The Wonderful World of Organosilicon Chemistry[††]

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INTRODUCTION

There is no better evidence for increasing interest in the chemistry of organosilicon compounds than the statistics from the Ninth International Symposium on Organosilicon Chemistry. The Edinburgh silicon meeting was attended by more than 500 participants from about 30 countries. The program included 5 plenary lectures, 30 invited lectures, 62 oral papers, and over 200 poster presentations. The latter were divided into seven topics: gas phase studies; siloxanes and silicones; electronic, ceramic, and polymer materials; spectroscopy and structural studies; biological aspects; industrial aspects; and theoretical aspects.

Here we present a summary of some of the important recent findings reported at the Edinburgh symposium. Our coverage is necessarily selective, for the immense amount of results reported has forced us to prune and graft. Undoubtedly we have omitted from this summary many equally important and useful contributions (in particular we make no mention of advances in the use of silicon compounds in organic synthesis). This review will be organized around five main topics:

1. The chemistry of silicon in low coordination states;
2. Sterically shielded silicon compounds;
3. Di-, oligo- and polysilanes;

4. Five and six-coordinate silicon species; and
5. New materials based on silicon.

SILICON IN LOW COORDINATION STATES

The species in this class include silylenes $RR'Si:$, silylenium ions R_3Si^+, and numerous pi-bonded species $RR'Si=E$ where E is C, Si, N, P, O, or S. The properties, and especially the reactivity, of low-coordinate silicon compounds depend very much on the nature of the substituents at the silicon atom. Small substituents tend to enhance reactivity, enabling the application of these species in synthesis and in mechanistic studies. Increasing the steric bulk of the substituents stabilizes low-coordinate silicon compounds and lowers their reactivity; this goal can also be reached by incorporating the (sometimes highly) reactive species in the coordination sphere of a transition metal. At the two preceding ISOSC meetings in St. Louis in 1987 and Kyoto in 1984, generation and detection of unsaturated silicon compounds were already major points of interest. Now, with the ability to synthesize stable samples of these derivatives, a vast area of rich synthetic possibilities in organosilicon chemistry has been opened up. Low-coordinate silicon compounds react readily with polar reagents and, in addition, typically undergo cycloaddition reactions with various unsaturated substrates, leading to new classes of organosilicon compounds. Investigations of this kind were one focal point of the Edinburgh symposium.

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The first stable silylene, decamethylsilicocene, was reported in 1986 by P. Jutzi and coworkers. This compound, $(\eta^5\text{-}C_5Me_5)_2Si$: (1) ($\delta\ ^{29}Si = -398!$), can be regarded as a hypervalent silicon nucleophile. Jutzi and his group have now started to explore the synthetic potential of 1 and have already found some remarkable reactions:

The reaction of 1 with protic substrates, for example two equivalents of 1,2-dihydroxybenzene, leads to the first stable silylenium ion, present in solution as $[(Me_5C_5)_2SiH]^+$ $[C_6H_4(OH)_3OC_6H_4]^-$. Although silylenium ions are known in the gas phase, their possible existence in solution has long been controversial.

Reacting HBF_4 with 1 cleaves off one equivalent of C_5Me_5H yielding $[Me_5C_5Si]^+BF_4^-$, which formally eliminates BF_3 to give $\frac{1}{4}[Me_5C_5(F)Si]_4$. An intermediate was detected spectroscopically, which may be the disilene $(Me_5C_5)(F)Si=Si(F)(C_5Me_5)$ or the fluorine-bridged silylene $(Me_5C_5\ddot{S}iF)_2$.

Carbonylgold chloride, $(CO)AuCl$, reacts with 1 to form the deep red silylene-metal complex $(C_5Me_5)_2Si$–$AuCl$. The addition of electron-donating compounds like Me_3CCN easily transforms the silylene complex into a derivative with ylidic ligands, e.g. 2.


1

2
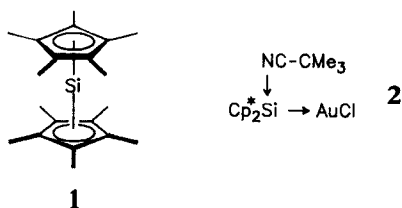
The sterically strongly crowded diadamantyl silylene Ad_2Si: (3), liberated by thermolysis or photolysis from 1,1-diadamantylsiliranes, was described by P. Gaspar. This reactive silylene was generated with the goal of producing a species having a triplet ground state by increasing the bond angle at the divalent silicon atom. However, the stereospecific addition of Ad_2Si: to olefins is consistent with a singlet, rather than a triplet, ground state.
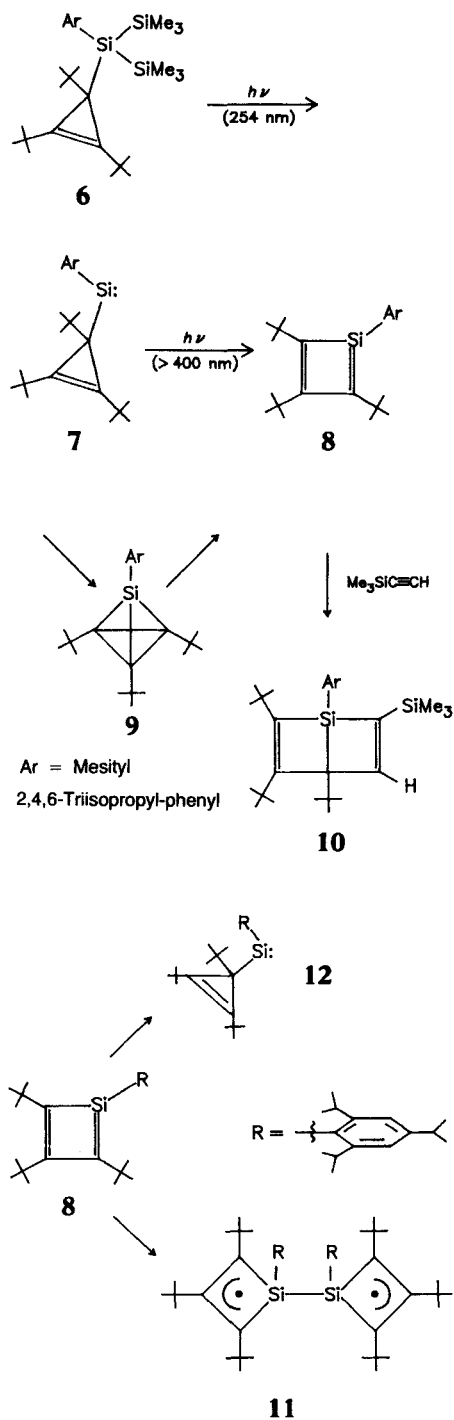

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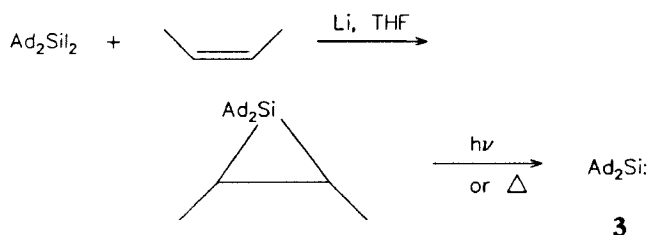
Using the now classical method of photolysis of polysilanes, M. Kira has matrix-isolated the first

vinyl-substituted silylene, actually containing two vinyl groups (4). Another classical route, dehalogenation of dichlorosilanes with alkali metal vapor has been used by E. A. Volnina to generate cyclic silylenes 5. The latter were trapped by insertion into Si–H bonds.
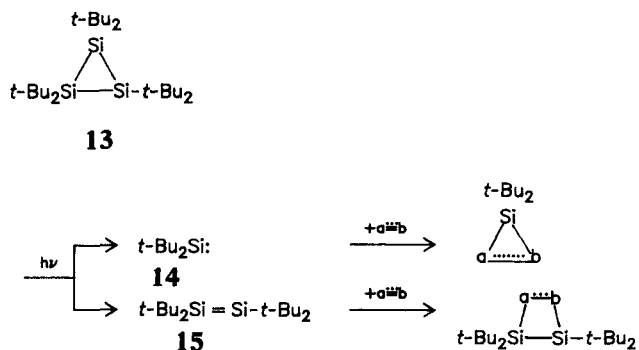

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5
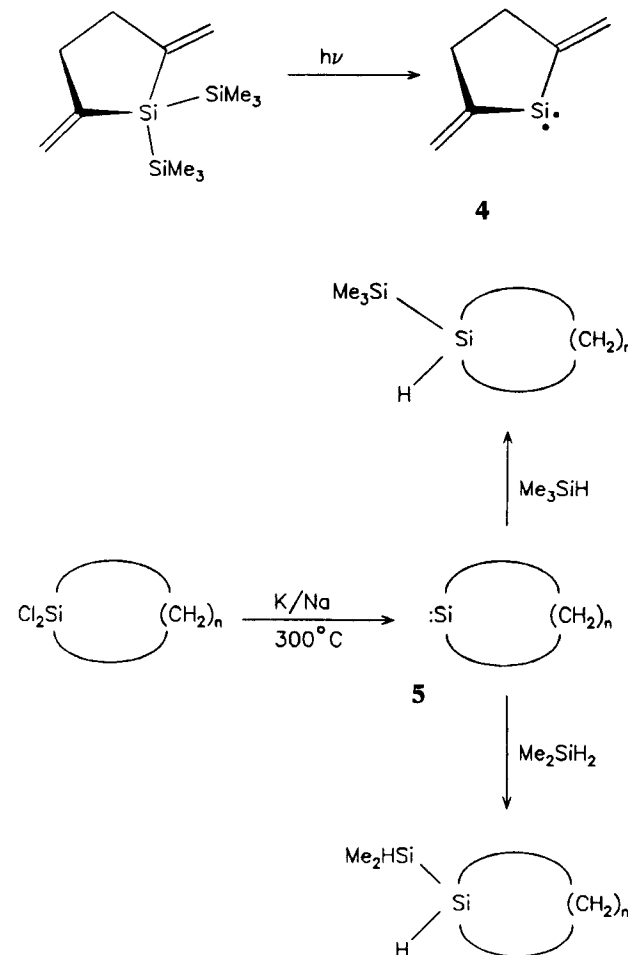
M. Fink reported the isolation of cyclopropenylsilylene 7 obtained by photolysis of the bis-Me_3Si substituted precursor 6 in a 3-methylpentane matrix. This silylene is a precursor to a variety of novel silicon rings. Further photolysis converts 7 to silacyclobutadiene 8, which can be trapped with trimethylsilylacetylene, undergoing cycloaddition to give the surprisingly stable sila-Dewar benzene, 10. The isomerization of 7 to 8 evidently occurs through intermediate formation of the silatetrahedron 9, arising from an intramolecular π-addition of the silylene to the double bond. Dimerization of 8 leads to the unusually stable diradical 11, which has a half-life of more than 8 h at room temperature. Even more surprising is the simultaneous isomerization of 8 to the silylene 12, which is stable in solution at low temperatures.
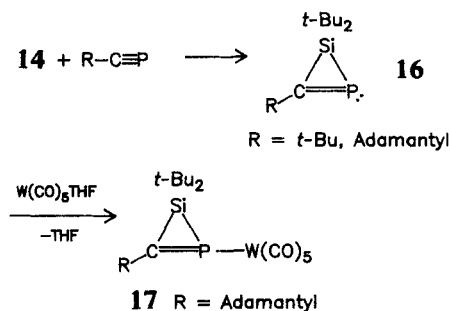
As shown earlier by Weidenbruch photolysis of the productive source, hexa-t-butylcyclotrisilane (13)

with phosphaalkynes, from which stable phosphasilirenes (16) are isolable. The structure of the three-membered ring compound 16 has been confirmed by X-ray crystallography of its end-on P-coordinated complex with $W(CO)_5$. The P=C double bond length in 17 of 1.686 Å is similar to that in open-chain phosphaalkenes.

