SILICON - SYNTHESIS AND REACTIVITY

ANNUAL SURVEY COVERING THE YEAR 1973

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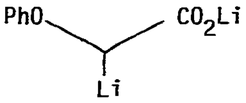
CONTENTS

I. INTRODUCTION

In an effort to maintain some degree of currency for a review which must abstract an ever-increasing number of publications, the approach to coverage has been selective instead of inclusive. No attempt was made to report on the patent literature, dissertations, or the organosilicon chemistry of polymers. In addition, other areas were treated in sion of alkyl halides to alkanes by complex metal hydrides ranging in composition from $LiCuH_2$ to Li_5CuH_6 [427]. Reactions of such species with enones and cyclic ketones to give reduction products are also reported.

Turning to boron ate complexes, dilithiophenoxyacetate (540) has been combined with a variety of trialkylboranes to afford, upon hydrolysis, alkylacetic acids [428]. For example, trioctylborane and 540 give decanoic acid (90%) apparently via 541.



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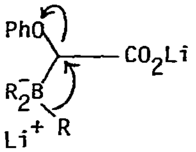

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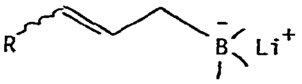
Allylic boron ate complexes 542 have been found to combine in a head to tail fashion with allyl chlorides and bromides 543 to give coupled products 544 in fair to excellent yields [429]. The related complexes 545 have been added to acrolein to yield homopropargyl alcohols 546 and α-allenic alcohols 547 at low and room temperature, respectively [430].



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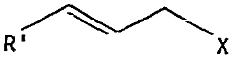

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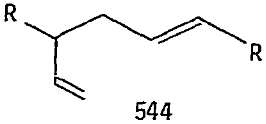

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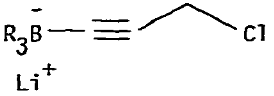

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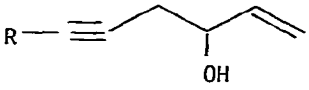

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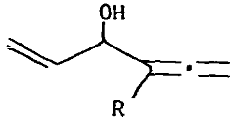
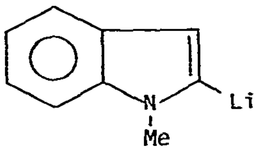


547

Lithioindoles such as 548 and vinyllithium have been combined with trialkylboranes (R_3B), iodine, and H_2O_2 to afford 549 [431] and trisubstituted olefins such as 550 [432], respectively.



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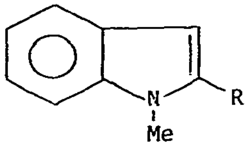

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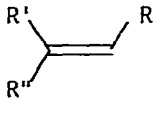

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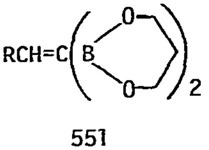
Migration of the methyl group from boron to carbon in the conversion of 551 to 552 by two equivalents of methyllithium is said to occur during the oxidation step with H_2O_2 [433]. Several possible intermediates are discussed.



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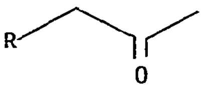
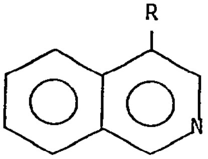


552

Other papers in this area discussed steric effects in the reactions of certain trialkylboranes with lithium and sodium hydrides [434], the synthesis of new germyl aluminates such as 553 by reduction of aryl digermanes by $LiAlH_4$ [435], and the preparation of 4-alkylisoquinolines 554 by combination of isoquinoline, $LiAlH_4$, and alkyl halides [436].

$(Ph_3Ge\text{-}AlH_3)^-Li^+$

553



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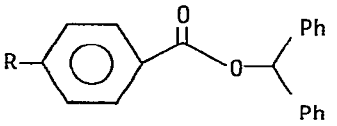
13. REDUCTIONS AND RADICAL-ANIONS

Several benzhydryl benzoates (555) have been found to undergo deoxygenation with lithium naphthalenide to afford ketones 556 [437]. Acetates of sterically hindered secondary alcohols and of tertiary alcohols are converted by lithium in ethylamine to alkanes rather than to alcohols [438]. The process is illustrated by the conversion of caryolan-1-ol acetate to caryolane (90%).



