SILICON - SYNTHESIS AND REACTIVITY

ANNUAL SURVEY COVERING THE YEAR 1974

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CONTENTS

I. INTRODUCTION

The scope of this review includes, with few exceptions, only those publications which are included in volumes 80 and 81 of Chemical Abstracts. The reader is referred to the introduction of the previous review[1] for a statement of selectivity in scope within the above material.

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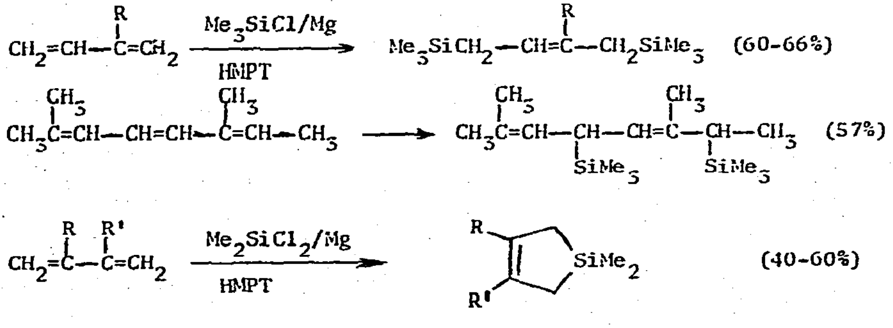
[1] Silicon - Synthesis and reactivity; Annual Survey covering the year 1973 see J. Organometal. Chem., 83(1974)65-154.

II. REVIEWS

Review articles involving silicon have appeared in the following areas: annual reviews on the general chemistry of organosilanes[1-4], hydrosilylation[5], carbofunctional silanes[6], organometallic synthesis of carbosilanes[7], fluxional organosilicon compounds[8], organosilyl free radicals[9], fluorinated derivatives of organosilanes[10], silicon analogues of olefins and ketones[11], adducts of silicon tetrafluoride[12], molecular rearrangements of oxygen-containing carbofunctional silanes[13], formation of alkoxy derivatives of chlorosilanes[14], preparation and properties of O-silyl hydroxylamines and oximes[15], compounds containing the B-O-Si moiety[16], organosilicon peroxides[17], silylphosphines[18], compounds containing silicon-metal bonds[19-21] or silicon-carbon-metal bonds[21,22] silacyclobutane ring-opening reactions[23], heterocycloalkanes containing silicon as a ring atom[24], the preparation and properties of the Si-Si bond[25] and biological aspects of organosilicon chemistry[26,27].

III. FORMATION OF THE SILICON-CARBON BOND

The trimethylchlorosilane-Mg-hexamethylphosphortriamide (HMPT) system continues to be a powerful method for the formation of silicon-carbon bonds. Dienes, for example, undergo bis(trimethylsilylation).[28]

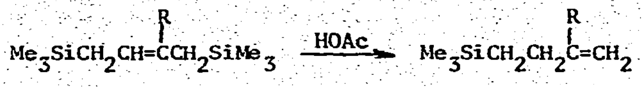


$$CH_2{=}CH{-}\overset{R}{C}{=}CH_2 \xrightarrow[HMPT]{Me_3SiCl/Mg} Me_3SiCH_2{-}CH{=}\overset{R}{C}{-}CH_2SiMe_3 \quad (60\text{-}66\%)$$

$$CH_3\overset{CH_3}{C}{=}CH{-}CH{=}CH{-}\overset{CH_3}{C}{=}CH{-}CH_3 \longrightarrow CH_3\overset{CH_3}{C}{=}CH{-}\underset{SiMe_3}{CH}{-}CH{=}\overset{CH_3}{C}{-}\underset{SiMe_3}{CH}{-}CH_3 \quad (57\%)$$

$$CH_2{=}\overset{R}{C}{-}\overset{R'}{C}{=}CH_2 \xrightarrow[HMPT]{Me_2SiCl_2/Mg} \quad (40\text{-}60\%)$$

Several of these adducts were monodesilylated in fair yields by refluxing acetic acid.

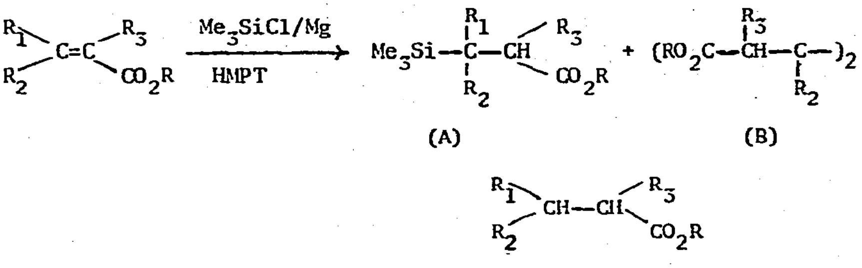


$$Me_3SiCH_2CH{=}\overset{R}{C}CH_2SiMe_3 \xrightarrow{HOAc} Me_3SiCH_2CH_2\overset{R}{C}{=}CH_2$$

Vinyltrimethylsilane is converted into <u>trans</u>-bis(trimethylsilyl)-ethylene in high yield, together with some higher silylated products.[29]

$$Me_3SiCH{=}CH_2 \xrightarrow{Me_3SiCl/Mg} \underline{t}\text{-}Me_3SiCH{=}CHSiMe_3 + (Me_3Si)_2CHCH_2SiMe_3 + (Me_3Si)_2CHCH(SiMe_3)_2$$

A variety of reaction pathways is exhibited by α,β-unsaturated esters; the success of the reaction and the relative amounts of each product depend strongly on the substituent groups, R.[30]

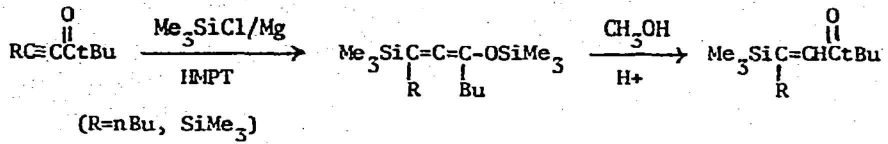


(A) (B)

(C)

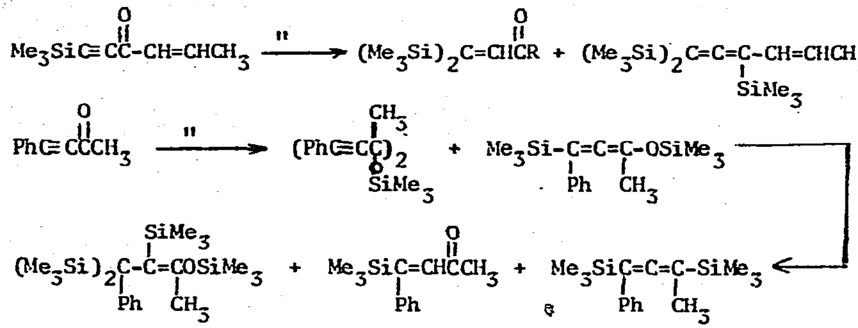
Group				Yield (%)				
R1	R2	R3	R	Recovered	A	B	C	
Ph	H	H	Et		55	9		
Ph	H	H	CH_2Ph		60	8.5		
Ph	H	Ph	Me		50		10	
Ph	H	CO_2Et	Et	30	76		2	
H	H	Me	Me	polymerization				
H	H	Br	Me	polymerization				
H	H	Me	nBu	10	30	50		$TiCl_4$ catalyst employed
Me	H	H	nBu	10	10	70		
Me	Me	H	nBu	5	10	70		
Me	H	CO_2Et	Et	15		50		
H	CO_2Me	H	Me		1	75		
CO_2Me	H	H	Me			80		

α,β-Acetylenic ketones afford bis-silylated allenoxysilanes which may be hydrolyzed to the monosilyl α,β-unsaturated ketones.[31] In some cases, the intermediate allenoxysilanes undergo further C-silylation, and for enolizable ketones, silyl enol and dimerization products are also found.



$$RC\equiv C\overset{O}{\overset{\|}{C}}tBu \xrightarrow[HMPT]{Me_3SiCl/Mg} Me_3Si\underset{R}{C}=C=\underset{Bu}{C}-OSiMe_3 \xrightarrow[H+]{CH_3OH} Me_3Si\underset{R}{C}=CH\overset{O}{\overset{\|}{C}}tBu$$

(R=nBu, $SiMe_3$)



$$Me_3SiC\equiv C\overset{O}{\overset{\|}{C}}-CH=CHCH_3 \xrightarrow{''} (Me_3Si)_2C=CH\overset{O}{\overset{\|}{C}}R + (Me_3Si)_2C=C=\underset{SiMe_3}{C}-CH=CHCH_3$$

$$PhC\equiv C\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{''} (PhC\equiv C\overset{CH_3}{\underset{\underset{SiMe_3}{O}}{C}})_2 + Me_3Si-\underset{Ph}{C}=C=\underset{CH_3}{C}-OSiMe_3$$

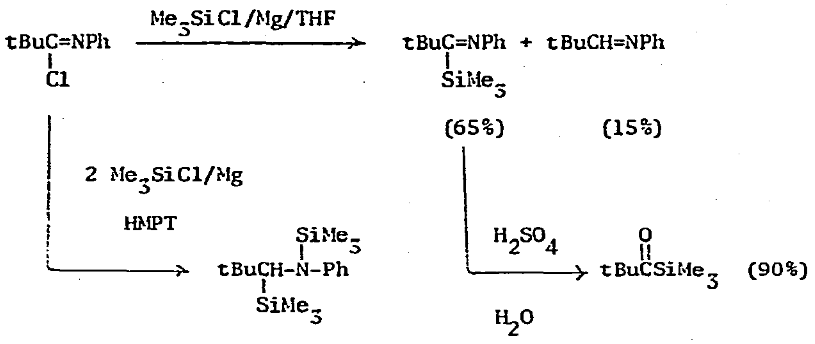
$$(Me_3Si)_2\overset{SiMe_3}{\underset{Ph}{C}}-\underset{CH_3}{C}=COSiMe_3 + Me_3Si\underset{Ph}{C}=CH\overset{O}{\overset{\|}{C}}CH_3 + Me_3Si\underset{Ph}{C}=C=\underset{CH_3}{C}-SiMe_3$$

Partial or total silylation of geminal polychlorocarbons can be effected by the $Me_3SiCl/Mg/HMPT$ system.[32]

Halide	Product	Yield
CCl_4	Cl_3CSiMe_3	45
$HCCl_3$	HCl_2SiMe_3	35
	+ $Cl_2C(SiMe_3)_2$+Cl_3CSiMe_3	21+7
$MeCCl_3$	$MeCCl_2SiMe_3$	80
Me_2CCl_2	$Me_2CClSiMe_3$	10
$PhCCl_3$	$PhCCl_2SiMe_3$	80
p-$ClC_6H_4CCl_3$	p-$ClC_6H_4CCl_2SiMe_3$	70
Ph_2CCl_2	$Ph_2CClSiMe_3$ + $Ph_2CHSiMe_3$	65
$PhCHCl_2$	$PhCHClSiMe_3$ + $PhCH_2SiMe_3$	50
$Cl_2C=CCl_2$	$Cl_2C=C(Cl)SiMe_3$	35
Me_2CCl_2	$Me_2C(SiMe_3)_2$	55

Halide	Product	Yield
H_2CCl_2	$H_2C(SiMe_3)_2$	30
H_2CBr_2	$H_2C(SiMe_3)_2$	50
$PhCHCl_2$	$PhCH(SiMe_3)_2$	75
Ph_2CCl_2	$Ph_2C(SiMe_3)_2$	65
CCl_3CCl_3	$Me_3SiC{\equiv}CSiMe_3$	50
$Cl_2C{=}CCl_2$	$Me_3SiC{\equiv}CSiMe_3$	65
$(Cl_2C{=}CCl)_2$	$(Me_3Si)_3CC{\equiv}CC(SiMe_3)_3$	65

N-Phenylpivalimidoyl chloride gives the product of mono- or bis-silylation, depending on the stoichiometry employed. Hydrolysis of the monosilylated product affords good yields of α-silylketone.[33]

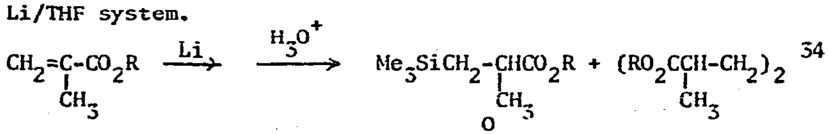


$$\underset{Cl}{tBuC}{=}NPh \xrightarrow{Me_3SiCl/Mg/THF} \underset{\underset{(65\%)}{SiMe_3}}{tBuC}{=}NPh + \underset{(15\%)}{tBuCH{=}NPh}$$

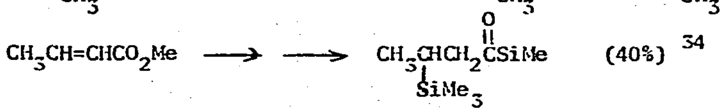
$$\underset{SiMe_3}{tBuC}{=}NPh \xrightarrow[H_2O]{H_2SO_4} tBu\overset{O}{\overset{\|}{C}}SiMe_3 \quad (90\%)$$

$$\underset{Cl}{tBuC}{=}NPh \xrightarrow[HMPT]{2\ Me_3SiCl/Mg} tBu\underset{SiMe_3}{C}H{-}\overset{SiMe_3}{N}{-}Ph$$

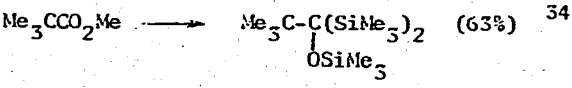
The following transformations have been reported using the Me_3SiCl/-Li/THF system.



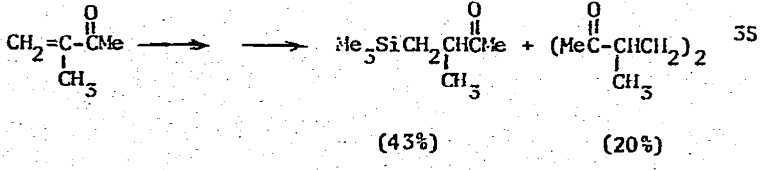
$$CH_2{=}\underset{CH_3}{C}{-}CO_2R \xrightarrow{Li} \xrightarrow{H_3O^+} Me_3SiCH_2{-}\underset{CH_3}{C}HCO_2R + (RO_2C\underset{CH_3}{C}H{-}CH_2)_2 \quad [34]$$



$$CH_3CH{=}CHCO_2Me \longrightarrow \longrightarrow CH_3\underset{SiMe_3}{C}HCH_2\overset{O}{\overset{\|}{C}}SiMe \quad (40\%) \quad [34]$$



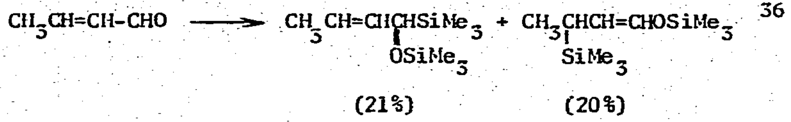
$$Me_3CCO_2Me \longrightarrow Me_3C{-}\underset{OSiMe_3}{C}(SiMe_3)_2 \quad (63\%) \quad [34]$$



$$CH_2{=}\underset{CH_3}{C}{-}\overset{O}{\overset{\|}{C}}Me \longrightarrow \longrightarrow \underset{(43\%)}{Me_3SiCH_2\underset{CH_3}{C}H\overset{O}{\overset{\|}{C}}Me} + \underset{(20\%)}{(Me\overset{O}{\overset{\|}{C}}{-}\underset{CH_3}{C}HCH_2)_2} \quad [35]$$

(carvone underwent similar reaction while α-ionone was disilylated at the carbonyl group)

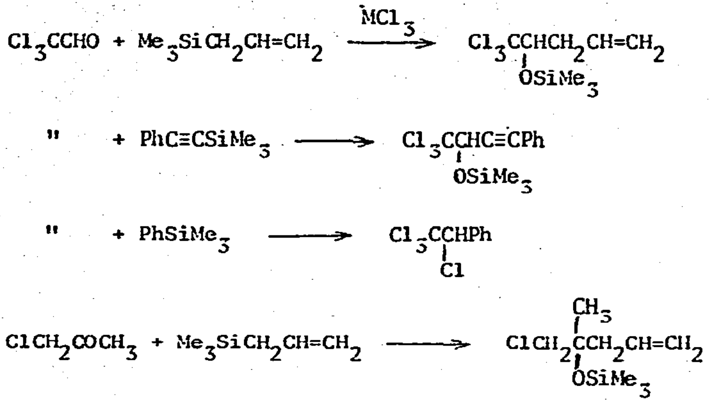
$CH_2{=}CH{-}CHO \longrightarrow Me_3SiCH_2CH{=}CHOSiMe_3$ (70%) [36]



$CH_3CH{=}CH{-}CHO \longrightarrow CH_3CH{=}CH\underset{OSiMe_3}{C}HSiMe_3 + CH_3\underset{SiMe_3}{C}HCH{=}CHOSiMe_3$ [36]

(21%) (20%)

Both chloral and chloroacetone undergo carbonyl addition of Si-ethynyl, Si-allyl, and Si-phenyl compounds under Lewis acid catalysis as shown below.[37]



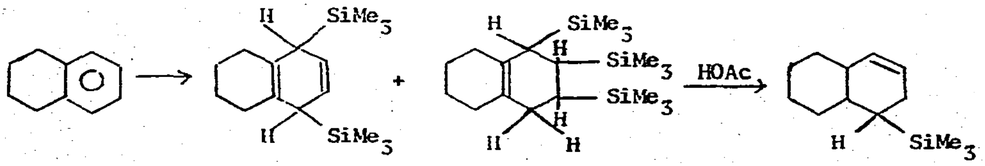
$$Cl_3CCHO + Me_3SiCH_2CH{=}CH_2 \xrightarrow{MCl_3} Cl_3C\underset{OSiMe_3}{C}HCH_2CH{=}CH_2$$

$$\text{"} + PhC{\equiv}CSiMe_3 \longrightarrow Cl_3C\underset{OSiMe_3}{C}HC{\equiv}CPh$$

$$\text{"} + PhSiMe_3 \longrightarrow Cl_3C\underset{Cl}{C}HPh$$

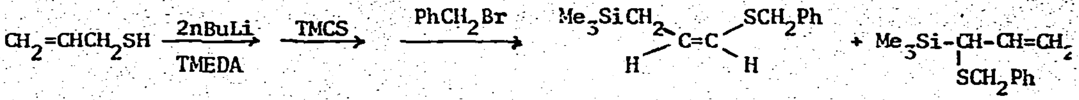
$$ClCH_2COCH_3 + Me_3SiCH_2CH{=}CH_2 \longrightarrow ClCH_2\overset{CH_3}{\underset{OSiMe_3}{C}}CH_2CH{=}CH_2$$

Tetralin is silylated in the presence of lithium and Me_3SiCl/THF; acetic acid degrades the tetrasilylated product as shown.[38]



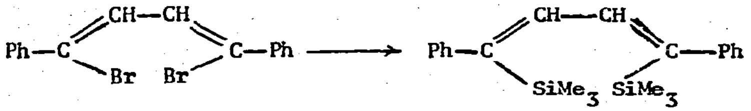
Derivatization of various organolithium and organomagnesium reagents with trimethylchlorosilane (TMCS) has led to the formation of a number of new organosilanes.

$Cl_3CP(O)(OEt)_2 \xrightarrow[THF]{nBuLi} (EtO)_2(O)PCCl_2Li \xrightarrow{TMCS} (EtO)_2(O)PCCl_2SiMe_3$ (70%)[39]

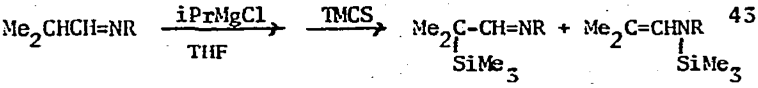


$Ph_3PbCH_2CH=CCl_2 \xrightarrow[-95°]{nBuLi} Li(CCl_2CHCH_2) \xrightarrow{TMCS} Me_3SiCCl_2CH=CH_2$ (99%) [41]

$ClCH_2CH=CHCl \xrightarrow[THF]{TMCS/Mg} \underline{t}\text{-}Me_3SiCH_2CH=CHSiMe_3$ (80%) [42]



[42]



$Me_2CHCH=NR \xrightarrow[THF]{iPrMgCl} \xrightarrow{TMCS} Me_2\underset{SiMe_3}{C}-CH=NR + Me_2C=CH\underset{SiMe_3}{N}R$ [43]

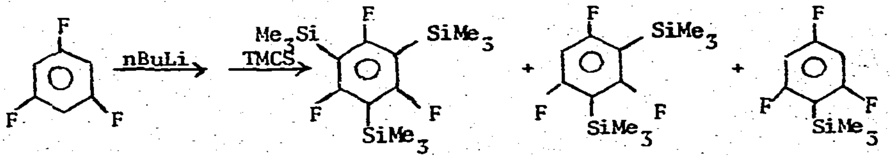
(A) (B)

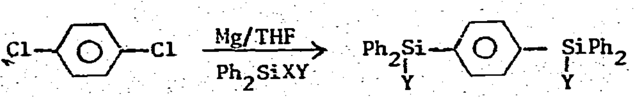
R	A(%)	B(%)
Ph	0	100
Me	6	94
Et	21	79
nPr	23	77
iPr	100	0
iBu	88	12
tBu	100	0

(The C-silyl isomer could be converted into the N-silyl isomer with Me_3SiBr catalyst for all but R = tBu, iPr and Ph)

Tetraadamantylsilane has been synthesized in 18% yield from the reaction of $SiCl_4$ with sodium and adamantyl chloride.[44]

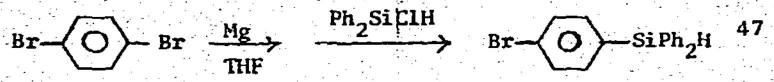
The following arylsilanes have been prepared by coupling reactions.[45]



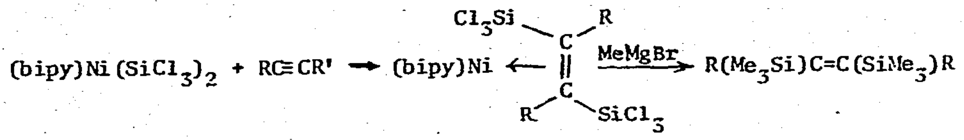


[46]

[X(Y) = Cl(H); $OCH_3(OCH_3)$; $Cl(OCH_3)$; OEt(OEt)]



Details of a bissilylation reaction of acetylenes have been reported using bis(trichlorosilyl)bipyridylnickel(II) as catalyst.[48]



REACTION OF $Ni(bipy)(SiX_3)_2$ WITH ACETYLENES; FOLLOWED BY METHYLATION

SiX_3	Acetylene	Product	Yield(%)	*cis/trans*
$SiCl_3$	PhC≡CPh	$Ph(Me_3Si)C=C(SiMe_3)Ph$	49	0/100
$SiCl_3$	PhC≡CH	$Ph(Me_3Si)C=C(SiMe_3)H$	47	73/27
$SiCl_3$	PhC≡CMe	$Ph(Me_3Si)C=C(SiMe_3)Me$	38	92/8
$SiCl_3$	n-BuC≡C-n-Bu	$n\text{-}Bu(Me_3Si)C=C(SiMe_3)n\text{-}Bu$	44	not determined
$SiMeCl_2$	PhC≡CPh	$Ph(Me_3Si)C=C(SiMe_3)Ph$	52	0/100
$SiMeCl_2$	PhC≡CH	$Ph(Me_3Si)C=C(SiMe_3)H$	49	67/33
$SiMeCl_2$	PhC≡CMe	$Ph(Me_3Si)C=C(SiMe_3)Me$	45	93/7
$SiMeCl_2$	n-BuC≡C-n-Bu	$n\text{-}Bu(Me_3Si)C=C(SiMe_3)\text{-}n\text{-}Bu$	52	not determined

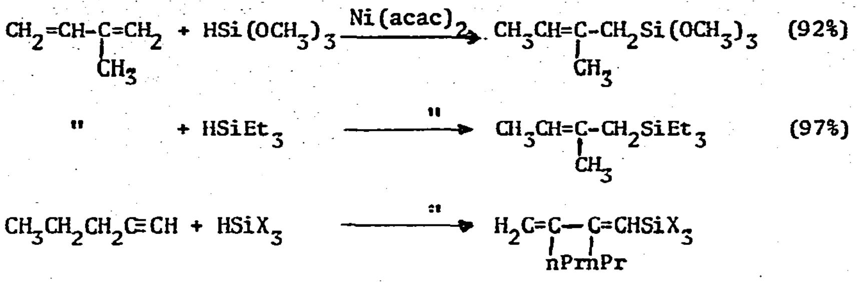
The bis silyl complex used above can be prepared as shown.[49] These

$$Ni(bipy)R_2 + 3\ HSiX_3 \rightarrow Ni(bipy)(SiX_3)_2 + RSiX_3 + H_2 + RH$$

$$(R=Me,\ Et;\ X_3=Cl_3,\ MeCl_2)$$

silicon-nickel complexes were inactive as hydrosilylation catalysts for olefins, but other organonickel species were found to be catalysts for hydrosilylation [$Ni(bipy)Et_2$; $Ni(PPh_3)$(cyclopentadienyl) Et; Ni(cyclopentadienyl)$_2$].

Ziegler-type systems of the form $M(acac)_n\ AlEt_3$ (M=Ni,Co or Fe) catalyze the hydrosilylation of 1,3-dienes and terminal acetylenes. The latter undergo dimerization concomitant with addition.[50]



$$CH_2{=}CH{-}\underset{CH_3}{C}{=}CH_2 + HSi(OCH_3)_3 \xrightarrow{Ni(acac)_2} CH_3CH{=}\underset{CH_3}{C}{-}CH_2Si(OCH_3)_3 \quad (92\%)$$

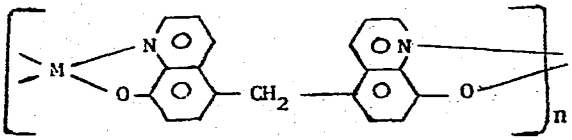
$$'' \quad + HSiEt_3 \xrightarrow{''} CH_3CH{=}\underset{CH_3}{C}{-}CH_2SiEt_3 \quad (97\%)$$

$$CH_3CH_2CH_2C{\equiv}CH + HSiX_3 \xrightarrow{''} H_2C{=}\underset{nPr}{C}{-}\underset{nPr}{C}{=}CHSiX_3$$

(X=OEt, Et, Me)

The reaction of tetracarbonyldichlorodirhodium with dimethylaminomethylated styrene-divinylbenzene copolymers afforded a polymer-supported hydrosilylation catalyst.[51] In another study, Rh, Pd and Pt complexes were prepared whose t-phosphine, t-amine, cyano or pyridine ligands were bonded directly or through alkylsiloxy linkages to an inorganic support (alumina, silica, zeolite). Some of these showed high activity and could be recycled.[52] A polymeric catalyst formed by the absorption of Pt(IV) ions on an anion-exchange resin gives excellent conversions of alkylaryl and arylsilanes and olefins or acetylenes to hydrosilylated products. In addition, the catalyst may be used many times without significant loss in activity.[53]

Chelate complexes of Pt, Rh, Pd and Ni of the form shown were prepared. Those containing Pt or Rh were most active as hydrosilylation catalysts.[54]



1,4-Hydrosilylation of 1,3-dienes occurs when mixtures of $Cr(CO)_6$, a 1,3-diene, and X_3SiH are irradiated.[55] The monoolefinic products, often produced in near quantitative yields, do not undergo further addition.

$$CH_2{=}CHCH{=}CH_2 + X_3SiH \longrightarrow \underline{c}\text{-}CH_3CH{=}CH\text{-}CH_2SiX_3$$

$$[X_3{=}Me_3,\ Ph_2H,\ (OEt)_3,\ Me_2H]$$

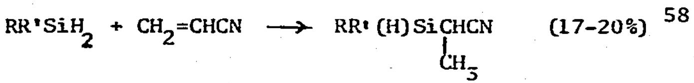
Optimum reaction conditions have been determined for the hydrosilylation of 1,3-butadiene with trichlorosilane using the $(p\text{-}RC_6H_4CN)_2$-$PdCl_2$ (R=H, Me, MeO, Me_2N) and $(p\text{-}Me_2NC_6H_4CN)_2PdBr_2$ catalyst systems.[56]

Copper-containing catalysts which effect the addition of trichlorosilane to acrylonitrile at 120° have been reported.[57]

$$CH_2{=}CHCN + HSiCl_3 \xrightarrow{cat.} Cl_3SiCH_2CH_2CN$$

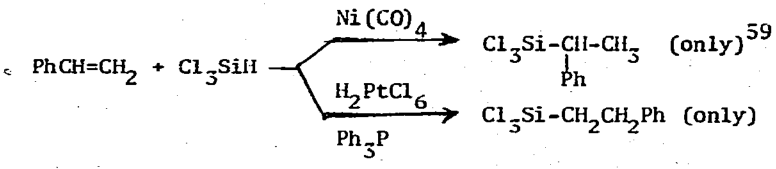
Catalyst	Adduct Yield (%)
Cu_2O - $C_6H_{11}NC$	70
Cu_2O - tBuNC	42
CuCl - $C_6H_{11}NC$	78
CuCl - tBuNC	56
$Cu(acac)_2$ - $C_6H_{11}NC$	75

The following hydrosilylations have also been carried out under various conditions.



$$RR'SiH_2 + CH_2{=}CHCN \longrightarrow RR'(H)Si\underset{\displaystyle CH_3}{CH}CN \qquad (17\text{-}20\%)\ ^{58}$$

(R=R'=Ph; R=CH_3, R'=Ph)



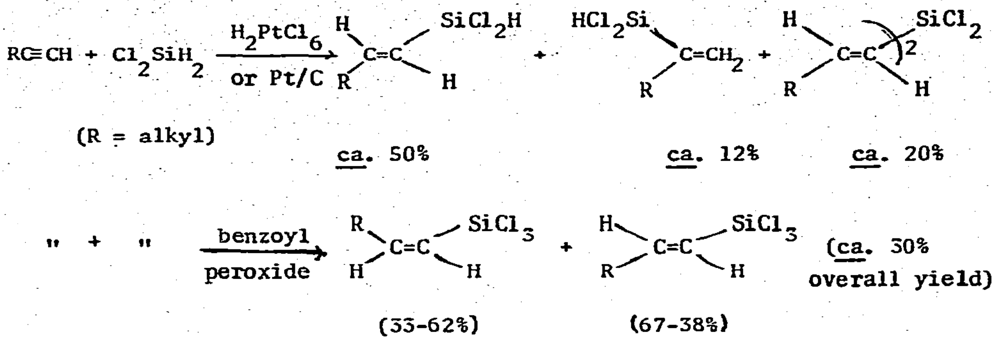
$$PhCH{=}CH_2 + Cl_3SiH \xrightarrow{Ni(CO)_4} Cl_3Si\text{-}\underset{\displaystyle Ph}{CH}\text{-}CH_3 \quad (only)^{59}$$

$$PhCH{=}CH_2 + Cl_3SiH \xrightarrow[Ph_3P]{H_2PtCl_6} Cl_3Si\text{-}CH_2CH_2Ph \quad (only)$$

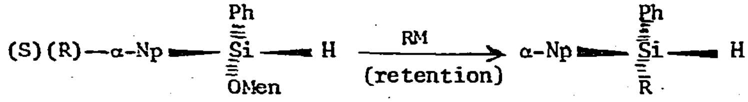
$$R\text{-}C{\equiv}CH + R'_3SiH \xrightarrow{(PhP)_3RhCl} RCH{=}CHSiCl_3 \quad ^{60}$$

(R=nPr, nHex; R'_3=EtMe_2, PhMe_2, Et_3) (cis/trans ratio of 65/35 to 81/19; note predominant anti-addition)

The stereochemistry of addition of dichlorosilane to terminal acetylenes with various catalyst systems has been investigated.[61]

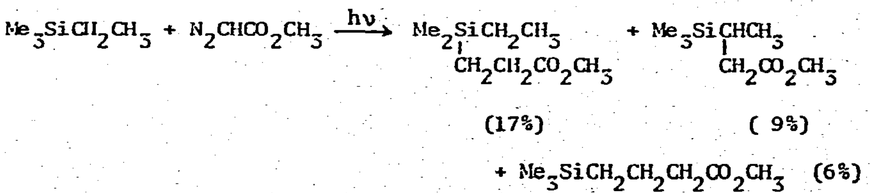


A method for the synthesis of monofunctional chiral organosilanes has been described which involves coupling bifunctional asymmetric silanes with saturated, vinylic, or aryl organometallic reagents (M=Li, Mg).