17 R = Adamantyl

A similar reaction carried out with phenyl isothiocyanate did not give rise to a product of [2 + 1] cycloaddition to the C=N double bond, but rather to its isomer 18. This silathiirane is assumed to undergo σ-dimerization to give the isolated six-membered ring 19. The [3 + 1] addition product of 14 with tri-t-butylazide could not be isolated; loss of nitrogen gives the silaneimine 20, a stable Si=N-compound that had also been synthesized by N. Wiberg using an alternative approach. 20 undergoes further ene-reaction with photolytically formed isobutene to give the final product 21.

[2 + 2] cycloaddition of 15 as well as of stable disilenes like $mes_2Si=Simes_2$ (22) to numerous multiply bonded compounds have been thoroughly investigated. 22 or 15 undergo [2 + 2] cycloadditions with dienes and unsymmetrically substituted

yields di-t-butylsilylene 14 and the marginally stable tetra-t-butyldisilene 15. Both of these may be trapped by addition to various unsaturated reagents. For example 14 undergoes [2 + 1] addition to the triple bond of nitriles to give silaazirines, which, presumably owing to the high ring strain, undergo spontaneous σ-dimerization to give 1,4- or 1,3-diaza-2,5-disila-1(6),3-cyclohexadienes. Formation of the silaazirine intermediates could be confirmed indirectly by the analogous reaction of 14
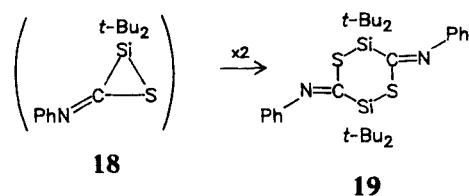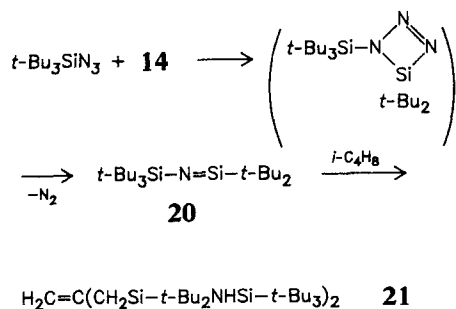
t-Bu$_3$SiN$_3$ + **14** $\longrightarrow$ $\left(\begin{array}{c} t\text{-Bu}_3\text{Si}-\text{N} \\ \text{Si} \\ t\text{-Bu}_2 \end{array} \right)$

$\xrightarrow[-N_2]{}$ t-Bu$_3$Si-N=Si-t-Bu$_2$ $\xrightarrow{i\text{-C}_4\text{H}_8}$

20
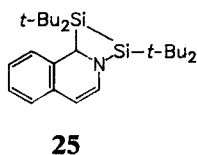
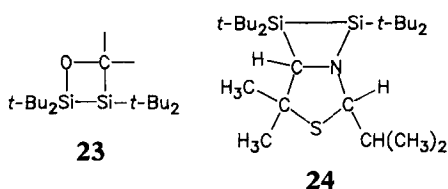H$_2$C=C(CH$_2$Si-t-Bu$_2$NHSi-t-Bu$_3$)$_2$ **21**

alkynes as well as with C=O double bonds; for example:

> With 1,3-cyclohexadiene or 1,3-diphenylisoben-zofuran the [2 + 2] products were obtained, and none of the [2 + 4] cycloadducts;
>
> 1,2,3-Oxadisiletanes **23** resulted as the products of the [2 + 2] addition to ketones;
>
> Reaction of **15** with 3-thiazoline leads to **24**, with isoquinoline **25** is formed.

23

24

25

Scheme 1 summarizes the cycloaddition behavior of **15**.

It appears that silylenes play a role in the well-known, classic Rochow reaction for direct synthesis of methylchlorosilanes. This was demonstrated by M. P. Clarke who prepared RClSi: (R = Me or Cl) *directly* by passing CH$_3$Cl over Si-powder (+ 4% Cu). Of course Me$_2$SiCl$_2$ and MeSiCl$_3$ are the main products, but when 1,3-butadiene was present in the reaction zone 1-sila-3-cyclopentenes were formed establishing that the silylenes were present.
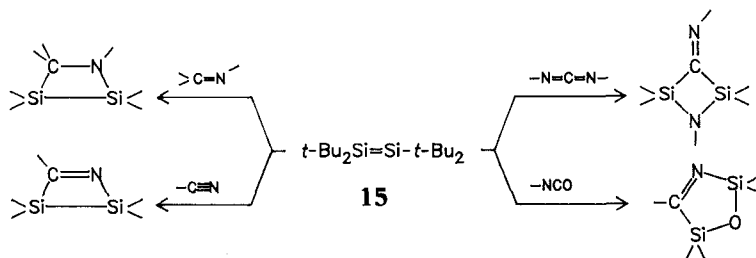
Interesting new structures have also been reported from reactions of disilenes, compounds containing a silicon–silicon double bond first synthesized in 1981. M. Driess described the "butterfly" molecule 1,3-diphospha-2,4-disilabicyclo[1.1.0]butane **26**, prepared by reaction of **22** with white phosphorus. Compound **26** behaves as a Lewis base, combining with W(CO)$_5$THF (to **27**), Ni(COD)$_2$ (to **28**), and (PPh$_3$)$_2$Pt(C$_2$H$_4$) (to **29**). Reaction with selenium converts **26** to the asterane **30** and pyrolysis yields a similar structure, the trisilaasterane **31**. These products show that there is more than a single reaction site in **26**. Compounds having a tricyclo[1.1.1]pentane structure were formed by insertion into the P–P bond; breakage of Si–P bonds was also observed, but only at elevated temperatures. The lone pairs on phosphorus could also be complexed with transition metals leaving the rest of the molecule intact. Remarkably, when E-1,2-di-t-butyl-1,2-dimesityldisilene is used in the reaction with white phosphorus, a bicyclobutane is formed with

26 δ^{29}Si~-50 ppm
J (SiP)~ 77Hz

27

28

29

30

31

t-Bu$_2$Si=Si-t-Bu$_2$

15

SCHEME 1
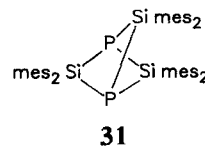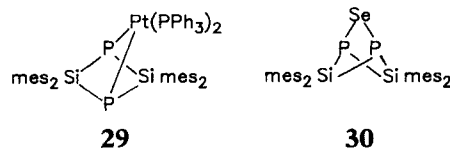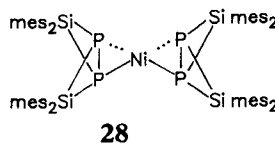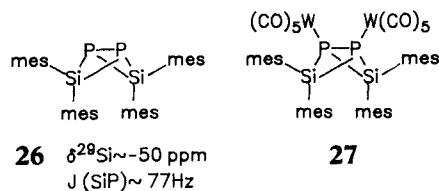
inversion of stereochemistry at silicon, the first such instance of inversion observed for a disilene reaction.

Cyclopolysilanes **32** are well-known sources for silylenes when photolyzed. In addition H. Watanabe demonstrated that heteroatom-containing cyclic polysilanes **33** also extrude silylenes. If the heteroatom is oxygen, Si_2O-three membered rings are obtained. If the heteroatom is nitrogen (**34**), the reaction pathway is complicated: depending on the substituents at silicon and nitrogen, disilaazirines, silylenes, silaneimines, and disilenes are produced as reactive intermediates in competition.

Silylene extrusion reactions were employed by W. Ando and coworkers to prepare strained silaalkyne ring compounds. Thus compound **35**, from $Cl(SiMe_2)_6Cl$ and $BrMgC\equiv CMgBr$, gives cycloheptyne **36** upon irradiation or pyrolysis.

32

33

34

35

36
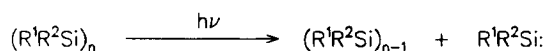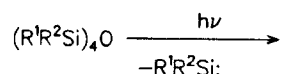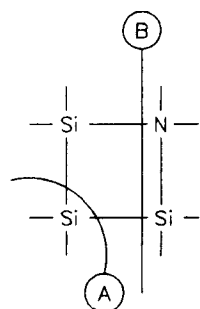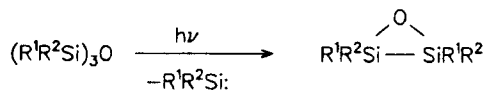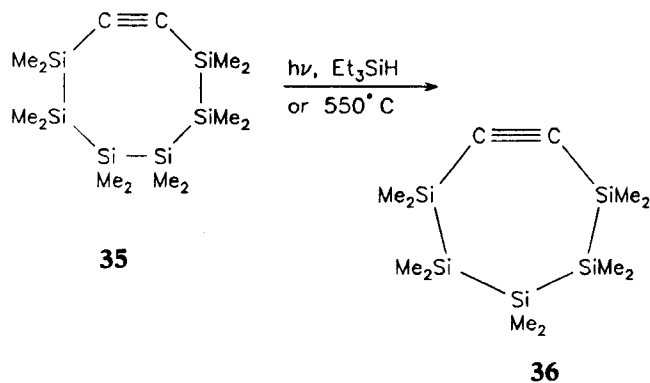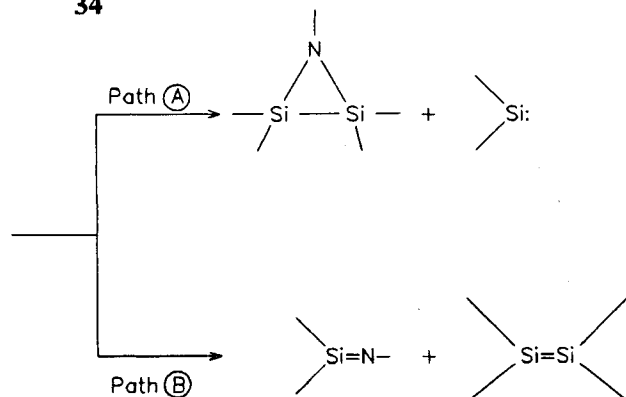
The cycloaddition potential of silenes ($\searrow Si=C\diagup$) was described by N. Auner. The ability of highly reactive dichloroneopentylsilene $Cl_2Si=CHCH_2{}'Bu$ to form [2 + 2] as well as [2 + 4] cycloadducts with dienes of low reactivity is attributed to the electronic influence on the Si=C-bond by the two chlorine atoms. Thus, C_5R_5H (R = H, Me), furans, anthracene, and naphthalene (**37**) yield [2 + 4] products whereas [2 + 2] cycloadducts are formed with norbornene, quadricyclane, aldehydes, ketones, butadienes, and acetylenes respectively. The [2 + 2] cycloaddition is favored over the [2 + 4] mechanism using norbornadiene and 1,3-cyclohexadiene as trapping agents. The quite different cycloaddition behavior of $Cl_2Si=CHCH_2{}'Bu$ compared to that of diorganosubstituted neopentylsilenes thus leads to a fascinating field of chemistry. The [2 + 2] compounds can be further transformed into the thermodynamically more stable Diels-Alder and catenated compounds (e.g. **38** → **39** + **40**).
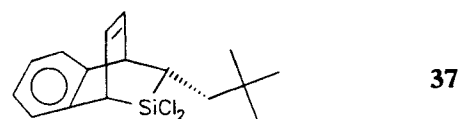
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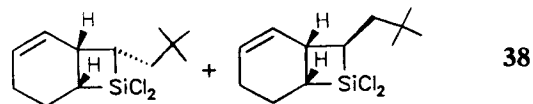
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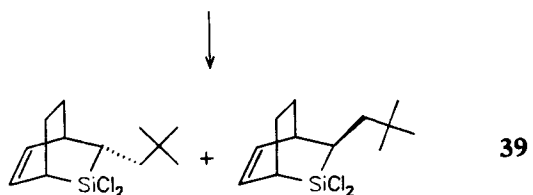
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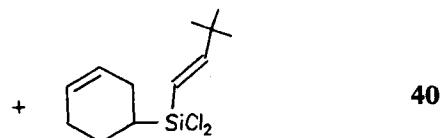
40