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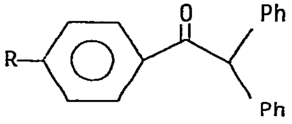
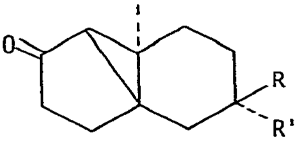


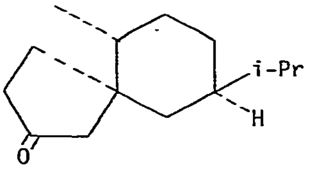
556

Four more tricyclodecan-3-ones have been reduced by lithium in liquid ammonia as illustrated by the conversion of 557 and 558 to 559 and 560, respectively [439] The results are discussed in terms of equilibration of intermediate carbanions and the rate of protonation of kinetically generated anions.



557 (R=i-Pr, R'=H)

558 (R=H, R'=i-Pr)



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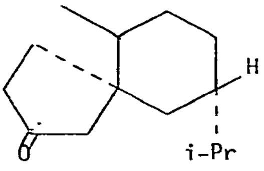
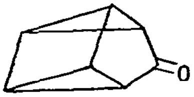


560

Lithium-ammonia reduction of several bridged dicyclopropyl ketones to afford products in which both cyclopropane rings have been cleaved has been ascribed to two electron reductions occurring by pericyclic processes [440]. The process is illustrated by the conversion of 561 to 562, 563, and other products. That carbanions are involved has been demonstrated by deuterolysis [441].



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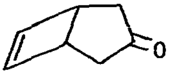

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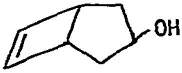
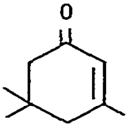


563

A large excess of "lithium bronze" ($Li \cdot 4NH_3$) has been found not to be necessary to effect convenient reduction of α,β-unsaturated ketones to saturated ones [442]. For example, this reagent converts 564 to 565 (97-98%). More normal "lithium blue" reductions have been employed in the conversion of 566 to 567 [443] and in a study of the stereochemistry of the reductions of 568 to 569 [444].



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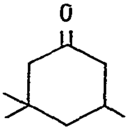

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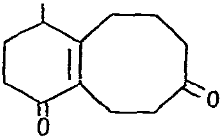

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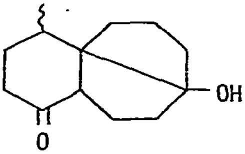

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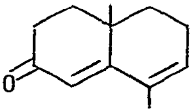

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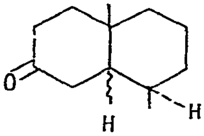
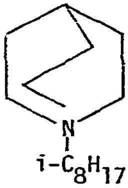


569

Lithium anthracenide has been alkylated by s-octyl fluoride with 42% inversion and 58% racemization, and by 570 to give 571 via ring opening [445]. The results are said to verify that such reactions can proceed by both S_N2 and by electron transfer processes.



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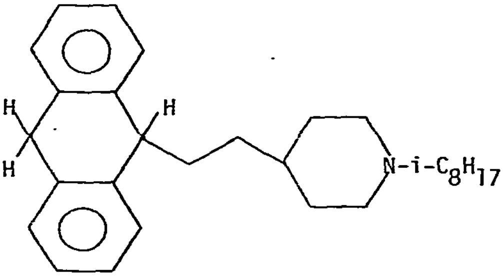
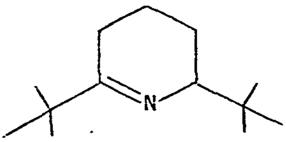


571

Alkali metal reductions of isomeric terphenyls and of biphenyl in HMPA have resulted in some cleavage of the Ar-Ar bonds since up to 25% of dihydrobiphenyls and -benzene were obtained, respectively [446]. New, severely hindered nitrogen bases such as 572 have been obtained by lithium-ammonia reduction of 2,6-di-t-butylpyridine [447]. Additional examples of reductive silylation of monoaromatics have been described as illustrated by the conversion of p-cresol to 573 using chlorodimethylsilane and lithium in THF [448].