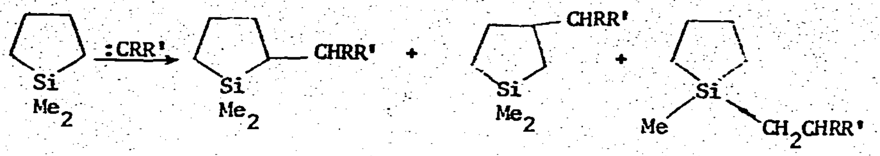


In the case of (R)(R)—Ph-α-Np(-)MenOSiCl, the chlorine is replaced with inversion of configuration. With dialkoxysilanes, the less bulky alkoxy group is substituted with retention of configuration.[62] The use of allylic organometallic reagents or benzyl magnesium chloride led to both inversion and retention products with Si-H and Si-OMe substrates, but reaction with the chlorosilane still proceeded with inversion.[63]

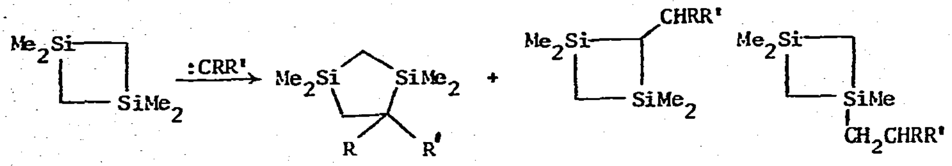
Carboalkoxycarbenes, generated from photolysis of diazo precursors, have been found to insert into both α- and β-silyl C-H bonds, as well as strained Si-C bonds.[64]



$$Me_3SiCH_2CH_3 + N_2CHCO_2CH_3 \xrightarrow{h\nu} \underset{CH_2CH_2CO_2CH_3}{Me_2SiCH_2CH_3} \ (17\%) + \underset{CH_2CO_2CH_3}{Me_3SiCHCH_3} \ (9\%) + Me_3SiCH_2CH_2CH_2CO_2CH_3 \ (6\%)$$



Relative reactivity per bond			
R = H, R' = CO_2CH_3	1.6	2.0	1.0
R = R' = CO_2CH_3	7.0	11.9	1.0



R=H, R'=CO_2CH_3	14%	33%	53%
R=R'=CO_2CH_3	5%	50%	45%

Copper-catalyzed decomposition of methyl diazoacetate in the presence of the Si-H bond serves as a general method for the preparation of α-silyl esters.[65]

$$RR'R''SiH + N_2CHCO_2Me \xrightarrow{Cu} RR'R''SiCH_2CO_2Me \quad (44\text{-}90\%)$$

R=R'=R"=Et

R=H, R'=Me, R"=Ph

R=R'=Me_3Si, R"=Me

R=R'=R"=Me_3Si

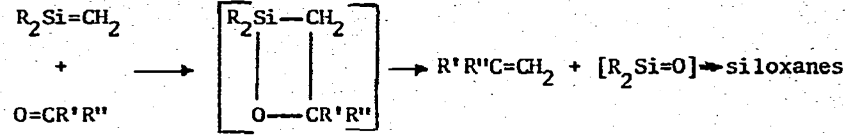
R=R'=Me, R"=Ph

Treatment of the appropriate metalloid tetrabromide with phenyl(trichloromethyl)mercury affords a general method for the preparation of mixed trihalomethyl(tribromo) Group IV compounds.[66]

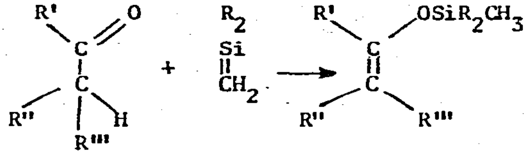
$$SiBr_4 + PhHgCCl_3 \xrightarrow[120^\circ]{NaI} BrCCl_2SiBr_3 \quad (30\%)$$

Experimental evidence continues to mount in support of the existence of a silicon-carbon double bond. The reaction of such a species (generated by the pyrolysis of silacyclobutanes) with ketones and aldehydes results in either silyl enol ethers (path A) or olefins <u>via</u>, possibly, a "pseudo Wittig" pathway (B).[67]

(A)



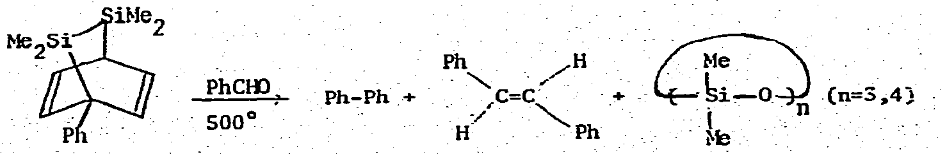
(B)



Enolizable carbonyl compounds gave low yields of "pseudo-Wittig" olefins because of enol ether formation.

Carbonyl Compound	Yield (% based on consumed silacyclobutane)	
	Enol Ether	Olefin
$Me_2C=O$	32	4
$(CH_2)_5C=O$	62	9
Ph(C=O)Me	22	65
$M-FC_6H_4(C=O)Me$	34	69
$Ph_2C=O$	--	97
$Me(CH_2)_5CHO$	26	26
PhCHO	--	54
$Ph_2C=O$	--	65
$Me(CH_2)_5CHO$	not determined	44

The transformation shown below has been interpreted in terms of species containing Si=Si, Si=C and Si=O bonds.[68]



When dimethylsilacyclobutane was pyrolyzed in the presence of silicon-halogen bonds, adducts were formed indicative of polarity in the sense $(\delta+)Me_2Si{=}CH_2\ (\delta-)$ within this intermediate species.[69]

Halosilane	Products (% Yield)			
SiF_4	$F_3SiCH_2SiMe_2F$ (44)	+		(trace)
$HSiCl_3$	$HCl_2SiCH_2SiMe_2Cl$ (22)	+	"	(trace)
$SiCl_4$	$Cl_3SiCH_2SiMe_2Cl$ (20)	+	"	(3)
$MeSiCl_3$	$Cl_2MeSiCH_2SiMe_2Cl$ (16)	+	"	(16)
Me_2SiCl	$ClMe_2SiCH_2SiMe_2Cl$ (13)	+	"	(25)
Me_3SiCl	$Me_3SiCH_2SiMe_2Cl$ (<2)	+	"	(40)
CF_4	no adduct	+	"	(46)

An investigation of the pyrolysis of 1,1-dimethylsilacyclobutane under high vacuum indicated that dimerization of the $Me_2Si{=}CH_2$ formed occurred in the gas phase, but that polymerization to $(Me_2SiCH_2)_n$ occurred on the surface of a cold trap.[70]

The high-temperature formation of vinyl silanes from hydrosilanes and vinyl chloride is markedly improved by the addition of small quantities of Freons to the reaction mixtures.[71]

Palladium(II) compounds have been found to catalyze the cleavage of the silicon-carbon bond.[72] Chlorosilanes are inert to Si-C cleavage.

$$Me_4Si \xrightarrow[H_2O]{Pd(II)} Me_3SiOSiMe_3 + CH_4 + C_2H_6$$

$$Me_3SiPh \xrightarrow[H_2O]{PdCl_2 \text{ or } Li_2PdCl_4} Me_3SiOSiMe_3 + PhH + Ph\text{-}Ph$$

$$Me_3SiOSiMe_3 + PdCl_2 \longrightarrow Me_3SiOSiMe_2Cl + [MePdCl]$$

If olefins (styrene, cyclohexene) are present during the cleavage reactions, transfer of methyl or phenyl groups occurs from silane to olefin.

$$PhCH{=}CH_2 + Me_4Si + LiPdCl_3 \xrightarrow[120°]{CH_3CN} PhCH{=}CHCH_3 \qquad (66\%)$$

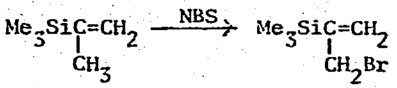
(23%)

IV. CARBOFUNCTIONAL SILANES

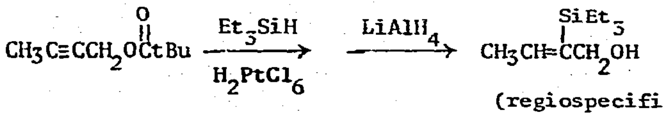
The following routes to some functionalized alkenylsilanes have been reported.

$$Me_3SiC\equiv CCH_2OH \xrightarrow{LiAlH_4} \underline{trans}\text{-}Me_3SiCH{=}CHCH_2OH$$ [73]

$$Me_3SiCH{=}CHCH_2OH \longrightarrow Me_3SiCH{=}CHCH_2X \quad (X{=}Cl,\ I)$$

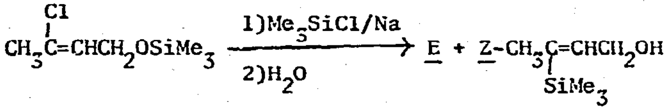


$$Me_3Si\underset{CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow{NBS} Me_3Si\underset{CH_2Br}{\underset{|}{C}}{=}CH_2$$

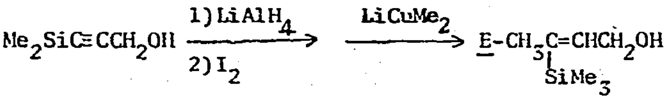


$$CH_3C\equiv CCH_2O\overset{O}{\overset{\|}{C}}tBu \xrightarrow[H_2PtCl_6]{Et_3SiH} \xrightarrow{LiAlH_4} CH_3CH{=}\overset{SiEt_3}{\overset{|}{C}}CH_2OH$$

(regiospecific)

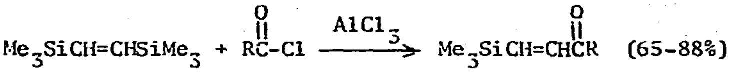


$$CH_3\overset{Cl}{\overset{|}{C}}{=}CHCH_2OSiMe_3 \xrightarrow[2)H_2O]{1)Me_3SiCl/Na} \underline{E} + \underline{Z}\text{-}CH_3\underset{SiMe_3}{\underset{|}{C}}{=}CHCH_2OH$$



$$Me_2SiC\equiv CCH_2OH \xrightarrow[2)I_2]{1)LiAlH_4} \xrightarrow{LiCuMe_2} \underline{E}\text{-}CH_3\underset{SiMe_3}{\underset{|}{C}}{=}CHCH_2OH$$

$$Me_3SiCH{=}CH_2 + Me_3SiCl \xrightarrow[FeCl_3]{HMPT/Mg} Me_3SiCH{=}CHSiMe_3$$ [74]



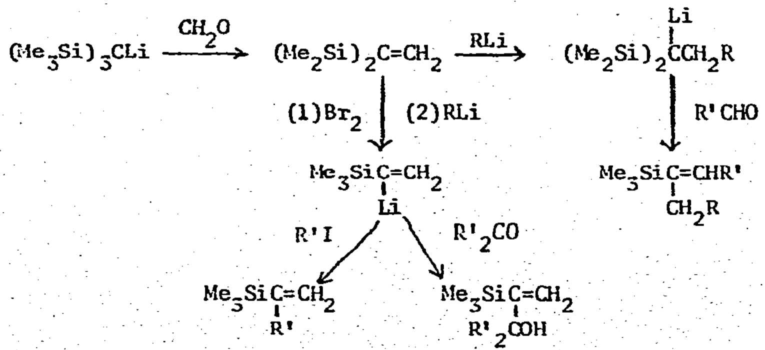
$$Me_3SiCH{=}CHSiMe_3 + R\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow{AlCl_3} Me_3SiCH{=}CH\overset{O}{\overset{\|}{C}}R \quad (65\text{-}88\%)$$ [75]

(R=Me, Ph, tBu)

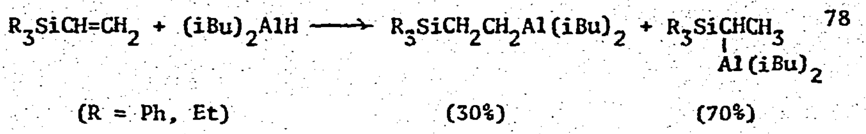
$$R_3Si^*Cl \xrightarrow{BrMgC\equiv COEt} R_3Si^*\text{-}C\equiv COEt \xrightarrow{\Delta} R_3Si^*\text{-}CH{=}C{=}O$$ [76]

$(R_3Si^* = MePh\text{-}1\text{-}C_{10}H_7Si)$

Peterson olefination reactions have led to new pathways to alkenylsilanes.[77]

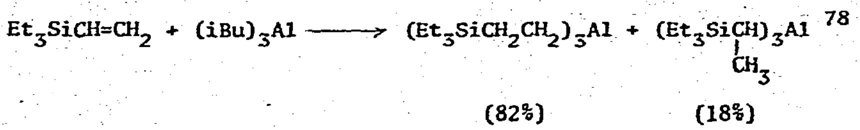


A number of reactions involving addition to the double bond of vinylsilanes have been investigated.



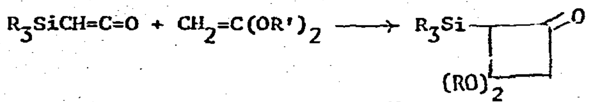
$$\mathrm{R_3SiCH{=}CH_2 + (iBu)_2AlH \longrightarrow R_3SiCH_2CH_2Al(iBu)_2 + R_3Si\underset{\underset{\displaystyle Al(iBu)_2}{|}}{C}HCH_3}$$ [78]

(R = Ph, Et) (30%) (70%)

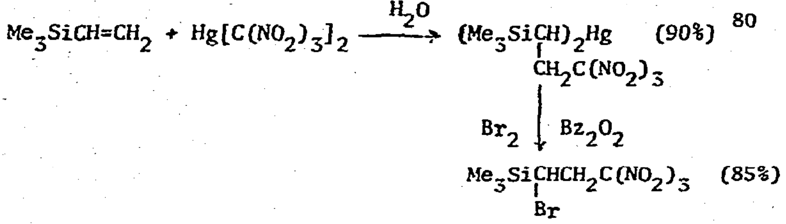


$$\mathrm{Et_3SiCH{=}CH_2 + (iBu)_3Al \longrightarrow (Et_3SiCH_2CH_2)_3Al + (Et_3Si\underset{\underset{\displaystyle CH_3}{|}}{C}H)_3Al}$$ [78]

(82%) (18%)



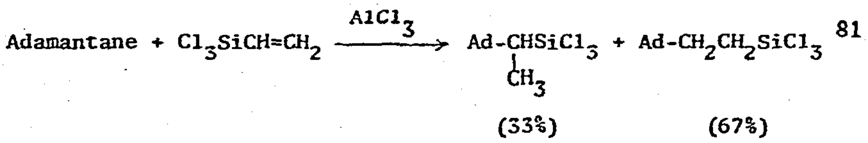
(50%) [79]



$$\mathrm{Me_3SiCH{=}CH_2 + Hg[C(NO_2)_3]_2 \xrightarrow{H_2O} (Me_3Si\underset{\underset{\displaystyle CH_2C(NO_2)_3}{|}}{C}H)_2Hg}$$ (90%) [80]

$$\Big\downarrow \mathrm{Br_2,\ Bz_2O_2}$$

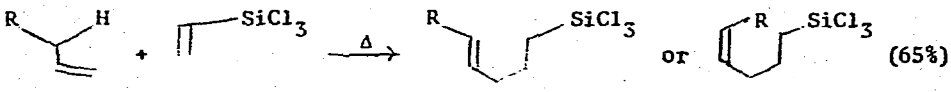
$$\mathrm{Me_3Si\underset{\underset{\displaystyle Br}{|}}{C}HCH_2C(NO_2)_3}$$ (85%)



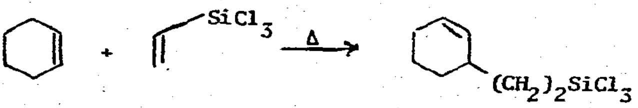
$$\mathrm{Adamantane + Cl_3SiCH{=}CH_2 \xrightarrow{AlCl_3} Ad\text{-}\underset{\underset{\displaystyle CH_3}{|}}{C}HSiCl_3 + Ad\text{-}CH_2CH_2SiCl_3}$$ [81]

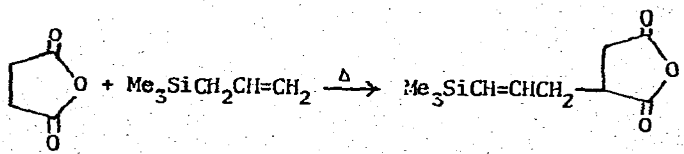
(33%) (67%)

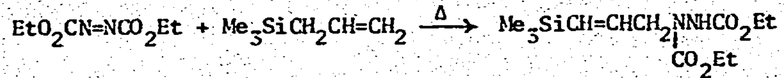
Ene reactions of alkenylsilanes afford entry into a variety of unsaturated organosilanes.[82]



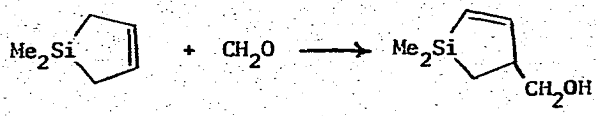
(R = nPr, nBu, n-Pent)





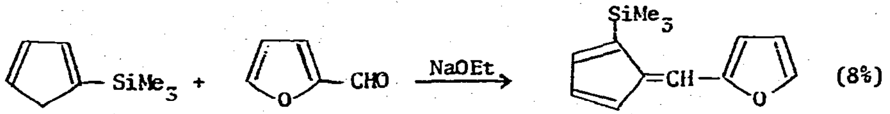


$$EtO_2CN{=}NCO_2Et + Me_3SiCH_2CH{=}CH_2 \xrightarrow{\Delta} Me_3SiCH{=}CHCH_2\underset{CO_2Et}{N}NHCO_2Et$$

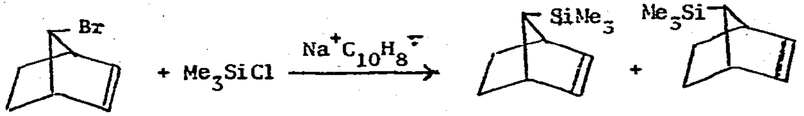


$$Cl_3SiCH{=}CH_2 + Me_3SiCH_2CH{=}CH_2 \xrightarrow{\Delta} Cl_3Si(CH_2)_3CH{=}CHSiMe_3$$

Reaction of 1-trimethylsilylcyclopentadiene with furfural gave low yields of the fulvenic product.[83]



The preparation and reactions of the following unsaturated silanes have also been reported.



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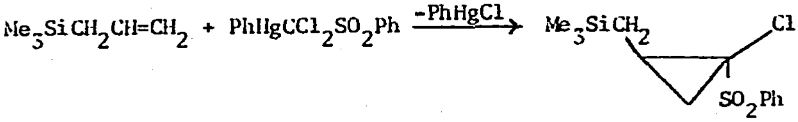
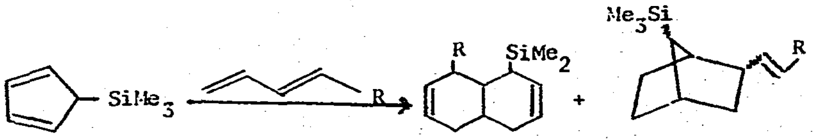


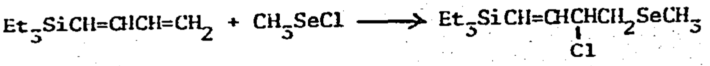
85

(47%; 1:1 cis + trans)



86

(R=H, CH3)



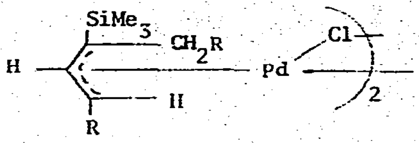
$$Et_3SiCH{=}CHCH{=}CH_2 + CH_3SeCl \longrightarrow Et_3SiCH{=}CH\underset{Cl}{C}HCH_2SeCH_3$$

87

Factors influencing the ease and mode of addition of alkane- and arene-sulfonyl chlorides to homologues of $Me_3SiC{\equiv}C\text{-}CH{=}CH_2$ have been investigated.[88]

Metal complexes originating from vinylsilanes have been prepared by several groups.

$Me_3SiCH=CHR + (PhCN)_2PdCl_2 \longrightarrow$

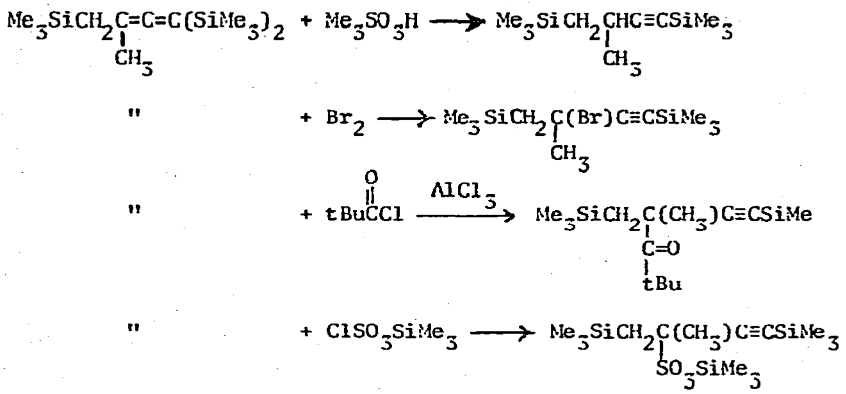


89

$$R_{4-n}Si(CH=CH_2)_n + CuCl \longrightarrow R_{4-n}Si(CH=CH_2)_n \cdot 2CuCl$$ [90]

(n=2,3)

Electrophilic reagents effected the cleavage of the allenic silane shown below.[91]



$$Me_3SiCH_2\underset{CH_3}{\underset{|}{C}}=C=C(SiMe_3)_2 + Me_3SO_3H \longrightarrow Me_3SiCH_2\underset{CH_3}{\underset{|}{C}}HC\equiv CSiMe_3$$

$$\text{"} \quad + Br_2 \longrightarrow Me_3SiCH_2\underset{CH_3}{\underset{|}{C}}(Br)C\equiv CSiMe_3$$

$$\text{"} \quad + tBu\overset{O}{\overset{\|}{C}}Cl \xrightarrow{AlCl_3} Me_3SiCH_2\underset{\underset{\underset{tBu}{|}}{C=O}}{\underset{|}{C}}(CH_3)C\equiv CSiMe$$

$$\text{"} \quad + ClSO_3SiMe_3 \longrightarrow Me_3SiCH_2\underset{SO_3SiMe_3}{\underset{|}{C}}(CH_3)C\equiv CSiMe_3$$

Sulfonating agents [$ClSO_2(OSiMe_3)$, SO_3-dioxane] react with acetylenic or allenic silanes as indicated.[92]

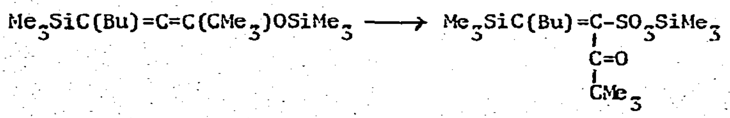
$RCH_2C\equiv CSiMe_3 \longrightarrow RCH_2C\equiv CSO_3SiMe_3$

(R=H, Ph, Me_3C, Me_3Si)

$RCH_2C\equiv CSiMe_3 \longrightarrow Me_3SiOSO_2CH_2C\equiv CSiMe_3$

(R=HO, Me_3SiO)

$(Me_3Si)_2C=C=C(CMe_3)OSiMe_3 \longrightarrow (Me_3Si)_2C=C=C(CMe_3)SO_3SiMe_3$



$$Me_3SiC(Bu)=C=C(CMe_3)OSiMe_3 \longrightarrow Me_3SiC(Bu)=\underset{\underset{\underset{CMe_3}{|}}{C=O}}{\underset{|}{C}}-SO_3SiMe_3$$

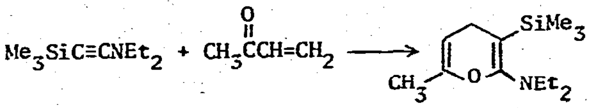
Silyl yneamines are preparable in good yields as follows:[93]

$$Et_3SiC{\equiv}CBr + Et_3N \xrightarrow{95°} Et_3SiC{\equiv}CNEt_2 + EtBr$$

(80%)

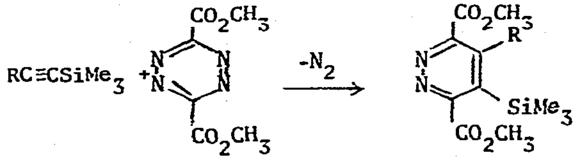
$$Me_3SiC{\equiv}C\text{-}OEt + LiNEt_2 \longrightarrow Me_3SiC{\equiv}CNEt_2 \quad (54\%)$$

The latter yneamine underwent cycloaddition to 3-buten-2-one



(20%)

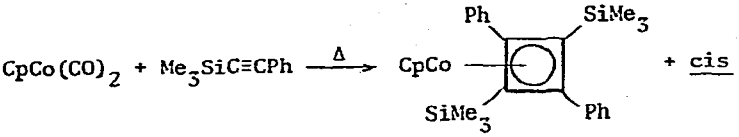
A cycloaddition-cycloreversion process forms silylated pyridazines from acetylenic silanes.[94]



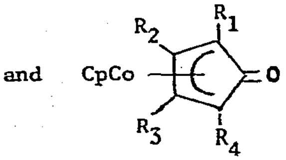
(R=H, $SiMe_3$)

Reactions between transition metal complexes and alkynyl silanes have afforded novel species (Cp=cyclopentadienyl).

$$CpNb(CO)_3 + Ph_3SiC{\equiv}CPh \xrightarrow{h\nu} CpNb(CO)(Ph_3SiC{\equiv}CPh)_2$$ [95]



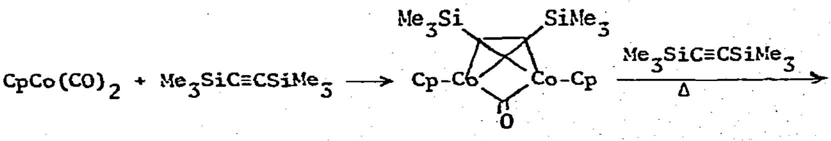
[96]

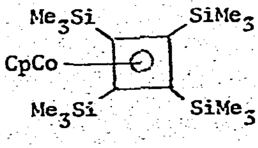


R_1, R_4 = Ph; R_2, R_3 = $SiMe_3$

R_1, R_3 = Ph; R_2, R_4 = $SiMe_3$

R_2, R_3 = Ph; R_1, R_4 = $SiMe_3$



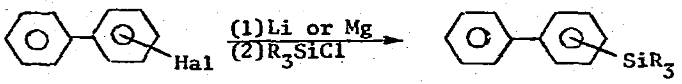


[97]

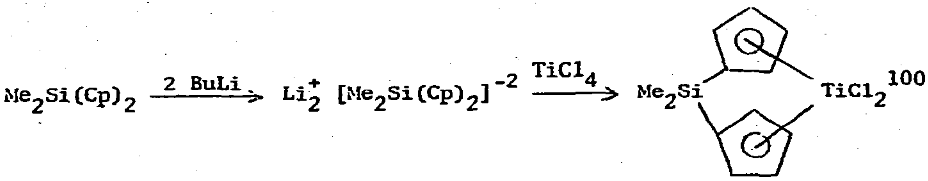
A silicon-containing compound is among the first examples of polynuclear mixed organocopper compounds.[98]

$$(\underline{o}\text{-}Me_2NC_6H_4)_4Cu_6Br_2 + 2\ LiC{\equiv}CSiMe_3 \longrightarrow (\underline{o}\text{-}Me_2NC_6H_4)_4Cu_6(C{\equiv}CSiMe_3)_2$$

A number of biphenylyl silanes have been prepared and their thermostability investigated.[99]

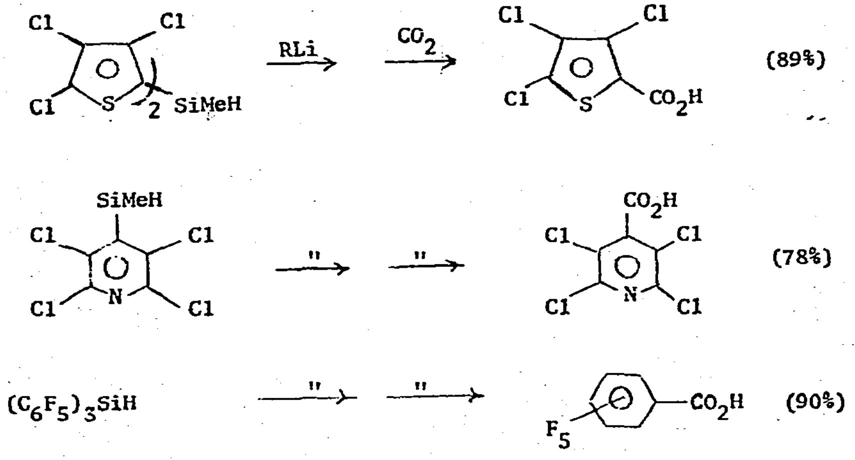


Silicon-containing aryl-metal complexes can be synthesized as shown.



$$PhSiMe_3 + (NH_3)_3Cr(CO)_3 \xrightarrow{dioxane} (MeSiPh)Cr(CO)_3 \quad ^{101}$$

Bis- and tris-(perhaloaryl) silanes undergo cleavage with butyl- or methyllithium to afford good yields of the corresponding perhaloaryllithiums.[102]

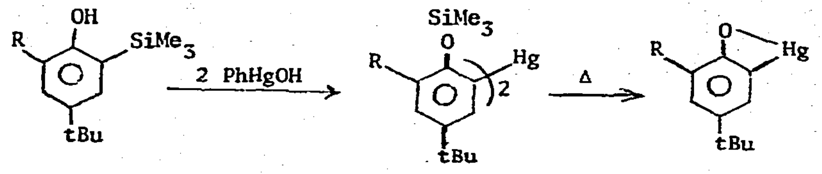


$$(C_6F_5)_2SiMeH + 2\ RM \longrightarrow 2\ C_6F_5M + R_2SiMeH \quad ^{103}$$

The effects of M = Li, MgX and the nature of R on the extent and position (C-Si or C-F) of attack were studied in this last report.

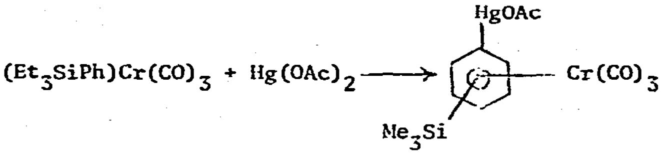
Tetraphenylsilane has been reported to be inert to Si-C bond cleavage by potassium in ammonia.[104]

Treatment of some aromatic silanes with mercury reagents has been reported.