Generation of silenes from diazo compounds, reported by W. Ando, has led to some remarkable new silicon ring compounds. From Me₃SiC(=N₂)Li and dichloropolysilanes Cl(SiMe₂)ₙCl bis-diazo compounds **41** and **42** are obtained. Pyrolysis of **41** gives, probably through rearrangement to a conjugated diene intermediate, the disilacyclobutene **43**. Pyrolysis of **42** leads, again through a proposed diene intermediate **44**, to the trisilaasterane **45** in 30% yield.


41

43

42

44

45
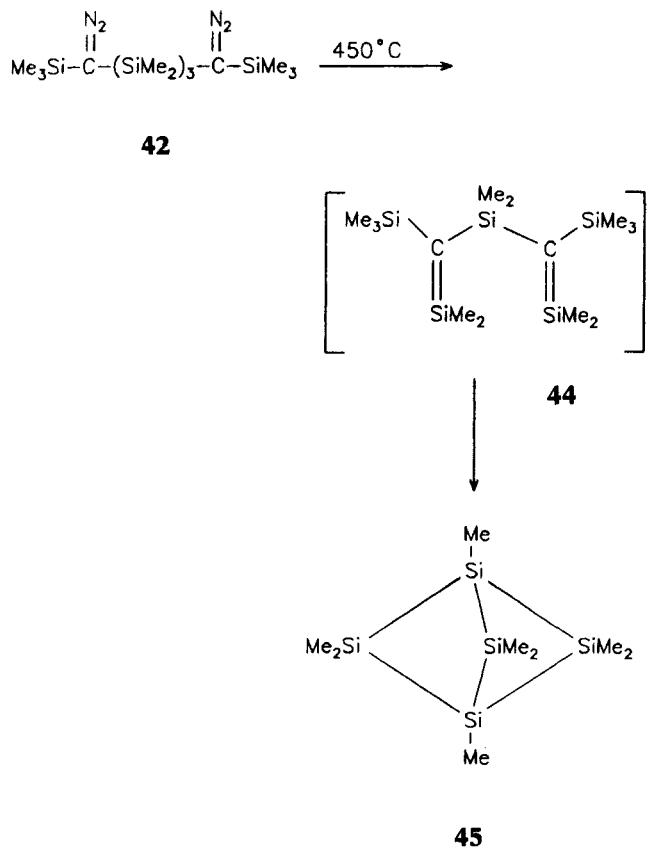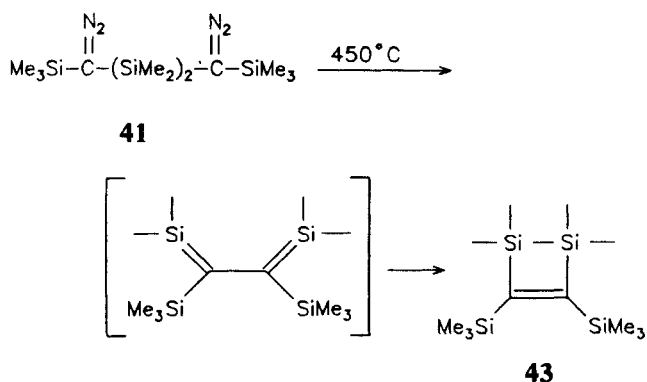
The pioneering papers of A. Brook and N. Wiberg on the synthesis of stable silenes and the research done by H. Bock and G. Maier concerning the PE-spectroscopic studies on H₂Si=CH₂ repre-

sent milestones in silene chemistry. Now the silene/Lewis base adducts of R(H)Si=CH₂/(CD₃)₂O (R = H, Me) have been characterized by NMR at − 140°C by J. Grobe and N. Auner. The method of silene production and the preparation of the NMR samples along with the chemical shifts of the ¹H and ¹³C nuclei definitely show that the character of the molecule is unsaturated and that the silenes are able to exist at − 196°C without donors.

Good results were also reported from the field of "silaaromatics," where F. Bickelhaupt and Y. van den Winkel have added new members to that class of compounds. The flash pyrolysis of 9,10-dihydro-9-silaanthracenes yields 9-substituted derivatives **46**, which could be trapped and identified UV-spectroscopically in an argon-matrix at 15K.

A, B, C, D = H, Ph, CH₂Ph
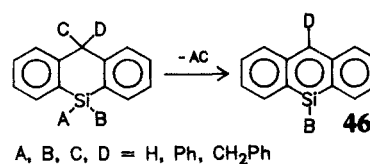
In the same context a contribution by P. Jutzi answers the question as to the existence of "nonclassical" silabenzene anions. The X-ray structures of crown-ether-stabilized lithium silacyclohexadienides **47** and **48** show that they exist as solvent separated ion pairs with free silacyclohexadienide anions. The SiC₅ framework is planar (as is the case for the isoelectronic neutral λ⁵-phosphinines **49** (Dimroth, Märkl)) and the endocyclic Si–C distances are shorter than the rather long exocyclic ones. The NMR data suggests that π-bonding in these R₂SiC₅H⁻ anions is quasiaromatic.

Li[12−crown−4]₂⁺

49

47 : R, R'=CH₃

48 : R=C(CH₃)₃, R'=H
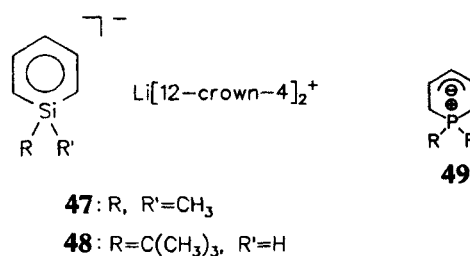
W. C. Joo employed NMR-spectroscopy to prove the monomeric existence of the 2,3,4,5-tetraphenyl-1-silacyclopentadienyl anions (TPSCp²⁻) (**50**) in solution with the negative charge being located at the silicon atom. However, the X-ray structure of the 1-methyl-1-sodium-derivative Me–TPSCp⁻Na⁺ (**51**) reveals a dimer in the solid state. In solution this decomposes into the species **52** and **53**, which have been trapped by polar reagents HX.

Further news of unsaturated Si-compounds includes the following: K. Tamao has produced Si=N-intermediates by thermal decomposition of 1-aza-

50

51

Me—TPSCp⁻

THF

52   **53**

54

$$Me_2Si: \quad + \quad S{=}C{=}S \quad \longrightarrow \quad \textbf{54} \quad \longrightarrow$$

