2Al}{|}}{\underset{\underset{R_2Al^{a)}}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{\backslash}}{C}}{-}SiHme_2$$

(68)

By an hydrolysis of these intermediates, the compounds *169*, *170*, *171* are formed.

d) Cyclization to *89*. By addition of 2 mole R_2AlH to be triple bond, C–C bonds with free rotation are obtained. Cyclization can thus be accomplished by both cis and trans intermediates.

---

[a] It cannot be determined to which of the C atoms the R_2Al group is attached.

e) Hydrogenation of the CH_2Br group in *119* by reaction (64). The hydrogenation of the CH_2Br group in *119* to form compounds *162*, *167*, *168*, *170*, *171* is shown in reaction (64).

f) isobutylation of the Si–H group in *119*:

$$\equiv SiH + R_2AlH \longrightarrow \equiv SiR + RAlH_2 \quad (R = \text{isobutyl}) \tag{69}$$

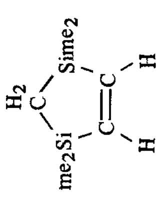
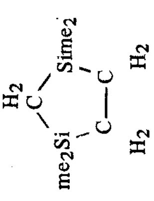
3. Reaction of $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2$ with R_2AlH in Pentane

Compound *119* was dissolves in pentane (without Lewis bases) and a pentane solution of a double molar amount of R_2AlH (R = isobutyl) was added over 1 h (45 °C). As with the reaction in ether, vigorous gas evolution was initially observed, decreasing later. That indicated cyclization (reaction (66)) and the HBr reaction (reaction (67)). Reaction of the CH_2Br group was monitored by nmr measurements. After 4 h, the corresponding resonances had disappeared completely. As was found in the last reaction, no signals indicating the free cyclic compounds *87* and *89* were observed. However, cyclization has already occurred before hydrolytic work-up, as all CH_2Br groups which can undergo cyclization have disappeared from the nmr spectrum. After hydrolysis (4 h, 0 °C, 4 N H_2SO_4) the resonances of the cyclic compounds *87* and *88* are observed. Separation by gas chromatography in combination with nmr-investigations leads to the identification of the compounds listed in Table 13. When the reaction is carried out at 0 °C, the same products are formed though the reaction time is prolonged. Compound *171* represents the main product. It is formed from *119* by repeated hydroalumination (reaction (68)), followed by hydrogenation of the CH_2Br group (reaction (64)) and substitution of the SiH group (reaction (69)). Cyclization to *87* and to compound *89*, also occurs (reaction (66)).

4. Reaction of $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiClme_2$ *177* and $me_2(CH_2Cl)Si{-}C{\equiv}C{-}SiHme_2$ *178* with R_2AlH in Diethylether

The procedure was similar to that described in section 2. In the reaction of *177*, a threefold molar excess of R_2AlH was used. It led to the same products (same%) (Table 14) as the reaction with $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2$ *119* (see Table 13). The hydrogenation of the SiCl group in *177* is favored with R_2AlH. All subsequent reactions correspond to those in Section 2. In the reaction of $me_2(CH_2Cl)Si{-}C{\equiv}C{-}SiHme_2$ *178* the influence of the CH_2Cl group in *119* may be seen. As indicated in Table 14, the cyclic compounds *87* and *89* are each obtained only in 2% yield. This is due to a very low mobility of the Cl atom in the CH_2Cl group. The addition of R_2AlH to the triple bond is not influenced by the CH_2Cl group. The products containing CH_2Br and CH_2Cl groups are not listed in Table 14; a polymeric residue is not formed in significant amounts with *178*.

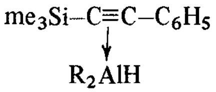
Table 14. Reaction of $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiClme_2$ *177* and $me_2(CH_2Cl)Si{-}C{\equiv}C{-}SiHme_2$ *178* with RAlH; R = isobutyl in ether

Compounds formed following hydrolysis	Starting materials $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiClme_2$ *177*	$me_2(CH_2Cl)Si{-}C{\equiv}C{-}SiHme_2$ *178*
	% of the compounds formed in the reaction mixture	
 *87*	40	2
 *89*	2	2
$me_3Si{-}C{\equiv}C{-}SiHme_2$ *162*	15	15
trans-$me_3Si{-}CH{=}CH{-}SiHme_2$ *167*	10	20
cis-$me_3Si{-}CH{=}CH{-}SiHme_2$ *168*	5	10
$me_3Si{-}CH_2{-}CH_2{-}SiHme_2$ *170*	5	15
$me_3Si{-}CH_2{-}CH_2{-}Sime_2{-}C_4H_9$ *171*	5	5

5. Influence of Lewis Bases on the Addition of R_2AlH to Disilylethynes and an Cyclization

The addition of R_2AlH to $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2$ *119* to form the cis compound and the subsequent cyclization to *87* represent the favored reactions in ether and dioxane. In the presence of N-methyl-pyrrolidine (strong Lewis base), the reaction of the same starting materials are basically different, since addition and cyclization do not occur at all, but the reaction leads to $me_3Si{-}C{\equiv}C{-}SiHme_2$ *162* (Table 13).

The effect of the Lewis base on the addition of R_2AlH was observed with $me_3Si{-}C{\equiv}C{-}C_6H_5$ *174*; in the presence of R_3N cis addition of the R_2AlH occurs, whereas without a Lewis base R_2AlH is added in the trans position. This behavior is interpreted in terms of a polarization of compound *174* by a +I effect of the me_3Si group indicated by the formula $me_3Si{-}\overset{\delta+}{C}{\equiv}\overset{\delta-}{C}{-}C_6H_5$ *175* which then forms a π complex

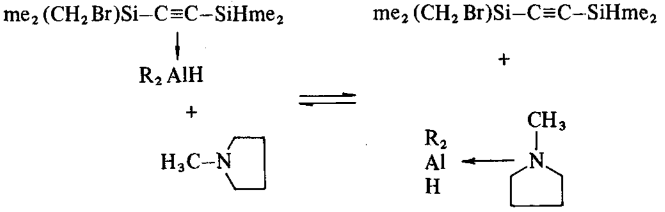


$$\begin{array}{c} me_3Si{-}C{\equiv}C{-}C_6H_5 \\ \downarrow \\ R_2AlH \end{array}$$

Disilylethyne is expected to react as an even stronger Lewis base, competing with other Lewis bases. This explains the results of the reactions in (49). That no addition of R_2AlH to

$$me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2 \quad \textit{119}$$

occurs in the presence of N-methylpyrrolidine (strong Lewis base) is illustrated by reaction (70). The equilibrium is forced to the right by the N-methylpyrrolidine so that no formation of the π complex *176* can occur and addition is prevented.

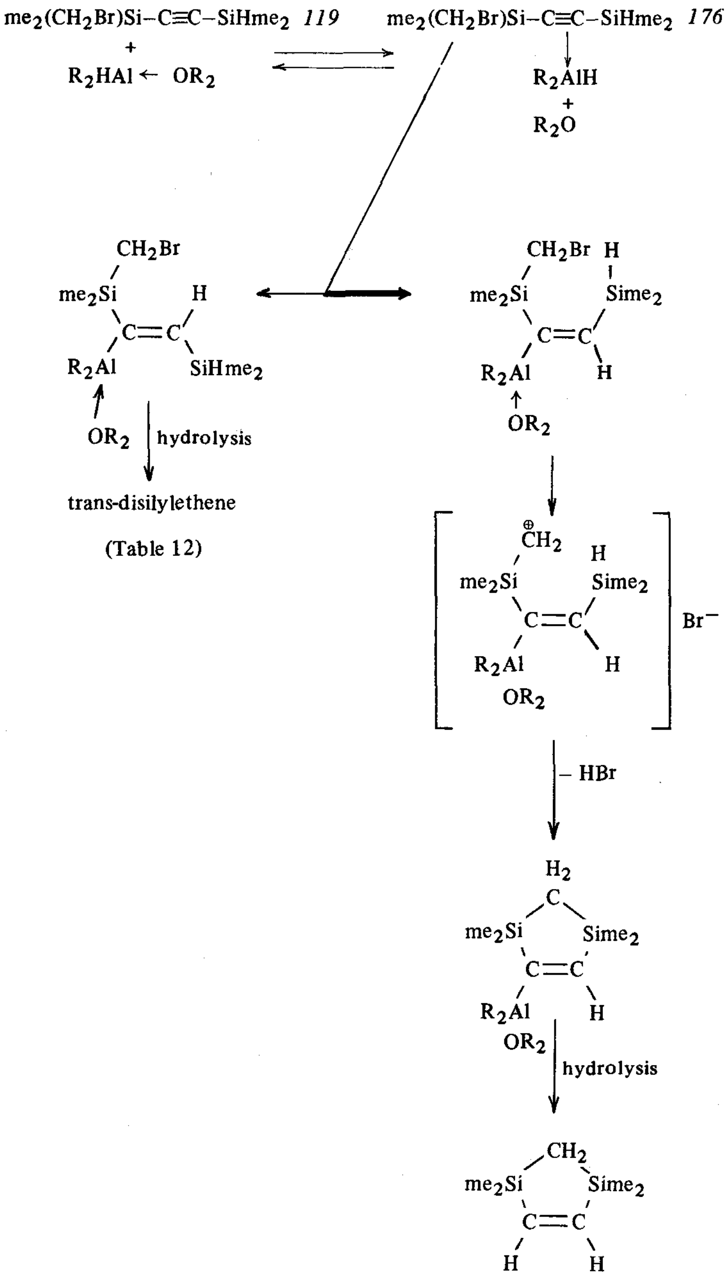


(70)

In the presence of weaker Lewis bases (dioxane, ether) the complex $R_2HAl \leftarrow OR_2$ is less stable. The equilibrium is not displaced as with N-methylpyrrolidine. The π complex is formed and additions proceeds. As in the reaction of the monosilylethyne, a cis addition of R_2AlH is dominant in the presence of a Lewis base, so the conditions for the formation of compound *87* are fulfilled.

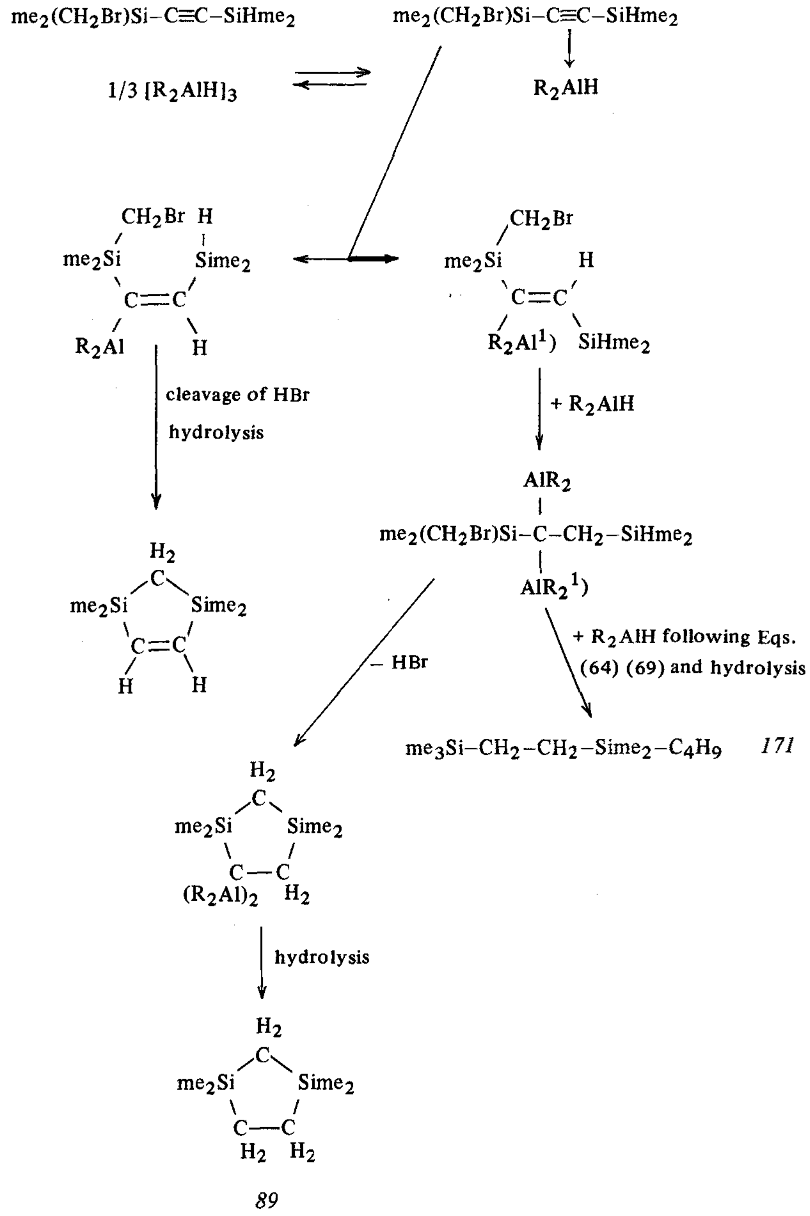
An explanation for the cyclization of disilylethyne to *87* and disilylethane to *89* may be as follows: Cyclization of $me_2(CH_2Br)Si{-}CH_2{-}CH_2{-}SiHme_2$ with R_2AlH was not successful. After the addition of R_2AlH to trans-$me_2(CH_2Br)Si{-}CH{=}CH{-}SiHme_2$, the cyclic compound *89* is obtained after hydrolysis. Addition of the R_2Al group forms a disilylethane in which the

Table 15. Sequence of cyclization of *119* to 1,1,3,3-tetramethyl-1,3-disilacyclopentene *87*



87

Table 16. Reaction sequence of $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2$ *119* with R_2AlH without Lewis base in pentane (Table 13)



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[1] It cannot be determined to which of the C atoms the R_2Al group is attached.

reactivity of the other substituents (CH_2Br, SiH) is greatly enhanced. Increasing reactivity of the CH_2X group in the compounds R_2AlCH_2X, $R_2AlCH_2{-}CH_2X$, $R_2Al{-}CH_2{-}CH_2{-}CH_2X$ (R = alkyl, X = Cl, Br, I); ether solvent was also observed earlier[52]. The sequence of cyclization of (119) to *87* and *89* is illustrated in Table 15.

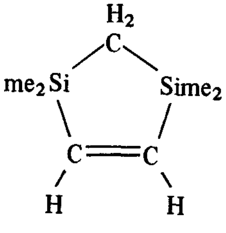
The reaction (in pentane) of $me_2(CH_2Br)Si{-}C{\equiv}C{-}SiHme_2$ *119* with R_2AlH in the absence of a Lewis base gives a completely different result. $me_3Si{-}CH_2{-}CH_2{-}Sime_2{-}C_4H_9$ *171* is obtained in 70% yield, whereas only 2% yield of *87* and 10% yield of *89* are observed (Table 13).

In the absence of a Lewis base, R_2AlH addition occurs in the trans position (as with the monosilylethyne *174* and compound (87) cannot be formed. The reaction sequence is shown in Table 16.

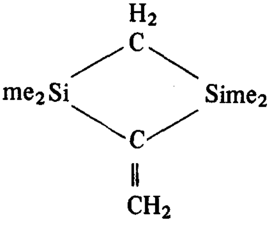
The addition of two R_2AlH molecules to *119* was presumed to lead to the geminal structure (see Table 16); this was proved by subsequent deuterolysis[53].

E. Synthesis and Reactions of Trisilacyclohexane *179* and of Trisilacycloheptene-6 *180*

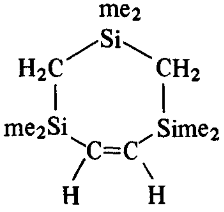
The syntheses of 1,1,3,3-tetramethyl-1,3-trisilacyclopentene *87* and of 1,1,3,3-tetramethyl-1,3-disila-4-methylene-cyclobutane *88* are described in Section C. By adding Br_2 or HBr, the ring system is cleaved as a first reaction step (35). For syntheses of carbosilanes, information on the corresponding six- or seven-membered ring systems was required. Therefore, the synthesis of the compounds *179* and *180* was investigated (54).



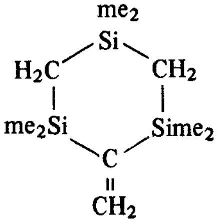
87



88



180

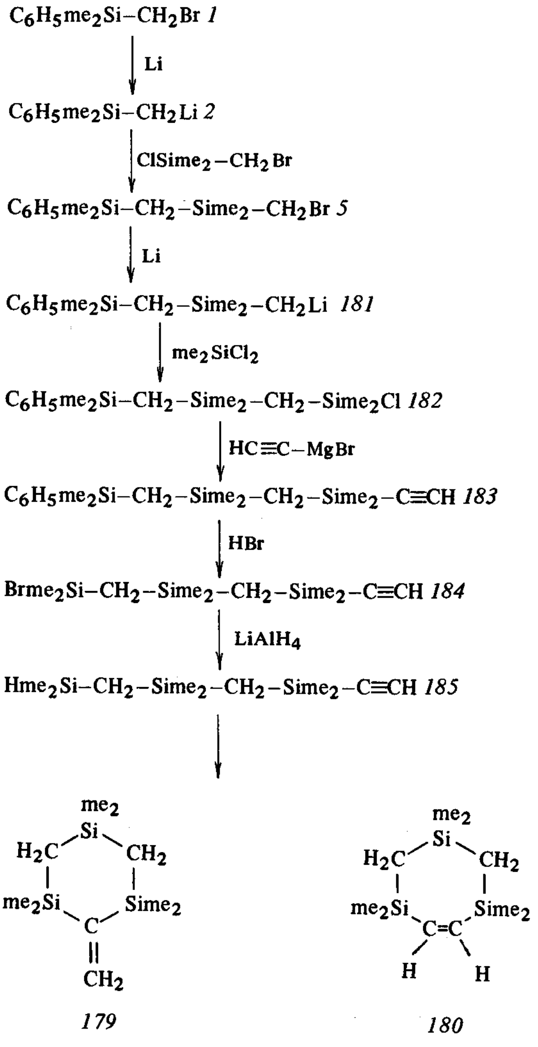


179

Experience in the synthesis of *87* and *88* using Wurtz' reactions of SiH-containing compounds with 1,2- and 1,1-dihalogenethenes suggested that they are of little use for the formation of *179* and *180*.

Table 17 represents the synthetic procedure.