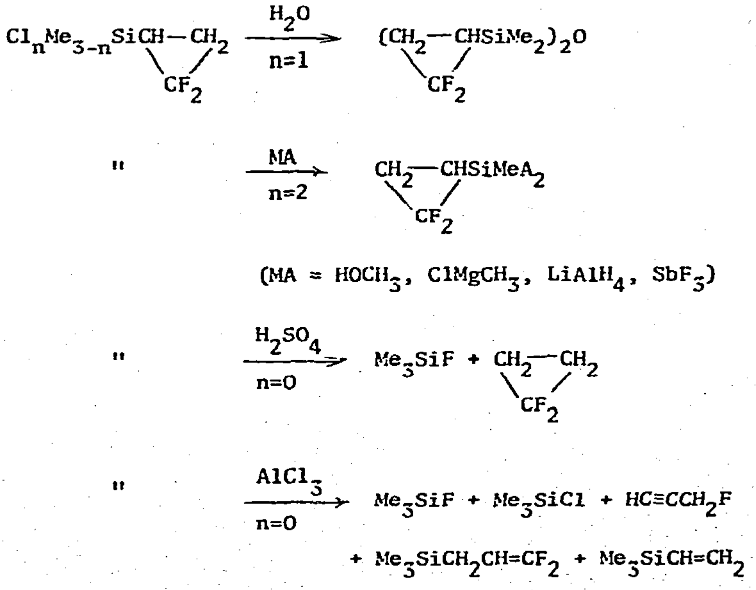
(R=Me, tBu)

105



106

In contrast to the lability of other β-halo-substituted alkylsilanes, 2,2-difluorocyclopropylsilanes are highly resistant to β-elimination.[107]



$$Cl_nMe_{3-n}\underset{CF_2}{SiCH-CH_2} \xrightarrow[n=1]{H_2O} (\underset{CF_2}{CH_2-CHSiMe_2})_2O$$

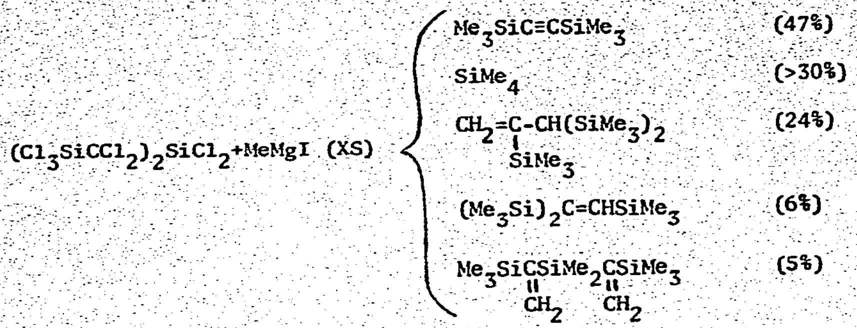
$$'' \xrightarrow[n=2]{MA} \underset{CF_2}{CH_2-CHSiMeA_2}$$

(MA = $HOCH_3$, $ClMgCH_3$, $LiAlH_4$, SbF_3)

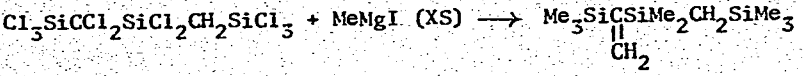
$$'' \xrightarrow[n=0]{H_2SO_4} Me_3SiF + \underset{CF_2}{CH_2-CH_2}$$

$$'' \xrightarrow[n=0]{AlCl_3} Me_3SiF + Me_3SiCl + HC{\equiv}CCH_2F + Me_3SiCH_2CH{=}CF_2 + Me_3SiCH{=}CH_2$$

Treatment of some polychlorocarbosilanes leads to products of elimination and rearrangement. A silacyclopropane intermediate is postulated as a precursor to the latter.[108]



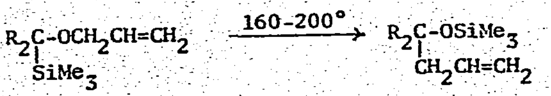
$$(Cl_3SiCCl_2)_2SiCl_2 + MeMgI\ (XS) \longrightarrow \begin{cases} Me_3SiC{\equiv}CSiMe_3 & (47\%) \\ SiMe_4 & (>30\%) \\ CH_2{=}\underset{\displaystyle SiMe_3}{\underset{|}{C}}{-}CH(SiMe_3)_2 & (24\%) \\ (Me_3Si)_2C{=}CHSiMe_3 & (6\%) \\ Me_3Si\underset{\displaystyle CH_2}{\underset{\|}{C}}SiMe_2\underset{\displaystyle CH_2}{\underset{\|}{C}}SiMe_3 & (5\%) \end{cases}$$



$$Cl_3SiCCl_2SiCl_2CH_2SiCl_3 + MeMgI\ (XS) \longrightarrow Me_3Si\underset{\displaystyle CH_2}{\underset{\|}{C}}SiMe_2CH_2SiMe_3$$

$$Me_3SiCCl_2SiCl_2CHClSiCl_3 + MeMgI\ (XS) \longrightarrow (Me_3Si)_2C{=}CHSiMe_3$$

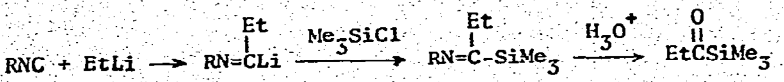
A (trimethylsilylmethyl)allyl ether system undergoes a high-yield pericyclic rearrangement upon heating.[109]



$$R_2\underset{\displaystyle SiMe_3}{\underset{|}{C}}{-}OCH_2CH{=}CH_2 \xrightarrow{160\text{-}200^\circ} R_2\underset{\displaystyle CH_2CH{=}CH_2}{\underset{|}{C}}{-}OSiMe_3$$

(R + R = o,o'-biphenylene, R = Ph)

The reaction of organolithium reagents with isonitriles affords a lithium aldimine which can be derivatized with chlorotrimethylsilane and the adduct hydrolyzed to the α-silyl ketones.[110]

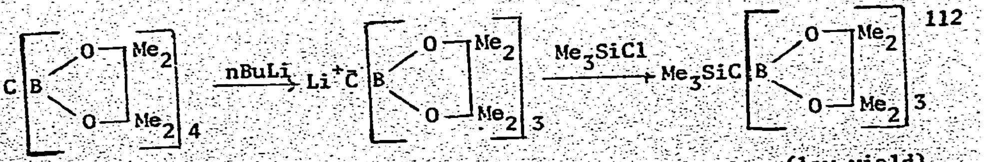


$$RNC + EtLi \longrightarrow RN{=}\overset{\displaystyle Et}{\overset{|}{C}}Li \xrightarrow{Me_3SiCl} RN{=}\overset{\displaystyle Et}{\overset{|}{C}}{-}SiMe_3 \xrightarrow{H_3O^+} Et\overset{\displaystyle O}{\overset{\|}{C}}SiMe_3$$

(R = 1,1,3,3-tetramethylbutyl) (80%) (50%)

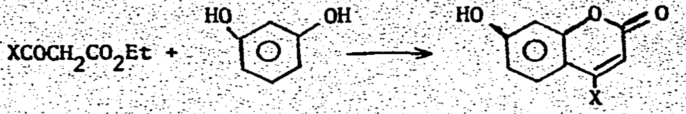
The synthesis and reactivities of the following systems have appeared.

$$Ph_2SnH_2 + Ph_3SiCO_2H \xrightarrow{-H_2} Ph_2Sn(O_2CSiPh_3)_2$$ [111]



112

(low yield)



113

(X = $Me_3Si(CH_2)_n$, $Me_3Si(CH_2)_nC_6H_4$; the ketoesters were prepared from the ketones $XCOCH_3$, and preparative details for the ketones are also given)

$$Et_3SiCH_2COCl \xrightarrow{CH_2N_2} Et_3SiCH_2COCHN_2 \begin{cases} \xrightarrow{PPh_3} Et_3SiCH_2COCH{=}NN{=}PPh_3 \\ \xrightarrow{Br_2} Et_3SiCH_2COCHBr_2 \\ \xrightarrow{AcOH} Et_3SiCH_2CHCH_2OAc \end{cases} \quad 114$$

$$'' \xrightarrow{NaN_3} Et_3SiCH_2NCO \quad 114$$

$$Me_3Si(CH_2)_3SCOCH_3 \xrightarrow{h\nu} \underset{(23\%)}{CH_3CHO} + \underset{(41\%)}{Me_3Si(CH_2)_3SCH_3} + \underset{(4\%)}{[Me_3Si(CH_2)_3]_2S_2} + \underset{(6\%)}{Me_3SiCH_2CH_2CH_3} \quad 115$$

$$Me_3Si(CH_2)_3SCOCH_3 \xrightarrow{h\nu} \underset{(32\%)}{CH_3CHO} + \underset{(25\%)}{Me_3Si(CH_2)_2SCH_3} + \underset{(14\%)}{[Me_3Si(CH_2)_2]_2S} + \underset{(16\%)}{Me_3SiEt} + \underset{(7\%)}{[Me_3Si(CH_2)_2]_2S} \quad 115$$

$$\begin{tikzcd}
Me_3Si(CH_2)_nSCOCH_3 \arrow[r, "OH^-"] & Me_3Si(CH_2)_n SH \arrow[r, "HCl", "CH_2O"'] & Me_3Si(CH_2)_nSCH_2Cl \arrow[d, "LiAlH_4"] \\
 & Me_3Si(CH_2)_nSO_2CH_3 & Me_3Si(CH_2)_nSCH_3 \arrow[l, "{[ox]}"']
\end{tikzcd} \quad 116$$

(n = 2,3)

$$Et_3SiCH_2SEt_3 \xrightarrow[HOAc]{H_2O_2} \underset{(56\%)}{Et_3SiCH_2SO_2Et} + \underset{(10\%)}{(Et_3Si)_2O} \quad 117$$

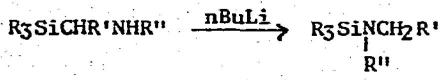
Aminomethylsilanes may be prepared from the novel aminomethyllithium reagents.[118]

$$CH_3(R)NCH_2Li + Me_3SiCl \longrightarrow CH_3(R)NCH_2SiMe_3$$

$[R = PhCH_2, Me_2NCH_2CH_2, CH_3(OCH_2CH_2)_3, HOCH_2CH_2, PhCH{=}CHCH_2]$

$$CH_3N(CH_2Li)_2 + 2\ Me_3SiCl \longrightarrow CH_3N(CH_3SiMe_3)_2$$

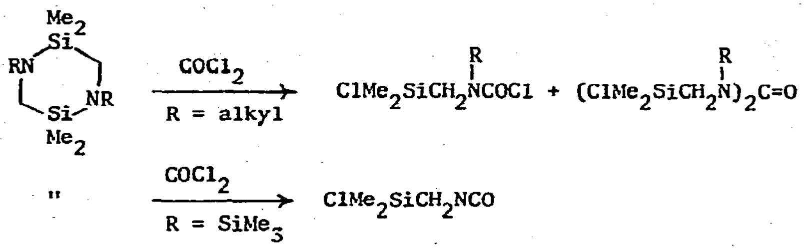
A rearrangement of aminomethylsilanes involving a 1,2-silyl group migration has been discovered.[119]



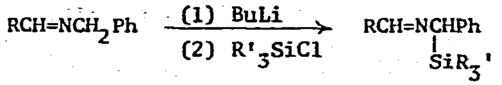
$$R_3SiCHR'NHR'' \xrightarrow{nBuLi} R_3Si\underset{R''}{N}CH_2R'$$

(R' = H, Ph; R" = alkyl; no rearrangement occurs for R" = Ph)

Carbamyl chlorides, ureas or isocyanates are products which arise from phosgene treatment of the heterocycles shown below.[120]



Silyl azomethines were prepared from a metalation route.[121]

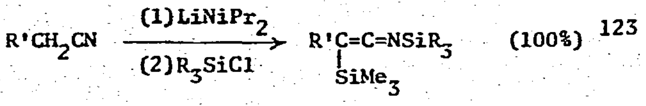


$$RCH{=}NCH_2Ph \xrightarrow[(2)\ R'_3SiCl]{(1)\ BuLi} RCH{=}N\underset{SiR_3'}{C}HPh$$

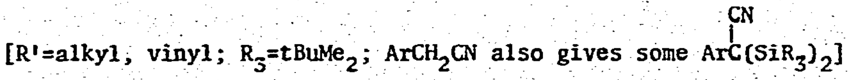
$$CH_3\text{-}CH{=}N\text{-}C_6H_{11} \xrightarrow{\text{"}} R_3'SiCH_2CH{=}CH\text{-}C_6H_{11}$$

The chemistry of some unsaturated silicon-nitrogen compounds has been investigated.

$$Me_3SiCl + Ag_2(CN)_2 \longrightarrow Me_3SiN{=}C{=}NSiMe_3 \quad ^{122}$$



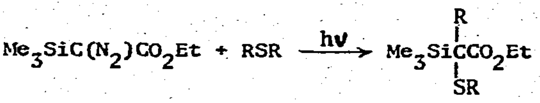
$$R'CH_2CN \xrightarrow[(2)R_3SiCl]{(1)LiNiPr_2} R'\underset{SiMe_3}{C}{=}C{=}NSiR_3 \quad (100\%) \quad ^{123}$$



[R'=alkyl, vinyl; R_3=tBuMe$_2$; $ArCH_2CN$ also gives some $Ar\overset{CN}{C}(SiR_3)_2$]

$$\mathrm{R'R''CHCN} \xrightarrow[\mathrm{R_3SiCl}]{\mathrm{LiNiPr_2}} \mathrm{R'R''C{=}C{=}NSiR_3}\ (87\text{-}100\%)$$ [123]

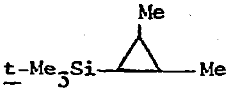
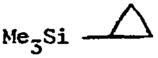
α-Silyldiazomethyl reagents were employed to generate some carbon-sulfur bond insertion products.[124]



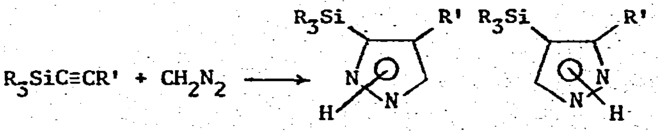
$$\mathrm{Me_3SiC(N_2)CO_2Et} + \mathrm{RSR} \xrightarrow{h\nu} \mathrm{Me_3Si\overset{R}{\underset{SR}{C}}CO_2Et}$$

(R = Me, Et, iPr)

The photochemical reaction of diazomethyltrimethylsilane with substrates has been studied.[125] Similar results were obtained with copper-(II) chloride catalysis.

Substrate	Products (%)
t-$\mathrm{CH_3CH{=}CHCH_3}$	 (23) + t-$\mathrm{Me_3SiCH{=}CHSiMe_3}$ (61)
$\mathrm{CH_2{=}CH_2}$	 (17) + + t-$\mathrm{Me_3SiCH{=}CHSiMe_3}$ (30)+ $\mathrm{C_8H_{20}Si_2}$ (19)
$\mathrm{(CH_3)_2C{=}C(CH_3)_2}$ or $\mathrm{F_2C{=}CF_2}$ or $\mathrm{CF_3CF{=}CF_2}$	(no cyclopropane) + t-$\mathrm{Me_3SiCH{=}CHSiMe_3}$ (30) + $\mathrm{C_8H_{20}Si_2}$ (30)
$\mathrm{Me_3SiH}$	$\mathrm{Me_3SiCH_2SiMe_3}$ (66)

Silyl derivatives were included among a large number of acetylenes whose behavior towards diazomethane and 2-diazopropane was studied.[126]

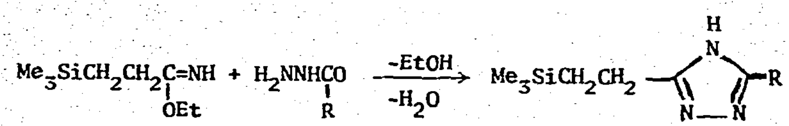


(A) (B)

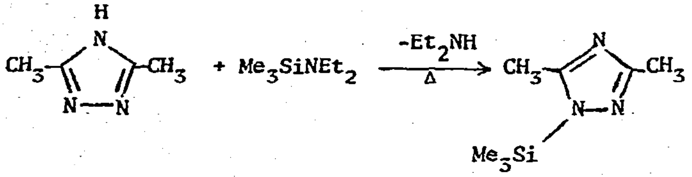
(R=Me, Ph; R'=H, Ph, Me, Me$_3$Si, CH$_2$OH, CHO, CO$_2$Me)

The predominant product for all acetylenes was A; this product ($R'=CO_2Me$) afforded a cyclopropene upon photolysis.

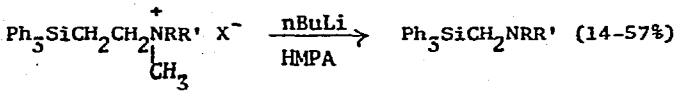
Some silicon-containing triazoles have been prepared.[127]



($R = H, CH_3$)



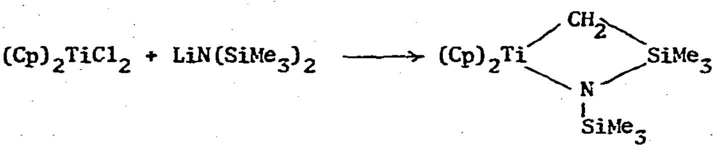
Animomethylsilanes are produced when 2-silyl-substituted ethylammonium salts are treated with n-butyllithium. No such product was obtained when R = Me, R' = Ph, however.[128]



$$Ph_3SiCH_2CH_2\overset{+}{N}RR'(CH_3)\ X^- \xrightarrow[HMPA]{nBuLi} Ph_3SiCH_2NRR'\ (14\text{-}57\%)$$

($R = R' = Me, Et; R = Me, R' = iPr$)

A novel heterocycle was formed from titanocene dichloride and lithium bis(trimethylsilyl) amide.[129]



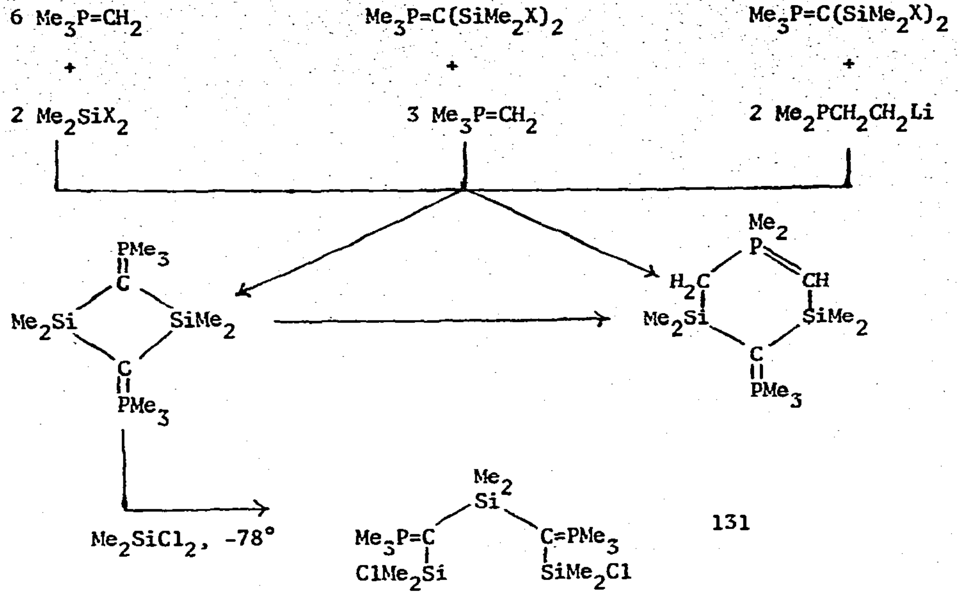
Various silylmethyl phosphines have been characterized. With R = Me and X = S, a bis-adduct, $(Me_3Si)_2CHP(S)Ph_2$, was obtained.[130]

$$R_3SiCl + LiCH_2P(X)Ph_2 \longrightarrow R_3SiCH_2P(X)Ph_2$$

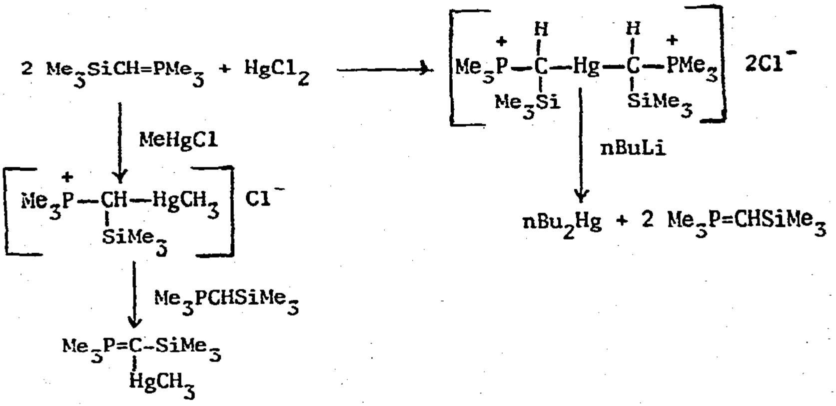
(R = Et, Ph, naphthyl; X = O or S)

$$Et_3SiCH_2MgCl + PhPOCl_2 \longrightarrow Et_3SiCH_2P(O)PhCH_2SiEt_3$$

Interesting chemistry continues to be discovered in the silyl-ylid area.



131



132

Transfer of silyl groups from transition metal complexes to ylids has been observed.[133] Substitution reactions were also reported.

$LnMSiMe_3 + R_3P{=}CHR' \longrightarrow R_3P{=}CR'SiMe_3$

[$LnM = Cp(CO)_3Mo$, $Cp(CO)_3W$, $Cp(CO)_2Fe$; R = alkyl, R' = H,Me,$SiMe_3$]

$Cp(CO)_2FeSiMe_2Cl + Me_2S(O){=}CH_2 \longrightarrow Me_2S(O){=}CHSiMe_2Fe(CO)_2Cp$

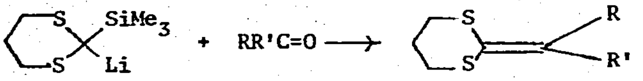
$\quad '' \quad + Me_3P{=}CHSiMe_3 \longrightarrow Me_3PC(SiMe_3)SiMe_2Fe(CO)_2Cp$

Trimethylsilylmetal compounds are formed quickly and cleanly by the addition of bis(trimethylsilyl) mercury to metal sand.[134]

$(Me_3SiCH_2)Hg + 2M \longrightarrow 2\ Me_3SiCH_2M + Hg$

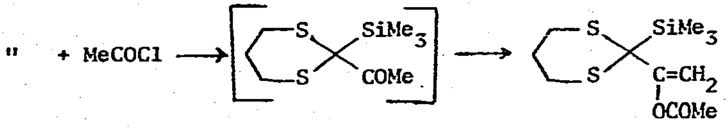
(M = Na, K, Rb, Cs)

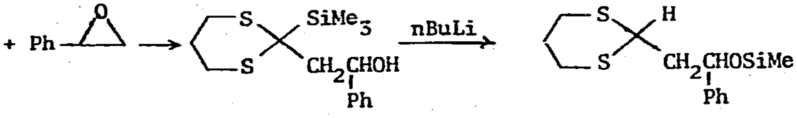
Reactions of 2-lithio-2-trimethylsilyl-1,3-dithiane with a number of electrophilic reagents proceed as shown.[135]

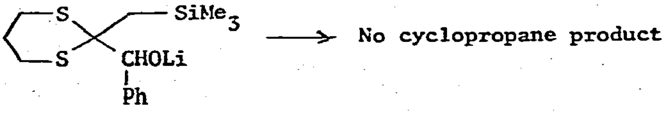


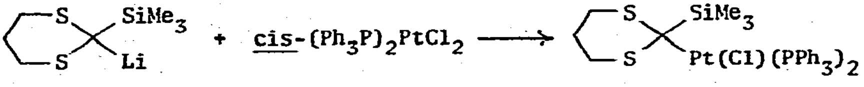
(45-75%)

(R,R' = alkyl, aryl, H, vinyl, Me_2N)









Silylmethyl-lithium or -sodium reagents may be prepared via the alkoxide-induced cleavage of silicon-carbon bonds.[136]

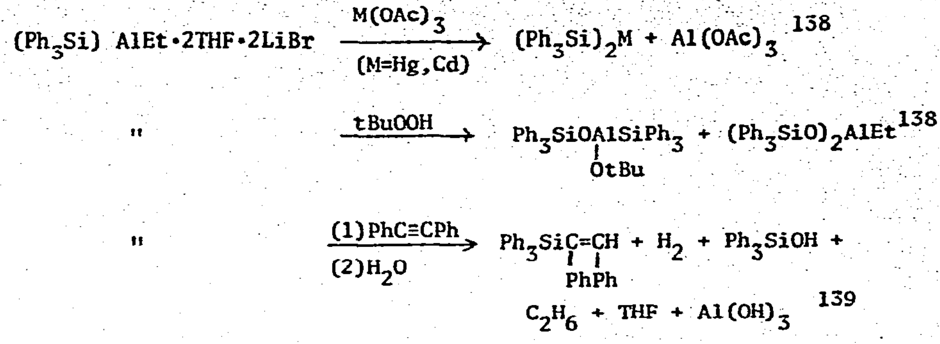
$(Me_3Si)_nCH_{4-n} + MOMe \xrightarrow{HMPA} [(Me_3Si)_nCH_{3-n}]^-M^+ + MeOSiMe_3$

(n = 2-4; M = Li, Na)

$(Me_3Si)_2CHPh + NaOMe \xrightarrow{HMPA} Me_3SiCH(Ph)Li + MeOSiMe_3$

High yields of 1,7-bis(dimethylsilyl)-m-carborane have been realized by the reaction of the 1,7-dilithio reagent with dimethylchlorosilane.[137]

Some reactions of a silylaluminum species have been investigated.



$$(Ph_3Si)\ AlEt \cdot 2THF \cdot 2LiBr \xrightarrow[(M=Hg,Cd)]{M(OAc)_3} (Ph_3Si)_2M + Al(OAc)_3 \quad ^{138}$$

$$'' \xrightarrow{tBuOOH} Ph_3Si\underset{\substack{|\\OtBu}}{Al}SiPh_3 + (Ph_3SiO)_2AlEt \quad ^{138}$$

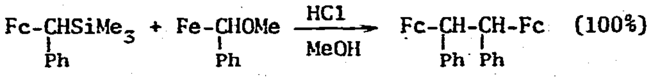
$$'' \xrightarrow[(2)H_2O]{(1)PhC\equiv CPh} Ph_3Si\underset{\substack{|\\Ph}}{C}=\underset{\substack{|\\Ph}}{CH} + H_2 + Ph_3SiOH + C_2H_6 + THF + Al(OH)_3 \quad ^{139}$$

Ferrocenylmethylsilanes are known to be cleaved by acids at the carbon-silicon bond. In the presence of ferric chloride or other oxidants [I_2, $Ce(SO_4)_2$, $Cu(OAc)_2$], cleavage occurs in methanol to give the methyl ether.[140]

$$Fc\text{-}CH_2SiMe_2R \xrightarrow{MeOH} \begin{cases} \xrightarrow{acid} Fc\text{-}CH_3 + Me_3SiOMe \\ \xrightarrow{FeCl_3} Fc\text{-}CH_2OMe + Me_2RSiOMe + FeCl_2 + HCl \end{cases}$$

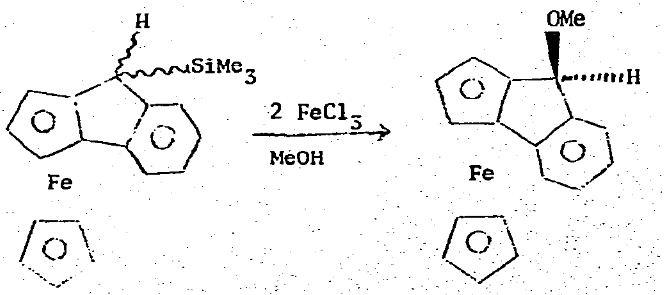
(Fc = ferrocenyl; R = alkyl, aryl, $SiMe_3$, OMe)

Coupling was observed when α(trimethylsilyl)benzyl ferrocene and α-(methoxy)benzyl ferrocene were treated with methanolic HCl. Pairing of radical species was postulated.[141]

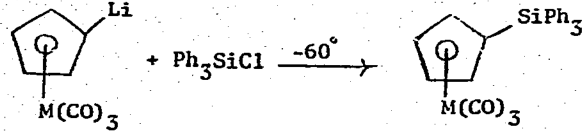


$$Fc\text{-}\underset{\substack{|\\Ph}}{CH}SiMe_3 + Fe\text{-}\underset{\substack{|\\Ph}}{CH}OMe \xrightarrow[MeOH]{HCl} Fc\text{-}\underset{\substack{|\\Ph}}{CH}\text{-}\underset{\substack{|\\Ph}}{CH}\text{-}Fc \quad (100\%)$$

Treatment of either exo- or endo-1-(trimethylsilyl)-2,3-ferrocenoindane with ferric chloride in methanol affords the exo-ether and no coupling products.[142]



Cyclopentadienyl-metal complexes may be metalated and derivatized to afford silyl-substituted complexes.[143]



(M = Mn, 25%; Re, 63%)

Certain mercurials react with methylidenetricobalt nonacarbonyl to yield methylidene-substituted species.[144] No product was obtained,

$$Hg(CHBrSiMe_3)_2 + HCCo_3(CO)_9 \longrightarrow Me_3SiCH_2CCo_3(CO)_9 \quad (70\%)$$

however, when $Hg(CH_2SiMe_3)_2$ was employed.

Lively interest continues to center about the stabilizing effect of trimethylsilylmethyl ligands attached to a central metal atom. The following chemistry has appeared in this area (R = Me_3SiCH_2 in the equations below).

$$\begin{tikzcd}
3(Me_3SiCH_2)_2Hg + 2\ Al/Hg \arrow[r, "110^\circ"] & 2\ (Me_2SiCH_2)_3Al + 3Hg \arrow[dl, "MeNH_2"] \\
{[(Me_3SiCH_2)_2AlNHMe]_2 + Me_4Si} &
\end{tikzcd}$$ [145]

$$R'_3SiCH_2Cl + SnCl_2 \xrightarrow[\Delta]{\text{ethereal solvent}} R'_3SiCH_2SnCl_3$$ [146]

(R'_3 = alkyl, aryl, halo, alkoxy)

$$R_3SnLi + CH_3CH_2Br \longrightarrow R_3SnCH_2CH_3$$ [147]

" $+ (CH_3)_3CCl \longrightarrow R_3SnH + R_3SnSnR_3$

" $+ (CH_3)_3CBr \longrightarrow R_3SnBr + R_3SnSnR_3$

" $+ PhCl \longrightarrow R_3SnSnR_3$

" $+ PhCOCl \longrightarrow R_3SnCOPh$

" $+ ClCH_2CO_2Et \longrightarrow R_3SnSnR_3$

" $+ ClHgCH_3 \longrightarrow R_3SnCH_3 + R_3SnSnR_3$

$R_3SnLi + Ph_2CO \longrightarrow Ph_2CHOH + R_3SnSnR_3$

" $+ PhC{\equiv}CH \longrightarrow PhC(Li){=}CHSiR_3 + R_3SnH + PhC{\equiv}CLi$

" $+ Ph_2C{=}CH_2 \longrightarrow Ph_2C{=}CHLi$

" $+ Me_3COOCMe_3 \longrightarrow R_3SnOCMe_3 + Me_3COLi$ [148]

" $+ (PhCO_2)_2 \longrightarrow R_3SnSnR_3 + PhCO_2Li$ [148]

" $+ (PhCO_2)_2 \longrightarrow R_3SnSnR_3 + PhCO_2Li$ [148]

$2\ R_3MH + Et_2Cd \longrightarrow (R_3M)_2Cd + EtH$ [149]

(M = Sn, Ge)

$(R_3M)_2Cd + (PhCO_2)_2 \longrightarrow Cd(O_2CPh)_2 + R_3SnO_2CPh$

$(R_3Sn)_2Cd + Li \longrightarrow R_3SnLi \xrightarrow{Et_3SiBr} R_3SnSiEt_3$

$(R_3M)_2Cd + Hg \longrightarrow (R_3Sn)_2Hg$ or $(R_3Ge)_2Hg$

$(R_3Sn)_2Cd + Hg(CH_2CO_2Me)_2 \longrightarrow Cd(CH_2CO_2Me)_2 + (R_3Sn)_2Hg$

$(R_3Sn)_2M + 2\ I_2 \longrightarrow MI_2 + 2\ (R_3Sn)_2SnI$

(M = Cd, Hg)

$R_2Hg \xrightarrow[100\ h]{200^\circ} Me_4Si + RHgCH_2SiMe_2CH_2CH_2SiMe_3 + Hg$ (5% conversion)[150]

$R_2Hg + HgX_2 \xrightarrow[20^\circ]{EtOH} 2\ RHgX$ (X = Cl, Br, I) (100%) [150]

$(Me_3Si_2CHLi + MCl_3 \longrightarrow [(Me_3Si)_2CH]_3M$; (M = Sc, Y, Ti, V, Cr)[151]

" $+ MCl_4 \longrightarrow [(Me_3Si)_2CH]_3MCl$; (M = Zr, Hf) [151]

" $+ Cp_2TiCl_2 \longrightarrow Cp_2TiCH(SiMe_3)_2$ [151]

$RM + (Cp_2TiCl)_2 \longrightarrow Cp_2TiR_2$ [152]

$RM + (CpTiCl_2)_n \longrightarrow CpTiR_3$ [152]

(M = Li, MgCl)

$CpFe(CO)_2SiMe_{2-n}Cl_nCH_2Cl \xrightarrow{100^\circ} CpFe(CO)_2CH_2SiMe_{2-n}Cl_{n+1}$ [153]

(n = 0-2)

$(Cp_2TiCl)_2 + RLi \longrightarrow Cp_2TiR$ [154]

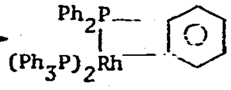
$Cp_2TiCl_2 + RLi \longrightarrow CpTiR_3$ [154]

$$\begin{tikzcd}
TlCl_3 + 2\,RLi \arrow[r] & R_2TlCl \arrow[r, "TiOCOiPr"] \arrow[d, "Br_2NC_5H_5"] & R_2TiOCOiPr \arrow[d, "Hg(OCOiPr)_2"] \\
 & {[RTlClBr]} \arrow[r, "TlOCOiPr"] \arrow[d, "Me_4Sn"] & RTl(OCOiPr)_2 \arrow[d, "Me_4Sn"] \\
 & MeRTlBr \arrow[r, "TlOCOiPr"] & MeRTlOCOiPr
\end{tikzcd}$$ [155]

$$\begin{tikzcd}
Cr(CO)_6 + RLi \arrow[r, "Me_4NBr"] & Me_4N[(CO)_5CrC(O)R] \arrow[r, "\Delta"] \arrow[dl, "AcCl{,}\ CH_2Cl_2"'] \arrow[d, "I_2"] \arrow[dr, "AcCl{,}\ MeCN"] & (CO)_5Cr\overset{O^-}{C}CH_2NMe_3 \\
Me_4N[(CO)_5CrCl] & Me_4N[(CO)_5CrI] & (CO)_5CrNCMe
\end{tikzcd}$$ [156]

$(CO)_5CrC(OEt)R \xrightarrow{HX} (CO)_5CrC(X)CH_3 \quad (X = OR,\ NH_2)$ [156]

$(Ph_3P)_3RhCl + RMgCl \longrightarrow$



$+ RH$ [157]

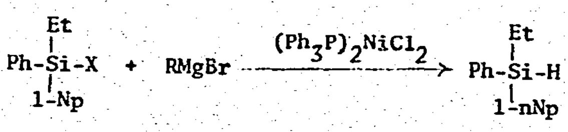
$(Ph_3P)_3RhCl + R_4M$ " $(M = Ti,\ Zr)$ [157]

$(Ph_3P)_3RhCl + HMe_2SiCH_2Cl \xrightarrow{Mg} (Ph_3P)_4RhH + Rh + Me_3SiH + kMe_2SiH$ [157]

V. SILAFUNCTIONAL COMPOUNDS

1. Si-H

Saturated Grignard reagents activated by nickel complexes reduce halo- and alkoxysilanes stereospecifically. Retention of configuration occurs for X = OMe and F, but inversion is observed for X = Cl.[158]



$$Ph\text{-}\underset{1\text{-}Np}{\overset{Et}{Si}}\text{-}X + RMgBr \xrightarrow{(Ph_3P)_2NiCl_2} Ph\text{-}\underset{1\text{-}nNp}{\overset{Et}{Si}}\text{-}H$$

(R = Et, nPr, iPr, nBu, iBu)

Vinylsilanes ($X = CH_2{=}CH$) are also reduced while deuterosilanes ($X{=}D$) undergo H-D exchange.

The syntheses of bifunctional, optically active phenyl-α-naphthyl-(-)-menthoxysilanes (Ph-α-Np(-)MenOSiX, X = H, Cl, OMe, OEt) have been described.[159]

Trichlorosilane, but not trifluoro- or trimethylsilane, reacts with cyanogen chloride.[160]

$$HSiCl_3 + ClCN + NEt_3 \longrightarrow NCSiCl_3 + NEt_3{\cdot}HCl$$

$$(80\%)$$

2. Si-Group VII

A method for the transformation of Si-H bonds into Si-Cl bonds employs homogeneous cupic chloride solutions.[161]

$$R_3SiH + CuCl_2 \xrightarrow{CH_3CN} R_3SiCl + CuCl$$

(R = iPr, Et)

High yields (96-99%) of chlorosilanes (R_3SiCl) are realized by reaction of R_3SiH with chlorobenzene and colloidal nickel.[162]

Ligand exchanges among silicon, germanium and tin compounds were found to proceed as shown.[163]

$$Bu_3SnOMe + R_3SiX \longrightarrow Bu_3SnX + R_3SiOMe \quad (X = F, Cl, Br, I)$$

$$(Bu_3Sn)_2O + 2\ Me_3SiX \longrightarrow 2\ Bu_3SnX + (Me_3Si)_2O \quad (X = Cl, Br)$$

$$Bn_3SnOAc + Me_3SiX \longrightarrow Bu_3SnX + Me_3SiOAc \quad (X = Cl, Br)$$

$$Bu_3SnY + Me_2SiCl_2 \longrightarrow Bu_3SnCl + Me_2SiClY \quad (Y = OMe, OAc)$$

$$Bu_3SnY_2 + R_3SiX \longrightarrow Bu_2SnXY + R_3SiOMe \quad (X = F, Cl, Br, I)$$

Mixed products were not obtained with an excess of halosilane; only tin dihalides resulted.