$$\tfrac{1}{2}\, Me_2Si \underset{S}{\overset{S}{<}} SiMe_2$$

55   **56**

57

RMgX

hν

58

ROH
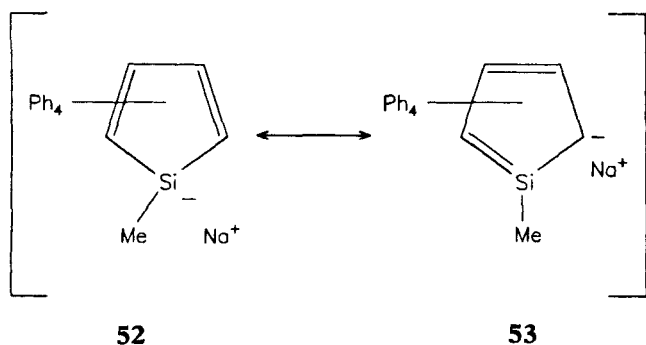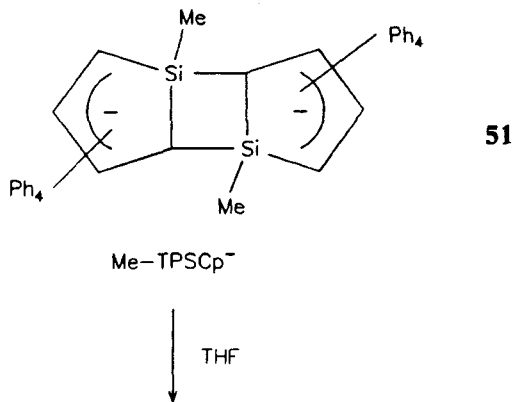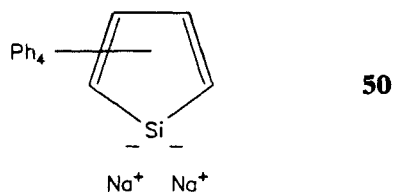
2-silacyclobutanes. Y. van den Winkel reported the NMR-spectroscopic characterization of phospha-silenes $R^1P{=}SiR^2R^3$ [$\delta\ ^{31}P \approx 130$ for $R^1 = 2,4,6$-$^tBu_3C_6H_2$, ≈ 70 for $R^1 = 2,4,6$-$^iPr_3C_6H_2$ (Is) or $2,4,6$-$Et_3C_6H_2$ (Es); $\delta\ ^{29}Si = 150$–190 ($R^2, R^3 = $ Is, Es, mes, or Bu^t); $^1J(PSi) \approx 152$ Hz]. V. N. Khabashesku isolated silanones $R_2Si{=}O$ in a matrix at 12 K [R = MeO, ν(SiO) = 1247; R = Ph, ν = 1205; R = Me, $\nu = 1210$ cm^{-1}]. S. Ijadi-Maghsoodi and T. J. Barton produced silathiones **54** by a) gas phase decomposition of (allylthio)dimethylsilane and b) reaction of dimethylsilylene with CS_2. **55** isomerizes into **56** under the conditions of the gas phase pyrolysis. A. Brook reported the reaction of his classic silene (**57**) with Grignard reagents; the products obtained suggest intramolecular migration of Me₃Si– and Me₃Si–O-groups. J. R. Wilking and P. Gaspar photolyzed (mesMe₂Si)₂ obtaining mesMe₂SiH and mesMeSi=CH₂; the latter could not be isolated but instead dimerized to E/Z isomers of the corresponding 1,3-disilacyclobutane. As expected the silene can be trapped by Me₃SiOMe, alcohols, acetone, and conjugated dienes. In a similar way M. Kira trapped the silene **58** with ROH to prove its existence indirectly.
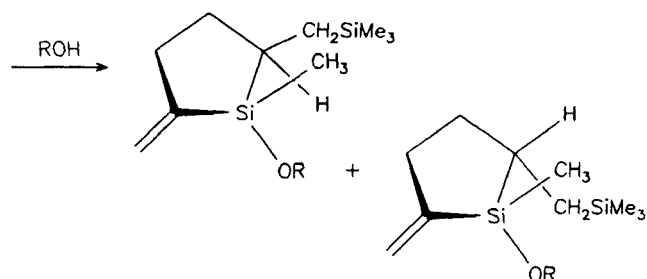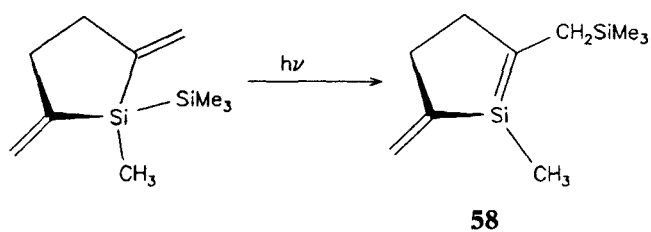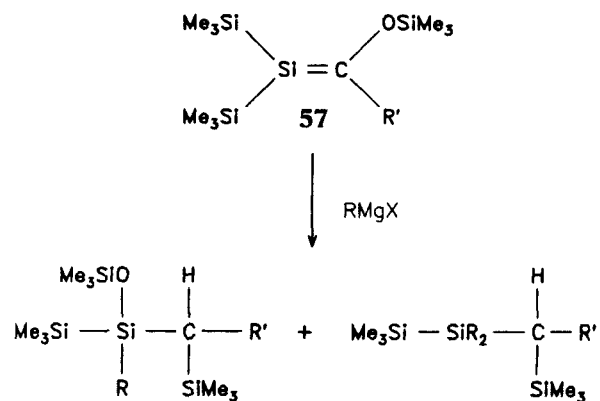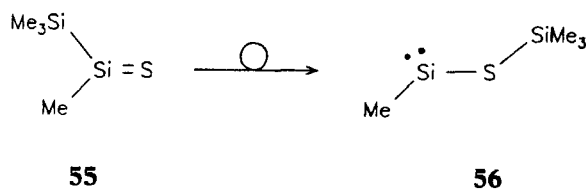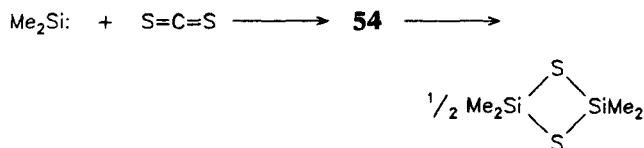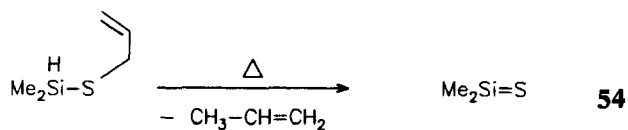
Silylenes, Silenes, and Disilenes in the Coordination Sphere of Transition Metals

Transition metal complexes are well established as useful catalysts for reactions of organosilicon compounds. Much of this chemistry is based on empirical observations, and surprisingly little is known about how transformations of silicon species occur at a metal center. Research on transition metal–silicon compounds has now increased dramatically, partly because of mechanistic considerations, but also because of the discovery that reactive intermediates—silylenes, silenes and disilenes—can be stabilized by binding to a transition metal.

In recent years Ch. Zybill had been successful in preparing silylene complexes of the type **59a,b** (M = Cr, d ≈ 2.28 Å; M = Fe, d ≈ 2.18 Å) in which the silicon atom is coordinated to an additional donor. New results show that compounds **60** liberate silylene when photolyzed; the silylene can be trapped by dimethylbutadiene to form silacyclopentene **61**. In addition he presented results that suggest the absence of coordinating donors in the silylene complexes $(CO)_4Fe=Si(SC_4H_9)_2$ and $Cp_2^*(CO)_2Re=SiBu'_2$.

$(CO)_4Fe=SiR_2 \cdot HMPT$

$(R = Me, OC_4H_9, SC_4H_9, Cl)$ **59a**

$(CO)_5Cr=SiR_2 \cdot HMPT$

$(R = Me, OC_4H_9, Cl)$ **59b**

60   **61**
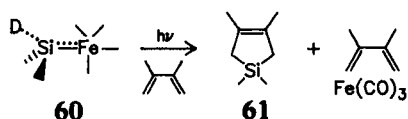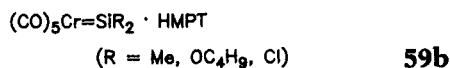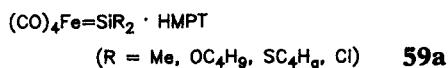
According to dynamic NMR studies carried out by D. Tilley, when $[Cp^*(PMe_3)_2Ru=SiPh_2(NCMe)]^+$ is dissolved in CH_2Cl_2 the acetonitrile is lost, forming the base-free cationic species $[Cp^*(PMe_3)_2Ru=SiPh_2]^+$. The related cation $[Cp^*(PMe_3)_2Ru=Si(SR)_2]^+$ [R = p-tol, δ ^{29}Si = 251 (r.t.), 259 (−80°C), $J(SiP)$ = 34 Hz; R = Et, δ ^{29}Si = 264 (−60°C)] is remarkably stable even in the solid state. The same group has also synthesized a stable Ru–silene complex: starting with the 16-electron compound $Cp^*(PR_3)RuCl$, the silene complex **62** is obtained by reaction with Grignard reagent $ClMgCH_2SiR'_2H$. The Si–CH_2 bond length of

62
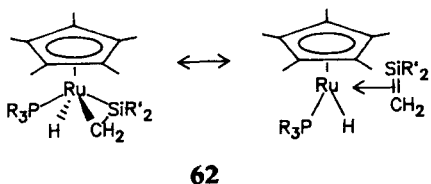
1.78 Å is intermediate between that for a free silene (1.70–1.76 Å) and a silacyclopropane (1.87–1.91 Å), indicating partial double bond character for the Si–C bond in **62**. $^1J_{CH}$ = 143.3 Hz is also consistent with partial double bonding. From an analogous synthesis $Cp^*(PMe_3)Ir(\eta^2\text{-}CH_2=SiR_2)$ (R = Me; R = Ph, δ $^{13}C(CH_2)$ = 33.37, $^1J_{CH}$ = 142.3 Hz, $d(Si=CH_2)$ = 1.81, $d(Ir–Si)$ = 2.317, $d(Ir–CH_2)$ = 2.189 Å) were also isolated.

Two additional silene transition metal compounds, described by D. Berry, showed NMR and structural data in good agreement with the findings mentioned above. For $Cp_2M(\eta^2\text{-}CH_2=SiMe_2)$ (M = Mo, W) the tungsten complex exhibits $d(Si=C)$ = 1.80 Å and $^1J_{CH}$ = 137 Hz. Disilenes have low oxidation potentials for the π-electrons in the Si=Si double bond and should therefore be good π-bases toward transition elements. Complexes **63** between stable disilenes and bis(phosphine)platinum moieties can be made directly.

63   R = Mesityl
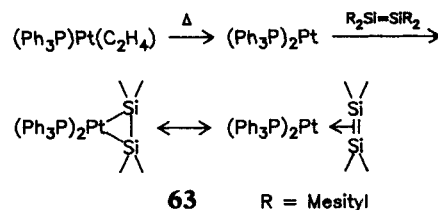
Similar complexes **64** and **65** are obtained when $(diphos)PtCl_2/Li$ or $(diphos)Pt(CH_2=CH_2)$ are reacted with dihydrodisilanes. These reactions allow an easy synthesis of complexes of disilenes, which are themselves unstable. When reacted with H_2, O_2, and NH_3 **65** suffers cleavage of the Si–Si bond leading to **66**, **67**, and **68**.

$R = Me, i\text{-}Pr, Ph$

64

a. R = Ph
b. R = Cy

a. R' = i-Pr
b. R' = Me
c. R' = Ph

65

a. R = Ph, R' = i-Pr
b. R = Ph, R' = Me
c. R = Cy, R' = Ph
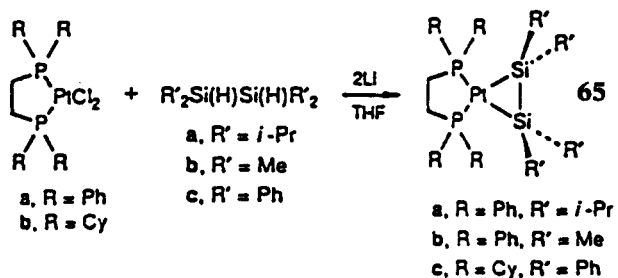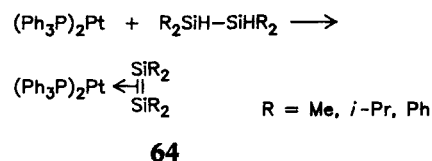
In related studies D. Berry reported the synthesis of stable molybdenum and tungsten disilene complexes, as well as a number of their reactions

66

67

a, R = i-Pr
b, R = Me

68

L = CO, PMe₃

69
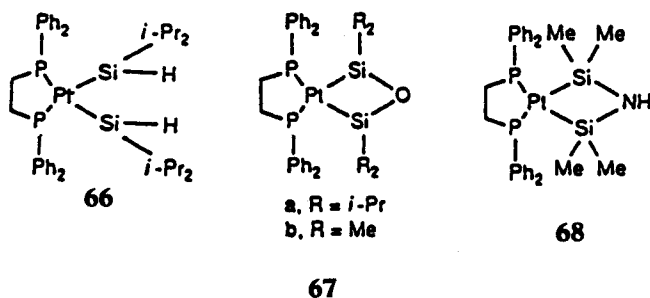
(Scheme 2), most of which also proceed with breaking of the Si–Si bond. A striking development by the same group is the preparation of the first silaneimine stabilized by complexing to a transition metal, in this case zirconium (**69**). The complex shows a Si=N distance of 1.69 Å, compared with the usual bond lengths of 1.58 Å for Si=N and 1.64–1.78 Å for Si–N.