Table 17. Synthesis of *179* and *180* by cycloaddition of $me_2HSi-CH_2-Sime_2-CH_2-Sime_2-C{\equiv}CH$

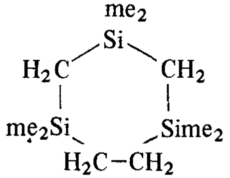


The starting substance $\mathrm{Clme_2SiCH_2Br}$ (primary bromination product of $\mathrm{me_3SiCl}$) leads to compound *1* by phenylation with $\mathrm{C_6H_5MgBr}$, which is then converted to compound *2* by adding a Li suspension in diethylether at –20 °C. A subsequent reaction of *2* with $\mathrm{me_2SiCl(CH_2Br)}$ to compound *5* does not give uniform products even at –78 °C. Besides compound *5*, the substances $\mathrm{C_6H_5Sime_3}$, $\mathrm{C_6H_5Sime_2{-}CH_2Br}$ and $\mathrm{me_2ClSi{-}CH_2{-}Sime_2{-}CH_2Br}$ are formed. Adding an ether solution of *2* to $\mathrm{me_2SiCl(CH_2Br)}$ at –78 °C, compound *5* is obtained in 60–70% yield. The formation of $\mathrm{C_6H_5Sime_3}$ may result from hydrogenation of the Li intermediate by the ether; the formation of $\mathrm{C_6H_5Sime_2(CH_2Br)}$ and $\mathrm{me_2ClSi{-}CH_2{-}Sime_2{-}CH_2Br}$ is due to a halogen-metal exchange followed by a coupling reaction since both compounds are obtained in 1 : 1 molar ratio:

$$\begin{array}{l} \mathrm{C_6H_5Sime_2{-}CH_2Li + me_2ClSi{-}CH_2Br} \longrightarrow \\ \qquad \longrightarrow \mathrm{C_6H_5Sime_2{-}CH_2Br + me_2ClSi{-}CH_2Li} \qquad\qquad (71) \\ \qquad\qquad\qquad\qquad\quad \big\downarrow \; \mathrm{+\, me_2ClSi{-}CH_2Br} \\ \qquad\qquad \mathrm{meClSi{-}CH_2{-}Sime_2{-}CH_2Br + LiCl} \end{array}$$

A further metal-halogen exchange to form a chain with 3 Si atoms is not observed even at low temperature (9). Compound *181* is formed from *5* in high yield (95 %); by dropwise addition of the Li compound *181* to an excess of $\mathrm{me_2SiCl_2}$ which prevents coupling at both sides, compound *182* is obtained in satisfactory yields and can be distilled under vacuum without decomposition. The formation of *183* by reaction of *182* with HC≡CMgBr can be readily achieved. As in the formation of the Grignard reagent in THF, a small amount of BrMgC≡CMgBr is formed and a disubstituted ethyne is found as a by-product which remains in the residue after distillation. The formation of *184* from *183* by cleavage with HBr at –38 °C occurs easily. Under the conditions used, no addition of HBr to the C≡C bond is observed. Finally, reduction to *185* is carried out (54).

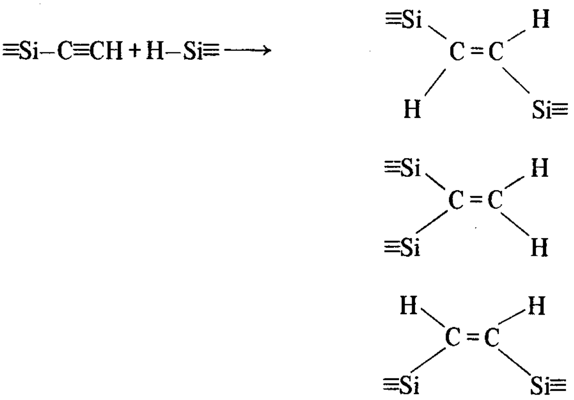
The formation of compound *179* and *180* from *185* is accomplished by the addition of the SiH group to the ethyne group in the same molecule. Addition reactions of hydrosilanes to silylethynes in presence of catalysts are well known (35-37,55). In particular $\mathrm{H_2PtCl_6 \cdot 6\,H_2O}$ in isopropanol with organic peroxides and amines is used. With peroxides alone, cis and trans ethynes are formed in a 3 : 1 and 4 : 1 ratio respectively, while in the presence of $\mathrm{H_2PtCl_6.6H_2O}$ the cis compound is not obtained.



186

After these investigations, the cyclization of *185* was accomplished with $H_2PtCl_6 . 6H_2O$ in cyclohexane under reflux. The reaction product was distilled and *179*, *180* and *186* were isolated[54].

Pare compound *179* can be isolated by gas chromatography (100 °C, phenyl silicon oil type O S 26.14 (PE) on Sterchamol, 6 m column, 1 atm helium). By a study of the nmr, i.r. and mass spectra, compound *179* is identified, and compared with that produced by a different synthesis[54]. The yield was 30 %. As the following possibilities for a hydrosilylation exist, this low yield is not surprising:



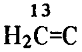
trans-1,2-disilylethene

1,1-disilylethene

cis-1,2-disilylethene

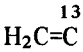
Addition may also occur intra- or intermolecularly, which is undesirable.

In the nmr spectrum of *179* four resonances having relative intensity of 2 : 12 : 6 : 4 are observed and assigned to this compound. The C–13 satellites of the vinyl group form a doublet with a characteristic coupling constant $J_{^{13}CH}$ = 156.6 Hz for the *a* coordination



$H_2\overset{13}{C}=C$

a



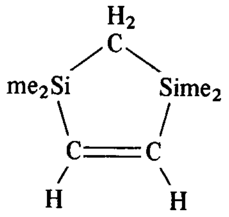
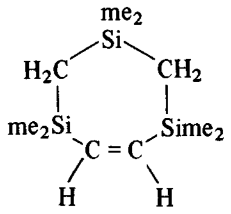
$H_2C=\overset{13}{C}$

b

The C–13 satellites of the *b* coordination are not considered. The ring size can be derived from measurement of the ^{29}Si satellites of the Si–CH_2–Si bridges. That coupling constants decrease with increasing ring size is known from nmr investigations on carbosilanes[1]. A coupling constant $J_{^{29}Si-H}$ = 8.1 Hz agrees with the ring size of compound *179*. In the i.r. spectrum, an absorption line is found at 1568 cm^{-1}. In unsaturated carbosilanes, the absorption of a 1,1-disilyl-ethyne is observed at 1560–1620 cm^{-1}[145], which confirms the structure of *179*.

The second fraction of the gas chromatogram contains the compounds *180* and *186*. The formation of *180* is the first example of a synthesis of a cis-1,2-disilylethene by hydrosilylation in the presence of $H_2PtCl_6 \cdot 6\,H_2O$. Four signals of relative intensity 2 : 12 : 6 : 4 are found in the nmr spectrum of *180*. The

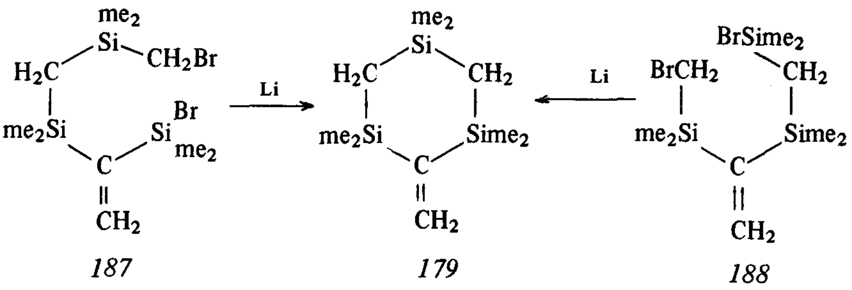
C–13 satellites of the vinyl resonance offer a simple means of determining the structure of *180*. As these signals are very weak, they are difficult to detect. However, sufficient amounts of compound *87* (1,3-disilacyclopentene) were provided by an organometallic synthesis[35, 54)], for comparison with the C–13 satellites in the vinyl group of both compounds:

	$J_{^{13}C-H}$	$J_{cis H-H}$
	143,4 Hz	15,2 Hz
	134,4 Hz	19,9 Hz

In both cases, the C–13 satellites are consistent with a doublet of doublets. The difference in the values is due to different ring strain. The coupling constant $J_{^{29}Si-CH_2}$ = 8.4 Hz for the $Si-CH_2-Si$ bridging group indicates a seven-membered ring structure. In the i.r. spectrum of *180*, the absorption line of the vinyl group is observed at 1460 cm^{-1}, while in previous investigations that of 1,2-disilylethenes was found in the region of 1480–1500 cm^{-1} (45). Compound *186*, the second component of the gas chromatographic separation, was identified by its mass and pmr spectra. $J_{^{29}Si-CH_2}$ = 8.4 Hz indicates the seven-membered ring structure. *186* does not react with HBr or Br_2. The formation of *186* follows hydrogenation of the SiH-containing starting material under the catalytic influence of $H_2PtCl_6 \cdot 6\,H_2O$.

1. Synthesis of Compound *179* by Cyclization with Li

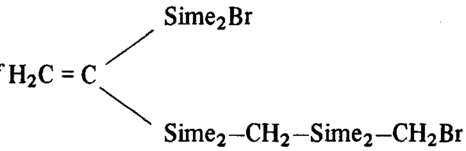
The following possibilities are given for a cyclization to form *179*:



(72)

Investigations on the synthesis of compounds *187* and *188* are reported below.

a) Synthesis of $H_2C = C$ *187*



$$H_2C=C\begin{cases} Sime_2Br \\ Sime_2{-}CH_2{-}Sime_2{-}CH_2Br \end{cases}$$

The synthesis of *187* is accomplished by addition of a corresponding SiH derivative to suitable Si compounds bearing an acetylenic group. Reactions (73) and (74) are considerable:

$$\underset{200}{me_2BrSiH} + \underset{189}{HC{\equiv}C{-}Sime_2{-}CH_2{-}Sime_2{-}CH_2Br} \longrightarrow 187 \qquad (73)$$

$$\underset{190}{me_2BrSi{-}C{\equiv}CH} + \underset{181}{HSime_2{-}CH_2{-}Sime_2{-}CH_2Br} \longrightarrow 187 \qquad (74)$$

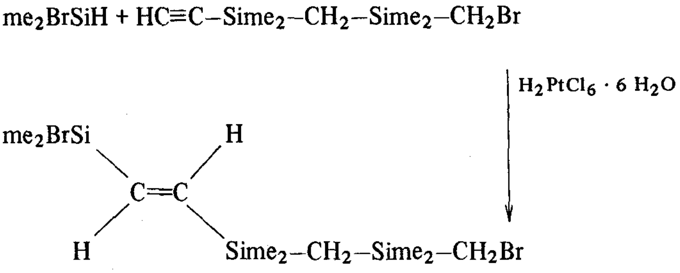
me_2BrSiH may be obtained as indicated here:

$$me_2SiCl_2 \xrightarrow{C_6H_5MgBr} C_6H_5me_2SiCl \xrightarrow{LiAlH_4} C_6H_5me_2SiH \xrightarrow{HBr} me_2BrSiH \quad (75)$$

Compound *5* (see Table 17) is the starting material for the synthesis of *189*.

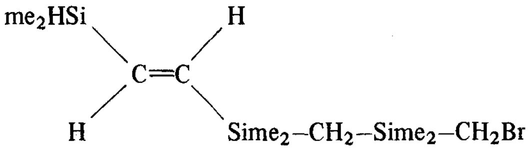
$$\begin{tikzcd} C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH_2Br \arrow[r, "Br_2"] & \underset{192}{Brme_2Si{-}CH_2{-}Sime_2{-}CH_2Br} \arrow[d, "HC{\equiv}CMgBr"'] & (76) \\ & \underset{189}{HC{\equiv}C{-}Sime_2{-}CH_2{-}Sime_2{-}CH_2Br} & \end{tikzcd}$$

The synthesis of *192* is accomplished easily. The reaction of *192* with $HC{\equiv}CMgBr$ yields compound *189* and the disilylated ethyne $BrCH_2{-}Sime_2{-}CH_2{-}Sime_2{-}C{\equiv}C{-}Sime_2{-}CH_2Sime_2{-}CH_2Br$ *197*. The hydrosilylation of me_2BrSiH and *189* quantitatively forms the trans compound *193* when $H_2PtCl_6 \cdot 6\,H_2O$ is present. In the vinyl region of the nmr spectrum, an AB signal is found ($J_{AB} = 22.4$ Hz), which indicates the formation of the trans-1,2-disilyl-ethene *193*.



193 (77)

The structure of *193* is confirmed by reaction with $LiAlH_4$, which forms *194*.



194

In the pmr spectrum, a septet is observed for the H–Si groups with a splitting of each line by the neighboring vinylic proton. The spectrum is assigned to compound *194*. The route given in reaction (73) is not a suitable procedure for the synthesis of *187*.

In the synthesis of *187* by reaction (74), the compound *191* is required. It can be obtained from *5* (see Table 16):

$$\begin{tikzcd} C_6H_5me_2Si{-}CH_2{-}Sime_2{-}CH_2Br \arrow[r, "Br_2"] & BrSime_2{-}CH_2{-}Sime_2CH_2Br \arrow[d, "LiAlH_4"] \\ & me_2HSi{-}CH_2{-}Sime_2{-}CH_2Br \end{tikzcd} \quad (78)$$

191

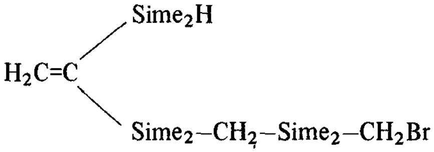
$m_2BrSi{-}C{\equiv}CH$ *190* is prepared by

$$C_6H_5me_2SiCl \xrightarrow{HC\equiv CMgBr} C_6H_5me_2Si{-}C{\equiv}CH \xrightarrow{HBr} Brme_2Si{-}C{\equiv}CH \quad (79)$$

$BrMgC{\equiv}CMgBr$ is also formed in the preparation of $HC{\equiv}CMgBr$: the byproduct $C_6H_5me_2Si{-}C{\equiv}C{-}Sime_2C_6H_5$ undergoes cleavage with HBr to

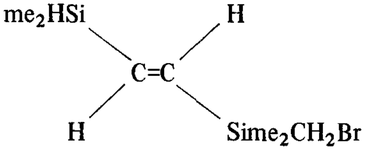
$$Brme_2Si{-}C{\equiv}C{-}Sime_2Br.$$

Compound *190* is obtained in an unsatisfactory yield. In the reaction of *190* with *191* (reaction (74)), 1,1- and 1,2-(trans)disilylethene are formed. All impurities which result from the preparation of the starting material can be separated easily by distillation when the addition reaction is accomplished, so only addition products remain, but to avoid thermal decomposition, no distillative separation was carried out. In the nmr spectrum of the addition products, two different groups of AB-type signals are found in the vinyl region. The lowfield vinyl signal is assigned to the trans-1,2-disilylethene *193* (39,5% yield) already reported. The second group represents *187* which is primarily identified from the coupling constant J_{AB} = 4.2 Hz. The structure is proved by the reaction with $LiAlH_4$ to *195*·



195

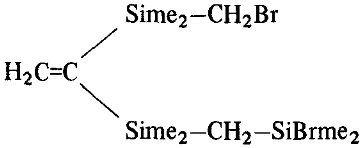
195 gives a septet for the HSi region without further splitting, indicating that not further protons are attached to the neighboring C atom; *195* can be obtained pure. For that purpose $H_2PtCl_6 \cdot 6\,H_2O$ is added to the mixture of *194* and *195* followed by dilution in ether and shaking with water. Vigorous H_2 evolution occurs. After separation of the ether phase and drying with anhydrous $CaCl_2$, pure compound *195* is obtained. Compound *194* was cleaved by the catalytic activity of $H_2PtCl_6 \cdot 6\,H_2O$. A similar H_2 evolution is observed with compound *196*.



196

This reaction does not occur with 1,1 disilylethenes.

b) Synthesis of



188

By analogy with reactions (73) and (74) in Section 1, the synthesis of *188* should be accomplished via rections (80) and (81):

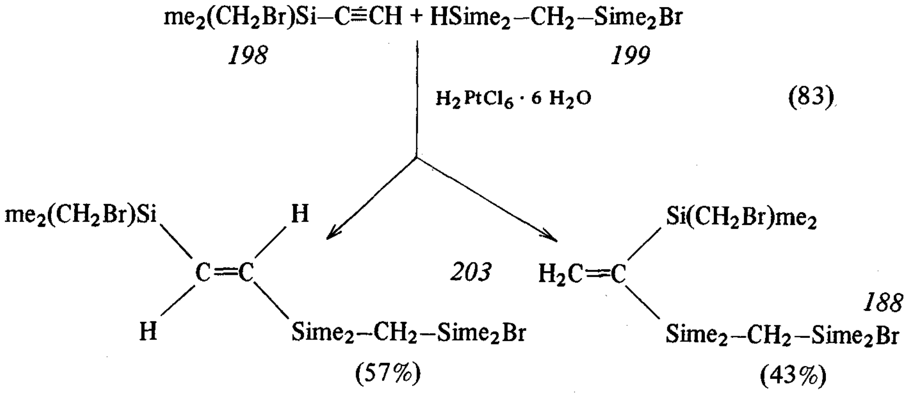
$$\underset{198}{me_2(CH_2Br)Si{-}C{\equiv}CH} + \underset{199}{HSime_2{-}CH_2{-}Sime_2Br} \longrightarrow 188 \qquad (80)$$

$$\underset{200}{me_2(CH_2Br)SiH} + \underset{201}{HC{\equiv}C{-}Sime_2{-}CH_2{-}Sime_2Br} \longrightarrow 188 \qquad (81)$$

Compound *198* is readily obtained from $me_2(CH_2Br)SiCl$ and $HC{\equiv}CMgBr$. The formation of compound *199* is by reaction (82).