Equilibrium constants have been reported for scrambling of the substituent pairs Cl/Br, Cl/I, Br/I, Cl/OMe, Br/OMe, Cl/OPh, Cl/SMe and

Br/SMe between the Me_2Si and MeGe moieties. Lower atomic number halogens favor silicon attachment in halogen/halogen redistribution. Halogens favor germanium in halogen/OR systems, while the opposite is true for halogen /SR exchange.[164]

Chlorosilanes react with cobalt carbonyl species to give low yields of a variety of products.[165]

$$Co_2(CO)_8 + MeSiCl_3 \xrightarrow{THF} RCCo_3(CO)_9 \; [R = C_4H_9, HO(CH_2)_4]$$

$$Co_2(CO)_8 + SiCl_4 \xrightarrow{THF} Cl_3SiOCCo_3(CO)_9$$

$$NaCo(CO)_4 + MeSiCl_3 \xrightarrow{THF} HO(CH_2)_4CCo_3(CO)_9$$

$$'' \quad + SiCl_4 \xrightarrow{THF} Co_4(CO)_{10}$$

$$'' \quad + MeSiCl_3 \xrightarrow{Et_2O} MeCl_2SiOCCo_3(CO)_9$$

$$'' \quad + SiCl_4 \xrightarrow{Et_2O} Cl_3SiOCCo_3(CO)_9$$

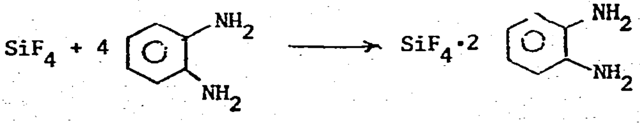
A number of halosilane adducts to electron-donor organic compounds have been reported.

$$SiCl_nOMe)_{4-n} + Me_2NCHO \longrightarrow 1{:}2 \text{ adduct } {}^{166}$$

$$(n = 0\text{-}4)$$

$$'' \quad + H_2NCRO \longrightarrow 1{:}(n+2) \text{ adduct } {}^{166}$$

$$(R = Me, H, Ph)$$



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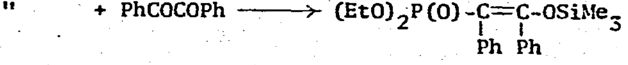
The fluorosilanes $PhMeSiF_2$, Ph_2SiF_2, $PhSiF_3$ and Et_3SiF formed adducts with $MeNO_2$, $PhNO_2$, Me_2NAc, Me_2SO, $(Me_3N)_3PO$, PhF and PhCOMe.[168]

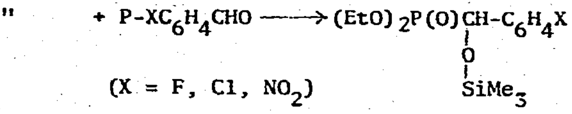
3. Si-Group VI

Phosphorous reagents have been employed in the preparation of alkoxysilanes from carbonyl-containing compounds.

$(EtO)_2POSiMe_3 + CF_3COCF_3 \longrightarrow (EtO)_2P(O)C(CF_3)_2OSiMe_3$ 169

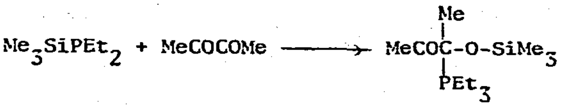


$'' + PhCOCOPh \longrightarrow (EtO)_2P(O)\text{-}\underset{Ph}{C}{=}\underset{Ph}{C}\text{-}OSiMe_3$ 170

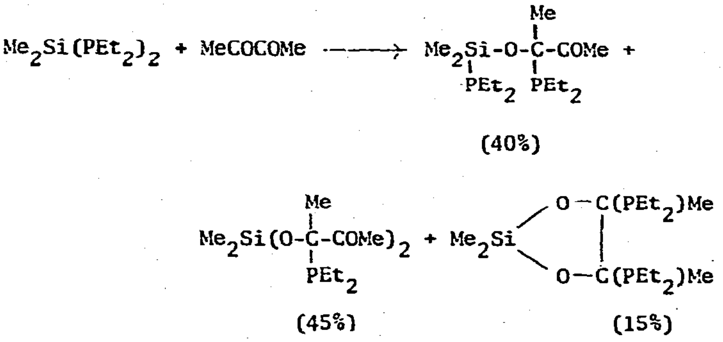


$'' + p\text{-}XC_6H_4CHO \longrightarrow (EtO)_2P(O)\underset{\underset{SiMe_3}{O}}{CH}\text{-}C_6H_4X$

$(X = F, Cl, NO_2)$



$Me_3SiPEt_2 + MeCOCOMe \longrightarrow MeCO\overset{Me}{\underset{PEt_3}{C}}\text{-}O\text{-}SiMe_3$ 171

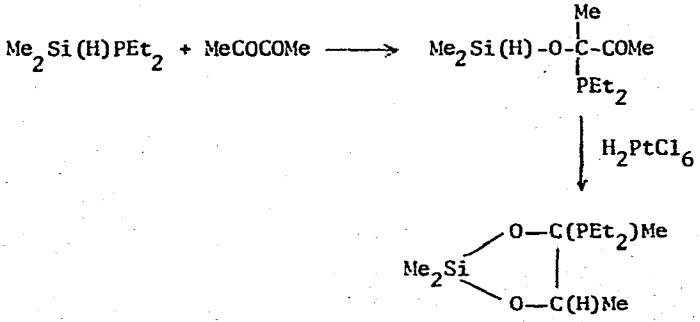


$Me_2Si(PEt_2)_2 + MeCOCOMe \longrightarrow \underset{PEt_2}{Me_2Si}\text{-}O\text{-}\overset{Me}{\underset{PEt_2}{C}}\text{-}COMe +$

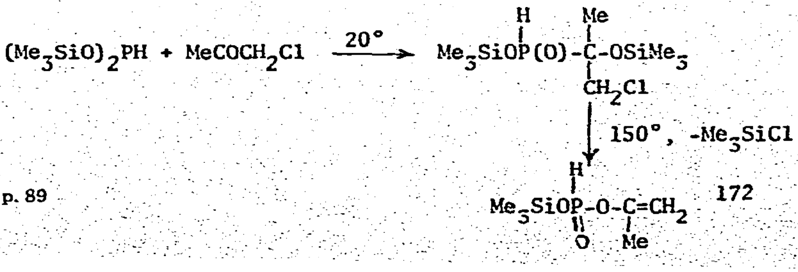
(40%)

$Me_2Si(O\text{-}\overset{Me}{\underset{PEt_2}{C}}\text{-}COMe)_2 + Me_2Si\langle{}^{O-C(PEt_2)Me}_{O-C(PEt_2)Me}$ 171

(45%) (15%)

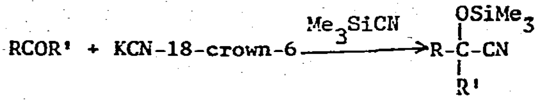


$Me_2Si(H)PEt_2 + MeCOCOMe \longrightarrow Me_2Si(H)\text{-}O\text{-}\overset{Me}{\underset{PEt_2}{C}}\text{-}COMe \xrightarrow{H_2PtCl_6} Me_2Si\langle{}^{O-C(PEt_2)Me}_{O-C(H)Me}$ 171



$(Me_3SiO)_2PH + MeCOCH_2Cl \xrightarrow{20°} Me_3SiO\overset{H}{P}(O)\text{-}\overset{Me}{\underset{CH_2Cl}{C}}\text{-}OSiMe_3 \xrightarrow{150°,\ -Me_3SiCl} Me_3SiO\overset{H}{\underset{O}{P}}\text{-}O\text{-}\underset{Me}{C}{=}CH_2$ 172

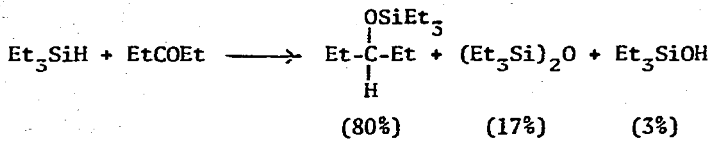
Crown ether complexes of alkali metal cyanides are efficient catalysts for carbonyl cyanosilylation.[173]



$$\mathrm{RCOR' + KCN\text{-}18\text{-}crown\text{-}6 \xrightarrow{Me_3SiCN} R\text{-}\overset{OSiMe_3}{\underset{R'}{C}}\text{-}CN}$$

(R, R' = alkyl, H)

Electrolysis of a mixture of triethylsilane and 3-pentanone affords the alkoxysilane as part of the product mixture.[174]



$$\mathrm{Et_3SiH + EtCOEt \longrightarrow \underset{(80\%)}{Et\text{-}\overset{OSiEt_3}{\underset{H}{C}}\text{-}Et} + \underset{(17\%)}{(Et_3Si)_2O} + \underset{(3\%)}{Et_3SiOH}}$$

A number of oxinatosilanes, some containing chelated structures, were prepared from chlorosilanes and 8-hydroxyquinoline.[175]

The ease of condensation of alcohols with dimesitylchlorosilane (Ms_2SiHCl) was investigated as a function of the steric bulk of the alcohol.[176]

Siloxyalkenes can be ozonized to the corresponding silyl esters, although migration of silicon to an adjacent position occurred with some systems.

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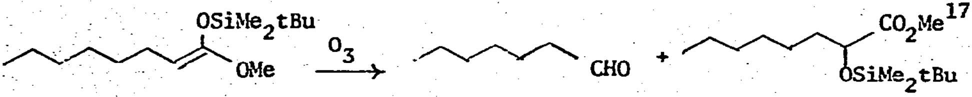

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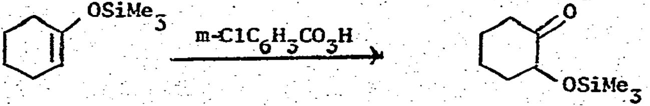
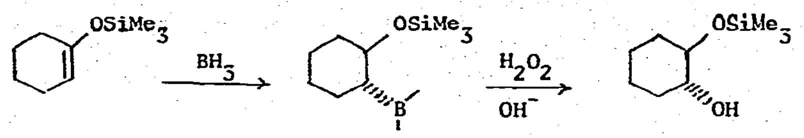
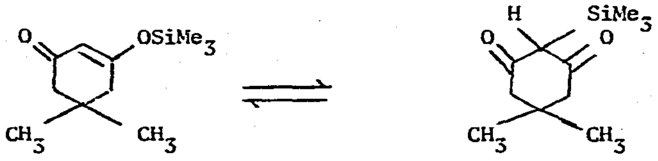
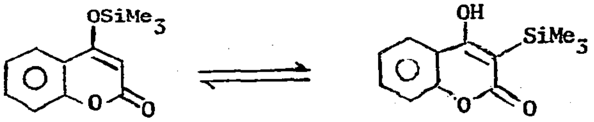


Hydroboration-oxidation of cyclic silyl enol ethers afforded the alcohol derived from introduction of boron <u>beta</u> to the siloxy function. The intermediate organoboranes were only stable in cyclic systems and led to elimination in acyclic substrates.[179]

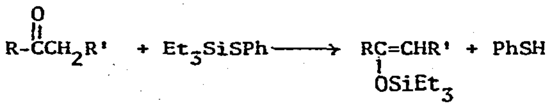


Certain silyl-substituted keto-enols undergo O-C rearrangements in solution.[180]

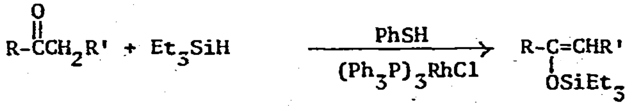




Easily enolizable ketones are converted into silyl enol ethers by triethylsilylthiophenoxide. The process can be made catalytic in thiophenol.[181]



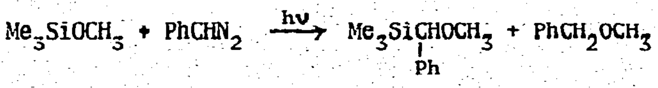
$$\text{R-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_2\text{R'} + \text{Et}_3\text{SiSPh} \longrightarrow \text{R}\underset{\text{OSiEt}_3}{\underset{|}{\text{C}}}\text{=CHR'} + \text{PhSH}$$



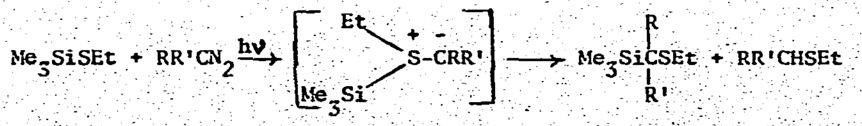
$$\text{R-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_2\text{R'} + \text{Et}_3\text{SiH} \xrightarrow[(\text{Ph}_3\text{P})_3\text{RhCl}]{\text{PhSH}} \text{R-}\underset{\text{OSiEt}_3}{\underset{|}{\text{C}}}\text{=CHR'}$$

(R = Ph, R' = CN; R = Me, R' = CO_2Me; R = Me, R' = COMe)

An overall insertion of carbenes into Si-O and Si-S bonds has been found to occur; these may arise via a silyl group shift from carbene-complexed heteroatom to carbon.[182]

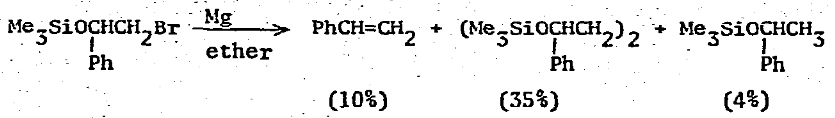


$$\text{Me}_3\text{SiOCH}_3 + \text{PhCHN}_2 \xrightarrow{h\nu} \text{Me}_3\text{Si}\underset{\text{Ph}}{\underset{|}{\text{C}}}\text{HOCH}_3 + \text{PhCH}_2\text{OCH}_3$$



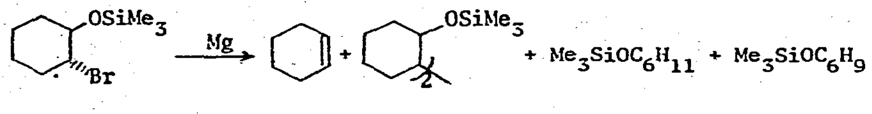
(R = H, R' = CO_2Et; R = H, R' = Ph; R = R' = Ph)

In addition to the expected elimination products, 2-bromoalkoxysilanes and magnesium also afford products of coupling and disproportionation.[183]



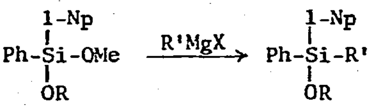
$$\text{Me}_3\text{SiO}\underset{\text{Ph}}{\text{C}}\text{HCH}_2\text{Br} \xrightarrow[\text{ether}]{\text{Mg}} \text{PhCH=CH}_2 + (\text{Me}_3\text{SiO}\underset{\text{Ph}}{\text{C}}\text{HCH}_2)_2 + \text{Me}_3\text{SiO}\underset{\text{Ph}}{\text{C}}\text{HCH}_3$$

(10%) (35%) (4%)

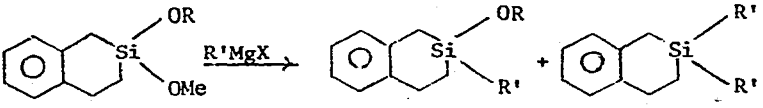


(10%) (31%) (19%) (16%)

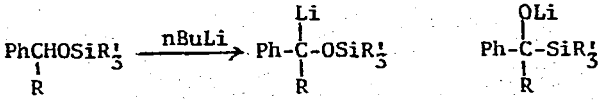
The selectivity between alkoxy groups in the reaction of diaryl methoxyalkoxysilanes with Grignard reagents and the stereochemical changes accompanying substitution have been determined. Phenyl-α-naphthylmethoxyborneoxy (or -menthoxy-) silane undergo replacement of only the methoxy group (with retention) using aromatic or saturated RMgX in ether, while allylic and benzylic Grignards substitute the bulkier alkoxy group with inversion. In THF and DMF, only methoxy is substituted with retention. For the cyclic silanes, both methoxy and menthoxy groups are substituted with retention.[184]



$$\text{Ph-}\overset{\text{1-Np}}{\underset{\text{OR}}{\text{Si}}}\text{-OMe} \xrightarrow{\text{R'MgX}} \text{Ph-}\overset{\text{1-Np}}{\underset{\text{OR}}{\text{Si}}}\text{-R'}$$



1,2-Anionic rearrangement of the silyl group has been observed in metalated benzyloxyorganosilanes.[185] Rearrangement was shown to occur stereospecifically with inversion at benzyl carbon.[186]



$$\text{Ph}\underset{\text{R}}{\text{C}}\text{HOSiR}'_3 \xrightarrow{\text{nBuLi}} \text{Ph-}\overset{\text{Li}}{\underset{\text{R}}{\text{C}}}\text{-OSiR}'_3 \qquad \text{Ph-}\overset{\text{OLi}}{\underset{\text{R}}{\text{C}}}\text{-SiR}'_3$$

(R = H, CH_3, $SiMe_3$; R' = alkyl, Ph)

The relative rates of silyl ether cleavage by phosgene as a function of the alkoxy group were determined. Slower rates were found for bulky alkoxy groups and for unsaturated alkoxy groups.[187]

$$R_3SiOR' + COCl_2 \longrightarrow R_3SiCl + R'OCOCl$$

Some success at the hydrogenolysis of alkoxysilanes has been reported, although fully saturated alkoxysilanes only reacted to low conversion.[188]

$$PhCH_2OSiMe_3 + H_2 \xrightarrow{Pd/C} PhCH_3 + (Me_3Si)_2O$$

Alkoxy- or acetoxystannyl compounds readily exchanged those groups for halogen when treated with halosilanes.[189] No mixed products were

$$Bu_3SnOR + R'_3SiX \longrightarrow Bu_3SnX + R'_3SiOR$$

$$(R = Me,\ COCH_3,\ OSnBu_3;\ X = Cl,\ Br)$$

observed from the reaction of $Bu_2Sn(OR)_2$ with halosilanes.

Exchange of acetoxy for alkoxy groups on silicon in ethynylsilanes has been carried out successfully.[190]

$$HC{\equiv}C\text{-}SiR_{3-n}(OMe)_n \xrightarrow[pTsOH]{Ac_2O} HC{\equiv}C\text{-}SiR_{3-n}(OAc)_n$$

$$(n = 1\text{-}3) \qquad\qquad (21\text{-}65\%)$$

Preparative methods and chemistry in the area of O-silylated oximes have been reported as follows.

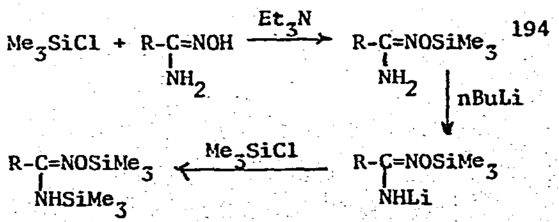
$$2\ R\text{-}CH{=}NOH + (Me_3Si)_2NH \longrightarrow RCH{=}NOSiMe_3 + NH_3 \quad {}^{191,192}$$

$$(R,R' = alkyl,\ aryl,\ H)$$

$$6\ RR'C{=}NOH + (Me_3SiNH)_3 \longrightarrow 3\ (RR'C{=}NO)_2SiMe_2 + 3\ NH_3 \quad {}^{193}$$

$$(R,R' = alkyl,\ aryl,\ H)$$

Preparations of amidoximes have also been described.



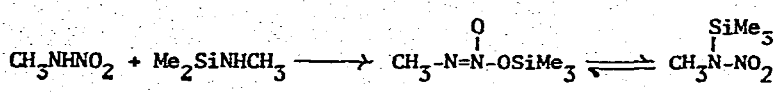
$$\begin{tikzcd} Me_3SiCl + R\text{-}\underset{NH_2}{C}{=}NOH \arrow[r, "Et_3N"] & R\text{-}\underset{NH_2}{C}{=}NOSiMe_3 \ {}^{194} \arrow[d, "nBuLi"] \\ R\text{-}\underset{NHSiMe_3}{C}{=}NOSiMe_3 & R\text{-}\underset{NHLi}{C}{=}NOSiMe_3 \arrow[l, "Me_3SiCl"'] \end{tikzcd}$$

A report on the potential explosion hazard involved in ketoximes and their silyl derivatives has appeared.[195]

N-sulfinyl-O-trimethylsilylhydroxylamine is prepared as shown.[196]

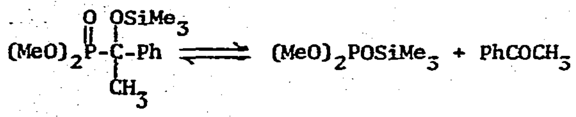
$$(Me_3Si)_2NOSiMe_3 + SOCl_2 \longrightarrow Me_3Si\text{-}O\text{-}N{=}S{=}O + 2\ Me_3SiCl$$

Nitramines may also be silylated to yield tautomeric mixtures of O- and N-silyated material.[197] The O-silyl material is more stable the bulkier the silyl group.



$$CH_3NHNO_2 + Me_2SiNHCH_3 \longrightarrow CH_3\text{-}N{=}\overset{O}{\overset{|}{N}}\text{-}OSiMe_3 \rightleftharpoons CH_3\overset{SiMe_3}{\overset{|}{N}}\text{-}NO_2$$

Dimethyl [α-methyl-α-(trimethylsiloxy)benzyl]phosphonate thermolyzes to dimethyl trimethylsilylphosphite. The reaction is reversible.[198]



$$(MeO)_2\overset{O}{\overset{\|}{P}}\text{-}\underset{CH_3}{\overset{OSiMe_3}{C}}\text{-}Ph \rightleftharpoons (MeO)_2POSiMe_3 + PhCOCH_3$$

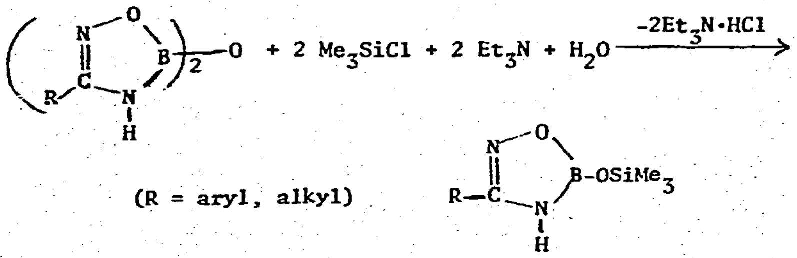
Tetrakis(trimethylsiloxy)phosphonium salts have been prepared in high yield.[199]

$$Me_3SiI + (Me_3SiO)_3PO \longrightarrow (Me_3SiO)_4P^+I^- \quad (100\%)$$

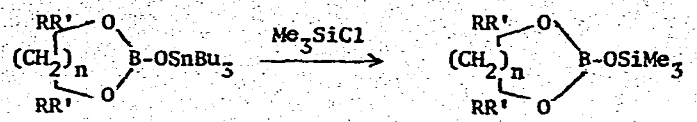
$$Me_3SiI + Me_nP(O)(OSiMe_3)_m \longrightarrow MenP^+(OSiMe_3)_{m+1}I^-$$

$(n \neq m = 1 \text{ or } 2)$

Siloxated oxadiazaboroles are synthesized as shown.[200]



Cleavage of trialkylstannyloxy- or germyloxy-substituted 1,3,2-dioxaborolanes with chlorotrimethylsilane affords the corresponding silyl derivatives.[201]



(n = 0,1; R,R' = Me, H)

Dimethyl(triphenylsiloxy)aluminum undergoes ligand isomerization upon strong heating.[202]

$$Me_2Al\text{-}O\text{-}SiPh \xrightarrow[50h]{250°} MePhAl\text{-}OSiMePh_2 + Ph_2Al\text{-}O\text{-}SiMe_2Ph$$

Monosodium salts of organosilanetriols were prepared and used to synthesize organoaluminosiloxanes.[203]

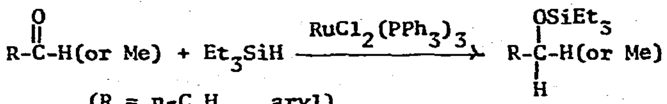
$$3RSi(OH)_2ONa + AlCl_3 \longrightarrow [RSi(OH)_2O]_3Al + 3\ NaCl$$

(R = alkyl, aralkyl, vinyl, Ph)

A trimethylsiloxy vanadium compound has been characterized.[204]

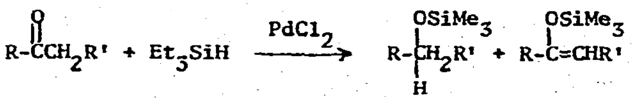
$$3\ Cl_3VO + 3\ HN(SiMe_3)_2 \longrightarrow (Me_3SiO)_3V{=}NSiMe_3 + 2\ Cl_3V{=}NSiMe_3 + 3\ HCl$$

A number of catalysts have been found effective for the hydrosilylation of ketones. In one report, a ruthenium complex affords good yields (55-74%) of silyl ethers. This catalyst was not as active, however as the analogous $RhCl(PPh_3)_3$. The use of palladium chloride affords mixtures of silyl ether and silyl enol ethers.[206] Addition of phenylthiol raised the reaction rate and increased the relative yield of silyl enol ether to 80-90%.



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}H(or\ Me) + Et_3SiH \xrightarrow{RuCl_2(PPh_3)_3} R\text{-}\underset{\underset{H}{|}}{\overset{\overset{OSiEt_3}{|}}{C}}\text{-}H(or\ Me) \quad 205$$

(R = n-C_5H_{11}, aryl)



$$R\text{-}\overset{\overset{O}{\|}}{C}CH_2R' + Et_3SiH \xrightarrow{PdCl_2} R\text{-}\underset{\underset{H}{|}}{\overset{\overset{OSiMe_3}{|}}{C}}H_2R' + R\text{-}\overset{\overset{OSiMe_3}{|}}{C}{=}CHR'$$

(R = alkyl, aryl; R' = H, alkyl)

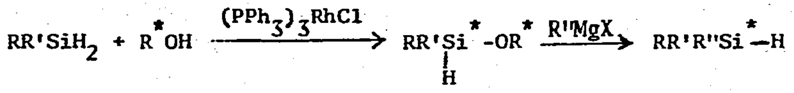
Hydridometallocarboranes of formula 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ and 2,2-$(Ph_3P)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$ were found to catalyze the quantitative hydrosilylation of acetophenone with diphenylsilane.[207]

Optical yields of up to 46% are obtained by the asymmetric hydrosilylation of ketones by a chiral phosphine-rhodium complex.[208]

$$\text{1-NpPhSiH}_2 + \text{RCOR} \xrightarrow{[(C_8H_{14})_2\text{RhCl}]_2} (+)\text{-1-NpPhHSiOCHR}_2$$

(R = alkyl, Ph)

The reaction of optically active alcohols with prochiral silanes ($RR'SiH_2$) affords silyl ethers which can be converted to optically active silyl hydrides.[209]



$$RR'SiH_2 + R^{*}OH \xrightarrow{(PPh_3)_3RhCl} RR'\underset{\underset{H}{|}}{Si^{*}}\text{-}OR^{*} \xrightarrow{R'MgX} RR'R''Si^{*}\text{—}H$$

The chiral complex $[Rh\text{-}((R)\text{-}PhCH_2MePhP)_2H_2S_2]^{+}ClO_4^{-}$, where S = solvent, has also been used for the generation of chiral organosilanes in the hydrosilylation of ketones by 1-NpPhSiH_2.[210]

Fluoride ion was found to catalyze the conversion of aromatic aldehydes into silyl ethers.[211]

$$ArCHO + Et_3SiH \xrightarrow[CH_3CN]{CsF} ArCH_2OSiEt_3$$

Generation of β-silylethyl radicals in aromatic solvents led to the conclusion of high reactivity for these species.[212] A similar conclusion

$$\begin{aligned} Et_3SiCH_2CH_2CO_3tBu &\xrightarrow[\Delta]{\text{Cumene}} Et_4Si + PhCMe_2\text{-}CMe_2Ph \\ '' \quad &\xrightarrow[\Delta]{PhCl} C_6H_4(Cl)CH_2CH_2SiEt_3 \\ '' \quad &\xrightarrow{Et_3SnSnEt_3} Et_3SiCH_2CH_2CO_2SnEt_3 + Et_3SnOtBu \end{aligned}$$

was reached for α-silylmethyl radicals generated from the thermolysis of cumyl triethylsilylperacetate.[213]

Bis(trimethylsilyl)peroxide was found to undergo numerous reactions not observed with its non-silicon counterpart, di-_t_-butylperoxide.[214]

$$Me_3Si\text{-}O\text{-}O\text{-}SiMe_3 \xrightarrow{RM} Me_3SiOR + MOSiMe_3$$

(R = alkyl, aryl; M = Li or MgX)

$$'' \xrightarrow{NaOEt} Me_3SiOEt + NaOOSiMe_3$$

$$'' \xrightarrow{NaAlH_2(OR)_2} H_2 + NaAl(OSiMe_3)_2(OR)_2$$

$$'' \xrightarrow[\text{or } Ni(CO)_4]{\text{alkali metals,}} Me_3SiOM \text{ or } Ni(OSiMe_3)_2$$

$$'' \xrightarrow{SO_3} (Me_3Si)_2SO_4$$

Certain oxidations can also be effected in high yields.

$$Me_3Si\text{-}O\text{-}O\text{-}SiMe_3 \xrightarrow{Me_2S} Me_2SO + (Me_3Si)_2O \text{ (HMDS)}$$

$$'' \xrightarrow{Me_2SO} Me_2SO_2 + \text{HMDS}$$

$$'' \xrightarrow{P(OEt)_3} OP(OEt)_3 + \text{HMDS}$$

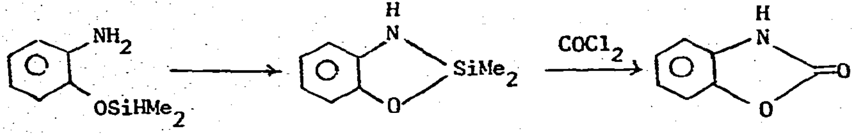
$$'' \xrightarrow{EPh_3} OEPh_3 + \text{HMDS}$$

(E = P, As, Sb)

The reaction of triphenylsilylhydroperoxide with phenyl isocyanate afforded the products shown.[215]

$$Ph_3SiOOH + PhNCO \xrightarrow[-O_2]{-CO_2} PhNH_2 + (Ph_3Si)_2O + (PhNH)_2CO$$

Reports concerning the preparation and chemistry of the following cyclosiloxanes have appeared.