STERICALLY CROWDED SILICON COMPOUNDS

Some fascinating chemistry of tetravalent silicon was presented by N. Wiberg in his lecture on "sterically overloaded organosilicon compounds." Tri-*t*-butylsilyl groups 'Bu₃Si ("Supersilyl") are especially suitable components of highly hindered Si compounds due to their extreme space requirements, their remarkable inertness, and their easy accessability. Substitution of normal silyl groups (e.g. Me₃Si) by 'Bu₃Si groups leads to silicon compounds with unusual bond lengths and angles, as well as unexpected stability and activity.

Starting materials are 'Bu₃SiHal (**70**), 'Bu₃SiOSO₂CF₃ (**71**), and 'Bu₃Si–N=N–NH–Si'Bu₃ (**72**). **71** is used to synthesize 'Bu₃SiNH₂ and 'Bu₃SiPH₂ while **72** serves as a precursor for 'Bu₃Si–E–Si'Bu₃ (E = O, S, NH). Reduction of **70** or oxidation of the metal silyl compounds MSi'Bu₃ leads to the short-lived 'Bu₃Si–radical, which mainly suffers dimerization at low temperatures to give 'Bu₃Si–Si'Bu₃ (**73**, mp 162°C, d(Si–Si) = 2.70 Å!). At higher temperatures 'Bu₃SiH is formed by H-
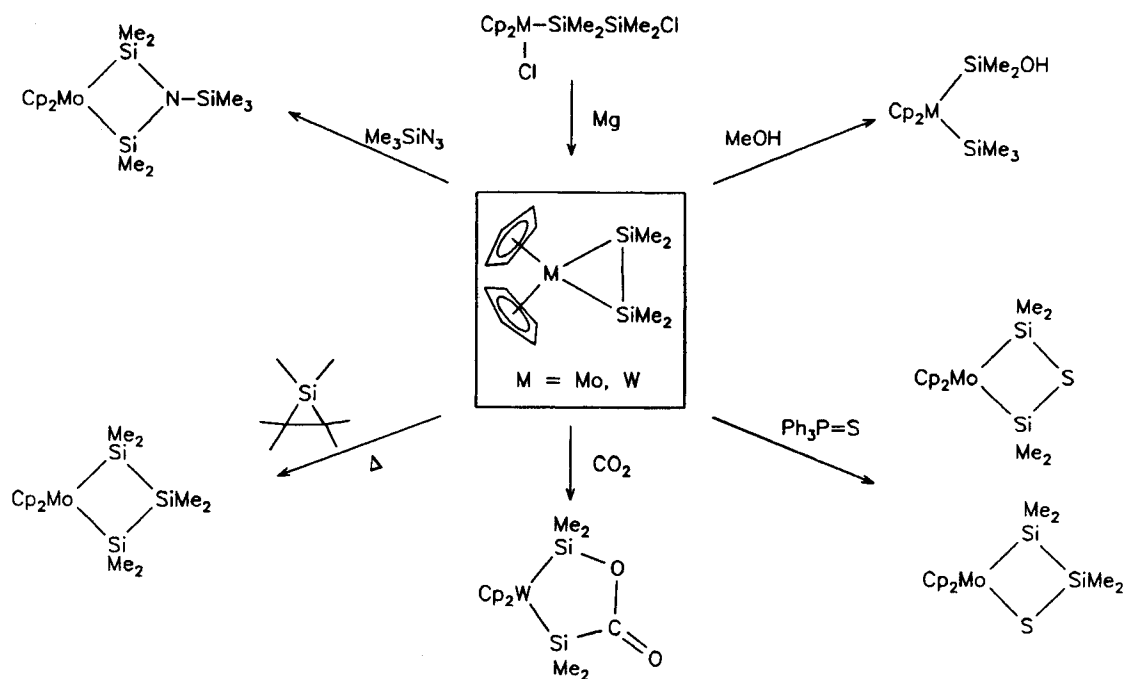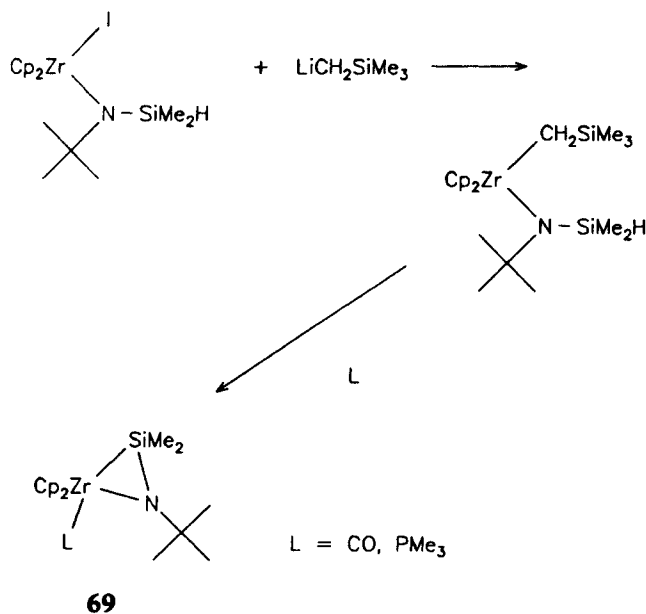
SCHEME 2

abstraction. When thermolyzed, **73** will again decompose into the "monomeric" radical, which leads to further interesting chemical reactions. With P_4, for example, it reacts to form **74**, whose structure is related to that of the well-known compound Li_3P_7; NO and **73** yield $^tBu_3SiON=NOSi^tBu_3$. Supersilylsodium, $^tBu_3SiNa$ (**75**), contains the anion $^tBu_3Si^-$, a strong base isoelectronic to $^tBu_3P$. Compound **75** likewise adds to the double bonds of N_2O (to **76**) and $N_3SiCl^tBu_2$ (to **77**). The adducts are labile and decompose with the elimination of N_2. In addition, $^tBu_3Si^-$ acts as a nucleophile and displaces halide in compounds such as LiCl, $MgBr_2$, PhCl, Me_3SiCl, PF_3, and S_2Cl_2. In cases where the outgoing halogen is less negatively polarized and/or is sterically protected, nucleophilic attack of $^tBu_3Si^-$ occurs frequently on halogen yielding supersilyl halides. The extraordinary shielding effects of the supersilyl group enabled the synthesis of several stable unsaturated silicon compounds like **20** (essentially linear Si=N–Si skeleton, d(Si=N) = 1.568 Å), $Me_2Si=N(Si^tBu_3)$, $Me_2Si=C(SiMe_3)(Si^tBu_3)$, and $^tBu_2Si=P(Si^tBu_3)$. The bis(supersilyl)triazene **78** is the first stable triazene stabilized only by silyl groups that has been isolated and characterized by X-ray crystallography. Remarkably it loses N_2 only when heated to more than 150°C.

74

78
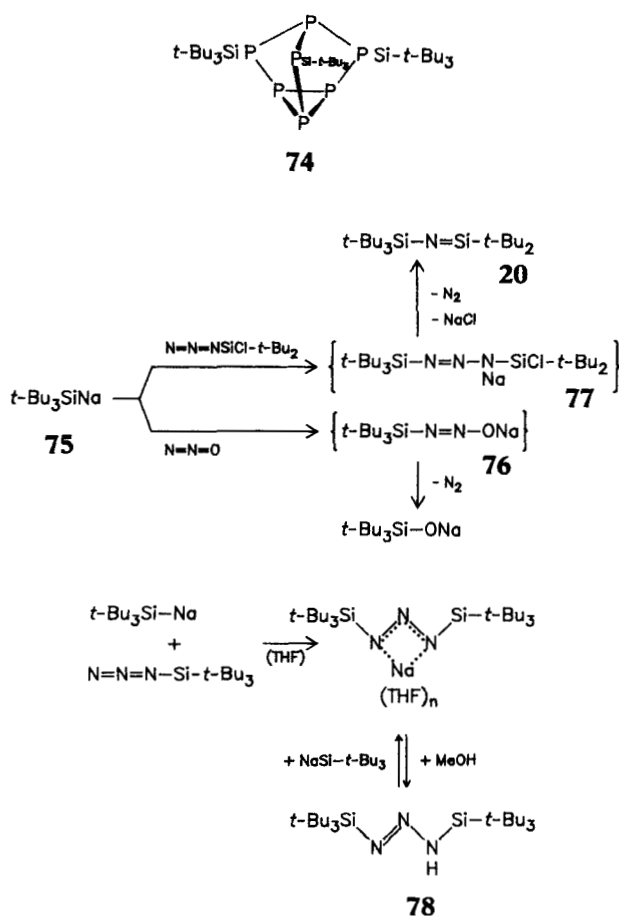
The enormous synthetic potential of **75** is demonstrated by the following impressive reactions:

Tetramer $(^tBu_3SiAl)_4$ is formed in the reaction with AlCl.

$^tBu_3Si–SiCl_3$ (from **75** and $SiCl_4$) and sodium yield products that give $(^tBu_3Si–SiH)_3$ or $(^tBu_3Si–SiH_2)_2$ when methanolyzed.

Similarly exciting results were reported using the $(Me_3Si)_2CH$ ("bisyl") group. The pioneer in this field, M. F. Lappert, took the participants on a tour through the periodic table comprising 16 years of research at Sussex. Bisyl compounds are remarkably useful in the synthesis of homoleptic organoelement compounds in unusual (low) states of oxidation and coordination numbers. Limitations allow us to quote just a few of the recent results: he reported the X-ray structure of Mg(bisyl)$_2$, which shows agostic contacts to neighboring molecules, and discussed a series of new lanthanoid compounds, as well as the two astonishingly stable radicals (bisyl)$_2$P· and (bisyl)$_2$As·.

The steric and electronic features of the Me_3Si group were applied by H. H. Karsch to influence the coordination properties of phosphino methanide ligands $[R_2P–CXY]^-$ (X, Y = H, PMe_2, $SiMe_3$). Numerous examples show that high coordination numbers (as in hexacoordinate $X_2Si[(Me_2P)_2C(SiMe_3)]_2$ (X = Cl, Me)) (**79**), oxidative bond formations (C–C, P–C, P–P), silyl rearrangements, and methyl transfer (Si→Al) are possible and may be governed by the choice of substituents. X-ray studies of the low valent compounds $E[(Me_2P)_2C(SiMe_3)]_2$ (**80**: E = Si, Ge, Sn, Pb) allow a direct comparison with detailed information about the kind of bonding and the role of the "lone pair" in such species. Especially noteworthy is the synthesis of the first divalent Si compound with σ-bonded ligands, **80** (E = Si), being stable at ambient temperatures.

79   E=Si, **80**
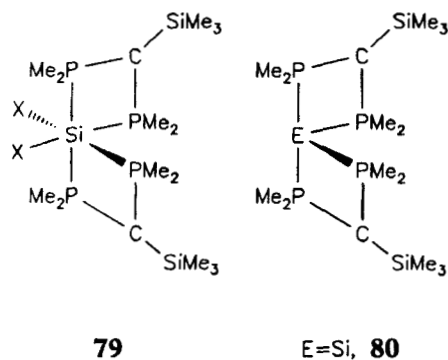
P. D. Lickiss enlarged the palette of silylated methanes by the synthesis of **81** and **82**. Compound **81** is completely unreactive toward trifluoroethanol, but **82**, although even more hindered, sol-

volyzes rapidly. This reaction probably proceeds through a phenyl-bridged cation **83**.

