SILAFUNCTIONAL COMPOUNDS: SYNTHESIS AND REACTIVITY *

Annual Survey for the Year 1984

Joyce Y. Corey
Department of Chemistry
University of Missouri-St. Louis
St. Louis, Missouri 63121 U.S.A.

CONTENTS

I. INTRODUCTION

This survey summarizes the synthesis and reactivity of silafunctional compounds as reported in Volumes 100 and 101 of Chemical Abstracts. Dissertations and the chemistry of silicon polymers are not covered but some patents that contain synthetic details are included. Sections III through IX concern the formation and reactivity of the indicated bonds and each section begin with a brief summary of the contents. The last sections gather together the various reports concerning silicon derivatives with more than four ligands and reactions that eliminate Me_3SiX units.

II. REVIEWS

A general review of carbon-functional organosilicon derivatives[1] was published as well as brief discussions of recent topics in silicon chemistry [2] and new silicon compounds [3]. The following specific classes of organosilicon compounds were surveyed: silacyclohexadienyl anions [4], 1,3,2-dioxasilaheterocycles [5], silaethenes [6], silylenes [7,8,9,10], silyl anions [11], polysilanes [12], trimethylsilyldiazomethane [13] and odorous organosilanes [14].

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*Previous review see R.B. King and J.P. Oliver (Eds.), J. Organomet.Chem. Library, 17(1985)163-309.

The reactions of organopolysilanes with organic peroxides has been summarized [15]. The steric effects in organosilicon chemistry [16] and in organosilicon radicals [17] has been reviewed. Silylation techniques applied to gas chromatography [18] have been covered briefly as well as the use of hydrosilanes as silylating, agents for hydroxyl groups [19].

Silafunctional derivatives have been used in various aspects of organic synthesis. These silafunctional derivatives include isocyanates [20,21], siloxyfurans and siloxyoxazoles [22], hydrosilanes [23], silyl enol ethers [24] and transition metal trialkylsilane complexes [25]. General surveys of silicon compounds in organic synthesis also appeared [26,27,28 and 29] as has the use of fluorodesilylation [30].

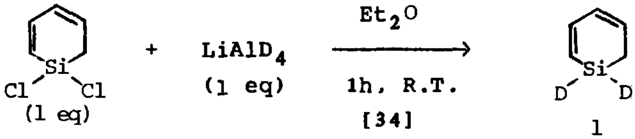
Developments in the area of biologically active organosilicon compounds have been summarized [31].

III. Silicon-Hydrogen

Silicon-hydrogen bonds are usually formed by reduction of chlorosilanes. A patent reports the use of MgH_2 to prepare SiH_4 from $SiCl_4$ in THF or glyme [32]. LAH reduction of halo- and alkoxy-derivatives is promoted by ultrasound in hydrocarbon solvents [33] and an example is shown in Eqn. 1 to illustrate the method. Formation of deuterated silacyclohexadiene is shown in Eqn. 2. Dimethylsilane is formed in 15% yield on reaction of Me_2SiCl_2 with Na in xylene at 440°. The major product, the oligomers of $(Me_2Si)_x$ when heated to 710° gave a gas mixture whose major components were Me_2SiH_2 (51 pts) and $(MeSiH)_2$ (20 pts) [35]

$$\underset{\text{R=tetrahydro-2-furyl}}{RSi(OMe)Me_2 + LiAlH_4} \xrightarrow[25°/3h]{\text{pentane}} \underset{(100\%)}{RSiHMe_2} \qquad (1)$$

[33]



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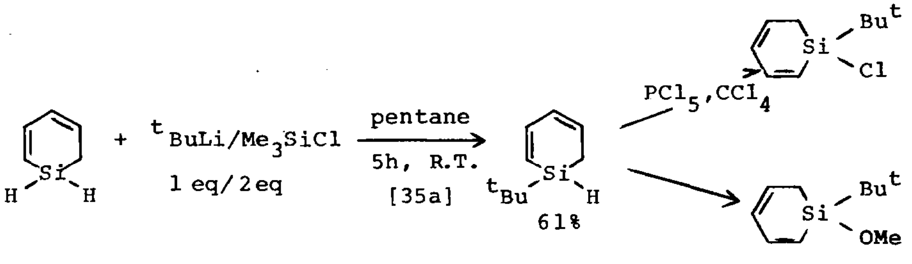
(2)

Hydrosilanes may be converted to other silafunctional derivatives. The combination, $tBuLi/Me_3SiCl$ with silacyclohexadiene resulted in incorporation of a *t*Bu group (Eqn. 3) [35a] The SiH bond may be halogenated or converted to an alkoxide as shown in Eqn. 3. The mechanism of the photobromination of hydrosilanes in CCl_4 has been reported. The ratio of the rate constant for k_{HSiCl_3}/k_{HSiPh_3} is about 1 but in the dark only $HSiPh_3$ reacts [36]. Hydrosilanes, $RSiMe_2H$, are cleaved by $KHCO_3/30\%H_2O_2$ in MeOH/THF (1:1) to give ROH (100%)[37].



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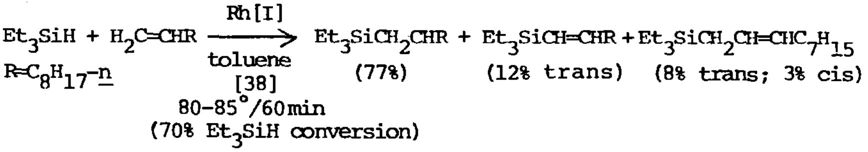
Hydrosilanes are used to prepare silicon-carbon bonds through hydrosilylation of olefins. The Rh(I) catalyzed hydrosilylation of $C_8H_{17}CH=CH_2$ with Et_3SiH was shown to give vinyl- and allylsilanes in addition to the expected tetraalkysilane (an example is shown in Eqn. 4) [38]. A comparison of product distribution with catalyst is shown in Eqn. 5. The two component Ziegler catalyst of $Rh(acac)_3$-R_3Al also gave a vinylsilane from $Et_3SiH + PhCH=CH_2$ [39] (Eqn. 6). This same catalyst promotes hydrosilylation of internal but not terminal alkynes (Eqn. 6). Hydrosilylation of benzaldehyde by $HSiPhMe_2$ in $Bu_4N^+F^-$/HMPA gave $PhCH_2(OSiMe_2Ph)$ in 91% yield [40]. This same combination of reagents ($PhMe_2SiH$/TBAF/HMPA) was used to synthesize 2-aminoalcohols (Eqn. 7). An assymetric hydrosilylation catalyst is formed "in situ" by adding a slight two-molar excess of optically active $2\text{-}Ph_2PC_6H_4CH_2NHCHMePh$ to $[Rh(COD)Cl]_2$. When the catalyst is used for the addition of Ph_2SiH_2 to PhCOMe (Rh/subst = 1:500), 93% hydrosilylation occurs and the optical yield of PhCHMeOH obtained after hydrolysis is 52.7% ee [41]. Aminomethylsilanes are formed from hydrosilanes and $(R_2N)_2CH_2$ (Eqn. 8).

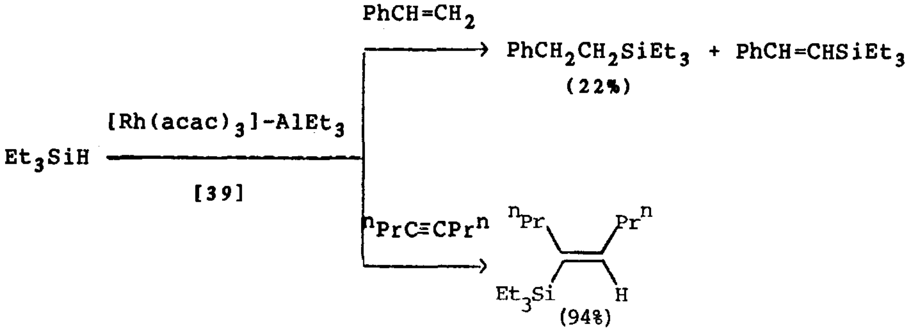


$$\underset{R=C_8H_{17}\text{-}\underline{n}}{Et_3SiH + H_2C{=}CHR} \xrightarrow[\substack{\text{toluene}\\ [38]\\ 80\text{-}85^\circ/60\text{min}\\ (70\%\ Et_3SiH\ \text{conversion})}]{Rh[I]} \underset{(77\%)}{Et_3SiCH_2CHR} + \underset{(12\%\ \text{trans})}{Et_3SiCH{=}CHR} + \underset{(8\%\ \text{trans};\ 3\%\ \text{cis})}{Et_3SiCH_2CH{=}CHC_7H_{15}} \qquad (4)$$

$$R_3SiH + H_2C{=}CHR \xrightarrow[\text{[38]}]{cat/C_6H_6} R_3SiC_8H_{17} + R_3SiCH{=}CHC_6H_8 + R_3SiCH_2CH{=}CHC_5H_{11} \qquad (5)$$

$R{=}C_6H_{13}$-n

	$R_3SiC_8H_{17}$	$R_3SiCH{=}CHC_6H_8$		$R_3SiCH_2CH{=}CHC_5H_{11}$	
	%	% trans	% cis	% trans	% cis
$RhClL_3$	60	32	-	5	3
$Ru_3(CO)_{12}$	11	47	-	32	11
$H_2PtCl_6{\cdot}6H_2O$	96				



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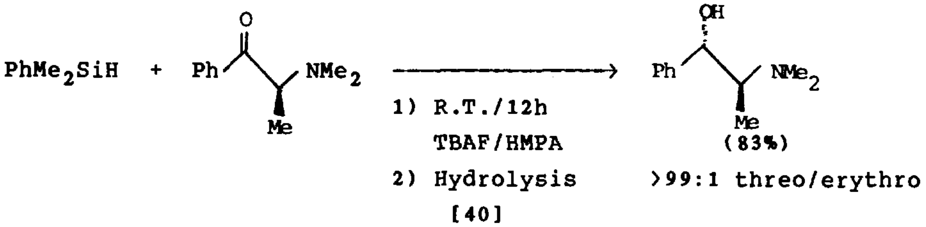


(7)

$$Me_2NCH_2NMe_2 + Me_nHSiCl_{3-n} \xrightarrow[\text{[42]}]{THF,\ R.T.} Me_2NCH_2SiCl_{3-n}Me_n \qquad (8)$$

n=0(67%); 1(57%); 2(68%)

Trichlorosilane has been used to deoxygenate phosphine oxides. When an attempt was made to reduce 7-phosphanobornenes in refluxing benzene, dihydrophosphindoles were obtained, but the combination, $HSiCl_3$/py gave the expected deoxygenated products [43]. Ring cleavage occurred in benzazaphospholes on addition of $HSiCl_3$ in refluxing benzene to give both 2-$MeNHC_6H_4CH_2PHPh$ (20%) and 2-$MeNHC_6H_4CH_2P(O)HPh$ (61%) [44]. Reduction of $MeCCl_3$ to $MeCHCl_2$ occurs with Et_3SiH/tBu_2O_2 [45]. The combination of $Et_3SiH/HClO_4$ in

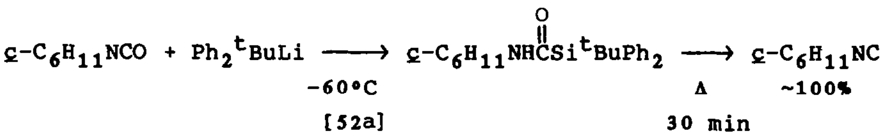
CH_2Cl_2 hydrogenates olefins and converts PhCOMe to PhEt in 74% yield [46]. Aryl halides undergo reductive formylation under 50 psi CO in the presence of poly(methylhydrosiloxane) (PMHS). When PhI is treated with PMHS and PdL_4 ($L=PPh_3$) with added HMPA at 80°C, 96% (GC) PhCHO is obtained after 20 h. Treatment of $p\text{-}ClC_6H_4Br$ with $PMHS/PdL_4/PhCH_2)_3N$ at 110° gave $4\text{-}ClC_6H_4CHO$ (54%) [47].

Multiple-IR-photon decomposition of $EtSiH_3$ proceeds by elimination of SiH_4 which involves H atoms β to silicon [48]. Laser driven reactions of SiH_4 and C_2H_4 generated uniform powders of β-SiC [49]. The generation of $KSiH_3$ from SiH_4 in glyme proceeds at a more rapid rate if dispersed Na/K alloy is used (20 h to convert 10 g of SiH_4) and use of pure dispersed K reduces the time even further (11-12 h) [50].

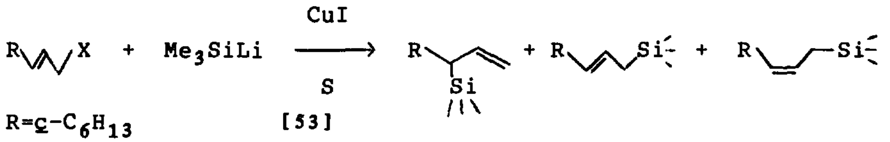
From a comparison of the reactivities of thermally generated SiH_2 and reactions of recoiling Si atoms it was demonstrated that singlet silylene is an important intermediate in the hot atom chemistry of silicon [51]. Reaction of **1** (Eqn. 2) with $CF_3C{\equiv}CCF_3$ in an autoclave at 90° for 5 h produced the Diels-Alder product, silabicycloactadiene, which provided $D_2Si{=}CH_2$ upon flash pyrolysis. The silaethene is stable in Ar at 10 K [34].

IV. Silicon-Group I, II, III

Silyllithium derivatives are used in syntheses either alone or with added CuI. In general, Me_3SiLi is produced from $Me_6Si_2/MeLi$ and $Ar_xR_{3-x}SiLi$ from reaction of a silylchloride with Li in THF. An illustration of this latter method is the formation of a green-black solution of $Ph_2{}^tBuSiLi$ from $Ph_2{}^tBuSiCl$ and Li in THF at R.T. in 6 h [52a]. The previously unknown ${}^tBu_3SiNa$ (formulated as $[Na(THF)_4][Na(SiBu_3{}^t)_2]$ has been generated from ${}^tBu_3SiBr$ and Na wire in THF [52b]. Examples of the synthetic uses of silyllithium agents are shown in Eqns. 9-11. Addition of Me_3SiLi to chiral naphthyl oxazoline followed by MeI gave 1,1,2-trisubstituted 1,2-dihydronaphthalenes that are *trans* [55].



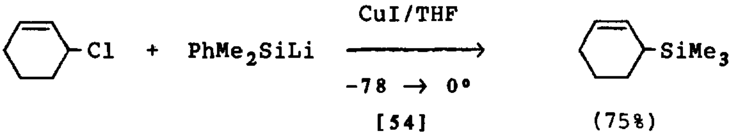
$$\underline{c}\text{-}C_6H_{11}NCO + Ph_2{}^tBuLi \xrightarrow[\substack{-60^\circ C\\ [52a]}]{} \underline{c}\text{-}C_6H_{11}NH\overset{O}{\overset{\|}{C}}Si{}^tBuPh_2 \xrightarrow[\substack{\Delta\\ 30\ min}]{} \underset{\sim 100\%}{\underline{c}\text{-}C_6H_{11}NC} \qquad (9)$$



(10)

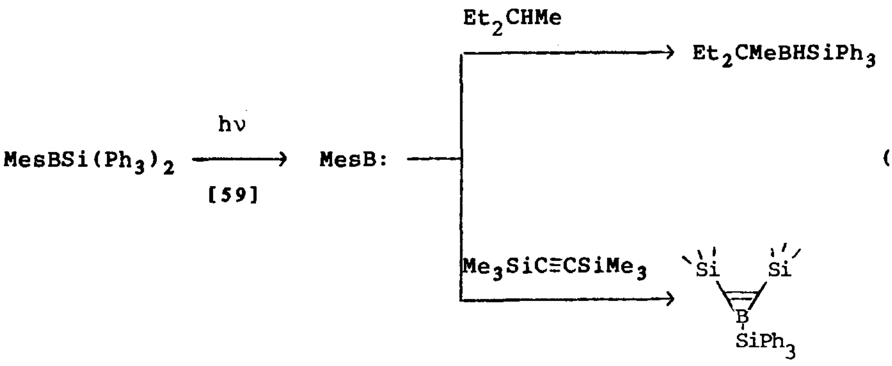
T	S	X	%a	Pts	Pts	Pts
7-25°	HMPA	Cl	80	87	13	0
		Br	80	60	13	27
-60°	$HMPA/Et_2O$	Cl	87	98	2	0
		Br	79	77	5	18

a. % conversion



(11)

Calcium atoms insert into Si-Cl bonds to give organosilylcalcium chlorides [56]. Silyl-substituted carboranes (with SiC bonds) are formed when RLnI (formed from $PhCB_{10}H_{10}CLi$ and LnI_2 in THF/C_6H_6 at -10 to 0°) is treated with Me_3SiCl [57]. When nido-$(Me_3Si)_2C_4B_4H_6$ is heated at 210° for 3d in a sealed tube, nido-$(Me_3Si)_2C_4B_8H_{10}$ is formed in 82% yield [58]. Silyllithium reagents couple with boron-halogen bonds to give silylborane derivatives. When Ph_3SiLi was added to BBr_3 in hexane, $B(SiPh_3)_3$ was isolated in 64% yield [59]. Derivatives of the type $RB(SiPh_3)_2$ (R=Me, Mesityl) were similarly prepared. These latter derivatives are precursors to boranediyls which were trapped by Et_2CHMe or $Me_3SiC{\equiv}CSiMe_3$ (Eqn. 12). Silylation of arylhalides and vinyl iodides occurs with $Me_3Si\}_3Al$ in the presence of a metal catalyst as shown in Eqn. 13.



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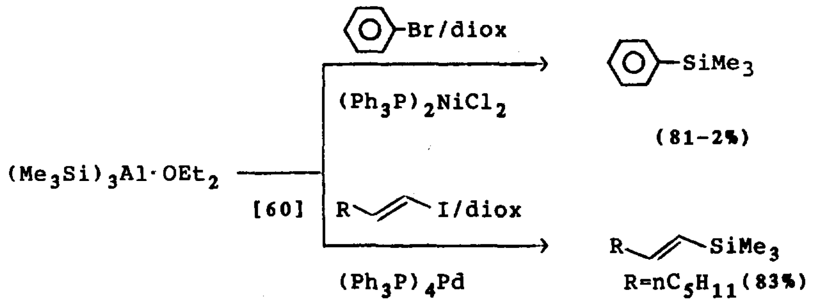


(13)

V. Silicon-Group IV

This section concerns the formation and reactivity of derivatives that contain one or more silicon-silicon bonds and will be covered in the sequence: 1. Disilenes; 2. Disilanes; 3. Linear Polysilanes; 4. Cyclic Polysilanes; 5. Heterocycles with Si-Si Bonds; 6. Silicon-Tin Derivatives.

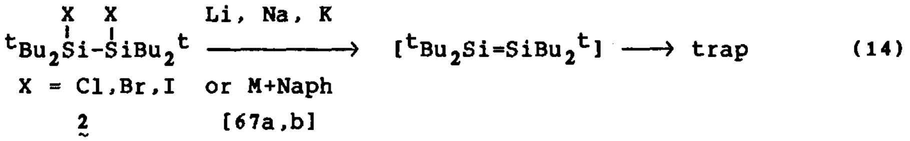
1. Disilenes

Photolysis of linear trisilanes is the usual route to disilenes through dimerization of the initially generated silylene. In most cases the substituents on silicon must be bulky groups to prevent further condensation reactions from occurring. The 266 nm laser photolysis of $(Me_3Si)_2SiPhMe$ at room temperature in cyclohexane gave a short-lived transient ($t_{1/2} < 20\mu s$) at 440 nm tentatively assigned to PhMeSi:. If the solvent is carefully deoxygenated a more persistent transient at 380 nm is generated. In the same study the transient at 440 nm reacts faster with 2,3-dimethylbutadiene than Et_3SiH but the transient at 380 reacts with neither additive. No free radicals such as $\cdot SiMePhSiMe_3$ were detected by pulsed photolysis ESR. These observations may support concerted elimination of Me_6Si_2 from the trisilane precursor [61].

A second route to disilenes is through the photolysis of a cyclotrisilane. Again, bulky substituents are required for isolation of solid disilene derivatives although several peralkyl-systems have been generated with a finite stability in solution. When the cyclotrisilane, $(R_2Si)_3(R{=}2{,}6\text{-}Et_2C_6H_3\text{-})$, is photolyzed in 3MP (~100K) for 25 min. disilene is generated in >50% yield [62]. A similar photolysis of $[(^tBuCH_2)_2Si]_3$ afforded a mixture of disilene and silylene whose presence was inferred from trapping reactions [63]. Extension of this strategy to cyclotetrasilanes appears to be successful. When $[^iPr_2Si]_4$ is photolyzed in $^cC_6H_{12}$ solution a species with λ_{max} = 320 nm is generated which was assigned to cyclotrisilane. Continued photolysis (7h) have a new species with λ_{max} = 400, assigned to the disilene, $^{i}Pr_2Si = SiPr^{i}_2$. Additional photolysis destroyed the yellow species [64].

The first disilenes that exhibit cis and trans isomers have been formed by the two previously described routes. Photolysis (254 nm) of $Mes(R)Si(SiMe_3)_2$ in pentane provides $Mes(R)Si{=}Si(R)Mes$ [$R={}^{t}Bu$(95% trans at R.T.) and $N(SiMe_3)_2$ (95% cis at -60°C)] [65]. Photolysis of cis and trans cyclotrisilane isomers of $(^{t}BuMesSi)_3$ proceeds with retention to give disilenes with an initial Z/E ratio of 7.1/1 (from cis-cyclotrisilane) and 0.38/1 (from trans-cyclotrisilane). Continued photolysis of cis$(^{t}BuMesSi)_3$ produced a photostationary ratio of Z/E $^{t}BuMesSi{=}SiMesBu^{t}$ of 3.5/1 [66]. When trans-$Mes(^{t}Bu)Si{=}Si(Bu^{t})Mes$ is photolyzed (λ =350 nm) a mixture of trans/cis = 10/5.9 is formed. However the cis form reverts to trans on standing [65]. Thermal isomerization of disilene above room temperature appears to occur by rotation about the Si-Si double bond (isomerization is not affected by trapping agents such as butadienes) [66].

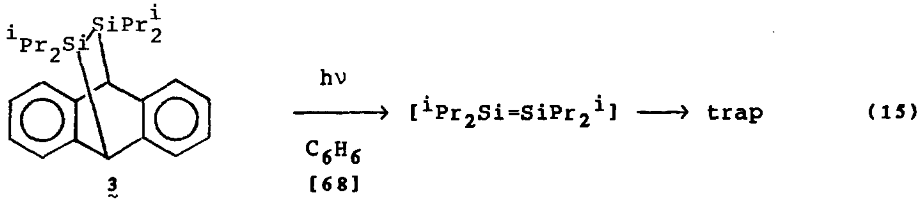
Other methods for generation of peralkyldisilenes have been reported from the disilane (Eqn. 14), a dibenzo-disilabicylco[2.2.2]octa-2,5-diene (Eqn. 15) and 1,2-disilacyclohex-4-enes (Eqn. 16) but the formation of disilenes were inferred from trapping reactions.



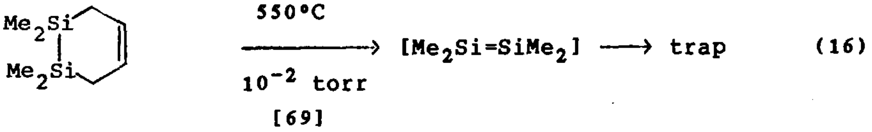
$$^{t}Bu_2\overset{X}{\overset{|}{Si}}-\overset{X}{\overset{|}{Si}}Bu_2{}^{t}\ \xrightarrow[\text{or M+Naph [67a,b]}]{\text{Li, Na, K}}\ [^{t}Bu_2Si{=}SiBu_2{}^{t}] \longrightarrow \text{trap} \qquad (14)$$

X = Cl,Br,I

2



$$\mathbf{3}\ \xrightarrow[C_6H_6\ [68]]{h\nu}\ [^{i}Pr_2Si{=}SiPr_2{}^{i}] \longrightarrow \text{trap} \qquad (15)$$



$$\xrightarrow[10^{-2}\ \text{torr}\ [69]]{550°C}\ [Me_2Si{=}SiMe_2] \longrightarrow \text{trap} \qquad (16)$$

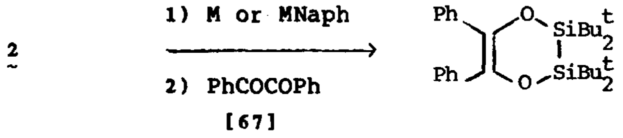
In cases where unstable disilenes are formed, trapping reactions are employed to "prove" their presence. The additives normally used are alcohols (Eqns. 17-19) PhCOCOPh (Eqn. 20a), or transfer from one diene to another (Eqn. 20b).

$$(R_2Si)_3 \xrightarrow[\text{[63]}]{h\nu} R_2Si{=}SiR_2 + R_2Si\colon \xrightarrow{EtOH} EtO(SiR_2)_2H + R_2Si(OEt)H \qquad (17)$$

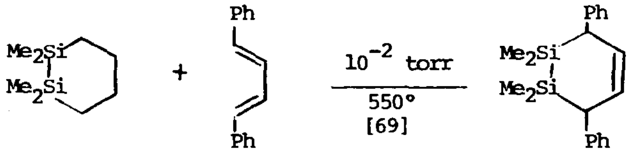
$R{=}CH_2Bu^t$

$$\underset{\sim}{3} + MeOH \xrightarrow[\text{[68]}]{h\nu} \underset{(41\%)}{MeO[Si(Pr^i)_2]_2H} \qquad (18)$$

$$({}^iPr_2Si)_4 \xrightarrow[\substack{EtOH/\underline{c}\text{-}C_6H_{12}\\ \text{[64]}}]{h\nu/40h} \underset{(68\%)}{H(SiPr^i_2)_2OEt} + \underset{(33\%)}{{}^iPr_2Si(OEt)H} + \text{other products} \qquad (19)$$



(20a)



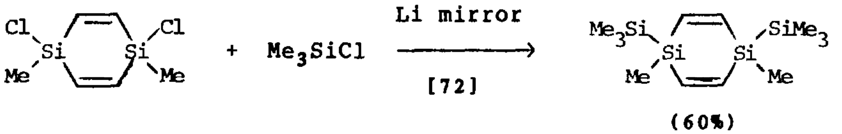
(20b)

Addition of diazomethane to $Ar_2Si=SiAr_2$ ($Ar=2,6\text{-}Me_2C_6H_3$) gave 1,2-disilacyclopropane in 30% yield [70]. The reactions of this new ring system are described in section V-5.

In the chemical vapor deposition of Si from SiH_4, the species, Si_2, was observed and is proposed as a precursor to nucleation of Si [71a].

2. Disilanes

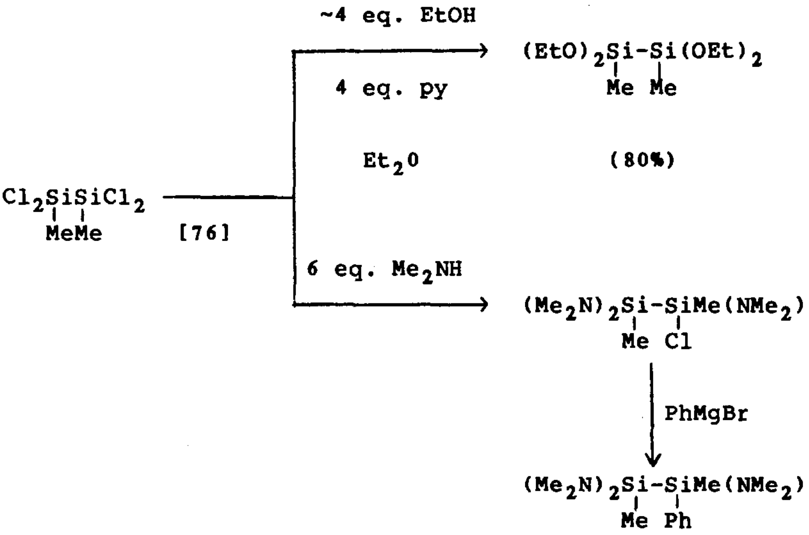
A possible synthesis of 1,2-difunctional disilanes may occur as an extension of the observation that $Ph_2HSi)_2$ is formed from Ph_2SiH_2 when Rh(I) catalysts are added, although workup tends to give $O(SiHPh_2)_2$[71b]. Silicon-silicon bonds are usually formed by condensation of chlorosilanes with alkali metals. An interesting application of this approach is shown in Eqn. 21 in the synthesis of a 1,4-bis-trimethyl-1,4-disilacyclohexadiene.



(21)

(60%)
81% *cis*; 19% *trans*

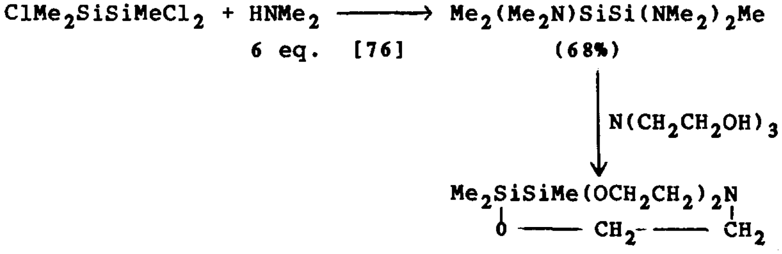
Most other new disilanes result from substitution chemistry. Pentamethylbromosilane is formed in 72% yield from Me_5Si_2OEt and CH_3COBr [73]. A mixture of $Me_2Si_2H_4$ and $Me_2Si_2Cl_4$ and $AlCl_3$ at 90° gives $MeH_2SiSiHClMe$ and $MeCl_2SiSiH_2Me$ initially. After about 60 minutes two additional derivatives, $MeCl_2SiSiHClMe$ and $MeHClSi)_2$ are also present [74]. When $MeCl_2Si)_2$ is reacted with ^tBuLi in n-hexane (0-5°), $Me^tBuClSi)_2$ is generated in 54% yield [75], but addition of PhMgBr to $MeCl_2Si)_2$ gave $MeCl_2SiSiPhMeCl$ (13%) [76]. Substitution reactions of chlorinated disilanes are shown in Eqns. 22 and 23. When Me_3SiOLi is added $ClMe_2SiSiMe_2Cl$ two reaction products (Eqn. 24) are observed but the rate of the second substitution step is significantly lower than the first ($k_1/k_2 \sim 30$). This result implies that partial substitution or a stepwise replacement of two different nucleophiles should be feasible. This is in contrast to the reaction of $Me_3SiSiMeCl_2$ with Me_3SiOLi which gives a mixture of $Me_3SiSi(OSiMe_3)MeCl$ and $Me_3SiSiMe(OSiMe_3)_2$ [73].



$$\mathrm{Cl_2\underset{Me}{Si}\underset{Me}{Si}Cl_2}\ [76] \xrightarrow[\text{4 eq. py, Et}_2\text{O}]{\sim\text{4 eq. EtOH}} \mathrm{(EtO)_2\underset{Me}{Si}{-}\underset{Me}{Si}(OEt)_2}\ (80\%)$$

$$\mathrm{Cl_2\underset{Me}{Si}\underset{Me}{Si}Cl_2} \xrightarrow{\text{6 eq. Me}_2\text{NH}} \mathrm{(Me_2N)_2\underset{Me}{Si}{-}\underset{Cl}{Si}Me(NMe_2)} \xrightarrow{\text{PhMgBr}} \mathrm{(Me_2N)_2\underset{Me}{Si}{-}\underset{Ph}{Si}Me(NMe_2)}$$

(22)



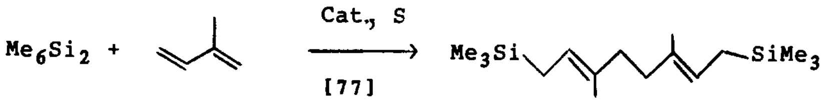
$$\mathrm{ClMe_2SiSiMeCl_2} + \underset{\text{6 eq.}}{\mathrm{HNMe_2}} \xrightarrow[{[76]}]{} \underset{(68\%)}{\mathrm{Me_2(Me_2N)SiSi(NMe_2)_2Me}} \xrightarrow{\mathrm{N(CH_2CH_2OH)_3}} \mathrm{Me_2SiSiMe(OCH_2CH_2)_2N}$$

(23)

$$\mathrm{ClMe_2SiSiMe_2Cl} + \mathrm{Me_3SiOLi} \xrightarrow[{[73]}]{k_1} \mathrm{Me_3SiOSiMe_2SiMe_2Cl} \xrightarrow{k_2} \mathrm{Me_3SiOSiMe_2)_2}$$

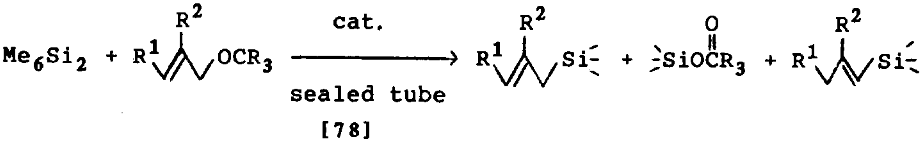
(24)

The combination R_6Si_2/Pd(O or II) or $R_4Si_2Cl_2$/Pd (O or II) has been shown to add to dienes or allylic esters and is a reducing agent for benzylidene dichlorides. Examples of these processes are shown in Eqns. 25-29.