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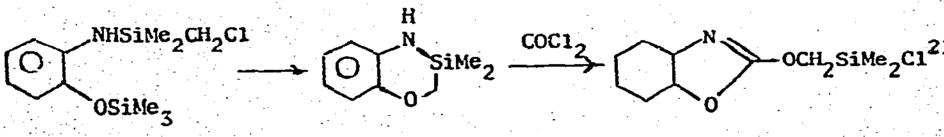

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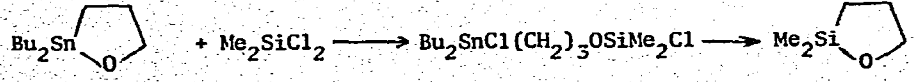

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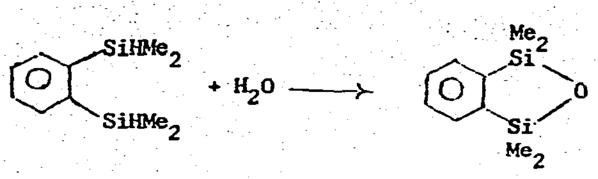

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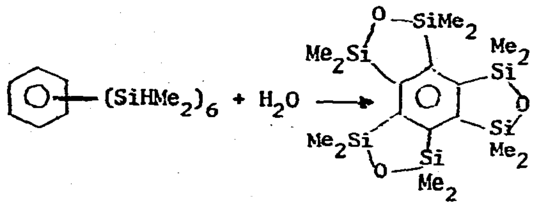

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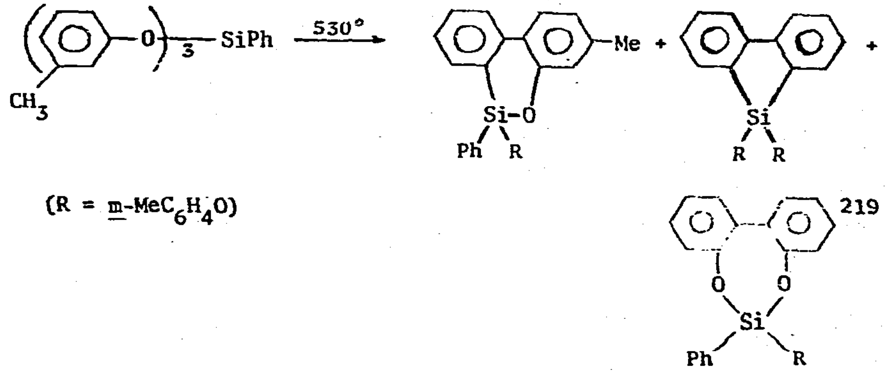
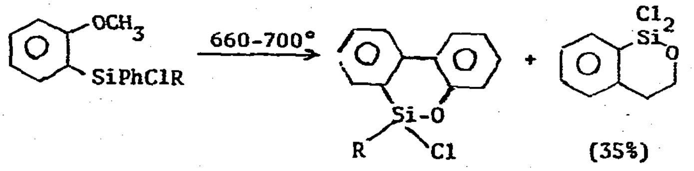


(R = m-MeC$_6$H$_4$O)

219



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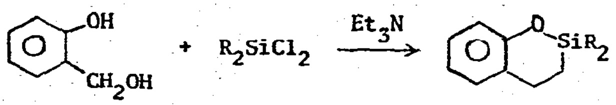
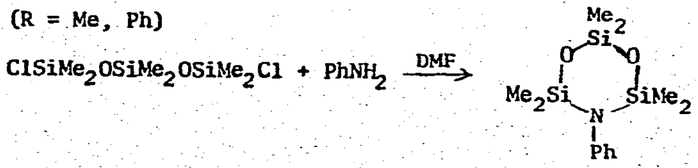
(R = Cl, Me, Ph) (40-57%)



221

(R = Me, Ph)



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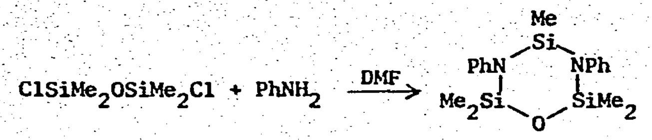

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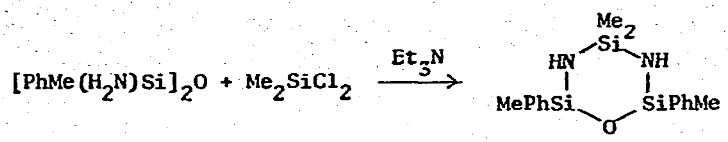

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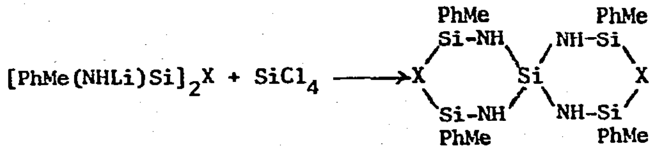

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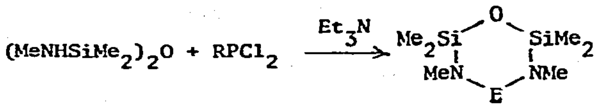
(X = O, N)



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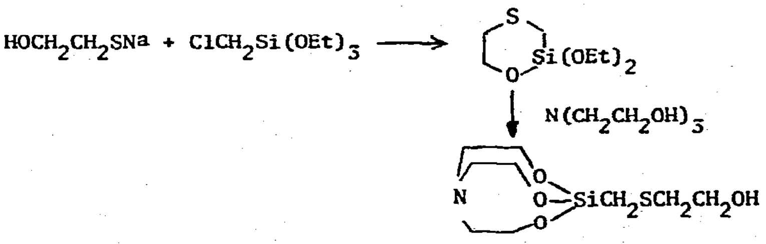
(R = Ph, Me; E = PMe, PPh)

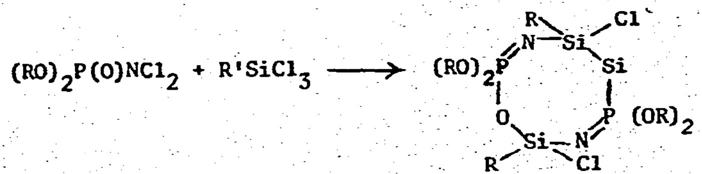
(E = $Me_2P^+I^-$, $PhMeP^+I^-$, $MeP^+CS_2^-$, $PhP^+CS_2^-$, $[MeP^+]_2[COI_2]^{-2}$, MeP(S), PhP(S) and $MeP{=}NSiMe_3$ were also prepared)



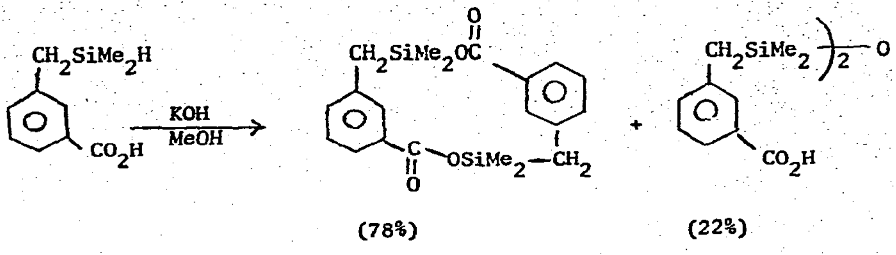
225

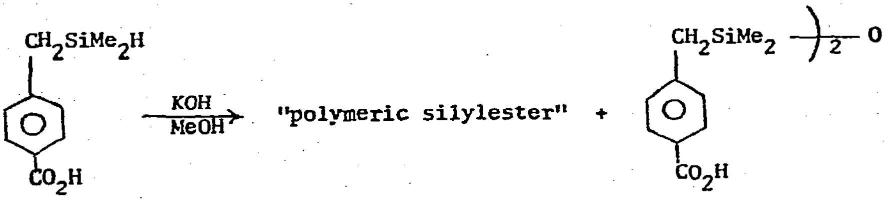
(Other silatranes containing the groups $BrCH_2$,[226] $Br(CH_2)_3$,[226] $H_2N(CH_2)_3$[227] and $H_2NCH_2CH_2NH(CH_2)_3$[227] have also been reported.)

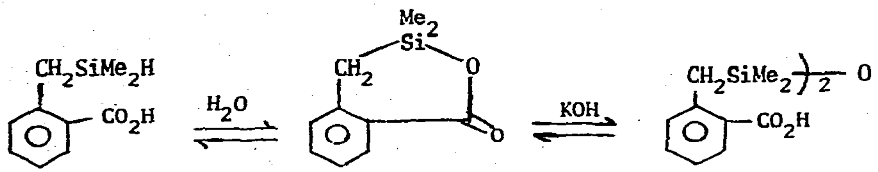
Eight-membered cyclic compounds were obtained quantitatively from the reaction of dialkyl dichlorophosphoramidates with chlorosilanes.[228]



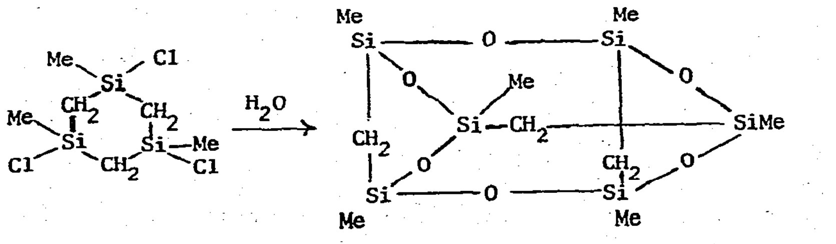
The behavior of (dimethylsilylmethyl)-substituted benzoic acids towards lactone formation has been investigated.[229]



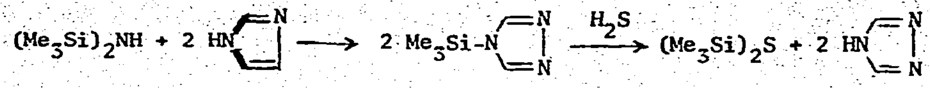


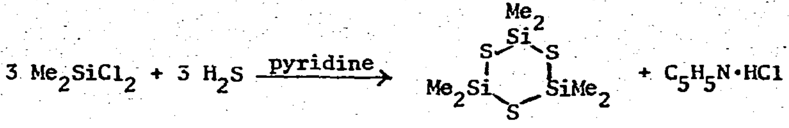


A novel silicon cage compound was obtained from the controlled hydrolysis of $Cl_3Me_3(SiCH_2)_3$.[230]



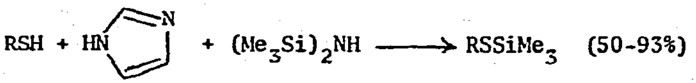
Detailed preparations of hexamethyldisilthiane and hexamethylcyclotrisilthiane are now available[231]





(83%)

Imidazole catalyzes the reactions of thiols with hexamethyldisilazane, probably <u>via</u> the intermediacy of 1-trimethylsilylimidazole, to afford trimethylsilylthioethers[232]



(R = $C_{10}H_{22}$, Ph, Ph_2CH, C_6H_{11}, $(CH_2)_2$, t-amyl)

Bis(alkoxysilyl)sulfides were prepared as follows.[233]

$$2\ RR'(OR'')SiCl + H_2S \xrightarrow{Et_3N} [RR'(OR'')Si]_2S \quad (58\text{-}82\%)$$

(R,R' = Me, Et, Ph; R'' = n-alkyl, isoalkyl)

Some metal sulfides can be obtained upon treating their oxides with hexamethyldisilthiane[234]

$$(Me_3Si)_2S + MO_2 \longrightarrow (Me_2Si)_2O + MS_2 \quad (25\text{-}70\%)$$

(M = Ba, Pb, Mn)

Both mineral acids and carboxylic acids are silylated in high yields by hexamethyldisilthiane.[235]

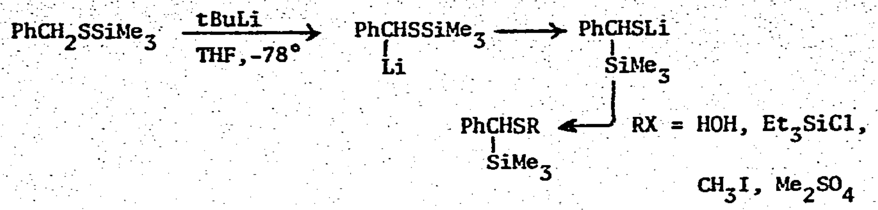
$$(Me_3Si)_2S + H_2SO_4 \longrightarrow (Me_3Si)_2SO_2 \quad (93\%)$$

$$'' \quad + H_3PO_4 \longrightarrow (Me_3Si)_3PO \quad (96\%)$$

$$'' \quad + H_3BO_3 \longrightarrow (Me_3SiO)_3B \quad (82\%)$$

$$'' \quad + RCO_2H \longrightarrow Me_3SiO\overset{O}{\overset{\|}{C}}R \quad (80\text{-}90\%)$$

A sulfur to carbon rearrangement is effected in benzylthiotrimethylsilane upon metalation with t-butyllithium.[236] Lithium disiopropylamide



$$PhCH_2SSiMe_3 \xrightarrow[\text{THF},-78°]{tBuLi} \underset{Li}{PhCH}SSiMe_3 \longrightarrow \underset{SiMe_3}{PhCH}SLi \longrightarrow \underset{SiMe_3}{PhCH}SR \quad RX = HOH,\ Et_3SiCl,\ CH_3I,\ Me_2SO_4$$

may also be used for the metalation. Small amounts of products arising from Si-S cleavage and Si-methyl metalation were also found in the t-butyllithium reactions.

Various trialkoxysilanethiolates were prepared by the reaction of trialkoxysilanethiols with metals.[237]

$$(RO)_3SiSH + M \longrightarrow (RO)_3SiSM + 1/2\ H_2 \quad (100\%)$$

(R = n-, sec-, tert-, iso-alkyl, Me; M = Li, Na, K)

$$(RO)_3SiSH + M \longrightarrow [(RO)_3SiS]_2M + H_2 \quad (90\%)$$

(M = Ca, Sr, Ba)

Hydrolysis of trialkoxysilanethiols afforded the corresponding trialkoxysilanols[238]

$$(RO)_3SiSH + H_2O \longrightarrow (RO)_3SiOH$$

(R = iPr, s-Bu, t-Bu, Am)

The methylselenosilanes $MeSeSiH_3$, $(MeSe)_2SiH_2$, $MeSeSiH_2Me$ have been prepared using the following reaction type.[239]

$$LiAl(SeMe)_4 + 2\ H_2SiBr_2 \longrightarrow 2\ (MeSe)_2SiH_2 + LiBr + AlBr_3$$

4. Si - Group V

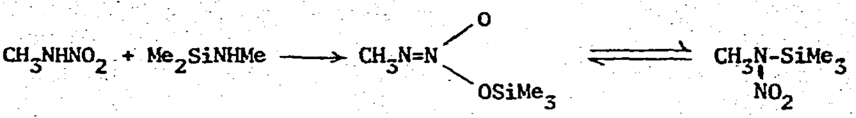
In contrast to the behavior of chlorotrimethylsilane, iodosilane reacts with bis[bis(trifluoromethyl)amino] mercury to give the previously unknown N,N-bis(trifluoromethyl)silylamine.[240]

$$[(CF_3)_2N]_2Hg + 2\ Me_3SiCl \longrightarrow 2\ Me_3SiF + 2\ CF_3N{=}CF_2 + HgCl_2$$

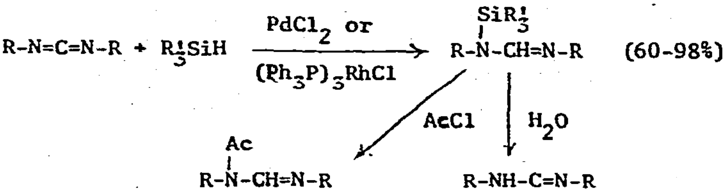
$$\text{"} \quad + 2\ SiH_3I \longrightarrow (CF_3)_2NSiH_3 + CF_3N{=}CF_2 + SiH_3F + HgI_2$$

(37%)

Silylation of methylnitramine affords tautomeric adducts which are sensitive to hydrolysis. The silver salt of methylnitramine is silylated by chlorotrimethylsilane to afford the same adducts.[241]



Hydrosilylation of carbodiimides offers a high-yield route to N-silylformamidines. These may be hydrolyzed or acetylated.[242]



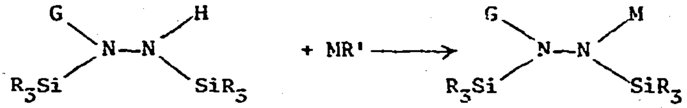
(R = iPr, C_6H_{11}; R' = Ph, Et, Me)

Arylazotriphenylsilanes have been prepared from the corresponding hydrazines.[243]

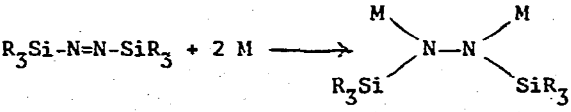
$$p\text{-}XC_6H_4NHNH_2 \xrightarrow{Ph_3SiCl} p\text{-}XC_6H_4NHNHSiPh_3 \xrightarrow{\text{chloranil}} X\text{-}C_6H_4N{=}NSiPh_3$$

(X = H, Cl, CH_3) (41-68%) (12-45%)

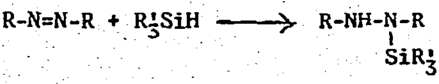
The preparation of metalated silylhydrazines has been carried out by two routes.[244]



(G = H or R_3Si; M = Li, Na, K)



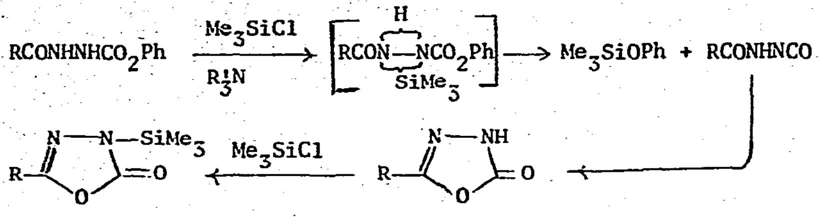
Azo compounds afford adducts with silanes.[245]



$$R\text{-}N{=}N\text{-}R + R'_3SiH \longrightarrow R\text{-}NH\text{-}\underset{SiR'_3}{N}\text{-}R$$

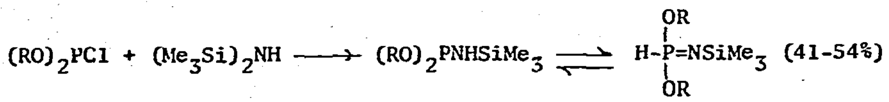
(R = CO_2Me, CO_2Et, Ph; R' = Et, Ph)

Thermally stable (200-300°C) N-silyl-1,3,4-oxadiazolin-2-ones are accessible as shown.[246]



(R = Me, tBu, Ph, $CH=CHCH_3$)

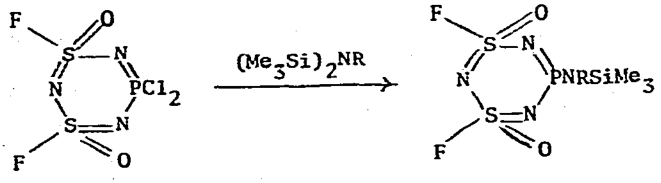
A number of silylated amidophosphates have been prepared.[247]



$$(RO)_2PCl + (Me_3Si)_2NH \longrightarrow (RO)_2PNHSiMe_3 \rightleftharpoons H\text{-}\overset{OR}{\underset{OR}{P}}{=}NSiMe_3 \quad (41\text{-}54\%)$$

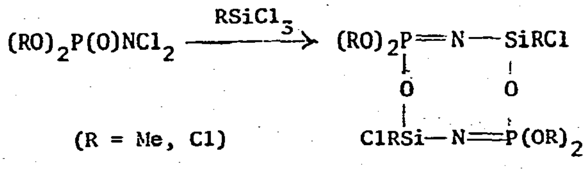
$$(RO)_2PCl + 2(Me_3Si)_2NMe \longrightarrow MeN\,[P(OR)_2]_2 \quad (43\text{-}46\%)$$

Other phosphorus chemistry involving silylamines is shown below.



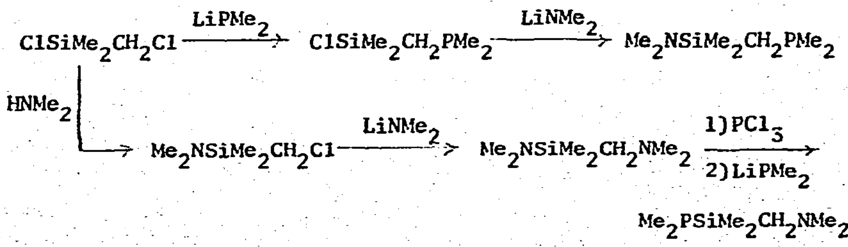
248

(R = H, Me, Et)



249

(R = Me, Cl)



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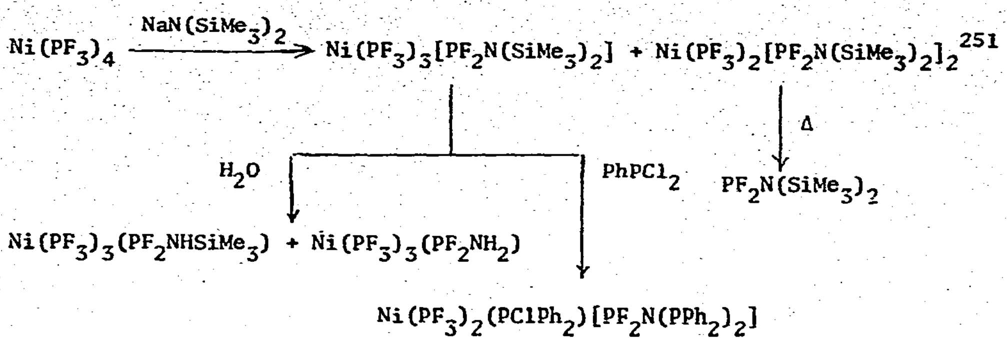


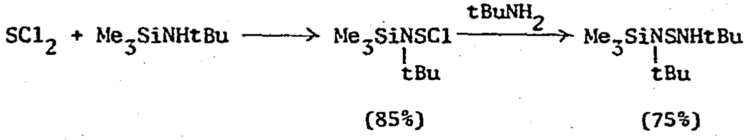
$$Ni(PF_3)_4 \xrightarrow{NaN(SiMe_3)_2} Ni(PF_3)_3[PF_2N(SiMe_3)_2] + Ni(PF_3)_2[PF_2N(SiMe_3)_2]_2$$[251]

$$Ni(PF_3)_3[PF_2N(SiMe_3)_2] \xrightarrow{H_2O} Ni(PF_3)_3(PF_2NHSiMe_3) + Ni(PF_3)_3(PF_2NH_2)$$

$$Ni(PF_3)_3[PF_2N(SiMe_3)_2] \xrightarrow{PhPCl_2} Ni(PF_3)_2(PClPh_2)[PF_2N(PPh_2)_2]$$

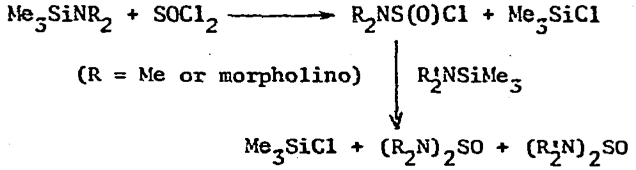
$$Ni(PF_3)_2[PF_2N(SiMe_3)_2]_2 \xrightarrow{\Delta} PF_2N(SiMe_3)_2$$

Sulfur dichloride reacts with N-silyl amines.[252]



$$SCl_2 + Me_3SiNHtBu \longrightarrow \underset{(85\%)}{Me_3Si\underset{tBu}{N}SCl} \xrightarrow{tBuNH_2} \underset{(75\%)}{Me_3Si\underset{tBu}{N}SNHtBu}$$

The preparation of aminosulfinyl chlorides and their reaction with the Si-N bond have been examined.[253]



$$Me_3SiNR_2 + SOCl_2 \longrightarrow R_2NS(O)Cl + Me_3SiCl$$

(R = Me or morpholino)

$$R_2NS(O)Cl \xrightarrow{R'_2NSiMe_3} Me_3SiCl + (R_2N)_2SO + (R'_2N)_2SO$$

$$2\ Me_2NS(O)Cl + R''N(SiMe_3)_2 \longrightarrow (Me_2N)_2SO + R''NSO + Me_3SiCl$$

(R'' = nPr, nBu)

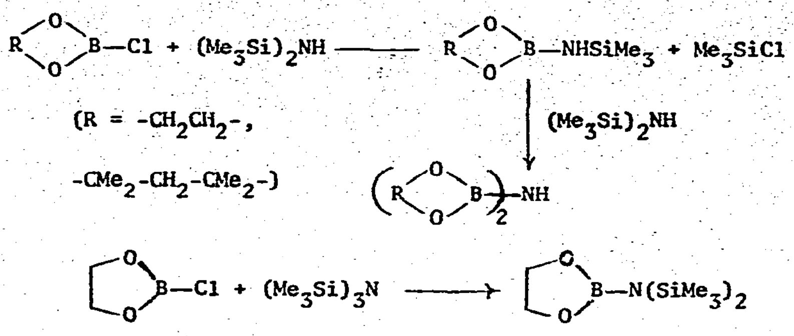
$$Me_3SiNSO + Me_2NS(O)Cl \longrightarrow Me_2NSNSO + SO_2 + Me_3SiCl$$

Silylamines are cleaved by diphenylselenium dichloride.[254]

$$PhSeCl_2 + Me_3SiNMe_2 \xrightarrow{-Me_3SiCl} Ph_2Se(NMe_2)Cl$$

$$PhSeCl_2 + (Me_3Si)_2NH \xrightarrow{-Me_3SiCl} [Ph_2Se{=}N{=}SePh_2]^+Cl^-$$

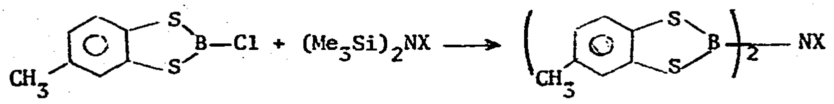
N-Silylated 2-amino-1,3,2-dioxaborolanes and dioxaborinanes are preparable in high yields.[255]



(R = -CH$_2$CH$_2$-,

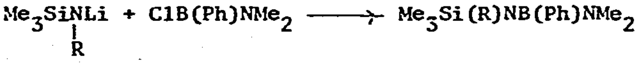
-CMe$_2$-CH$_2$-CMe$_2$-)

The 2-chloroborole shown below reacts similarly with hexamethyldisilazane.[256]



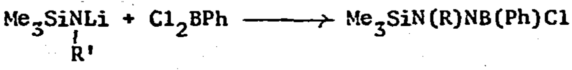
(X = H, SiMe$_3$)

The reaction of phenyl(dimethylamino)chloroborane with N-lithiosilylamines forms stable silylaminoboranes, but the stability of similar products obtained from phenyl(dichloro)borane was dependent on structure.[257]



$$\underset{\mathrm{R}}{\mathrm{Me_3Si\overset{}{N}Li}} + \mathrm{ClB(Ph)NMe_2} \longrightarrow \mathrm{Me_3Si(R)NB(Ph)NMe_2}$$

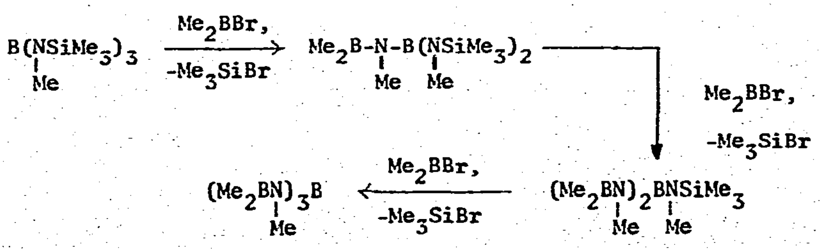
(R = iPr, Et, Me stable)



$$\underset{\mathrm{R'}}{\mathrm{Me_3SiNLi}} + \mathrm{Cl_2BPh} \longrightarrow \mathrm{Me_3SiN(R)NB(Ph)Cl}$$

[R' = tBu, iPr stable; Et, Me unstable to give 1/3(RNBPh)$_3$ + Me$_3$SiCl]

Stepwise cleavage by Me$_2$BBr of the Si-N bonds in B(NMeSiMe$_3$)$_3$can be carried out and all members of the cleavage sequence can be isolated.[258]



$$\underset{\mathrm{Me}}{\mathrm{B(NSiMe_3)_3}} \xrightarrow[-\mathrm{Me_3SiBr}]{\mathrm{Me_2BBr,}} \mathrm{Me_2B\text{-}\underset{Me}{N}\text{-}B(\underset{Me}{N}SiMe_3)_2} \xrightarrow[-\mathrm{Me_3SiBr}]{\mathrm{Me_2BBr,}} \mathrm{(Me_2\underset{Me}{BN})_2B\underset{Me}{N}SiMe_3} \xrightarrow[-\mathrm{Me_3SiBr}]{\mathrm{Me_2BBr,}} \mathrm{(Me_2\underset{Me}{BN})_3B}$$

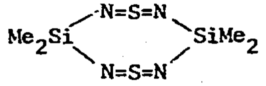
Tris(trimethylstannyl)amine reacts with chlorosilanes to form silyl stannylamines.[259]

$$(Me_3Sn)_3N + Me_{4-n}SiCl_n \longrightarrow (Me_3Sn)_2NSiMe_{4-n}Cl_{n-1} \quad (n = 1\text{-}4)$$

$$2(Me_3Sn)_2NSiMe_3 + S_4N_4 \longrightarrow (Me_3SnN)_2S + Me_3SnNSNSiMe_3$$

$$2(Me_3Sn)_2NSiMe_2NCS + S_4N_2 \longrightarrow Me_4Sn + Me_2SnN_2S_2 +$$

$$2\ Me_3SnNSNSiMe_2NCS \xrightarrow{-Me_3SnNCS}$$

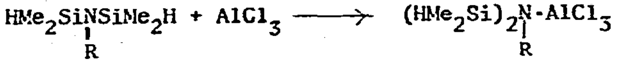


A new 4-coordinate thorium compound containing silylamino ligands has been reported. Attempts at introduction of a fourth such ligand were unsuccessful.[260]

$$ThCl_4 + LiN(SiMe_3)_2 \xrightarrow{THF} ClTh[N(SiMe_3)_2]_3$$

Numerous aminofluorosilanes have been obtained from mixtures of tetrafluorosilane and primary and secondary amines in the presence of dehydrofluorinating agents such as $LiAlH_4$, $NaBH_4$, B_2H_6 and electropositive metals.[261]

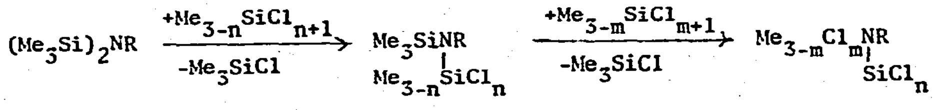
Complexes stable to 100° were formed between silazanes and aluminum chloride.[262]



$$HMe_2Si\underset{\displaystyle R}{\underset{|}{N}}SiMe_2H + AlCl_3 \longrightarrow (HMe_2Si)_2\underset{\displaystyle R}{\underset{|}{N}}\text{-}AlCl_3$$

(R = H, Et)

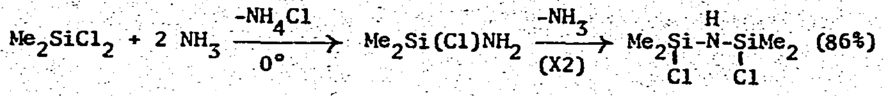
Disilazanes have been transsilylated by some chlorosilanes; the reactivity order was found to be $Me_2SiCl_2 < CH_3SiCl_3 > SiCl_4$.[263]



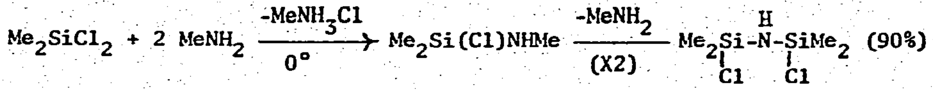
$$(Me_3Si)_2NR \xrightarrow[-Me_3SiCl]{+Me_{3-n}SiCl_{n+1}} \begin{matrix} Me_3SiNR \\ | \\ Me_{3-n}SiCl_n \end{matrix} \xrightarrow[-Me_3SiCl]{+Me_{3-m}SiCl_{m+1}} \begin{matrix} Me_{3-m}Cl_mNR \\ | \\ SiCl_n \end{matrix}$$

(n = 1-3; R = H, Me)

Simple, high yield, routes to tetramethyl- and pentamethyl-1,3-dichlorodisilazanes have been described.[264]



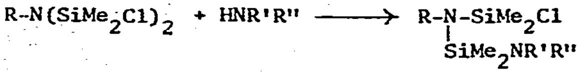
$$Me_2SiCl_2 + 2\ NH_3 \xrightarrow[0°]{-NH_4Cl} Me_2Si(Cl)NH_2 \xrightarrow[(X2)]{-NH_3} Me_2\underset{Cl}{Si}-\overset{H}{N}-\underset{Cl}{Si}Me_2\ (86\%)$$



$$Me_2SiCl_2 + 2\ MeNH_2 \xrightarrow[0°]{-MeNH_3Cl} Me_2Si(Cl)NHMe \xrightarrow[(X2)]{-MeNH_2} Me_2\underset{Cl}{Si}-\overset{H}{N}-\underset{Cl}{Si}Me_2\ (90\%)$$

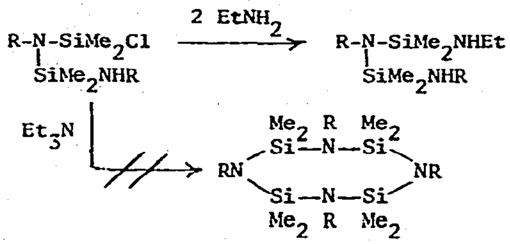
In contrast, ethylamine gives only dimethylchloroethylaminosilane under similar conditions.

A number of 1-chloro-3-dialkylamino disilazanes were prepared as indicated below.[265] These could be transformed into disiltriazanes, but not into cyclosilazanes.



$$R\text{-}N(SiMe_2Cl)_2 + HNR'R'' \longrightarrow R-\underset{SiMe_2NR'R''}{N}-SiMe_2Cl$$

(R = Me, Et; R' = H, Me, Et; R'' = n-, iso-, tert-, cyclo-alkyl)



Thermolysis of bis(trimethylsilyl)diimine has been found to proceed as follows.[266]

$$2\ Me_3SiN{=}NSiMe_3 \xrightarrow{0°} (Me_3Si)_2N\text{-}N(SiMe_3)_2 + N_2$$

(74%)

$$2\ \text{"} \xrightarrow{-50°} (Me_3Si)_2N\text{-}N{=}N\text{-}N(SiMe_3)_2\ (88\%)$$

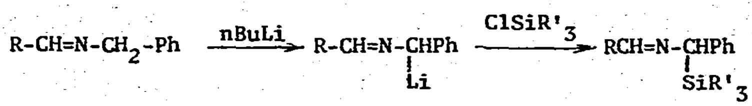
$$3\ \text{"} \xrightarrow{-150°} (Me_3Si)_3N + N_2 + (Me_3Si)_2NNHSiMe_3$$

$$+ (Me_3Si)_2NH + \text{above two products}$$

Products containing N-H bonds appear to arise *via* hydrogen abstraction by intermediate silylhydrazyl and silylamino radicals.[267,268]

Alkali metals (Li, Na, K) reduce bis(trimethylsilyl)diimine to the dianion or radical anion; the latter is unstable towards decomposition into nitrogen plus the metal bis(trimethylsilyl)amide or the metal bis(trimethylsilyl)amide, tris(trimethylsilyl)hydrazide and azide.[269]

Metalation and subsequent silylation of aldimines afforded a series of C-silylated products.[270]



$$R\text{-}CH{=}N\text{-}CH_2\text{-}Ph \xrightarrow{nBuLi} R\text{-}CH{=}N\text{-}\underset{Li}{CHPh} \xrightarrow{ClSiR'_3} RCH{=}N\text{-}\underset{SiR'_3}{CHPh}$$

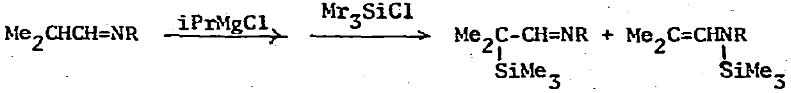
$(R = Ph,\ p\text{-}Me_2NC_6H_4,\ C_6H_{11};\ R' = Me,\ Ar)$

N-trimethylsilylketimine reacts with bis(benzonitrile)palladium dichloride to afford an N-silylketimine complex.[271]

$$(PhCN)_2PdCl_2 + 2\ Ph_2C{=}NSiMe_3 \longrightarrow (Ph_2CNSiMe_3)_2PdCl_2$$

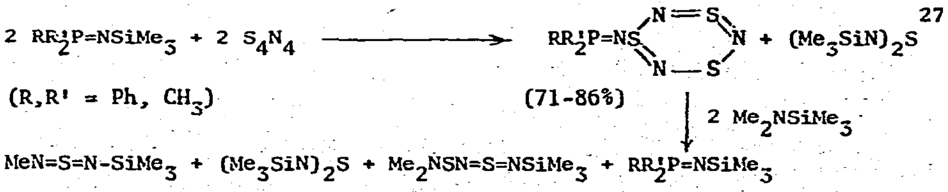
(67%)

Aldimines can be metalated by isopropylmagnesium chloride. Subsequent silylation affords mixtures of N- and C-cilylated products that are interconvertable when heated or treated with halosilanes. The amount of N-silyl material at equilibrium is governed by the steric requirements of R.[272]



$$Me_2CHCH{=}NR \xrightarrow{iPrMgCl} \xrightarrow{Mr_3SiCl} Me_2\underset{SiMe_3}{C}\text{-}CH{=}NR + Me_2C{=}CH\underset{SiMe_3}{N}R$$

The following silyliminophosphorane chemistry has appeared.