81

82

83
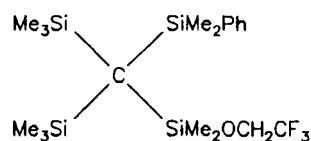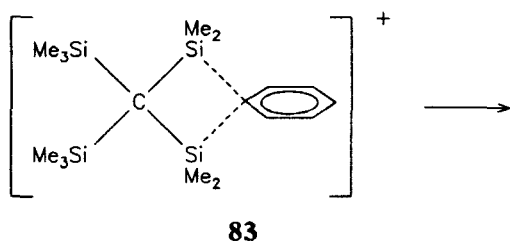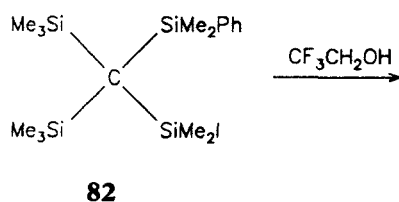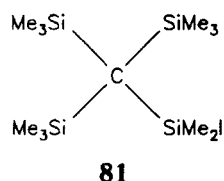
(Me₃Si)₃CSiBr₃—a potential precursor for the "disilyne" (Me₃Si)₃C–Si≡Si–C(SiMe₃)₃—was prepared by S. M. Whittaker. In addition the trisyl ligand (Me₃Si)₃C was used by W.-W. du Mont for the synthesis of several selenium compounds, including trisyl-Se$_x$-trisyl (x = 2, 3), trisylSeI, and **84**. Finally H. J. Breunig has been successful in the preparation of [bisyl-Sb]₄.

84
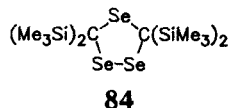
DI-, OLIGO- AND POLYSILANES

The polysilanes continue to be of great interest. Structural aspects of cyclic and linear oligosilanes were reviewed by L. Parkànyi, who presented correlations between the bond distances of those compounds [d(Si–Si) = 2.22–2.70 Å, d(Si=Si) = 2.14–2.16 Å] and the substitution pattern at silicon. The Si–Si bond lengths depend greatly on the substituent bulk, indicating the primary importance of steric interactions.

Electronic interactions are important when the silicon atoms are linked to small and electron-withdrawing substituents or bound to transition metal atoms. In small ring systems the Si–Si distances conform to what is expected, becoming shorter as the ring size increases. The Si–Si bond lengths in permethylated macro rings with negligible ring strain increase slightly with the size of the ring.

The synthesis of polysilanes is usually achieved by condensation reaction of halogenomono-, di-, or trisilanes in the presence of alkali metals. H. Matsumoto has carried out the cocondensation of 1,1,2,2-tetrachloro-1,2-diisopropylsilane and 1,2-dichloro-1,1,2,2-tetraisopropyldisilane with Li in THF yielding the "ladderlike" polysilane oligomers (RSiSiR)$_n$(R₂SiSiR₂)₂ (**85**) (n = 1–4). However, condensation of 2,2,3,3-tetrabromo-1,4-di-t-butyl-1,1,4,4-tetramethyltetrasilane with Na gave the remarkable octasilacubane (RSi)₈ (**86**). An X-ray structure determination disclosed a slightly distorted cube-like framework. The high oxidation potential of **86** (0.48 V vs. saturated calomel electrode) reflects the great strain energy of the cage Si₈-lattice.

85

86

R = i-Pr, n = 1-4   R = t-BuMe₂Si
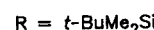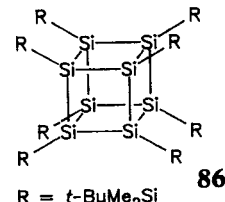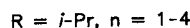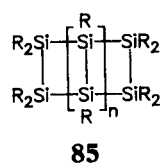
The growing industrial importance of polysilanes and polycarbosilanes as SiC-precursors has aroused interest in both the synthesis of functional di- and trisilanes and the decomposition pathways of polysilanes when subjected to thermolysis and/or photolysis. The group of E. Hengge has investigated the first aspect: K. Hassler and U. Katzenbeisser reported the synthesis and properties of bromo- and iododi- and trisilanes X$_n$Si₂H$_{6-n}$ and X$_n$Si₃H$_{8-n}$ (X = Br, I) by cleavage of Si-aryl bonds with HX; H. Stüger described those of tetrasilanes X(SiH₂)₄X (X = Br, Cl, F); and M. Eibl and E. Hengge presented new transition metal cyclosilanyl compounds Si₆Me₁₁ML$_n$, ML$_n$ = Fe(CO)₂Cp, Mo(CO)₃Cp, Mn(CO)₅.

The decomposition of the model compounds Si₄Me₁₀ (branched and linear) occurs along different pathways depending on the conditions. I. M. T. Davidson showed that the thermal gas phase decomposition primarily leads to organosilyl radicals, which become transformed into silylenes in secondary reactions. These species then isomerize to stable products. Photolysis in solution, however, leads directly to silylenes as initial products in the first step.

Relatively little work was presented on polysilane high polymers, which have recently excited so much interest for their applications in high tech-

nology. However, work by two different groups leading to the first ordered polysilanes was reported. The Tohoku University group synthesized alternating copolymers **87** by the novel anionic polymerization of the disilane fragment from the bridged biphenyl, **88**. Before quenching, the lithium-terminated "living polymer" may be used as an initiator for polymerization of alkenes such as methyl methacrylate to give polysilane–alkene copolymers. Ordered polymers of AAB type **89** were also reported by the Wisconsin group, by condensation of a dibromotrisilane, **90**. In this reaction a high molecular weight ($M_w \approx 830,000$) randomized fraction is produced as well as a low molecular weight ($M_w \approx 8500$) ordered fraction.

also adopt a planar all-trans conformation, although (^{n}Bu$_2$Si)$_n$ and (^{n}Pent$_2$Si)$_n$ exist in a $\frac{7}{3}$ helical arrangement. The polymer (^{n}BuSi^{n}Hex)$_n$ has now been studied by Asuke and was found to have a conformation with only two-dimensional order at all temperatures from -100 to $+250°$C. From -20 to $+200°$C (^{n}BuSi^{n}Hex)$_n$ exists in a columnar liquid–crystalline mesophase, an arrangement that may be common for many polysilanes.

PENTA- AND HEXACOORDINATE SI-COMPOUNDS

Hypervalent Si species have aroused much interest and research activity in the recent years, partly because they may be reaction intermediates in nearly all substitution reactions at the Si atom. R. Damrauer has studied such reactions in the gas phase. A large number of hypervalent derivatives have been synthesized and studied recently, especially in the group of R. Corriu, so that today a pattern of "structure and reactivity" is gradually emerging and being understood.

Results presented by R. Corriu in his lecture "Reactivity of Penta- and Hexacoordinate Species of Silicon" show that nucleophiles often react more rapidly with pentacoordinate than with tetracoordinate Si compounds. Thus, the Grignard reagent ^{i}PrMgBr reacts 150 times faster with PhSiF$_4^-$K$^+$ than with PhSiF$_3$, and ketones and aldehydes form alcohols with HSi(OEt)$_4^-$K$^+$ spontaneously while no reaction occurs with HSi(OEt)$_3$. In this context, pentacoordinate dihydridosilanes in many reactions show a surprisingly high reactivity compared to that of tetracoordinated analogs. In agreement with these results, the reactivity of hexacoordinate compounds, whose existence in solutions has been proved by NMR methods, is distinctively different from those of the tetra- and pentacoordinate compounds.

In general, the actual substitution reaction on silicon is often preceded by Si-pentacoordination, a fact shown by K. Tamao's X-ray investigations on novel pentacoordinate anionic silicates containing a bent fluoride-bridge between two silicon atoms (e.g. **91** and **92**) along with his mechanistic inves-

A paper by L. Leites reported thorough infrared and Raman spectroscopic studies on (Me$_2$Si)$_n$ and (Et$_2$Si)$_n$, confirming that these two polymers exist in a planar, trans-zig-zag conformation. From earlier work it is known that (^{n}Pr$_2$Si)$_n$ and (^{n}Hex$_2$Si)$_n$

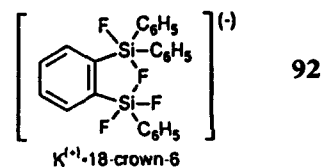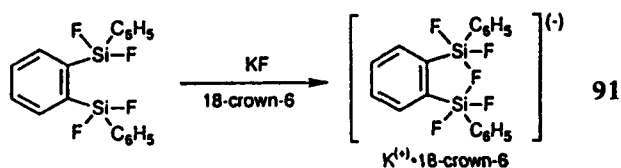$$R-SiX_3 + H_2O_2 \xrightarrow[\text{THF, MeOH}]{\text{KF, KHCO}_3} R-OH$$

transition state
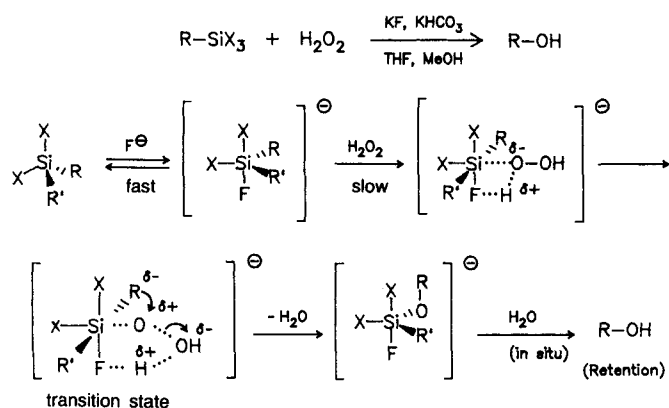
SCHEME 3

tigations on the H_2O_2 oxidation of Si–C bonds in F, Cl, OR, or NR_2 functionalized silanes (Scheme 3).