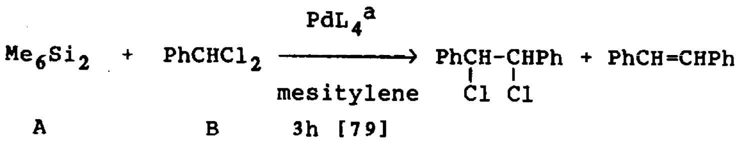

(25)

Cat.	S	T(t)	%
$PdCl_2L_2^a$	C_6H_6	160(16)	3
	CH_2Cl_2	130(19)	tr^b
	-	60(12)	70
$Pd(OAc)_2$	-	120(94)	87

a. L=PhCN b. $CuCl_2$ added


(26)

R^1	R^2	R^3	cat	T(t)	%	%	%
H	H	Me	Pd(0)	180(2)	48	100	48
			Rh(I)	160(24)	100	100	0
H	Me	Me	Pd(0)	150(10)	100	100	0
			Rh(I)	160(24)	31	31	0

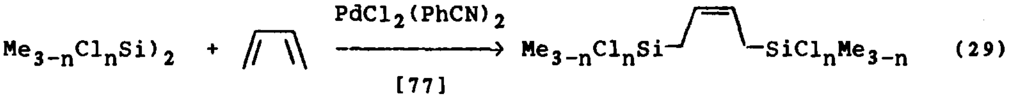

(27)

$$\underset{A}{Me_6Si_2} + \underset{B}{PhCHCl_2} \xrightarrow[\text{mesitylene, 3h [79]}]{PdL_4{}^a} \underset{\;\;\;\;Cl\;\;\;Cl}{PhCH\text{-}CHPh} + PhCH{=}CHPh$$

A/B	%	%
2/1	0	78
1/1	65	18

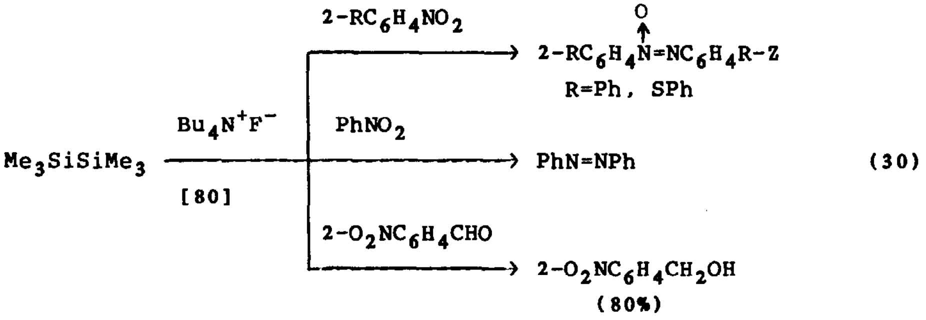
a. $L=PPh_3$

$$\underset{2\text{ eq.}}{Me_4Si_2Cl_2} + \underset{1\text{ eq}}{PhCCl_3} \xrightarrow[\text{[79]}]{6h} \underset{(49\%)}{PhCCl_2CCl_2Ph} + \underset{\substack{E/Z\ =\ 30/70 \\ (45\%)}}{PhCCl{=}CClPh} \qquad (28)$$

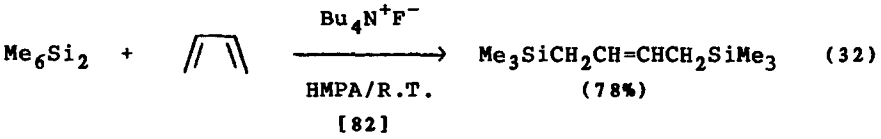


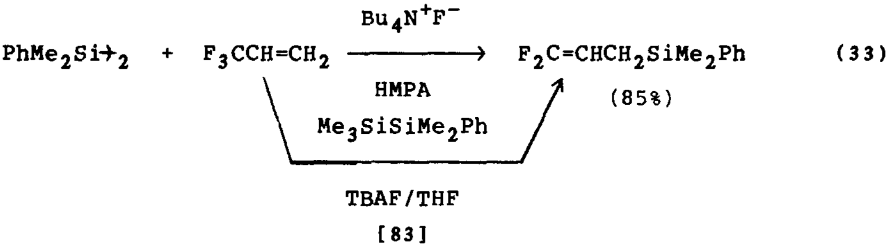
Mole % Cat.	T(t)	n	%
2	60(18)	1	49
2.5	60(24)	2	50
1	60(15)	1	69
1	60(77)	2	20

The combination of $Me_6Si_2/Bu_4N^+F^-$ functions as a reducing agent towards aldehydes and nitro groups and undergoes 1,4-addition to butadiene. This combined reagent is also the basis of the preparation of difluoroallylsilanes. These applications are summarized in Eqns. 30-33.



$$Me_6Si_2 + RCHO \xrightarrow[\text{HMPA/THF [81]}]{Bu_4N^+F^-} RCH(OH)SiMe_3 \quad R{=}decyl\ (67\%) \qquad (31)$$





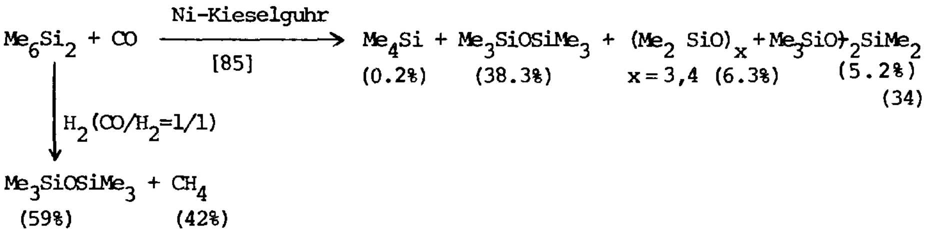
$$PhMe_2Si{+}_2 + F_3CCH{=}CH_2 \xrightarrow[\text{HMPA}]{Bu_4N^+F^-} \underset{(85\%)}{F_2C{=}CHCH_2SiMe_2Ph} \qquad (33)$$

$Me_3SiSiMe_2Ph$

TBAF/THF

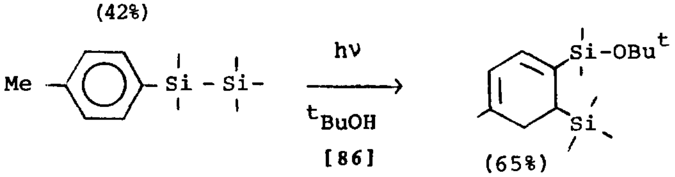
[83]

The reaction of hydrogen radicals with Me_6Si_2 (Hg-sensitized photolysis) proceeds at room temperature to give Me_3SiH and $Me_3Si^{\bullet}$ [84]. Nickel-Kieselguhr catalyzes the reduction of CO by Me_6Si_2. The products of the reaction contain O from CO and are shown in Eqn. 34. Photolysis of aryldisilanes in the presence of ^tBuOH give silylcyclohexadiene (Eqn. 35) as well as ring-opened products. Pyrolysis of Si_2H_6 provided hydrogenated amorphous Si films [87].



$$Me_6Si_2 + CO \xrightarrow[\text{[85]}]{\text{Ni-Kieselguhr}} \underset{(0.2\%)}{Me_4Si} + \underset{(38.3\%)}{Me_3SiOSiMe_3} + \underset{x=3,4\ (6.3\%)}{(Me_2\,SiO)_x} + \underset{(5.2\%)}{Me_3SiO{+}_2SiMe_2} \qquad (34)$$

$$Me_6Si_2 \xrightarrow{H_2(CO/H_2=1/1)} \underset{(59\%)}{Me_3SiOSiMe_3} + \underset{(42\%)}{CH_4}$$

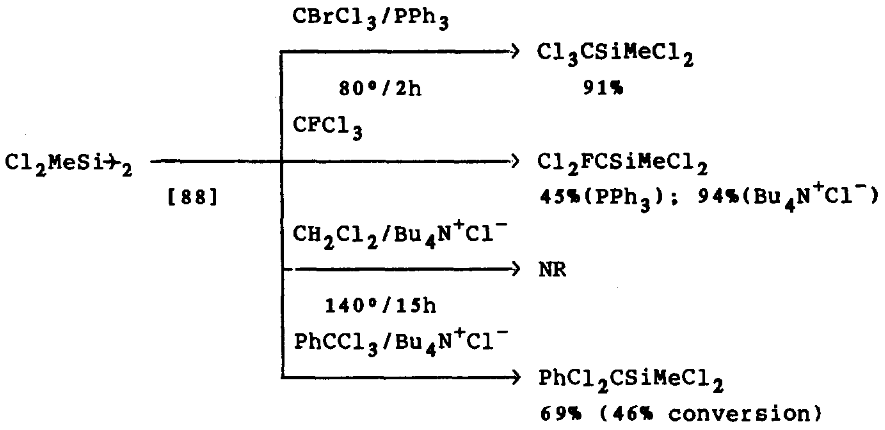


(35)

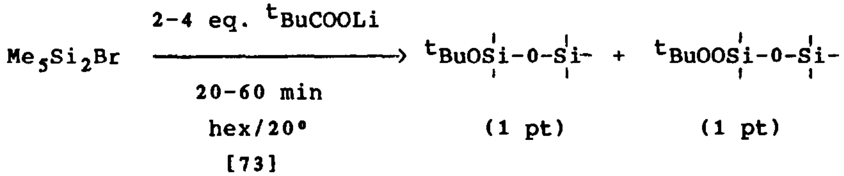
The cleavage of Si-Si bonds occurs in the presence of bases and can be used as a method for preparation of functional monosilanes. The reaction of $Cl_2SiMe{+}_2$ with CCl_4 as a function of base is shown in Eqn. 36. Other examples illustrating possible variations are shown in Eqn. 37 and 38.

$$Cl_2(Me)Si{+}_2 + CCl_4 \xrightarrow{\text{cat./T/t}} Cl_3CSiMeCl_2 \qquad (36)$$

[88]	%
PPh_3/80/2	100
Bu_4NCl/80/2	98
Et_3N/80/6	31



(37)



$$Me_5Si_2Br \xrightarrow[\substack{20\text{-}60\ min \\ hex/20° \\ [73]}]{2\text{-}4\ eq.\ {}^tBuCOOLi} {}^tBuOSi\text{-}O\text{-}Si\text{-} + {}^tBuOOSi\text{-}O\text{-}Si\text{-} \quad (38)$$

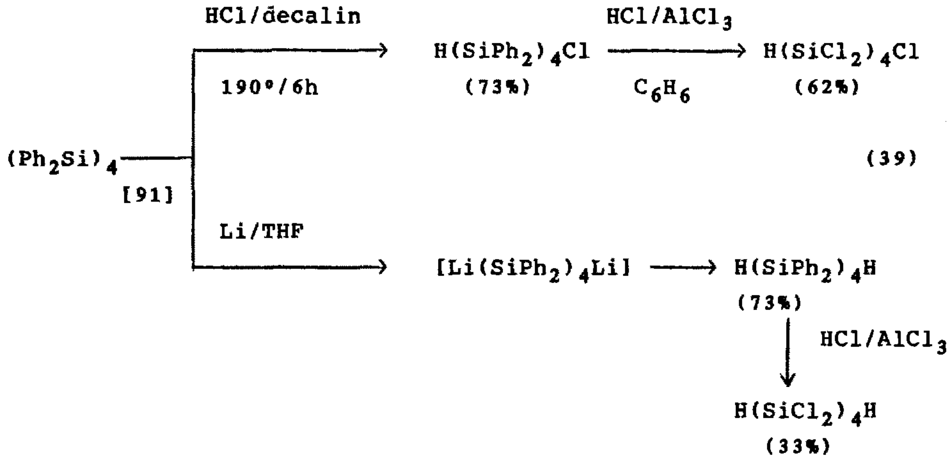
(1 pt) (1 pt)

3. Linear Polysilanes

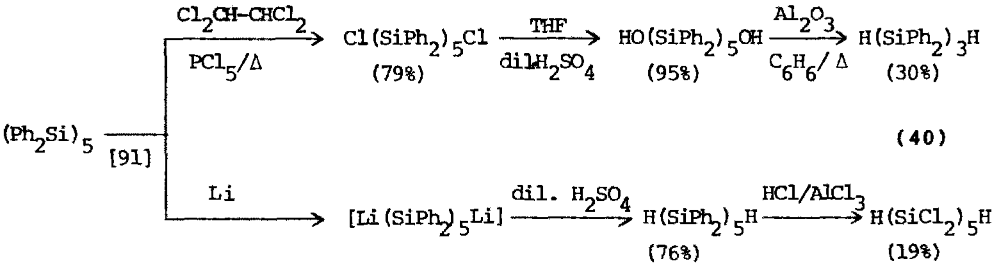
The Hg($^3P_1$) sensitized photolysis of H_2/SiH_4 mixtures provides Si_2H_6, Si_3H_8 and Si_4H_{10}. The origin of the last two products is believed to be an activated disilane which decomposes mainly into SiH_2 and SiH_4 (followed by subsequent reactions) [89].

One approach to linear polysilanes is through ring cleavage of cyclopolysilanes. When Si_4Me_8 is reacted with Cl_2 in n-hexane, $Cl(SiMe_2)_4Cl$ is produced in 68% yield. A similar reaction with Br_2 in pet ether at -20° gives $Br(SiMe_2)_4Br$ (38%) [90]. In contrast to bromination, iodination (pet ether/c-C_6H_{12} at -40°) gives a high yield of $I(SiMe_2)_4I$ (93%) but higher cyclopolysilanes are converted in low yields: $I(SiMe_2)_5I$ in 24% yield from $(Me_2Si)_5$ and $I(SiMe_2)_6I$ in 27% yield from $(Me_2Si)_6$ [90]. Prolonged photolysis of $(^iPr_2Si)_4$ (64h) gave $H(^iPr_2Si)_3H$ (28% yield) but this system also provided disilene products [64].

An extensive study of conditions required for ring cleavage of $(Ph_2Si)_x$ (x = 4,5) and subsequent dephenylation has been published. The ring opening of $(Ph_2Si)_4$ by Li and HCl as well as subsequent conversions is shown in Eqn. 39, and of $(Ph_2Si)_5$ in Eqn. 40. A specific synthesis of $H(SiCl_2)_xH$ (x = 6,7) is shown in Eqn. 41.



(39)

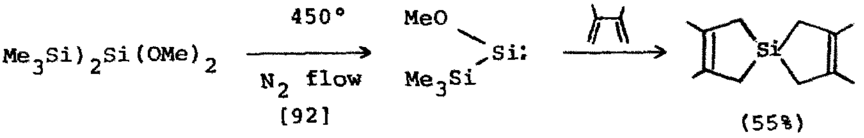


(40)

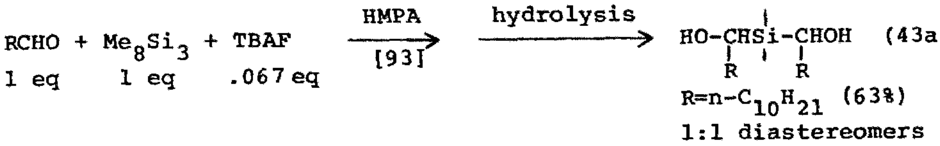
$$Li(SiPh_2)_xLi \xrightarrow[\text{dioxane}]{HPh_2SiCl} H(SiPh_2)_{x+2}H \xrightarrow[C_6H_6]{HCl/AlCl_3} H(SiCl_2)_{x+2}H \qquad (41)$$

[91] x=4(55%); 5(62%) x=4(25%); 5(25%)

The trisilane, $Me_3Si\rangle_2Si(OMe)_2$ is a "one-pot silicon atom synthon" as shown in the pyrolysis reaction illustrated in Eqn. 42. In an effort to determine whether F^- attacks Me_8Si_3 on an internal Si to give Me_3Si^- or a terminal Si to give a disilanyl anion, $Me_5Si_2^-$ the reaction in the presence of aldehyde and diene traps was studied. The results seem to favor disilanyl anion formation (Eqns. 43a and 43b). The addition order is important in observing successive "insertion" into the SiSi bonds of Me_8 Si_3 . When CO_2 is added to $(Me_3Si)_3SiLi$ in THF the expected carboxylic acid, $(Me_3Si)_3SiCO_2H$ is obtained. An attempt to generate silaethylenes from this source failed [94].

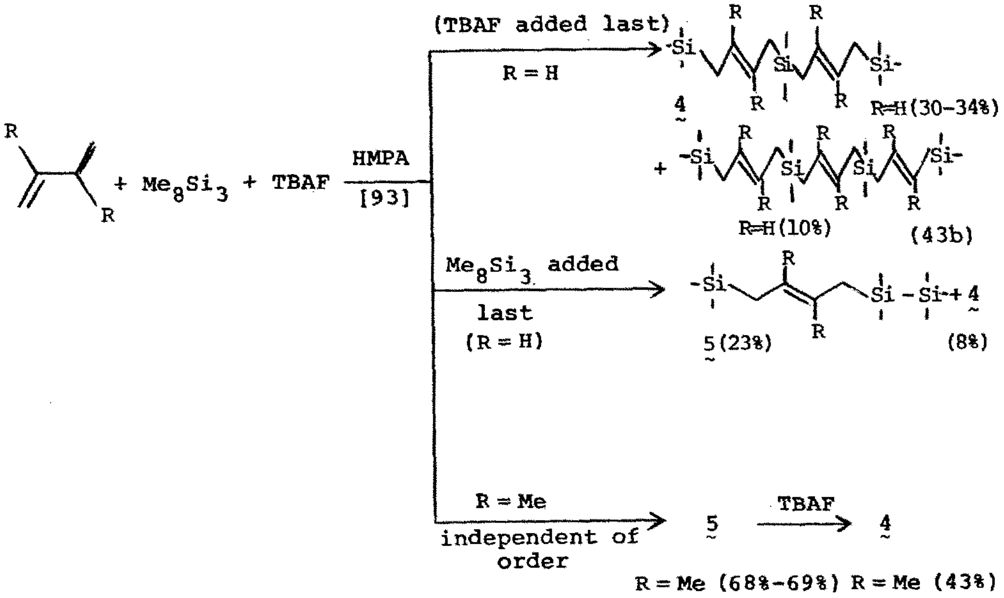


(42)



$$RCHO + Me_8Si_3 + TBAF \xrightarrow[{[93]}]{HMPA} \xrightarrow{hydrolysis} HO-\underset{R}{CH}-\overset{|}{\underset{|}{Si}}-\underset{R}{CH}OH$$

(43a)



(43b)

Thermolysis of poly(dimethylsilylene) at 440° gave Me_2SiH_2 (15%) and oligomer (85%). When the oligomer was heated to 720° a gas (86%) was generated which contained Me_3SiH (51%) and $Me_2SiH\text{+}_2$ (18%) [95].

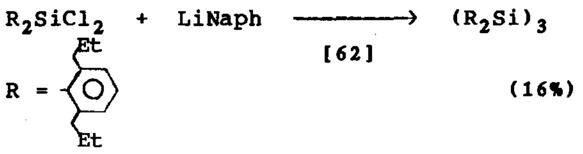
4. Cyclopolysilanes

The major development this year has been the generation of cyclotrisilanes. Hexaneopentylcyclotrisilane is formed from condensation of R_2SiCl_2 with Li in THF (Eqn. 44) and Li/Naph was used for condensation in the cases of $^tBu_2SiCl_2$, Ar_2SiCl_2 and $^tBu(Ar)SiCl_2$ (Eqns. 45-47).

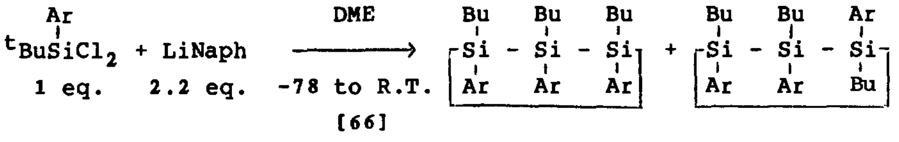
$$\underset{1\ \text{eq.}}{(^tBuCH_2)_2SiCl_2} + \underset{2.2\ \text{eq.}}{Li} \xrightarrow[\text{[63]}]{\text{THF/0°/9h}} \underset{(14\%)}{[(tBuCH_2)_2Si]_3} \qquad (44)$$

$$\underset{1\ \text{eq.}}{^tBu_2SiI_2} + \underset{2.3\ \text{eq}}{LiNaph^a} \xrightarrow[\substack{-78°\text{-> R.T.}\\ \text{[67b]}}]{\text{THF}} \underset{\substack{(72\%)\\ \text{(air stable)}}}{(^tBu_2Si)_3} \qquad (45)$$

a. Added to silane



$$R_2SiCl_2 + LiNaph \xrightarrow[\text{[62]}]{} \underset{(16\%)}{(R_2Si)_3} \qquad (46)$$



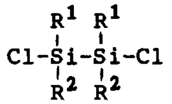
$$\underset{1\ \text{eq.}}{^tBu\overset{Ar}{Si}Cl_2} + \underset{2.2\ \text{eq.}}{LiNaph} \xrightarrow[\substack{-78\ \text{to R.T.}\\ \text{[66]}}]{\text{DME}} \underset{(7\%)}{\boxed{\overset{Bu}{\underset{Ar}{Si}} - \overset{Bu}{\underset{Ar}{Si}} - \overset{Bu}{\underset{Ar}{Si}}}} + \underset{(38\%)}{\boxed{\overset{Bu}{\underset{Ar}{Si}} - \overset{Bu}{\underset{Ar}{Si}} - \overset{Ar}{\underset{Bu}{Si}}}} \qquad (47)$$

Ar=Mes

An extensive study of the lithium condensation of $RR'SiCl_2$ has shown that the cyclopolysilane ring size that is favored is related to the bulk of the substituent. The results are summarized in Eqn. 48. An attempt to condense $^tBu_2SiCl_2$ with Li under a variety of conditions gave $H(^tBu_2SiSiBu^t{}_2)H$ plus many other products [96]. An alternate route to alkylpolysilanes is the condensation of 1,2-dichlorodisilanes (Eqn. 49).

$$R^1R^2SiCl_2 + Li \xrightarrow[{[96]}]{} [R^1R^2Si]_n \qquad (48)$$

R^1	R^2	mol	Li,mol	T(°C)/t(hr)	n	Yd(isol)
Et	Et	0.05	0.12	3.5/43	5	49
Pr	Pr	0.05	0.12	2.5/41	5	36
^iPr	^iPr	0.25	0.54	2.0/1	4	74
					7	9
Bu	Bu	0.04	0.096	3.5/98	5	67
^iBu	^iBu	0.05	0.12	2.5/25	4	36
					5	10
^sBu	^sBu	0.034	0.084	2.0/1	4	(61)



$$\underset{R^2\ \ R^2}{\overset{R^1\ \ R^1}{Cl-Si-Si-Cl}} + Li \xrightarrow[{[97]}]{} [R^1R^2Si]_n \qquad (49)$$

n = 4,5

$R^1 = R^2 = {}^iPr$

$R^1 = R^2 = {}^iPr, Me$

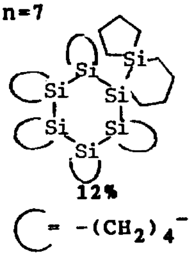
Me_3SiCH_2, Me

Condensation of dichlorosilacyclopentane and dichlorosilacyclohexane gives organosilicon rotanes. The ring size distribution is a function of the conditions used and results for $(CH_2)_4SiCl_2$ are summarized in Eqn. 50, and for $(CH_2)_5SiCl_2$ in Eqn. 51.

$(CH_2)_4SiCl_2 \xrightarrow[{[98]}]{}$ (50)

Li(2 eq), THF (non-equil.) → $[(CH_2)_4Si]_n$ **6**
n=5-12
max wt. % at n=6
wt. % n=5 ~ n=7

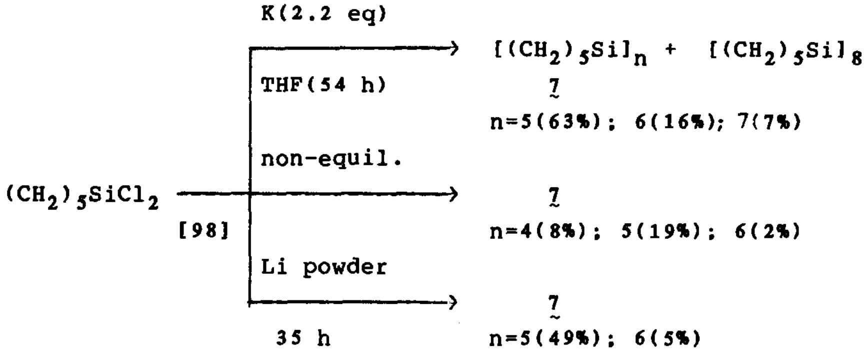
Li(2.2 eq) (thermodynamic conditions) → **6**
n=5(2%);
6(28%)
1(7%)



12%

$= -(CH_2)_4-$

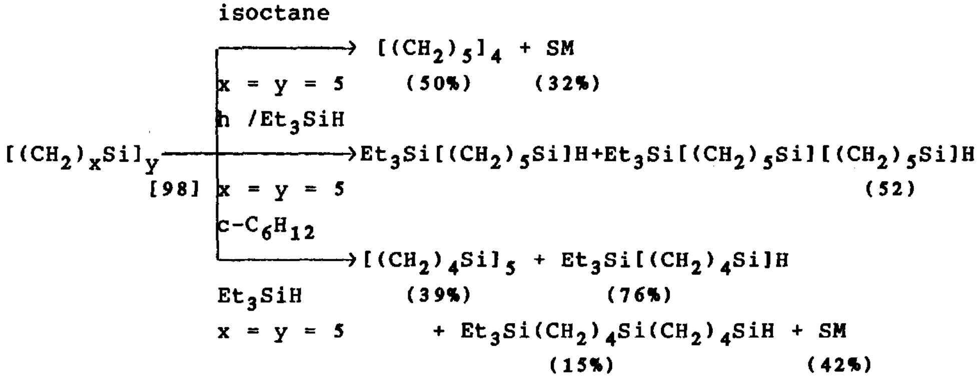
Li(2.2 eq) $Ph_3SiSiMe_3$ → **6**
n=5(1%); 6(80%); 7(4%)



(51)

A less common entry into cyclopolysilanes is the dimerization (or oligomerization) of disilenes. An example of the equivalent of the dimerization of the disilene, $R_2Si=SiR_2(R={}^iPr)$, has been published. Photolysis of 3 (Eqn. 15) in $\underset{\sim}{c}$-C_6H_{12} at RT for 12h gave $[{}^iPr_2Si]_4$ in 30% yield [68].

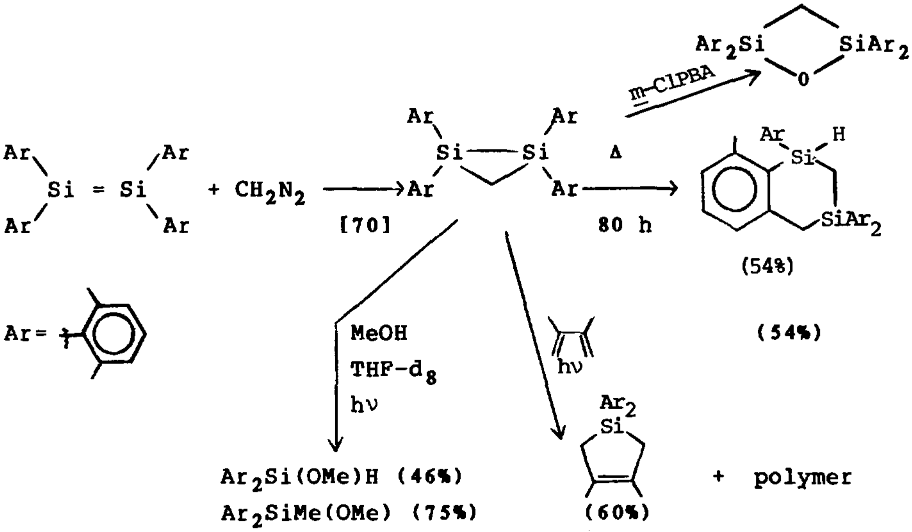
One of the important reactions of cyclopolysilanes is the photolytic extrusion of silylene. In the simplest cyclopolysilane, $(R_2Si)_3$, disilenes are also produced and these processes were discussed in section V-1. The photolysis of $(Me_2Si)_6$ in an argon matrix gave Me_2Si and when irradiated at 450 nm the silylene converts to 1-methylsilene [99]. Laser flash photolysis of $(Me_2Si)_6$ at 350 nm produced Me_2Si and the rates of reaction of the silylene with $HSiEt_3$ ($\underset{\sim}{c}$-C_5H_{10}) and with MeOH (THF) were determined to be $2 \times 10^6 M^{-1}s^{-1}$ and $3 \times 10^7 M^{-1}s^{-1}$ respectively [100]. Photolysis of the rotanes has been reported and the results are summarized in Eqn. 52. Thermolysis of $[(CH_2)_4Si]_6$ at 220°(3d) gave $[(CH_2)_4Si)_x$, x=5(15%); 6(80%); 7(5%) [98].



(52)

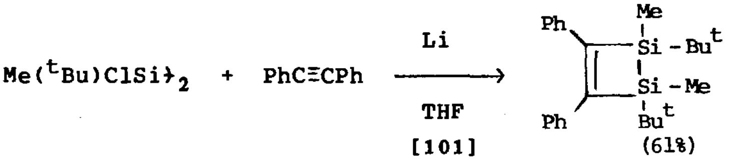
4. Heterocycles

The smallest heterocycle with a silicon-silicon bond has been generated from reaction of diazomethane with a disilene at -196°C. The disilacyclopropane is a source of silylenes and silenes on photolysis. Thermolysis provides a rearrangement product. Oxidation results in insertion of O into the Si-Si bond. These processes are summarized in Eqn. 53.



(53)

The reaction of 1,2-dichlorosilanes with alkali metals to give disilene was described in Eqn. 14. When this reaction was run in the presence of the trap, tolan, a disilacyclobutene was isolated (Eqn. 54). A similar trapping reaction with 1,3-cyclohexadiene is shown in Eqn. 55.



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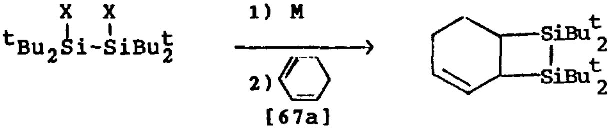
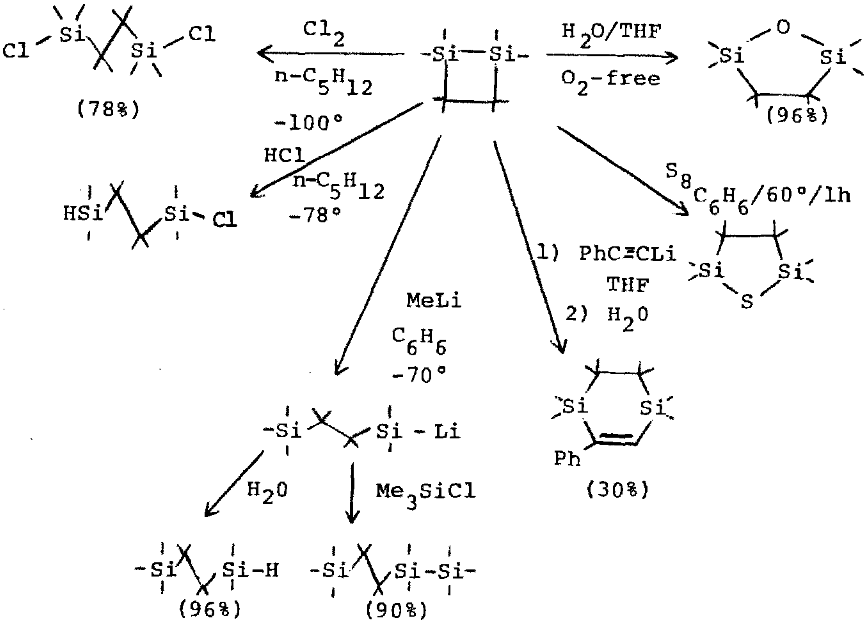


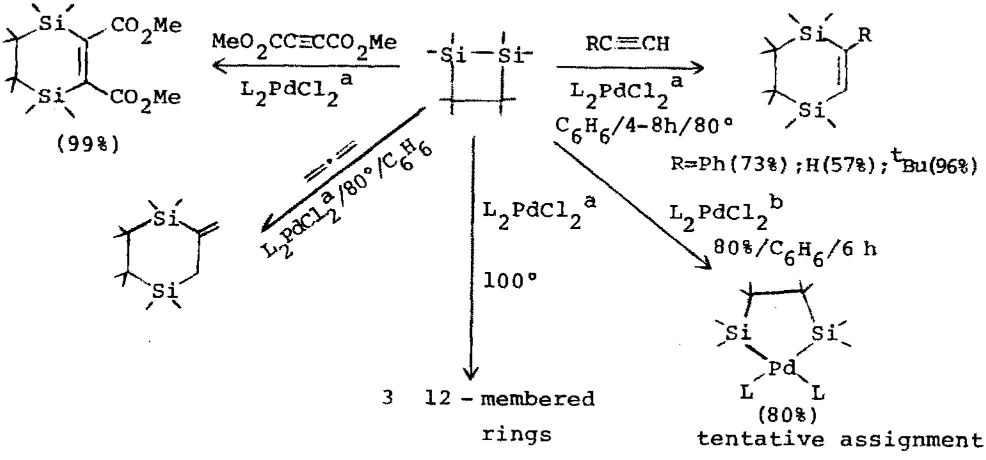
(55)

An extensive study of the cleavage and insertion chemistry of disilacyclobutane has been published [102]. The non-catalyzed processes are summarized in Scheme 1 and the catalyzed processes in Scheme 2.

Scheme 1 [102]

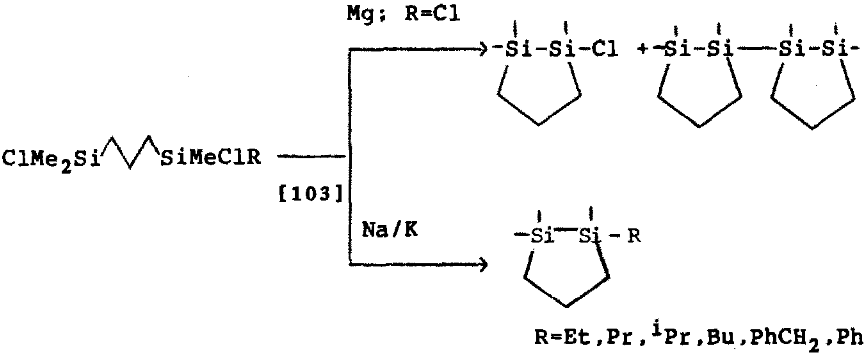


Scheme 2 [102]

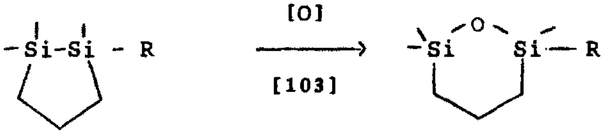


a. Catalytic; L = PPh_3 b. Stoichiometric; L = PPh_3

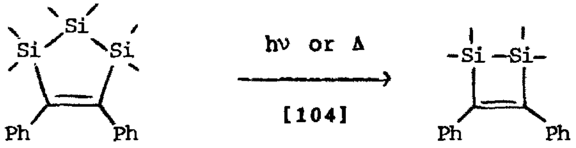
Disilacyclopentanes have been formed from condensation of $ClMe_2Si(CH_2)_3SiMeClR$ with Na/K, Li or Mg as shown in Eqn. 56. The Si-Si bond is susceptible to oxidation as shown in Eqn. 57. Photolysis and thermolysis of 1,2,3-trisilacyclopentane generates silylene but only in the case of thermolysis is the central Si ejected (Eqn. 58) regiospecifically.



(56)

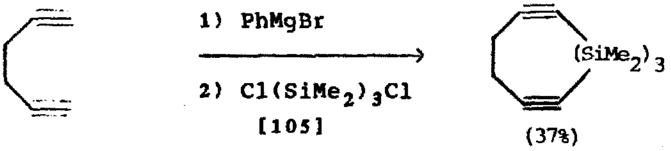


(57)

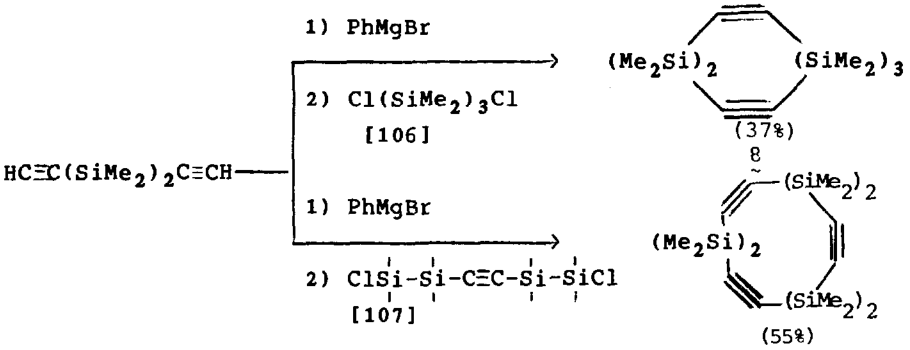


(58)

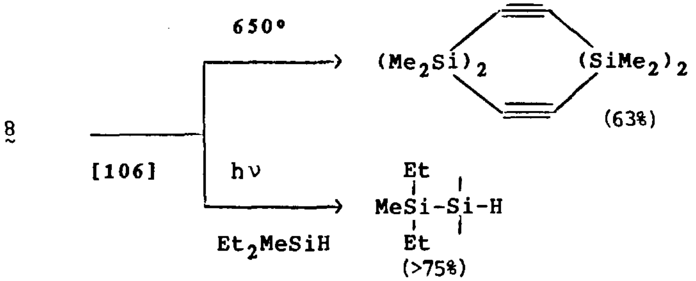
Large-membered rings varying in size from 9 to 12 atoms with Si-Si as well as Si-Si-Si linkages are formed from condensation of alkynes and $Cl(SiMe_3)_3Cl$ (Eqns. 59 and 60) or 1,2-dialkynyldisilanes (Eqn. 60). Such ring systems can generate silylenes thermally or photolytically (Eqn. 62).



(59)

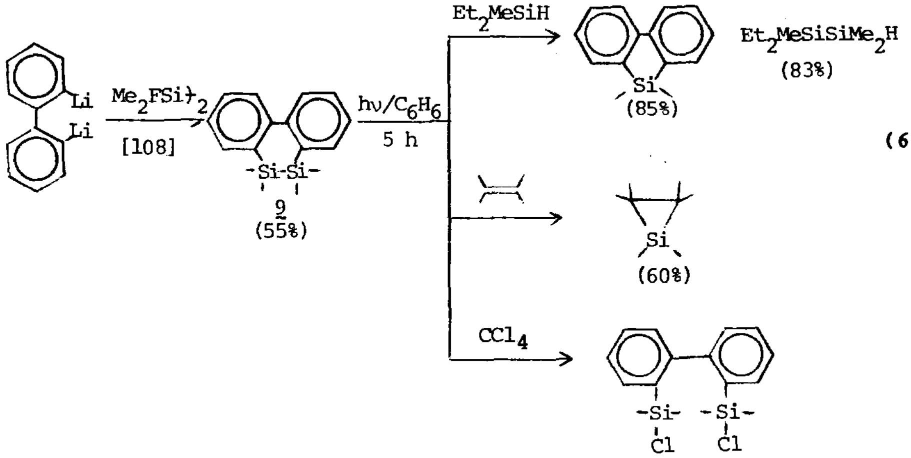


(60)

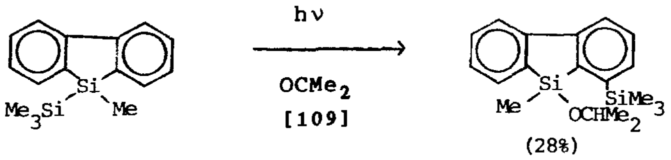


(61)

Dibenzosilacyclohexadiene, 9, is formed from the reaction of o,o′-dilithiobiphenyl with $Me_2FSi\!\!\nearrow_2$ (Eqn. 62). Photolysis of 9 provides dimethylsilylene and the process may occur through a diradical (Eqn. 62). Photolysis of the dibenzosilole isomer gave rearrangement products (Eqn. 63).

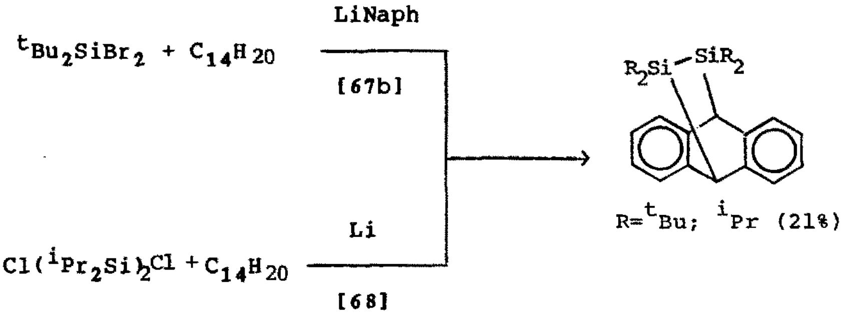


(62)



(63)

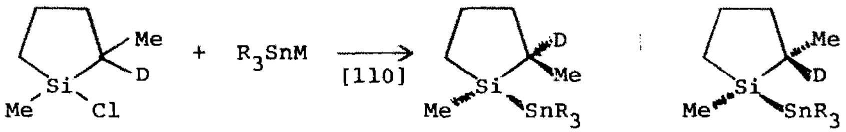
Bridged anthracene systems are formed from both dichlorodisilanes and dibromosilanes as shown in Eqns. 64.



(64)

5. Si-Sn

Trialkylstannyl anions condense with chlorosilanes to give stannylsilanes. The selectivity with cis-and trans-chlorosilacyclopentanes is poor and depends on the method used to generate the stannylanion. Typical results are shown in Eqn. 65.



(65)

E/Z	R_3SnM Generation	%(E/Z)
25/75	$Bu_3SnCl/Li/xsTHF^a$	38(55/45)
35/65	$Bu_3SnCl/Li/xsTHF^b$	22(59/41)
25/75	$Bu_6Sn_2/BuLi/DME^a$	16(42/58)
35/65	$Bu_3SnH/KH/THF^a$	23(56/44)
25/75	$Bu_3SnH/{}^iPrMgCl/Et_2O^a$	7(71/29)
50/50	$Me_6Sn_2/BuLi/THF^a$	88(54/46)
44/56	$Me_3SnBr/Li/xsTHF^b$	52(47/53)
25/75	$Me_3Sn_2/BuLi/DME^a$	72(70/30)
63/37	$Me_6Sn_2/BuLi/DME^b$	20(52/48)

Stannocene is lithiated by BuLi and addition of Me_3SiCl gave 1,1'-bis(trimethylsilyl)stannocene. Stepwise lithiation/silylation also gave the 1,1',3,3'-tetrakistrimethylsilyl derivative as well as the 1,1',2,2',4,4'-hexakis derivative [111].