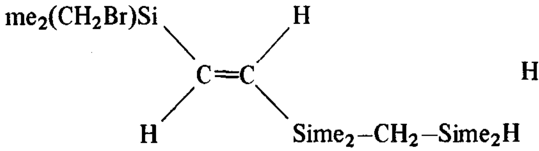
$$\begin{tikzcd}
C_6H_5me_2Si{-}CH_2Li + me_2SiCl_2 \arrow[r] & C_6H_5me_2Si{-}CH_2{-}Sime_2Cl \arrow[d, "LiAlH_4"] & \\
& C_6H_5me_2Si{-}CH_2{-}Sime_2H \quad 202 \arrow[d, "HBr"] & (82) \\
& Brme_2Si{-}CH_2{-}Sime_2H \quad 199 &
\end{tikzcd}$$

In the reaction of $C_6H_5me_2Si{-}CH_2{-}Sime_2H$ with HBr (at −30° to −78 °C) H_2 is evolved from the SiH group, which has to be considered in this procedure. The reaction of *198* with *199* is shown in reaction (83):

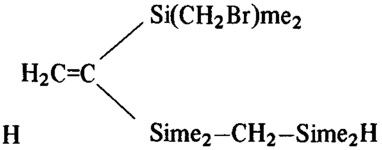


(83)

The hydrosilylation catalyzed by $H_2PtCl_6 \cdot 6\ H_2O$ leads to compound *188* in 43% yield. The pmr spectrum shows an AB signal in the vinyl region (J = 22.5 Hz) which is assigned to *203*; at higher field a singlet which results from an identical chemical shift of the two vinyl protons is found for *188*. Improved characterization is obtained by a reaction with $LiAlH_4$ forming *204* and *205*.



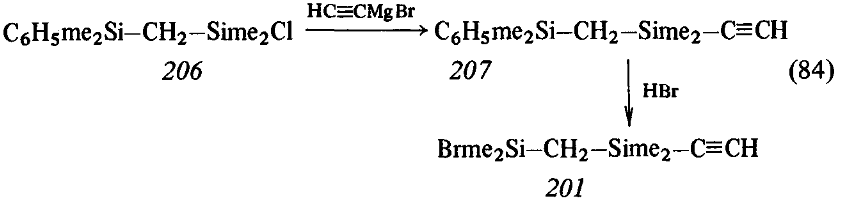
204



205

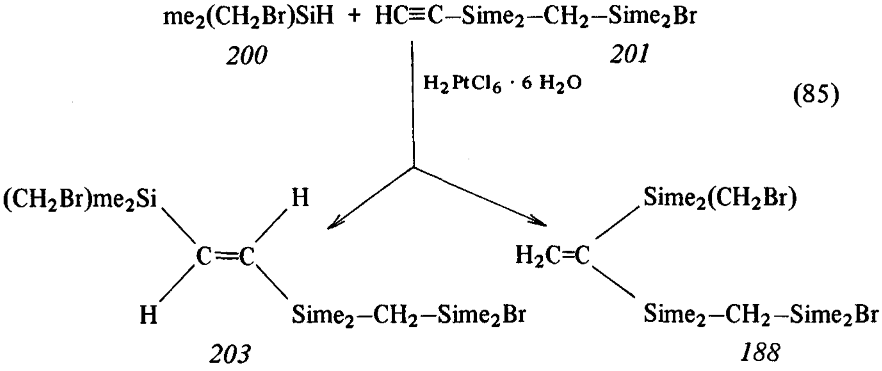
The newly introduced protons cause splitting of the neighboring group. So that the spectra can be definitely assigned. The vinyl region (AB signal and singlet) is not changed. Nine lines are found for the Si–H group in both compounds[54)].

For the synthesis of *188* (reaction 81), compound $\mathrm{me_2(CH_2Br)SiH}$ *200* is prepared from $\mathrm{me_2(CH_2Br)SiCl}$ and $\mathrm{LiAlH_4}$. Compound *201* is obtained following this reaction sequence.



$$\begin{tikzcd} \underset{206}{\mathrm{C_6H_5me_2Si{-}CH_2{-}Sime_2Cl}} \arrow[r, "\mathrm{HC{\equiv}CMgBr}"] & \underset{207}{\mathrm{C_6H_5me_2Si{-}CH_2{-}Sime_2{-}C{\equiv}CH}} \arrow[d, "\mathrm{HBr}"] \\ & \underset{201}{\mathrm{Brme_2Si{-}CH_2{-}Sime_2{-}C{\equiv}CH}} \end{tikzcd} \qquad (84)$$

Hydrolysis in presence of $\mathrm{H_2PtCl_6 \cdot 6\,H_2O}$ (reaction (85)) yields 60% of the trans compound *203* and 40% of compound *188*:



(85)

c) Cyclization of the Compounds 187 and 188 to Trisilacyclohexane 179

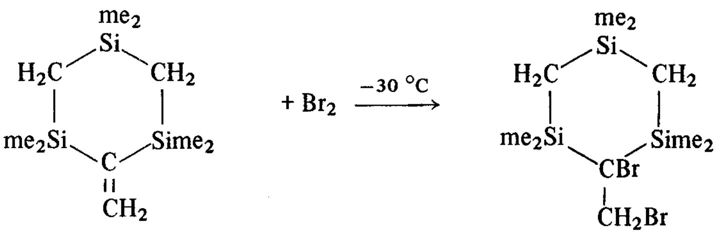
The compounds *187* and *188* and their SiH-containing derivatives are available for cyclization by reaction (72). The cyclization of the SiH-containing compound *195* occurs in ether at 20 °C to *179* without significant side-reactions. Compound *187* was reacted in a mixture with the isomeric trans compound

193. The reaction in ether occurs slowly and is completed by heating under reflux for 24 h. Compound *179* is obtained pure in 49% yield by distillation. In 45% yield compound *188* and its SiH-derivative react with Li to form the cyclic compound *179*. SiH compounds are advantageous for cyclization reactions, as the reaction occurs clearly with precipitation of LiH and no Si–Si bonds are formed[54)].

2. Reactions of the Cyclic Compounds *179* and *180*

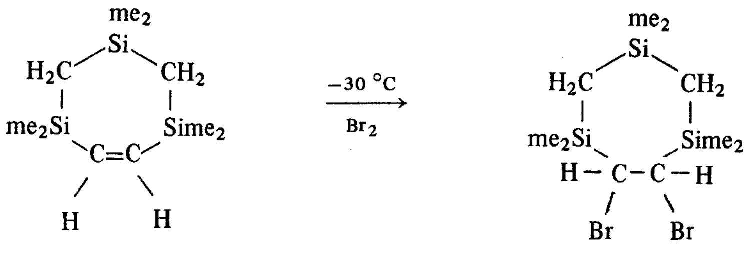
a) Addition of Br_2

In the compounds *179* and *180* are reacted in CCl_4 at –30 °C with very dilute Br_2 solutions in CCl_4 (addition of the Br_2 solution in small quantities), the formation of very pure products can be observed from the nmr spectrum:



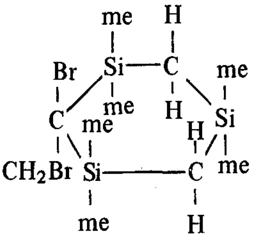
179 *208*

(86)

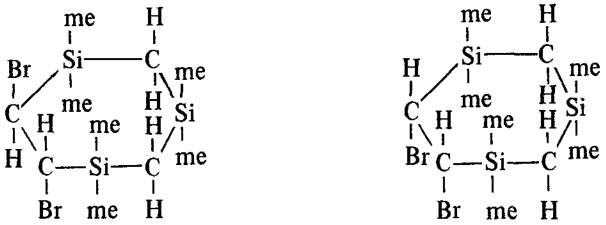


180 *209*

Higher reactivity of the seven-membered ring *179* is observed when both compounds are reacted in an mixture. The addition products *208* and *209* are stable at room temperature for several weeks and form crystals after some days. The pmr spectrum deserves some interest, the upper and lower side of both rings are altered by bromination.



208a



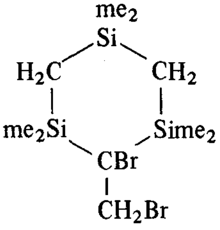
209

In *208* (simplified planar structure), the protons of the upper and lower sides have a different chemical environment. The expected seven resonances are obtained with appropriate relative intensities in the nmr spectrum.

Two stereoisomers of the brominated seven-membered ring *209* are expected to result from trans (compound *b*) and cis-(compound *c*) addition. The nmr spectrum may enable distinction of the two isomers.

In compound *b*, the Si–CH_3 and Si–CH_2–Si protons of the neighboring C–C group have different chemical environments depending on the side of the ring to which the substituents are attached. The protons of the other $Sime_2$ groups and the CHBr groups do not differ in chemical environments. In compound *c*, all protons on the upper side of the ring differ from those on the lower side. The six resonances in the nmr spectrum give clear proof of the formation of compound *b* (trans addition)[54].

The two products of bromination *208* and *209* can be thermally decomposed with β-elimination. If the mixture of both compounds is heated in a CCl_4 solution, the brominated seven-membered ring *209* is more stable. Compound *208* is cleaved quantitatively between 60 and 70 °C with β-elimination.



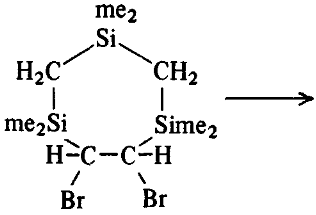
208

$$\longrightarrow H_2C = CBr{-}Sime_2{-}CH_2{-}Sime_2{-}CH_2{-}Sime_2Br \qquad (87)$$

210

In the nmr spectrum, the resulting compound *210* gives an AB signal in the vinyl region (J = 1.4 Hz).

The brominated seven-membered ring *209* decomposes with difficulty, undergoing β-elimination at 70 °C.



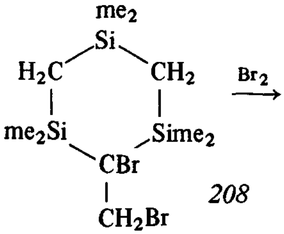
$HBrC{=}C{-}Sime_2{-}CH_2{-}Sime_2{-}CH_2{-}Sime_2Br$ (88)

211

The corresponding bromination product of the five-membered ring decomposes with β-elimination even when a boiling stone is added[39].

b) Ring Cleavage of 35 and 36 with Br$_2$

The six-membered ring *35* reacts with only a high concentration of Br_2, quantitatively giving:



208

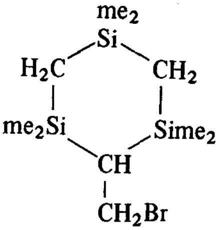
$BrH_2C{-}CBr_2{-}Sime_2{-}CH_2{-}Sime_2{-}CH_2{-}Sime_2Br$ (89)

212

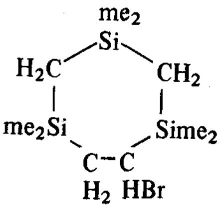
The seven-membered ring *209* is cleaved more readily by Br_2 though more side-reactions occur. In the nmr spectrum the resonance of a $CHBr_2{-}CHBr_2$ is observed.

c) Reaction of Compounds 179 and 180 with HBr

Formation of *213* and *214* is primarily expected.



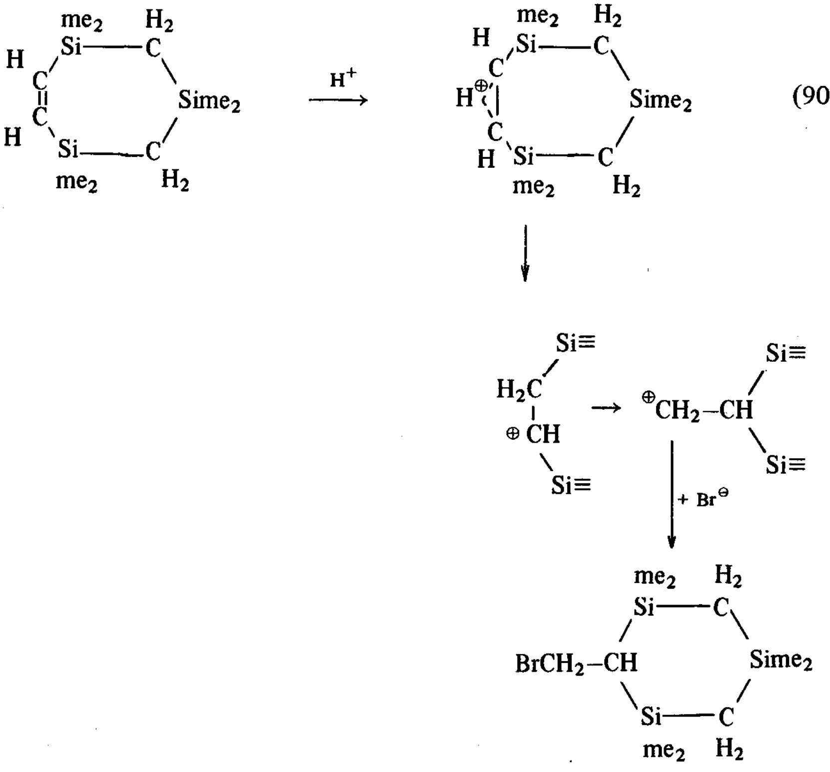
213



214

The six-membered ring *179* readily reacts to *179* in CCl_4 at –30 °C when HBr and N_2 (in a 5 : 1 ratio) are passed through the solution. The pmr spectrum shows the expected resonances, e.g. a doublet at low field and a triplet at high field (rel. intensity 2 : 1). Unreacted starting compound and the first cleavage products of *213* are present in the mixture[54].

In the reaction of *180* with HBr an unexpected process occurs. Under mild conditions (HBr + N_2 in a 1 : 5 ratio at –78 °C, CH_2Cl_2 solution a low-temperature spectrum at –78 °C shows that compound *213* is formed. This product is identical with compound *179*, which indicates that the HBr addition of *180* occurs with ring contraction to the six-membered ring system by reaction (90):



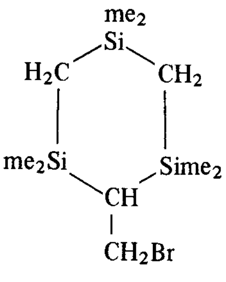
(90)

213

No ring contraction occurs in the reaction of the five-membered ring *87* with HBr, but the HBr addition product is formed because the four-membered ring system of 1,3-disilacyclobutane is relatively instable and is easily cleaved by HBr[34].

d) Ring Cleavage of 213 by β-Elimination

The same product should be obtained from the reaction of compounds *179* and *180* with HBr owing to the ring contraction of the seven-membered ring *180* by the action of HBr. This was proved by the following procedure[54].



213

$$H_2C{=}CH{-}Sime_2{-}CH_2{-}Sime_2{-}CH_2{-}Sime_2Br$$

215

$$\Big\downarrow {+}\,HBr$$

$$H_2BrC{-}CH_2{-}Sime_2{-}CH_2{-}Sime_2{-}CH_2{-}Sime_2Br$$

216

$$\Big\downarrow$$

$$H_2C{=}CH_2$$

$$+$$

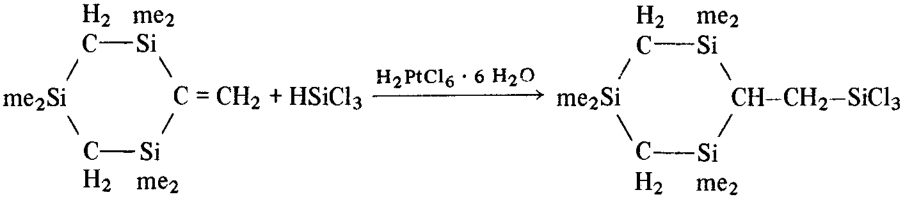
$$Brme_2Si{-}CH_2{-}Sime_2{-}CH_2{-}Sime_2Br$$

217 (91)

In the nmr spectrum, compound *215* gives an AB signal for the $H_2C{=}C$ group (J = 16.5 Hz). A triplet of one half of the intensity is found with a shift to higher field and is assigned to the C=CH group (J = 16.5 Hz). The HBr addition product *216* gives an A_2B_2 spectrum and is clearly identified. A simple nmr spectrum is obtained for *217*[54].

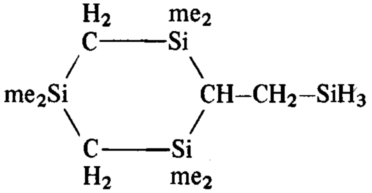
e) Addition of $HSiCl_3$ and $HSime_2Br$ to Trisilacyclohexane 179

The addition of $HSiCl_3$ to compound *179* occurs quantitatively over 10 h (at 40 °C) in the presence of $H_2PtCl_6 \cdot 6\,H_2O$ to form compound *218*:



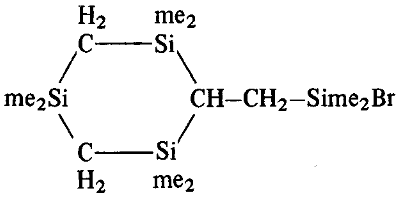
218 (92)

Compound *218* is distilled off and isolated as crystals (m.p. 55–57 °C). The nmr spectrum affords a clear identification. Compound *219* is obtained by reaction of *218* with $LiAlH_4$:

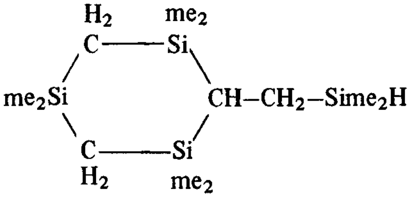


219

By a similar route, but at a distinctly slower rate, the reaction of *179* occurs with me_2BrSiH. After three days of heating to 90–100 °C about 70% of *179* has reacted to compound *220*, but this cannot be completely separated from the starting material.



220



221

For better identification, *220* is converted to *221* by $LiAlH_4$. The nmr spectrum gives a nonet for the SiH region. For the neighboring CH_2 bridging group of the SiH group, a doublet is formed, each line splitting to another doublet.

In both reactions a 1,1,1-trisilylethane derivative can be formed by addition of a SiH group to compound *179*.

F. Final Considerations

The investigations carried out on the organometallic synthesis of carbosilanes and presented in this paper indicate the progress achieved in this field in the years between 1967 and 1971 in cooperation with Dr. P. Schober, Dr. M. Hähnke and Dr. G. Maas. The yields of these syntheses are not all satisfactory yet, in most cases with the cyclization reaction. There is no doubt that the procedures described can be extended and simplified. However, it is also apparent that only some of the compounds (and their derivatives) which arise from the pyrolysis of the methylchlorosilanes and of tetramethylsilane can be obtained by organometallic synthesis[38]. The development of this field of chemistry requires extensive advances in methods for synthesis.

I am grateful to Dr. N. Braunagel for the translation of this paper.