$2\ RR'_2P{=}NSiMe_3 + 2\ S_4N_4 \longrightarrow$ … $+ (Me_3SiN)_2S$ [27

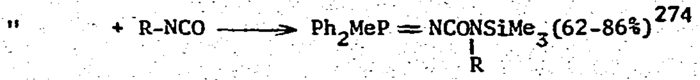
$(R,R' = Ph,\ CH_3)$ (71-86%)

$2\ Me_2NSiMe_3$

$MeN{=}S{=}N\text{-}SiMe_3 + (Me_3SiN)_2S + Me_2NSN{=}S{=}NSiMe_3 + RR'_2P{=}NSiMe_3$

$$Ph_2MeP{=}NSiMe_3 + Ac_2O \longrightarrow Ph_2MeP{=}NCOMe + AcOSiMe_3 \quad ^{274}$$

(98%)



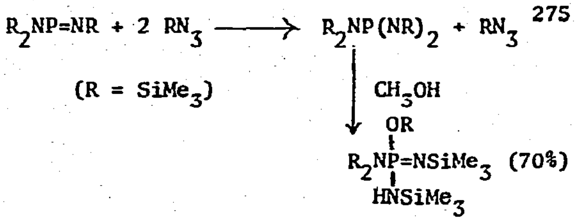
$$\text{"} \quad + R\text{-}NCO \longrightarrow Ph_2MeP{=}NCO\underset{R}{N}SiMe_3\ (62\text{-}86\%)^{274}$$

(R = Me, Et)

$$Ph_2MeP{=}NSiMe_3 + PhNCO \longrightarrow \underset{(38\%)}{Ph\text{-}N{=}C{=}N\text{-}Ph} + \underset{(15\%)}{Ph\text{-}N{=}C{=}N\text{-}SiMe_3}\ ^{274}$$

$$+ \underset{(91\%)}{Ph_2MePO} + \underset{(57\%)}{Me_3SiNCO}$$

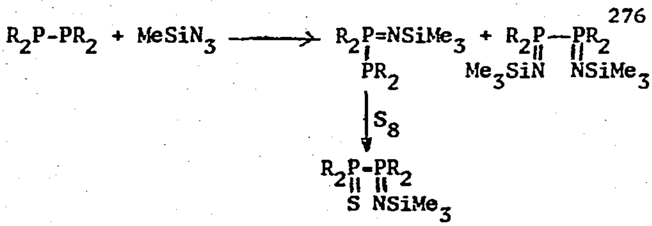
$$\text{"} \quad + CS_2 \longrightarrow \underset{(98\%)}{Me_3SiNCS} + \underset{(76\%)}{Ph_2MeP{=}S}\ ^{274}$$



$$R_2NP{=}NR + 2\ RN_3 \longrightarrow R_2NP(NR)_2 + RN_3\ ^{275}$$

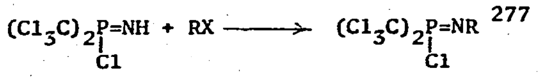
$$(R = SiMe_3)$$

$$R_2NP(NR)_2 \xrightarrow{CH_3OH} R_2N\overset{OR}{\underset{HNSiMe_3}{P}}{=}NSiMe_3\ (70\%)$$



$$R_2P\text{-}PR_2 + MeSiN_3 \longrightarrow R_2\underset{PR_2}{P}{=}NSiMe_3 + R_2\underset{Me_3SiN}{\overset{\|}{P}}\text{—}\underset{NSiMe_3}{\overset{\|}{P}}R_2\ ^{276}$$

$$R_2\underset{PR_2}{P}{=}NSiMe_3 \xrightarrow{S_8} R_2\underset{S}{\overset{\|}{P}}\text{-}\underset{NSiMe_3}{\overset{\|}{P}}R_2$$



$$(Cl_3C)_2\underset{Cl}{P}{=}NH + RX \longrightarrow (Cl_3C)_2\underset{Cl}{P}{=}NR\ ^{277}$$

$$(R = SiCl_3,\ X = Cl;\ SiBr_3,\ X = Br;\ SiMe_2Cl,\ X = Cl)$$

$$(Me_3Si)_2NLi + PX_3 \longrightarrow (Me_3Si)_2NP{=}NSiMe_3 \quad (59\text{-}61\%)^{278}$$

$$(X = Br,\ Cl)$$

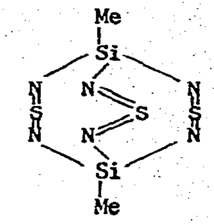
$$(Me_3Si)_2NP{=}NSiMe_3 \xrightarrow{[(Me_3Si)_2N]_2PN_3} (Me_3Si)_2NP({=}NSiMe_3)_2$$

$$Ph_2P(CH_2)_nPPh_2 + 2\ Me_3SiN_3 \longrightarrow Me_3SiN{=}P(Ph_2)[CH_2]_nP(Ph)_2{=}NSiMe_3\ ^{279}$$

$$(90\text{-}98\%)$$

$$Me_3SiN{=}SF_2{=}NSiMe_3 + 2\ SF_4 \xrightarrow[CsF]{100°} F_2S{=}N\text{-}SF_4\text{-}N{=}SF_2 + 2\ Me_3SiF\ ^{280}$$

A bicyclic compound is produced by the reaction of methyltrichlorosilane with N,N'-bis(trimethylstannyl)sulfur diimide.[281]

$2\ MeSiCl_3 + 3\ Me_3SnNSNSnMe_3 \longrightarrow 6\ Me_3SnCl +$  (44%)

De- and trans-silylation reactions of silyl sulfur diimides proceed as follows.[282]

$R_2S(=NSiMe_3)_2 + Ph_2PCl \longrightarrow R_2S(=NPPh_2)_2$

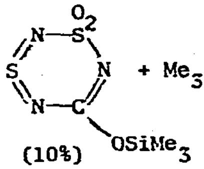
$'' \quad + Me_2PCl \longrightarrow R_2S(=NSiMe_3)(=NPMe_2PMe)Cl^-$

$'' \quad + Me_2SiCl_2 \longrightarrow R_2S(=NSiMe_2Cl)_2$

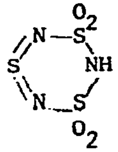
$'' \quad + MeSiCl_3 \longrightarrow R_2S(=NSiMeCl_2)_2$

$'' \quad + AlMe_3 \longrightarrow Me_3SiN{=}SR_2{=}N(AlMe_3)SiMe_3$

New heterocycles result from the interaction of N,N'-bis(trimethylsilyl) sulfur diimide and chlorosulfinyl isocyanate and imidobissulfonic acid chloride.[283]

$Me_3SiNSNSiMe_3 + ClSO_2NCO \longrightarrow$  $+ Me_3SiCl$

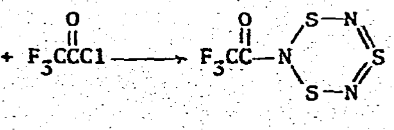
(10%)

$'' \quad + HN(SO_2Cl)_2 \longrightarrow$  $+ 2\ Me_3SiCl$

(7%)

Other reactions of the silyl sulfur diimide are shown below.[284]

$Me_3SiNSNSiMe_3 + Cl_2 \longrightarrow Me_3SiN{=}S{=}NCl \quad (82\%)$

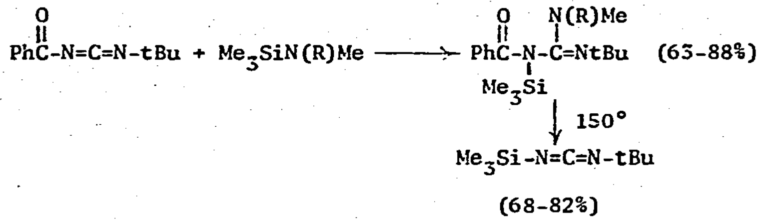
'' 

$+ F_3C\overset{O}{\overset{\|}{C}}Cl \longrightarrow$

$$Me_3SiNSNSiMe_3 + SCl_2 \longrightarrow (Me_3SiNSN)_2S$$

$$(Me_3Si)_2NNa + SOF_4 \longrightarrow (Me_3SiN{=})_3S$$

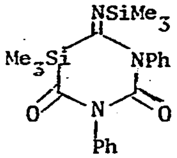
A facile insertion reaction of silylamines with benzoyl-t-butylcarbodiimide leads to a preparative method for trimethylsilylcarbodiimide.[28]



$$PhC(=O){-}N{=}C{=}N{-}tBu + Me_3SiN(R)Me \longrightarrow PhC(=O){-}N(SiMe_3){-}C(N(R)Me){=}NtBu \quad (63\text{-}88\%) \xrightarrow{150°} Me_3Si{-}N{=}C{=}N{-}tBu \quad (68\text{-}82\%)$$

An isocyanurate is formed from phenyl isocyanate and silyldiimides.[286]

$$Me_3SiNCNSiMe_3 + PhNCO \longrightarrow$$



(82%)

Sulfur diimides were obtained as shown.[287]

$$3\ Me_3SiNHSiMe_3 + N_3S_3Cl_3 \xrightarrow{pyridine} 3\ Me_3SiNSNSiMe_3 \quad (37\%)$$

$$\begin{tikzcd} Me_3SiNHSiMe_3 + PhSCl \arrow[r] & PhNHSiMe_3 \ (32\%) \arrow[d, "N_3S_3Cl_3"] \\ & PhSNSNSiMe_3 \ (45\%) \end{tikzcd}$$

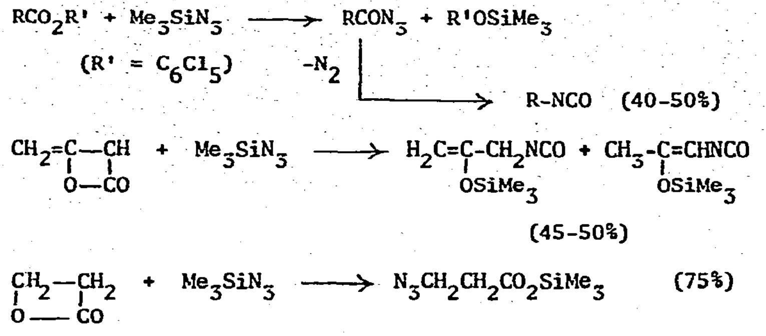
Trimethylsilylnitrene is fixed by reaction with transition metal complexes.[288]

$$Me_3SiN_3 + Ru_3(CO)_{12} \longrightarrow Ru_3(CO)_{10}NSiMe_3 \quad (5\%)$$

$$'' \quad + C_5H_5Co(CO)_2 \longrightarrow Co_3(CO)(C_5H_5)_3NSiMe_3 \quad (54\%)$$

$$'' \quad + Rh_3(C_5H_5)_3(CO)_2 \longrightarrow Rh_3(C_5H_5)_3(CO)NSiMe_3 \quad (48\%)$$

The reaction of trimethylsilylazide with organic esters affords silicon-containing species.[289]



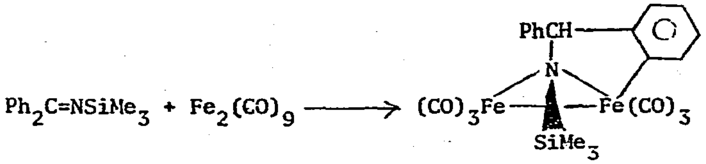
$$RCO_2R' + Me_3SiN_3 \longrightarrow RCON_3 + R'OSiMe_3$$

$$(R' = C_6Cl_5) \qquad RCON_3 \xrightarrow{-N_2} R\text{-}NCO \quad (40\text{-}50\%)$$

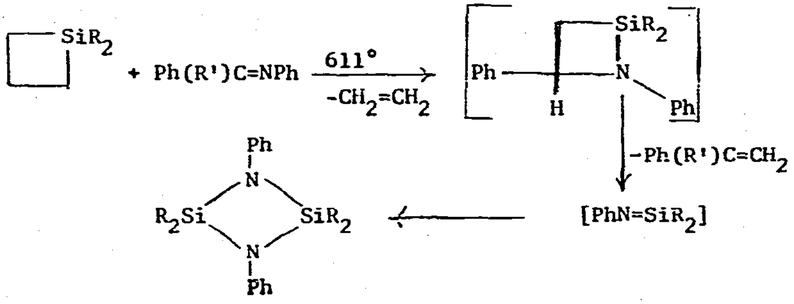
$$+ Me_3SiN_3 \longrightarrow H_2C{=}C(OSiMe_3)\text{-}CH_2NCO + CH_3\text{-}C(OSiMe_3){=}CHNCO \quad (45\text{-}50\%)$$

$$+ Me_3SiN_3 \longrightarrow N_3CH_2CH_2CO_2SiMe_3 \quad (75\%)$$

An iron complex is formed between diironenneacarbonyl and N-trimethylsilylbenzophenonimine.[290]



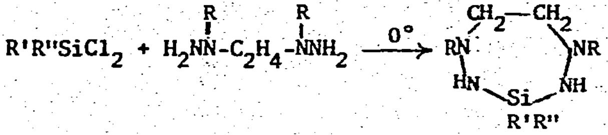
Evidence for a species containing a silicon-nitrogen double bond has been reported.[291]



(25-41%)

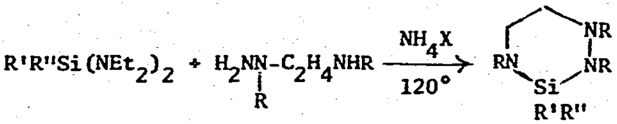
The preparation, characterization, and reactions of a series of isocyanato- and isothiocyanatosilanes and halosilanes have been reported. These are of the form $HSi(NCQ)_3$, $Si(NCQ)_4$, $HSiX(NCQ)_2$ and $HSiX_2(NCQ)$ (Q = 0 or S; X = Cl, Br and I).[292]

The heterocyclic chemistry of silicon-nitrogen compounds has been an active area of investigation.



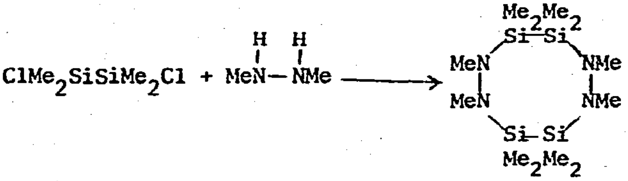
293

(R = Me, Bu; R' = Me, Et; R" = Me, Et, Ph, vinyl)

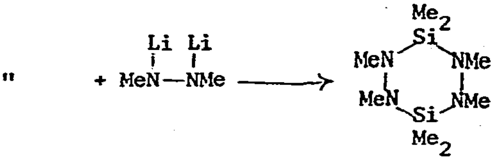


293

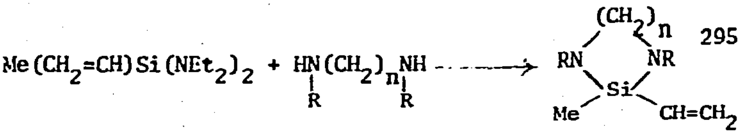
(R = Me, Bu, iPr; R' = Me, iR" = Me, Ph, vinyl)



(57%) 294

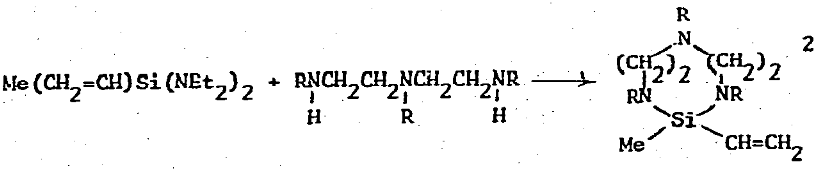


294



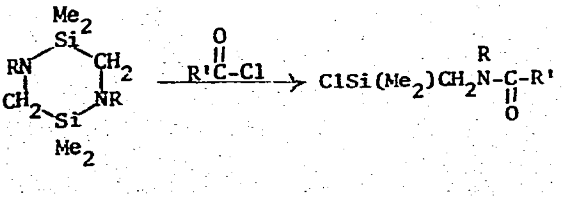
295

(R = alkyl: n = 2,3) (n = 2, 82%)

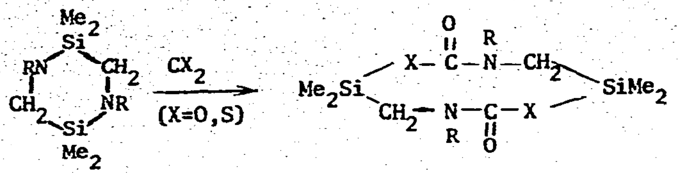


295

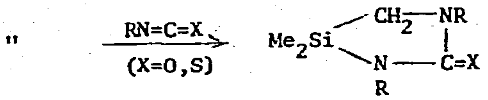
(R = Me, 59%)



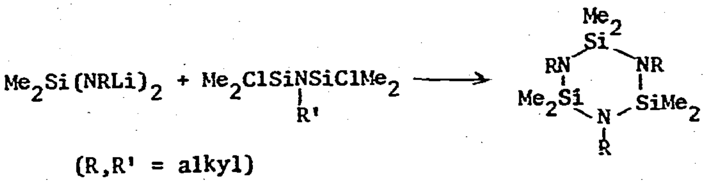
(R' = Me, 92%) 296



(92-95%)[296]

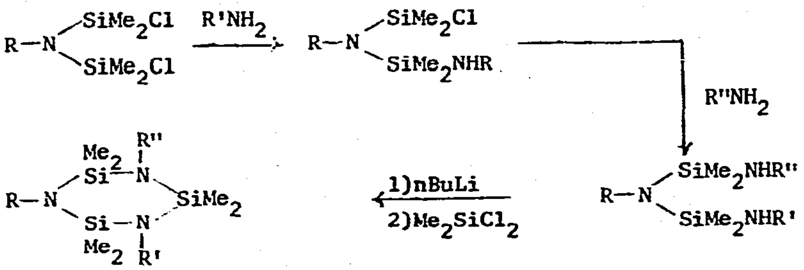


(90-95%)[296]



(34-41%)[297]

(R,R' = alkyl)

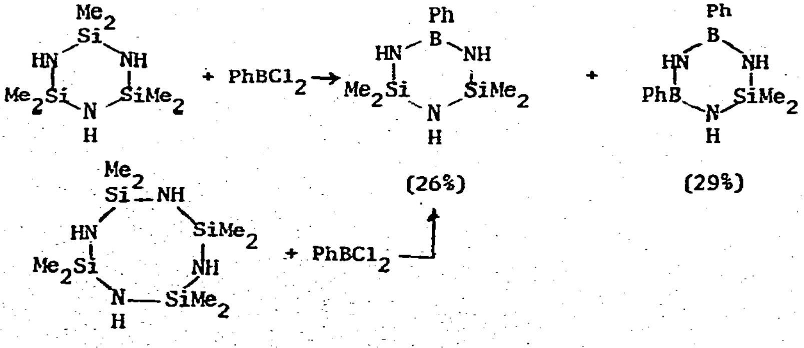


298

(60%)

(60%)

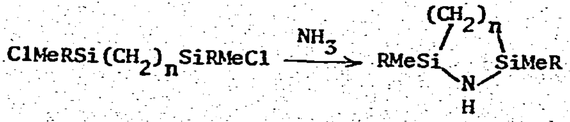
(R ≠ R' ≠ R'' = alkyl)



299

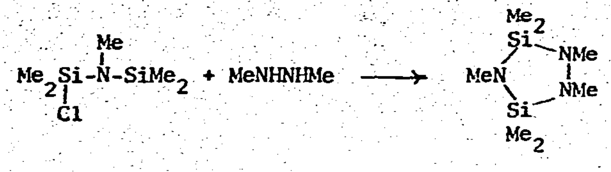
(26%)

(29%)

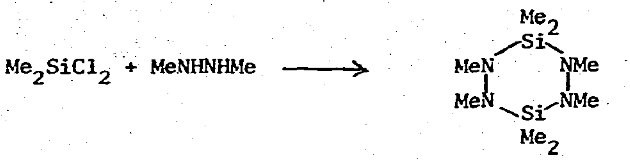


(73-91%)[300]

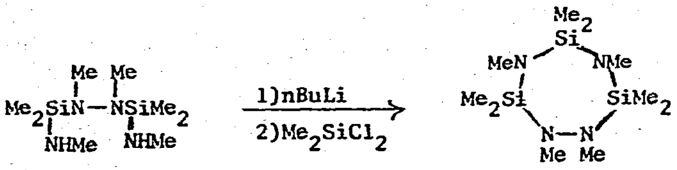
(R = Me, Ph; n = 1-3)



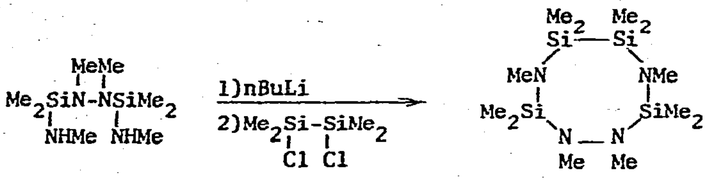
(20%) 301



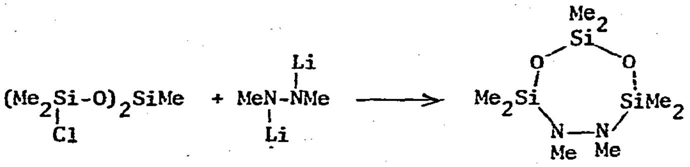
(42%) 301



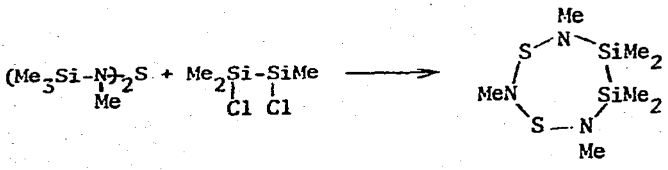
(52%) 301



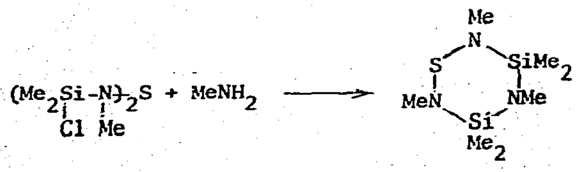
301



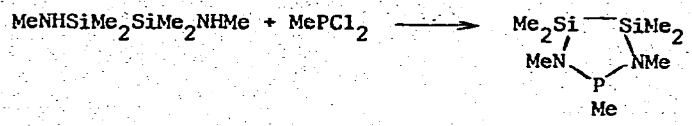
(25%) 301



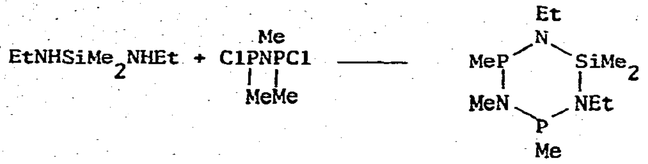
(72%) 302



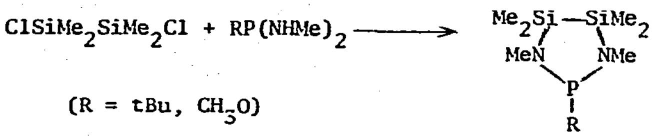
(89%) 302



303

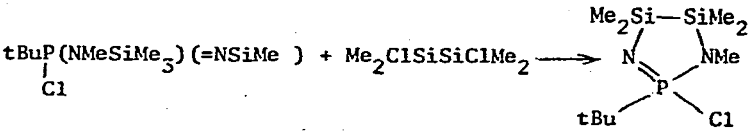


303

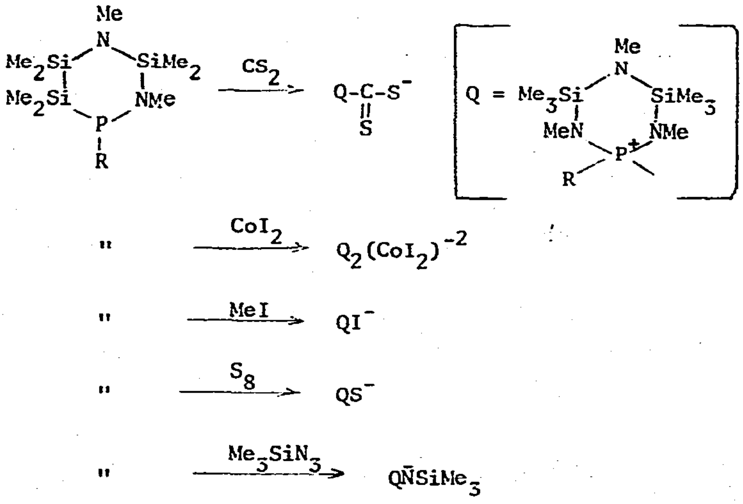


(R=tBu, 34%) 304

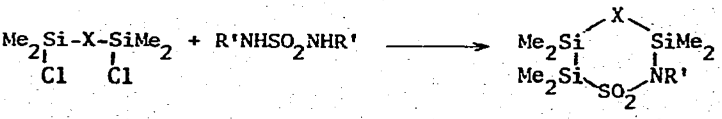
(R = tBu, CH_3O)



(52%) 304

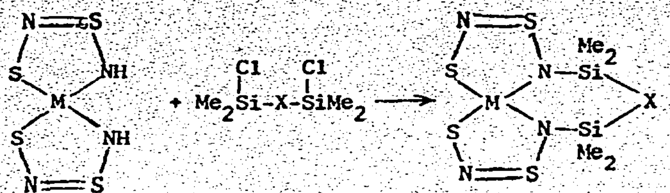


305

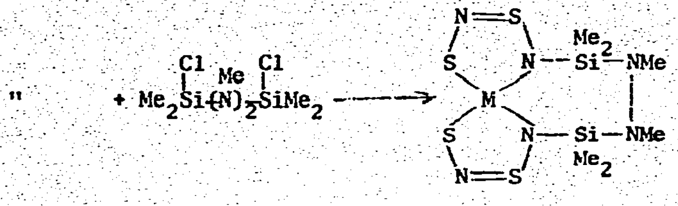


(30%) 306

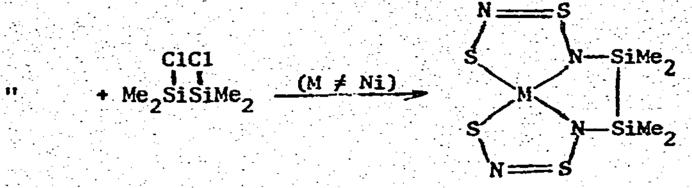
(X = O, NR; R = $SiMe_3$, Me; R' = H, alkyl)



307

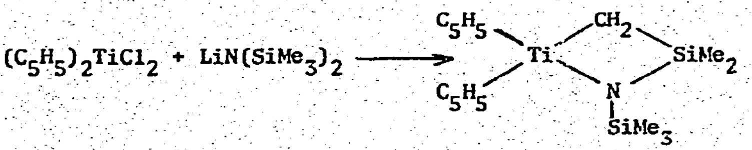


307



307

(M = Ni, Co; X = O, S)



308

The preparation and chemical reactivities of a number of silylphosphine species have been investigated.

$4\ BrSiF_3 + MAl(PH_2)_4 \longrightarrow \underset{(60\%)}{F_3SiPH_2} + AlBr_3 + MBr$ (M = Li, Na) [309]

(Br_2SiF_2 and Br_3SiF did not yield silylphosphines)

$F_3SiPH_2 + IE(CF_3)_2 \longrightarrow F_3SiI + (CF_3)_2EPH_2$ (E = P, As) [309]

$MeSiHCl_2 + MeSiH(PH_2)_2 \xrightarrow{80°} 2\ Me(H)Si(Cl)PH_2$ [310]

$SiCl_4 + MeSiH(PH_2)_2 \xrightarrow{50°} Me(H)Si(Cl)PH_2 + Cl_3SiPH_2$ [310]

(Cl_3SiPH_2 dec. to PH_3 and Si-P polymers at 50°)

$SiBr_4 + MeSiH(PH_2)_2 \xrightarrow{25°} Me(H)Si(Br)PH_2 + Br_3SiPH_2 + Br_2Si(PH_2)_2$ [310]

$Br_3SiF + MeSiH(PH_2)_2 \longrightarrow Me(H)Si(Br)PH_2 + FSiBr_2PH_2$ [310]

$R_3SiPH_2 + LiPEt_2 \longrightarrow R_3SiPLi_2 \xrightarrow{CH_3Cl} R_3SiPMe_2$ [311]

$(R_3 = Me_2H,\ MeH_2,\ H_3)$

$R_3SiPH_2 + LiPHMe \longrightarrow R_3SiPHLi \underset{}{\overset{2\ X}{\rightleftarrows}} (R_3Si)_2PLi + LiPH_2$ [311]

$(Me_3Si)_2PLi + CH_3Cl \longrightarrow (Me_3Si)_2PCH_3$ [311]

$(MeH_2Si)_2PLi + MeH_2SiBr \longrightarrow (MeH_2Si)_3P$ [311]

$$\begin{tikzcd}
R_3SiPHLi + AlCl_3 \arrow[r] & LiAl(PHSiR_3)_4 \arrow[d, "4\ R_3SiBr"] \\
& (R_3Si)_2PH + AlBr_3
\end{tikzcd}$$ [311]

$H_3SiPH_2 + F_3CMI \xrightarrow{-25°} F_3CM(PH_2)_2 \quad (M = P,\ As)$ [312]

(70%)

$Me_3SiPMe_2 + (CF_3)_2PH \longrightarrow Me_3SiP(CF_3)_2 + Me_2PH$ [313]

$F_3SiBr + Me_3SnEH_2 \longrightarrow F_3SiEH_2 \quad (E = P,\ As)$ [314]

(70%)

$H_3SiPH_2 + HNRR' \longrightarrow H_3SiNRR' + PH_3$ [315]

(R, R' = alkyl) (100%)

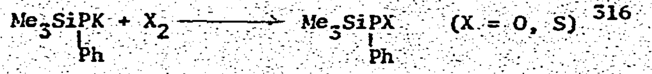
$H_3SiPH_2 + HXCN \longrightarrow H_3SiNCX \quad (X = O,\ S)$ [315]

(80%)

" $+ HN_3 \longrightarrow H_3SiN_3$ [315]

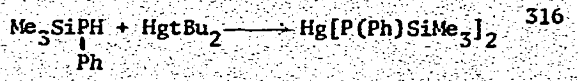
" $+ H_2NCN \longrightarrow H_3SiNCNSiH_3$ [315]

(100%)

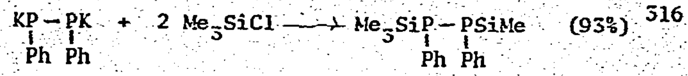


$Me_3SiP(Ph)K + X_2 \longrightarrow Me_3SiP(Ph)X \quad (X = O,\ S)$ [316]

(70-73%)



$Me_3SiP(Ph)H + HgtBu_2 \longrightarrow Hg[P(Ph)SiMe_3]_2$ [316]



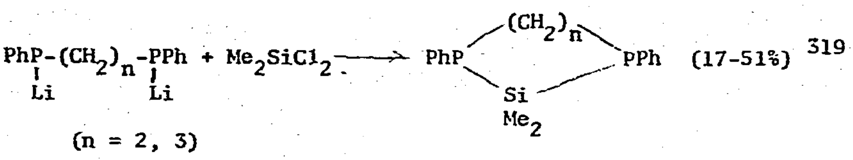
$KP(Ph)-P(Ph)K + 2\ Me_3SiCl \rightarrow Me_3SiP(Ph)-P(Ph)SiMe$ (93%) [316]

$PhPK_2 + 2\ Me_3SiCl \rightarrow (Me_3Si)_2PPh$ (64%) [317]

$Me_2PH + BuLi \rightarrow Me_2PLi \xrightarrow{AlCl_3} LiAl(PMe_2)_4$ [318]

$'' \qquad '' \xrightarrow{R_3SiX} R_3SiPMe_2$ (68-80%) [318]

$(R_3 = H_3, MeH_2, Me_2H, Me_3)$



$PhP(Li)-(CH_2)_n-P(Li)Ph + Me_2SiCl_2 \rightarrow$ (17-51%) [319]

$(n = 2, 3)$

Exceptionally stable dialkylarsenido-transition metal complexes containing silyl groups have been prepared.[320]

$C_5H_5(CO)_3MoAsMe_2 + Me_3SiCH_2Cl \rightarrow [C_5H_5(CO)_3MoAsMe_2CH_2SiMe_3]^+Cl^-$

$C_5H_5(CO)_3WAsMe_2 + Me_3SiI \rightarrow [C_5H_5(CO)_3WAsMe_2SiMe_3]^+I^-$

$(Me_3Si)_3Sb + Ni(CO)_4 \rightarrow (Me_3Si)_3Sb-Ni(CO)_3$ (60%) [321]

5. Si-Metal

Several trifluorosilylpentaboranes have been prepared and characterized.[322]

$LiB_5H_8 + SiF_4 \xrightarrow[-78°]{ether} 2-F_3SiB_5H_8 + 1-F_3SiB_5H_8$

(45%) (1%)