VI. SILICON-GROUP V

The chemistry of Silicon-Group V is covered in the sequence: 1. Acyclic Silyl Amines, 2. Silicon-Nitrogen Heterocycles, 3. Miscellaneous Methods for SiN Formation, 4. Silicon-Nitrogen Bond Cleavage, 5. Reactions at N in Si-N Derivatives and Silylamides as Ligands, 6. Silylphosphines and 7. Silylarsines

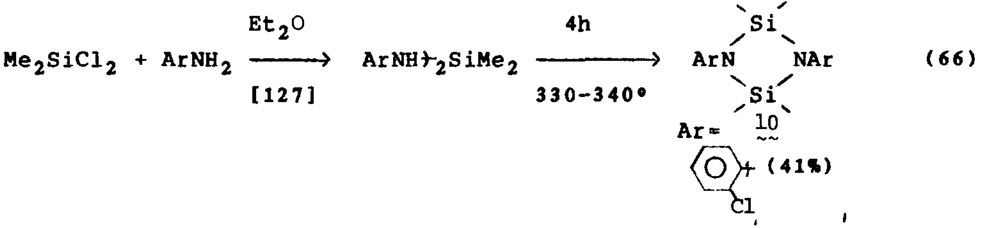
1. Acyclic Silyl Amines

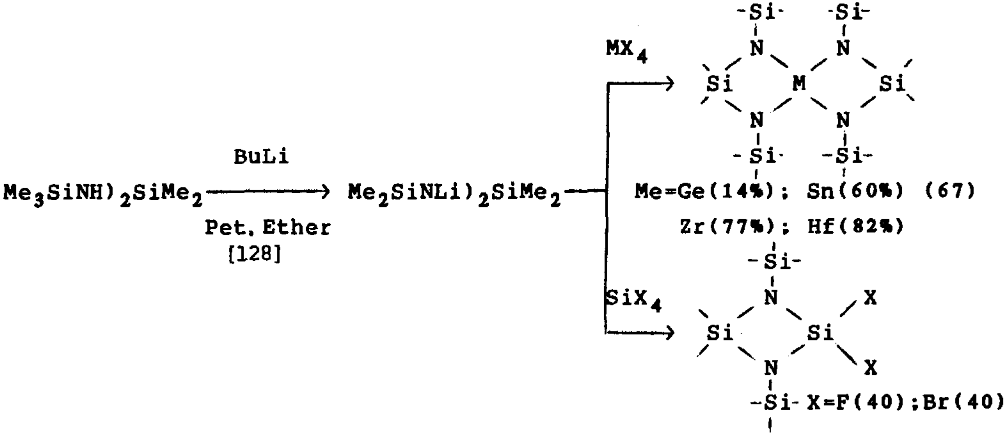
The standard methods for silicon-nitrogen bond formation (aminolysis of chlorosilanes, chlorosilane and metal amides and exchange) are summarized in Table 1.

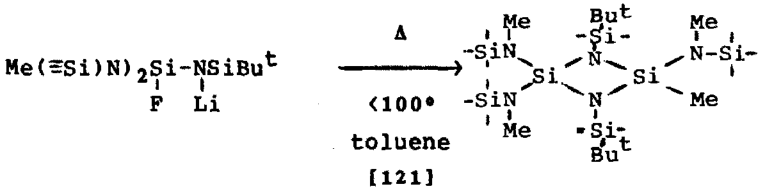
2. Silicon-Nitrogen Heterocycles

Heterocycles that include one or more Si-N ring bonds are included in this section. The material is organized in terms of increasing ring size followed by selected aspects of the reactivity of the silazane heterocycles.

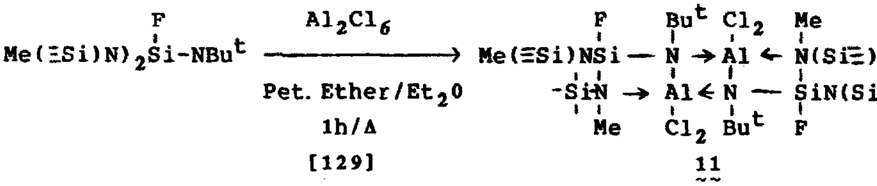
The usual preparations of cyclodisilazanes involve reaction of a dichlorosilane with a primary amine. Such a route is shown in Eqn. 66 for the aryl derivative, 10, which exhibits a unique coplanar conformation possibly due to interaction of the o-chloro substituent with silicon. Other entries to cyclodisilazanes involve condensation of amide such as $Me_3SiN(M)\text{)}_2SiMe_2$ with metal halides (Eqn. 67) or "elimination" of LiF from the unit, Si(F)N(M) and dimerization of the resultant silaimine (Eqn. 68,69)







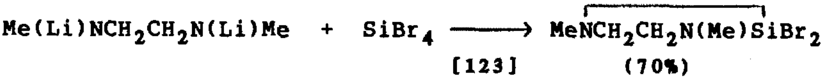
(68)



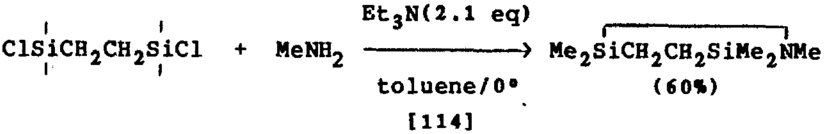
(69)

11

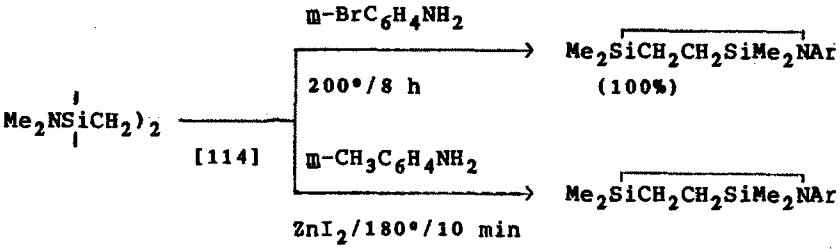
Five membered disilazanes have been generated both from the amide Me(Li)NCH$_2$CH$_2$N(Li)Me (Eqn. 70) and by condensation of ClSi(Me)$_2$CH$_2$CH$_2$Si(Me)$_2$Cl and MeNH$_2$ (Eqn. 71). The high temperature exchange/extrusion of Me$_2$N(Me)$_2$SiCH$_2$$\!\!+_2$ with ArNH$_2$ shown in Eqn. 72 occurs at a lower temperature and a faster rate if catalytic amounts of ZnI$_2$ are added. The first cycloalumadisiladiazane was reported (Eqn. 73).



$$Me(Li)NCH_2CH_2N(Li)Me + SiBr_4 \xrightarrow[\text{[123]}]{} \overline{MeNCH_2CH_2N(Me)Si}Br_2 \quad (70\%) \qquad (70)$$



$$ClSiCH_2CH_2SiCl + MeNH_2 \xrightarrow[\text{toluene/0° [114]}]{Et_3N(2.1\ eq)} \overline{Me_2SiCH_2CH_2SiMe_2N}Me \quad (60\%) \qquad (71)$$



$$Me_2NSiCH_2)_2 \xrightarrow[\text{200°/8 h}]{\text{[114]};\ m\text{-}BrC_6H_4NH_2} \overline{Me_2SiCH_2CH_2SiMe_2N}Ar \quad (100\%)$$

$$Me_2NSiCH_2)_2 \xrightarrow[ZnI_2/180°/10\ min]{\text{[114]};\ m\text{-}CH_3C_6H_4NH_2} \overline{Me_2SiCH_2CH_2SiMe_2N}Ar \qquad (72)$$

TABLE I. Formation of Acylic Silylamines

Silane	Nitrogen Reactant	Product	%	Ref
Aminolysis				
$ClSiR_3$[a]	$\underline{o}$-XC_6H_4NMeH[b]	$\underline{o}$-$XC_6H_4NMeSiR_3$	16-88	112
$ClSiMe_3$	$MeNRH$[c]	$MeNRSiMe_3$	90	113
$ClSiMe_2CH_2)_2$	Me_2NH	$Me_2NSiMe_2CH_2)_2$	90	114
	Et_2NH	$Et_2NSiMe_2CH_2)_2$	51	114
$Me_2SiCl_2/MeSiCl_3$	1) $^tBuOH/Et_3N$	$^tBuOMe_2SiNHPh$	87	115
	2) $PhNH_2$			
Et_2SiHCl	$H_2NCH_2Pr^i$	$Et_2Si(H)NHCH_2Pr^i$		116
$MeSiCl_3$	$MeNH_2$	$MeSi(NHMe)_3$		117,118
Coupling with Metal Amides				
$ClSiMe_3$	$LiNMeNMe_2$	$Me_3SiNMeNMe_2$		119
	$MeS(=NR')NRLi$	$MeS(=NR')NRSiMe_3$		120
		$R=R'=SiMe_3$	92	
		$R=R'=^tBu$	48	
$F_2Si^iPr^tBu$	$LiNHBu^t$	$^iPr^tBuSi(F)NHBu^t$	73	121
F_2SiMes_2	$LiNHBu^t$	$Mes_2Si(F)NHBu^t$	78	121
$F_2Si(NMeSiMe_3)_2$	$LiNHR$[d]	$[Me_3SiNMe]_2Si(F)NHR$	78	121
$F_3Si[C(SiMe_3)_3]$	$LiNHAd$	$(Me_3Si)_2CHSiF_2NAd(SiMe_3)$		122
	$LiNH_2$	$(Me_3Si)_3CSiF_2)_2NH$	49	122
Br_4Si	$LiNMe_2$	$(Me_2N)_nSiBr_{4-n}$		
		$n=2$	84	123
		3	66	123

TABLE I. (Cont.) Formation of Acylic Silylamines

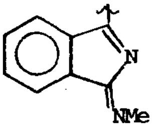
Silane	Nitrogen Reactant	Product	%	Ref
Exchange				
$Et_2NSiMe_2OPr^i$	$XC_6H_4NH_2$[e]	$(^iPrO)Me_2SiNHC_6H_4X$	95	115
$Et_2NSiMe(OPr^i)_2$	$XC_6H_4NH_2$	$(^iPrO)_2MeSiNHC_6H_4X$	98	115
$HN(SiMe_3)_2$	$HONH_2 \cdot H_2SO_2/CO_2$	$Me_3SiON(SiMe_3)CO_2SiMe_3$	79	124
	H_2NCONH_2[f]	$(Me_3SiNH)_2CO$	98	125
	$NaNHSO_2CF_3$	$Me_3SiN(Na)SO_2CF_3$		126

Footnotes

a. R=Me, Et, Ph, Bu, etc.

b. X=Cl, Br

c. R=

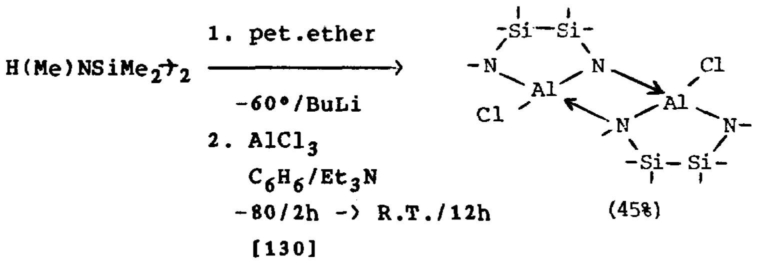


d. $R=SiMe_2Bu^t$

e. $X=NEt_2$

f. Presence of $Me_3SiNH\}_2CO$;

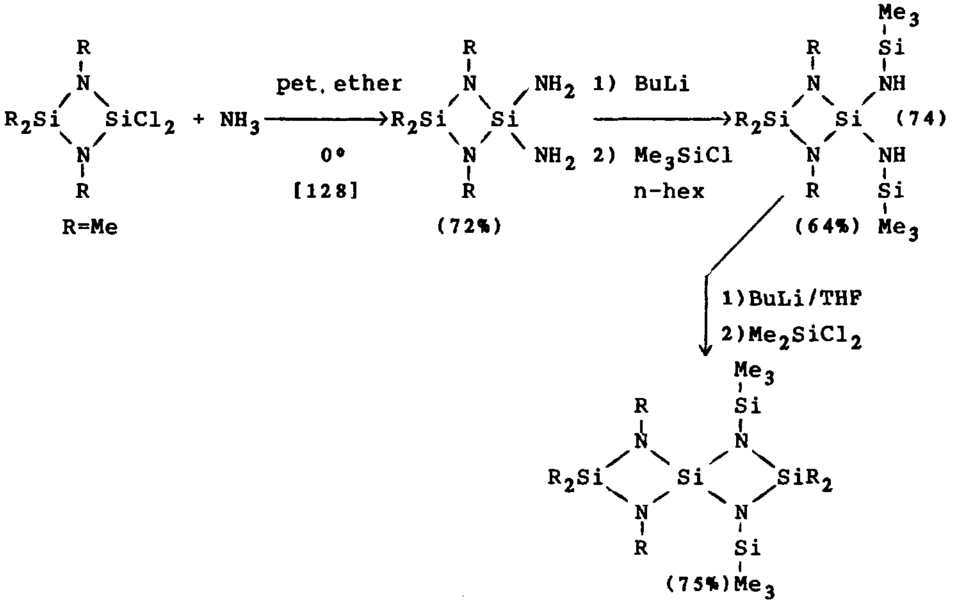
Reaction on Kg scale.



(73)

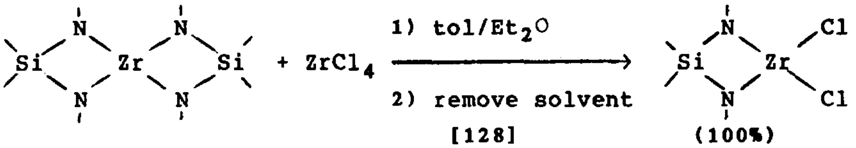
Condensation of $MeClSiR(CH_2)_4SiR'ClMe$ with $MeNH_2$ provided the seven-membered ring $MeR\overline{Si(CH_2)_4SiMeRN}Me$ (R=Me,Et) [131].

The spirobicycloheptane system with Si as the spiro center could not be prepared by the route shown in Eqn. 67 but was prepared by a stepwise procedure shown in Eqn. 74. Hydrolysis of 11 (Eqn. 69) cleaved the Si-N bonds and gave the aluminum analog of cyclodisilazane (Eqn. 75). Redistribution of the spirocyclic metal silylamides occurs in the presence of MCl_4 (Eqn. 76).



(74)

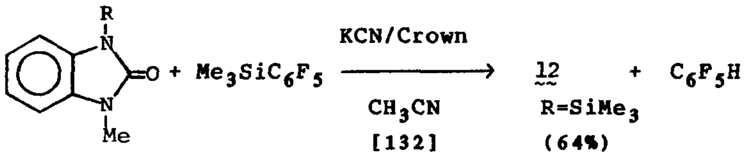
$$\underset{\sim}{11} + H_2O \xrightarrow[3h/R.T.\ [129]]{Et_2O} {}^tBu(H)\overline{NAlCl_2N(H)Bu^t}AlCl_2 \quad (35\%) \qquad (75)$$



(76)

3. Miscellaneous Methods for SiN Formation

The NH bond can be silylated with $Me_3SiC_6F_5$ (Eqn. 77) as well as by $HSiMe_3$ (Eqn. 78). Disproportionation of $(RO)_{3-n}R_nSiNHR'$ occurs in the presence of $TiCl_4$ (Eqn. 79). Thermolysis of siloxyisocyanates resulted in O to N rearrangement (Eqn. 80). A silylsubstituted triazene was formed from silylazide and $NaSiR_3$ (Eqn. 81).

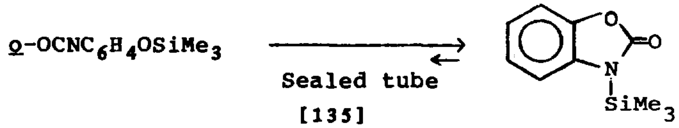


(77)

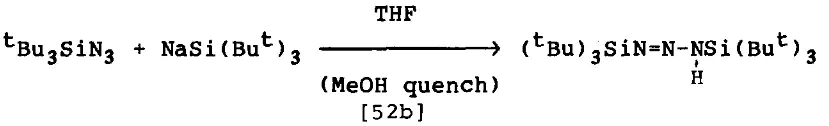
12 R=H

$$(CF_3SO_2)_2NH \;+\; \underset{(xs)}{HSiMe_3} \;\xrightarrow[\substack{\text{FED Reactor}\\ [126]}]{}\; \underset{(92\%)}{(CF_3SO_2)_2NSiMe_3} \qquad (78)$$

$$PhOSiEt_2NHCH_2Ph + 2TiCl_4 \xrightarrow[[133,134]]{} Et_2Si(NHCH_2Ph)_2 \cdot 2TiCl_4 \qquad (79)$$



(80)



$$ {}^{t}Bu_3SiN_3 + NaSi(Bu^t)_3 \xrightarrow[\text{(MeOH quench)}]{\text{THF}} ({}^{t}Bu)_3SiN{=}N{-}\underset{H}{N}Si(Bu^t)_3 \qquad (81) $$

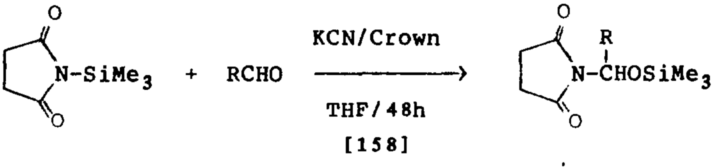
[52b]

4. Silicon Nitrogen Bond Cleavage

The silicon-nitrogen bond is cleaved by acylhalides and inorganic halides and thus silyl amines and other silicon-nitrogen reagents are useful as synthetic intermediates. Examples of this synthetic use are given in Table II. The general utility of low molecular weight silicon-nitrogen-phosphorous reagents in formation of $(RPN)_n$ and $(RR'PN)_n$ (R,R'=alkyl, aryl) polymers (generated by cleavage of SiN bonds) has been reviewed [151].

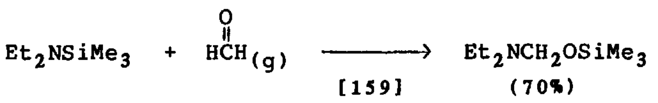
The silicon-nitrogen bond is also cleaved by oxygen-containing reagents, and particulary by water in most aqueous workups. The kinetics for the hydrolysis of $Me_3SiN(Ar)CO_2Et$ and $ArSiMe_2NPhCO_2Et$ (silylurethanes) in aqueous buffers has been determined [152, 153]. The rate of methanolysis of $Me_2\overline{SiOSiMe_2OSiMe_2N}Ar$ to $ArNH_2$ and $MeO(Me_2SiO)_3H$ has also been reported [154].

Silicon-nitrogen derivatives have a variety of other synthetic uses. The combination of $(BzO)_2/(Me_3Si)_2NH$ is an epoxidation agent at room temperature in CH_2Cl_2 [155]. An aprotic diazotization method has been developed from $PhNR(SiMe_3)$ and O=NX (X=Cl,Br,I; generated from $O{=}NOC_5H_{11}{}^i$ and Me_3SiX) in CH_2Cl_2 (25°) to give $PhN_2{}^+X^-$ and Me_3SiOR (R=H, $SiMe_3$) [156]. Silylcarboxamides react with silylepoxides, $Me_3Si\overline{CHCH_2O}$, in the presence of Me_3SiONa to give $Me_3SiOCH_2C(SiMe_3)HNMeCOH$ (38%) [157]. Silylamines add to carbonyl derivatives to give both 1,2- and 1,4-addition products (Eqns. 82-84). The dianion formed from $CH_3\overset{O}{C}NHSiMe_3$ condenses with electrophiles to give amides (Eqn. 85). Anionic 1,3-rearrangement of Me_3Si from N to C is shown in Eqn. 86.

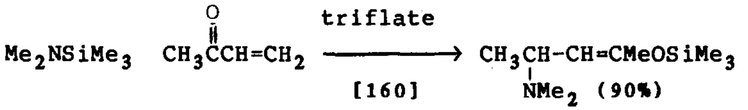


(82)

R=^{i}Pr(87%); Ph(96%)

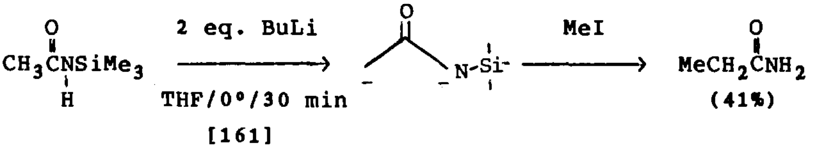


$$ Et_2NSiMe_3 + H\overset{O}{\overset{\|}{C}}H_{(g)} \xrightarrow[\text{[159]}]{} Et_2NCH_2OSiMe_3 \ (70\%) \qquad (83) $$

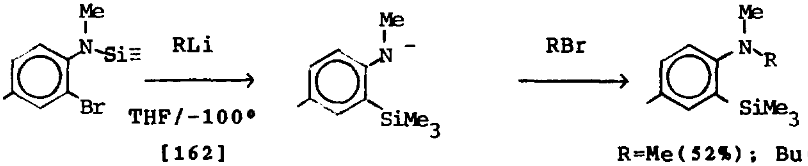


$$Me_2NSiMe_3 \quad CH_3\overset{O}{\overset{\|}{C}}CH{=}CH_2 \xrightarrow[\text{[160]}]{\text{triflate}} CH_3\underset{NMe_2}{\underset{|}{C}H}{-}CH{=}CMeOSiMe_3 \ (90\%)$$

(84)



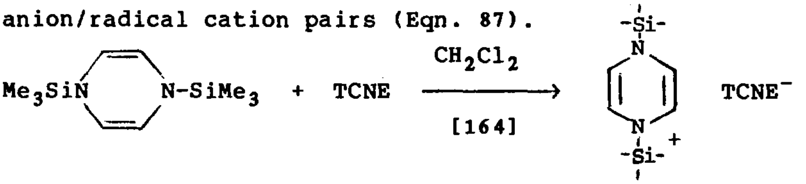
(85)



R=Me(52%); Bu(16%) (86)

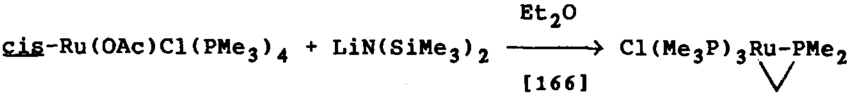
5. Reactions at N in Si-N Derivatives

The formation of silylamino radicals from photolysis of R'(R_3Si)NCl has been reported [163]. N-Silylpyrazines react with TCNE via an SET process to give solvent-separated radical anion/radical cation pairs (Eqn. 87).



(87)

The acidity of a series of secondary amines in THF was measured. Silylamines are more acidic than dialkylamines containing groups of similar size and $Me_3Si)_2NH$ had the greatest acidity of those examined (pK = 29.5) [165]. A novel example of the non-nucleophilic but strong base character of $LiN(SiMe_3)_2$ is shown in Eqn. 88. The formation of both metal and nonmetal silylamides is shown in Table III.



$$\underline{cis}\text{-}Ru(OAc)Cl(PMe_3)_4 + LiN(SiMe_3)_2 \xrightarrow[\text{[166]}]{Et_2O} Cl(Me_3P)_3Ru{-}PMe_2$$

(88)

The use of $(Me_3Si)_2N^-$ ligands as a substituent at phosphorous is quite common. The reactivity of the $Si_2N{-}P{-}C$ linkage has been summarized [180]. Some examples of the chemistry of $(Me_3Si)_2NPRR'$, $Me_2\overline{SiCH_2CH_2SiMe_2N}R$, $(Me_3Si)_2NP{=}NSiMe_3$ and $(Me_3Si)_2NP{=}PN(SiMe_3)_2$ are shown in Eqns. 89-92.

TABLE II. Cleavage of SiN Bonds by Organic and Inorganic Halides

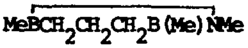
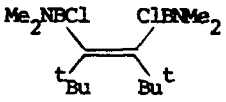
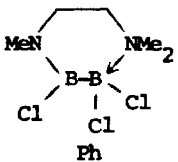
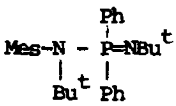
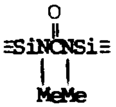
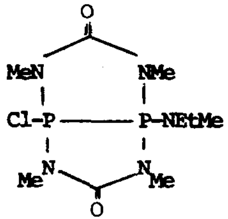
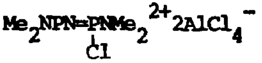
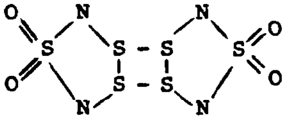
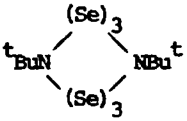
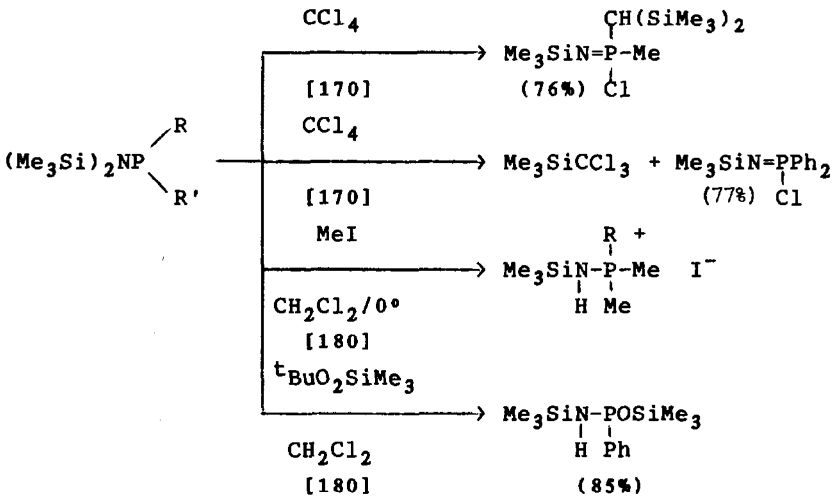
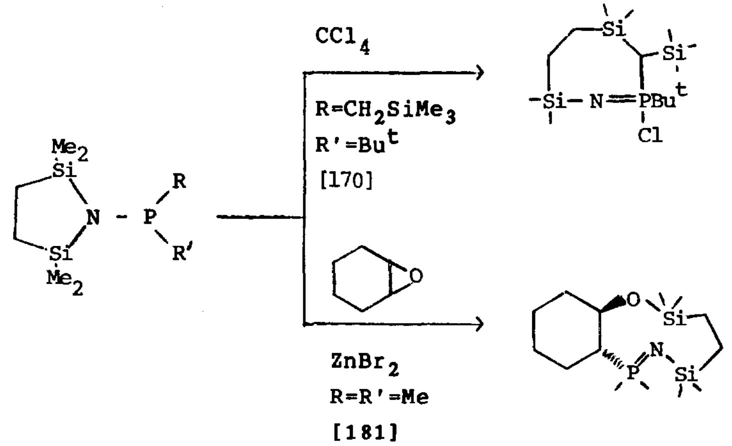
Halide Reagent	SiN	Product[a]	%	Ref
Organic Halides				
$Me\overset{O}{\overset{\|}{C}}Cl$	$Me_3Si)_2NOSiMe_3$	$Me\overset{O}{\overset{\|}{C}}NHOH$	85	136
	$Me_3SiNHBu^t$	$^tBuN(H)\overset{O}{\overset{\|}{C}}CH_3$	88	137
$Ph\overset{O}{\overset{\|}{C}}Cl$	$Me_3Si\}_2NOSiMe_3$	$Ph\overset{O}{\overset{\|}{C}}NHOH$	95	136
	$Me_3Si\}_2NH$	$Ph\overset{O}{\overset{\|}{C}}NHSiMe_3$	85	137
	Me_3SiNEt_2	$Ph\overset{O}{\overset{\|}{C}}NEt_2$	67	137
$Cl\overset{O}{\overset{\|}{C}}Cl$	$^iBu\overset{O}{\overset{\|}{C}}N(SiMe_3)_2$	$^iBu\overset{O}{\overset{\|}{C}}NCO$	45	138
$Cl\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Cl$	Me_3SiNEt_2 (1 eq)	$Et_2N\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Cl$	36	137
	Me_3SiNEt_2 (2 eq)	$Et_2N\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}NEt_2$	61	137
	$Me_3Si\}_2NH$	$-[NH\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\}_x$		137
Inorganic Halides				
$Cl_2BN(SiMe_3)_2$	Me_3SiNMe_2	$(Me_3Si)_2NB(Cl)NMe_2$	94	139
$Cl(Me)BCH_2\}_2$	$Me_3Si\}_2NMe$	 $MeBCH_2CH_2CH_2B(Me)NMe$		140
$\underline{cis}$-$Cl_2BCBu^t{=})_2$	Me_3SiNMe_2		70	141
B_2Cl_4	$Me_2NC_2H_4N(Me)SiMe_3$			142
$ClPPh_2$	$Me\overset{NBu^t}{\overset{\|}{S}}N(SiMe_3)Bu^t$		48	120

TABLE II. (Cont.) Cleavage of SiN Bonds by Organic and Inorganic Halides

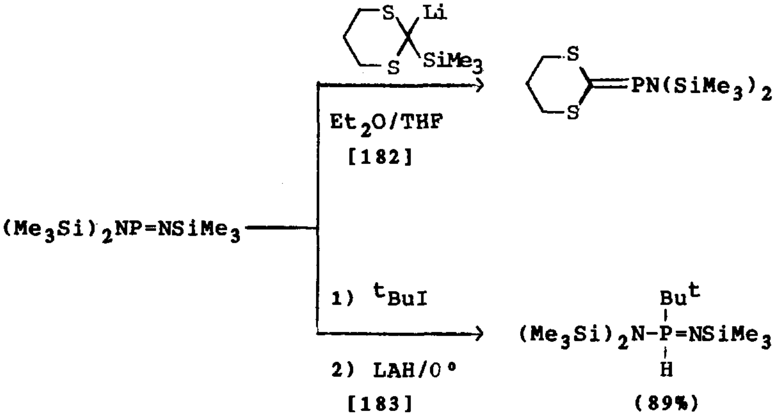
Halide Reagent	SiN	Product[a]	%	Ref
Inorganic Halides				
$Cl_2PNMeEt$	 $\equiv\mathrm{Si}\underset{\mathrm{Me}}{\mathrm{N}}\overset{\mathrm{O}}{\overset{\parallel}{\mathrm{C}}}\underset{\mathrm{Me}}{\mathrm{N}}\mathrm{Si}\equiv$			143
$ClPNMe_2^+AlCl_4^-$	Me_3SiN_3	 $\mathrm{Me_2NPN{=}\underset{Cl}{P}NMe_2}^{2+}\,2\mathrm{AlCl_4}^-$		144
Cl_2S(2 eq)	$[(Me_3Si)N]_2SO_2$		80	145
Cl_2SO_2	$(Ph_2PN)(SN)_2/Me_3SiN{=})_2S$	$Ph_2PS_3N_5$	70	146
$(ClSN)N_2PPh_2$	Me_3SiNMe_2	$(Ph_2PN)_2(NSNMe_2)$		147
Cl_2SeO	$Me_3SiNLiBu^t$			148
FCs	$Ph_2CO/Me_3SiN{=})_2C$	$Ph_2C{=}NCN$	62-70	149
Cl_3TiCp	$Me_3SiNMeNMe_2$	$CpTiCl_2NMeNMe_2$	57	119
$BrMn(CO)_5$	$(Me_3Si)_2NP(=NSiMe_3)_2$	$[(OC)_3MnNSiMe_3]_2$		150


(Me3Si)2NP(R)R'
CCl4
[170]
Me3SiN=P(CH(SiMe3)2)(Me)Cl
(76%)
CCl4
[170]
Me3SiCCl3 + Me3SiN=PPh2Cl
(77%)
MeI
CH2Cl2/0°
[180]
Me3SiN(H)-P(R)(Me)-Me + I−
tBuO2SiMe3
CH2Cl2
[180]
Me3SiN(H)-P(Ph)OSiMe3
(85%)

(89)

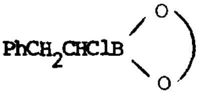
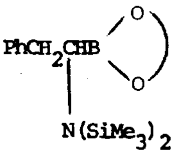
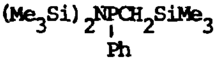
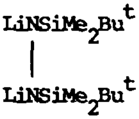
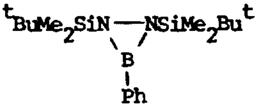
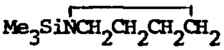

Me2
Si
N - P
R
R'
Si
Me2
CCl4
R=CH2SiMe3
R'=But
[170]
Si
Si
Si
N
PBut
Cl
O
ZnBr2
R=R'=Me
[181]
O
Si
N
P
Si

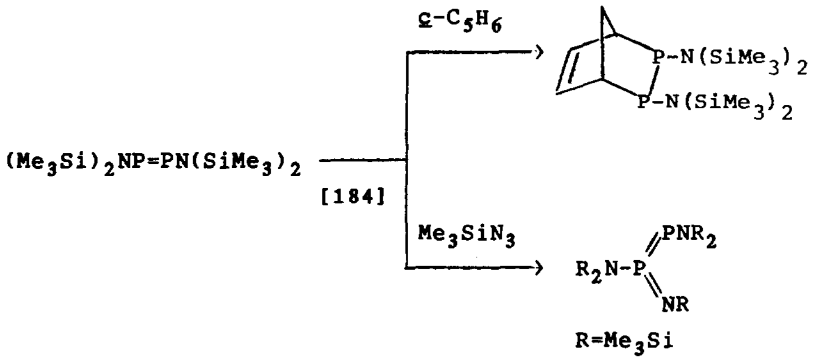
(90)


S
Li
S
SiMe3
Et2O/THF
[182]
S
S
PN(SiMe3)2
(Me3Si)2NP=NSiMe3
1) tBuI
2) LAH/0°
[183]
But
(Me3Si)2N-P(H)=NSiMe3
(89%)

(91)

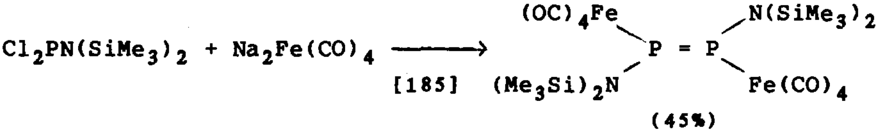
TABLE III. Formation of Metal and Nonmetal Silylamides

$MN(R)SiMe_3$	Metal/Nonmetal Halide[a]	Product	%	Ref
$LiN(SiMe_3)_2$	BCl_3	$(Me_3Si)_2NBCl_2$	76	139
			85	167
	$BrCH_2C\equiv CH/Me_3SiCl$	$Me_3SiC\equiv CCH_2N(SiMe_3)_2$	78	168
	$ClP{=}C(SiMe_3)_2$	$(Me_3Si)_2C{=}PN(SiMe_3)_2$	59	169
	Cl_2PPh/Me_3SiCH_2MgCl	 $(Me_3Si)_2N\underset{Ph}{P}CH_2SiMe_3$	61	170
	Cl_2PMes	$(Me_3Si)_2NP(Mes)Cl$	~100	171
	$MnBr_2$	$Mn[N(SiMe_3)_2]_2 \cdot THF$		172
 $\begin{array}{l}LiNSiMe_2Bu^t\\ \vert\\ LiNSiMe_2Bu^t\end{array}$	$F_2BN(SiMe_3)_2$		85	173
$LiN(SiMe_3)P(Bu^t)_2$	$Cl_2PN(SiMe_3)_2$	$(Me_3Si)_2NP{=}NP(Bu^t)_2$	36	174
$LiN(SiMe_3)Bu^t$	$VO(OBu^t)_2Cl$	$VO(OBu^t)_2[NBu^t(SiMe_3)]$	56	175
$NaN(SiMe_3)_2$	MeI	$MeN(SiMe_3)_2$	75	176
	$Br(CH_2)_4Br$			176
	$MeOCH_2Cl/MeMgBr$	$MeOCH_2N(SiMe_3)_2$	82	177
	EuI_2/dme	$Eu[N(SiMe_3)_2](dme)_2$	79	178
	EuI_2/Et_2O	$Na\{Eu[N(SiMe_3)_2]_3\}$	41	178
$Zn[N(SiMe_3)_2]_2$	Et_2Zn	$EtZnN(SiMe_3)_2$		179

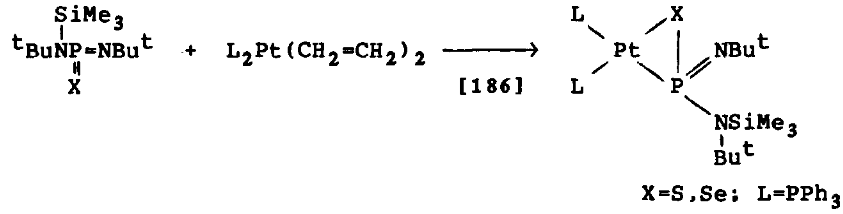


(92)

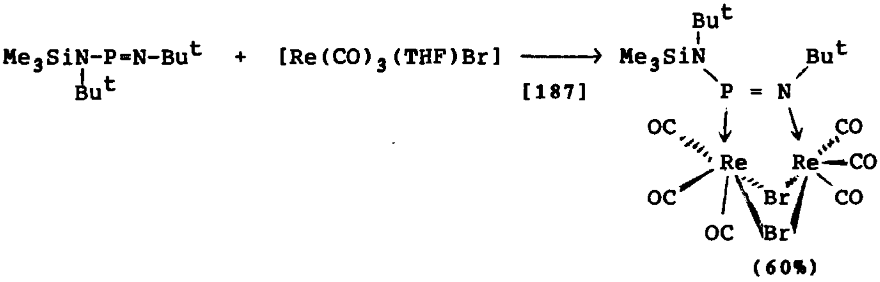
The reaction of silylamidophosphines with various metal substrates is shown in Eqns. 93-95. Mixed sandwich derivatives with azoborolinyl ligands were prepared [188]. The oxidation and electrochemical studies of bis(azaborolinyl)cobalt have appeared [189,190]. Cleavage of CO by $(Me_3SiN)_2ZrMe_2$ gave an 80% yield of the two products: $\{[(Me_3Si)_2N]_2ZrMe\}_2O$ and $[(Me_3Si)_2N]_2Zr[(OC(Me)=CMe_2](Me)$ [191].



(93)



(94)



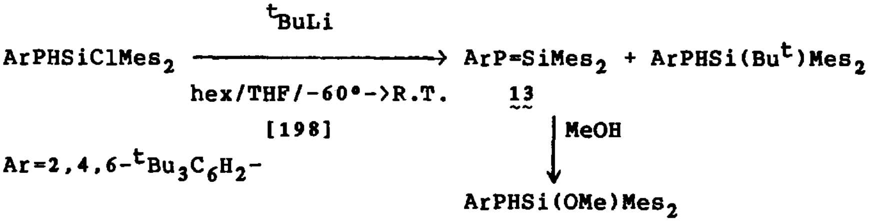
(95)

A $B_6N_7^-$ phenalene was prepared from $Me_3SiN(SnMe_3)_2$ + $B(SMe)_3$ [192].