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The Chemistry of Silicon-Transition-Metal Compounds

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1. Introduction

The growing interest in compounds possessing covalent metal-metal bonds opened up a new area of organosilicon chemistry. The first complex in which silicon is bonded to a transition metal, $(CH_3)_3SiFe(CO)_2(\pi\text{-}C_5H_5)$, was prepared in 1956[191]. After a period of incubation, rapid development began in 1966. The main lines of research derived from:

a) comparisons with the corresponding σ-alkyl, -germyl, -stannyl, and (in some cases) -plumbyl transition-metal complexes (reviewed in[2–5, 7, 10, 11]),

b) the possibility of bond-strengthening or multiple bonding, in a VB approach by π back-bonding from filled *d* orbitals of the transition metal into empty *d* orbitals of the silicon atom;

c) the industrial importance of catalytic processes such as hydrosilylation of olefins (reviewed in[6, 9]) or polymerization of cyclic organosilicons.
There have been only two previous reviews dealing exclusively with silicon-transition-metal compounds[1, 8].

Up to the end of 1972, more than 350 compounds containing silicon-transition-metal bonds had been synthesized, but their distribution among the d-block elements is by no means uniform. It can be inferred that the stability of such complexes decreases from right to left in a transition series and with increasing oxidation state of the transition metal. Nevertheless, it is remarkable that no silyl derivatives of the vanadium group have been prepared and that there are few nickel or palladium derivatives, as can be seen in the complete list of compounds given in Section 6.

Abstracting structural units from this list, we find that, in the majority of compounds, one silyl group "Si" is bonded to one transition metal "M" (*Ia–If* in Fig. 1). In some 40 compounds, two, three or four silicons are attached to a metal center (*II–IV*). Some of these units can also appear as ionic species (*Id, Ie, IIb*). The remaining ligands L are CO, π-cyclopentadienyl or PR^1_3 groups in most compounds. In some special cases, L is found to be methylcyclopentadienyl, C_6H_6, alkene, AsR^1_3, SbR^1_3, H, halogen, or a phenyl, germyl, stannyl or other transition-metal group. Some compounds of types *Ia*, *Ie*, and *IIa* have been synthesized in which two adjacent sites of M are occupied by a bidentate ligand. In one of the reviews in this volume compounds containing di-, tri-, and tetrasilane units are specially mentioned (*Ib*).

Furthermore, one silicon can connect two or three transition-metal units, whether bonded to each other or not (*Va–Vc*, *VI*).

Structure *If* was one of the first known examples of hydrogen bridges between a transition metal and a main-group element other than boron. There are many interesting features in syntheses, bonding properties, and reactions of silicon-transition-metal compounds which can only be outlined in this article, which covers the literature up to 1973. But any survey achieves its aim if it stimulates further interest and research in its specific area.

Ia $L_nM\text{-}Si$ $n = 1, 2, 3, 4, 5$

Ib $L_nM\text{-}Si_m$ $n = 3, 4, 5; m = 2, 3, 4$ and $L_nM{-}Si_m{-}ML_n$ $m = 2, 3$

Ic $L_nM\text{-}SiR_4$ and $L_nM{-}SiR_4R'$

Id $[L_nM\text{-}Si]^-$ n = 3, 4

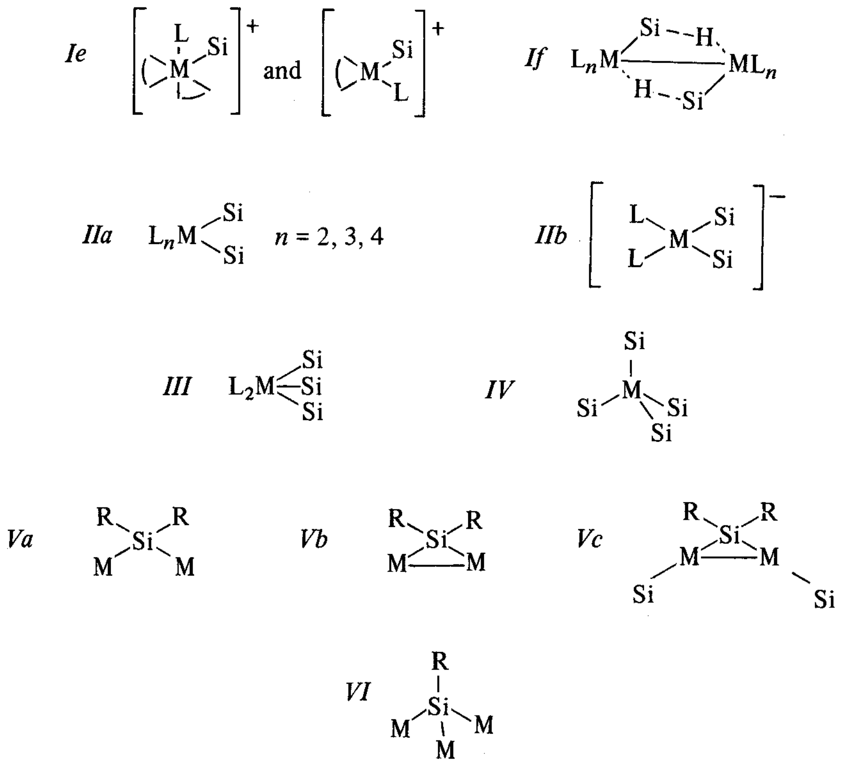


Fig. 1. Simplified scheme of structural types

2. Methods of Synthesis

2.1. "Alkali Halide" Route

In this convenient preparative route, an alkali metal salt is formed as a by-product of the synthesis of the desired silicon-transition-metal derivative. The two possibilities are (a) action of a silyl alkali derivative on a transition-metal-halide complex and (b) reaction of a transition-metal carbonyl anion with a silicon halide.

Route (a) is severely limited by the availability of the silyl alkali reagents. $KSiH_3$[14), $LiSiph_3$[a) 27, 50, 155, 156), $LiSimeph_2$[62, 64), $LiSime_2ph$[64), and $KSiph_3$[129) have been used in the synthesis of Ti-, Zr-, Hf-, Fe-, Pt-, and Au-Si compounds. The reactions are carried out in cooled etheral solvents, the yield of the silyl metal derivative varying between 13 (Eq. (1)) and 90% (Eq. (2)):

$$Fe(CO)_2cpBr + KSiH_3 \longrightarrow Fe(CO)_2cp(SiH_3) + KBr \qquad (1)$$

$$Zrcp_2Cl_2 + LiSiph_3 \longrightarrow Zrcp_2Cl(Siph_3) + LiCl \qquad (2)$$

The formation of $Pt(Pet_3)_2H(Siph_3)$ (20% yield) in the reaction of $LiSiph_3$ with $Pt(Pet_3)_2Cl_2$[27) is noteworthy and can most easily be explained by participation of the tetrahydrofuran solvent.

Route (b) was applied in 1956 by Piper and Wilkinson[191) to the preparation of the "prototype" $Fe(CO)_2cp(Sime_3)$, according to Eq. (3),

$$Na[Fe(CO)_2cp] + ClSime_3 \xrightarrow{THF} Fe(CO)_2cp(Sime_3) + NaCl \qquad (3)$$

and many other Si-Fe compounds were subsequently prepared under analogous conditions[23, 78, 154, 178, 180).

Some effects of specific substituents and solvents may be mentioned. Whereas $Mn(CO)_5(SiH_3)$[18, 19, 21) and $Co(CO)_4(SiH_3)$[17, 20) are formed readily from silyl iodide and sodium carbonyl metallate in ethers,

$$Na[Co(CO)_4] + ISiH_3 \longrightarrow Co(CO)_4(SiH_3) + NaI \qquad (4)$$

the best yields of $Mn(CO)_5(Sime_3)$ are obtained from dry $Na[Mn(CO)_5]$ and trimethylchlorosilane[40). $Na[Co(CO)_4]$ reacts very slowly with triphenylchlorosilane in THF to produce $CoCl_2$ and hexamethyldisiloxane as principal products. To obtain a triphenylsilyl cobalt complex by this method, the nucleophilicity of the cobaltate group must be increased by substitution of the carbonyl group by triphenylphosphine[80):

$$\begin{aligned} &Na[Co(CO)_3(Pph_3)] + ClSiph_3 \xrightarrow{THF} \\ &\qquad trans\text{-}[Co(CO)_3(Pph_3)(Siph_3)] + NaCl \qquad (5)\end{aligned}$$

Selection of the solvent is of special importance in the preparation of group-VI metal-silicon compounds. Cyclohexane or methylcyclohexane is recommended by Malisch[169, 170) because polar solvents lead to cleavage of the

---

a) For abbreviations see Section 6.

Si-M bond. As generally found in organometallic chemistry, the "alkali salt" method may be unsatisfactory in certain cases because of side reactions involving alkali metal-halogen exchange.

2.2. Elimination Reactions

Besides the elimination of alkali halides in the reaction between the silyl and metal reagents, several types of reactions in which other simple molecules are liberated have been widely employed. These methods, which include elimination of hydrogen, oxidative eliminations and ligand displacement reactions, are often interrelated.

Hydrogen is evolved in the reaction of cobalt[15)] or platinum hydrides[35, 36)] with silanes HSiRR'R″ containing at least one electron-withdrawing R substituent:

$$\mathrm{Co(Pph_3)_3H_3 + HSiR_3 \rightleftharpoons Co(Pph_3)_3H_2(SiR_3) + H_2} \qquad (6)$$

$$\mathrm{trans\text{-}[Pt(PR^1_3)_2XH] + HSiRR'R'' \rightleftharpoons trans\text{-}[Pt(PR^1_3)_2X(SiRR'R'')] + H_2} \qquad (7)$$

Both reactions are reversible. Using a dichloroplatinum complex as starting material, formation of the silyl-platinum bond is achieved in the presence of triethylamine:

$$\mathrm{cis\text{-}[Pt(QR^1_3)_2Cl_2] + HSiR_3 + Net_3 \longrightarrow} \\ \mathrm{trans\text{-}[Pt(QR^1_3)_2Cl(SiR_3)] + [et_3NH]Cl} \qquad (8)$$

Again the ease of reaction depends very much on Q (P, As) and the substituents R^1 and R[63, 64)]. The preparation of a compound containing an optically active silicon center, trans-(+)-Pt(Pme$_2$ph)$_2$Cl[Si*meph(1-naphthyl)], showed that these complexes are formed with retention of configuration at the silicon[96)]. The stereochemical characteristics are also retained in the syntheses of cobalt carbonyls according to Eq. (9)[210)]:

$$\mathrm{Co_2(CO)_8 + 2\ HSiR_3 \longrightarrow 2\ Co(CO)_4(SiR_3) + H_2} \qquad (9)$$

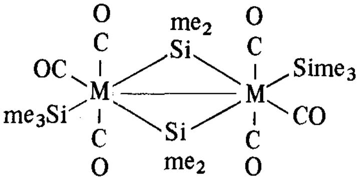
Reaction (9) was discovered by Chalk and Harrod[59, 60)] and later investigated by MacDiarmid[25, 26, 111, 118)]. The authors showed that it proceeds in two steps. The primary reaction product is $HCo(CO)_4$ which is thought to be responsible for the catalytic activity of $Co_2(CO)_8$ in the hydrosilylation of olefins:

$$\mathrm{Co_2(CO)_8 + HSiR_3 \longrightarrow Co(CO)_4(SiR_3) + HCo(CO)_4} \qquad (10)$$

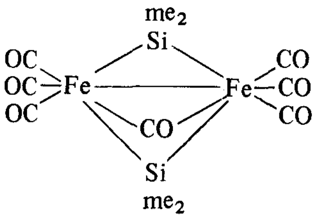
$$\mathrm{HCo(CO)_4 + HSiR_3 \longrightarrow Co(CO)_4(SiR_3) + H_2} \qquad (11)$$

The principle of reacting a silicon hydride $HSiR_3$ with a polynuclear carbonyl (or carbonyl cyclopentadienyl derivative) was successfully applied to other transition metals such as Mo[137], Mn[40, 137, 181, 207], Re[135, 137, 207], Fe[137,146,207], Ru[74,160], Os[159,161], and Ni[137] to give MSi, MSi_2, and (for M = Ru and Os only) SiM-MSi units. The reactions were carried out in sealed tubes in the absence of solvent or in hydrocarbon solvents, thermally or under uv irradiation.

With $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, if pentamethyldisilane is used as the silane component, both metal-metal and silicon-silicon bonds are broken to yield di-μ-(dimethylsilylene) complexes[47]:



On the other hand, 1,1,2,2-tetramethyldisilane reacts with $Fe(CO)_5$ to build up a binuclear structure with three bridging groups[166]:



There are few reports of reactions involving silanes of the type H_2SiR_2 or H_3SiR. H_2Siph_2 and H_2Siet_2 react with $Co_2(CO)_8$ to give $Co(CO)_4(SiHR_2)$[60], $Co_2(CO)_7(SiR_2)$[30] [μ-diorganylsilyl-μ-carbonyl-bis(tricarbonylcobalt)], and $Co_4(CO)_{14}(SiR_2)$[101] [with the suggested structure $(OC)_4CoSiR_2OCCo_3(CO)_9$].

A short paper mentions that H_3Siph and $Co_2(CO)_8$ react to give $Co_3(CO)_{11}(Siph)$[30]. In most such reactions not only hydrogen but also CO is eliminated. Uv irradiation of $Fe(CO)_5$ or $M(CO)_n$cp in the presence of a silane at low temperatures liberates only CO[138, 139]

$$Fe(CO)_5 + HSiCl_3 \longrightarrow Fe(CO)_4H(SiCl_3) + CO \qquad (12)$$

$$Co(CO)_2cp + HSiCl_3 \longrightarrow Co(CO)cp(H)(SiCl_3) + CO \qquad (13)$$

whereas the thermal reaction of $Fe(CO)_5$ and $HSiCl_3$ produces $Fe(CO)_4(SiCl_3)_2$ or $[Fe(CO)_4SiCl_2]_2$, depending upon the conditions, as was shown by

Graham[137, 141]. Reactions of the type shown in Eqs. (12) and (13) pertain to oxidative eliminations or oxidative addition-elimination reactions. Further examples in which the transition metals increase their oxidation number by two and their coordination number by one are seen in the interaction of rhodium(I)[61, 126, 127, 186], iridium(I)[122, 123] and ruthenium(0) complexes[160] with silicon hydrides:

$$\mathrm{Rh(Pph_3)_3Cl + HSiR_3 \longrightarrow Rh(Pph_3)_2Cl(H)(SiR_3) + Pph_3} \qquad (14)$$

$$\mathrm{Ir(Pph_3)_3(CO)H + HSiR_3 \longrightarrow Ir(Pph_3)_2(CO)H_2(SiR_3) + Pph_3} \qquad (15)$$

$$\mathrm{Ru(CO)_3(Pph_3)_2 + 2\ HSiR_3 \longrightarrow Ru(CO)_2(Pph_3)_2(SiR_3)_2 + CO + H_2} \qquad (16)$$

$$\mathrm{Rh(CO)_2cp + 2\ HSiCl_2R \longrightarrow Rh(CO)cp(SiCl_2R) + CO + H_2} \qquad (17)$$

Treatment of platinum(0) complexes with silicon hydrides[65, 66, 97, 102, 221]

$$\mathrm{Pt(Pph_3)_4 + HSiR_3 \longrightarrow Pt(Pph_3)_2H(SiR_3) + 2\ Pph_3} \qquad (18)$$

$$\mathrm{Pt(Pph_3)_2H(SiR_3) + HSiR_3 \longrightarrow Pt(Pph_3)_2(SiR_3)_2 + H_2} \qquad (19)$$

or disilanes[205, 206]

$$\mathrm{Pt(Pph_3)_4 + Si_2Cl_6 \longrightarrow Pt(Pph_3)_2(SiCl_3)_2 + 2\ Pph_3} \qquad (20)$$

similarly produces compounds with a silicon atom attached to platinum(II). Finally, some ligand displacement reactions have been reported in which the oxidation state of the transition metal is not altered. Cobalt[210], iridium[108], and platinum complexes[70, 71] undergo exchange reactions involving two different SiR_3, or SiR_3 and ElR_3 moieties (El = Ge, Sn):

$$\mathrm{ML_{\mathit{n}}(ElR'_3) + HSiR_3 \longrightarrow ML_{\mathit{n}}(SiR_3) + HElR'_3} \qquad (21)$$

CO groups in silyl-transition-metal carbonyls can be replaced by PR^1_3 groups or bidentate phosphorus ligands:

$$\mathrm{M(CO)_{\mathit{n}}(SiR_3) + PR^1_3 \longrightarrow M(CO)_{\mathit{n}-1}(PR^1_3)(SiR_3) + CO} \qquad (22)$$

Such reactions do not affect the Si-M bond but lead to new derivatives which are treated in some detail in Section 4.2.

2.3. Oxidative Addition Reactions

In this special type of reaction, three-coordinated or square-planar complexes of certain transition metals (Rh, Ir, Pt) add silanes to form penta- or hexacoordinate complexes, respectively, both the oxidation number and coordination number of the transition metal increasing by two,

$$\mathrm{Rh(CO)_2cp + HSiR_3 \longrightarrow Rh(CO)_2cp(H)(SiR_3)}\ ^{186)} \qquad (23)$$

$$\mathrm{M(PR^1_3)_2(CO)Cl + HSiR_3 \longrightarrow M(PR^1_3)_2(CO)Cl(H)(SiR_3)\ (M = Rh, Ir).} \qquad (24)$$

The stability of the adducts increases with increasingly electronegative substitution on the silicon[58, 122]. Reactions are reversible in some cases[54, 61, 124] and there is an evident connexion to homogeneous catalysis[56].

The only isolated silyl derivative of hexacoordinated platinum was prepared by Ebsworth[36, 37] according to Eq. (25),

$$\mathrm{trans\text{-}[Pt(Pet_3)_2I_2] + H_3SiI \longrightarrow Pt(Pet_3)_2I_2(H)(SiH_2I)} \qquad (25)$$

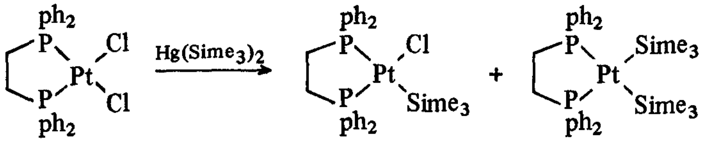
although the complex can be detected by nmr in solutions of $\mathrm{Pt(Pet_3)_2I(SiH_2I)}$ containing HI. Hexacoordination may occur in an intermediate of the elimination process (7).