C. Brelière and R. Corriu achieved the synthesis of **93**, the first stable salt containing *two* hexacoordinate silylanions in *one* molecule, as well as the preparation of coordinatively stabilized silylenium ions (e.g. **94**) by oxidation of hypervalent hydridosilane **95** with a silver salt.
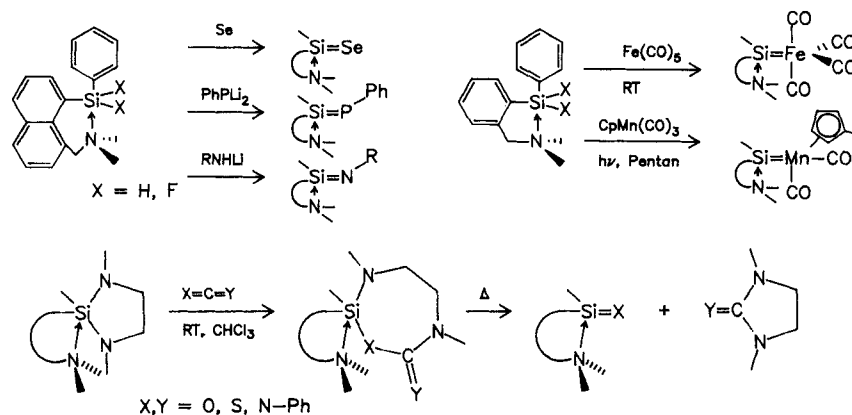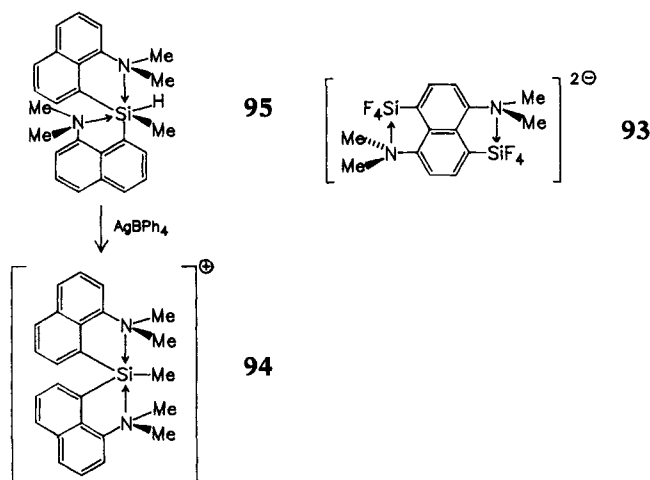
The *inter*molecular stabilization of silicon compounds having low coordination numbers by Lewis bases is well established; G. F. Lanneau and R. Corriu now show that a comparable (or even better?) stabilization is possible by *intra*molecular coordination. This approach has led to the isolation of the first stable silathione ($\diagdown$ Si=S) and the synthesis of further unsaturated Si compounds—among them two silylene transition metal complexes (Scheme 4).

SILICON MATERIALS

"Silicon Compounds in the Materials Sciences" will obviously be one of the dominating themes of silicon symposia yet to come. The active participation of international industrial enterprises at the Edinburgh meeting suggests that the time is now favorable for harvesting the results of many years of research in the form of new and useful materials.

An elegant transition from synthetic work to efficient application of the products in the field of Si materials was presented by H. Schmidbaur in his lecture on the synthesis of small polysilylalkanes—especially those of the "methane series" $C(SiH_3)_nH_{4-n}$ ($n = 1-4$)—which are utilized as feedstock gases for PE-CVD (*plasma enhanced chemical vapor deposition*). The synthetically oriented Si chemist must first of all understand the importance of hydrogen-containing amorphous silicon (a-Si:H) as a semiconductor material before he will accept the destruction of such ingeniously synthesized and aesthetic molecules as, for example, tetrasilylmethane $C(SiH_3)_4$ (**96**) by PE-CVD. The optoelectronic properties (especially the characteristic semiconductor energy band-gap ΔE_g) of a-Si:H can be altered by introducing carbon or germanium as alloy constituents, and in standard technology CH_4 or GeH_4 are employed as sources for C and Ge

SCHEME 4

in the PE-CVD process. The properties of a-SiC:H films generated by these techniques are not fully satisfactory, however, and alternative sources for C (and Ge) may therefore offer distinct advantages. Disilyl- and trisilylmethane obtained from cheap starting materials have satisfied the expectations that the microstructure of the films can be adjusted by the selection of compounds having appropriate stoichiometry and constitution. Thus, Schmidbaur's group succeeded in the production of a-SiC: H films with a high photoconductivity and a large "optical gap" using $H_2C(SiH_3)_2$ (bp 15°C); the results were optimized applying $HC(SiH_3)_3$ (bp 61°C) as film source. The PE-CVD of **96**, synthesized by the sequence $PhSiH_2X \rightarrow C(SiH_2Ph)_4 \rightarrow C(SiH_2Br)_4 \rightarrow$ **96** (bp 86.5°C) is being investigated at this time— an increase in the quality of the a-SiC:H films is expected. In addition there is a strong interest in the synthesis of alternative compounds like $MeC(SiH_3)_3$, $Me_2C(SiH_3)_2$, or $MeSiH_2SiH_3$ and $H_3SiCH_2CH_2SiH_3$ targeted for the use in PE-CVD.

In his plenary lecture "The Wonderful World of Silicon on Unsaturated Carbon—From Gas Phase Rearrangements to Ceramic Fibers," T. J. Barton was able to demonstrate the close relationship of the reactivity of organosilicon compounds in the gas phase and the polymeric or solid state. He first reported observations concerning the thermally induced behavior of organosilanes with silicon bonded to (or otherwise interacting with) unsaturated carbon. This discussion included both divalent and tetravalent Si interacting intramolecularly with olefinic and acetylenic units to (almost) inevitably produce molecular rearrangement; examples are given in Equations 1 and 2. Barton then moved to the solid state where he reviewed the efforts on the synthesis (Equation 3) and study of silicon–acetylene and silicon–diacetylene polymers and their conversion to silicon carbide fibers. He finished with the presentation of studies on catalytically polymerized diethynylsilanes, systems that are electrical conductors and possess truly unique nonlinear optical properties; in the case of polydiethynylsilanes

$$(3)$$
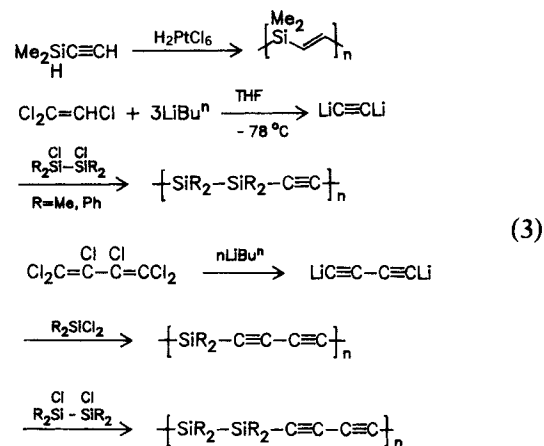
these are due to the structure of the fully conjugated backbone in which there may be four- (**97**) or five-membered rings (**98**).
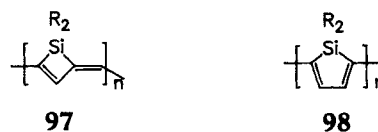
Several new polymers containing silicon with other organic moieties were reported in a series of papers from the Montpellier group. Only a few examples (**99–102**) are illustrated here.

99

100

101

$$(1)$$

$$(2)$$

$$-\!\!\left(\!C\!\equiv\!C-C\!\equiv\!C-\underset{\underset{R^2}{|}}{\overset{\overset{R^1}{|}}{Si}}-Fc-\underset{\underset{R^2}{|}}{\overset{\overset{R^1}{|}}{Si}}-C\!\equiv\!C-C\!\equiv\!C-\underset{\underset{R^4}{|}}{\overset{\overset{R^3}{|}}{Si}}\!-\!\!\right)_{\!n}$$
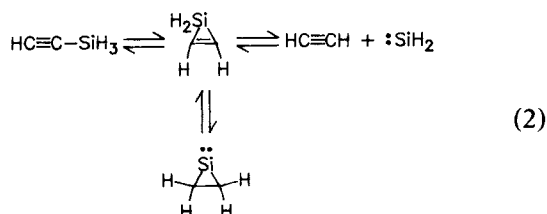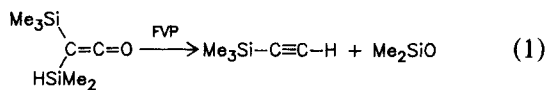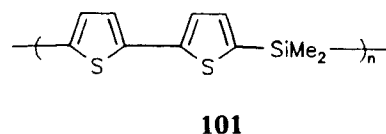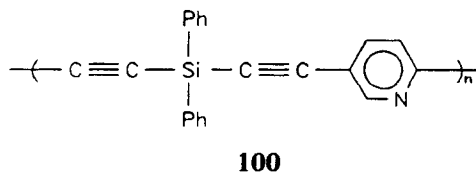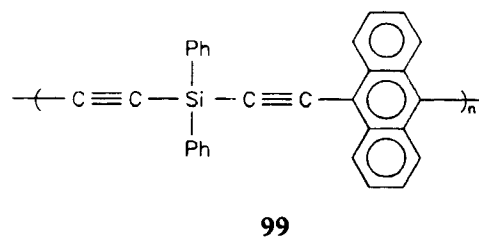
102

A simple route to cycloethynylsilanes has been developed by E. Hengge and A. Baumegger. They treated a mixture of dichlorodiorganosilanes and ethyne with Na/K-alloy yielding $(Me_2SiC\equiv C)_n$ ($n = 3–12$; $n = 4$ see **103**), $(Ph_2SiC\equiv C)_5$, and catenated dimethyldiphenyl-3,6-disilaocta-1,4,7-triyne. An analogous reaction using mono- and 1,4-dihalogenopermethylcyclohexasilane led to the corresponding ethynylundecamethylcyclohexasilane and 1,4-diethynyldecamethylcyclohexasilane—the first examples of cyclohexasilane–ethyne compounds. Employing similar synthetic routes, $\sigma(Si–Si)$-π-conjugated cyclic ethynylsilanes **104** and **105** were obtained by R. West and T. Iwahara by reacting the Grignard reagent $BrMgC\equiv C-SiR_2-SiR_2-C\equiv CMgBr$ with $ClSiR_2' SiR_2'Cl$ (giving **104**) and $Cl_2SiR'-SiR'Cl_2$ respectively (giving **105**).

$$\begin{array}{ccc} Me_2Si\!-\!C\!\equiv\!C\!-\!SiMe_2 \\ {\scriptstyle |}\qquad\qquad{\scriptstyle |} \\ C\qquad\qquad C \\ {\scriptstyle |||}\qquad\qquad{\scriptstyle |||} \\ C\qquad\qquad C \\ {\scriptstyle |}\qquad\qquad{\scriptstyle |} \\ Me_2Si\!-\!C\!\equiv\!C\!-\!SiMe_2 \end{array}$$

103

$$\begin{array}{cc} R_2Si\!-\!C\!\equiv\!C\!-\!SiR'_2 \\ {\scriptstyle |}\qquad\qquad{\scriptstyle |} \\ R_2Si\!-\!C\!\equiv\!C\!-\!SiR'_2 \end{array} \qquad \begin{array}{cc} R_2Si\!-\!C\!\equiv\!C\!-\!\underset{\underset{R'}{|}}{\overset{\overset{R'}{|}}{Si}}\!-\!C\!\equiv\!C\!-\!SiR_2 \\ R_2Si\!-\!C\!\equiv\!C\!-\!\underset{\underset{R'}{|}}{\overset{\overset{R'}{|}}{Si}}\!-\!C\!\equiv\!C\!-\!SiR_2 \end{array}$$

$(R' = i\text{-}C_3H_7)$

$\lambda_{max} = 250\ nm$ $\lambda_{max} = 260\ nm$

104   **105**

The extensive work at Dow-Corning Corporation on preceramic polymers was summarized in a plenary lecture by W. Atwell. An interesting development is the formation of solid silicon carbide parts from a suspension of finely-divided silicon carbide powder in a polysiloxane polymer. The resulting mixture can be injection-molded to produce a desired shape and then pyrolyzed to SiC. A similar process, but using a polysilane polymer as the binder, is now carried out in Japan.