6. Silylphosphines

A new method for the formation of Si-P bonds has been developed from silyliminophosphine. When $Hg(SiMe_3)_2$ is added to (E)-$(Me_3Si)_2NP{=}NSiMe_3$ in HMPT (Ar/40°/2h) $Me_3SiP[N(SiMe_3)_2]_2$ (63%) is formed [193]. The usual method of formation of SiP bonds is the condensation of LiP with a halosilane, although there are several variations of this theme as shown in Table IV. Deprotonation of PH bonds can give a mixture of products due to decomposition. An example is the reaction of $[(Me_3Si)_2P]_2PH$ with ${}^tBuLi$ which gives $LiP[P(SiMe_3)_2]_2$ initially but PP cleavage occurs with time and $(Me_3Si)_2PP(Li)SiMe_3$ and $LiP(SiMe_3)_2$ are produced [204]. When $P_7(SiMe_3)_2$ and Li_3P_7 (ratio=2/1) are mixed $LiP_7(SiMe_3)_2$ forms and when the ratio is 1/2 the product is $Li_2P_7SiMe_3$ [205].

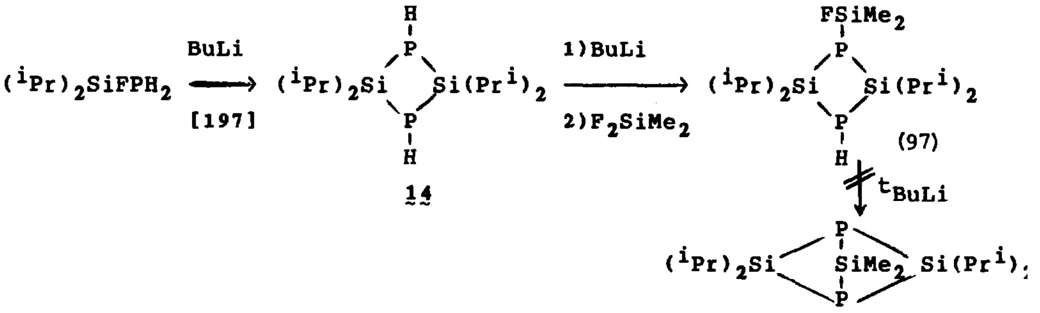
The reaction of the atom sequence, -PHSiX (X=Cl,F), with RLi follows the patterns that have been established for comparable NHSiX sequences. When the groups at both P and Si are sufficiently bulky, phosphasilaalkenes are produced although the extreme O_2 sensitivity precluded isolation (Eqn. 96). The half-life for **13** was 1 day at 25° and about 1 week (-60°C). The presence of **13** in solution was inferred from the trapping reaction also shown in Eqn. 96. The generation of a head-to-tail dimer **14** in Eqn. 97 may imply a P=Si intermediate. An attempt to bridge the two P centers in **14** failed.



$$\mathrm{ArPHSiClMes_2} \xrightarrow[\text{hex/THF/-60°->R.T.}\ [198]]{{}^t\mathrm{BuLi}} \underset{\mathbf{13}}{\mathrm{ArP{=}SiMes_2}} + \mathrm{ArPHSi(Bu^t)Mes_2} \quad (96)$$

$$\mathrm{ArP{=}SiMes_2}\ \xrightarrow{\mathrm{MeOH}}\ \mathrm{ArPHSi(OMe)Mes_2}$$

$Ar=2,4,6\text{-}{}^tBu_3C_6H_2\text{-}$



(97)

TABLE IV. Formation of SiP Bonds from Phi and Halosilanes.

Phosphorous Precursor	Halosilane	Product	%	Ref
Na/K/P_4	$ClSi(SiMe_3)_3$(10 eq) + $ClSiMe_3$(1 eq)	$P_6Si_4(SiMe_3)_8$	40-70	194
P_4/^tBuLi	$ClSiMe_3$	$P_4(SiMe_3)Bu^t_3$[a]		195
P_4/MeLi	$ClSiMe_3$	$P_7(SiMe_3)_3$	1pt	196
		$P_7(SiMe_3)_2Me$	3.3pts	
PH_3/BuLi	$F_2Si(Pr^i)_2$, 0.5 eq	$(^iPr)_2Si(PH_2)_2$	30	197
	$F_2Si(Pr^i)_2$, 1 eq	$(^iPr)_2Si(PH_2)F$	28	197
H_2PPh/BuLi	$F_2Si(Bu^t)_2$, 0.5 eq	$(^tBu)_2Si(PHPh)_2$	16	197
	$F_2Si(Bu^t)_2$, leq	$(^tBu)_3Si(PHPh)F$	52	197
H_2PAr/BuLi[b]	Cl_2SiMes_2[c]	$(Mes)_2SiClPHAr$		198
	$ClSiMe_2Bu^t$	$^tBuMe_2SiPHAr$		199
o-$(H_2P)_2C_6H_4$/RLi	$ClSiMe_3$	*o*-$[(Me_3Si)_2P]_2C_6H_4$		200
$\mathrm{H\overline{PCH_2CH{=}CHCH}Me}$/RLi	$ClSiMe_3$	$\mathrm{Me_3Si\overline{PCH_2CH{=}CHCH}Me}$		201
$H(^tBuP)_3H$	$ClSiMe_3$	$Me_3Si(^tBuP)_3SiMe_3$[d]	94	202
$LiPPh_2$	$\mathrm{RMe\overline{SiCH_2CH_2CH_2}}$[e]	$Ph_2PMe(R)(CH_2)_3Li$		203

---

a. $(Me_3Si)_2PBu^t$, $P(SiMe_3)_3$ also formed.

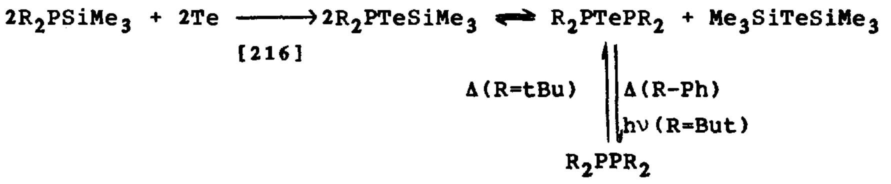
b. Ar=2,4,6-$(^tBu)_3C_6H_2$

c. Mes=Mesityl

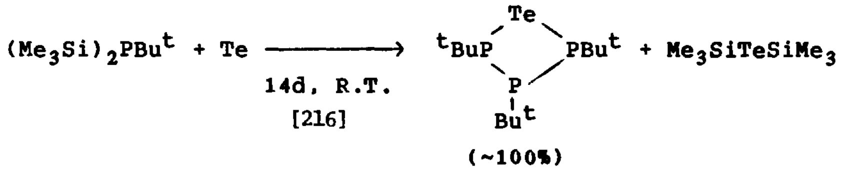
d. Primarily threo-erythro

e. R=Me, *m*-tolyl

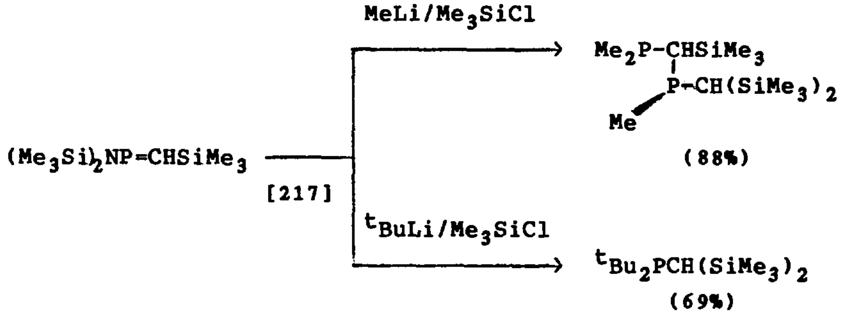
The SiP bond is cleaved by nonmetal halides, C=O containing reagents, alcohols and by RLi as summarized in Table V. When P_4 is added to $LiP(SiMe_3)_2$ (1/4 eq) $LiP_{13}.4THF$ is produced but when there are 2 eq. of $LiP(SiMe_3)_2$, Li_3P_7 and $P(SiMe_3)_3$ are generated [204]. Elemental Te cleaves Si-P bonds as shown in Eqns. 98 and 99. When methylenephosphines are treated with RLi/Me_3SiCl cleavage of PR bonds and addition to P=C are both observed (Eqn. 100).



(98)



(99)



(100)

VII. Silicon-Group VI.

Derivatives that contain silicon-oxygen bonds are described in the sequence: 1. Silylating Agents; 2. Alkoxysilanes and Related Derivatives; 3. Linear Siloxanes; 4. Cyclic Siloxanes and Heterocycles with SiO Bonds; 5. Silyl Enol Ethers, Formation and Chemistry; 6. Silicon-Oxygen Bond Cleavage; 7. Synthetic Uses; 8. Silicon-Sulfur, Silicon-Tellurium Derivatives.

TABLE V. Cleavage of SiP Bonds

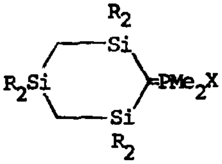
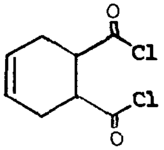
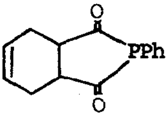
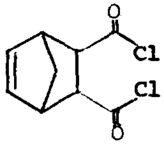
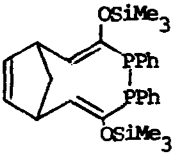
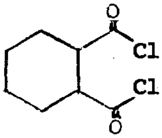
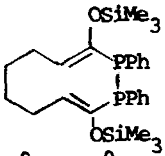
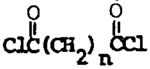
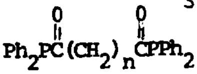
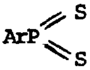
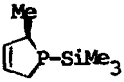
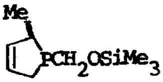
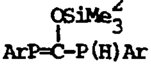
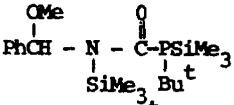
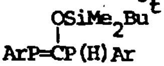
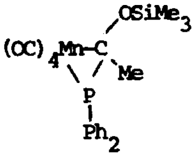
Reagent	Silyl Phosphine	Product	%	Ref
Nonmetal Halides				
$X_2CSiR_2CH_2SiR_2CH_2SiR_2$	Me_3SiPMe_2			
		R X		
		Cl Cl	37	206
		F Cl	29	206
		Me Br	78	206
 $ClC(=O)CH_3$	$Me_3Si[N(SiMe_3)_2]_2$	$AcP[N(SiMe_3)_2]_2$		193
	$(Me_3Si)_2PPh$		81	207
	$(Me_3Si)_2PPh$		82	207
	$(Me_3Si)_2PPh$		>75	208
 $ClC(=O)(CH_2)_nC(=O)Cl$	Me_3SiPPh_2	 $Ph_2PC(=O)(CH_2)_nC(=O)PPh_2$		209
		n=1	72	
		n=2	58	
		n=3	81	
Cl_2S_2	$(Me_3Si)_2PAr$		72	210
Carbonyl Reagents				
H_2CO				211

TABLE V. (Cont) Cleavage of SiP Bonds

Reagent	Silyl Phosphine	Product	%	Ref
Carbonyl Reagents				
$O{=}C(NMe_2)_2$	$\underline{o}$-$[(Me_3Si)_2P]_2C_6H_4$	$\underline{o}$-$(Me_2NCH{=}P)_2C_6H_4$		200
$O{=}C{=}CPh_2$	$ArP(Li)SiMe_2Bu^t$	$ArP{=}C{=}CPh_2$	58	199
$O{=}C{=}PAr$	$ArP(H)SiMe_3$	 $ArP{=}\overset{OSiMe_3}{\overset{\vert}{C}}{-}P(H)Ar$		212
$O{=}C{=}NCH(OMe)Ph$	$(Me_3Si)_2PBu^t$	 $Ph\overset{OMe}{\overset{\vert}{C}}H - \underset{SiMe_3}{\underset{\vert}{N}} - \overset{O}{\overset{\Vert}{C}}{-}\underset{Bu^t}{\underset{\vert}{P}}SiMe_3$	85	213
$O{=}C{=}O$	$ArP(H)SiMe_2Bu^t$	 $ArP{=}\overset{OSiMe_2Bu^t}{\overset{\vert}{C}}P(H)Ar$	81	214
$(OC)_5MnMe$	Me_3SiPPh_2		75	215
Alcohols				
MeOH	$Me_3SiP[N(SiMe_3)_2]_2$	$HP[N(SiMe_3)_2]$		193
	$P_4(SiMe_3)Bu_3^t$	$P_4Bu_3^tH$	85	195
Lithium Reagents				
nBuLi	$P_4(SiMe_3)Bu_3^t$	$LiP_4(Bu^t)_3$		195

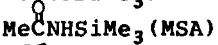
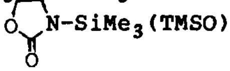
1. Silylating Agents

No new silylating agents have been reported but a method has been developed to generate variously substituted $R_2SiXOSO_2CF_3$ species by cleavage of SiC, SiCl and SiH bonds (Eqn. 101). Reagents such as $H_3SiOSO_2CF_3$ which disproportionate readily and $Cl_3SiOSO_2CF_3$ could both be prepared by this method. An improved method for the preparation of $Me_3SiO_3SiCF_3$ is shown in Eqn. 102 from TMSO [N-(trimethylsilyl)-2-oxazolidinone]. The results of other agents used to prepare silyltriflate are shown in Eqn. 102 for comparison.

$$R_2SiXY + CF_3SO_3H \xrightarrow[\text{[218a,218b]}]{} R_2SiXOSO_2CF_3 + HY \qquad (101)$$

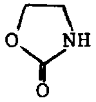
R	X	Y	%
Me	H	Cl	95
Me	H	Ph	86
H	H	Ph	(not isolated)
Cl	Cl	Ph	85
Me	Me	Me	~100

$$\text{Silylating Agent} + CF_3SO_3H \xrightarrow[\text{[219]}]{} Me_3SiO_3SCF_3 \qquad (102)$$

	Time	%
$MeC(OSiMe_3) = NSiMe_3$ (BSA)	5m	43
 $MeC(=O)NHSiMe_3$ (MSA)	5m	35
	30m	-
 $Cl_3CC(=O)OSiMe_3$	5m	40
	2m	80

A good catalyst for silylation of alcohols by $^tBuMe_2SiCl/Et_3N$ is 1,1,3,3-tetramethylguanidine [220]. The use of TMSO as a silylating agent is shown in Eqn. 103.

$$RH + TMSO \xrightarrow[\text{[219]}]{CF_3SO_3H} RSiMe_3 + \qquad (103)$$



Time	R	%
5m	$PhCO_2$	95
30m^a	EtS	82
10m	PhS	93

a. DBU cat.

2. Alkoxysilanes and Related Derivatives

The more standard methods for forming SiO bonds (SiCl + HR; SiCl + $^-$OM or $^-$OR; exchange) are shown in Table VI. The formation of $\mathrm{C(SiMe_2OH)_4}$ in 69% from addition of AgOCN to $\mathrm{C(SiMe_2I)_4}$ in moist ether has been reported [242].

Hydrosilanes react with alcohols to form alkoxysilanes but catalysts are required. The simplest seems to be piperidine (Eqns. 104, 105) or $\mathrm{ZnCl_2}$ (Eqn. 106). It has been shown that the dimeric Ru species, $\mathrm{[LRu(CO)_2Cl_2]_2}$ ($\mathrm{L{=}R_3P}$; R=Me,Et) were active catalysts for alcoholysis of $\mathrm{Et_3SiH}$ but that $\mathrm{L_2Ru(CO)_2Cl_2}$ derivatives are not active [245b]. Ethanolysis of $\mathrm{Me_3SiO[Si(H)(Me)O]_nSiMe_3}$ (n=50) has been accomplished with Rh and Ir catalysts anchored on silica [245c].

$$\mathrm{RSiMe_2H + HON{=}CMe_2 \xrightarrow[50^\circ/3\ h]{piperidine} RSiMe_2ON{=}CMe_2} \qquad (104)$$

R = 2-thienyl [243] (41%)

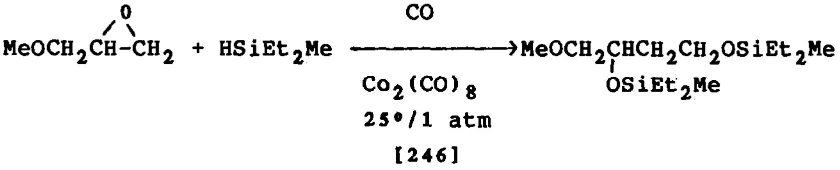
$$\mathrm{Ph_3SiH + EtOH \xrightarrow[R.T./20\ h]{piperidine} Ph_3SiOEt} \qquad (105)$$

[244] (78%)

$$\mathrm{R_2MeSiH + HOCH_2C{\equiv}CH \xrightarrow[[245a]]{ZnCl_2} HC{\equiv}CCH_2OSiMeR_2} \qquad (106)$$

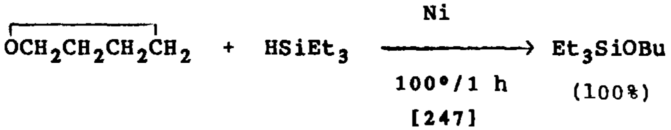
$\mathrm{R={}^iPr,\ {}^iBu}$, pentyl (25-30%)

Ring opening of oxiranes, THF and dioxacycloalkanes occurs in the presence of HSi/metal catalyst as shown in Eqn.s 107-109. Acetals are converted to ethers by SiH (Eqn. 110).



$$\mathrm{MeOCH_2\overset{O}{CH{-}CH_2} + HSiEt_2Me \xrightarrow[Co_2(CO)_8,\ 25^\circ/1\ atm]{CO} MeOCH_2\underset{OSiEt_2Me}{CH}CH_2CH_2OSiEt_2Me} \qquad (107)$$

[246]



$$\mathrm{\overline{OCH_2CH_2CH_2CH_2} + HSiEt_3 \xrightarrow[100^\circ/1\ h]{Ni} Et_3SiOBu} \qquad (108)$$

[247] (100%)

TABLE VI. Formation of Alkoxysilanes from Chlorosilanes, Anions and Miscellaneous Sources

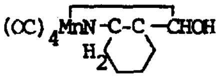
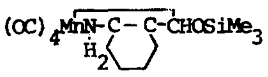
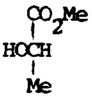
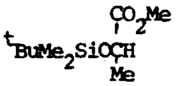
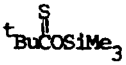
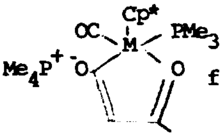
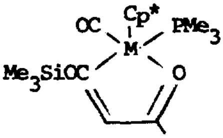
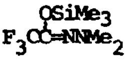
Organic Substrate	Silane	Product	%	Ref
Alcohols/Acids				
EtOH	$SiCl_4$(1/1)[a]	$EtOSiCl_3$	90	221
	$SiCl_4$(2/1)[a]	$(EtO)_2SiCl_2$	95	221
	$SiCl_4$(3/1)[a]	$(EtO)_3SiCl$	80	221
	$SiCl_4$(4/1)[a]	$(EtO)_4Si$	82	221
$^{i}PrOH$	$SiBr_4$	$^{i}PrOSiBr_3$	75	123
		$(^{i}PrO)_2SiBr_2$	19[b]	123
		$(^{i}PrO)_3SiBr$	64	123
PhC(O)N(R')OH[c]	R_2SiCl_2[c]	$[PhC(O)N(R')O]_2SiR_2$		222
$ArOCH_2CO_2H$	$Me_2PhSiCl$	$ArOCH_2CO_2SiPhMe_2$		223
	Me_3SiCl[d]		52	224
MeOH	$TrisSiMe_2I$	$TrisSiMe_2OH$	90	225
	$TrisSiPh_2I$	$(Me_3Si)_2C(SiPh_2Me)SiMe_2OH$	90	225
 $HO\underset{Me}{\overset{CO_2Me}{CH}}$	$^{t}BuMe_2SiCl$[e]	 $^{t}BuMe_2SiO\underset{Me}{\overset{CO_2Me}{CH}}$	90	226a
$HONH_2\cdot HCl$	$R_2SiFNHBu^t$	$R_2SiFONH_2$		226b
Anions				
Ag_2CrO_4	$^{i}PrPh_2SiCl$	$^{i}PrPh_2SiO)_2CrO_2$	93	227
	$BuPh_2SiCl$	$BuPh_2SiO)_2CrO_2$	96	228
	$C_8H_{17}Ph_2SiCl$	$C_8H_{17}Ph_2SiO)_2CrO_2$	95	229
	$MePh_2SiCl$	$MePh_2SiO)_2CrO_2$	97	230
	$EtPh_2SiCl$	$EtPh_2SiO)_2CrO_2$	94	231
$Me_2NCO_2^-$	Me_3SiCl	$Me_2NCO_2SiMe_3$	95	232 233
$[^{i}Bu_2NCO_2]^-[^{i}Bu_2NH_2^+]$	Me_3SiCl	$^{i}Bu_2NCO_2SiMe_3$	86	233

TABLE VI. (Cont.) Formation of Alkoxysilanes from Chlorosilanes, Anions and Miscellaneous Sources

Organic Substrate	Silane	Product	%	Ref
Alcohols/Acids				
$[RNHCO_2^-]Et_3NH^+$	Me_3SiCl	$MeN(SiMe_3)CO_2SiMe_3$	67	233
$^tBuLi/CO$; PhCHO	Me_3SiCl	$^tBuCOC(Ph)HOSiMe_3$	95	234
$^tBuLi/CO/CS_2$	Me_3SiCl	 $^tBu\overset{\overset{S}{\|}}{C}OSiMe_3$	64	235
Miscellaneous				
CrO_3	$^iBuPh_2SiOH$	$^iBuPh_2SiO\text{)}_2CrO_2$	98	236
 f	$Me_3SiO_3SCF_3$		93	237
$Et\overline{OCHO(CH_2)_3O}$	Me_3SiOPr	Me_3SiOEt	100	238
Me_2EtCOH	$Me_2NCO_2SiMe_3$	$Me_3SiOCMe_2Et$		239
$(Me_3SiOCH_2CH_2)_3N$	$F_3CCO_2(CH_2)_3SiF_3$	$F_3CCO_2(CH_2)_3Si(OCH_2CH_2)_3N$		240
$F_3CCONHNMe_2$	Me_3SiCl	 $F_3C\overset{OSiMe_3}{\overset{\|}{C}}{=}NNMe_2$	90	241a
Ac_2NNHAc	Me_3SiCl	$Me_3SiO(Me)\overline{COCMe{=}N{-}N}Ac$		241b

a. Ratio of $EtOH/SiCl_4$ b. low yield attributed to disproportionation during distillation

c. R'=Ph, tolyl; R=Me, Ph d. $(Me_3Si)_2NH$ added

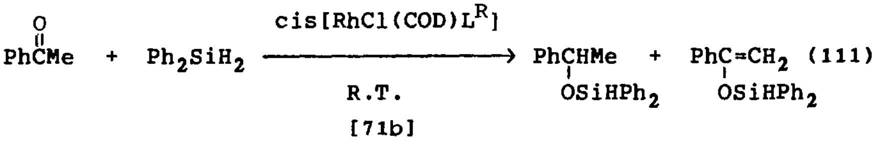
e. Et_3N and 4-(dimethylamino)pyridine present F. $Cp^*=Me_5C_5$

$$\overline{OCH_2OCH_2CH_2CH_2} + HSiEt_3 \xrightarrow[100°/1\ h]{Ni/ZnCl_2} \underset{(96\%)}{Et_3SiOCH_2CH_2CH_2OMe} \qquad (109)$$

[248]

$$MeCH(OPr)_2 + HSiEt_3 \xrightarrow[[249]]{ZnI_2} EtOPr + Et_3SiOPr \qquad (110)$$

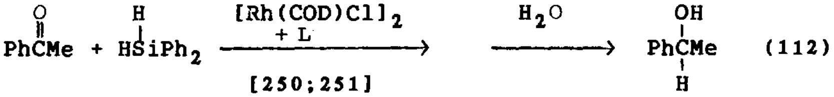
Hydrosilanes add to carbonyl derivatives in the presence of *cis* or *trans* $[RhCl(COD)L^{Me}]$ (L^{Me} = $\overline{CNMeCH_2CH_2NMe}$) to give both the siloxy- and silyl enol derivatives (Eqn. 111). Catalysts have been developed from addition of appropriate base ligands to $[Rh(COD)Cl]_2$. The catalysts can be generated *in situ* and up to 97.6% ee was observed in the alcohol products. Examples are shown in Eqn. 112. A similar tactic was used to make amines (Eqn. 113). Silanes also add to ketones in the presence of $ZnCl_2$ (Eqn. 114).



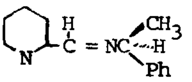
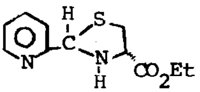
$$Ph\overset{O}{\overset{\|}{C}}Me + Ph_2SiH_2 \xrightarrow[R.T.]{cis[RhCl(COD)L^R]} Ph\underset{OSiHPh_2}{CHMe} + Ph\underset{OSiHPh_2}{C}{=}CH_2 \qquad (111)$$

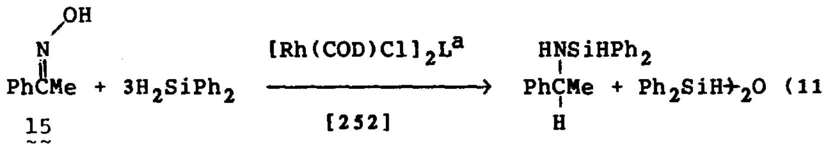
[71b]

$:\overline{CN(R)CH_2CH_2NR}$			
	R=Me	(76%)	(24%)
	R=Ph	(98%)	(2%)



$$Ph\overset{O}{\overset{\|}{C}}Me + H\overset{H}{Si}Ph_2 \xrightarrow[[250;251]]{[Rh(COD)Cl]_2 + L} \xrightarrow{H_2O} Ph\overset{OH}{\underset{H}{C}}Me \qquad (112)$$

L	Rh/L	time	%	%ee
	1/13	41	96	57.3(R)
	1/13		100	97.6(R)

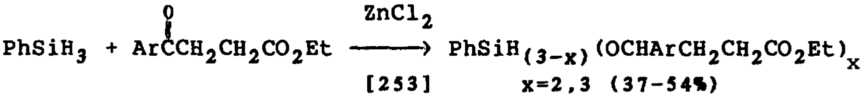


$$\underset{15}{\mathrm{Ph\overset{\overset{OH}{N}}{\|}{C}Me}} + 3H_2SiPh_2 \xrightarrow[{[252]}]{[Rh(COD)Cl]_2L^a} \mathrm{Ph\overset{HNSiHPh_2}{\underset{H}{C}}Me} + (Ph_2SiH)_2O \quad (113)$$

R	Rh/15	Rh/P	t	%	%ee
Me	1/100	1/2	44^b	54	4.5(R)
	1/100	1/4	96^b	60	14.4(R)
Et	1/200	1/2	144^c	20	18.9(R)
^{i}Pr	1/200	1/2	44^d	30	12.7(R)

a. L=(R,R)-(-)-P,P-[1,3-dioxolane-4,5-bis(methylene)bis-(diphenylphosphine)]

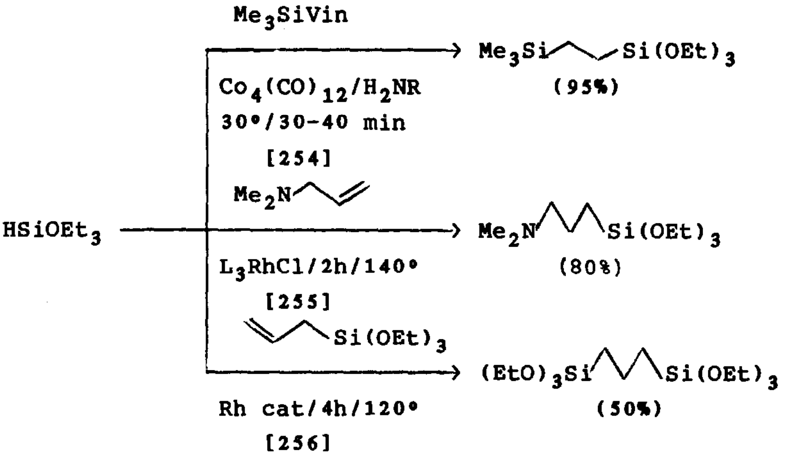
b. -10 -> 25°. c. 25° d. 50°



$$PhSiH_3 + \mathrm{Ar\overset{O}{\overset{\|}{C}}CH_2CH_2CO_2Et} \xrightarrow[{[253]}]{ZnCl_2} PhSiH_{(3-x)}(OCHArCH_2CH_2CO_2Et)_x \quad (114)$$

$$x=2,3\ (37\text{-}54\%)$$

Alkoxysilanes can be prepared by more indirect routes which include addition of $HSi(OEt)_3$ to olefins (Eqn. 115), a metathesis reaction of $(EtO)_3SiVin$ (Eqn. 116), a form of exchange from triflates (Eqn. 117) and by a variety of rearrangement processes (Eqns. 118-122). Particularly noteworthy in this latter group is the new anionic rearrangement shown in Eqn. 118. Silyl groups also migrate between trans diaxial OH functions of carbohydrates [265].



(115)

$$2(EtO)_3SiCH{=}CH_2 \xrightarrow[\text{sealed ampoule}]{120^\circ} (EtO)_3SiCH{=}CHSi(OEt)_3 + CH_2{=}CH_2 \quad (116)$$

[257]

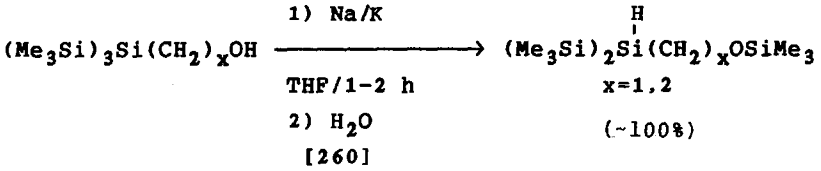
Catalyst	trans/cis	%
$RuCl_2L_2$	5/1	69
$RuCl_3L_3$	5/1	63
$Ru(acac)_3$	4/1	51
RuH_2L_4	6/1	42

$$RMe_2SiO_3SCF_3 \xrightarrow[{[258]}]{R={}^tBu,\ (PhCH_2)_3NO} (PhCH_2)_3NOSiMe_2Bu^t]^+O_3SCF_3^- \quad (117)$$

$$RMe_2SiO_3SCF_3 \xrightarrow[{[259]}]{M(CO)_2(dppe)LSO_2} [M(CO)_2(dppe)LSO_2SiMe_3]^+SO_3CF_3^-$$

$L=P(Pr^i)_3$

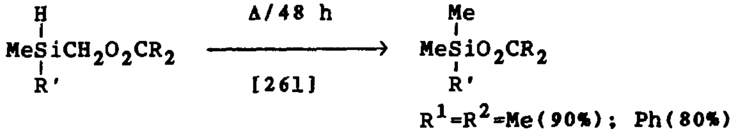
M=Mo, W(60%)



$$(Me_3Si)_3Si(CH_2)_xOH \xrightarrow[\text{THF/1-2 h; 2) } H_2O;\ [260]]{\text{1) Na/K}} (Me_3Si)_2\overset{H}{Si}(CH_2)_xOSiMe_3 \quad (118)$$

x=1,2

(~100%)

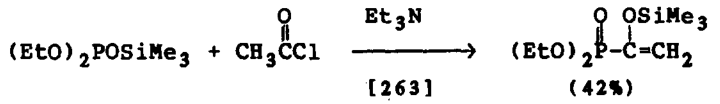


$$Me\overset{H}{\underset{R'}{Si}}CH_2O_2CR_2 \xrightarrow[{[261]}]{\Delta/48\ h} Me\overset{Me}{\underset{R'}{Si}}O_2CR_2 \quad (119)$$

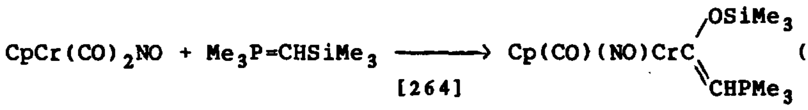
$R^1=R^2=Me(90\%)$; Ph(80%)

$$(Me_3Si)_3CSiMe_2OMe + CF_3CO_2H \xrightarrow[{[262]}]{RT/30\ min} (Me_3Si)_2C(SiMe_2O_2CCF_3)_2 \quad (120)$$

(74%)



$$(EtO)_2POSiMe_3 + CH_3\overset{O}{\overset{\|}{C}}Cl \xrightarrow[{[263]}]{Et_3N} (EtO)_2\overset{O}{\overset{\|}{P}}-\overset{OSiMe_3}{\overset{|}{C}}=CH_2 \ (42\%) \qquad (121)$$



$$CpCr(CO)_2NO + Me_3P=CHSiMe_3 \xrightarrow[{[264]}]{} Cp(CO)(NO)CrC\begin{matrix}/OSiMe_3\\ \backslash CHPMe_3\end{matrix} \qquad (122)$$

Silicon sesquioxide has been prepared from Si_2Br_6 and SO_3 [266]. When either Me_2SiCl_2 or Me_3SiCl is added to graphitic oxide (pyridine present) intercalated graphite bound $-OSiMe_2OH$ and $OSiMe_3$ are formed [267]. Trimethyl polyphosphate, formed from addition of $Me_3SiOSiMe_3$ to P_2O_5, is a mixture of cyclic trimer and tetramer as well as linear dimer and tetramer [268]. The collision induced dissociation of Me_3SiO^- (formed in the gas phase from Me_4Si/OH^-) forms CH_4 and dimethylsilanone enolate [269].

3. Linear Siloxanes

Carbon monoxide is reduced in the presence of Me_6Si_2 when Ni-Kieselguhr catalyst is added (Eqn. 123). When the reduction is performed in the presence of H_2 ($CO/H_2 = 1/1$), $Me_3Si)_2O$ is formed in 59% yield (9% yield of other siloxanes) [85]. From labelling studies it was shown that the O in the siloxanes is derived from CO. When F_2SiR_2 is reacted with KOH variously substituted disiloxanes are produced (Eqn. 124). Addition of PhCHO to $PhSiCl_3$ ($h\nu/NiCl_2/SnCl_2/12h/120°$) gave $Cl_2(Ph)Si)_2O$ (22%) [76].

$$\underset{}{Me_6Si_2} + CO \xrightarrow[{[85]}]{\text{Ni-Kieselguhr}} \underset{(0.2\%)}{Me_4Si} + \underset{(38.3\%)}{Me_3SiOSiMe_3} + \underset{\substack{x=3,4\\(6.3\%)}}{(Me_2SiO)_x} \qquad (123)$$

$$+ \underset{(5.2\%)}{Me_3SiO)_2SiMe_2} + \underset{(7.3\%)}{CH_4}$$

$$\underset{R=Pr^i}{F_2SiR_2} + KOH \xrightarrow[{[270]}]{} \underset{X=F,\ OH}{XR_2Si)_2O} + FR_2SiOSiR_2OH \qquad (124)$$

When D_3 is treated with $AcOSiMe_3$ or Me_3SiOMe in the presence of CF_3SO_3H ring opening occurs to give $Me_3Si(OSiMe_2)_3OAc$ [271] and $Me_3Si(OSiMe_2)_3OMe$ [$Me_3Si(OSiMe_2)_6OMe$ is a minor product] [272] respectively. When silicic acid is adsorbed on $Fe(OH)_3$ then silylated the following derivatives were formed: $R_3SiOSiR_3$, $R_3Si(OSiR_2)_xOSiR_3$, (x=1,2), $(R_2SiO)_4$ and R_4Si ($R{=}OSiMe_3$) [273]. Hydrolytic condensation of $(EtO)_4Si/EtOH$ gave $Et[OSi(OEt)_2]_nOEt$ (n=2-4) [274].

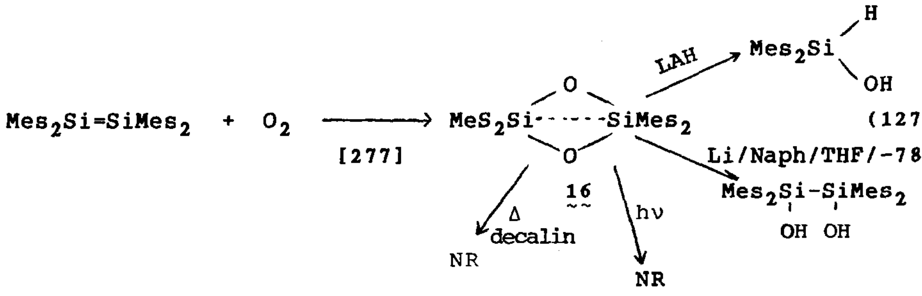
A more directed synthesis of siloxanes is accomplished by coupling of silanols with chlorosilanes or hydrosilanes as shown in Eqns. 125, 126.

$$CH_2{=}CHSiCl_3 + HO(SiMe_2O)_2H \xrightarrow[\text{[275]}]{py/C_6H_6} \underset{(47\%)}{Cl_2VinSiO(SiMe_2O)_2SiVinCl_2} \qquad (125)$$

$$H(SiMe_2O)_nSiMe_2H + Ph_2Si(OH)_2 \xrightarrow[\text{[276]}]{ZnCl_2} \underset{n=1-5}{Ph_3SiO(SiMe_2O)_nSiMe_2H} \qquad (126)$$

4. Cyclic Siloxanes and Heterocycles with SiO Bonds

The smallest cyclosiloxane, D_2, has been generated through the reaction of a disilene with O_2 (Eqn. 127a). The O_2 derivative 16 is unique in terms of having a very short O...O distance. Indeed, when 16 is reduced with Li/Naph, the disilane $(Mes)_2(HO)SiSi(OH)(Mes)_2$, is formed [277]. A similar approach has generated D_3 from oxidation of a cyclotrisilane (Eqn. 127b)



(127a)

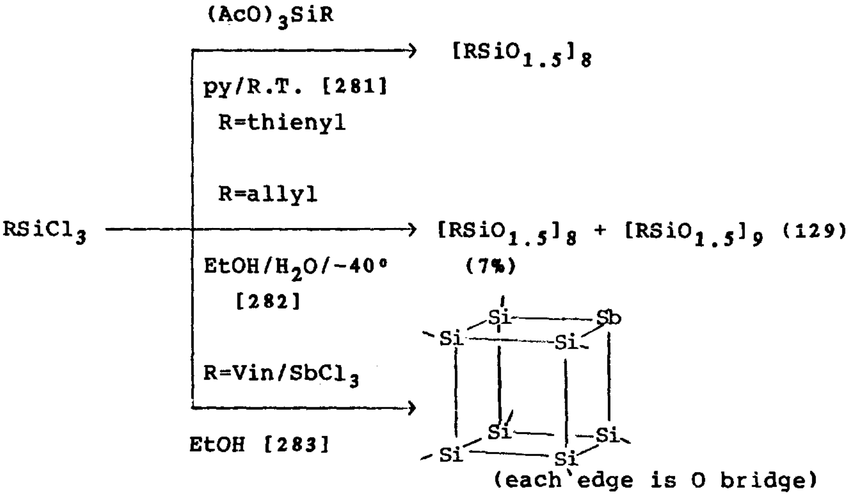
$$(^tBu_2Si)_3 + m\text{-}ClC_6H_4CO_3H \xrightarrow[\text{[278]}]{CHCl_3} \underset{(90\%)}{(^tBu_2SiO)_3} \qquad (127b)$$

The usual route to cyclopolysiloxanes is through hydrolysis of dichlorosilanes (Eqn. 127c) or a trichlorosilane (Eqn. 128). Sesquisiloxanes are normally formed from trichlorosilanes (Eqn. 129). The competition of intermolecular vs. intramolecular condensation of $HO(SiMe_2O)_5H$ catalyzed by RSO_3H ($R=Me, CF_3$) has been reported. The rates of the competing reactions are about equal in dioxane and in CH_2Cl_2 formation of cyclic and linear derivatives are independent of initial concentration [284]. The cyclic siloxane, $(Me_2SiO)_5$, may be useful in the control of flies and cockroaches [285].

$$Me_2SiCl_2 \xrightarrow[35° \ [279]]{C_6H_{13}SO_3Na/HCl/H_2O} (Me_2SiO)_n \quad n=4(47\%);\ 5(13\%)$$

$$Me_2SiCl_2 \xrightarrow[[280]]{(F_{2n+1}C_n)SO_3M/HCl/H_2O} (Me_2SiO)_n \quad n=4(79\%);\ 5(16\%);\ 6(3\%) \qquad (127c)$$

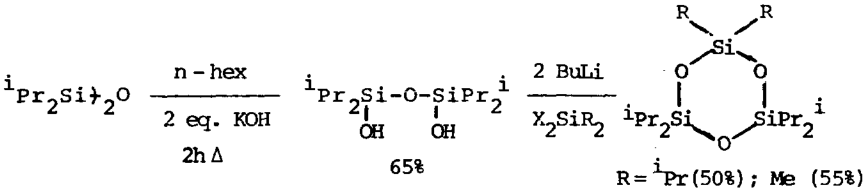
$$\underset{R=\text{thienyl}}{RSiCl_3} + H_2O \xrightarrow[-7° \ [281]]{Et_2O/py} \underset{(47\%)}{[(HO)(R)SiO]_4} \qquad (128)$$



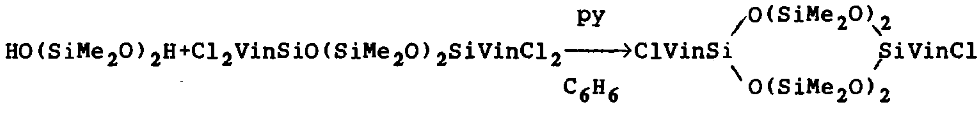
(129)

(each edge is O bridge)

A more directed synthesis of cyclopolysiloxanes is shown in Eqns. 130 and 131.