2.4. Mercurial Method

Bis(trimethylsilyl)mercury (a convenient source of $\mathrm{Sime_3}$ groups in organometallic reactions) was successfully used by Glockling for the preparation of trimethylsilyl complexes of platinum:

$$\mathrm{cis\text{-}[Pt(Pet_3)_2Cl_2] + Hg(Sime_3)_2 \longrightarrow trans\text{-}[Pt(Pet_3)_2Cl(Sime_3)] + ClSime_3 + Hg.} \qquad (26)$$

The second halogen atom cannot be substituted because of the very high trans effect of the $\mathrm{Sime_3}$ group[105, 106]. If, therefore, a cis-chelating phosphine such as bis(diphenylphosphino)ethane (diphos) is used, either one or both chlorine atoms can be replaced by $\mathrm{Sime_3}$ groups, while mercury and trimethylchlorosilane are other products in these reactions which are carried out in refluxing benzene[69–71, 109]:



(27)

Only two other examples are reported: (28) involving both chloride replacement and oxidative addition to Ir(I)[132], and (29) employing $\mathrm{Hg(SiCl_3)_2}$ as mercurial reagent[41]:

$$\mathrm{trans\text{-}[Ir(Pet_3)_2(CO)Cl] + 2\ Hg(Sime_3)_2 \longrightarrow Ir(Pet_3)_2(CO)(Sime_3)_2(HgSime_3) + Hg + ClSime_3} \qquad (28)$$

$$Mn_2(CO)_{10} + Hg(SiCl_3)_2 \longrightarrow 2\,Mn(CO)_5(SiCl_3) + Hg. \qquad (29)$$

3. Spectroscopic and Structural Investigations. The Si-M Bond

There have been numerous spectroscopic and structural studies on the properties of the silicon-transitions metal bond. Infrared studies on the substituents of the Si and M centers were the usual starting point, so these will be the first to be discussed.

3.1. Studies of the Silicon Ligand

The values of the SiH stretching frequencies in compounds of the type $ML_m(SiH_nR_{3-n})$ compared with SiH_nR_{4-n} show a weakening of the Si-H bond, which is consistent with very low effective electronegativity values of the transition-metal residue ML_m. Smith[209] suggests that the electronegativity or inductive power of each substituent R^i in a silane $HSiR^1R^2R^3$ can be expressed in E values derived from ν(SiH), so that:

$$\nu(\mathrm{SiH}) = \sum_{i=1}^{3} E_i.$$

Table 1 compares the E values of some familiar substituents and of ML_m groups. The hypothetical compound $[Fe(CO)_2cp]_2SiH_2$ is calculated to have a mean SiH stretching frequency as low as 2037 cm^{-1}.

Table 1. E values [cm^{-1}] for some substituents R in $HSiR^1R^2R^3$

R	*E*	Ref.	R	*E*	Ref.	R	*E*	Ref.
F	761	209)	ph	709	209)	$Mn(CO)_5$	683	21)
Cl	753	209)	me	706	209)	$Fe(CO)_2cp$	656[1]	14, 154)
Br	756	209)	et	699	209)	$M(CO)_3cp$	651	115)
I	729	129)	cyclohexyl	692	209)	(M = Cr, Mo, W)		
H	725	209)	$Fe(CO)_4H$	692	24)	$Pt(Pet_3)_2Cl$	635[1]	36)
$Co(CO)_4$	710	20)	me_3Si	683	49)			

[1] Mean value.

The available nmr coupling constants $J(^{29}SiH)$[20, 21] are consistent with the ν(SiH) values and fit the correlation curve given by Bürger[49]. The ^{19}F nmr signal of $Co(CO)_4(SiF_3)$ occurs at extremely low field (−82.8 ppm, SiF_4 scale) because of the paramagnetic effect to the Co atom; the large coupling constant $J(^{29}SiF)$ of 370 Hz indicates the electropositive character of the transition-metal group[144]. The ^{35}Cl nqr frequency is relatively little changed in going from $SiCl_4$ to $Co(CO)_4(SiCl_3)$, presumably owing to blocking of any field gradient changes by the SiCl $d\pi p\pi$-bonding[48)].

X-ray data of
$Zrcp_2Cl(Siph_3)$[175)],
$[(me_3Si)(CO)_3Ru(Sime_2)]_2$[75)],
$Mn(CO)_5[Si(Sime_3)_3]$[182)],
$Co(CO)_4(SiF_3)$[100)],
$Co(CO)_4(SiCl_3)$[195)],
$Fe(CO)cpH(SiCl_3)_2$[171)], and
$Rh(Pph_3)_2Cl(H)(SiCl_3)$[176)]

show that the geometry at the silicon atom deviates slightly but significantly from a tetrahedral one: the mean R-Si-R angle in the SiR_3 or bridging SiR_2 groups varies from 103° to 106°. The SiC distances in the Zr complex (1.913 Å) and in the bridging $Sime_2$ group of the Ru complex (1.92 Å) are somewhat longer than in $Sime_4$, $Siph_4$ (1.87 Å[103)]) or in the terminal Ru-$Sime_3$ group (1.88 Å). The same relation holds for the SiSi distances in the manganese carbonyl (2.374 Å) and in $Si(Sime_3)_4$[31)] (2.361 Å), whereas the SiCl distances of 2.03–2.06 Å in the above-mentioned compounds compare favourably with those usually found in chlorosilanes. The SiF distance in $Co(CO)_4(SiF_3)$ could not be given very exactly because of undetermined thermal correction factors. Similar silicon-atom geometry is found in $W_2(CO)_8H_2(Siet_2)_2$[34)] possessing W-H-Si bridges (SiC 1.895 Å, $\sphericalangle$ CSiC 101°).

Infrared and ^{19}F nmr spectra indicate a five-coordinated silicon in $(ph_3P)_2Pt \cdot SiF_4$ and the ir data alone suggest octahedral silicon in the NH_3 adduct $(ph_3P)_2Pt \cdot SiF_4 \cdot NH_3$[94)]. Based on a ^{19}F nmr. study, a dynamic $Fe \rightarrow Si$ interaction in $(OC)_4Fe[Pme_2CH_2CH_2SiF_3]$ is discussed[114)].

3.2. Studies of the Transition-metal Ligand

Since the great majority of the known silyl-transition-metal compounds contain carbonyl groups, the 2000 cm^{-1} region in the infrared has been widely used for structural analysis. The number, position, and intensity of the carbonyl stretching frequencies provide information about the geometrical arrangement of carbonyl and silyl ligands around the transition metal, about inductive effects caused by adjacent substituents, about the oxidation state of the transition metal[58)] and about rotational isomerization. The SiR_3 groups in $M(CO)_m(SiR_3)_n$ can initially be assumed to be point masses when applying the $M(CO)_m$ selection rules. That is, a $M(CO)_5(SiR_3)$ or $M(CO)_4(SiR_3)$ molecule with SiR_3 in axial positions should have three infrared-active CO stretchings ($2A_1 + E$) exhibiting C_{4v} (of which a B_1 mode is only Raman-active) and C_{3v} symmetry, respectively. This pattern can be altered by intermolecular effects in the condensed phase or solvent, or by molecular asymmetry, *e.g.* asymmetric substitution on the silicon, as in $Co(CO)_4(SiH_2me)$ (Table 2). Table 2 shows some examples from the Co series, the wave-numbers for the silyl derivatives being grouped in the range of hydrogen or methyl compounds.

Table 2. CO stretching vibrations in tetracarbonylcobalt compounds [cm^{-1}]

Compound	Phase		ν CO		Ref.
		A_1	A_1	E	
$Co(CO)_4(SiF_3)$	Gas	2128	2073	2049	116)
$Co(CO)_4(SiCl_3)$	Gas	2125	2071	2049	116)
	Cyclohexane	2117	2062	2037	84)
$Co(CO)_4(H)$		2119	2053	2030	172)
$Co(CO)_4(CH_3)$		2111	2046	2031	172)
$Co(CO)_4(SiH_3)$	Gas	2105	2050	2025	20)
$Co(CO)_4(SiH_2me)$	Gas	2102	2043	2021, 2015	116)
$Co(CO)_4(Sime_3)$	Gas	2100	2041	2009	116)
$Co(CO)_4(Siph_3)$	[1]	2097	2035	2009	59, 84)
$Co(CO)_4(Siet_3)$	[1]	2089	2027	1997	59, 84)
$Co(CO)_4[Si(Ome)_3]$	[1]	2103	2038	2017	59, 84)

[1] Mean values from solutions in C_7H_{16}-[59] and $C_{16}H_{34}$[84].

The two A_1 stretchings of axial (ax) and equatorial (eq) CO groups are extensively coupled[84, 87, 216]. Approximate force-field calculations have been made which neglect coupling with other molecular vibrations and take into account only two CO stretching force constants (f^{ax}, f^{eq}) and two CO/CO stretch-stretch interaction force constants ($f^{ax,eq}$, $f^{eq,eq}$). To avoid vagueness, a relationship between $f^{ax,eq}$ and $f^{eq,eq}$ must be assumed. A well-known method was developed by Cotton and Kraihanzel[72], modified by Stone[12, 83, 84] and further simplified by MacDiarmid[116]. The use of additional data such as ^{13}C shifts[87] or band intensities[44] has been recently proposed.

The values for f(CO) range from 16.5 to 18.0 mdyn/Å and depend on the silicon substituents. Most authors calculate f^{ax} to be greater than f^{eq}, which seems plausible considering the symmetry of the participating d orbitals of Co and the π orbitals of the CO groups. For $Co(CO)_4(SiCl_3)$, which was investigated several times, the following differences ($f^{ax} - f^{eq}$) were determined: 0.93[216], 0.69[91], 0.58[84], 0.42 (using ^{13}C data)[87], –0.06[116]. Each method of calculation allows some deductions to be drawn in a series of related compounds, although great difficulties arise in trying to interpret the data so obtained. The generally accepted bonding picture involves some π-acceptor capacity for the SiR_3 group[12, 39, 146] and a complicated interrelation both of inductive effects operating through the σ system and of mesomeric metal-ligand-π interactions must be considered[112]. These effects are weighted in different ways[84, 116, 146, 215]. Stone[84] pointed out that for $Co(CO)_4(ElR_3)$, with El a group-IV element, the force constants f(CO), as well as the dπdπ-bonding between Co and El, increase with increasing R polarity constants (σ^*), as expected on the basis of an inductive effect. In compounds with highly electronegative R, dπdπ-

bonding in the silicon derivative is less significant than in those of germanium and tin, probably because of greater pπdπ competition between Si and R. MacDiarmid[116)] emphasized π interactions between SiR_3 and CO groups in the trans position, f^{ax} being predominantly affected by changes in π-bonding.

Similar studies were made on compounds of the type
$M(CO)_5(SiR_3)$[8, 21, 83, 88, 112, 142, 207, 208, 215)] and
$Fe(CO)_4(SiR_3)_2$[90, 139, 146)] and
$[Fe(CO)_4SiCl_2]_2$[85, 89)].
In the latter complexes[24, 137, 146)] and the related compounds
$Fe(CO)_4H(SiR_3)$[24, 139)],
$Ru(CO)_4(SiR_3)_2$[160)],
$Os(CO)_4H(SiR_3)$[161)], and
$Mn(CO)_4(Pph_3)(SiR_3)$[207)]

the four-band spectrum in the ν CO region proves the cis-arrangement for the two non-carbonyl ligands. $Os(CO)_4(Sime_3)_2$, $Os(CO)_4(Sime_3)(Snme_3)$[161)] and $Ru(CO)_4(SiR_3)(Snme_3)$[160)] consist of a mixture of cis- and trans-isomers, while the triethylsilyl analogue $Os(CO)_4(Siet_3)_2$ [161)] and the halides $Os(CO)_4X(Sime_3)$ and $Ru(CO)_4X(Sime_3)$ (X = Br, I)[16)] have only one strong carbonyl absorption in the infrared, which is typical of a trans configuration. Recent communications reported stereochemical non-rigidity and cis-trans isomerization in $Ru(CO)_4(SiCl_3)_2$[192)] and $Os(CO)_4(Sime_nCl_{3-n})$[193)]. Other examples of stereochemically non-rigid structures are $Fe_2(CO)_7(Sime_3)_2$[166)] and $Fe(CO)_2cp(SiCl_2me)$[81, 82, 137)]. Measurements of CO stretching absorptions were also helpful in detecting ionic species[18, 24, 28, 140, 141)] (see Section 4.3).

Few vibrational spectra of silyl-transition-metal carbonyls have been extended to the middle and far ir regions[20–22, 24, 145, 146, 147)] and completed by Raman data[93)] to permit normal coordinate analyses[91, 216)]. The frequency ranges for the M-C stretchings and δ MCO bendings are 400–510 cm^{-1} and 480–660 cm^{-1}, respectively. Distinct coupling of several coordinates is concluded from the eigenvectors of the lower vibrational modes: the effect on the SiM stretching force constants is explained below (Section 3.3).

In phosphine complexes, the ν MP modes (around 400 cm^{-1})[36, 64, 205)] are often obscured by aryl-group vibrations. Main efforts for the determination of stereochemistry are concentrated on ^{31}P nmr spectroscopy, especially in the case of platinum(II) and platinum(IV) complexes[36, 37)] (^{195}Pt nucleus: spin $\frac{1}{2}$, 31% abundant). Silyl groups have been found to have a very great trans effect of inductive origin. It causes a very low value of $J(^{195}Pt-^{31}P)$ in cis-$[Pt(Pme_2ph)_2(Simeph_2)_2]$ (1559 Hz), reflecting the covalency of the Pt-P bond[64, 128)]. In trans-$[Pt(PR_3^1)_2X(SiR_3)]$ it leads to exceptionally low values of the Pt-halogen (X) stretching frequencies which are also sensitive to the nature of the R substituents on the silicon[62, 63)]. ν (PtCl) and ν (PtBr) lie in the region of 235–275 cm^{-1} and 155–175 cm^{-1}, respectively; the coupling constants $J(^{195}Pt-^{31}P)$ are in the range 2630–2880 Hz. Long-range couplings are also significant in this class of compounds [*e.g.* $J(^{195}\text{Pt-Si-C-}^{1}\text{H})$71, 107), $J(^{195}\text{Pt-Si-}^{1}\text{H})$36, 37)].

In a number of hydrido complexes $M(H)L_m(SiR_3)_n$ the MH bond has been proved by ir (ν MH 1940–2140 cm^{-1}) and ^1H nmr spectroscopy [τ MH 15–24 ppm, J(MH)]65, 69, 71, 97, 102, 122, 126, 127, 135, 138, 139, 141, 161, 186).

3.3. Studies of the Silicon-Metal Bond

The silicon-transition-metal bond is presently viewed as a σ bond which is additionally stabilized in most cases by some partial dπdπ interactions due to donation from filled d orbitals of the metal to empty silicon d orbitals of appropriate symmetry. X-ray diffraction studies have contributed valuable information to this picture. From Table 3 it can be seen that all observed SiM distances, with the exception of the last three, are significantly shorter than would be expected on the basis of the covalent radii [$r_{\text{cov}}(\text{Si}) = 1.17$ Å]. Estimation of covalent radii for the transition metals is certainly a very difficult problem, but errors in these values can probably not explain differences up to 0.28 Å. The shortest Si-M bond was found in the rhodium compound176) which consists of discrete, highly distorted trigonal bipyramids with apical phosphines ($\sphericalangle$ PRhP 161.7°) and $SiCl_3$, H, and Cl^1 in the trigonal plane ($\sphericalangle$ SiRhP 98.3°, $\sphericalangle$ SiRhCl^1 115.9°). There is consequently no π-bonding ligand trans to and competing with the silyl group. In the trigonal bipyramidal cobalt complexes, the SiCo distance decreases significantly with substitution of electronegative atoms on the silicon100, 195, 194). Considering the similarity of d(SiCo) in the fluoro and chloro derivatives, it is suggested that the shortening is effected not only by the electron-withdrawing ligand contracting the metal d orbitals but also by some dπdπ back-bonding172).

Simple molecular-orbital calculations using an extended Hückel approach on $Co(CO)_4(SiF_3)$ and $Co(CO)_4(SiCl_3)$ show a relatively small contribution of SiCo π interactions (6–8% of total bonding)39). In both compounds the equatorial carbonyl groups are displaced out of the basal plane in the direction of the axial silyl group; this, together with evidence from mass spectra202), may suggest a direct pπdπ interaction between the silicon and these carbonyls8, 39). Some relatively high bond-dissociation energies have been reported from mass-spectral studies

[$Co(CO)_4(SiF_3)$200) 105 ± 12,
$Co(CO)_4(SiF_2me)$201) 127 ± 15,
$Co(CO)_4(SiCl_3)$202) 126 ± 25 kcal/mol].

Finally, in the d^0 complex $Zrcp_2(Cl)(Siph_3)$, where no dπdπ back-donation is to be expected, an extremely long SiM distance is found175).

Table 3. SiM distances (Å) in silyl-transition-metal complexes obtained by X-ray diffraction studies

Compound	d(SiM) obsd.	calcd.	Ref.
$Rh(Pph_3)_2H(Cl)(SiCl_3) \cdot x\ HSiCl_3$	2.203	2.48	176)
$Co(CO)_4(SiF_3)$	2.226	2.51	100)
$Co(CO)_4(SiCl_3)$	2.254	2.51	195)
$Co(CO)_4(SiH_3)$	2.381 1)	2.51	194)
$Fe(CO)cp(H)(SiCl_3)_2$	2.252	2.51	171)
trans-$[Pt(Pme_2ph)_2Cl(Simeph_2)]$	2.29	2.46	148)
$Mn(CO)_5(Sime_3)$	2.497	2.60	119)
$Mn(CO)_5[Si(Sime_3)_3]$	2.564	2.60	182)
$W_2(CO)_8H_2(Siet_2)_2$	2.586 (WSi) 2.703 (WSi')	2.79	34)
$[Ru(Si^1me_3)(CO)_3(Si^2me_2)]_2$	2.391 $(RuSi^2)$ 2.491 $(RuSi'^2)$ 2.507 $(RuSi^1)$	2.44	75)
$Zrcp_2(Cl)(Siph_3)$	2.813	2.62	175)

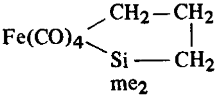
1) Electron diffraction.