An interesting contribution to "organosilicon preceramic polymer technology" was presented in J. Dunogues' lecture on new synthetic strategies on silicon carbide and carbonitride materials. During the last ten years silicon carbide and carbonitride-based materials have created considerable scientific interest due to their potential utilization in the aeronautical and space industry, and, more generally, in the production of a new generation of high performance engines. Concerning silicon carbide-based fibers the present industrial approach involves the following steps: $Me_2SiCl_2 \rightarrow$ polydimethylsilane (PDMS) $\rightarrow$ polycarbosilane (PCS)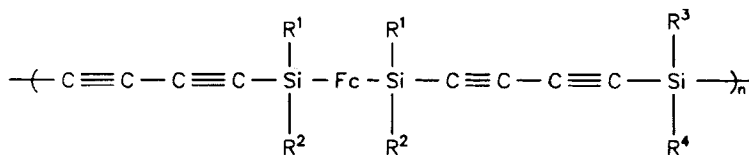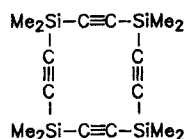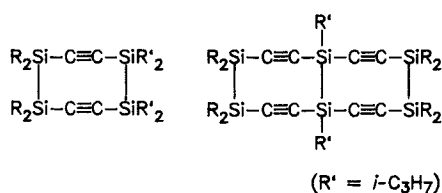 $\rightarrow$ "SiC." Dunogues offered two new strategies in polysilane chemistry: a) the synthesis of a modified PDMS from polycondensation of both Me_2SiCl_2 and $(ClHMeSi)_2CH_2$ and b) the preparation of PDMS by electrosynthesis of Me_2SiCl_2 according to a simple and very practical process. The former route can afford a soluble PDMS more easily converted into the corresponding PCS. The latter avoids the use of sodium and operates at room temperature. The author also proposed a preparation of linear and well defined PCS having the formula $HMe_2Si-(CH_2SiMeH)_nCH_2SiMe_2H$ from the well-known 1,3-disilacyclobutane $(Me_2SiCH_2)_2$, itself chemically or electrochemically prepared from $ClMe_2SiCH_2Cl$; this polysilapropylene constitutes a convenient model to investigate the mechanism of conversion of the organosilicon precursor into the corresponding SiC material. In contrast L. E. Gusel'nikov polymerized 1,2-disilacyclobutane $Me_2\overline{SiCH_2CH_2}SiMe_2$ at ambient temperatures obtaining a crystalline high molecular weight polymer containing Si–Si-units, $[-CH_2CH_2SiMe_2SiMe_2-]_n$.

Preceramic polymers leading to SiC/Si_3N_4 alloys are often produced from polysilazane sources. The cocondensation of $Me_2SiCl_2/ClHMeSiNR-SiHMeCl$ (R = H, Me) leads to a polysilacarbosilazane that can be thermolyzed to give N containing PCS. As Dunogues pointed out, the Si carbide nitride resulting from the pyrolysis of the latter differs from that obtained via the polysilazane, since treatment at $\approx 1500°C$ converts it into silicon carbide and not silicon nitride.

The chemistry of monomeric cyclosilazanes $(-\underset{|}{\overset{|}{Si}}-\underset{|}{N}-)_n$ ($n = 2–4$) pioneered by U. Wannagat and today being subjected to further research by U. Klingebiel is nowadays thought to be quite well understood. The mixture of mostly cyclic oligomers obtained in the ammonolysis of $MeSiHCl_2$ may be converted to cross linked products of higher molecular weight thermally or by treatment with ap-

propriate acids or bases. D. Seyferth reported a new method of achieving such crosslinking that involves treatment of the ammonolysis product of MeSiHCl₂ with H₃B·SMe₂. The crosslinking process involves formation of borazine rings via silazane ring opening by the BH₃ reagent. Pyrolysis in a stream of NH₃ of the resulting polymers at 1000°C gives amorphous B/Si/N-ceramics. Further heating of such materials under Ar at 1500°C causes formation of crystalline BN. However, BN appears to retard crystallization of Si₃N₄.

The most important organosilicon materials are of course the silicone polymers; at Edinburgh some 40 papers and posters reported new developments in polysiloxane.chemistry. Here we can note only a few highlights.

J. Rich reported the synthesis of new thermoplastic block copolymers of siloxanes with polyimide and polycarbonate. The intermediates for these polymers, for example **106** and **107**, were obtained by the recently discovered silylative decarbonylation of acid chlorides with methylchlorodisilanes. Siloxanes with cyclic structures in the main chain, **108**, were reported by N. N. Makarova and N. N. Kuzmin; they have properties intermediate to those of the very flexible alkylpolysilanes and the rigid polysilsesquioxanes. That siloxane cage structures may also be introduced into polymers was reported by R. Weidner. Treatment of spherocyclic tetraalkylammonium silicates R₄NOSiO₃ with silylating agents gives anions such as the cubane structure (Me₃SiO)₈(SiO₃)₈ (**109**); the Me₃SiO groups can be replaced by Me₂HSiO substituents, allowing further elaboration to polymeric materials. New sil-

oxanes with perfluoroalkyl ether side groups, for example **110**, have been prepared by M. Boileau from hydrosilylation of fluoroalkyl allyl ethers such as $C_6F_{13}CH_2CH_2OCH_2CH{=}CH_2$ by polymethylhydrosiloxane. J. Chojnowski reported syntheses of siloxanes with phosphorus-containing side groups **111**, made by anionic polymerization of the corresponding cyclotrisiloxanes; and the group of E. A. Chernyshev reported on siloxanes containing aryl metal carbonyl moieties **112**.
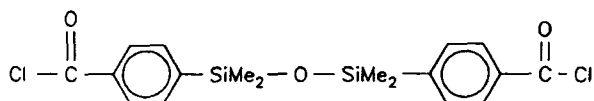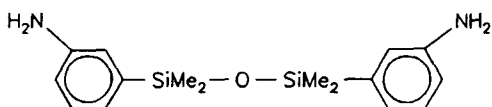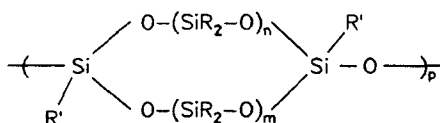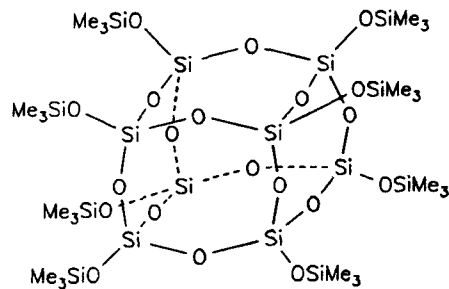
109

106

107

108 n,m=1–4

110

111 (X=nil, O, S)
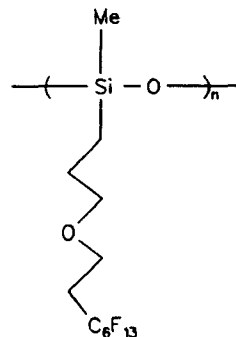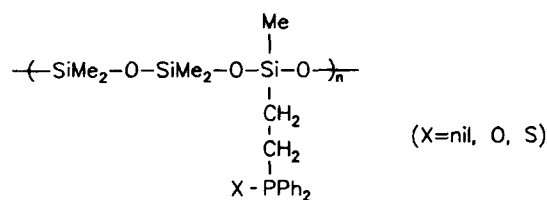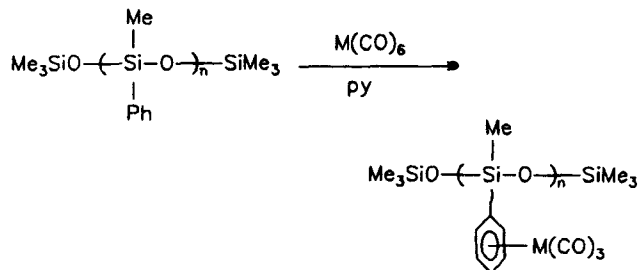
112

Of the several papers presented on physical studies of siloxanes, we will describe only the contributions by V. Litvinov. Line shape analysis of the ^{29}Si NMR resonance was employed to study $(Et_2SiO)_n$, which unlike $(Me_2SiO)_n$ forms a mesomorphic, thermotropic "liquid crystalline" phase. Crystallization from this phase gives an almost fully crystalline polymer. NMR relaxation data also shows that $(Et_2SiO)_n$ with two carbon atoms in the side chain forms the minimum in a curve of T_g versus side chain length. A complex interplay of steric restriction and interchain attraction is apparently responsible.

The importance of Si-containing materials was further underlined by an open discussion led by Aylett, West, Sakurai, Corriu, and Pachaly on the topic "Success and Future Trends of New Si-Materials." The discussion reflected hitherto achieved success as well as future expectations and industrial requirements in this research field.

Although every technology exacts an environmental cost, the organosilicon industry is relatively benign, as pointed out by A. Stroh in his lecture "Recycling—Magic or Tragic." Of the products from the Rochow direct synthesis, which is the basis of the silicone industry, more than 95% are used. Even the spent silicon is oxidized to useful SiO_2. Chlorine atoms in the direct synthesis are recaptured as HCl and repeatedly recycled. Silicone polymers are biologically almost inert, oxidizing slowly in the environment to relatively harmless organic compounds and silica. Thus as we move toward the twenty-first century, which perhaps will be the century of silicon as the twentieth has been the century of carbon, it is reassuring to know that organosilicon compounds are relatively "environment friendly."

This review does have to come to an end, although there are still several areas of Si-organic chemistry that should be mentioned, for example, the chemistry of silicon in pharmaceutical and natural materials; elegant results of research in the field of bio-organic silicon chemistry were given by R. Tacke (for those interested see *The Chemistry of Organic Silicon Compounds* part 2, Wiley, Chichester, pp. 1143–1206 (1989)). This report should be understood to be an appetizer for delving deeper into the wonderful world of organosilicon chemistry. The community of silicon chemists has grown—but it is not yet "sterically overcrowded."

APPENDIX: ORGANOSILICON LITERATURE

The literature on most aspects of organosilicon chemistry is well summarized in the books *The Chemistry of Organosilicon Compounds*, Parts 1 and 2, S. Patai and Z. Rappoport (eds), Wiley, Chichester, 1989. As a supplement to these useful books we provide here a list of articles in selected areas of organosilicon chemistry that have appeared since the beginning of 1988. Publications on silicon polymers are not listed, because the numbers are simply too large. Since the beginning of 1988, about 500 articles and patents have appeared on polysilanes, 400 on polycarbosilanes, 120 on polysilazanes and 800 on polysiloxanes. We call attention however to a particularly important review article on polysilanes by R. D. Miller and J. Michl, *Chem. Reviews* *89*, 1989, 1359.

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