(130)

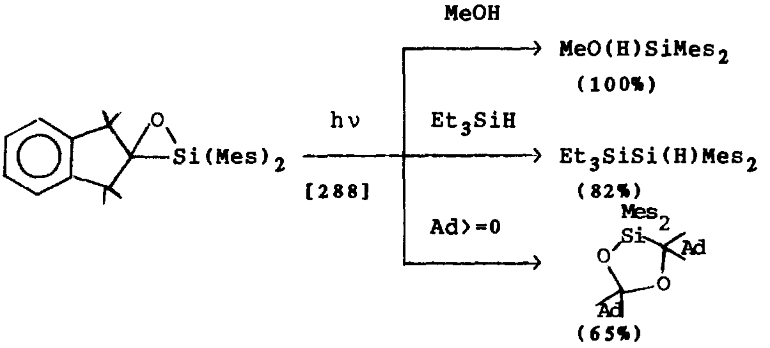


$$HO(SiMe_2O)_2H + Cl_2VinSiO(SiMe_2O)_2SiVinCl_2 \xrightarrow[C_6H_6]{py} ClVinSi\begin{matrix} O(SiMe_2O)_2 \\ O(SiMe_2O)_2 \end{matrix}SiVinCl$$

[275] (45%) (131)

Cyclopolysiloxanes are subject to ring-opening or polymerization reactions by either acids or bases. When AcCl is added to $(Me_2SiO)_4$ at 150°, $Me_2Si(OAc)Cl$ is formed if $ZnBr_2$ or $FeCl_3$ is added. About 74% of AcCl is consumed in 1h when $FeCl_3$ is present [286]. Ionic fluorides catalyze the polymerization of D_3 and D_4. Their effectiveness as catalysts decrease through the sequence, Me_4NF or $Bu_4NF.2H_2O > CsF > KF$ [287].

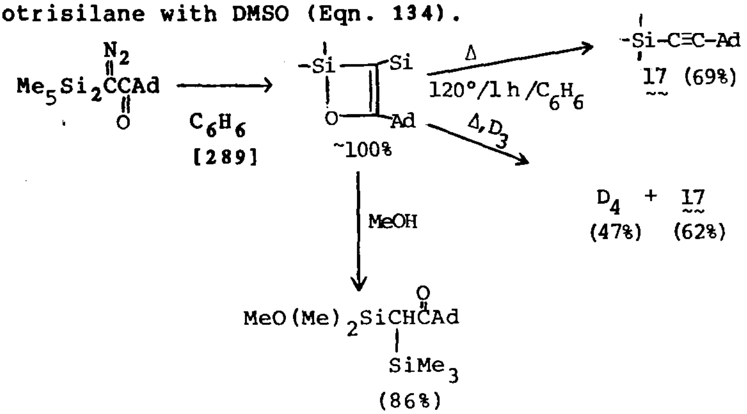
The oxasilacyclopropane ring functions as a source of silylenes but also undergoes insertion reactions with adamantanone as shown in Eqn. 132.



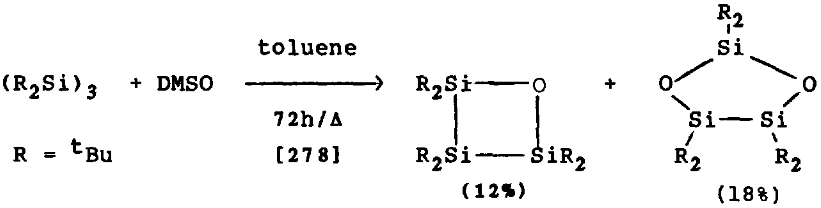
(132)

Pholoysis of the disilane, $Me_5Si_2C(N_2)COR$ (R=adamantyl) provided the novel unsaturated ring system, 1,2-silaoxetane (not isolated in pure form). Thermolysis of the silaoxetane appears to give a silanone as inferred from the trapping with D_3. Addition of

MeOH cleaves the ring. These reactions are summarized in Eqn. 133. An oxatrisilane is formed during the mild oxidation of cyclotrisilane with DMSO (Eqn. 134).

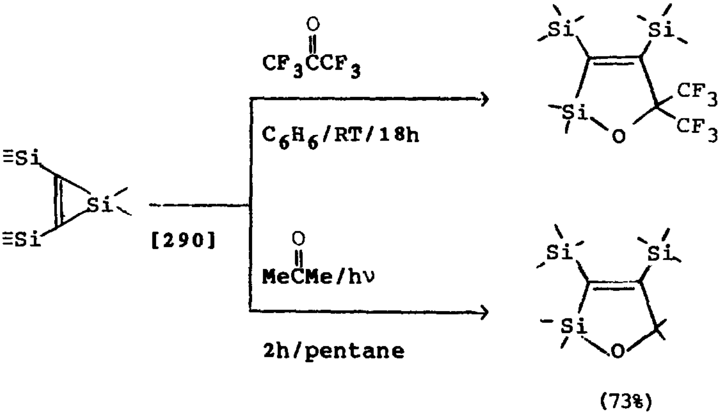


(133)

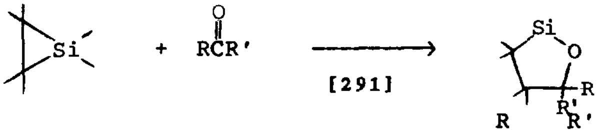


(134)

Insertion of carbonyls into silacyclopropane and silacyclopropene provides five-membered rings which contain a SiO bond (Eqns. 135 and 136). The formation of 1,3-dioxosilacyclopentane is shown in Eqn. 137, although it is doubtful that the product is monomeric as shown. The formation of rings with a BOSi sequence and an NSiO sequence is shown in Eqns. 138 and 139.

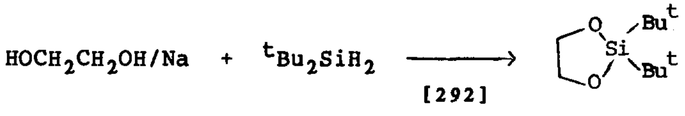


(135)



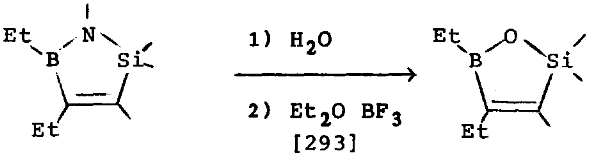
(136)

R	R'	%
Ph	H	52
Ph	Me	60

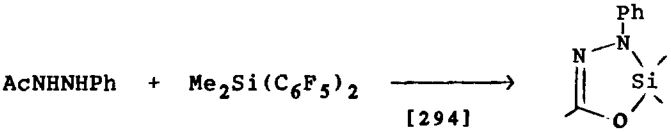


(70%)

(137)

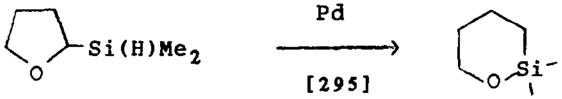


(138)

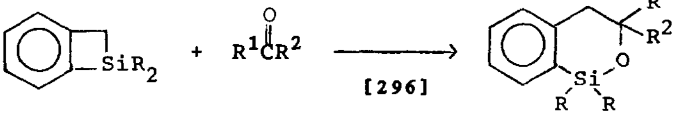


(139)

Oxasilacyclohexanes have been generated by a rearrangement reaction (Eqn. 140) and an insertion process (Eqn. 141). Metal carbonyl complexes of 10-sila-9-oxaphenanthrene have been generated as shown in Eqn. 142. The disiloxane, $O[Si(Me)_2CH_2Cl]_2$, has been converted to a cyclic derivative by reaction of the $-CH_2Cl$ substituent (Eqn. 143).

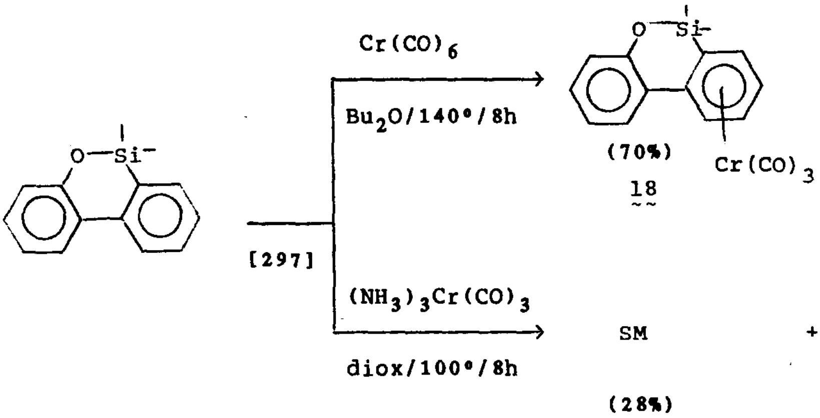


(140)

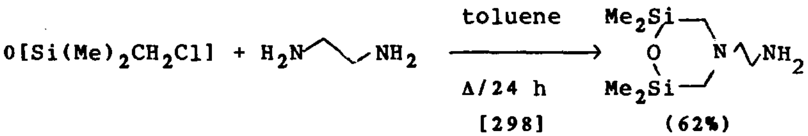


(141)

R = Me, Ph
R^1 = Me, Et, Pr
R^2 = H, Me, Et, Ph

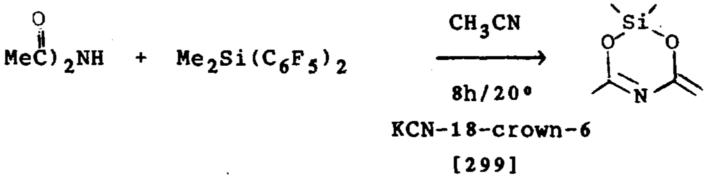


(142)

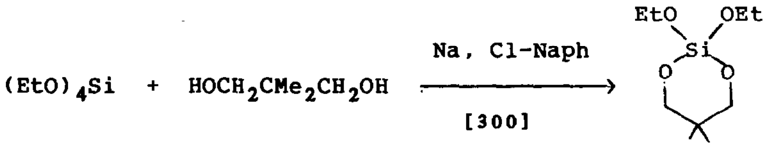


(143)

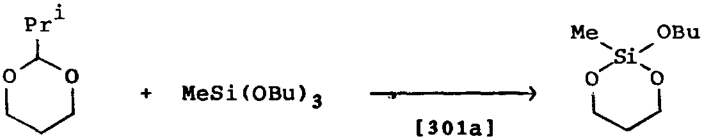
Six-membered rings with an OSiO sequence have been formed by silylation of N-acetylacetamide (Eqn. 144), alcoholysis of $Si(OEt)_4$ (Eqn. 145), exchange (Eqn. 146) and rearrangement (Eqn. 147).



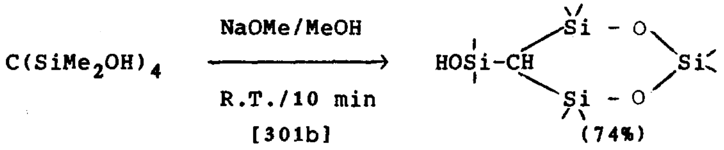
(144)



(145)



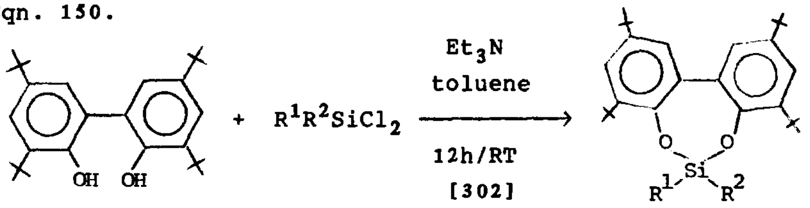
(146)



(147)

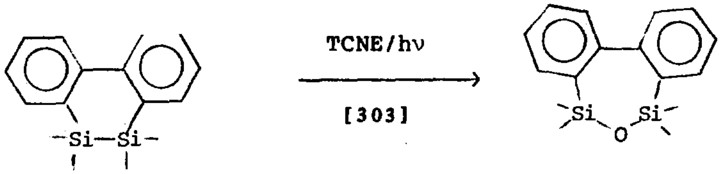
Condensation of $RSiH_3$ with cis-phloroglucitol resulted in good yields of 2,4,10-trioxa-3-silaadamantanes [301b]. When the ethanolamine derivative, $(Me_3SiOCH_2CH_2)(Me_3Si)NCO_2SiMe_3$, was treated with $ClCH_2SiMe_2Cl$, the new heterocycle, $Me_2SiOCH_2CH_2NRCH_2$ ($R=CH_2SiMe_2Cl$ and CH_2SiMe_3) was formed [301c]. Addition of ^tBuLi to $^tBu_2Si(F)ONHBu^t$, led to the cyclic silylhydroxylamine, $^tBu_2SiON(Bu^t)Si(Bu^t)_2ONBu^t$ [226b].

The seven-membered dibenzo[1,3,2]dioxasilepin ring system was formed from biphenol (Eqn. 148) and the dibenzo[1,3,2]oxadisilepin from oxidation of dibenzodisilacyclohexadiene (Eqn. 149). An effective trap for silanones is 1,3,2-disilaoxacyclopentane as shown in Eqn. 150.

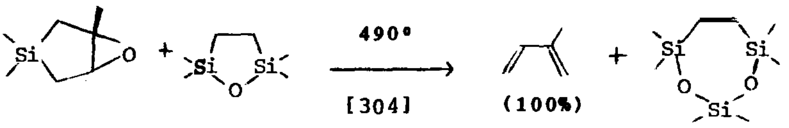


(148)

R^1	R^2	%
H	Me	77
Me	Me	47

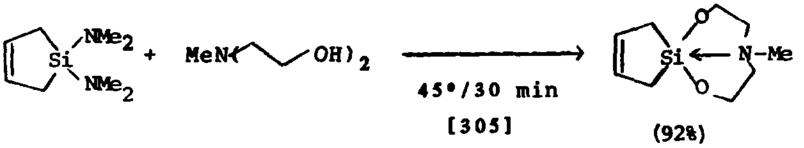


(149)

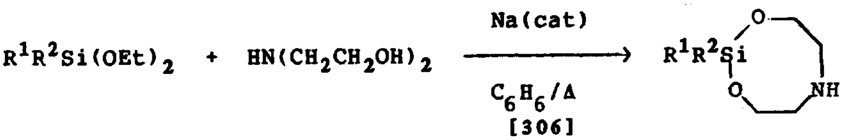


(150)

Interest in transannular interactions such as exist in silatranes has motivated the synthesis of 1,3-dioxa-6-aza-2-silacyclooctanes (Eqns. 151-153) and the disilane analog of silatrane (Eqn. 154).

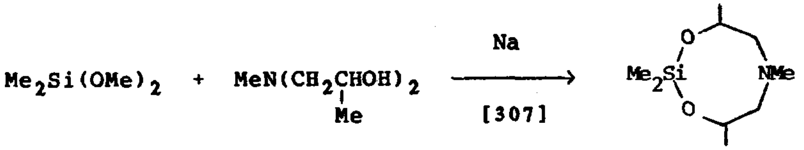


(151)

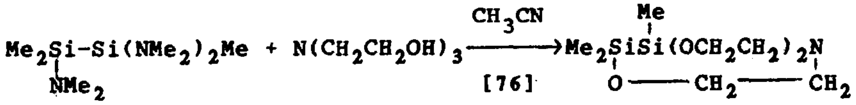


(152)

R^1	R^2	%
Ph	Me	44
Me	Me	52

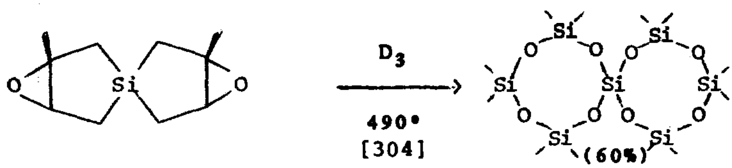


(153)



$$\mathrm{Me_2\underset{NMe_2}{Si}{-}Si(NMe_2)_2Me + N(CH_2CH_2OH)_3 \xrightarrow[[76]]{CH_3CN} Me_2\underset{O\text{———}CH_2\text{———}CH_2}{Si\overset{Me}{Si}(OCH_2CH_2)_2N}} \quad (154)$$

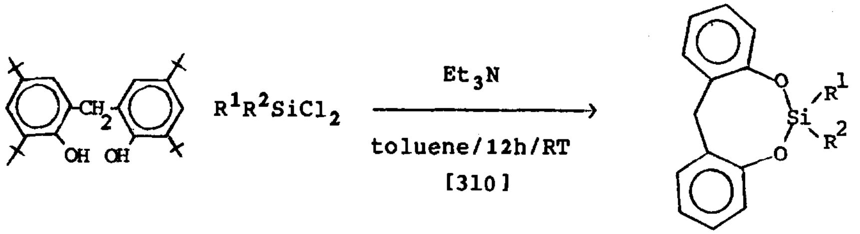
The intermediate "O=Si=O" has been trapped by D_3 to give the spiro-derivative shown in Eqn. 155. A derivative of D_4 has been reported from the reaction of R_2GeX_2 and $Ph_2Si(OH)_2$ (Eqn. 156). Reaction of methylene bisphenol with R_2SiCl_2 gives 12H-dibenzo-[d,g][1,3,2]dioxasilocin (Eqn. 157). These dioxasilocins are stabilizers for polyolefins and PVC [310]. When dichlorosilanes are treated with catechol the expected monomeric product is not observed but the dimeric dibenzotetraoxasiladecadione is formed (Eqn. 158).



(155)

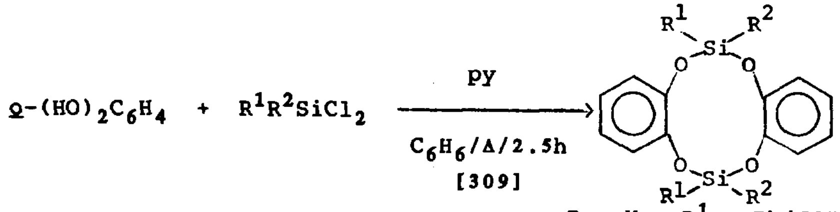
$$2R_2GeX_2 + 2Ph_2Si(OH)_2 \xrightarrow[\text{acetone}\ [308]]{4NEt_3} [R_2GeOSiPh_2O]_2 \qquad (156)$$

R=Ph,Me



(157)

R^1	R^2	%
H	Me	30
Me	Me	86
H	Ph	24

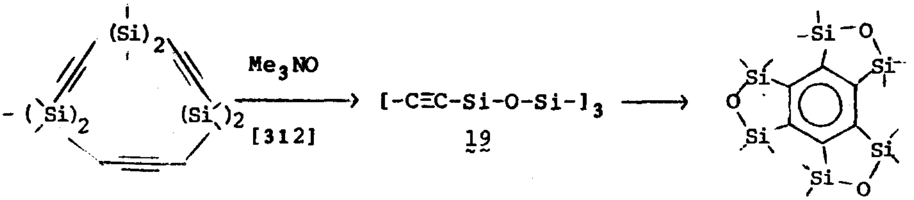


(158)

R = Me, R^1 = Ph(59%)

R = R^1 = Me(46%); Ph(60%)

A sila-14-crown-5 is formed from Vin(Me)Si(OEt)$_2$ and HO(CH$_2$)$_4$OH [Ti(OBu)$_4$, cat.] [311] and a 15-membered ring is formed on oxidation of 3,4,7,8,11,12-hexasilacyclododeca-1,5,9-triyne but 19 is unstable with respect to intramolecular cyclization (Eqn. 159).



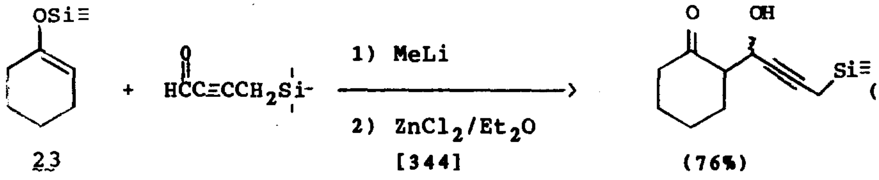
(159)

5. Silyl Enol Ethers: Formation and Chemistry

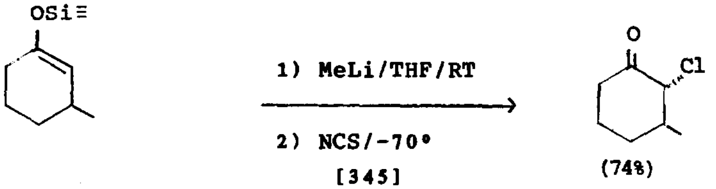
Silyl enol ethers and their chemistry will be described in terms of the structural type: C(OSiR$_3$)=C; C(OR)(OSiR$_3$)=C (R=alkyl or silyl); siloxydienes.

Several of the methods that were reported during this Survey Year for the synthesis of silyl enol ethers [C(OSiR$_3$)=C} are described in Table VII. It has been demonstrated that Me$_3$SiCl is not attacked by LDA or LOBA at -78°, therefore this combination can be used to deprotonate and silylate ketones (first entries in Table VII) [313]. A regio- and stereocontrolled synthesis of silyl enol ethers has been developed from enol boranes by exchange with N-trimethylsilylimidazole [319].

The principle use of silyl enol ethers is in applications to synthetic strategies. Many of these processes are acid catalyzed reactions as shown in Table VIII. Although less common, inorganic reagents added to silyl enol ethers may also provide novel compounds including thiadiazoles and oxathioles. These reactions are shown in Table IX. Silyl enol ethers also react on addition of MeLi followed by the organic substrate as demonstrated in Eqns. 160 and 161. Coupling processes are also initiated by oxidation both electrochemically (Eqn. 162) and chemically (Eqn. 163). Silyl enol ethers react with ketones to form silyloxycyclobutanones (Eqn. 164).



(160)



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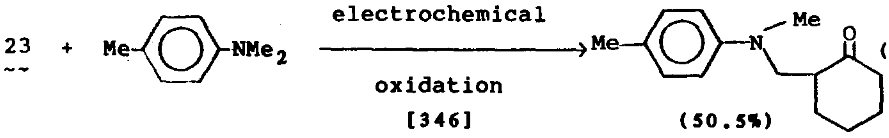


(162)

TABLE VII. Methods of Formation of Silyl Enol Ethers

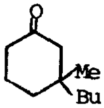
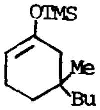
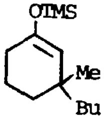
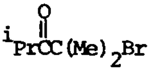
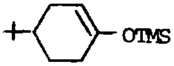
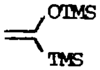
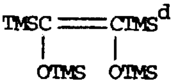
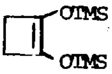
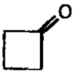
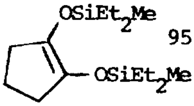
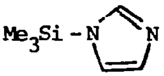
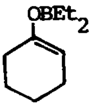
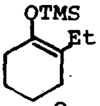
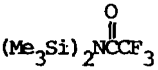
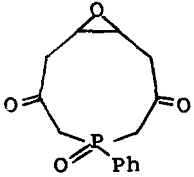
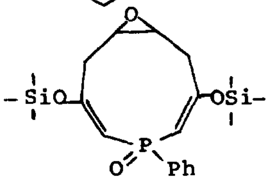
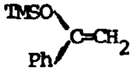
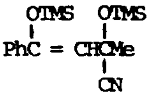
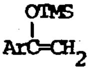
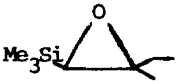
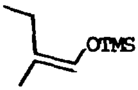
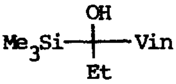
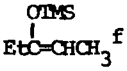
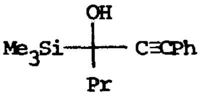
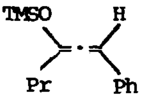
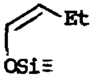
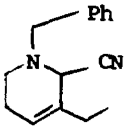
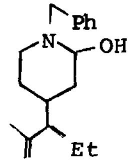
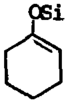
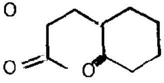
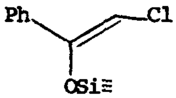
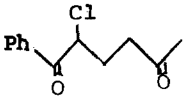
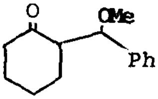
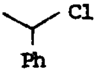
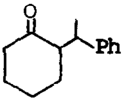
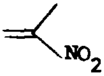
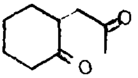
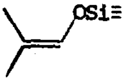
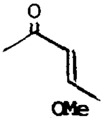
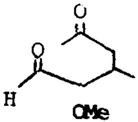
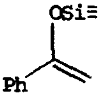
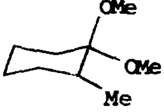
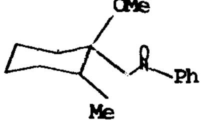
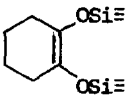
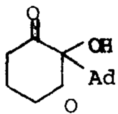
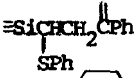
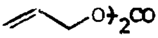
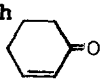
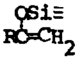
Silicon Source	Substrate	Conditions	Product	%	Ref
Me$_3$SiCl/LDA[a]	 20	THF/-78°	 21	90	313
			 22	10	
Me$_3$SiCl/LOBA[b]	20	THF/-78°	21	97	313
			22	3	
Me3SiCl/LiNPr$^i_2$	 $^{i}PrC\overset{\overset{O}{\|}}{C}(Me)_2Br$	-78	$^{i}PrC(OTMS)=CMe_2$	98	314
Me$_3$SiCl/Fe°[c]		Et$_2$O		98	315
Me$_3$SiCH$_2$Li	1. CO 2. Me$_3$SiCl	Et$_2$O/15°		75	316
	1. CO 2. Me$_3$SiCl	Et$_2$O/-78	 $\underset{OTMS}{\underset{\mid}{TMSC}}=\underset{OTMS}{\underset{\mid}{CTMS}}$[d]	33	316
Me$_3$SiCl/Na-K	EtO$_2$CCH$_2$CH$_2$CO$_2$Et			78	317
Et$_2$MeSiH/CO(50 atm) Co$_2$(CO)$_8$/PPh$_3$		175		95	318

TABLE VII. Methods of Formation of Silyl Enol Ethers (Cont.)

Silicon Source	Substrate	Conditions	Product	%	Ref
				73	319a
 $(Me_3Si)_2N\overset{O}{\overset{\|}{C}}CF_3$		60°/1 h			319b
$Me_3SiSnBu_3$	$BrCH_2COPh$	$PdCl_2$/80°[e]		81	320
Me_3SiCN	PhC(OH)=CHCOMe	120°/12 h	 $Ph\overset{OTMS}{\overset{\|}{C}}=CH\underset{CN}{\overset{OTMS}{C}}Me$	82	321
Me_3SiCN	 $Ar\overset{O}{\overset{\|}{C}}OAc$	KCN/Crown	 $Ar\overset{OTMS}{\overset{\|}{C}}=CH_2$		322
		$BF_3\cdot OEt_2$		68	323
 $Me_3Si-\underset{Et}{\overset{OH}{\|}}-Vin$		^tBuLi/-20°	 $Et\overset{OTMS}{\overset{\|}{C}}=CHCH_3$[f]		324
 $Me_3Si-\underset{Pr}{\overset{OH}{\|}}-C\equiv CPh$		^tBuLi/THF/-78			325

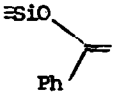
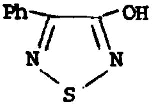
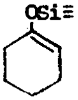
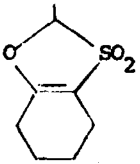
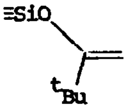
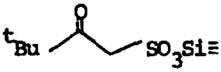
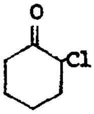
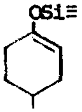
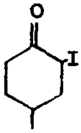
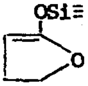
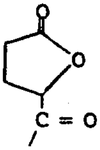
a. LDA=lithium diethylamide
b. lithium t-octyl-t-butylamide
c. Fe° from $FeCl_3$/MeMgBr
d. E/Z=1:1
e. $P(OMe)_3$ also added
f. Z/E = 95/5

TABLE VIII. Lewis Acid Catalyzed Reactions of Silyl Enol Ethers

Lewis Acid Catalyst	Silyl Enol Ether	Coreactant	Product	%	Ref
$BF_3 \cdot OEt_2$				94	326
	 23	 24		50	327
		24		60	328
Me_3SiI	23	$PhCH(OMe)_2$		89[a]	329
$TiCl_4$	23			61	330
	23			83	331
				90	332
	 25			95	333
$ZnCl_2$		AdCl		66	334
$ZnBr_2$	25	$Me_3SiCHClSPh$	 $\equiv \underset{SPh}{SiCH}CH_2\overset{O}{\overset{\|}{C}}Ph$	86	335
$Pd(OAc)_2$[b]	23			87	336
$PdCl_2$[c]	 $\overset{OSi\equiv}{RC}{=}CH_2$	PhCHO	 $\overset{O}{\overset{\|}{RC}}CH_2\underset{Ph}{CHOH}$	95	337

a. Erythro/threo-99/1 b. dppe added

TABLE IX. Reaction of Silyl Enol Ethers with Inorganic Reagents and Halogenated Organics

Inorganic or Halogenated Reagent	Silyl Enol Ether	Product	%	Ref
N_4S_4				338
$BrCH_2SO_2Br$/DBN	 23		70[a]	339
$ClSO_3Si$≡			85	340
SO_2Cl_2	23		80	341
NIS[b]			74	342
 $\mathrm{Cl\overset{O}{\overset{\|}{C}}CH_3}$			90	343

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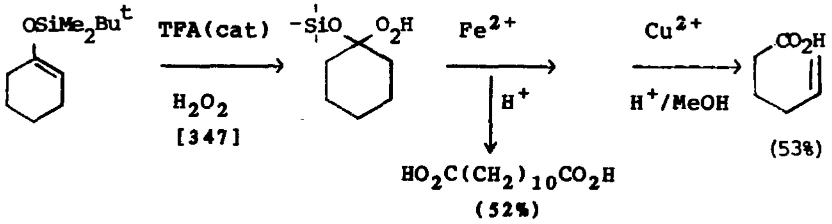
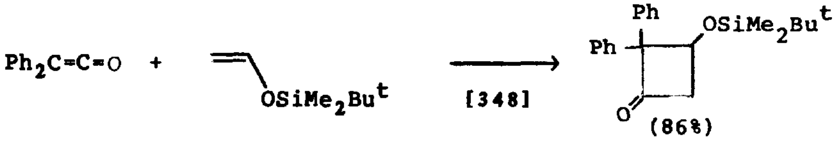
a. EtOH solvent

b. N-iodosuccinimide

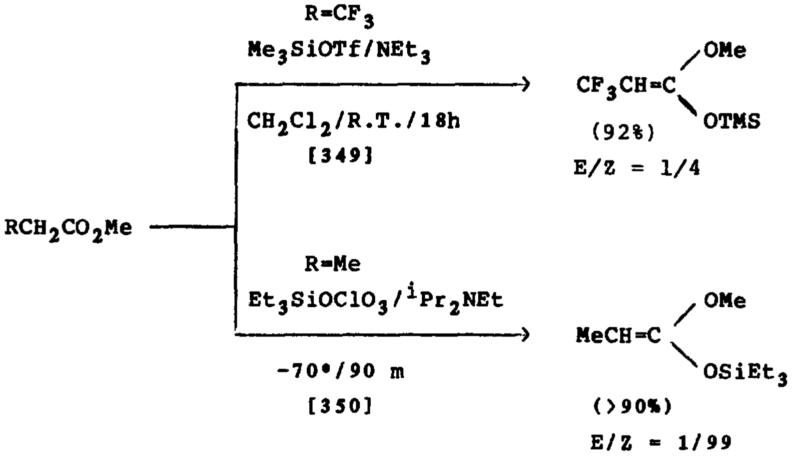


(163)

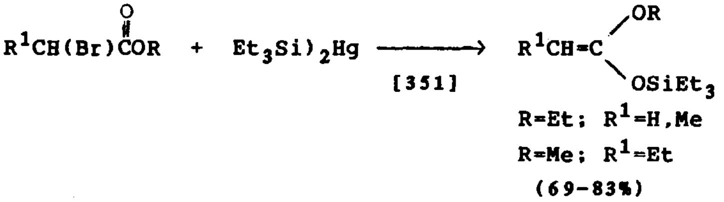


(164)

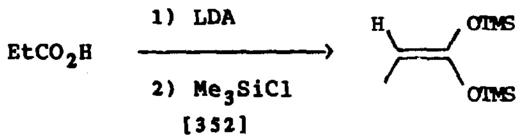
Silyl ketene acetals are usually formed from esters but the silicon source can vary from TMSOTf (Eqn. 165) to $Et_3SiOClO_3$ (Eqn. 165) to $(R_3Si)_2Hg$ (Eqn. 166). The use of Me_3SiCl/LDA/ester or acid also provides the acetal (Eqns. 167,168). The acetal, $Me_2C{=}C(OMe)OSiEt_3$, was formed by catalytic hydrosilylation of methyl methacrylate [353b].



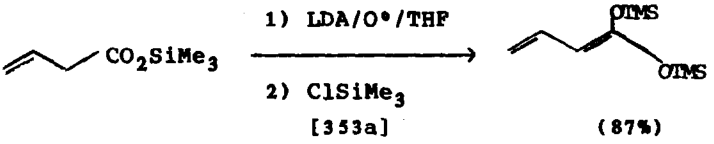
(165)



(166)



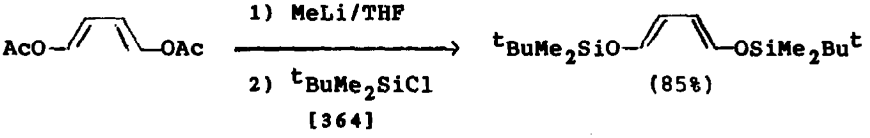
(167)



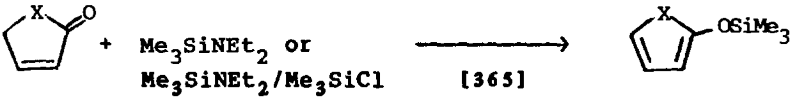
(168)

The synthetic uses of silyl ketene acetals are shown in Table X. The migration of $SiMe_3$ in a ketene acetal occurs under high pressure (10 Kbar) and provides a new synthesis of α-silylated esters [356].

The E,E-isomer of 1,4-siloxydiene has been prepared from E,E-AcOCH=CHCH=CHOAc as shown in Eqn. 169. A cyclic siloxydiene has been generated according to Eqn. 170.



(169)



(170)

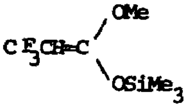
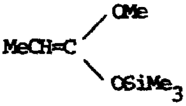
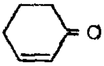
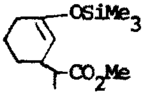
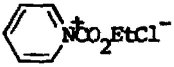
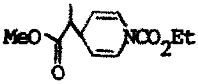
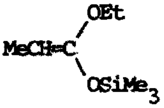
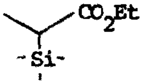
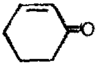
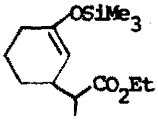
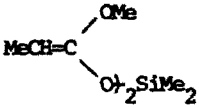
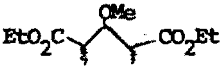
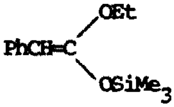
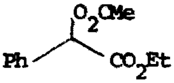
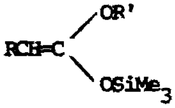
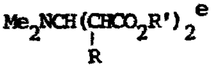
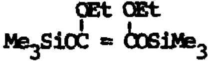
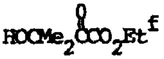
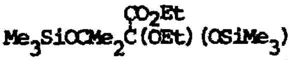
Temp/time	X	%
0°-RT/12h	NMe	70
-78/4 h	S	65

The incorporation of siloxydienes into synthetic strategies is shown in Table XI.