Other structural details of interest are an unusual *trans* square-pyramidal geometry about the iron in $Fe(CO)cp(H)(SiCl_3)_2$ 171), the existence of a strong Ru-Ru bond in the Ru_2Si_2 bridge plane of $[Ru(Sime_3)(CO)_3(Sime_2)]_2$ (this molecule containing three different Si-Ru bonds75)) and the apparent presence of three-center two-electron W-H-Si bonds in the tungsten complex $W_2(CO)_8H_2(Siet_2)_2$, which contains a planar central W_2Si_2 cluster in the form of a parallelogram with two different Si-W distances34). This tungsten complex is one of the few hydrogen-bridged silicon-transition-metal compounds34,99,125). Another compound of this class is $Re_2(CO)_8H_2Siph_2$ for which a symmetric ReHSiHRe bridge has been suggested across the Re-Re bond99). The Si-Re distance of 2.544 Å is shorter than the sum of covalent radii (2.68 Å), indicating some attraction. In the dimethylsilicon analog $Re_2(CO)_8H_2Sime_2$, the CH_3 proton resonance appears as a triplet caused by coupling (J = 1.5 Hz) with the bridging hydrogens134).

The pure nqr data of ^{59}Co in $Co(CO)_4(SiCl_3)$ and $Co(CO)_4(Siph_3)$ were interpreted in terms of σ and π interactions between Co and the SiR_3 group48). Measurements of dipole moments were performed for only three $Co(CO)_4(SiR_3)$ derivatives145) (R = Cl, ph, et; μ = 2.85, 1.25, 1.47 D) and for trans-$[Pt(Pme_2ph)_2Cl(Simeph_2)]$ (μ = 2.5 D)64). The polarity of the Si-M bond is $\overset{\delta-}{Si}–\overset{\delta+}{M}$ with a low partial moment215).

A moderate number of Si-M stretching frequencies have been located in the vibrational spectra of silyl-transition-metal complexes (Table 4). For the determination of reliable force constants, normal coordinate analyses are required; pseudodiatomic calculations[216] using [Si]-[Co] or $[R_3Si][ML_n]$ units give erroneous results because of strong mixing of internal coordinates. The only figure reported for a Si-M stretching force constant is f(SiCo) in $Co(CO)_4(SiCl_3)$, amounting to 1.32–1.43 mdyn/Å[91,216]. ν(SiCo) is coupled with ν_sSiCl_3 and δ_sSiCl_3 in the frequency pattern of 309, 549, and 179 cm^{-1}.

Table 4. "Si-M stretching frequencies" in silyl-transiton-metal complexes [cm^{-1}]

Compound	νSiM	cm^{-1}	Ref.
$Mn(CO)_5(SiH_3)$	SiMn	304	21)
$Mn(CO)_5(Sime_3)$		293	147)
$Mn(CO)_5(SiCl_3)$		291	147)
	SiFe	302	77)
$Co(CO)_4(SiH_3)$	SiCo	310	20)
$Co(CO)_4(SiCl_3)$		303	147)
		309	91, 216)
$Co(CO)_4(Sime_3)$		295	93, 147)
$Pt(Pet_3)_2X(SiR_3)$	SiPt	326–352	36, 106)
$Pt(Pet_3)_2(Geph_3)(Sime_3)$		337	106)
$Au(Pph_3)(Siph_3)$	SiAu	305	27)

4. Properties and Reactions

The silyl-transition-metal complexes completely tabulated in Section 6 and arbitrarily selected in Table 5 are a generally fairly stable and rather easily handled class of compounds provided the inert conditions, required in most cases during the preparation because of the sensitivity of the starting materials, are maintained. Some solid platinum[64] and rhodium complexes[127] are even stable in air. In solution, stability is very often reduced[27, 156, 169, 180, 186]. Light sensitivity is reported for several compounds of molybdenum, tungsten[169] and gold[27].

Particular chromium[198], ruthenium[16], cobalt[118, 138], platinum[37], and tungsten complexes[203] decompose even when stored at room temperature for an extended period. Partial decomposition is sometimes observed upon melting. Thermal stability was investigated in detail in some cobalt, manganese, iron[23] and ruthenium compounds. The decomposition products often vary according to the substituents on the silicon:
the silyl derivatives $Co(CO)_4(SiH_3)$[20] and $Mn(CO)_5(SiH_3)$[21] decompose on heating at 100 °C or 135 °C to yield SiH_4, H_2, CO and $HM(CO)_n$.

Table 5. Physical properties of arbitrarily selected silicon-transition-metal compounds

Compound	Colour	m.p. (°C)	Ref.
$Zrcp_2(Cl)(Siph_3)$	Orange	175–178 (dec.)	50, 156)
$Mn(CO)_5(SiH_3)$	White	25.5	19, 21)
$Mn(CO)_5(SiF_3)$	White	75	208)
$Mn(CO)_5(SiCl_3)$	White	130–131	137)
$Mn(CO)_5(Sime_3)$	White	26	40)
$Mn(CO)_5(Siph_3)$	White	160–163	142)
$Fe(CO)_4(H)(SiCl_3)$	Pale yellow	Liq.	139)
$Fe(CO)_2cp(Sime_3)$	Orange yellow	70	191)
$[Ru(CO)_4(Siet_3)]_2$	Bright yellow	150–152	160)
$Co_4(CO)_{14}Siph_2$	Dark red	78–80	101)
$Rh(Pph_3)_2H(Cl)(Sime_3)$	Yellow	92–97 (dec.)	127)
$Li[Ni(CO)_3(Siph_3)] \cdot 2$ THF	Yellow	99–101	163)
$Pt(Pph_3)_2(SiCl_3)_2$	White	210–212	66)
$Pt(Pet_3)_2I_2(H)(SiH_2I)$	Yellow	dec.	36)

$Co(CO)_4(Siph_3)$ releases Si_2ph_6 on pyrolysis at 200 °C$^{60)}$ whereas $Co(CO)_4(Sialkyl_3)$ yields $(alkyl_3Si)_2O$ at 150–190 °C$^{8)}$.
$Co(CO)_4(SiF_3)$ as a pure liquid undergoes complete decomposition in 18 hours at room temperature to give SiF_4, CO, Si, $Co_2(CO)_8$, and $Co_4(CO)_{12}$$^{118)}$.
$Ru(CO)_4I(Sime_3)$ on refluxing in hexane liberates CO and forms the binuclear complex $[Ru(CO)_3I(Sime_3)]_2$$^{16)}$.
The thermal stability of the chloroalkyl complexes $Rh(Pph_3)_2Cl(H)(SiCl_nme_{3-n})$ decreases markedly with increasing number of alkyl groups and a similar stability sequence is found in solution. The trimethyl compound dissociates instantly on dissolution in diglyme, $HSime_3$, $(me_3Si)_2O$, and $Rh(Pph_3)_2ClH_2$ being isolated$^{127)}$.

Of course, "stability" is a very complicated term influenced by numerous and diverse parameters. Thermodynamic stability means that the complex has a negative free energy of formation from its decomposition products. Unfortunately, thermodynamic evidence on the strength of Si-M bonds is almost completely lacking. Kinetic stability affects the possible pathways of decomposition, such as existence of potential coordination sites at the silicon or metal center, the ability of the latter to vary its oxidation state, nucleophilicity of the ligands, the associated possibility of concerted rearrangements$^{46)}$and so on. These introductory notes will be followed by a discussion of chemical reactivities.

Reactions are conveniently classified into three types, substitution at the silicon, substitution at the metal, and cleavage of the silicon-metal bond. Because of some interesting bonding features, we devote a section to reactions with nitrogen and phosphorus Lewis bases.

4.1. Substitution at the Silicon

Very little is known about substitution at the silicon. If a hydrogen halide[19, 21, 36, 37] or a halogen[65, 66] is allowed to react gently with some SiH complexes, hydrogen or hydrogen halide respectively are liberated:

$$Mn(CO)_5(SiH_3) + x\ HCl \longrightarrow Mn(CO)_5(SiCl_xH_{3-x}) + x\ H_2\ (x = 1\text{–}3) \qquad (30)$$

$$Pt(Pet_3)_2Cl(SiClH_2) + HCl \longrightarrow Pt(Pet_3)_2Cl(SiCl_xH_{3-x}) + H_2\ (x = 2, 3) \qquad (31)$$

$$Pt(diphos)(Siph_2H)_2 + Br_2 \longrightarrow Pt(diphos)(Siph_2Br) + HBr. \qquad (32)$$

In the platinum complexes, the halogen attached to the silicon was further substituted by me[65, 66], Ome, and Nme$_2$ groups[36, 37]. CCl$_4$ chlorinates the weak Si-H bond in Fe(CO)$_2$cp(Sime$_2$H)[152]. Fluorination of the silicon center is achieved by interaction of PF$_5$ on Co(CO)$_4$(SimeH$_2$)[110, 111] and AgBF$_4$ on Fe(CO)$_2$cp(SiCl$_3$)[173]. Triphenylphosphine is reported to reduce the platinum derivatives Pt(Pph$_3$)$_2$(SiX$_3$)$_2$ to silylene complexes Pt(Pph$_3$)$_2$(SiX$_2$)$_2$, being itself oxidized to Pph$_3$Cl$_2$[205]. (ph$_3$P)$_2$Pt · SiF$_4$ adds one NH$_3$ molecule to give (ph$_3$P)$_2$Pt · SiF$_4$ · NH$_3$ containing an octahedrally coordinated silicon[94].

4.2. Substitution at the Metal

A series of ligand displacement reactions has been investigated in which a phosphine replaces a carbonyl group, the ease of reaction depending on both M and the silyl residue. Triphenyl or trialkyl phosphine can remove only one CO molecule in Mn, Re, Co, and Fe complexes, even under forced conditions,

$$M(CO)_5(SiR_3) + Pph_3 \longrightarrow M(CO)_4(Pph_3)(SiR_3) + CO\ (M = Mn^{92, 197, 207, 208)}, Re^{208)}) \qquad (33)$$

$$Co(CO)_4(SiR_3) + PR^1_3 \longrightarrow Co(CO)_3(PR^1_3)(SiR_3) + CO^{19, 20, 28, 29, 80, 146, 184)} \qquad (34)$$

$$Fe(CO)_2cp(Sime_3) + PR^1_3 \xrightarrow{UV} Fe(CO)cp(PR^1_3)(Sime_3) + CO^{152, 154)} \qquad (35)$$

but two CO molecules in a Ru compound:

$$Ru(CO)_4(Sime_3)_2 + 2\ Pph_3 \longrightarrow Ru(CO)_2(Pph_3)_2(Sime_3)_2 + 2\ CO^{160)} \qquad (36)$$

UV irradiation of Mn(CO)$_5$(Sime$_3$) with excess PF$_3$ gave a mixture of Mn(CO)$_{5-n}$(PF$_3$)$_n$(Sime$_3$) where n = 1, 2, 3.[29, 40].

Chelating bidentate ligands such as 1,2-bis(diphenylphosphino)ethane-(diphos)[152, 197], cis-1,2-bis(diphenylphosphino)ethylene[152] and 2,2'-bipyridyl(bipy)[197] replace two moles of CO. In the reaction of the ditertiary phosphines (L) and Fe(CO)$_2$cp(Sime$_3$) there was some evidence for production of bridged derivatives of the type [(R$_3$Si)cp(CO)Fe]$_2$L[154]. Diphos and two cis-positioned phosphine groups are interchanged in a stepwise replacement reaction[64, 107]. In the case of trialkyl phosphines, Eq. (34) is only adequate for the trichlorosilyl cobalt complex. With the trialkylsilyl derivatives, the Si-Co bond is cleaved with formation of ionic species $[R_3SiPR^1_3]^+[Co(CO)_4]^-$[28]. A trace of water, however, is said to catalyze the conversion of the hexaethyl salt to $Co(CO)_3(Pet_3)(Siet_3)$ with elimination of CO[29]. Reaction (33) with $Mn(CO)_5(Siph_3)$, which must be carried out above 130 °C[197], was found to be autocatalytic[92]. Phosphites $P(OR)_3$ generally cleave Si-M bonds[77, 196, 197]; with the iron complex, substitution according to Eq. (35) occurred to a greater extent[152].

M-halogen bonds can be converted to M-H bonds by silanes $HSiR_3$, exchanging Cl for H[54], or by the usual sodium borohydride reduction of iodides[16]. CH_3I reacts very slowly with trans-$[Pt(Pet_3)_2Cl(SiClH_2)]$ in benzene to form CH_3Cl and trans-$[Pt(Pet_3)_2I(SiClH_2)]$[36].

After treatment of the rhodium compound shown in Eq. (37) with CO, the ir spectrum indicated an unstable hexacoordinate intermediate:

$$Rh(Pph_3)_2Cl(H)(SiCl_3) + CO \longrightarrow Rh(CO)(Pph_3)_2Cl(H)(SiCl_3). \qquad (37)$$

This subsequently lost $HSiCl_3$ to form $Rh(CO)(Pph_3)_2Cl$[127].

Some studies of Ru and Os chemistry have been reported by Stone. The metal-metal bonds in the complexes $[M(CO)_4(Sime_3)]_2$ are readily attacked by halogens, triphenylphosphine, trimethylsilane, and sodium amalgam. Sodium amalgam produces the anion $[M(CO)_4(Sime_3)]^-$ which reacts with main-group or transition-metal halide species to give a series of new complexes,[74, 160, 161] *e.g.*

$$\begin{aligned} &[Ru(CO)_4(Sime_3)]^- + \text{trans-}[Os(CO)_4(Sime_3)Br] \longrightarrow \\ &\qquad\qquad (me_3Si)Ru(CO)_4Os(CO)_4(Sime_3) + Br^- \qquad (38) \end{aligned}$$

which contains a linear SiRuOsSi sequence.

The monohalides (X = Br, I, cf. Eq. (39)) tend to liberate CO to form halogen-bridged complexes $[M(CO)_3(Sime_3)X]_2$. These are shown by ir and

$$[M(CO)_4(Sime_3)]_2 + X_2 \longrightarrow 2\ \text{trans-}[M(CO)_4(Sime_3)X] \qquad (39)$$

nmr spectroscopy to exist as mixtures of mer- and fac-isomers. Triphenylphosphine cleaves the halogen bridges of the dimeric species to give the monomeric and more stable compounds $M(CO)_3(Pph_3)(Sime_3)X$, which are less well prepared direct from $M(CO)_4(Sime_3)X$ and Pph_3[16]. Excess triphenylphosphine reacts with $[Ru(CO)_4(Sime_3)]_2$ in a complicated way to give $Ru(CO)_2(Pph_3)_2(Sime_3)_2$ and $Ru(CO)_3(Pph_3)_2$[160]. In reaction (40)

$$[Os(CO)_4(Sime_3)]_2 + HSime_3 \longrightarrow Os(CO)_4(Sime_3)_2 + Os(CO)_4(Sime_3)H \qquad (40)$$

the Os-Os bond is cleaved by the silane to form a Si-Os bond and an osmium hydride which regenerates the binuclear complex on heating[161]:

$$2\ Os(CO)_4(Sime_3)H \longrightarrow [Os(CO)_4(Sime_3)]_2 + H_2. \qquad (41)$$

4.3. Formation of Ionic Species and Adducts

Silyl-substituted transition-metal hydrides show remarkably high acidities, which decrease in the sequence
$Fe(CO)cp(H)(SiCl_3)_2 \gg Fe(CO)_4(H)(SiCl_3) > Fe(CO)_4(H)(Siph_3) > Mn(CO)_2cp(H)(SiCl_3) > Mn(CO)_2cp(H)(Siph_3)$.
$Fe(CO)cp(H)(SiCl_3)_2$ is a very strong acid in acetonitrile; its pK_a value of 2.6 shows it to be stronger than HBr or H_2SO_4 in this solvent, but weaker than $HClO_4$. A tetraphenylarsonium salt can be prepared in acetone:

$$Fe(CO)cp(H)(SiCl_3)_2 + [ph_4As]Cl \longrightarrow [ph_4As]^+[Fe(CO)cp(SiCl_3)_2]^- + HCl. \qquad (42)$$

The cyclopentadienyl-tricarbonyl iron salt $[Fe(CO)_3cp]^+[Fe(CO)cp(SiCl_3)_2]^-$ is one of the products from the interaction of the dimer $[Fe(CO)_2cp]_2$ with $HSiCl_3$. The other products are $Fe(CO)_2cp(SiCl_3)$, $Fe(CO)cp(H)(SiCl_3)_2$, and $[Fe(CO)_3cp]^+[FeCl_4]^-$, yields being very sensitive to the reaction conditions[141]. Anions of the weaker acids have been obtained in CH_2Cl_2 solution, *e.g.*

$$Fe(CO)_4(H)(SiR_3) + et_3N \longrightarrow [et_3NH]^+[Fe(CO)_4(SiR_3)]^- \quad (R = Cl, ph) \qquad (43)$$

$$Mn(CO)_2cp(H)(SiCl_3) + et_3N \longrightarrow [et_3NH]^+[Mn(CO)_2cp(SiCl_3)]^- \qquad (44)$$

and used for metathetical reactions leading to other metal-metal bonds[140]. $[Fe(CO)_4(Siph_3)]^-$ as well as $[Ni(CO)_3(Siph_3)]^-$ can also be prepared by a different route from the reaction of ph_3SiLi and $Fe(CO)_5$ or $Ni(CO)_4$[163].

In connexion with the work of Graham on the metal hydrides, some results of Aylett's group must be mentioned. These authors have found that $Fe(CO)_4(SiH_3)_2$ and $Fe(CO)_4(H)(SiH_3)$[13, 23, 24], as well as $Co(CO)_4(SiH_3)$ and $Mn(CO)_5(SiH_3)$[18, 19, 22], react with tertiary amines to produce "adducts", the stoichiometry being 1:2 with Nme_3 or pyridine, and 1:1 with 2,2'-bipyridyl. From comparison of the solid-state ir spectrum of $Fe(CO)_4(SiH_3)_2 \cdot 2\ Nme_3$ with other carbonyl ferrates, a partly ionic nature was deduced with one Nme_3 group coordinated to each silicon. The adducts of the three other compounds evidently contain the carbonyl metallate anions in the solid state and can be formulated as $[SiH_3 \cdot 2\ B]^+[Fe(CO)_4H]^-$ and $[SiH_3 \cdot 2\ B]^+[M(CO)_n]^-$, where B = Nme_3 and py, and 2 B = bipy. Amine adducts of $M(CO)_3cp(SiH_3)$ where M = Cr, Mo, W have been reported[115].