Boron insertion reactions have been used to prepare the first examples of apically substituted hexaborane(10) derivatives.[323]

H_2BCl + 1- or $2-Me_3SiB_5H_7Li \rightarrow 1-Me_3SiB_6H_9$ (5%)

Compounds containing germanium-silicon bonds are formed from difluorogermylene and chlorosilanes.[324]

$GeF_2 + Ph_{4-n}SiCl_n \rightarrow Ph_{4-n}SiGeF_2Cl_n$

$(n = 1-3)$

A somewhat improved preparation of an optically active mercurial has been reported, along with some of its reactions which proceed predominantly by retention.[325]

$$tBu_2Hg + (+)\text{-}R_3SiH \xrightarrow[9h]{100°} (-)\text{-}(R_3Si)_2Hg + 2iBuH$$

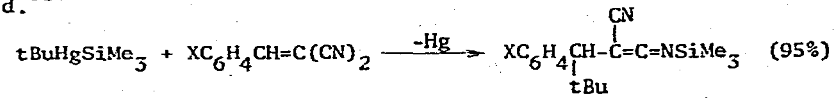
$(R_3 = \text{methyl-1-naphthyl-phenyl})$

$$(-)\text{-}(R_3Si)_2Hg + LiAlH_4 \longrightarrow (+)\text{-}R_3SiH$$

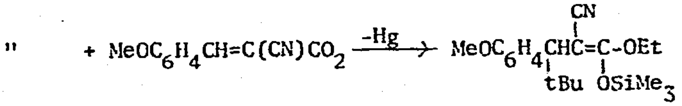
$$'' \quad + (BrCH_2)_2 \longrightarrow (-)\text{-}R_3SiBr$$

$$'' \quad \xrightarrow{h\nu} (-)\text{-}(R_3Si)_2$$

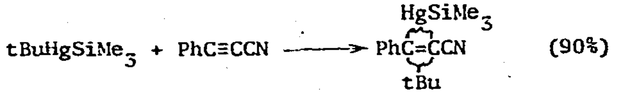
New chemistry of t-butyl(trimethylsilyl)mercury has been investigated.[326]



$$tBuHgSiMe_3 + XC_6H_4CH{=}C(CN)_2 \xrightarrow{-Hg} XC_6H_4\underset{tBu}{CH}\text{-}\overset{CN}{C}{=}C{=}NSiMe_3 \quad (95\%)$$



$$'' \quad + MeOC_6H_4CH{=}C(CN)CO_2 \xrightarrow{-Hg} MeOC_6H_4\underset{tBu}{CH}\overset{CN}{C}{=}\underset{OSiMe_3}{C}\text{-}OEt$$



$$tBuHgSiMe_3 + PhC{\equiv}CCN \longrightarrow Ph\underset{tBu}{C}{=}\overset{HgSiMe_3}{C}CN \quad (90\%)$$

A number of alkyl(trimethylsilyl)mercury compounds have been prepared, and their stability to heat and light investigated.[327]

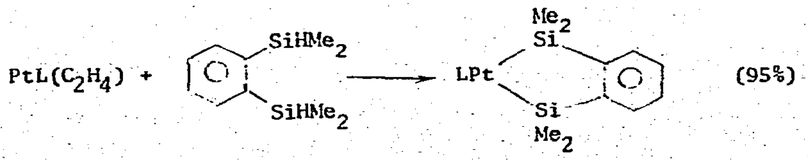
$$(Me_3Si)_2Hg + RHgX \xrightarrow{-40°} RHgSiMe_3$$

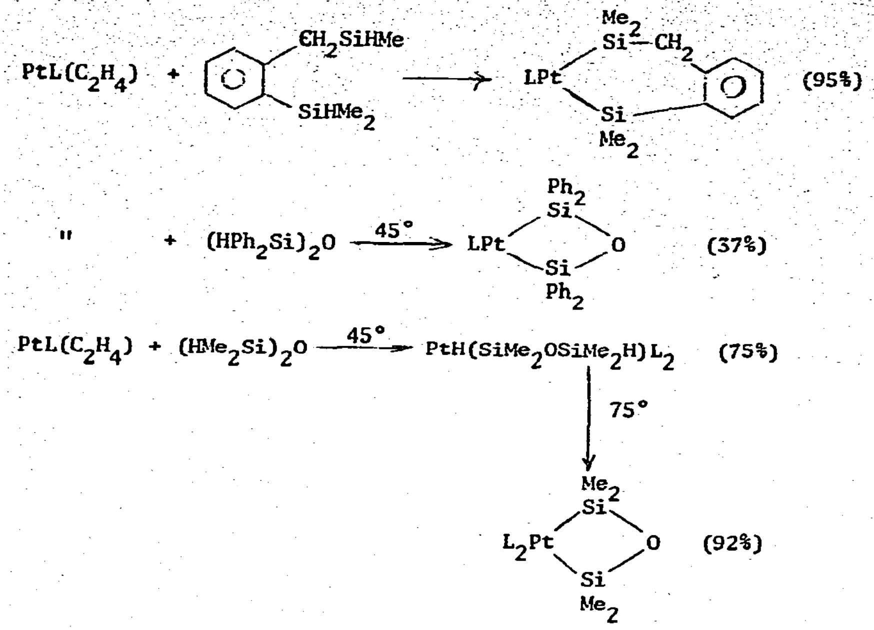
(R = Me, Et, Pr, iPr, tBu)

Conditions for the symmetrization reaction were also discussed.

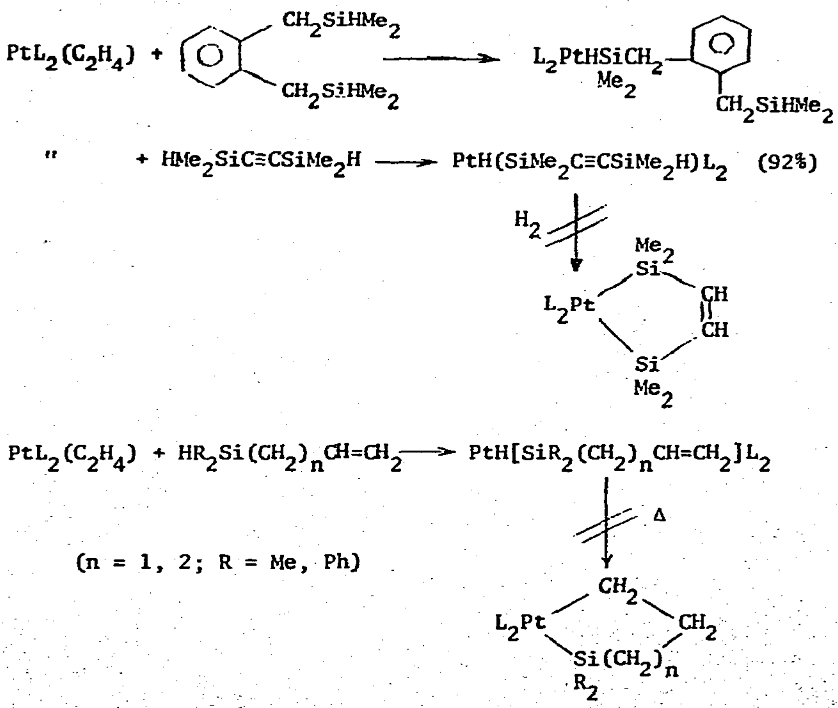
$$2\ RHgSiMe_3 \rightleftharpoons R_2Hg + (Me_3Si)_2Hg$$

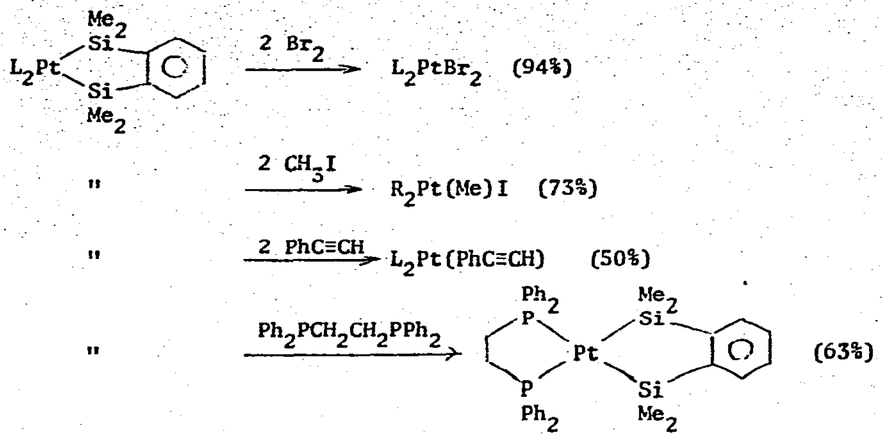
New work on silyl-platinum complexes has been reported. The chemistry of some cyclic compounds of this type is shown below ($L = PPh_3$)[328]





Attempts to prepare 7-membered ring systems only gave acyclic species.





Silyl-platinum complexes containing varied functionality in the silyl group have also been prepared ($L = PPh_3$).[329]

$$PtL_2(C_2H_4) + R_3SiH \longrightarrow PtH(SiR_3)L_2 \qquad (45\text{-}98\%)$$

$[R_3 = Ph_3,\ Ph_2Me,\ Ph_2H,\ PhMe(CH_2{=}CH),\ Et_3,\ (EtO)_3,\ Me(Me_3SiO)_2]$

$$PtL_2(C_2H_4) + Me_2ClSiH \longrightarrow Pt(SiMe_2Cl)_2L_2 \qquad (74\%)$$

$$PtL_2(PhC{\equiv}CR) + Ph_2MeSiH \longrightarrow PtH(SiMePh_2)L_2 \qquad (47\%)$$

$(R = H,\ Ph)$

$$Pt(PPh_2Me)_4 + R_3SiH \longrightarrow Pt(SiR_3)_2(PPn_2Me)_2 \qquad (60\text{-}70\%)$$

$(R_3 = Cl_3,\ Cl_2Me)$

A new method for the synthesis of silyl-platinum complexes has been described. ($L = PMe_2Ph$).[330]

$$PtMe_2L_2 + Ph_2SiH_2 \longrightarrow \underline{cis}\text{-}[Pt(SiHPh_2)_2L_2] \qquad (67\%)$$

$$\text{"} \quad + R_3SiH \longrightarrow \underline{cis}\text{-}[PtH(SiR_3)_2L_2] \qquad (18\text{-}64\%)$$

$(R = Ph,\ p\text{-}FC_6H_4)$

$$PtMe_2L_2 + Ph_2MeSiH \longrightarrow \underline{cis}\text{-}[Pt(SiMe_2Ph)_2L_2] \qquad (21\%)$$

$$PtMe(PMePh_2)_2 + Ph_2SiH_2 \longrightarrow \underline{cis}\text{-}[PtH(SiPh_2H)(PMePh_2)_2] \qquad (50\%)$$

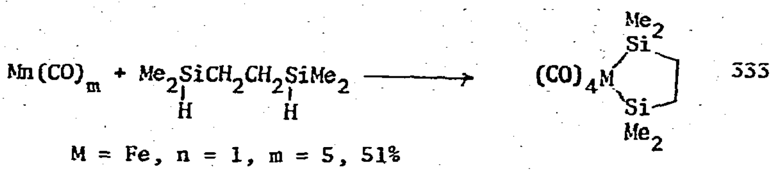
Reported chemistry of non-platinum transition metal-silicon bonds appeared as follows.

$$(C_5H_5)Fe(CO)_2SiR_3 + AgBF_4 \longrightarrow (C_5H_5)Fe(CO)_2SiF_3 \quad (75\%)^{331}$$

(R = Cl, OMe)

$$2\ Ph_{3-n}X_nSiH + M_2 \longrightarrow 2\ Ph_{3-n}X_nSiM + H_2 \quad ^{332}$$

[n = 1,2; X = Cl, C_6H_5; M = $Mn(CO)_5$, $Fe(CO)_2Cp$; the reactivities of these species with C_6H_5Li are described]



$$M_n(CO)_m + Me_2\underset{H}{Si}CH_2CH_2\underset{H}{Si}Me_2 \longrightarrow (CO)_4M(SiMe_2CH_2CH_2SiMe_2) \quad ^{333}$$

M = Fe, n = 1, m = 5, 51%

M = Ru, n = 3, m = 12, 89%

M = Os, n = 3, m = 12, 89%

$$Co_2(CO)_8 + Me_3\underset{H}{Si}CH_2CH_2\underset{H}{Si}Me_2 \longrightarrow [(CO)_4CoSi(Me_2)CH_2]_2 \quad (36\%)^{333}$$

$$\begin{array}{l} Hg(SiMe_3)_2 + Fe(CO)_5 \xrightarrow{h\nu} Hg[Fe(CO)_4SiMe_3]_2 \quad (28\%)^{334} \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow Hg(SiMe_3)_2 \\ \qquad\qquad\qquad\qquad\qquad (CO)_4Fe(SiMe_3)_2 \quad (78\%) \end{array}$$

An iron to carbon silyl group rearrangement has been observed under thermal or catalytic ($AlBr_3$) conditions.[335]

$$(C_5H_5)Fe(CO)_2SiMe_{2-n}Cl_nCH_2Cl \longrightarrow (C_5H_5)Fe(CO)_2CH_2SiMe_{2-n}Cl_{n+1}$$

(n = 0-2)

Cleavage of metal-metal bonds occurs when the silyl-iron complex shown is treated with electrophilic reagents.[336]

$$Me_3SiFe(CO)_2(C_5H_5) + A\text{-}B \longrightarrow Me_3SiA + BFe(CO)_2(C_5H_5)$$

(A = B = Cl; A = B = I; A = Cl, B = H; A = Cl, B = I;
A = CF_3, B = I)

Silyl-metal complexes have been formed by coupling reactions.[337]

$$Na[M(CO)_3C_5H_5] + Me_{4-n}SiX_n \longrightarrow Me_{4-n}X_{n-1}SiM(CO)_3C_5H_5$$

(n = 1-4; X = Br, Cl; M = Mo, W)

$$\mathrm{Na[Fe(CO)_2C_5H_5] + Me_{4-n}SiX_n \longrightarrow Me_{4-n}X_{n-1}SiFe(CO)_2C_5H_5}$$

$$(n = 1\text{-}3;\ X = \mathrm{Br, Cl})$$

$$\mathrm{Na[Mn(CO)_5] + Me_3SiBr \longrightarrow Me_3SiMn(CO)_5}$$

A mild halogenation method has been developed for transition metal-silicon hydrides.[338]

$$\mathrm{C_5H_5(CO)_3MSiHRR' + CCl_4 \longrightarrow C_5H_5(CO)_3MSiClRR'}$$

$$\mathrm{C_5H_5(CO)_3MSiHMe_2 + CBr_4 \longrightarrow C_5H_5(CO)_3MSiBrMe_2}$$

$$(\mathrm{M = Cr, Mo, W;\ RR' = Me_2, MeCl, Cl_2})$$

$$\mathrm{C_5H_5(CO)_5MnSiHCH_3Cl + CCl_4 \longrightarrow C_5H_5(CO)_5MnSiCl_2CH_3}$$

$$\mathrm{C_5H_5(CO)_2FeSiHRR' + CCl_4 \longrightarrow C_5H_5(CO)_2FeSiClRR'}$$

$$(\mathrm{RR' = MeCl, Cl_2})$$

Silylcobalt carbonyls have been synthesized and their reactions with some electrophilic reagents investigated.[339]

$$\mathrm{Co_2(CO)_8 + R_3SiH \longrightarrow R_3SiCo(CO)_4}$$

$$\mathrm{R_3SiCo(CO)_4 + HgX_2 \longrightarrow R_3SiX}$$

$$\text{"} \quad + \mathrm{HX} \xrightarrow[4000\ \mathrm{atm}]{90°} \mathrm{R_3SiX}$$

$$(\mathrm{R_3 = Me_2Cl, MeCl_2;\ X = Cl, Br})$$

Reactions of some transition metal complexes with fluorine-containing acids in glass apparatus resulted in the formation of salts. Boron trifluoride affords the tetrafluoroborate analogues of these salts.[340]

$$\begin{tikzcd}
\mathrm{(Ph_3P)_3Ir(CO)H + SiF_4} \arrow[dr, "\text{glass}"] & \\
 & \mathrm{[(Ph_3P)_3Ir(CO)H_2]SiF_5} \\
\text{"} \quad \mathrm{+ HF} \arrow[ur, "\text{silica}"'] &
\end{tikzcd}$$

$$\mathrm{(Ph_3P)_3Pt + HF \xrightarrow{silica} [(Ph_3P)_3PtH]SiF_5}$$

Preliminary results concerning the formation and reactions of vinyl-silyl-metal complexes have appeared.[341]

$$C_5H_5(CO)_nMNa + ClR_2SiCH{=}CH_2 \longrightarrow C_5H_5(CO)_nMSiR_2CH{=}CH_2$$

$$\begin{tikzcd} C_5H_5(CO)_nMSiCl_2CH{=}CH_2 + AgBF_4 \arrow[r] & C_5H_5(CO)_nMSiF_2CH{=}CH_2 \arrow[d, "AgBF_4"] \\ & C_5H_5(CO)_3MSiF_3 \end{tikzcd}$$

(R_2 = Me_2, Cl_2, MeCl; M = Fe, n = 2;
M = Mo, W, n = 3)

$$C_5H_5(CO)_2FeSiMe_2CH{=}CH_2 + HX \longrightarrow C_5H_5(CO)_2FeX + HSiMe_2CH{=}CH_2$$

(X = F, Cl, Br, I, CF_3CO_2, CCl_3CO_2)

$$\begin{tikzcd} & C_5H_5(CO)_2FeSiCl_2CH_2CH_2Br \\ C_5H_5(CO)_2FeSiCl_2CH{=}CH_2 \arrow[ur, "HBr"] \arrow[dr, "HF/BF_3"'] & \\ & C_5H_5(CO)_2FeSiF_3 \end{tikzcd}$$

New silicon-nickel complexes have been added to the limited number of this compound type.[342]

$$Ni(bipy)R_2 + 3\ HSiX_3 \longrightarrow \underset{(85\%)}{Ni(bipy)(SiX_3)_2} + RSiX_3 + H_2 + RH$$

(R = Me, Et; X_3 = Cl_3, $MeCl_2$)

Other hydrides [$HSiPhCl_2$, $HSiPh_2Me$, $HSi(m\text{-}CF_3C_6H_4)_2Me$, $HSi(OEt)_3$] gave no stable silicon-nickel complexes.

$$\begin{tikzcd} C_5H_5Ni(PPh_3)Et + HSiCl_3 \arrow[r, "-EtSiCl_3"] & C_5H_5Ni(PPh_3)SiCl_3 \quad (49\%) \arrow[d, "CH_3I"] \\ & MeSiCl_3 \quad (24\%) \end{tikzcd}$$

The bipyridyl complexes were inactive as olefin hydrosilylation catalysts. They were also found to undergo Si-Ni bond cleavage with HCl. The dichloromethyl complex reacted with tetracyanoethylene to give a 9% yield of $MeCl_2SiSiCl_2Me$.

Evidence for the formation of silyl-ruthenium complexes has been reported ($Ph_3P = L$).

$L_3RuCl_2 + Et_3SiH \longrightarrow L_3RuHCl$ [343]

" $+ (EtO)_3SiH \longrightarrow L_3RuHCl + L_3RuHSi(OEt)_3$ [343]

" $+ Cl_3SiH \longrightarrow L_3RuH(SiCl_3) + L_3Ru(SiCl_3)_2$ [343]

$L_3RuH_2 + R_3SiH \longrightarrow L_3RuH_3SiR_3$ [344]

[R_3 = Et_3, $EtMe_2$, $PhMe_2$, $(EtO)_3$, Et_2H, PhMeH, Ph_2H, PhH_2, cyclohexyl-H_2]

$Ru(CO)_4(SiMe_3)_2 + CDT \longrightarrow Ru(CO)_2(C_8H_9)SiMe_3$ [345]

(low yields)

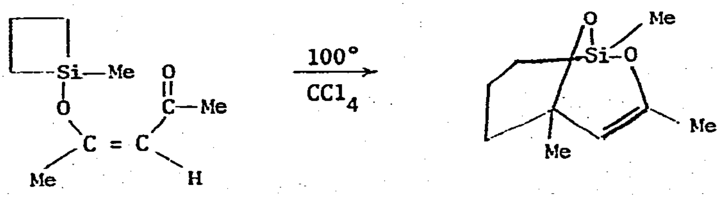
" $+ COD \longrightarrow Ru(CO)_2(C_8H_9)SiMe_3$ (19%) [345]

$Ru(CO)_4(SiMe_3) + COT \longrightarrow Ru(CO)_2(C_8H_9)SiMe_3$ (17%) [346]

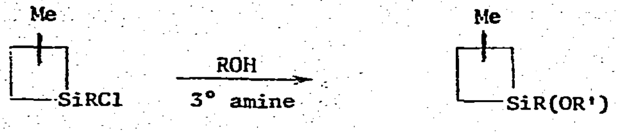
(CDT = all trans-cyclododeca-1,5,9-triene; COD = cycloocta-1,5-diene; COT = cycloocta-1,3,5- and 1,3,6-trienes; Ru complexes free of silicon were also obtained as products).

VI. SILACYCLIC COMPOUNDS

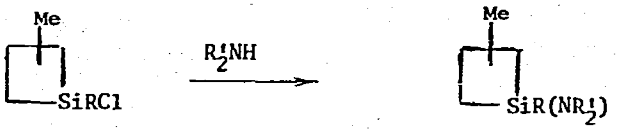
A silacyclobutane has been shown to undergo ring opening by internal nucleophilic displacement.[347]



Stereoselective syntheses (60-90%) of some silacyclobutanes were achieved by alcoholysis or amminolysis of 2- or 3-methyl-1-chloro-1-silacyclobutanes.[348]

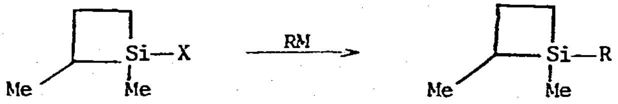


(R = H, Me; R' = Me, tBu, Ph)



(R = H, Me; R' = Me, Et)

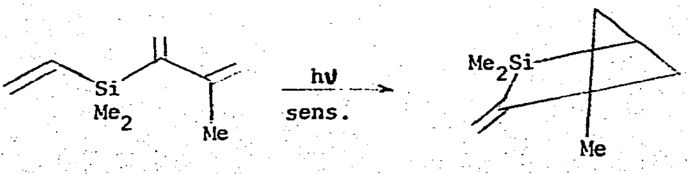
Reactions between organolithium or Grignard reagents and t-butoxy- dimethylamino- and fluorosilyl methyl-substituted silacyclobutanes have been investigated.[349]



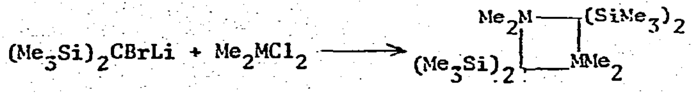
X = tBuO, Z/E = 15/85	RM = MeMgI, Z/E = 15/85
X = tBuO, Z/E = 10/90	RM = nBuLi, Z/E = 10/90

X = tBuO, Z/E = 65/35	RM = MeMgI, Z/E = 65/35
X = tBuO, Z/E = 80/20	RM = nBuLi, Z/E = 80/20
X = Me_2N, Z/E = 60/40	RM = nBuMgBr, Z/E = 60/40
X = F, Z/E = 60/40	RM = nBuLi or nBuMgBr, Z/E = 55/45

Photolysis of 2,4,4-trimethyl-4-sila-3-methylene-1,5-hexadiene led to the formation of a silabicyclic photoproduct. Other trienes did not undergo cyclization.[350]

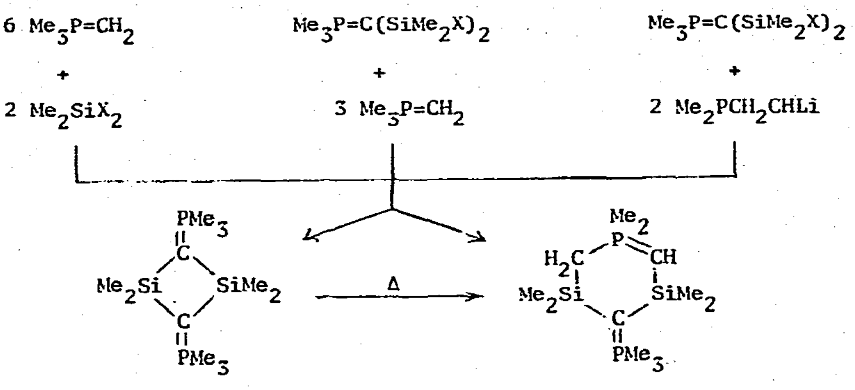


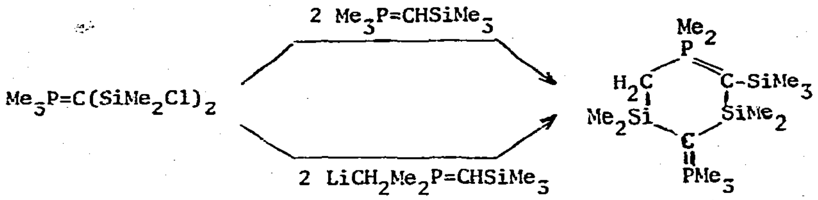
A series of 1,3-di-(Group IV)-metalloidal cyclobutanes has been prepared by a novel route.[351]



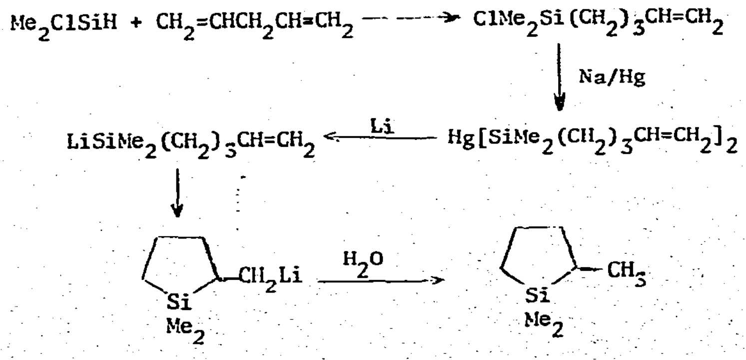
(M = Si, Ge, Sn)

Acyclic ylids have been used as precursors to silacyclic ylids.[352]

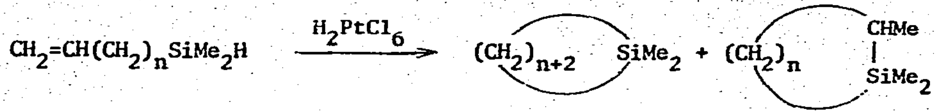




A new route to 5-membered silacycles utilizing the intramolecular addition of a silyllithium to a C=C bond has been developed.[353]

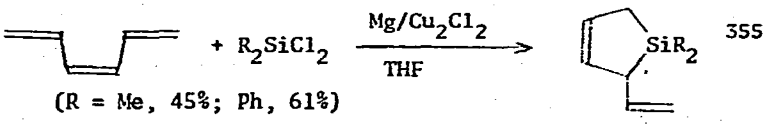


The effect of ring size on the utility of chloroplatinic acid-catalyzed intramolecular cyclization of alkenylsilanes has been examined.[354]

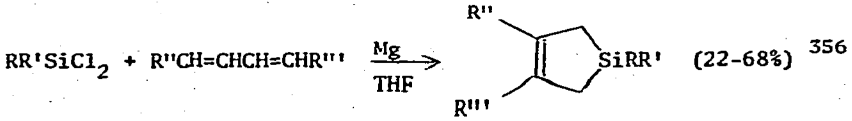


	Yield (%)	Distribution (%)	
n = 0, 1	0	0	0
n = 2	46	100	0
n = 3	58	10	90
n = 4	70	48	52
n = 5	16	46	54
n = 6	2	0	100

Silacyclopentenes have been obtained from chlorosilanes and conjugated dienes or trienes.

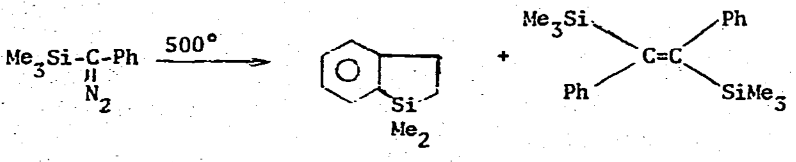


(R = Me, 45%; Ph, 61%)



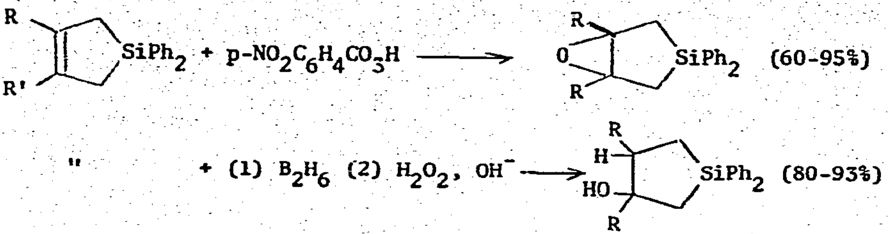
(R, R' = Me, Ph, H, vinyl, allyl; R", R"' = H, Me; the use of HMPT as co-solvent increases yields).

Thermolysis of an α-diazosilane affords a benzosilacyclopentene.[357]

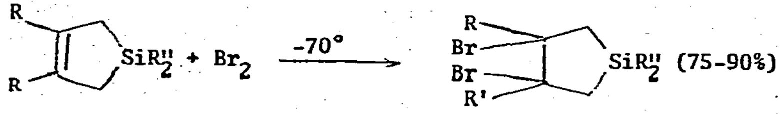


(15%)

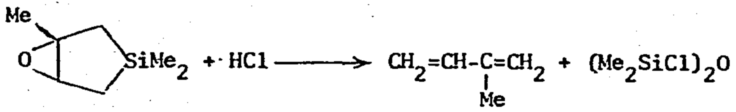
The reactivity of silacyclopentenes towards a number of reagents has been investigated.[358]

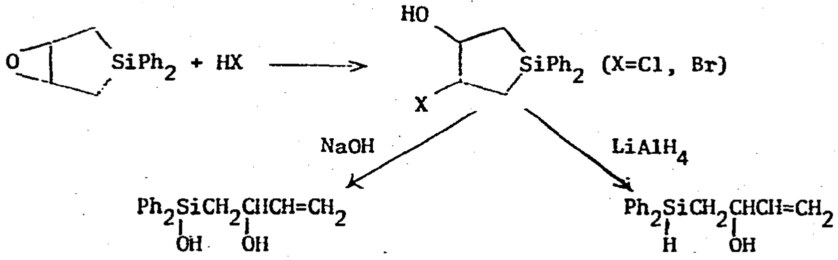


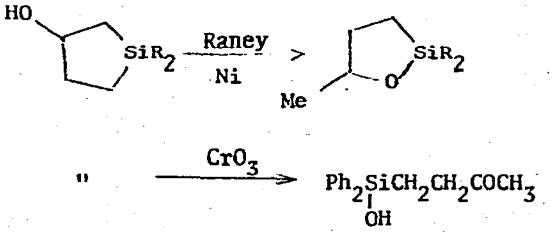
(R, R' = H, H; H, Me; Me, Me)



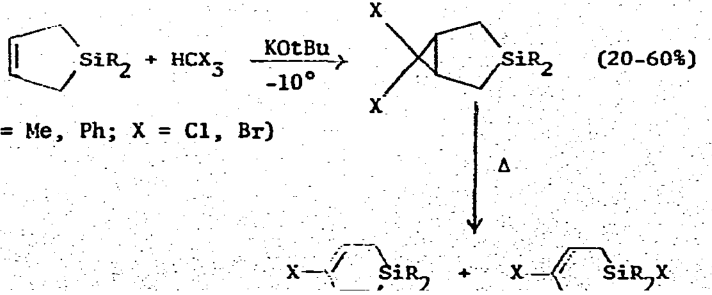
(R, R' = H, H; Me, Me; R" = Me or Ph)







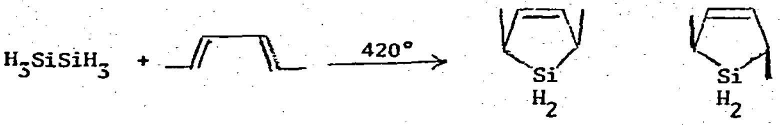
Silabicyclics are formed by the addition of dihalocarbenes to 1-silacyclopent-3-enes. The thermolysis of these species was investigated.[359]



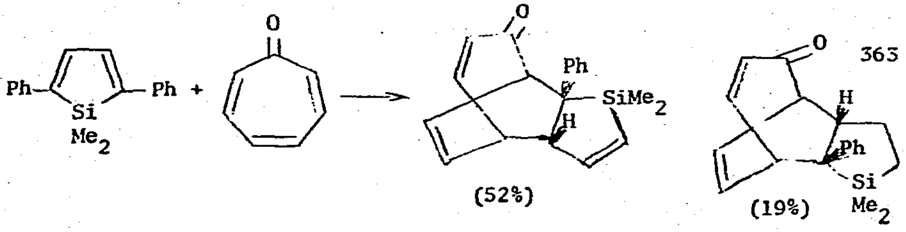
(R = Me, Ph; X = Cl, Br)

Silylene, generated from neutron irradiation of PH$_3$, has been found to react with 1,3-butadiene to form silacyclopent-3-ene.[360,361]

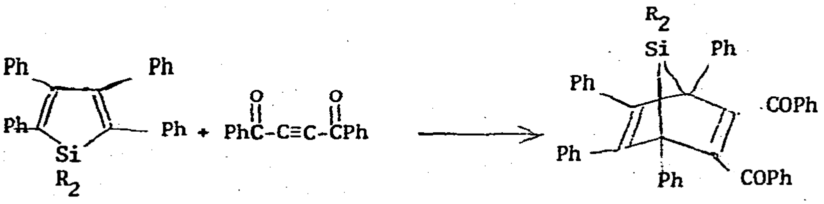
Thermally generated silylene (from disilane) reacted with *trans*, *trans*-2,4 hexadiene to afford a 1:1 mixture of silacyclopentene stereoisomers.[362]



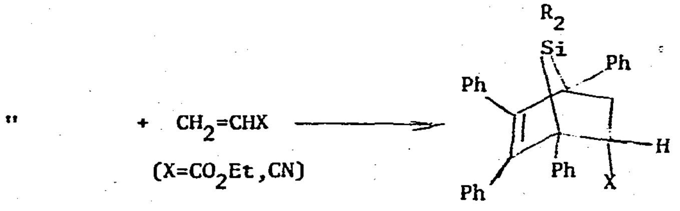
Cycloaddition reactions of silacyclopentadienes have been reported.