6. Silicon-Oxygen Bond Cleavage

In mixed tetrahydropyranyl, tert-butyldimethylsilyl derivatives, $RO(CH_2)_{10}OSiMe_2Bu^t$, the THP group is removed selectively by Me_2AlCl [374]. The RO group bound to silicon may be transferred to a variety of nonmetal and metal centers as illustrated in Table XII. The common characteristic of the reagents in Table XII is the presence of an element-halogen bond.

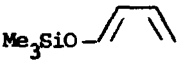
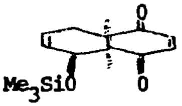
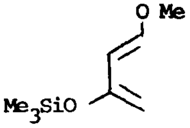
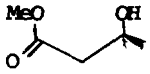
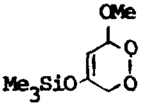
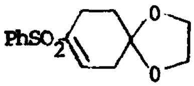
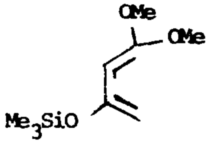
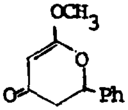
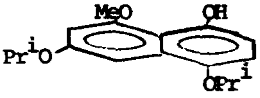
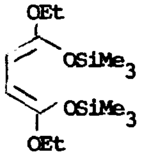
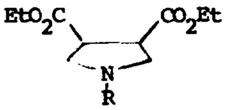
TABLE X. Silyl Ketene Acetals in Synthesis

Silyl Ketene Acetal	Substrate	Product	%	Ref
 $CF_3CH=C(OMe)(OSiMe_3)$	$Me_2C(OMe)_2$	$MeOC(Me)_2CH(CF_3)CO_2Me$	74	349
 $MeCH=C(OMe)(OSiMe_3)$			94[a]	354
			87	355
 $MeCH=C(OEt)(OSiMe_3)$	b		80	356
			80	357
 $(MeCH=C(OMe)O)_2SiMe_2$	$HC(OMe)_3$[c]		56	358
 $PhCH=C(OEt)(OSiMe_3)$	1) $Pb(OAc)_4$ 2) Et_3NHF		75	359
 $RCH=C(OR')(OSiMe_3)$	$Me_2NCH(OMe)_2$[d]	 $Me_2NCH(\underset{R}{CH}CO_2R')_2$[e]	27–65	360
$Me_2C=C(OMe)OSiMe_3$	^tBuCl[d]	$^tBu(Me)_2CO_2Me$	85	352
	c	$MeO_2CC(Me)_2C(Me)_2CO_2Me$		352
$Me_2C=C(OSiMe_3)_2$	$PhCHO$[e]	$HOCHPhCMe_2CO_2H$	86	361
 $Me_3SiO\overset{OEt}{C}=\overset{OEt}{C}OSiMe_3$	Me_2CO[d]	 $HOCMe_2\overset{O}{C}CO_2Et$[f]	~100	362
	Me_2CO	 $Me_3SiOCMe_2\overset{CO_2Et}{C}(OEt)(OSiMe_3)$	87	363

a. 1:1 diastereomeric mixture b. 10 Kbar pressure c. $TiCl_4$ cat.

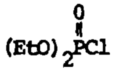
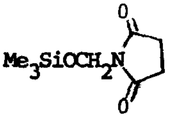
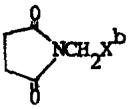
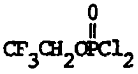
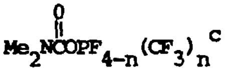
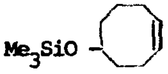
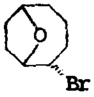
d. $ZnCl_2$ cat. e. R=Me,Et,Pr,^{i}Pr, Bu; R'=Me,Et,Pr f. after acid hydrolysis

TABLE XI. Siloxydienes in Synthesis

Siloxydiene	Coreactant	Product	%	Ref
			92	366
	PhCHO[a]			367
	$^1O_2$		28	368
	PhSO$_2$ Vin HOCH$_2$CH$_2$OH		85	369
	PhCHO[a]		85	370,371
	1)  2) ^{i}PrBr/K$_2$CO$_3$		69	372
	RN(CH$_2$SMe)$_2$	 [b]	51-95	373

a. Eu(hfc)$_3$ b. R=Me, PhCH$_2$, MeSCH$_2$

TABLE XII. Transfer of Oxygen Substituents from Silicon to Nonmetal and Metal Centers

ROSi≡	Halide	Product	%	Ref
$Me_3SiOP(OEt)_2$	CCl_4	 $(EtO)_2\overset{\overset{O}{\|}}{P}Cl$		375
$Me_3SiO_2CBu^t$	Ph_3CF[a]	$^tBuCO_2CPh_3$	94	376
	Me_3SiX		51-76	377
$Me_3SiOCH_2CF_3$	$POCl_3$	 $CF_3CH_2O\overset{\overset{O}{\|}}{P}Cl_2$	94	378
 $Me_3SiO\overset{\overset{O}{\|}}{C}NMe_2$	$(F_3C)_nPF_{5-n}$	 $Me_2N\overset{\overset{O}{\|}}{C}OPF_{4-n}(CF_3)_n$[c]		379
Me_3SiOCH_2Ph	PF_2Cl	$PhCH_2OPF_2$	82	380
$Me_3SiOCH_2Ad\text{-}1$	PF_2Cl	$1\text{-}AdOPF_2$	75	380
Me_3SiOMe	$TeClF_5$	$MeOTeClF_4$		381
Me_3SiO_2CMe	$H(CF_2)_6CH_2OSF_3$	$H(CF_2)_6CH_2O_2SF$	98	382
	Br_2		60	383
Me_3 SiOTf	$W(CH)L_4Cl$[d]	$W(CH)L_4(CF_3SO_3)$	96	384

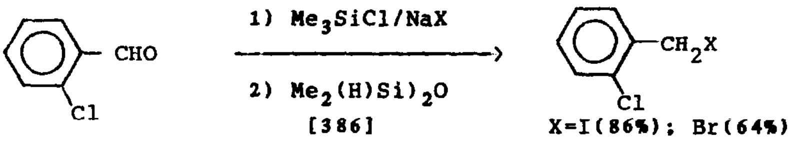
a. SiF_4 cat. b. X=Cl,Br,I. c. n=1,2,3 d. $L=PMe_3$

7. Synthetic Uses

Although several examples of uses of oxygen-containing functional groups at silicon were described in the previous two sections there are a series of examples that do not fit the patterns described for silyl enol ethers or in the cleavage of Si-O bonds by halogen-containing reagents and these miscelleneous processes are covered in this section.

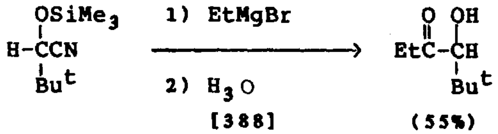
A method has been developed for the preparation of multigram quantities of trimethylsilyldiazomethane from the treatment of trimethylsilyl triflate with diazomethane (-78° in the presence of EtNPr^i_2) [385].

A synthesis of benzyl halides has been developed from halosilanes and 1,1,3,3-tetramethyldisiloxane (Eqn. 171). Adamantylsilanes can be formed from 1,3-AdCl_2 and $\text{Me}_3\text{SiOSiMe}_3$ (Eqn. 172). A synthesis of acyloins from silylated cyanohydrins is shown in Eqn. 173.



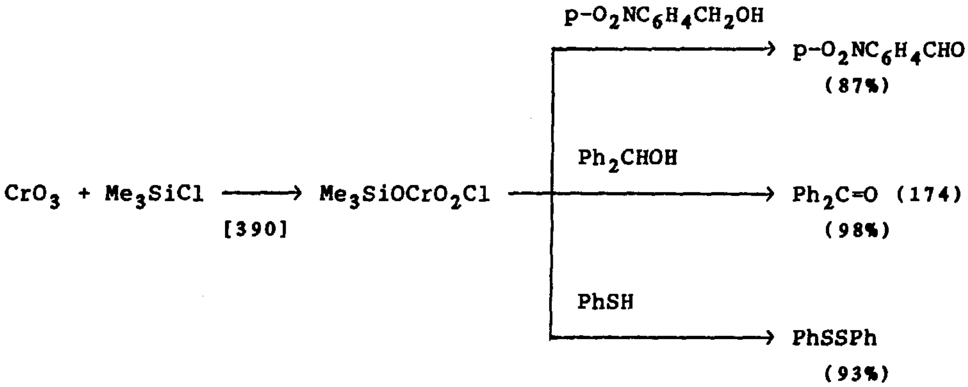
(171)

$$1,3\text{-AdCl}_2 \quad + \quad \text{Me}_2\text{SiOSiMe}_3 \xrightarrow[\text{[387]}]{\text{Na/HMPA}} 1\text{-Me}_3\text{SiAd} \qquad (172)$$



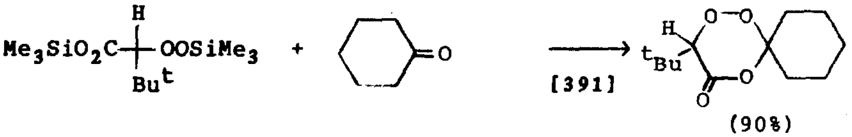
$$\text{H-}\overset{\text{OSiMe}_3}{\underset{\text{Bu}^t}{\text{C}}}\text{CN} \xrightarrow[\text{2) H}_3\text{O} \;\; [388]]{\text{1) EtMgBr}} \text{Et}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}\overset{\text{OH}}{\underset{\text{Bu}^t}{\text{C}}}\text{H} \;\; (55\%) \qquad (173)$$

Trimethylsilyl derivatives of peroxysulfuric acids can be formed by addition of SO_3 to $\text{Me}_3\text{SiO}_2\text{R}$ [389]. When CrO_3 and Me_3SiCl are mixed a red-orange liquid forms which is presumed to be $\text{Me}_3\text{SiOCrO}_2\text{Cl}$ [390]. This reagent constitutes a new oxidizing system (Eqn. 174).

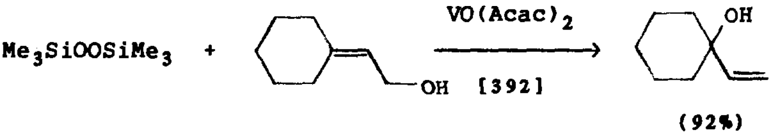


(174)

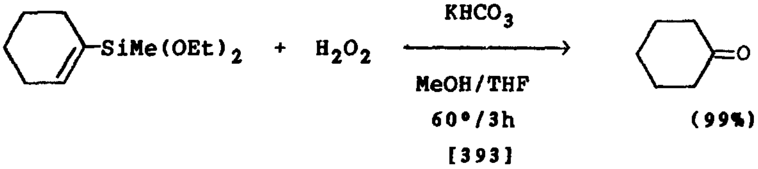
Reactions of peroxysilanes are shown in Eqns. 175 and 176. Oxidation of alkoxysilanes by H_2O_2 is shown in Eqn. 177 and a 1,3-diol synthesis also involving an alcoxysilane **26** shown in Eqn. 178.



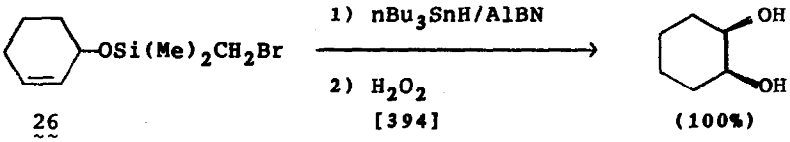
(175)



(176)



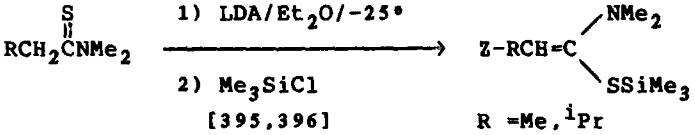
(177)



(178)

8. Silicon-Sulfur and Silicon Tellurium Derivatives

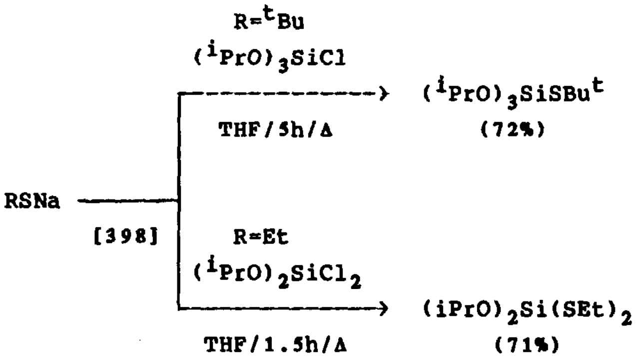
A common method for formation of silicon-sulfur bonds is quenching of a sulfur anion with Me_3SiCl. Several examples of this process with different substrates are shown in Eqns. 179-183. The reaction of R_3SiH with ArSSAr to give R_3SiSAr and ArSH has been studied by kinetic methods [400].



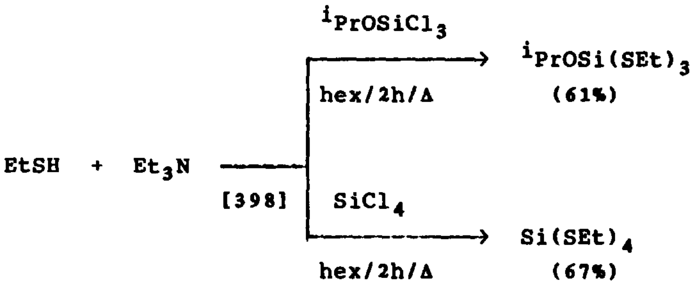
$$RCH_2\overset{\overset{S}{\|}}{C}NMe_2 \xrightarrow[\substack{2)\ Me_3SiCl \\ [395,396]}]{1)\ LDA/Et_2O/-25°} Z\text{-}RCH{=}C(NMe_2)(SSiMe_3) \quad R = Me, {}^iPr \qquad (179)$$

$$Ph_{4-n}SiCl_n + nNaS_2AsR_2 \xrightarrow[[397]]{} Ph_{4-n}Si(S_2AsR_2)_n \qquad (180)$$

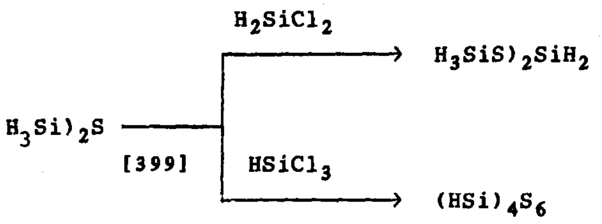
n	R	%
2	Me	80
1	Me	78
2	Ph	63
1	Ph	62



(181)

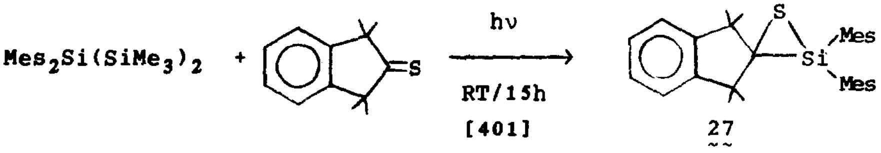


(182)

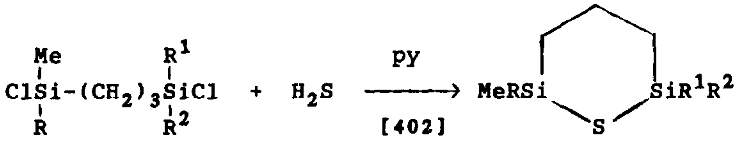


(183)

A silathiacyclopropane **27** has been prepared from a silylene and indanethione (Eqn. 184). The three membered ring is stable in the presence of air or moisture. Other heterocycles have been prepared from HS/SiCl (Eqns. 185 and 186), by pyrolysis of a mixture of 1,1,3,3-tetramethyldisiloxane and sulfur, (Eqn. 187) copyrolysis of silacyclobutane and cyclotrisilthione (Eqn. 188) and pyrolysis of a silathietane (Eqn. 189).



(184)

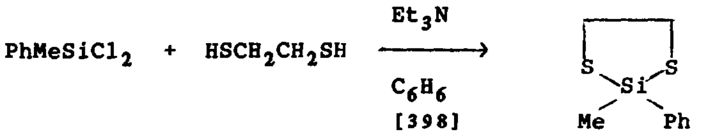


(185)

R = Me, Et

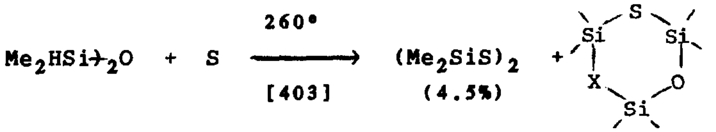
R^1 = Me, Et, Bu, Ph

R^2 = Et, Bu, Ph, Cl



(186)

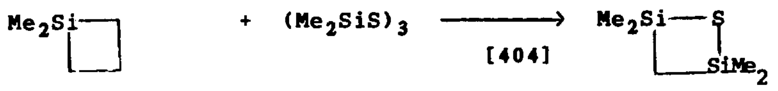
(71%)

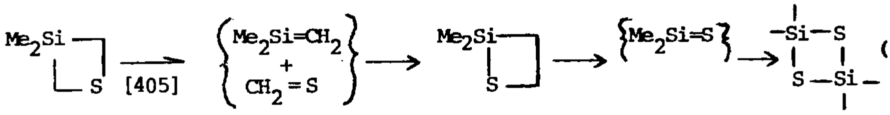


(187)

X = O (67%)

S (19%)


(188)


(189)

The silicon-sulfur bond is cleaved by halogen-containing reagents as illustrated in Table XIII. The silylsulfide, Et_3SiSBr, reacts with Grignard reagents to give Et_3SiSR (R=Et, Ph), but with BuLi a complex mixture containing Bu_2S, $(Et_3Si)_2S$, BuSSBu, $BuSSiEt_3$ and Et_3SiBr results [416]. The reaction of Ph_3SiSBr with cyclohexene gave cyclohexene sulfide and with $P(OEt)_3$, $(EtO)_3P{=}S$ was formed [416].

8. Silicon-Tellurium

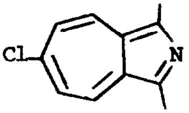
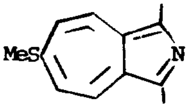
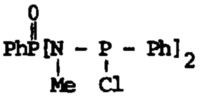
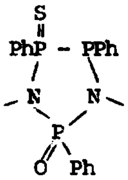
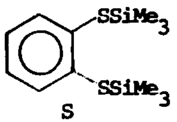
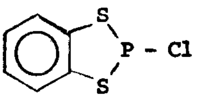
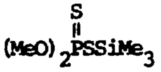
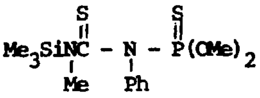
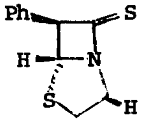
Addition of Te to PhMgBr gives PhTeMgBr which on addition of Me_3SiCl, gives three products (Eqn. 190). When MeOH is added to $PhTeSiMe_3$, PhTeH and $MeOSiMe_3$ are produced [418].

$$\mathrm{PhTeMgBr} + \mathrm{Me_3SiCl} \xrightarrow[\text{[417]}]{\text{THF}} \underset{(40\%)}{\mathrm{Me_3SiTePh}} + \underset{(10\%)}{\mathrm{(Me_3Si)_2Te}} + \underset{(45\%)}{\mathrm{Me_3SiO(CH_2)_4TePh}} \qquad (190)$$

VIII. Silicon-Halogen and Silicon Pseudohalogen

Most silafunctional derivatives are formed from chlorosilanes (many are commercially available) and several examples appeared in previous sections. The sequence followed in this section will be: 1. Methods of Formation of Halosilanes, 2. Applications of Halosilanes in Synthesis and 3. Formation and Chemistry of Pseudohalides.

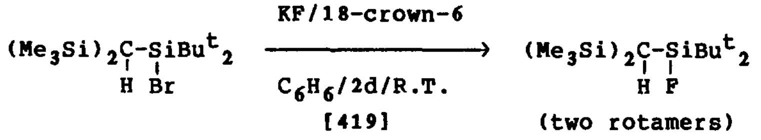
TABLE XIII. Cleavage of Silicon-Sulfur Bonds

Silicon-Sulfur Derivative	Corectant	Product	%	Ref
Me_3SiSPh	$PhCH_2Br$	$PhCH_2SPh$	97	406
	$WCl_4(SMe_2)_2$	$Me_2SCl_3W(\mu\text{-}SPh_2)WCl_3(SMe_2)$	13	407
Me_3SiSMe				408
	$GaCl_3$(1 eq)	Cl_2GaSMe	67	409
	$GaCl_3$(0.5 eq)	$ClGa(SMe)_2$	99	409
	$GaBr_3$(0.3 eq)	$Br_3Ga_2(SR)_3$	94	409
	$GaCl_3$(0.3 eq)	$Ga(SMe)_3$	87	409
$Me_3Si)_2S$	 $PhP(=O)[N(Me)-P(Cl)-Ph]_2$		54	410
	$M(OEt)_5/Et_4N^+Cl^-$	$(Et_4N)_4[M_6S_{17}]\cdot 3S^a$		411
	PCl_5			412
 $(MeO)_2P(=S)SSiMe_3$	MeN=C=NPh	 $Me_3SiN(Me)C(=S)-N(Ph)-P(=S)(OMe)_2$		413
$PhC\equiv CSSiMe_3$	 /CsF		55	414
$Me_2Si(SEt)_2$	$(MeO)_2CHR$	RCH(OMe)(SEt)		415

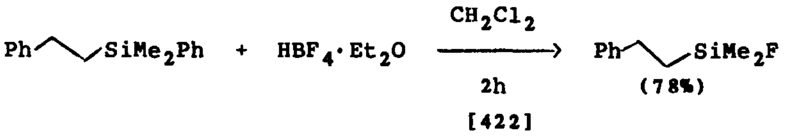
a. M=Nb,Ta; S=CH_3CN

1. Synthesis of Silicon-Halogen Bonds

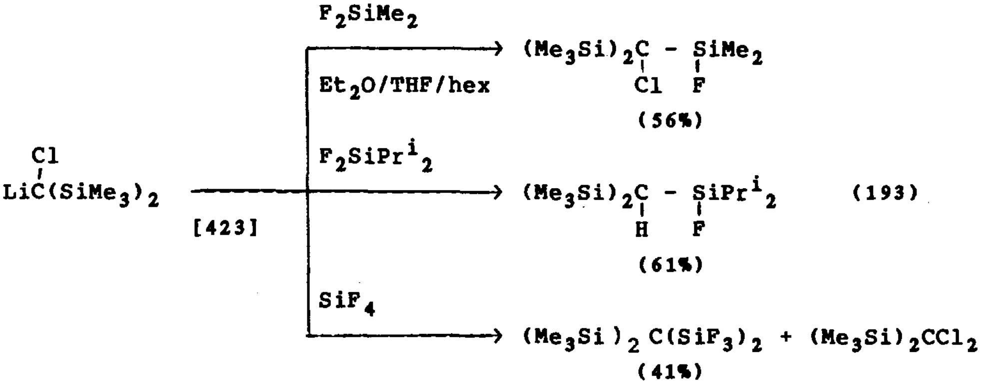
Silyl fluorides can be prepared from bromosilanes with KF/crown in C_6H_6 (Eqn. 191). When Me_3SiCl reacts with $AgBF_4$ in CH_3CN, Me_3SiF and $F_3B\cdot NCMe$ are formed and not the adduct $[Me_3SiNC{=}CMe]^+BF_4^-$ as originally proposed [420]. The difunctional dihydrosilane, RR^1SiH_2 (R, R^1 = Et, Vin) reacts with SbF_3 to give RR^1SiHF and then RR^1SiF_2. The yield of RR^1SiHF passes through a maximum [421]. Phenyl groups are cleaved from RMe_2SiPh by $HBF_4\cdot Et_2O$. An example is given in Eqn. 192 [422]. Partial substitution of fluorosilanes with organolithium reagents or Grignard reagents provides fluorosilanes as shown in Eqns. 193 and 194. Formation of a thia-silacyclooctane with exocyclic fluorine substituents is shown in Eqn. 195.



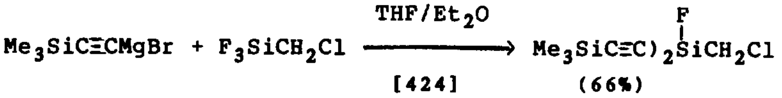
$$(Me_3Si)_2\underset{H}{C}-\underset{Br}{Si}Bu^t_2 \xrightarrow[C_6H_6/2d/R.T.\ [419]]{KF/18\text{-}crown\text{-}6} (Me_3Si)_2\underset{H}{C}-\underset{F}{Si}Bu^t_2 \quad \text{(two rotamers)} \qquad (191)$$



(192)

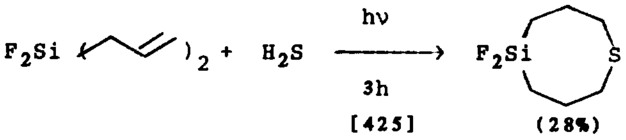


(193)



$$\mathrm{Me_3SiC{\equiv}CMgBr + F_3SiCH_2Cl \xrightarrow[\text{[424]}]{\text{THF/Et}_2\text{O}} Me_3SiC{\equiv}C)_2\overset{F}{Si}CH_2Cl}$$

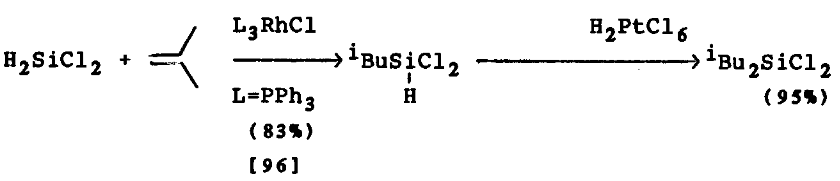
(66%) (194)



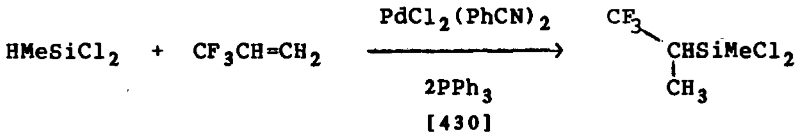
(195)

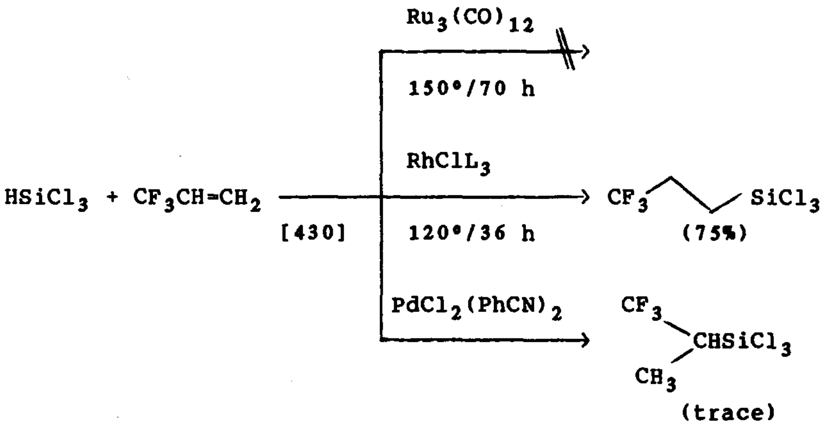
The reaction of MeCl with Si-Cu and added Sb catalyst provides a product mixture which consists of Me_2SiCl_2 (78%), $MeSiCl_3$ (18%) and Me_3SiCl (3%) [426]. Chlorination of R_2SiH_2 by CCl_4 occurs in the presence of $PdCl_2$ to give R_2SiCl_2 [R=^{i}Pr(76); ^{t}Bu(88%); ^{t}Bu(86%)] [96]. Addition of a 5 molar excess of ICl to $^tBu_3SiH$ gives $^tBu_3SiCl$ in 85% yield [427]. A Si-C bond in Me_4Si is cleaved by CCl_4 in the presence of 5 mol % I_2 to give Me_3SiCl in 100% yd. after 20 h at 30° [428]. The three component system $(Et_2N)_3P/CF_3Br/Me_nSiCl_{4-n}$ gives $MeSiCl_2CF_3$ and $MeSiCl(CF_3)_2$ [429].

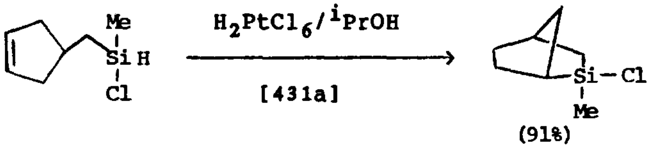
Addition of HSiCl< derivatives to olefins produces new chlorosilanes. Several different metal catalysts have been employed for this process. Reaction of H_2SiCl_2 with $RCH{=}CH_2$ (H_2PtCl_6 catalyst) provides the dichlorosilanes, $R^1_2SiCl_2$ [R^1=Et(77%); Pr(91%) and Bu(90%)] [96]. However, addition to $Me_2C{=}CH_2$ can be made to occur stepwise with appropriate choice of catalyst [Eqn. 196). The reaction of hydrosilane with trifluoropropene gives α-product as shown in Eqn. 197, but the catalyst can drive the reaction to the β-product (Eqn. 198). Bicycloheptane derivatives are formed from an intramolecular hydrosilylation process (Eqn. 199). Gas phases thermolysis of $HSiCl_3/Cl_3C_2H$ mixtures provide several products including $Cl_3SiCH{=}CCl_2$ and $Cl_3SiC{\equiv}CSiCl_3$ [431b]. Tetrasubstituted silanes, $R_2SiR^1_2$ undergo redistribution reactions in the presence of $HSiCl_3$ when H_2PtCl_6 is added. The smallest and least hindered R group migrates [431c].



(196)


(197)


(198)


(199)

Bromosilanes have been prepared from bromination of hydrosilanes (Eqn. 200) or siloxanes (Eqn. 201) or from a disilane and EDB (Eqn. 202). Addition of ICl to $TsiSiMe_2H$ in MeOH gives $TsiSiMe_2I$ (100%) yield but if the reaction is performed in CCl_4, both $TsiSiMe_2I$ and $TsSiMe_2Cl$ are formed in 77% and 23% yield respectively [433].

$$(Me_3Si)_2CHSiHBu^t_2 \xrightarrow[0° \; [419]]{Br_2/CCl_4} \underset{(100\%)}{(Me_3Si)_2CHSiBrBu^t_2} \qquad (200)$$

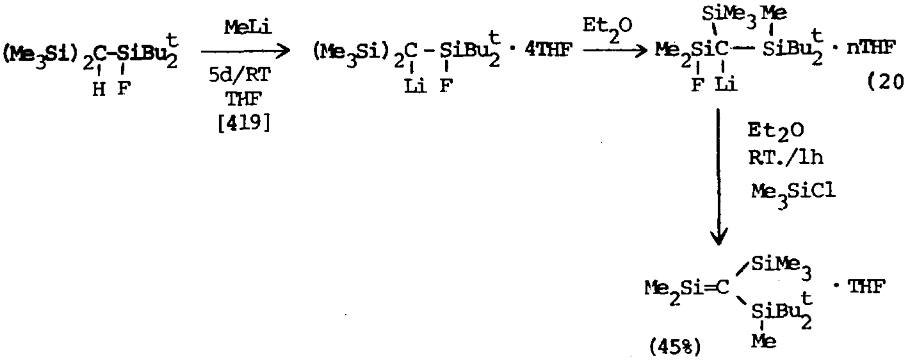
$$Me_3SiOSiMe_3 + Br_2 \xrightarrow[[432]]{PPh_3} \underset{(96\%)}{BrSiMe_3} \qquad (201)$$

$$\text{Me}_2\text{SiH}\!\!+_2 + \text{BrCH}_2\text{CH}_2\text{Br} \xrightarrow[{[431a]}]{\text{Ph}\overset{}{\underset{O}{C}}\text{O}\text{O}\underset{O}{C}\text{Ph}} \underset{(68\%)}{\text{BrMe}_2\text{SiH}} \qquad (202)$$

2. Applications of Halosilanes in Synthesis

Silaethenes have been generated from halosilanes by reaction with alkali metals (Eqn. 203) or from LiF elimination in the unit >Si(F)C(Li)< (Eqn. 204). This latter reaction is facilitated by the presence of Me_3SiCl.

$$\text{ClSiMe}_2\text{CH}_2\text{Cl} \xrightarrow[\substack{280\text{-}300^\circ \\ [434]}]{\text{K/Na}} \text{Me}_2\text{Si{=}CH}_2 \qquad (203)$$

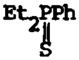
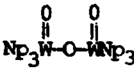
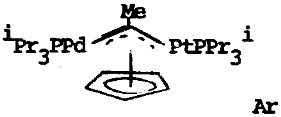
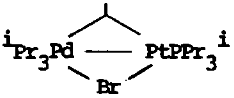
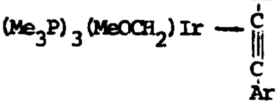
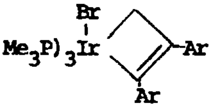


(204)

Several examples of the use of Me_3SiX in inorganic syntheses are shown in Table XIV. Most frequently the halosilane is used as a source of halogen although it may serve the purpose of water sponge as in the case of $Np_3W(O)OW(O)Np_3/Me_3SiCl$ to give $OWNp_3Cl$ [442]. The reduction potentials of Me_3SiX were measured in PhOMe and DMF and correlated with quantum chemical calculations [445].

Silyl halides are also employed in organic syntheses as shown in Table XV. In addition to the ether cleavage reactions in this Table a mild method for cleavage of methoxymethyl ethers with Me_3SiBr has been demonstrated [461]. Other functional groups such as esters, alkyl or silyl ethers and amides are stable in the presence of Me_3SiBr. The combination, $Me_3SiCl/NaI/Et_3N/MeCN$, has been used to replace MeO by H in the synthesis of 7b-methyl-7bH-cyclopent[c,d]indene [462]. Epoxides are converted to alcohols by

TABLE XIV. Use of Halosilanes in Inorganic Synthesis

Inorganic Reagent	Halosilane	Product	%	Ref
Main Group				
O=NOR	Me_3SiCl	O=NCl	95	435
	Me_3SiBr	O=NBr		
EtPhPSEt	Me_3SiI	 $Et_2\overset{}{P}(=S)Ph$	84	436
		$Et_3PPh^+I^-$	15	
$MeArSeNSO_2Ph$	Me_3SiCl	$MeArSeCl_2$	37	437
IF_5	Me_nSiF_{4-n}	$MeIF_4$		438
Transition Metals				
$Mo_2(O_2CCF_3)_4$	Me_3SiCl/C_2H_5CN	$Mo_2(O_2CCF_3)_2(C_2H_5CN)_2Cl_2\cdot$ $Mo_2(O_2CCF_3)_3(C_2H_5CN)Cl$		439
	$Me_3SiCl/SS\cdot dppb$[a]	$Mo_2Cl_4(S,S\text{-}dppb)_2$		440
	$Me_3SiCl/dppe$[b]	$\alpha\text{-}Mo_2Cl_4(dppe)_2$	40	441
	$Me_3SiCl/dppe$[c]	$\beta\text{-}Mo_2Cl_4(dppe)_2$	30	441
 $Np_3W(=O)\text{-}O\text{-}W(=O)Np_3$[d]	$MeSiCl/HCl$[e]	$WONp_3Cl$		442
$TaCl_3[N(SiMe_3)_2]_2$	Me_3SiBr	$\{TaBr_2(NSiMe_3)[N(SiMe_3)_2]\}_2$	25	443
	Me_3SiBr		95	444a
	Me_3SiBr			444b

a. S,S-dppb = $Ph_2PCH(CH_3)CH(CH_3)PPh_2$ b. toluene c. THF

d. $Np=Me_3CCH_2^-$ e. SiCl is a water sponge

TABLE XV. Use of Halosilanes in Organic Synthesis

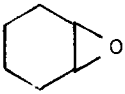
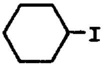
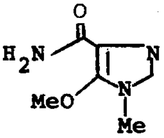
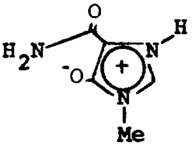
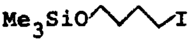
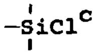
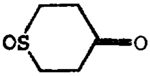
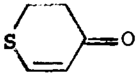
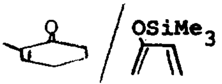
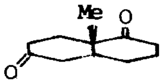
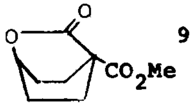
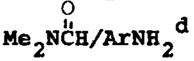
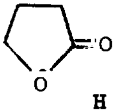
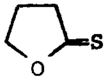
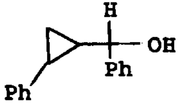
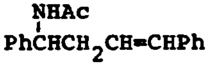
Organic Substrate	Halosilane	Product	%	Ref.
Ether Cleavage				
	Me_3SiCl/NaI		93	446
	Me_3SiCl/NaI + $(Me_2SiH)_2O$		75	447
	$Me_3SiCl/LiBr$ + $(Me_2SiH)_2O$		69	447
	Me_3SiF		60	448
THF	Me_3SiI/KI[a]			449
$CH_2(OMe)_2/(nBu)_2CHOH$	Me_3SiI	$^nBu_2CHOCH_2OMe$	80	450
Elimination of Water				
$PhCH_2CH{=}NOH$	$Me_3SiI/(Me_3Si)_2NH$	$PhCH_2CN$	84	451
$Ph_2C{=}NOH$	Me_3SiI	 $PhNH\overset{\overset{O}{\Vert}}{C}Ph$	80	451
$ArNHCO_2Ph$	Me_3SiCl/NEt_3	ArNC		452
 $R\overset{\overset{O}{\Vert}}{C}NHOH$[b]	 $-\underset{\vert}{\overset{\vert}{Si}}Cl$[c]	RNCO		453
	Me_3SiCl		86	454
Miscellaneous Reactions				
	Me_3SiI		40	455
	Me_3SiI		90	456
$R_2NCO_2CH_2Ph$	Me_3SiI	$R_2NH_2{}^+I^-$	70	457
 $Me_2N\overset{\overset{O}{\Vert}}{C}H/ArNH_2$[d]	Me_3SiI	ArNHCH=NAr		458

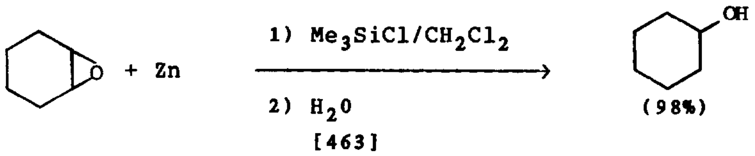
TABLE XV. (Cont.) Use of Halosilanes in Organic Synthesis

Organic Substrate	Halosilane	Product	%	Ref
Miscellaneous Reactions				
	1) LiNPr$_2^i$/Me$_3$SiCl 2) H$_2$S			459
	Me$_3$SiCl/AgBF$_4$/CH$_3$CN	 $\overset{NHAc}{PhCH}CH_2CH{=}CHPh$		460

a. No reaction in absence of KI b. R=Me, Me$_2$CHCH$_2$, Ph

c. PhSiCl$_3$, PhMeSiCl$_2$ or Me$_2$SiCl$_2$

d. Ar=C$_6$H$_5$, ClC$_6$H$_4$, C$_6$H$_4$Me, C$_6$H$_4$OMe the combined reagents Me_3SiCl/Zn (Eqn. 205). Oxidative cleavage of alkenylfluorosilanes provides a route to ketones (Eqn. 206).