MacDiarmid and his coworkers report the formation of ionic species containing trialkylsilyl groups. Nme_3 and PR^1_3 undergo instantaneous reactions in a hydrocarbon solvent with a deficiency of $Co(CO)_4(Sime_3)$ to give $[me_3SiNme_3]^+[Co(CO)_4]^-$ and $[me_3SiPR^1_3]^+[Co(CO)_4]^-$.
No phosphonium compound was formed when either the phosphorus or the

silicon was bonded to electronegative groups; in some cases there was a slow replacement to CO by PR^1_3 [28, 29]. $Mn(CO)_5(Sime_3)$ reacts only with the stronger base Nme_3 [29, 40]. The presence of the $[M(CO)_n]^-$ ion was unequivocally established by ir studies in the νCO region. Dimethylamine reacts with $Co(CO)_4(Sime_3)$ in an analogous way, yielding the rather unstable $[me_3SiN(H)me_2]^+[Co(CO)_4]^-$, but a simultaneous side reaction occurs, as shown in Eq. (45a): [131]

$$ML_n(Sime_3) + HNme_2 \underset{b}{\overset{a}{\rightleftharpoons}} me_3SiNme_2 + HML_n. \qquad (45)$$

Eq. (45a) also holds for $Fe(CO)_2cp(Sime_3)$ [38, 177]. The reverse reaction (45b), an amine-elimination process, can be used to prepare trimethylsilyl compounds of Cr, Mo, and W, where L_n is $(CO)_3cp$ [50,51].

Ammonia is reported to cleave the Si-M bond in $Co(CO)_4(SiH_3)$ and $Mn(CO)_5(SiH_3)$, giving $HM(CO)_n$ and $(H_3Si)_2NH$ as the primary products, whereas PH_3 does not react with $Co(CO)_4(SiH_3)$ [19, 22].

4.4. Cleavage of the Si-M Bond

Experimental data on this topic are very comprehensive. They can conveniently be divided into several types of reactions; the one concerning Lewis bases has already been anticipated in the second part of the previous chapter.

4.4.1. By Protonic Agents and Covalent Halides

The Si-M bond is cleaved by water, methanol, hydrogen halides or thiophenol [64, 98], at varying rates. The silicon products on hydrolysis (Eq. (46)) are disiloxanes or SiO_2,

$$2\,ML_n(SiR_3) + H_2O \longrightarrow \{(R_3Si)_2O\} + 2\,HML_n \qquad (46)$$

methanolysis produces R_3SiOme [17, 21, 25, 36, 38, 40, 105–107, 115, 118, 127, 177]. The Si-Fe bond in $Fe(CO)_2cp(Sime_3)$ is very resistant so that aqueous or methanolic KOH, or CH_3OH/HCl are required to disrupt it [177]. The reaction with HCl was often used as an important argument for the presence of a Si-M bond; it can follow two courses:

$$ML_n(SiR_3) + HCl \longrightarrow ClSiR_3 + HML_n \quad \text{or} \qquad (47)$$

$$ML_n(SiR_3) + HCl \longrightarrow HSiR_3 + ClML_n. \qquad (48)$$

Eq. (47) is valid for Co [17, 20], Fe [23, 24, 38, 177], Cr, Mo, W [115, 198], and some Pt complexes [62, 71, 107]. With $Fe(CO)_4(SiH_3)_2$, a stepwise reaction occurs via $Fe(CO)_4(H)(SiH_3)$ to $Fe(CO)_4H_2$ [23, 24]. Cleavage according to Eq. (48) is obtained with Zr[50, 156], Hf[155, 156] [HBr], Ni [157], Rh[127], and some other Pt complexes[62, 65, 66, 71]. The specific behaviour of Pt compounds is attributed to the influence of the group trans to the silyl group, as is indicated in Eqs. (49) and (50):

$$\text{cis-}[Pt(Pme_2ph)_2(Simeph_2)_2] + HCl \longrightarrow$$
$$HSimeph_2 + \text{trans-}[Pt(Pme_2ph)_2Cl(Simeph_2)] \qquad (49)$$

$$\text{trans-}[Pt(Pme_2ph)_2Cl(Simeph_2)] + HCl \longrightarrow$$
$$ClSimeph_2 + \text{trans-}[Pt(Pme_2ph)_2Cl(H)]. \qquad (50)$$

Two complexes, $Mn(CO)_5(Sime_3)$ and $[(me_3Si)Fe(COSime_3)(CO)_3]_2$ [179] are not attacked by HCl. For substitution reactions see Section 4.1.

The cleavages of silyl transition-metal compounds by halogens[26, 98] range from a stepwise elimination of the SiR_3 groups in
$Os(CO)_4(Sime_3)_2$ [16],
cis-$[Pt(Pme_2ph)_2(Simeph_2)_2]$[64],
or $Pt(diphos)(SiR_3)_2$ [66]
to the complete breakdown of the $Co(CO)_4(SiH_3)$ molecule yielding $CoBr_2$, $SiBr_4$, HBr, CO, and $COBr_2$ [17].

The reported reactions with covalent halides are mainly restricted to Co and Pt complexes. GeF_4 and me_2AsCl act on $Co(CO)_4(Sime_3)$ to give trimethylhalosilane, $Co(CO)_4(GeF_3)$ and unstable $Co(CO)_4(Asme_2)$, respectively[25, 26]. Mercuric halides HgX_2 cleave $Co(CO)_4(SiR_3)$ molecules to give $XSiR_3$ and $Hg[Co(CO)_4]_2$ [17, 20, 118].

When methyl iodide is heated with cis-$[Pt(Pme_2ph)_2(Simeph_2)_2]$ at 100 °C, $PtI_2(Pme_2ph)_2$ and dimethyldiphenylsilane, and also some methylphenyliodosilane, are obtained[64]. Ethylene dichloride reacts slowly with trans-$[Pt(Pet_3)_2Cl(Sime_3)]$ to give the corresponding chlorides $Pt(Pet_3)_2Cl_2$, $ClSime_3$, and ethylene[103]. Some other reactions have also been described[21, 40, 95, 115, 156].

4.4.2. By Displacement of the Silyl Ligand

Some reactions of Si-M bond formation by hydrogen elimination have been found to be reversible (Eqs. (6, 7)). Hydrogenolysis of silyl-platinum complexes has been extensively studied by Glockling. It was postulated to proceed via the formation of a hexa-coordinate platinum dihydride intermediate[106, 107]. In $Pt(PR^1_3)_2(SiR_3)_2$ one Pt-Si bond is readily hydrogenated (usually at 1 atm and 20 °C in the absence of added catalysts), but the other Pt-Si bond resists cleavage[71]. For the chelate complex $Pt(diphos)(Sime_3)_2$ the reaction with H_2 (at 1 atm) is temperature-dependent. At 40 °C one mole of trimethylsilane is produced together with $Pt(diphos)(H)(Sime_3)$; at 70 °C both $Sime_3$ groups are cleaved as $HSime_3$, the residue having the appropriate composition of $Pt_4(diphos)_3$ [71]. Hydrogenolysis of $Pt(diphos)Cl(Sime_3)$ has been used to obtain $Pt(diphos)Cl(H)$, the first cis-hydridohalide complex of platinum[69].

Organosilyl substituents on a transition metal can be replaced by other silyl groups[210] or, more readily, by germyl and stannyl groups[35, 160, 162, 169] because there is enhanced stability of El-M bonds in the order El = Sn $\gg$ Ge $>$ Si. Examples with some peculiarities are shown in Eqs. (51)–(53):

$$\mathrm{Pt(Pph_3)_2H[Si(C_6H_4CF_3{-}m)_3] + 2\,Cl_3SiH \longrightarrow Pt(Pph_3)_2(SiCl_3)_2 + [(m{-}CF_3C_6H_4)_3Si]_2 + H_2}^{65,\,66)} \tag{51}$$

$$\mathrm{Pt(diphos)Cl(Sime_3) + me_3GeH \xrightleftharpoons{} Pt(diphos)Cl(Geme_3) + me_3SiH}^{70,\,71)} \tag{52}$$

$$\mathrm{[Ru(CO)_4(Sime_3)_2]_2 + 2\,me_3SnH \longrightarrow Ru(CO)_4(Snme_3)_2 + 2\,me_3SiH}^{159,\,161)}. \tag{53}$$

However, $HSiCl_3$ can eliminate $HSnme_3$ or $HGeme_3$ from an Ir center in a reverse reaction[108] (Eq. (21)).

In one group of reductive-elimination reactions, an $HSiR_3$ molecule can be displaced from a silyl-substituted transition-metal hydride $ML_n(H)(SiR_3)$ by more efficient π-bonding ligands such as CO, PR^1_3, C_2H_4, acetylenes or N_2 which favor a lower oxidation state of M:

$$\mathrm{Rh(Pph_3)_2Cl(H)(SiCl_3) + CO \longrightarrow Rh(Pph_3)_2Cl(CO) + HSiCl_3}^{126,\,127,\,176)} \tag{54}$$

$$\mathrm{Mn(CO)_2cp(H)(Siph_3) + Pph_3 \longrightarrow Mn(CO)_2cp(Pph_3) + HSiph_3}^{125)} \tag{55}$$

$$\mathrm{Pt(Pph_3)_2(H)(Simeph_2) + phC{\equiv}CH \longrightarrow Pt(Pph_3)_2(phC{\equiv}CH) + HSimeph_2}^{97)} \tag{56}$$

$$\mathrm{Co(Pph_3)_3H_2[Si(Oet)_3] + N_2 \rightleftharpoons Co(Pph_3)_3H(N_2) + HSi(Oet)_3}^{15)}. \tag{57}$$

Eq. (54) also holds for PF_3 and C_2H_4 as exchanging ligands[127]. Reaction (55) has first-order kinetics. The rate-determining initial process is dissociation of the starting compound in which the single hydrogen on the M atom is thought to be already close enough to silicon to allow some degree of bonding interaction[125]. With a complex containing an optically active silicon center, cleavage according to Eq. (56) is reported to occur and the configuration at silicon is largely retained[97]; trans-[$Pt(Pet_3)_2Cl(Sime_3)$] and phenylacetylene interact in a complicated way, presumably involving a hexacoordinate intermediate. The products isolated include $RSime_3$, $Pt(Pet_3)_2(R)(C{\equiv}Cph)$ [R = H, Cl], trans-[$Pt(Pet_3)_2(C{\equiv}Cph)_2$], and trimethylstyrylsilane[106].

$Ni(bipy)(SiCl_3)_2$ adds diphenylacetylene to produce a complex with the postulated structure of [trans-α,α'-bis(trichlorosilyl)stilbene]bipyridylnickel(0) because methylation and subsequent work-up afforded trans-α,α'-bis(trimethylsilyl)-stilbene as the sole product[158].

4.4.3. By Insertion Reactions

While insertions of CO and SO_2 into C-M[183, 220] and less commonly into Ge-M[43] and Sn-M bonds[53] of alkyl, germyl, and stannyl transition-metal compounds are known, no such reactions have as yet been found in silicon-transition-metal chemistry[19, 20, 21, 38, 40, 43, 135]. This may be because the $d\pi d\pi$ interaction energy of the Si-M bond is thereby lost[19]. Bearing in mind that an analogous bonding model with partial $d\pi\sigma^*$ double-bonding character has been suggested for perfluoroalkyl-transition-metal derivatives[73] (these compounds indeed show little tendency to undergo C-M insertion reactions), it was logical to attempt some insertion reactions with highly fluorinated alkenes and alkynes.

Reactions were performed under UV irradiation in a hydrocarbon solvent at temperatures of 0–80 °C for 20–100 hours. Only three substrates $Mn(CO)_5(SiF_3)$[208], $Mn(CO)_5(Sime_3)$[67], and $Fe(CO)_2cp(Sime_3)$[42] and six reactants, C_2F_3H, C_2F_4, $CF_3CF{=}CF_2$, $CF_3C{\equiv}CH$, $CF_3C{\equiv}CCF_3$ and perfluorocyclobutene, have as yet been used. Working-up of the metal-containing residues was done mainly by chromatography, and the yield of the insertion products ranged from trace amounts to about 15%. Other products obtained were CO and fluorocarbon polymers, and frequent $FSime_3$ and silicon-free fluoroalkyl-metal compounds, as well as $Mn_2(CO)_{10}$. The following insertion products have been characterized:

$me_3SiCF{=}CFMn(CO)_5$,
$F_3SiCF_2CF_2Mn(CO)_5$, $me_3SiCF_2CF_2Mn(CO)_5$,
$me_3Si(H)C{=}C(CF_3)Mn(CO)_5$,
$me_3Si[CHC(CF_3)]_3Mn(CO)_5$,
$me_3Si(H)C{=}C(CF_3)Fe(CO)_2cp$,
$me_3Si(CF_3)C{=}C(CF_3)Mn(CO)_5$,
$me_3Si(CF_3)\underbrace{C{-}C(CF_3){=}C(CF_3)C}(CF_3)Mn(CO)_5$,
$me_3Si(CF_3)C{=}C(CF_3)Fe(CO)_2cp$.

5. Catalytic Processes

There has been a mutual fertilization between transition-metal complex-catalyzed interactions of silanes and olefins and attempted syntheses of silicon-transition-metal compounds.

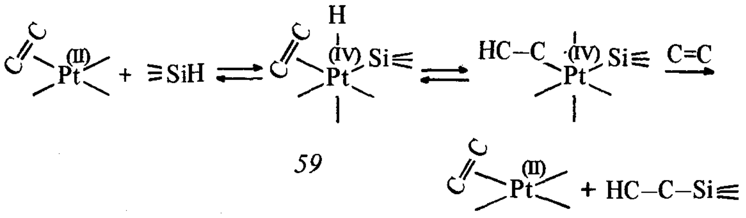
Hydrosilylation (or "hydrosilation"), addition of a silicon hydride to an olefin (Eq. (58)):

$$R_3SiH + CH_2{=}CHR^1 \xrightarrow{cat.} R_3SiCH_2CH_2R^1 \tag{58}$$

was discovered in 1947[212], and has become an exceedingly important laboratory and industrial process for the formation of silicon-carbon bonds. Among the catalysts for such reactions (which proceed as homogeneous processes) H_2PtCl_6 is by far the most common[213], but $[Pt(C_2H_4)Cl_2]_2$[58],

$Rh(Pph_3)_3Cl$[57, 58, 61, 127, 185], and $Co_2(CO)_8$[60, 121] have comparable activity. However, only a few silicon complexes of these transition elements are efficient catalysts[15, 61, 127]. Concurrent isomerization reactions occur and are reported to be markedly affected by the silane used.

A mechanism for catalysis by platinum compounds was proposed in 1965 by Chalk[58] and has since been supported by increasing knowledge about silylmetal systems and by the direct detection of Pt-Si[211] and Rh-Si[61, 185] complexes in the reaction mixtures. The suggested mechanism requires olefin coordination to the Pt(II) species (in the case of H_2PtCl_6 formed by reduction by the silicon hydride), oxidative addition of the silane, formation of an intermediate in which silicon and alkyl are both bonded to the platinum center, and reductive elimination of alkylsilane, probably assisted by coordination of more olefin:



59

(59)

The reaction is highly stereospecific with retention of the silicon center configuration[211].

Phosphine-substituted nickel(II)[32, 165, 222], nickel(0)[164], and palladium(0) complexes[120, 214] have recently been investigated and their mechanisms seem analogous to platinum-catalyzed hydrosilylation.

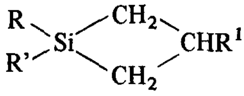
In contrast, the cobalt carbonyl-catalyzed additions follow a different major pathway, $HCo(CO)_4$ (formed according to Eq. (10)) being the central species[60, 121]:

$$HCo(CO)_4 + C{=}C \longrightarrow HC{-}C{-}Co(CO)_4 \xrightarrow{+\equiv SiH} HC{-}C{-}Si\equiv + HCo(CO)_4 \quad (60)$$

The silyl-cobalt complex also produced in Eq. (10) is not a catalytic species for hydrosilylation but it is for stereospecific hydrogen exchange[60, 210]:

$$R_3SiH + R'_3SiD \rightleftharpoons R_3SiD + R'_3SiH. \quad (61)$$

Finally, strained organosilicon heterocycles have been polymerized by neutral transition-metal complexes of the type $L^1_nML^2_m$ where L^1 = Pph_3, C_2H_4, CO, L^2 = H, me, Cl and m = 1, 2, giving polymers with a silicon-carbon backbone[76], *e.g.*

n  $\rightarrow [-RR'Si-CH_2-CHR^1-CH_2-]_n$. (62)

The initial step in the reaction mechanism is formulated as an oxidative addition of the silacyclobutane to the transition-metal complex attaching Si to M (ring expansion). It is followed by a transfer of L^2 from the metal to the silicon (ring opening) and polymer growth by insertion of further coordinated ring into the metal-carbon bond, similar to the mechanism proposed for olefin polymerization by Ziegler-type catalysts.

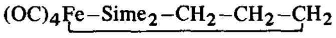
6. Complete List of Compounds

The following tables summarize the silicon-transition-metal compounds known up to 1973. The abbreviations used for organic substituents are:
me = CH_3, et = C_2H_5, pr = C_3H_7, bu = C_4H_{10}, ph = C_6H_5, bz = $CH_2C_6H_5$, cp = π-cyclopentadienyl, diphos = 1,2-bis(diphenylphosphino)-ethane.
The literature references for each compound are accompanied by letters characterizing the information contained: m = compound briefly mentioned, p = preparation and properties; r = reactions; and s = spectral or structural data.