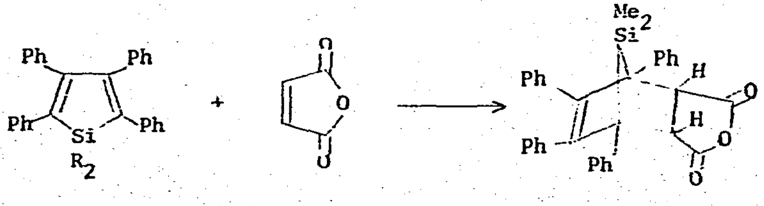
363



364



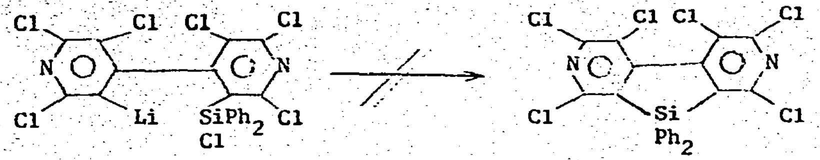
364
(X endo)



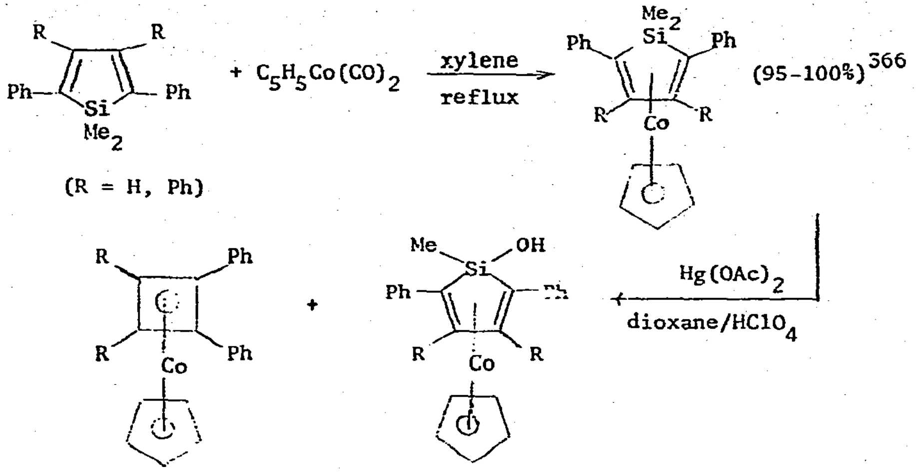
364

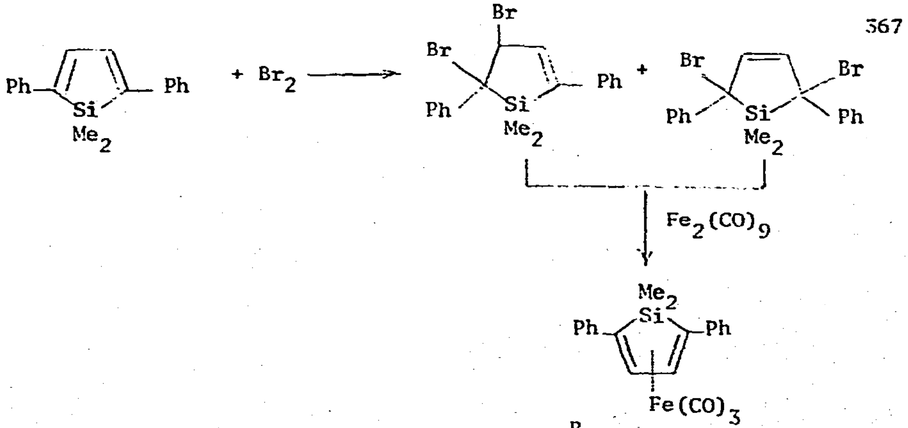
(R = Ph, Me, CH=CH$_2$)

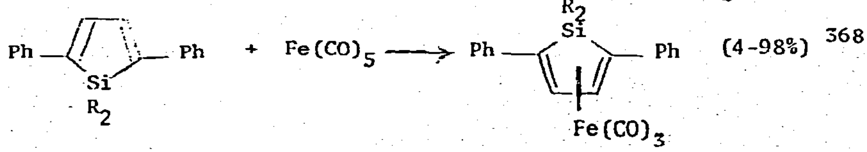
Attempts at the ring closure of perchlorobipyridyl chlorosilanes were unsuccessful.[365]

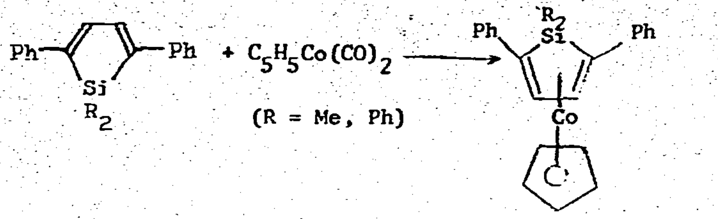


A number of transition metal complexes employing the silacyclopentadiene ring as ligand have been reported.



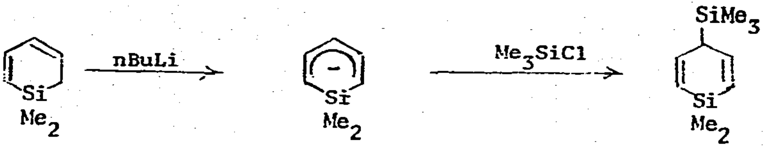




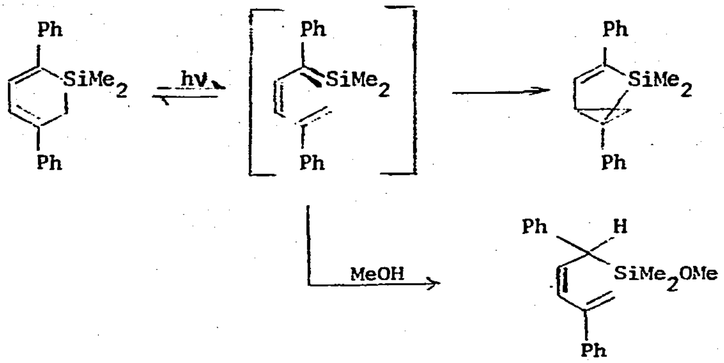


(81-87%)[368]

The following chemistry of silacyclohexadienes has appeared.

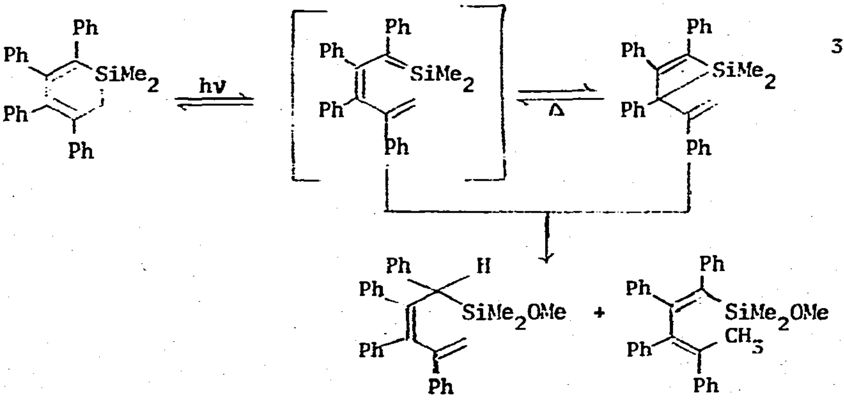


[369]

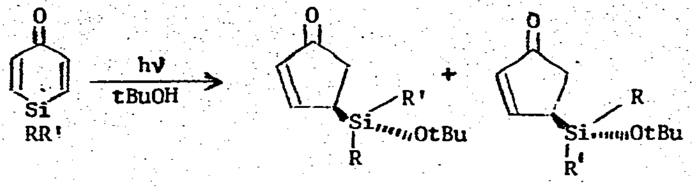


(38%)[370]

(50%)



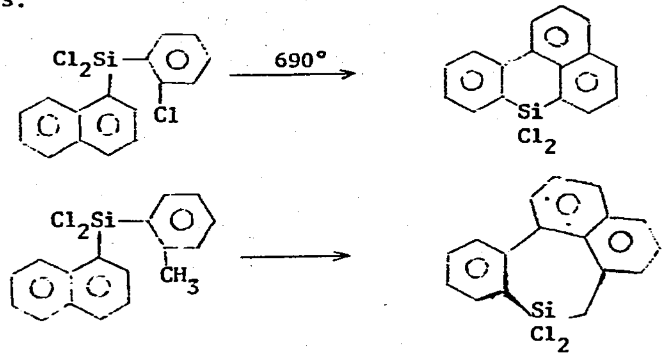
[370]



371

(R, R; = Me, Me; Ph, Ph; Me, Ph)

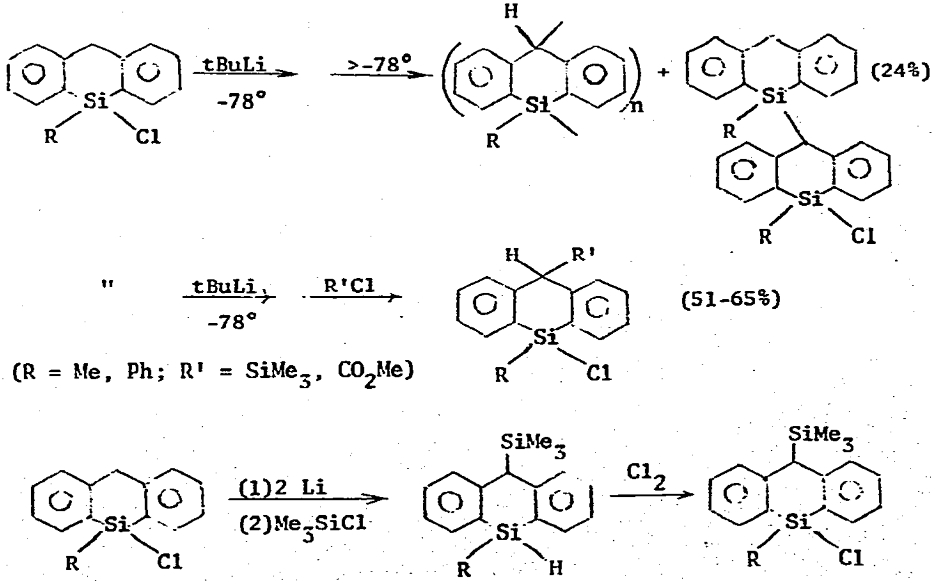
Thermolysis of arylsilanes affords polynuclear silicon-containing compounds.[372]



(20%)

(20%)

Substitution reactions at the 9- and 10- positions of 9,10-dihydro-9-silaanthracenes have been described.[373]

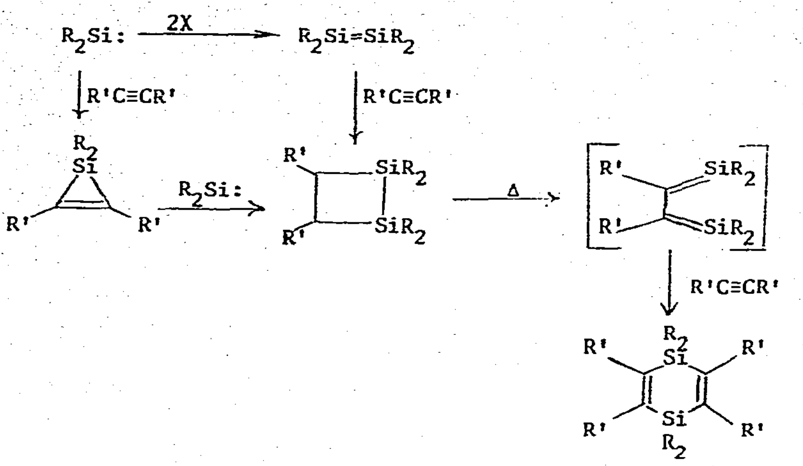


(24%)

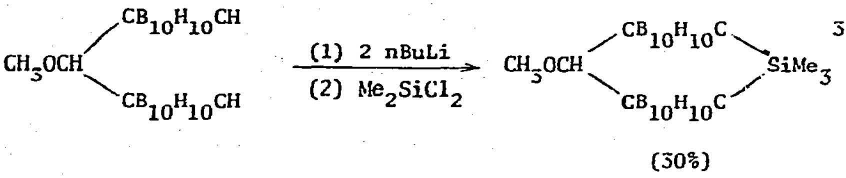
(51-65%)

(R = Me, Ph; R' = $SiMe_3$, CO_2Me)

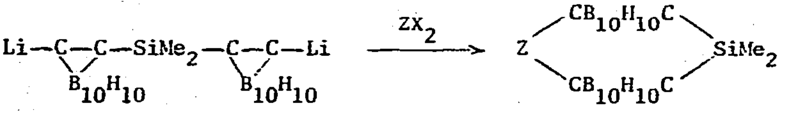
A new mechanistic route has been suggested as the pathway by which acetylenes afford 1,4-disilacyclohexa-2,5-dienes upon treatment with silylene generators.[374]



Silacyclic carboranes have been prepared as shown below.



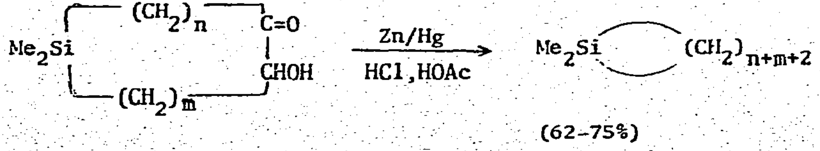
375



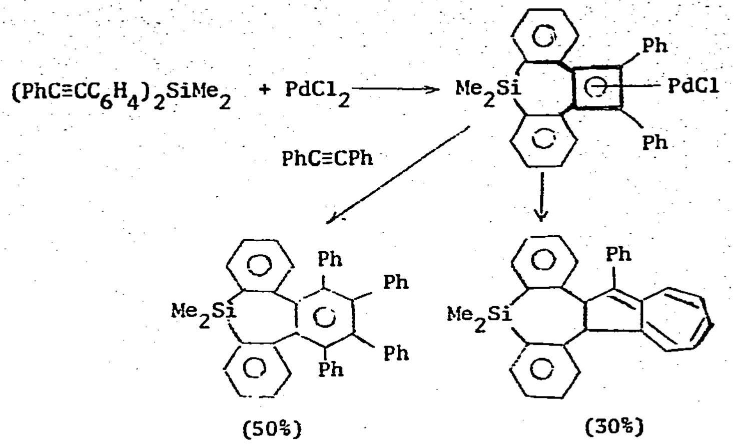
376

(Z = $SnMe_2$, $GeMe_2$, PPh, AsMe)

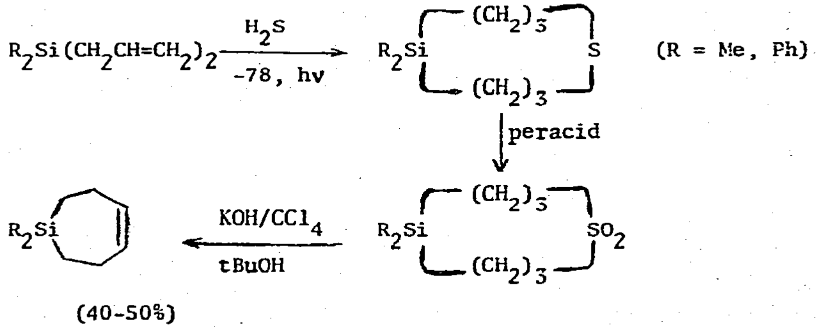
Synthetic schemes were investigated which led to the preparation of medium-sized silacycloalkanes by reduction of initially prepared acyloins. Acyloins of following ring size were prepared from available starting materials (size, % yield): 11 (8.8), 10 (4.8), 9 (1.6), 8 (11.8).[377]



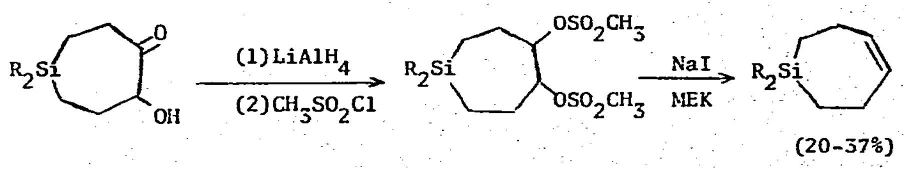
Palladium complexes afford silacycles from diacetylenes.[378]



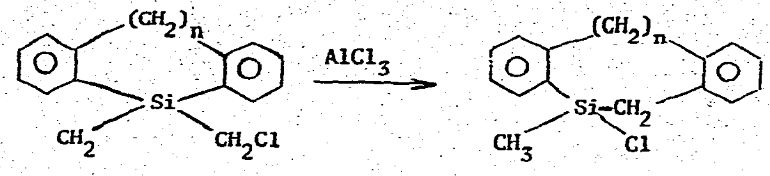
Photochemical addition of H_2S to diallylsilanes affords 10-25% isolated yields of the 1-sila-5-thiacyclooctanes. These can be transformed into silacycloheptenes.[379]



The silacycloheptenes were also prepared from the corresponding acyloins.

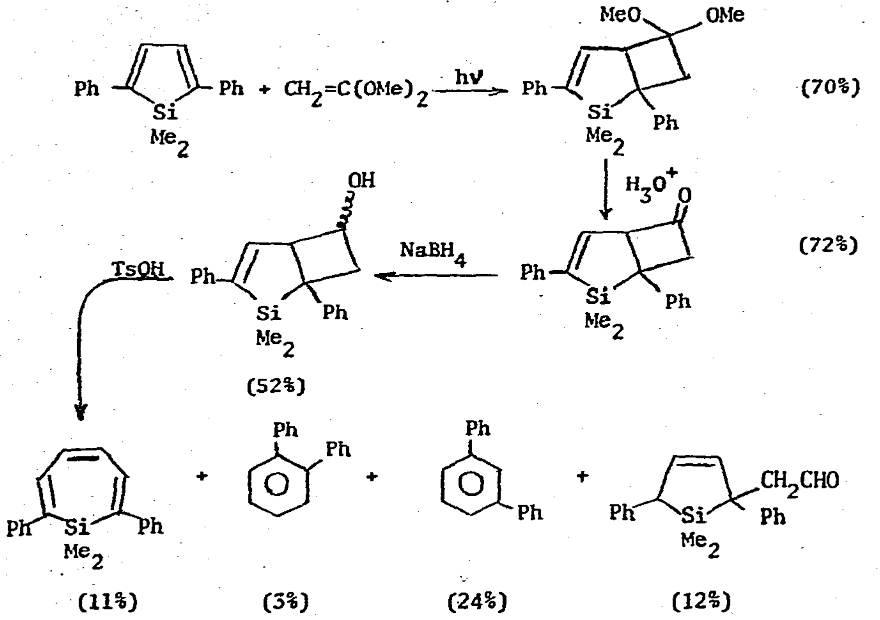


A ring-expansion reaction afforded entry into several dibenzosilacycles.[380]



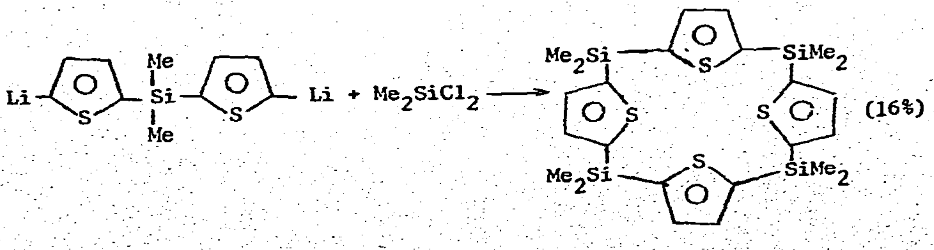
(n = 0-2)

A synthesis of the first nonannulated silacycloheptatriene has been achieved.[381]



The pyrolysis of tetramethylsilane at 700° afforded twenty characterizable compounds with bi- and polycyclic Si-C-Si frameworks; nine of these were 1,3,5,7-tetrasilaadamantanes.[382]

A novel macrocycle has been prepared containing thiophene moieties.[383]



VII. DISILANES AND POLYSILANES

A number of methods have been reported for the preparation of disilanes.

$(MeO)_3SiSi(OMe)_3 + 6\ BF_3 \longrightarrow Si_2F_2 + 6\ BF_2(OMe)$ [384]

(76%)

$HF_2SiSiF_2Br + SbF_3 \longrightarrow F_3SiSiF_2H$ [385]

$RR'SiHCl + M \xrightarrow{THF} RR'(H)SiSi(H)RR'$ [386]

(R, R' = alkyl, aryl, H; M = Mg or Na; mixed disilanes were also prepared)

$Me_3Ga + Si\ (mirror) \xrightarrow{250^\circ} Me_3SiSiMe_3$ [387]

$MePh\text{-}\alpha\text{-}Np\overset{*}{Si}Li + MePh\text{-}\alpha\text{-}Np\overset{*}{Si}Cl \longrightarrow (MePh\text{-}\alpha\text{-}Np)_2Si_2$ [388]

(meso + d,l)

$Cl_3SiSiCl_3 + 1{,}10\text{-phenanthroline} \longrightarrow Si_2Cl_6 \cdot C_{12}H_8N_2$ (65%) [389]

A difference in reactivity between dichloro- and methyl chloropolysilanes allows the preparation of monochloro permethylated polysilanes.[390]

$Cl(SiMe_2)_nCl + MeMgI \longrightarrow Me(SiMe_2)_nCl$ (58-90%)

(n = 2-6)

Polysilanes of high catenation number have been synthesized for the first time.[391]

$Cl(SiMe_2)_6Me + Cl(SiMe_2)_6Cl \xrightarrow{K} Me(SiMe_2)_nMe$ (n = 12, 18, 24)

Other polysilane chemistry has appeared as follows:

$$\left.\begin{array}{l} H_2Si[Si(OMe)_3]_2 + BF_3 \longrightarrow H_2Si(SiF_3)_2 \\ HSi[Si(OMe)_3]_3 + BF_3 \longrightarrow HSi(SiF_3)_3 \end{array}\right\} (60\text{-}70\%)$$ [392]

$H(SiH_2)_nH + BuLi \longrightarrow Bu(SiH_2)_nR$ [393]

(n = 3-5; R = H, Bu)

The polysilyl anions $H_3SiSiH_2^-$, $(H_3Si)_2SiH^-$, and $(H_3Si)_3Si^-$ have been prepared and characterized by NMR and IR spectroscopy.[394,395] These have been used in coupling reactions with $PhSiH_2Cl$ and C_2H_5Cl.[395]

Polysilanes have been employed as ligands in the formation of transition metal complexes.[396]

$$Me_5Si_2H + Mn_2(CO)_{10} \longrightarrow Me_5Si_2Mn(CO)_5 \quad (12\%)$$

$$Me_5Si_2Cl + NaMn(CO)_5 \longrightarrow Me_5Si_2Mn(CO)_5 \quad (26\%)$$

$$(Me_3Si)_3SiMe \xrightarrow{Li} Me(Me_3Si)_2SiLi \xrightarrow{BrMn(CO)_5} Me(Me_3Si)_2SiMn(CO)_5 \quad (30\%$$

$$(Me_3Si)_4Si \xrightarrow{Li} (Me_3Si)_3SiLi \xrightarrow{BrMn(CO)_4PPh_3} (Me_3Si)_3SiMn(CO)_4PPh_3 \quad (8\%)$$

$$(Me_3Si)_3SiCl + NaFe(CO)_2C_5H_5 \longrightarrow (Me_3Si)_3SiFe(CO)_2C_5H_5 \quad (18\%)$$

$$(ClMe_2Si)_4Si + NaFe(CO)_2C_5H_5 \longrightarrow [C_5H_5(CO)_2FeMe_2Si]_4Si \quad (5\%)$$

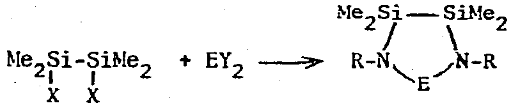
In addition to the above, the following compounds were similarly prepared.

$Me_nSi_mFe(CO)_2C_5H_5$ (n = 7, m = 3; n = 5, m = 2; n = 3, m = 1)

$Me_3SiMn(CO)_4PPh_3$

$Me_nSi_mMn(CO)_5$ (n = 9, m = r; n = 3, m = 1)

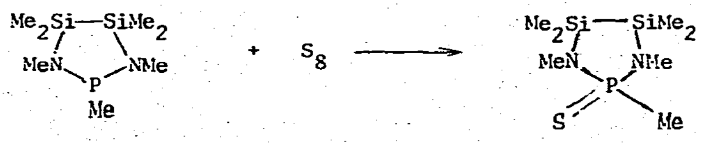
A variety of new ring systems containing di- or polysilyl moieties have been synthesized.



397

(X = NHMe; E = BPh, SiF_2, $GeCl_2$, PMe, AsCl, SbCl, SO, $SnBu_2$; R = Me

(X = Cl; EY_2 = X; $(Me_3SiNH)_2SO_2$; R = Me or Me_3Si)



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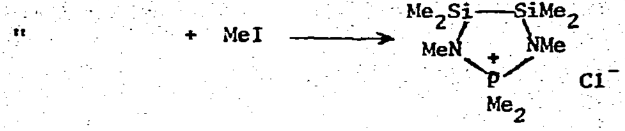

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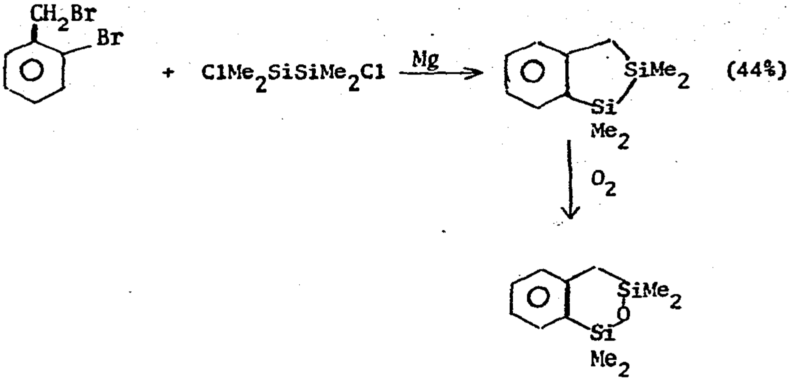

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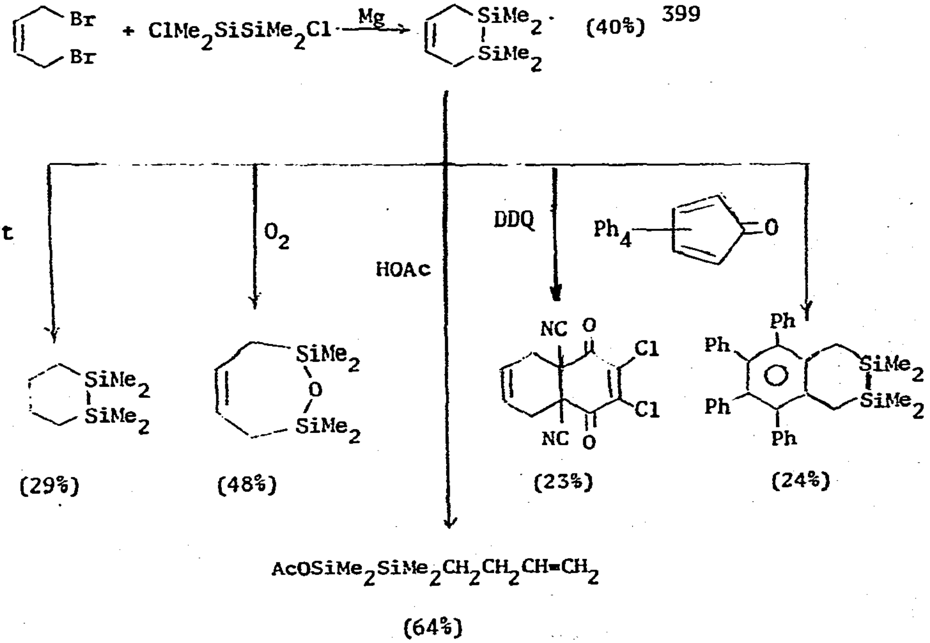

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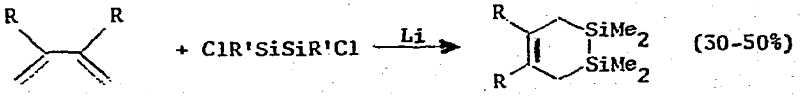
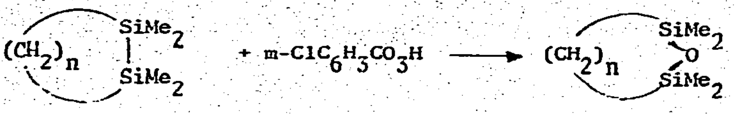


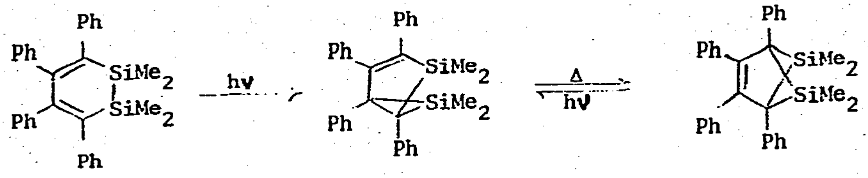
400

(R = H, Me; R' = Me, Et)



401

(n = 3-5; ease of oxidation dependent on ring strain)



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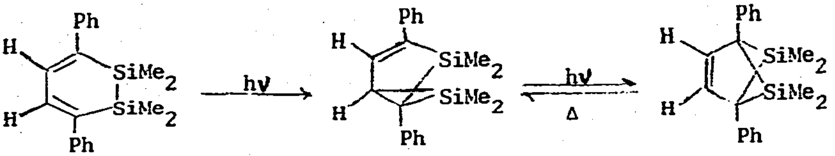
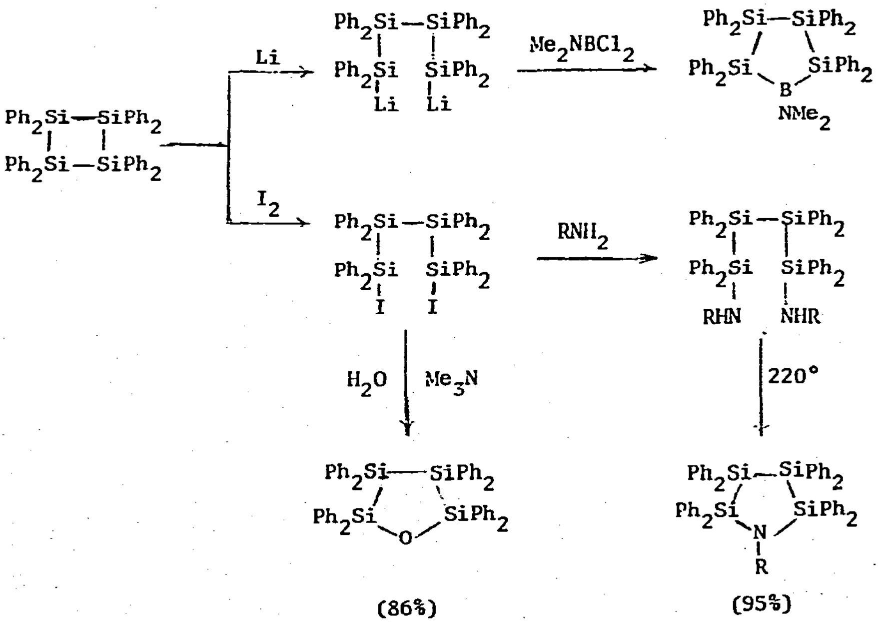


402

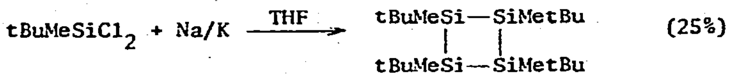
(Note reversal of thermal stabilities of photoproducts. This is the first proven example of a vinylsilacyclopropane-silacyclopentene rearrangement)



403

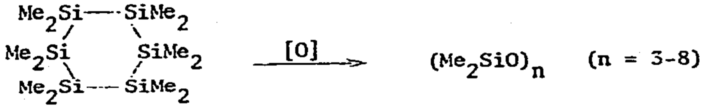
(No spectral evidence was found for electron delocalization in any of these heterocycles.)

A direct synthesis of a highly unreactive cyclotetrasilane has been reported. A 2:1 mixture of the all-trans compound and what appears to be an isomer containing a 1,2,3-cis arrangement of groups was isolated. these are found to be inert to oxygen, H_2SO_4 or HCl-$AlCl_3$, but can be reduced to a radical anion.[404]



Reaction of either 1,4-dilithiooctaphenyltetrasilane or 1,5-dilithiodecaphenylpentasilane with the dihalides Ph_2CCl_2, H_2CCl_2, CH_2Br_2 or $MeCCl_2Me$ gave no carbosilacyclic products.[405]

The reactivity of dodecamethylcyclohexasilane towards oxidizing agents has been investigated. Oxygen or hydrogen peroxide had little effect, but CrO_3, $K_2Cr_2O_7$ or $KMnO_4$ gave cyclic siloxanes.[406]



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