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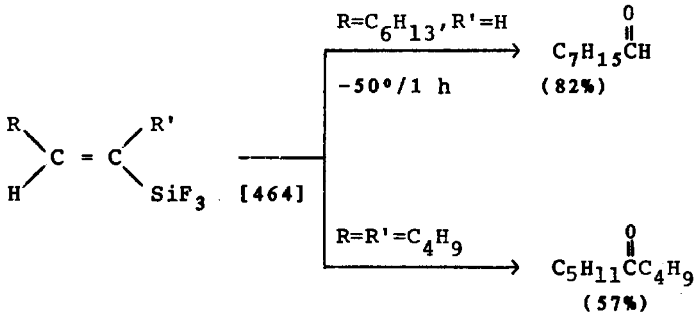
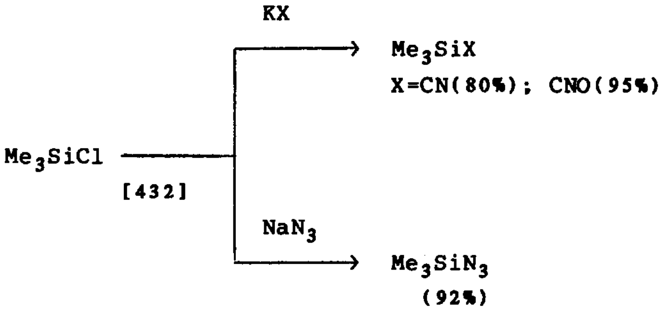


(206)

3. Formation and Chemistry of Pseudohalides

The usual method of formation of silyl pseudohalides is the reaction of a halosilane with a salt and several examples are shown in Eqns. 207-209. Trimethylsilyl cyanide has been prepared from $(Me_3SiO)_2SO_2$ (molten) and KCN in 67% yield [466]. A cyanate to isocyanate isomerization occurs when $(Me_3Si)_3CSiMe_2OCN$ is heated in diphenyl ether (195°C) [467]. Methyltricyanosilane is generated "in situ" from $MeSiCl_3$ /KCN/NaI/py in CH_3 CN [468].



(207)

$$\begin{tikzcd}[column sep=large] & {}^{t}Bu_3SiN_3 \; (74\%) \\ {}^{t}Bu_3SiI \arrow[ur, "NaN_3", "MeOH/84\ h"'] \arrow[dr, "KSCN", "MeOH/12\ h"'] \arrow[r, phantom, "{[427]}"] & \\ & {}^{t}Bu_3SiNCS \; (85\%) \end{tikzcd} \qquad (208)$$

$${}^{t}BuMe_2SiCl + NH_4SCN \xrightarrow[{[465]}]{} {}^{t}BuMe_2SiNCS \qquad (209)$$

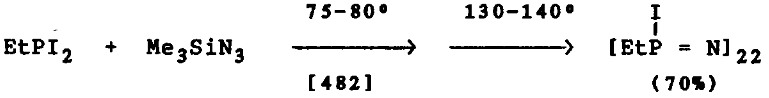
Silicon pseudohalides add to carbonyl groups and cleave ether-type linkages and these processes are shown in Table XVI. Examples of transfer and cleavage of the pseudohalogen in inorganic systems are shown in Eqns. 210-214.

$$\underline{mer}\text{-}CoMe_3L_3 + Me_3SiN_3 \xrightarrow[12\ h/R.T.\ [481]]{Pet.\ Ether} Me_4Si + \underline{mer}\text{-}CoMe_2(N_3)L_3 \; (60\%) \qquad (210)$$

$L=PMe_3$

$$\underline{fac}\text{-}RhMe_3L_3 + Me_3SiN_3 \xrightarrow[12\ h\ [481]]{toluene} RhMe_2N_3L_3 \qquad (211)$$

$L=PhMe_3$



$$EtPI_2 + Me_3SiN_3 \xrightarrow[{[482]}]{75-80°} \xrightarrow{130-140°} [Et\overset{I}{\overset{|}{P}} = N]_{22} \; (70\%) \qquad (212)$$

TABLE XVI. Uses of Pseudohalogens in Organic Synthesis

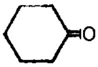
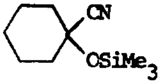
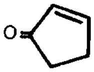
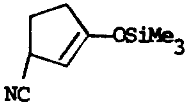
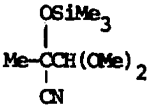
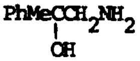
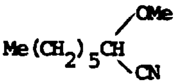
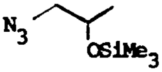
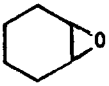
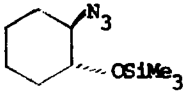
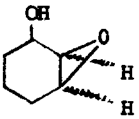
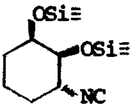
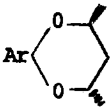
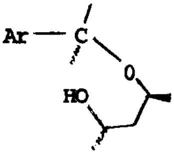
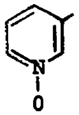
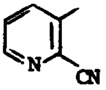
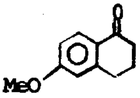
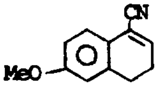
Organic Substrate	Silyl Pseudohalogen	Product	%	Ref
Addition to Carbonyls				
Me_2CO	Me_3SiCN/ZnI_2	$Me_2C(OSiMe_3)CN$	95	466
	Me_3SiCN/ZnI_2		75	466
	Me_3SiCN			469
 $Me\overset{O}{\overset{\|}{C}}CH(OMe)_2$	Me_3SiCN	 $Me-\underset{CN}{\overset{OSiMe_3}{C}}CH(OMe)_2$	83	470
	KCN/18-crown-6			
PhMeC=O	1) $MeSi(CN)_3$ 2) $LiAlH_4$	 $PhMe\underset{OH}{C}CH_2NH_2$	75	468
$4\text{-}RC_6H_4CHO^a$	$Me_3SiN_3/ZnCl_2$	$4\text{-}RC_6H_4CN$		471
Addition to Ethers, Acetals and Oxirane				
$Me(CH_2)_5CH(OMe)_2$	Me_3SiCN^b		89	472
$(RO)_4C^b$	Me_3SiCN	$(RO)_3CCN$	73-85	473
	$Me_3SiN_3/Ti(OPr^i)_4$		77	474
	$Me_3SiN_3/Ti(OPr^i)_4$			474
	Me_3SiCN/ZnI_2		71	475
 c	$Me_3SiCN/TiCl_4$		97.5	476

TABLE XVI. (Cont.) Uses of Pseudohalogens in Organic Synthesis

Organic Substrate	Silyl Pseudohalogen	Product	%	Ref
Miscellaneous				
$^{i}PrHC(SEt)_2$	$Me_3SiCN/SnCl_4$	$^{i}PrHC(SEt)CN$	93	477
$Et_2C(SEt)_2$	$Me_3SiCN/SnCl_4$	$Et_2C(SEt)CN$	78	477
 $Ph\overset{O}{\|}{C}Cl$	$Me_3SiCN/SnCl_4$	 $Ph\overset{O}{\|}{C}CN$	91	478
	 $Me_3SiCN/Me_2N\overset{O}{\|}{C}Cl$		90	479
	1) Me_3SiCN/BF_3 2) $POCl_3$			480

a. R=H,Me,OMe,Cl   b. electrolysis

c. R=Me,Et,Pr,^{i}Pr,Bu,^{i}Bu,$Me_2CH(CH_2)$ -

d. Ar=m-PhCOC$_6$H$_4$

$$Me_3SiCN \xrightarrow{[483]} \begin{cases} \xrightarrow[-80°]{SCl_2} Me_3SiCl + \underset{(82\%)}{S(CN)_2} \\ \xrightarrow[-80° \to 5-10°]{S_2Cl_2} \underset{(68\%)}{Me_3SiCl} + \underset{(68\%)}{S(CN)_2} + \underset{(72\%)}{Me_3SiSCN} \end{cases} \quad (213)$$

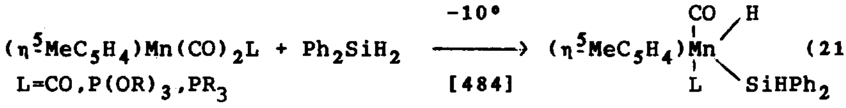
$$Me_3SiCN + SO_3 \xrightarrow[{[483]}]{} \underset{(72\%)}{Me_3SiO)_2SO_2} + SO_2 + (CN)_2 \quad (214)$$

IX. SILICON-METAL, SILICON-METALLOID, SILYL-SUBSTITUTED LIGANDS

The chemistry of derivatives that contain both silicon and metal atoms will be covered in the sequence: 1. Silicon-Transition Metal Bonds; 2. Silylmethyl ligands; 3. Silyl-substituted Ligands

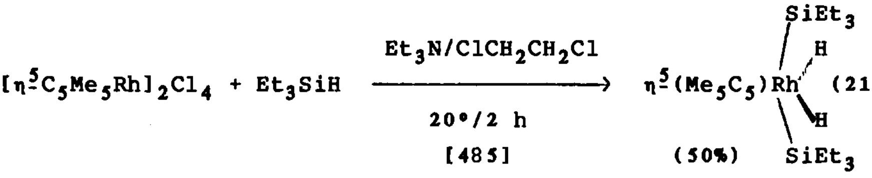
1. Silicon-Transition Metal Bonds

Hydrosilylation of metals can provide products of oxidative addition with formation of both metal-hydrogen and metal-silicon bonds. Examples have been reported for manganese (Eqn. 215), rhodium (Eqn. 216) and iridium (Eqn.s 217, 218). Exchange of hydrosilanes at cobalt centers has been demonstrated and is shown in Eqns. 219,220.

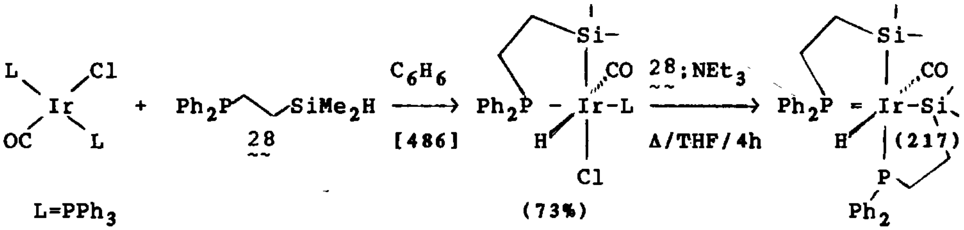


$$(\eta^5\text{-}MeC_5H_4)Mn(CO)_2L + Ph_2SiH_2 \xrightarrow[{[484]}]{-10°} (\eta^5\text{-}MeC_5H_4)Mn(CO)(L)(H)(SiHPh_2) \quad (215)$$

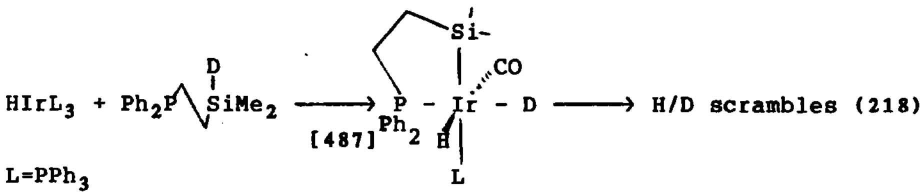
$L=CO, P(OR)_3, PR_3$



$$[\eta^5\text{-}C_5Me_5Rh]_2Cl_4 + Et_3SiH \xrightarrow[\substack{20°/2\ h \\ [485]}]{Et_3N/ClCH_2CH_2Cl} \underset{(50\%)}{\eta^5\text{-}(Me_5C_5)Rh(H)_2(SiEt_3)_2} \quad (216)$$



(217)



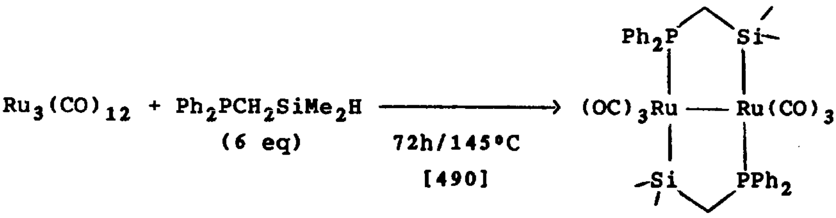
(218)

$$\begin{tikzcd}[column sep=large] R_3SiCo(CO)_4 \arrow[r, "h\nu", "25^\circ\ [488]"'] & {[R_3SiCo(CO)_3]} \arrow[r, "R^1{}_3SiH"] & {[R_3Si(R^1{}_3Si)HCo(CO)_3]} \arrow[d] \\ & & R^1{}_3SiCo(CO)_4 + R_3SiH \end{tikzcd} \quad (219)$$

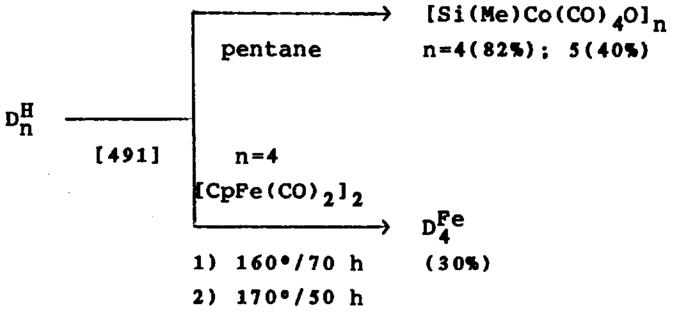
R=Me,Et,Ph

$\underline{cis}$-$\underline{mer}$-$HM(SiEt_3)(CO)_3L + Ph_3SiH \xrightleftharpoons{[489]}$ $\underline{cis}$-$\underline{mer}$-$HM(SiPh_3)(CO)_3L + Et_3SiH$
L=PPh$_3$ M=Fe,Ru (220)

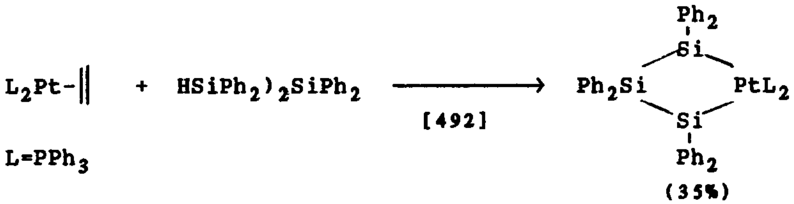
Several novel reactions of hydrosilanes have beeen reported in which the silyl group but not hydrogen is incorporated into the product. Examples include cleavage of metal-metal bonds in polynuclear carbonyls (Eqns. 221 and 222) and displacement of unsaturated hydrocarbons (Eqns. 223 and 224) from nickel triad metals.



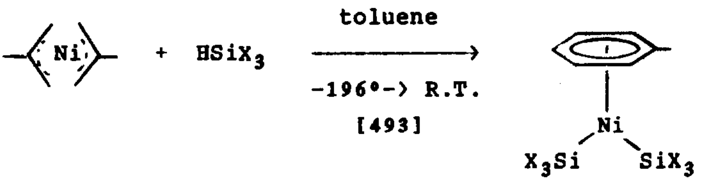
(221)



(222)

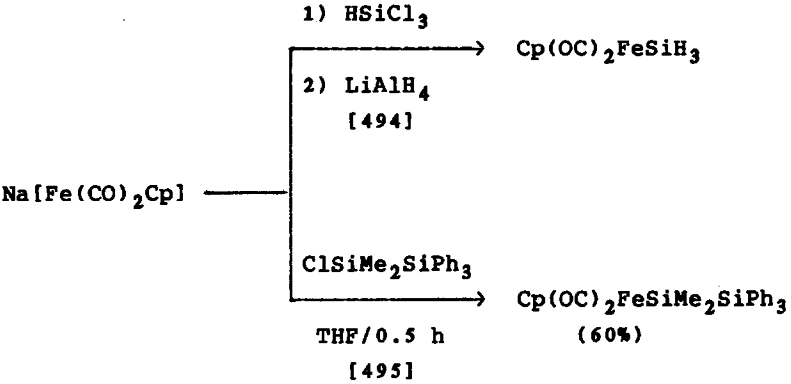


(223)



(224)

Metal carbonyl anions condense with chlorosilanes to provide silicon-metal bonded derivatives as shown in Eqns. 225-227. The reverse strategy of reacting a silyllithium reagent with a metal chloride is also successful (Eqn. 228).



$$Na[Fe(CO)_2Cp] \xrightarrow[\text{2) } LiAlH_4 \text{ [494]}]{\text{1) } HSiCl_3} Cp(OC)_2FeSiH_3$$

$$Na[Fe(CO)_2Cp] \xrightarrow[\text{THF/0.5 h [495]}]{ClSiMe_2SiPh_3} Cp(OC)_2FeSiMe_2SiPh_3 \text{ (60\%)}$$

(225)

$$CpRe(CO)(NO)H + BuLi \xrightarrow[\text{[496]}]{} CpRe(CO)(NO)Li \xrightarrow{Me_3SiCl} CpRe(CO)(NO)SiMe_3 \qquad (226)$$

$$K[Ru(C_5Me_5)(CO)_2] + HSiCl_3 \xrightarrow[\text{40 h [497]}]{\underline{c}-C_6H_{12}} C_5Me_5(OC)_2RuSi(H)Cl_2 \text{ (13\%)} \qquad (227)$$

$$M_2Cl_2(NMe_2)_4 + \underset{(2\ eq)}{(THF)_3LiSi(SiMe_3)_3} \xrightarrow[1h/R.T.]{hex} M_2[Si(SiMe_3)_3]_2(NMe_2)_4 \quad (228)$$

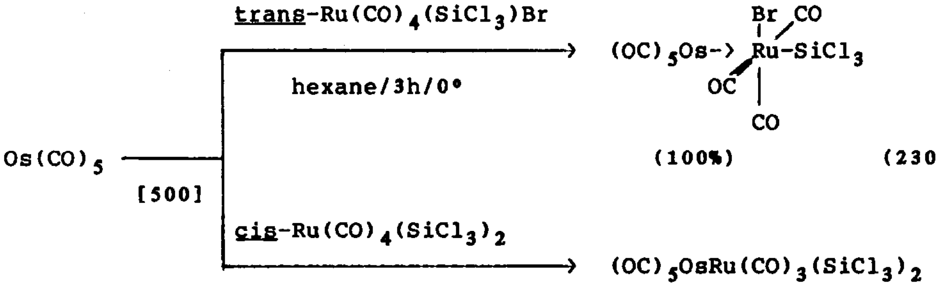
M=Mo(23%); W(25%)

[498]

There are several variations on the reactivity of organometallic derivatives of silicon. In metal carbonyl derivatives a CO ligand may be substituted without cleavage of the silicon-metal bond (Eqns. 229-231). Carbonyl anions may be alkylated without loss of the silicon substituent (Eqn. 232,233).

$$\underset{L=PPh_3}{Ru(CO)_3L(SiCl_3)_2} \xrightarrow[CH_2Cl_2/R.T./72h]{^{13}CO\ (2\ atm)} Ru(CO)_2(^{13}CO)L(SiCl_3)_2 \quad (229)$$

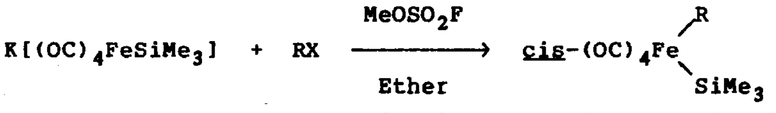
[499]



(230)

$$Cp(OC)_2FeSiH_3 + L \xrightarrow[{[494]}]{h\nu} Cp(CO)LFeSiH_3 \quad (231)$$

L=MeNC(39%); ${}^tBuNC(22\%)$



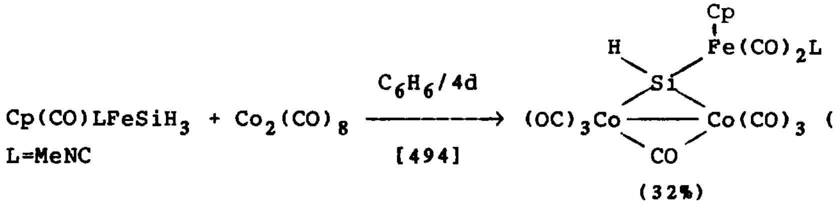
$$K[(OC)_4FeSiMe_3] + RX \xrightarrow[Ether]{MeOSO_2F} cis\text{-}(OC)_4Fe(R)(SiMe_3) \quad (232)$$

[501] R=Me(46%); Et(56%); $C_3H_5(34\%)$

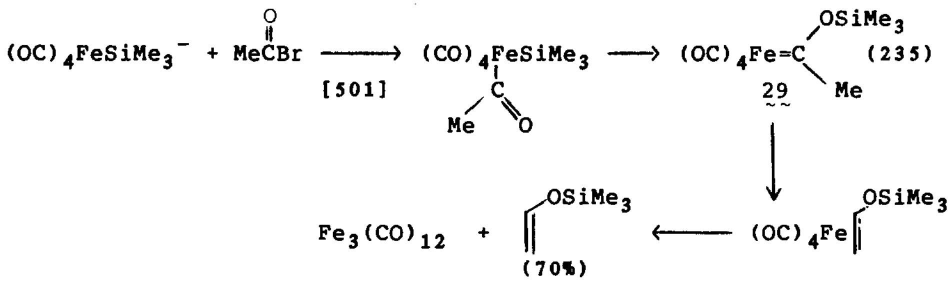
$$[(\eta^5\text{-}MeC_5H_4)(CO)_2SiPh_3Mn]^- + RX \xrightarrow{} \eta^5\text{-}MeC_5H_4Mn(CO)_2SiPh_3R \quad (233)$$

[502] R=Me(75%);Et(73%);$C_6H_5CH_2(56\%)$

The silyl group that is coordinated to the metal may undergo substitution chemistry without loss of the metal-silicon bond (Eqn. 234). However, a sequence of rearrangement steps involving coordinated silicon has been demonstrated as shown in Eqn. 235. If the α-carbon contains no hydrogens the carbene complex (**29**) is moderately stable.

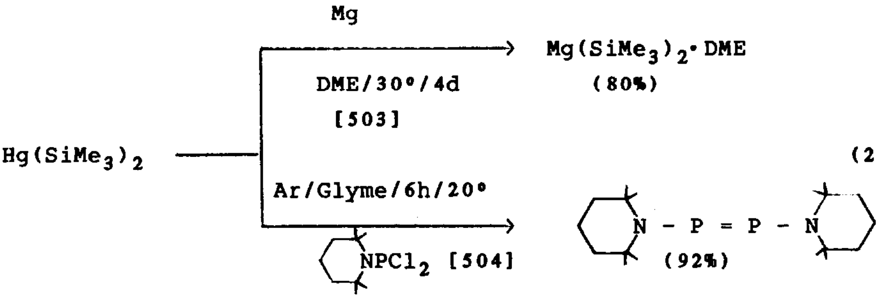


(234)

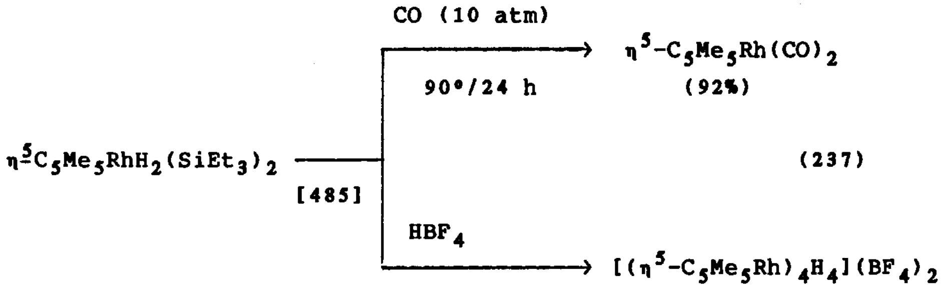


(235)

Several reactions of silylmetallic derivatives result in cleavage of the silicon-metal bond. Silyl mercury derivatives have been used for an improved synthesis of Me$_3$Si)$_2$Mg (silyl moiety transfers from one center to another) as well as in the synthesis of diphosphine (Eqn. 236). Electrolytic reduction of η^5-Cp(CO)$_2$FeSiPh$_3$ results in loss of SiPh$_3^-$ (observed as HSiPh$_3$) [505, 506]. Photolysis of *cis*-*mer*-HM(SiEt$_3$)(CO)$_3$L (L=2-methyltetrahydrofuran) at 100K resulted in reductive elimination (in part) of Et$_3$SiH to give M(CO)$_3$L and HM(SiEt$_3$)CO)$_2$L (M=Fe,Ru) [489]. The silicon-rhodium bond is cleaved by both CO and HBF$_4$ (Eqn. 237). Reductive elimination from a manganese center also occurs on addition of phosphine (Eqn. 238).

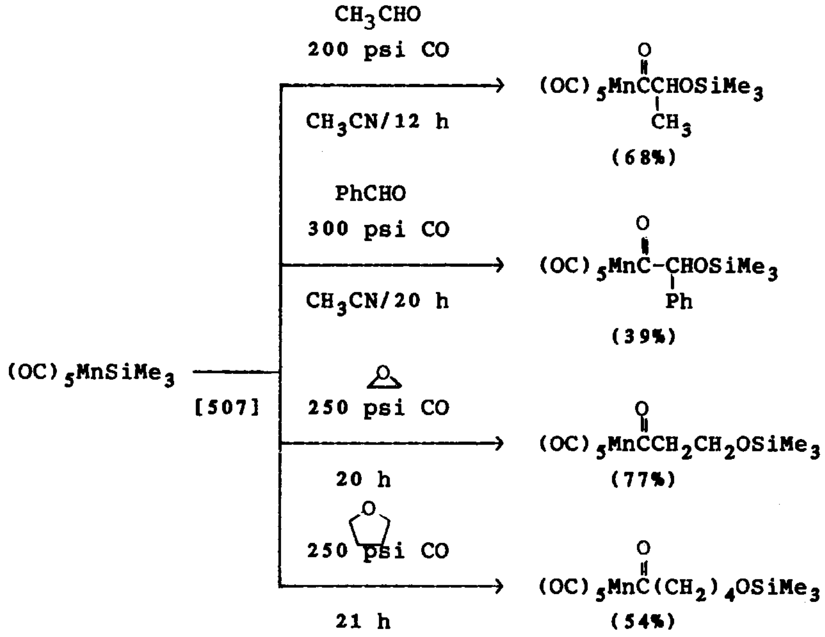


(236)

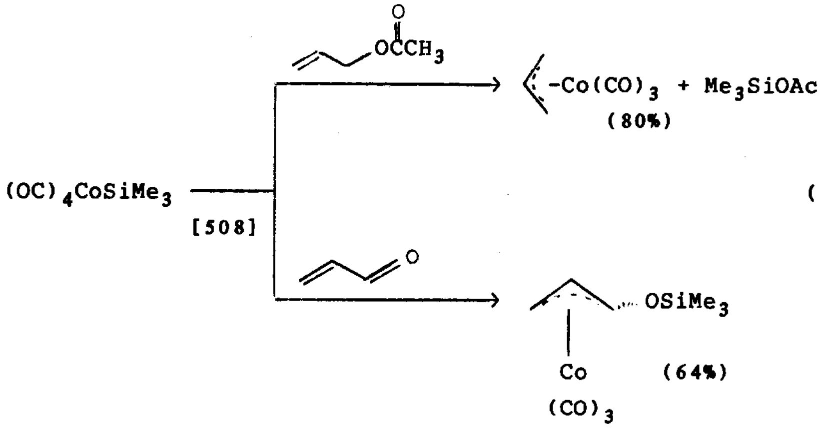


$$[\eta^5\text{-}C_5MeH_4Mn(CO)_2MeSiPh_3] + PPh_3 \xrightarrow[{[502]}]{C_6H_6/\Delta} \eta^5\text{-}C_5MeH_4Mn(CO)_2PPh_3 + RSiPh_3 \quad R=Me,H \qquad (238)$$

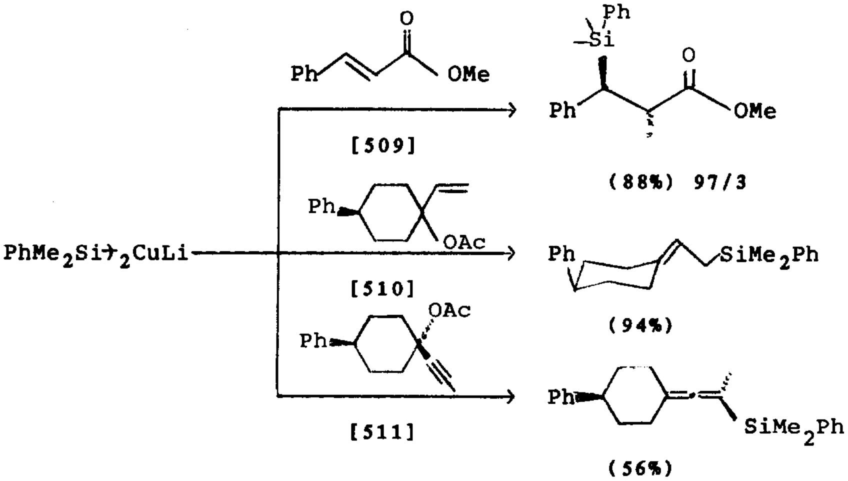
A mixture of aldehydes and CO or ether and CO inserts into the silicon manganese bond to provide manganese acyls (Eqn. 239) and a new synthesis of allylcobalt tricarbonyl utilizes cleavage of a silicon-cobalt bond (Eqn. 240). Silyl cuprates have been used in organic syntheses and examples are shown in Eqn. 241.



(239)



(240)



(241)

The kinetics of the reaction between $HFe(CO)_4SiCl_3$ and conjugated dienes has been determined. The reaction is first order in each reagent and probably occurs by H atom transfer (free radical mechanism) [512]. Addition of SiH to $RCH{=}CH_2$ is catalyzed by $Ph_3SiMn(CO)_5$. The catalyst is activated both thermally and photochemically but the product distribution differs in the two cases. On photolysis, $\geqslant SiCH_2CH_2R$ is formed exclusively whereas in the thermal activation alkenylsilanes and disilanes are formed in addition to the alkylsilane [513].

2. Silylmethyl Ligands

Improvements in the preparation of $(Me_3Si)_3CLi$ [from $(Me_3Si)_3CH$ and MeLi] have been summarized and include the use of MeLi generated from MeCl, removal of Et_2O (to leave THF) and destruction of excess MeLi by addition of Me_3SiOMe [514]. When $(Me_3Si)_3CH$ is added to powdered MeLi (THF/Δ/6h followed by 12 h at R.T.), solid $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ (65%) [515] forms. The same procedure has been used to prepare $[Li\{C(SiMe_2Ph)_3\}(THF)]$ (67%) [516]. Another route to α-silyl carbanions has been developed through reaction of $PhSCRR'SiMe_3$ with LiNaph. Equation 242 summarizes the preparation of phenylsulfides and conversion to the carbanion. Formation of phospinomethylsilanes is shown in Eqn. 243 and 244.

$$\begin{tikzcd}
PhSCH_2SiMe_3 \arrow[r, "1)nBuLi/THF/0°/0.5", "2)Me_3SiCl/1h\ [517]"'] \arrow[d, "2\ cycles\ 1)\ nBuLi\ 2)\ Me_3SiCl"'] & (Me_3Si)_2CHSPh\ (96\%) \arrow[r, "1)nBuLi", "2)RI"'] & (Me_3Si)_2CRSPh\ R=Me,Bu \arrow[d, "LiNaph\ THF/-78°"] \\
PhSC(SiMe_3)_3\ (52\%) \arrow[r, "LiNaph", "THF/-78°"'] & LiC(SiMe_3)_3 & LiC(R)(SiMe_3)_2
\end{tikzcd} \tag{242}$$

$$Me_{4-n}SiCl_n + LiCH_2PMe_2 \xrightarrow[{[518]}]{} Me_{4-n}Si(CH_2PMe_2)_n \tag{243}$$

n=1(72%); 2(38%); 3(31%); 4(40%)

$$Me_3SiCl + Ph_2PCH(Li)SiMe_3 \xrightarrow[{[519]}]{THF} Ph_2PCH(SiMe_3)_2\ (73\%) \tag{244}$$

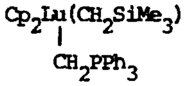
Many silylmethyl metal derivatives are formed by the reaction of $(Me_3Si)_xCH_{3-x}Li(MgX)$ with a suitable metal or metalloid derivative and examples are shown in Table XVII. There are more novel routes to silylmethyl ligand derivatives including exchange (Eqn. 245) and ring opening of a thoracyclobutane (Eqn. 246). A new silylmethyl substituted base has been prepared from 2-[bis-(trimethylsilyl)methyl]pyridine. Condensation with M^I derivatives gives dimeric derivatives as shown in Eqn. 247.

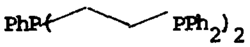
$$(Et_3Si)_2Hg + Me_{3-n}R_nSiCH_2Cl \xrightarrow[{[527]}]{} Me_{3-n}R_nSiCH_2)_2Hg \tag{245}$$

R = Cl, MeO

n = 0 -3

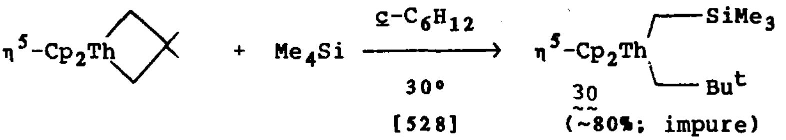
TABLE XVII. Reaction of Silylmethyl Organometallics with Metal and Metalloid Halides

$(Me_3Si)_xCH_{3-x}M$		Metal/Metalloid Halide	Product	%	Ref
X	M				
Main Group					
2	MgCl	$GeCl_2\cdot diox$	$\{[(Me_3Si)_2CH]_2Ge\}_2$		520
		$SbCl_3$	$(Me_3Si)_2CHSbCl_2$		521
		$AsCl_3$	$(Me_3Si)_2CHAsCl_2$		521
Transition Metal					
1	Li	IrCl(bdpp)[a]	$Me_3SiCH_2Ir(bdpp)$	48-59	522
1	MgCl	$LRuCl(PMe_3)_2$[b]	$LRuCH_2SiMe_3(PMe_3)_2$	73	523
3	Li	CuI	$[LiS_4]\{Cu[C(SiMe_3)_2)_2]_2\}$[c]	26	524
Lanthanide/Actinide					
1	Li	$Cp_2Lu(Cl)CH_2PPh_3$	 $Cp_2\underset{CH_2PPh_3}{Lu}(CH_2SiMe_3)$	83	525
1	Li	Cp_3ThCl	$Cp_3ThCH_2SiMe_3$	46	526

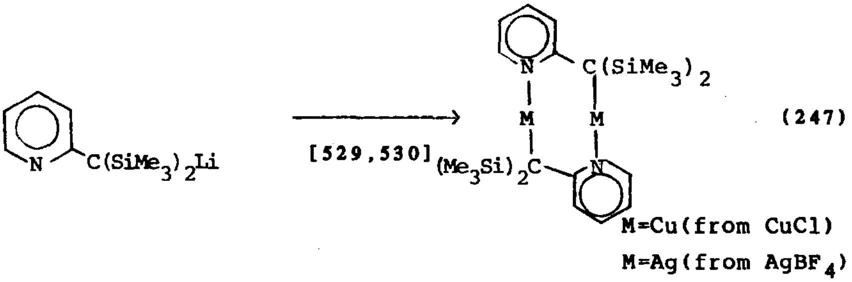
a. 

b. L= η^5-C_5Me_5

c. S = THF

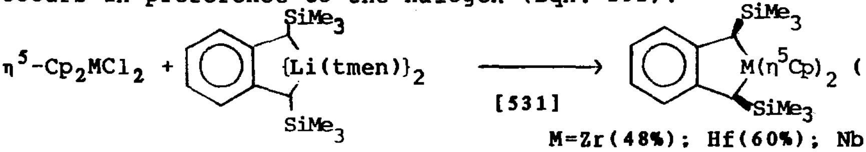


(246)



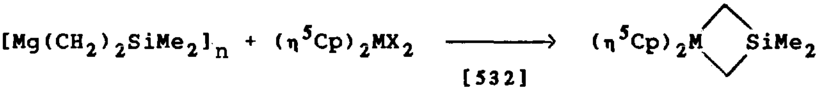
(247)

A variation of the reaction of silylmethyllithium reagents with metal halides produces both o-xylidene metal complexes (Eqn. 248) and 1-metalla-3-silacyclobutanes (Eqn. 249). Occasionally the reaction of $Me_3SiCH_2Li(MgR)$ gives unexpected cyclic products (Eqn. 250, 251) and in one case coupling with a coordinated carbonyl occurs in preference to the halogen (Eqn. 252).