List of compounds

Scandium group	
No silyl derivative known	
Titanium group	
$Ti(Siph_3)_4$	(130p)
$Ticp_2(Siph_3)_2$	(130p)
$Zrcp_2(Cl)(Siph_3)$	(50p, 156p, 175s)
$Hfcp_2(Cl)(Siph_3)$	(155p, 156p)
Vanadium group	
No silyl derivative known	
Chromium group	
$Cr(CO)_3cp(SiH_3)$	(115pr, 198p)
$Cr(CO)_2(C_6H_6)(H)(SiCl_3)$	(138m, 139ps)
$Cr(CO)_2(C_6H_6)(SiCl_3)_2$	(139m)
$Mo(CO)_3cp(SiR_3)$	[$R_3 = H_3$ (115pr, 198p), Cl_3 (137mp, 169p), Br_3, HCl_2, HClme (all 169p), me_3 (50m, 51m, 169p)]
$Mo(CO)_3cp(Sime_2Sime_2R)$	(R = Cl, Br, me) (170p)
$W(CO)_3cp(SiR_3)$	[$R_3 = H_3$ (115pr), Cl_3, Br_3, HCl_2, HClme, Cl_2me (all 169p), me_3 (50m, 51m, 169p)]
$W(CO)_3cp(Sime_2Sime_2R)$	(R = Cl, Br, me) (170p)
$[(OC)_5W]_2SiR_2$	(113m)
$W_2(CO)_8H_2(Siet_2)_2$	(34ps)
$[(OC)_5WSiI_2]_2$	(203p, 204m)
Manganese group	
$Mn(CO)_5(SiR_3)$	[$R_3 = H_3$ (18r, 19pr, 21prs, 22r), F_3 (208p), Cl_3 (40m, 41m, 112s, 137mp, 147s, 174m), Cl_2me (112s), me_3 (29m, 38m, 40p, 67r, 119ms, 147s, 181m), ph_3 (83s, 88ms, 92r, 142p, 196r, 197r, 215ms), $(C_6F_5)_3$ (207p)]
$Mn(CO)_5(Si_nR_{2n+1})$	[Si–chain = Si_2me_5 (47m, 181p), $(me_3Si)_2meSi$ (181p), $(me_3Si)_3Si$ (181p, 182s)]
$[Mn(CO)_5]_2SiH_2$	(21m)
$Mn(CO)_4(Pph_3)(SiR_3)$	[R = F (208p), ph (92r, 197r), C_6F_5 (207p)]

List of compounds (continued)

$Mn(CO)_n(PF_3)_{5-n}(Sime_3)$	(n = 2, 3, 4) (29m, 40m)
$Mn(CO)_3L(Siph_3)$	(L = diphos, bipy) (197m)
$[Mn(CO)_2L(SiCl_3)]^-$	[L = cp, C_5H_4me] (140ps)
$Mn(CO)_2cp(H)(SiR_3)$	[R = Cl (125m, 138m, 139ps), ph (125m)]
$Mn(CO)_2(C_5H_4me)(H)(Siph_3)$	(139ps)
$Mn(CO)_2cp(SnCl_3)(SiCl_3)$	(140ps)
$Mn(CO)_2(C_5H_4me)(SnR^1_3)(SiCl_3)$	(R^1_3 = Cl_3, $Clph_2$, Cl_2ph) (140ps)
$[Mn(CO)_2(C_5H_4me)(SiCl_3)]_2SnCl_2$	(140ps)
$Re(CO)_5(SiR_3)$	[R = F (208p), Cl (137mp), ph (83s, 88ms, 135m, 142ps, 215m), C_6F_5 (207p)]
$Re(CO)_5(Si_2me_5)$	(47m)
$Re(CO)_4(Pph_3)(SiF_3)$	(208p)
$Re(CO)_2cp(H)(Siph_3)$	(125m)
$[Re(CO)_4Siph_2]_2$	(33m)
$Re_2(CO)_9(H)(SiR_3)$	(R_3 = Cl_3, Cl_2me, Cl_2ph, $Clme_2$) (135ps)
Iron group	
$[Fe(CO)_4(SiR_3)]^-$	[R = Cl (140ps), ph (140ps, 163p)]
$Fe(CO)_4(H)(SiR_3)$	[R = H (23m, 24prs), Cl (138m, 139ps), me (178ps, 179s), ph (139ps)]
 $(OC)_4Fe{-}Sime_2{-}CH_2{-}CH_2{-}CH_2$	(76pr, 77r)
$Fe(CO)_4(SnR^1_3)(SiCl_3)$	(R^1_3 = Cl_3, Cl_2ph) (140ps)
$[Fe(CO)_4(SiCl_3)]_2SnCl_2$	(140ps)
$Fe(CO)_4(SiR_3)_2$	[R = H (23pr, 24prs), Cl (90ms, 137mp, 140rs, 141r, 146ps), me (178ps, 179s), et (90ms, 146s)]
$[Fe(CO)_4SiCl_2]_2$	(85ms, 89ms, 137mp, 141m)
$[Fe(CO)_4SiCl_3]_2$	(138m)
$Fe_2(CO)_7(Sime_3)_2$	(166ps)
$Fe(CO)_2cp(SiR_3)$	[R_3 = H_3 (14p), Hme_2 (154p), F_3 (173p, 208p), Cl_3 (86s, 137mp, 141ps, 180p), Cl_2me (81s, 82s, 137ms), Cl_2ph (180p), $Clme_2$ (154p), $Clph_2$ (180p), me_3 (38m, 42r, 43r, 141m, 152r, 177r, 187m, 188m, 191p), $(C_6F_5)_3$ (207p), (ph)(ph_4C_4) (78p)]

List of compounds (continued)

$C_2H_4[Sime_2Fe(CO)_2cp]_2$	(154p)
$Fe(CO)_2cp(Si_nR_{2n+1})$	[Si–chain = Si_2me_5 (153m, 154p, 188m), Si_2me_4R with R = Cl, Br (170p), Si_3me_7 and Si_4me_9 (153m, 154p)]
$Fe(CO)_2cp–(Si_nR_{2n})–Fe(CO)_2cp$	[Si–chain = Si_2me_4 (154p), Si_3me_6 (153m, 154p)]
$[Fe(CO)_2cp]_2Siph_2$	(68m)
$ph_2SiFe_2(CO)_3cp_2$	(68m)
$[Fe(CO)L(SiCl_3)_2]^-$	(L = cp, C_5H_4me) (141ps)
$Fe(CO)cp(H)(SiCl_3)_2$	(138m, 139ps, 141r, 171s)
$Fe(CO)cp(Pph_3)(Sime_3)$	(152ps, 187m)
$Fe(CO)cp[P(Oph)_3](Sime_3)$	(152ps)
$FeLcp(Sime_3)$	(L = diphos, cis-$ph_2PCH{=}CHPph_2$) (152ps)
$Fe(CO)cp(Sime_3)(diphos)Fe(CO)cp(Sime_3)$	(152m)
$[Ru(CO)_4(Sime_3)]^-$	(160pr)
$Ru(CO)_4X(SiCl_3)$	(X = Br, I) (16ps)
$Ru(CO)_4X(Sime_3)$	[X = Br, I (16ps), $Gebu_3$ (160p), $Snme_3$ (74m, 160p), $Snph_3$ (160p), $Mn(CO)_5$ (16p, 160ps), $Re(CO)_5$ (16p), $Os(CO)_4(Sime_3)$ (161p), $AuPph_3$ (160p)]
$Ru(CO)_4(Snme_3)(Siet_3)$	(160p)
$Ru(CO)_4(SiR_3)_2$	[R = Cl (192s, 193s), me (47r, 159m, 160ps, 162r)]
$[Ru(CO)_4(SiR_3)]_2$	[R_3 = Cl_3 (16r, 74m, 160ps), Cl_2me (160ps), me_3 (16ps, 47m, 159m, 160ps, 162m), et_3, pr_3, $(etO)_3$, ph_3 (all 160ps)]
$Ru(CO)_3(Pph_3)X(Sime_3)$	(X = H, I) (16ps)
$[Ru(CO)_3(Sime_3)X]_2$	[X = Br, I (16ps), μ-$Sime_2$ (47p, 75s)]
$Ru(CO)_2(Pph_3)_2(SiR_3)_2$	(R = Cl, me) (160ps)
$Ru_2(CO)_6(Sime_2)_3$	(47p)
$[Os(CO)_4(Sime_3)]^-$	(161r)
$Os(CO)_4X(Sime_3)$	[X = H (133m, 159m, 161ps), Br, I (16ps), me, HCF_2CF_2, $Snme_3$ (all 161ps), $Ru(CO)_4(Sime_3)$ (161p), $AuPph_3$ (159m)]
$Os(CO)_4(H)(Siet_3)$	(161ps)

List of compounds (continued)

$Os(CO)_4(SiR_3)_2$	[R_3 = Cl_3, Cl_2me, Clme$_2$ (all 193ms), me$_3$ (47r, 159p, 161ps, 162r, 193ms), et$_3$ (161ps)]
$[Os(CO)_4(SiR_3)]_2$	[R = me (16ps, 47r, 133m, 159p, 161ps, 162r), et (161ps)]
$Os(CO)_3(Pph_3)X(Sime_3)$	[X = Br, I (16ps), me (161ps)]
$[Os(CO)_3(Sime_3)X]_2$	[X = Br, I (16ps), μ-Sime$_2$ (47p)]
$Os_3(CO)_9(Sime_2)_3$	(47p)
Cobalt group	
$Co(CO)_4(SiR_3)$	[R_3 = H_3 (17mr, 20ps, 22r, 39m, 117m, 194s), H_2me (26p, 110r, 111r, 116s, 117m, 199r), Hph$_2$ (60p), F_3 (39s, 100s, 116s, 117m, 118pr, 144ms, 200s, 218m), F_2me (111r, 117m, 201s), Cl_3 (12ms, 26pr, 39ms, 48s, 59ps, 60ps, 84s, 87s, 91s, 116s, 117m, 145s, 146s, 147s, 174m, 184r, 195s, 202s, 215m, 216s, 217s, 218m), Cl_2ph (59ps, 60ps), me$_3$ (25p, 26p, 28r, 29r, 93s, 116s, 117m, 131r, 147s, 174m, 202s, 218m), et$_3$ (12ms, 28r, 29r, 59ps, 60ps, 84s, 145s, 146s, 210r, 215m, 218m), ph$_3$ (12ms, 48s, 59ps, 60ps, 80p, 84s, 87s, 145s, 146s, 190m, 215m, 218m), $(C_6F_5)_3$ (207p), (meO)$_3$ (84s, 145s, 146s, 215m, 218m), meph(1-naphthyl) (210p)]
$[Co(CO)_4]_2SiH_2$	(20m)
$Co(CO)_4(Si_2me_5)$	(168m)
$Co(CO)_3(PR^1_3)(SiCl_3)$	[R^1 = F (28m, 29m), me (28m), bu (184p)]
$Co(CO)_3(Pet_3)(SiR_3)$	[R = Cl (28m, 29m, 146s), et (146s)]
$Co(CO)_3(Pph_3)(SiR_3)$	[R = H (19m, 20m), me (28m, 29m), ph (79m, 80p)]
$Co(CO)cp(H)(SiCl_3)$	(138m, 139ps)
$Co(CO)cp(SiCl_3)_2$	(143m)
$Co(Pph_3)_3H_2(SiR_3)$	(R = F, etO) (15p)
$Co_3(CO)_9$(Si vinyl)	(150p)
$[Co_3(CO)_9Si]_2$	(151p)
$Co_2(CO)_7Siph_2$	(30m)
$Co_3(CO)_{11}Siph$	(30m)
$Co_4(CO)_{14}SiR_2$	(R = et, ph) (101p)

List of compounds (continued)

$Rh(CO)cp(H)(SiR_3)$	(R = ph, bz) (186ps)
$Rh(CO)cp(SiR_3)_2$	(R_3 = Cl_3, Cl_2me) (186ps)
$Rh(Pph_3)_2Cl(H)(SiR_3)$	[R_3 = Cl_3 (61p, 126m, 127ps, 176s), Cl_2me (61p, 127ps), Cl_2et, $Clme_2$, $Clet_2$, me_3 (all 127ps), $me(me_3SiO)_2$ (104m), et_3 (127ps, 185m), ph_3 (127ps), $(etO)_3$ (126m, 127ps)]
$Rh(Pph_3)_2Br(H)(SiR_3)$	[R_3 = Cl_3 (126m, 127ps), Cl_2me, Cl_2et, $Clme_2$, $Clet_2$, et_3 (all 127ps), $(etO)_3$ (126m, 127ps)]
$Rh(Pph_3)_2I(H)(SiR_3)$	(R = Cl, etO) (127ps)
$Rh(Qph_3)_2Cl(H)(SiR_3)$	(Q = As, Sb; R = Cl, etO) (126m, 127ps)
$Rhcp(alkene)(SiCl_3)_2$	(alkene = C_2H_4, cyclo-octene, cyclo-octadiene) (104m)
$Rh(Pph_3)_2(SiCl_3)_3$	(104m)
$Rh(CO)(Pph_3)_2Cl(H)(SiCl_3)$	(61p, 127s)
$Rh(CO)(Pet_3)_2Cl(H)(SiR_3)$	[R_3 = Cl_3 (61p), Cl_2me (61m)]
$Ir(CO)(Pph_3)_2H_2(SiR_3)$	[R_3 = Cl_3 (108ps, 122ps), Cl_2me (122ps), me_3 (108ps, 122ps), me_2ph (122ps), et_3 (54m), ph_3 (122ps), $(etO)_3$ (54m, 122ps, 123p)]
$Ir(CO)(Pph_3)_2Cl(H)(SiR_3)$	[R_3 = Cl_3, Cl_2et, Cl_2ph (58p), et_3 (54m), $(etO)_3$ (54m, 58p)]
$Ir(CO)(Pet_3)_2(HgSime_3)(Sime_3)_2$	(132ps)
$\{Ir(diphos)_2H[Sime_n(Oet)_{3-n}]\}^+$	(n = 0–3) (124p)
Nickel group	
$[Ni(CO)_3(Siph_3)]^-$	(163p)
$Ni(CO)cp(SiCl_3)$	(137m)
$Ni(bipy)(SiR_3)_2$	[R_3 = Cl_3 (157p, 158r), Cl_2me (157p)]
$Pd(PR^1_3)_2Cl(Sime_nCl_{3-n})$	(n = 0, 1; R not specified) (45m)
$Pd(PR^1_3)_2(Sime_nCl_{3-n})_2$	(n = 0, 1; R not specified) (45m)
$Pt(Pph_3)_2H(SiR_3)$	[R_3 = Cl_2me (102p, 221p), Hph_2, $meph_2$, et_3, ph_3, $(etO)_3$, $me_2(Hme_2SiO)$, $me(me_3SiO)_2$ (all 97p), meph(1-naphthyl) (98p); R = $p-FC_6H_4$, $m-FC_6H_4$, $p-CF_3C_6H_4$, $m-CF_3C_6H_4$ (65m, 66p)]

List of compounds (continued)

trans-$[Pt(Pme_2ph)_2Cl(SiR_3)]$	$[R_3$ = Cl_3 (63m, 128s), $meph_2$ (62m, 63m, 64prs, 128s, 148ms), meph(1-naphthyl) (96p, 98r); R = ph (64ps, 128s), m–FC_6H_4, p–FC_6H_4, m–ClC_6H_4 (64ps), p–ClC_6H_4 (63m, 64ps), m–meC_6H_4 (64ps), p–meC_6H_4, m–$CF_3C_6H_4$ (63m, 64ps), p–$CF_3C_6H_4$ (64ps, 128s), p–$meOC_6H_4$, p–$me_2NC_6H_4$, C_6F_5 (64ps)]
trans-$[Pt(Pme_2ph)_2Br(SiR_3)]$	$[R_3$ = $meph_2$ (62m, 64prs, 128s) meph(1-naphthyl) (98m); R = ph, p–meC_6H_4, m–$CF_3C_6H_4$, p–$me_2NC_6H_4$ (all 64ps)]
trans-$[Pt(Pme_2ph)_2I(SiR_3)]$	$[R_3$ = meph(1-naphthyl)] (98m)
$Pt(Pet_3)_2H(Siph_3)$	(27p)
trans-$[Pt(Pet_3)_2Cl(SiR_3)]$	$[R_3$ = H_3, H_2F (36ps), H_2Cl (35m, 36ps, 37m), HCl_2 (36ps, 37m), H_2(Ome), $H_2(Nme_2)$, HCl(Ome) (36ps), Cl_3 (37m), me_3 (105m, 106prs, 107r)]
trans-$[Pt(Pet_3)_2Br(SiR_3)]$	$[R_3$ = H_3 (36ps), H_2Cl, H_2Br (35m, 36ps)]
trans-$[Pt(Pet_3)_2I(SiR_3)]$	$[R_3$ = H_3 (36ps), H_2Cl (35m, 36ps), H_2Br (36ps), H_2I (35m, 36ps, 37ps), HCl_2, HI_2 (36ps)]
trans-$[Pt(Pet_3)_2L(Sime_3)]$	[L = ph (107m), $Geph_3$ (106ps, 107p)]
$Pt(PR^1_3)_2Cl(Sime_nCl_{3-n})$	(R not specified) (45m)
trans-$[Pt(Asme_2ph)_2Cl(SiR_3)]$	$[R_3$ = $meph_2$; R = ph, m–FC_6H_4, p–FC_6H_4, m–ClC_6H_4, p–ClC_6H_4, m–meC_6H_4, p–meC_6H_4, m–$CF_3C_6H_4$, p–$CF_3C_6H_4$, p–$me_2NC_6H_4$, p–$meOC_6H_4$ (all 64 ps)]
trans-$[Pt(Asme_2ph)_2Br(Siph_3)]$	(64ps)
$Pt(diphos)H(Sime_3)$	(70m, 71ps)
$Pt(diphos)Cl(SiR_3)$	$[R_3$ = me_3 (69r, 70m, 71prs), $meph_2$ (64ps)]
$Pt[CH_2(Pph_2)_2]Cl(Sime_3)$	(109m)
$[Pt(Pet_3)(diphos)(Sime_3)]^+$	(107p)
$[Pt(PCl_3)(SiCl_3)]_x$	(219m)
$Pt(diphos)(SiCl_2)$	(66m)
$Pt(Pph_3)_2 \cdot SiF_4$	(94p, 95r)
$Pt(Pph_3)_2 \cdot SiF_4 \cdot NH_3$	(94m)
$Pt(Pph_3)_2(SiR_3)_2$	$[R_3$ = Cl_3 (65m, 66pr, 205p, 206m, 221p), Cl_2me (102p, 221p), Br (205p)]

List of compounds (continued)

$Pt(Pph_3)_2(SimeCl_2)_2Pt(Pph_3)_2$	(102p)
$Pt(Pph_3)_2(SiR_2)_2$	(R = Cl, Br) (204m, 205p)
$(ph_3P)_2Pt-SiCl_2-Cph=Cph-SiCl_2$	(205m)
cis-$[Pt(Pme_2ph)_2(Simeph_2)_2]$	(62m, 64prs, 128s)
cis-$[Pt(Pmeph_2)_2(SiR_3)_2]$	[R_3 = Cl_3, Cl_2me (97m), me_2ph (63m, 64ps)]
$Pt(diphos)(SiR_3)_2$	[R_3 = Hph_2, Cl_3, $Brph_2$ (65m, 66pr), me_3 (70m, 71prs), $meph_2$ (64pr, 65m, 66pr), ph_3 (64m)]
$Pt[CH_2(Pph_2)_2](Sime_3)_2$	(109m)
$Pt(Pet_3)_2I_2(H)(SiH_2R)$	[R = Cl (36m), I (36ps, 37m)]
Copper group	
$Au(Pph_3)(Siph_3)$	(27p, 174ms)

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