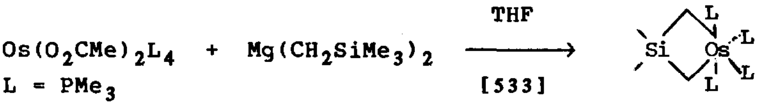
(248)

M=Zr(48%); Hf(60%); Nb(30%)



(249)

m=Ti(95%); Zr(44%);
Nb(48%); Mo(55%)



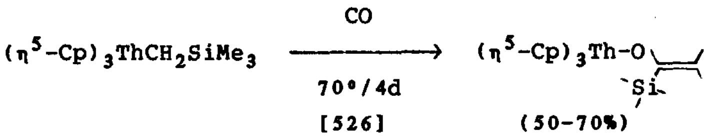
(250)

$$\underset{L=PPh_3}{IrClL_3} + \underset{(3\ eq)}{Me_3SiCH_2Li} \xrightarrow[2\ h\ [534]]{toluene} \overline{Ir(CHSiMe_3)(o\text{-}C_6H_4PPh_2})L \quad (251)$$

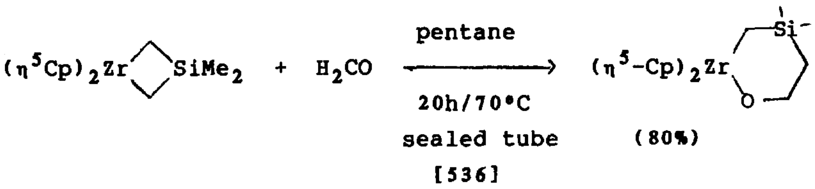
$$MoCl_2(CO)_2L_2 + Me_3SiCH_2MgCl \xrightarrow[-60\to R.T.]{Et_2O} MoCl(\eta^2\text{-}COCH_2SiMe_3)COL_3 \qquad (252)$$

L=PMe$_3$ 5 h   [535]   (60-70%)

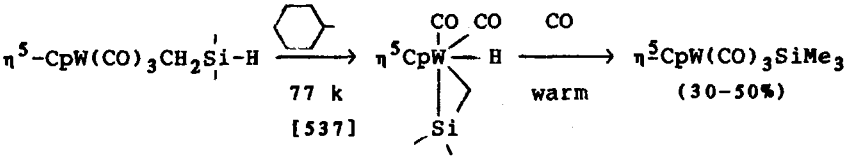
The reactions of silylmethylmetal derivatives can occur at the coordinated silylmethyl group (without loss of this group) or at the metal center without loss of the silylmethyl group. The thorium derivative, 30 (Eqn. 246) is converted to thorasilacyclobutane, $(\eta^5\text{-}Cp)_2\overline{ThCH_2SiMe_2CH_2}$ on heating at 30°C [528]. A migratory-insertion reaction occurs at the ThCH$_2$SiMe$_3$ group in the presence of CO (Eqn. 253) and insertion of paraformaldehyde into the Zr-C bond occurs in silazirconacyclobutane (Eqn. 254). One of the most novel reactions of a coordinated silylmethyl-substituent occurs in the photolysis of CpW(CO)$_3$CH$_2$SiMe$_2$H where spectroscopic results support a coordinated silene (Eqn. 255).



(253)

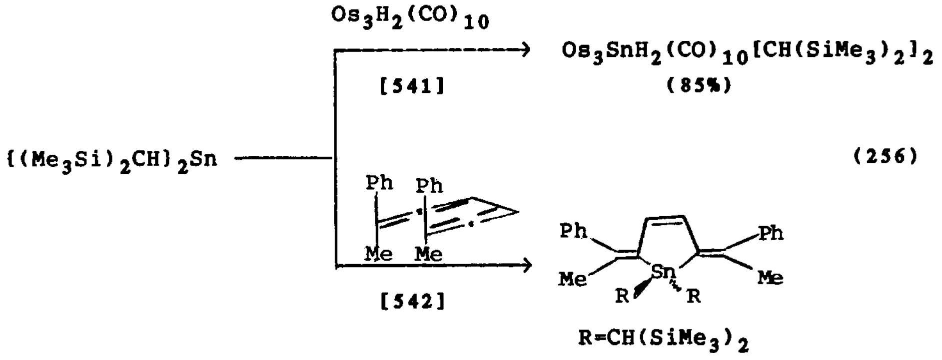


(254)

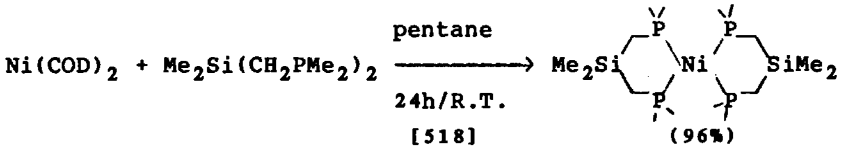


(255)

The reactions at the metal site in coordinated silylmethyl derivatives can be quite varied. When KH is added to Ga(CH$_2$SiMe$_3$)$_2$Br in glyme the complex, K[Ga(CH$_2$SiMe$_3$)$_2$H$_2$], 31, is isolated in 46% yield. Addition of Ga(CH$_2$SiMe$_3$)$_2$Br to 31 did not yield the hoped for Ga(CH$_2$SiMe$_3$)$_2$H [538]. When (Me$_3$Si)$_3$CSnMeCl$_2$ is treated with MeOK in MeOH/THF (reflux), cyclotristannoxane is produced (51% yield) [539]. The stannylene, $(Me_3Si)_2Sn$ reacts with 1,3-dienes to give 1,4-cycloadditions and with $Os_3H_2(CO)_{10}$ to give the first closed $SnOs_3$ cluster (Eqn. 256).



Substitution of metal-halogen bonds in $Mo_2Br_2R_4(R=CH_2SiMe_3)$ occurs on addition of LiOAr/py to give $Mo_2(OAr)_2R_4$ $(Ar=2,6\text{-}Me_2C_6H_3)$ [543]. When alkynes, RC≡CR (R=H,Me,Ph) are added to $W_2(\mu\text{-}CSiMe_3)_2R_4$ $(R=CH_2SiMe_3)$ coordination of the alkyne occurs in the first step followed by insertion of the alkyne into the bridging ligand to form $W_2(\mu\text{-}CSiMe_3)(\mu\text{-}C_3R_2SiMe_3)R_4$ [544]. Addition of bases such as PMe_3 to the homoleptic alkyl, $[Mn(CH_2SiMe_3)_2]_n$, results in depolymerization to the coordinated dimer, $Mn_2(CH_2SiMe_3)_4(PMe_3)_2$ [545]. Base exchange occurs when dmpe $(Me_2PCH_2CH_2PMe_2)$ is added to $Ni(CH_2SiMe_3)_2(py)_2$ to give $Ni(CH_2SiMe_3)_2dmpe$ in almost quantitative yield [546]. Coordination of silylmethylphosphines to both Ni and Rh centers have been reported (Eqns. 257 and 258).

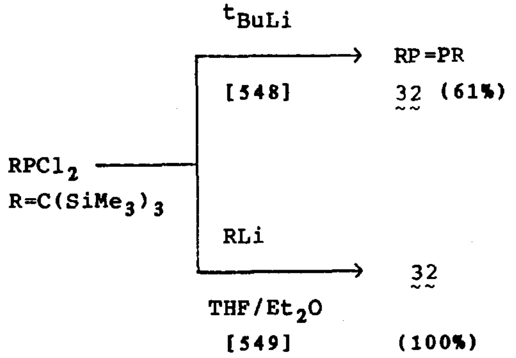


(257)

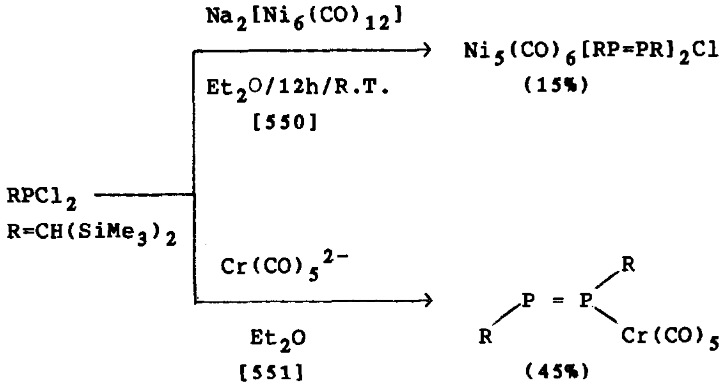
$$[\{RhCl(COD)\}_2] + \underset{R=CH(SiMe_3)_2}{ClPR_2} \xrightarrow[25°]{\text{toluene}} \underset{(54\%)}{(COD)ClRh(ClPR_2)_2} \quad (258)$$

[547]

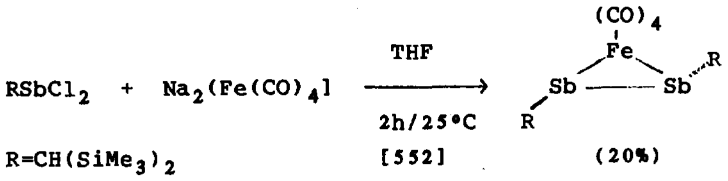
One of the major uses of the $-CH(SiMe_3)_2$ or $-C(SiMe_3)_3$ ligand is to stabilize diphosphines (distibenes, etc.). An approach to these El=El (El=P,Sb) systems is through the reaction of an organolithium or silyllithium reagent with $RPCl_2$ as shown in Eqn. 259. If a metal carbonyl anion is employed, derivatives where the metal portion is coordinated to the El=El unit are formed (Eqns. 260 and 261). When $RSbCl_2$ [$R=CH(SiMe_3)_2$] is treated with Mg/THF the cyclic polystibines, $(RSb)_3$ and $(RSb)_4$ are formed in a manner reminiscent of the condensation of R_2SiCl_2 with alkali metals [553].



(259)

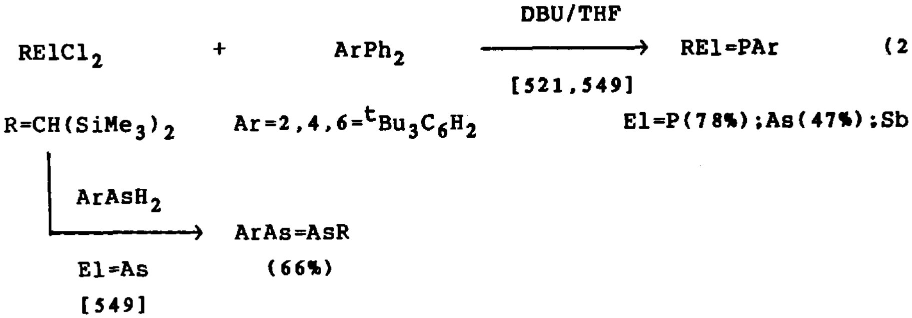


(260)



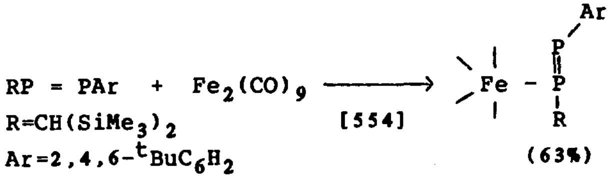
(261)

Unsymmetrical El=El' systems can be prepared from the reactions of $RElCl_2$ and $R'ElH_2$ as shown in Eqn. 262.

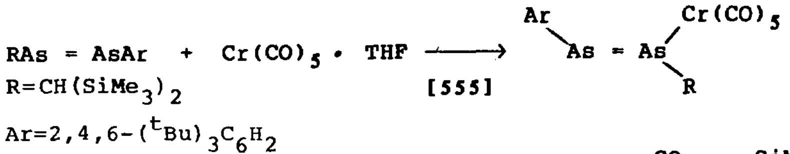


(262)

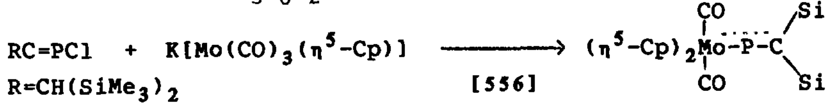
Coordination of El=El' to metals has been actively pursued. The possible coordination of $Me_2Si=CH_2$ is outlined in Eqn. 263 and examples from El=Group V are shown in Eqns. 264 and 265. Formation of a phosphavinyldiene-molybdenum complex is suggested for the product in the condensation reaction shown in Eqn. 266.



(263)

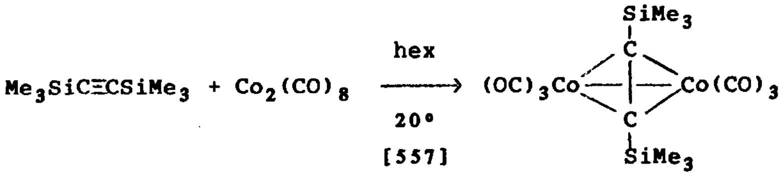


(264)



(265)

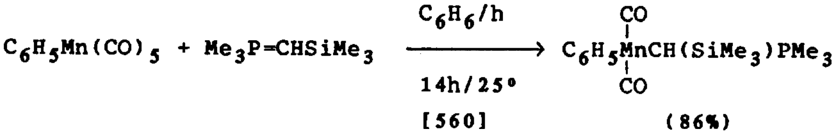
There are a few examples of silicon-carbon-metal sequences that are not silylmethyl derivatives but where the carbon is formally tetrahedral. These miscellaneous examples are shown in Eqns. 266 through 269.



(266)

$$\mathrm{Me_3SiCCo_3Cp_3CH + AgPF_6 \xrightarrow[\mathrm{CH_2Cl_2/10\ min}\ [558]]{\mathrm{NH_4PF_6}} [Me_3SiCCo_3Cp_3CH]^+PF_6^-} \quad (267)$$

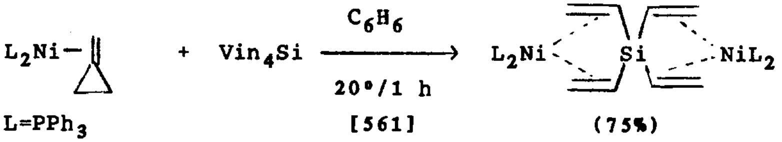
$$\mathrm{(Me_3Si)_2C_2B_4H_6 + Os_3(CO)_{12} \xrightarrow[[559]]{140^\circ} \underset{<3\%}{(OC)_3OsB_4H_4C_2(SiMe_3)_2}} \quad (268)$$



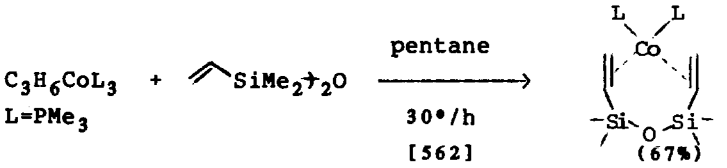
$$\mathrm{C_6H_5Mn(CO)_5 + Me_3P{=}CHSiMe_3 \xrightarrow[14h/25^\circ\ [560]]{C_6H_6/h} \underset{(86\%)}{C_6H_5\overset{CO}{\underset{CO}{Mn}}CH(SiMe_3)PMe_3}} \quad (269)$$

3. Silyl-Substituted Ligands

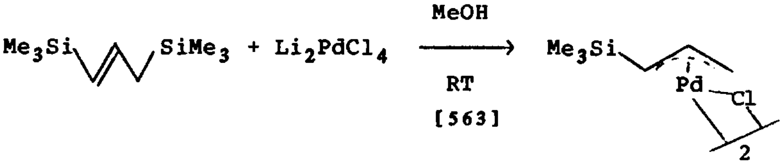
Vinyl and allylsilanes react with metal complexes to give substituted olefin and allyl complexes respectively. Examples are shown in Eqns. 270-274. A silylbutadiene complex was generated as shown in Eqn. 275.



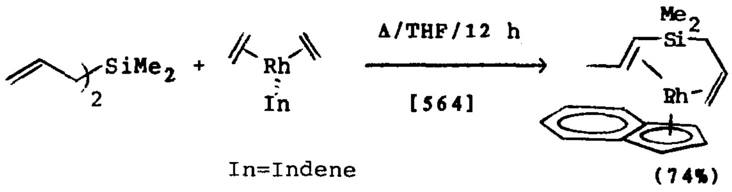
(270)



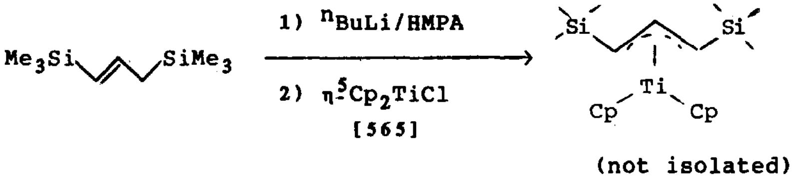
(271)



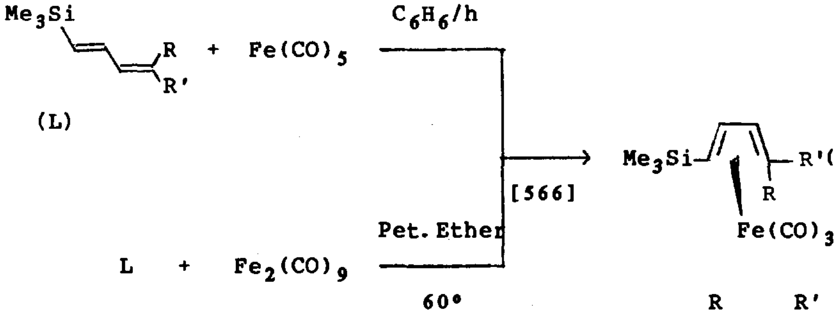
(272)



(273)



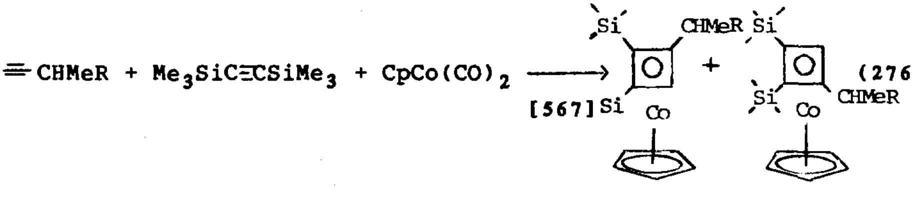
(274)



(275)

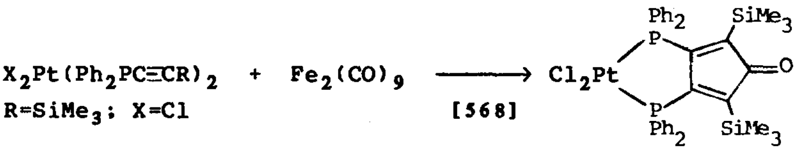
R	R'	%
H	H	75
Me	Me	80

Cyclic ligands that contain silyl-substituents can be prepared from condensation of silyl acetylenes in the presence of $CpCo(CO)_2$ (Eqn. 276) or by reaction of alkynylphosphines that are coordinated to Pt (Eqn. 277). Cyclohexadienes react with $Fe(CO)_5$ (Eqn. 278).

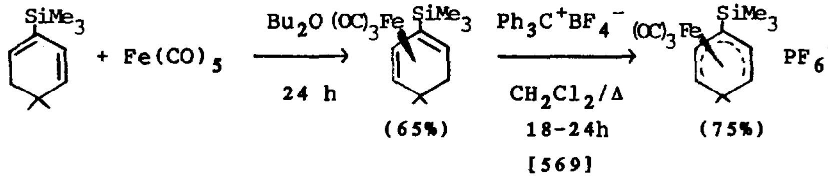


(276)

R=OH(34%); $OSiMe_3$(37%)



(277)

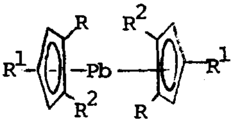


(278)

When an equimolar mixture of BuLi and TMEDA are added to $Me_3SiC_5H_5$ in hexane, $LiC_5H_4SiMe_3 \cdot TMEDA$ is formed. The crystal structure shows this to be the simplest metallocene [570]. Treating 1,2,4-$(Me_3Si)_3C_5H_2Li$ with quinuclidine, TMEDA and $(Me_2NCH_2CH_2)_2NMe$ provides 1:1 complexes with a metallocene structure [571]. Silylcyclopentadienyllithium derivatives react with metal halides to give plumbocenes (Eqn. 279) and titanocene derivatives (Eqn. 280). In a reverse approach coordinated Cp-ligands can be deprotonated with BuLi and quenched with Me_3SiCl (Eqn. 281).

$$2C_5(Me_3Si)_nH_{5-n}Li \quad + \quad PbCl_2 \xrightarrow[0°]{THF}$$

[572]



(279)

R	R^1	R^2	%
Me_3Si	H	H	7
Me_3Si	Me_3Si	H	9.8
Me_3Si	Me_3Si	Me_3Si	7.8

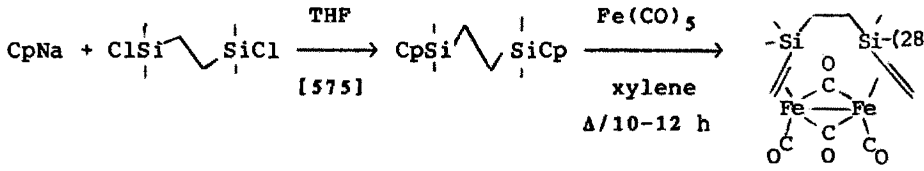
$$Me_3SiC_5H_4Li \quad + \quad \eta^5CpTiCl_3 \xrightarrow[[573]]{THF/Ar} Cp^{TMS}CpTiCl_2 \quad (280)$$

(76%)

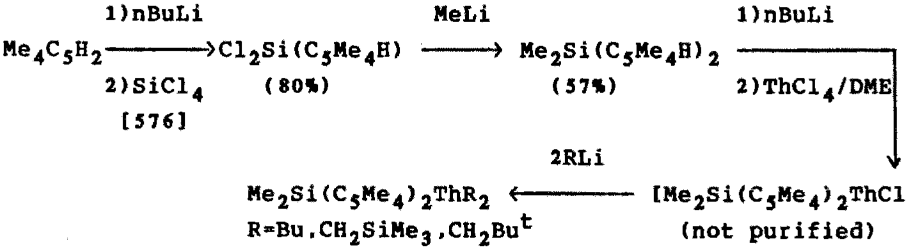
$$\eta^5\text{-}C_5H_5Fe(CO)_2Ph \xrightarrow[Me_3SiX]{BuLi/THF/-78°} \eta^5\text{-}Me_3SiC_5H_4Fe(CO)_2Ph \quad (281)$$

[574] (90%)

Two different silicon-substituted bridged cyclopentadienyl ligands have been prepared according to the sequences shown in Eqns. 282 and 283.



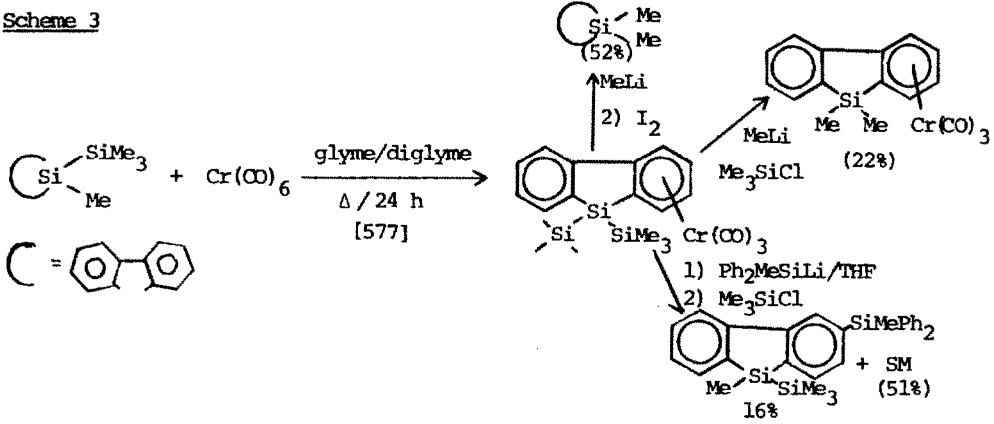
(282)



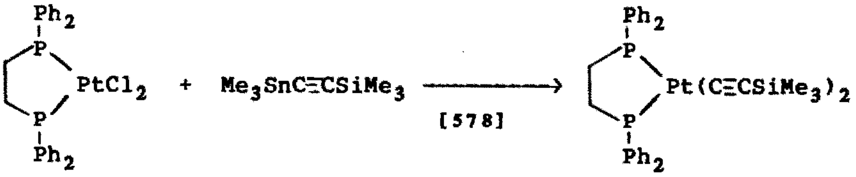
(283)

Silafluorene forms a complex on reaction with $Cr(CO)_6$. Exchange of groups at silicon in the complex occurs with alkyllithium but not silyllithium reagents. The metal can be removed with I_2. These various processes are summarized in Scheme 3.

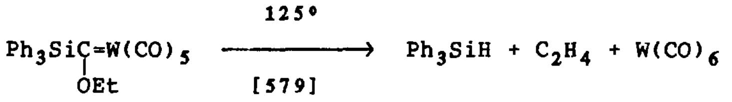
Scheme 3



Silylacetylide derivatives of Pt are prepared from L_2PtCl_2 and $Me_3SnC{\equiv}CSiMe_3$ (Eqn. 284). Thermolysis of a silylcarbene complex resulted in loss of the silicon moiety (Eqn. 285).



(284)

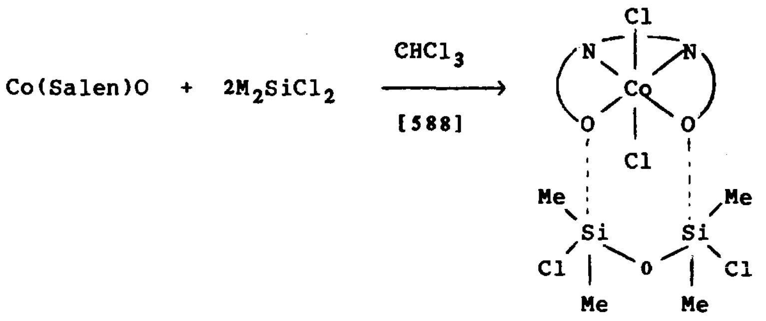


$$Ph_3Si\underset{\substack{|\\ \mathrm{OEt}}}{C}=W(CO)_5 \xrightarrow[{[579]}]{125^\circ} Ph_3SiH + C_2H_4 + W(CO)_6 \qquad (285)$$

X. Penta- and Hexacoordinated Silicon

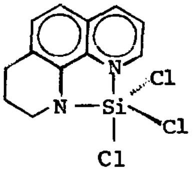
Extracoordinate derivatives of silicon have been prepared by reaction of an appropriate neutral ligand with R_2SiCl_2 or $SiCl_4$. Derivatives of 2,3-naphthalocyanatosilicon have been reported [580]. The ligand was prepared by refluxing α,α,α',α'-tetrabromo-o-xylene, fumaronitrile and NaI in DMF at 70° to give 2,3-naphthalenedicarbonitrile which was condensed to 1,3-diiminobenz(f) isoindoline in $MeOH/NH_3$. Reaction of the indoline with $SiCl_4$ in a mixture of tetrahydronaphthalene/$(nBu)_3N$ at reflux gave $SiNcCl_2$ which contained between 20-40% impurities and could not be purified. The $SiNc(OH)_2$ reacts in concentrated sulfuric acid to give $SiNc(OH)_2$ after hydrolysis. Further substitution of $SiNc(OH)_2$ occurs on addition of $(^n hex)_3SiCl$ in pyridine (reflux) to give $SiNc[OSi(hex\text{-}n)_3]_2$ [580]. Addition of $NaC{\equiv}CC_6H_4C{\equiv}CNa$ to $SiPcCl_2$ (Pc=phthalocyanato) in THF gave polymer, $[PcSiC{\equiv}CC_6H_4C{\equiv}C]_n$ in 85% yield [581]. A related derivative, $SiLCl_2$ (H_2L=tetra-2,3-pyridineporphyrazine), was formed from H_2L and $SiCl_4$ in the presence of quinoline and $C_6H_3Cl_3$ [582]. In all these derivatives silicon is six-coordinate.

Several Schiff base adducts were described during this Survey Year. Condensation of benzaldehyde with ring substituted anilines gave the imines PhCH=NAr (L) which react with $SiCl_4$ in CCl_4 to give $SiCl_4\cdot 2L$ [583]. Schiff bases of the type $o\text{-}HOC_6H_4CH{=}NC_6H_4)_2$ react with Me_2SiCl_2 in C_6H_6 to give complexes with 1:1 stoichiometry [584]. Hexacoordinate complexes, R_2SiR' (R=Me,Ph) were formed from bidentate tetrafunctional Schiff bases, $R'H_2$, where $R'H_2{=}HOCH_2CH_2N{=}CMe)_2$ etc. [585]. Binuclear complexes $NiL_2\cdot SiCl_4$ have been reported from the reaction of NiL_2 ($HL{=}R\text{-}2\text{-}HOC_6H_3CH{=}NOH$) and $SiCl_4$ in C_6H_6 but the adduct contains an Si-OH bond [586]. However, in the Cu(II) salicylaldoximate case, reaction with Me_2SiCl_2 gave a non-electrolyte product where the NOH moiety is still intact [587]. Condensation of substituted salicylaldehyde and ethylenediamine gives substituted salens which gave Co(salen)O on reaction with $CoCl_2$. When the cobalt complex is treated with two equivalents of Me_2SiCl_2 a 1:2 complex forms which is a non-electrolyte and formulated as a coordinated disiloxane is formed as shown in Eqn. 286.

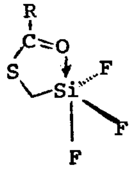


(286)

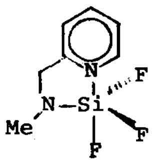
Neutral five coordinate complexes can be formed when one of the substituents at silicon contains a grouping that can coordinate to the silicon center. A five-membered ring is usually formed as shown for 33, 34 and 35, however an example of 5-coordinate silicon involving a six-membered ring, 36, has been described in non-polar solvents. Formation of 35 and 36 are shown in Eqns. 287 and 288.



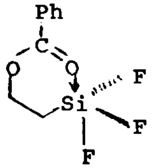
33
[589,590]



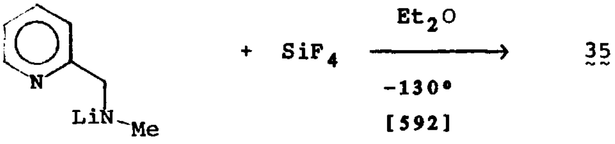
34
[591]



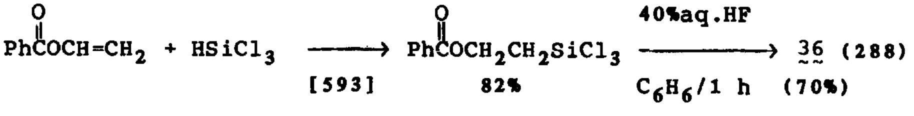
35
[592]



36
[593]

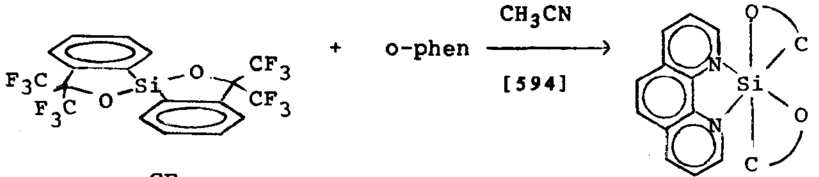


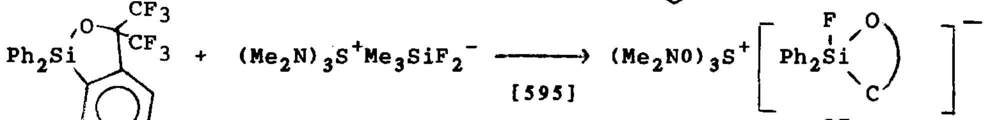
(287)



$$\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH{=}CH_2} + \mathrm{HSiCl_3} \xrightarrow[\text{[593]}]{} \underset{82\%}{\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH_2CH_2SiCl_3}} \xrightarrow[\mathrm{C_6H_6/1\ h}]{40\%\mathrm{aq.HF}} \underset{(70\%)}{36} \quad (288)$$

When o-phenanthroline is added to the spiro-derivative shown in Eqn. 280 a hexacoordinate species is formed. A five-coordinate, nonhygroscopic anion is formed from the related system that contains the unit $o\text{-}C_6H_4C(CF_3)_2O^-$ (Eqn. 281). The salt, 37, is a polymerization catalyst for methyl methacrylate.

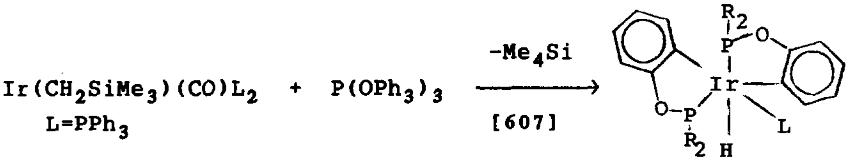

(289)


37 (290)
(90%)

Electron donating solvents coordinate to silicon in Et_3SiH [596]. Anionic organosilicon species may be studied by the flowing afterglow technique. A study of several species generated in the gas phase in the presence of N_2O shows that N_2O reacts with silyl anions but not pentacoordinate Si anions. Such a study demonstrates that addition of F^- to $Me_3SiCH=CH_2$ gave $Me_3SiF(Vin)^-$ and not $[Me_3SiCHCH_2F]^-$ [597].

XI. Elimination of Small Organosilanes in Synthetic Strategies

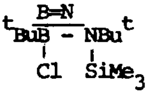
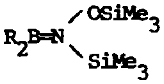
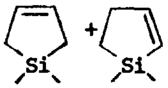
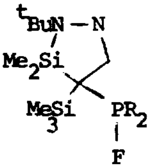
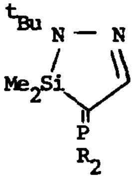
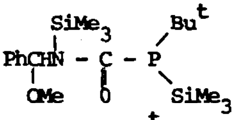
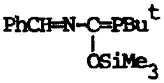
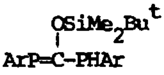
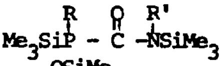
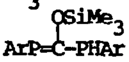
Although a few examples of the elimination of small molecules have appeared in previous sections the types of possible processes are summarized in this section. In most cases elimination of Me_3SiX occurs from a unit $Me_3SiEl\text{-}El'X$ such that $El=El'$ is produced. These processes are summarized in Table XVIII. Elimination of Me_3SiX occurs thermally or from deprotonation in the sequence $Me_3SiOEl\text{-}El'H$. These methods have resulted in the generation of B=N, Si=C, P=C, P=N and P=P derivatives. Elimination of Me_4Si occurs subsequent to orthometalation in the iridium derivative shown in Eqn. 291.


(291)

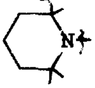
R=OPh; L=P(OPh)$_3$

Introduction of unsaturation in organic derivatives is accomplished by the same strategy. Fluoride ion induces a 1,2-elimination of o-$Me_3SiC_6H_4O_3SCF_3$ to give a benzyne intermedaite [608]. Similarly, addition of Bu_4NF to $Me_3SiCH_2CH=CHCH(R)SO_2Ph$

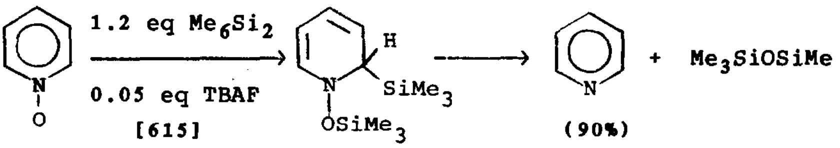
XVIII. Elimination of Me_3SiX in the Synthesis of Multiple Bonds Between Main Group Elements

Precursor	Me_3SiX Eliminated	Conditions (Initiator)	Product	Ref
 $\overset{B=N}{{}^{t}Bu\underset{Cl}{B}-\underset{SiMe_3}{N}Bu^{t}}$	Me_3SiCl	530°	${}^{t}BuB{\equiv}NBu^{t}$	598,599
$ClBR_2/(Me_3Si)NO$[a]	Me_3SiCl	-78°	 $R_2B{=}N\begin{matrix}OSiMe_3\\SiMe_3\end{matrix}$	599
$[ClBNSMe_3]_3$	Me_3SiCl	360°	$(BN)_4$	600
<u>Si=X</u>				
$Me_3SiCH_2SiMeHOMe$ + 	Me_3SiOMe	700°		601
$(MeO)_2MeSiN(SiMe_3)_2$	Me_3SiOMe		$MeO(Me)Si{=}NSiMe_3$	602
<u>P=X</u>				
	Me_3SiF	hex/Δ		603
	Me_3SiOMe	170-190°	 $PhCH{=}N{-}\underset{OSiMe_3}{C}{=}PBu^{t}$	213
 $ArP{=}\overset{OSiMe_2Bu^{t}}{C}{-}PHAr$	Me_3SiOLi	nBuLi/THF	$ArP{=}C{=}PAr$	214
 $Me_3Si\overset{R}{P}-\overset{O}{\overset{\Vert}{C}}-\overset{R'}{N}SiMe_3$	$Me_3SiOSiMe_3$	KOH/THF	$RP{=}C{=}NR'$	604
 $ArP{=}\overset{OSiMe_3}{C}{-}PHAr$	Me_3SiOLi	${}^{t}BuLi$	$ArP{=}C{=}PHr$	212
$RClPN(SiMe_3)_2$[c]	Me_3SiCl	120-130°/0.02mm	$RP{=}NSiMe_3$	605
$RClPP(Bu^{t})SiMe_3$[c]	Me_3SiCl	Δ	$RP{=}PBu^{t}$	606

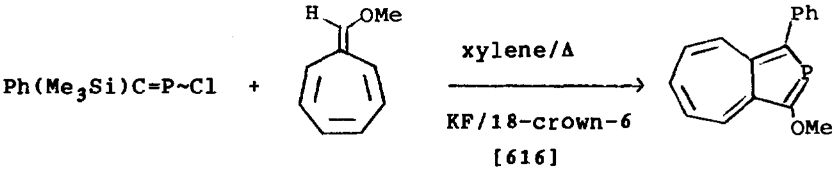
a. $R{=}CH_2CHMe_2$ b. $R{=}{}^{t}Bu$, ${}^{i}Pr$, Me, Mes, Ph; R' = ${}^{t}Bu$, ${}^{i}Pr$, Ph

c. 

results in a 1,4-elimination of Me_3SiO_2SPh to give the substituted butadiene, $CH_2=CH-CH=CHR$ [609]. When the alcohols, $RCH(OH)C(Me)HSiMe_3$ are treated with KH or acid, Me_3SiOH is lost and olefins are produced [610]. A silylation amination sequence for hydroxy nitrogen heterocycles involves elimination of Me_3SiOH and occurs in high yield if silylating agent is present to convert the silanol to disiloxane [611]. Isocyanates are formed by elimination of $Me_3SiOSiMe_3$ from $RC(OSiMe_3)=NOSiMe_3$ [612] and Me_3SiCl from $ArC(OSiMe_3)=NCl$ [613]. Pyrolysis of $MeO(Me_3SiO)C=CHCO_2Me$ at 500° eliminates Me_3SiOMe and forms the α-ketenic ester, $MeO_2CCH=C=O$ [614]. Heterocyclic N-oxides can be reduced by Me_6Si_2/TBAF. The intermediate is believed to be the silylated N-oxide as is shown in Eqn. 292. Cyclization of $Ph(Me_3Si)C=PCl$ to a phosphaazulene probably proceeds by elimination of Me_3SiCl (Eqn. 293).



(292)



(293)

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