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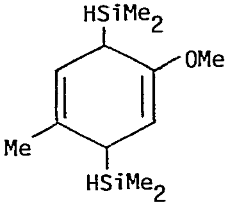
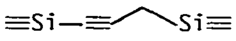


573

Other papers in this section discussed the preparation of 574 by reductive silylation of 575 (R = Me, $SiMe_3$) using chlorotrimethylsilane and lithium in THF [449], the synthesis of middle-ring cyclosilanes $(Me_2Si)_n$ (n = 8,9) from dichlorodimethylsilane and lithium in THF [450], the conversion of chloroalkoxides 576, prepared from Grignard reagents and chloroketones, to trisubstituted alkenes by lithium [451], and the preparation [452] and electrochemical behavior [453] of M^+Au^-.



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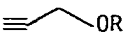

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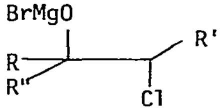


576

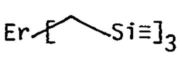
14. REACTIONS WITH INORGANIC AND ORGANOMETALLIC COMPOUNDS

As in the past, this section will be divided into the families of the periodic table proceeding from left to right. First, $LiMgH_3$ has been prepared by the addition of $LiMgPh_3$ to $LiAlH_4$ [454]. Other ate complexes described in this paper included $LiMgH_nR_{3-n}$ (n = 1,2; R = Me,Et,Bu), prepared from RLi and alkylmagnesium hydrides or MgH_2, and $LiMg_2H_5$, synthesized from n-butyllithium and MgH_2 in a 1:2 molar ratio.

Several new organic derivatives of lanthanides were reported in 1978. Thus, dicyclopentadienylerbium and -ytterbium chlorides have been combined with lithiotriphenylstannane to afford 577 (M = Er,Yb) [455]. A similar germanium derivative was likewise obtained from the erbium chloride reagent. Erbium(III) chloride itself was condensed with trimethylsilylmethyllithium to give 578 [456]. Ate complexes 579 (M = Er,Lu) were also obtained from the metal (III) chlorides and six equivalents of methyllithium in the presence of TMEDA [457].

Cp_2MSnPh_3

577



578

$(Me_6M)(Li{\cdot}TMEDA)_3$

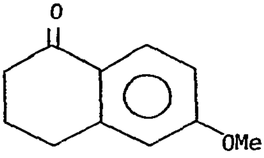
579

New thermally stable bis(cyclopentadienyl) derivatives 580 of thorium and uranium have been prepared from the corresponding new dichlorides and methyllithium [458]. Hydrogenation of 580 yielded the first organoactinide hydrides.

$$(Me_5C_5)_2MMe_2$$

580

A full paper described the titanium-induced reductive coupling of carbonyls to olefins as illustrated by the conversion of benzophenone to tetraphenylethylene (80%) and the mixed coupling of 581 and acetone to 582 (85%) [459]. The titanium metal is conveniently obtained from titanium(III) chloride and lithium metal.



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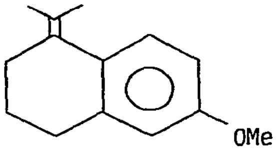
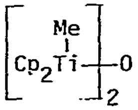


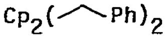
582

Several organotitanium systems were prepared from organolithium reagents including 583 from the dichloride and methyllithium [460], dibenzyl- and diphenyltitanium from 584 and 585 with benzyl- and phenyllithium, respectively [461], titanium, vanadium, chromium, and scandium systems such as 586 from 587 and appropriate halides [462], paramagnetic chelated derivatives such as 588 from 587, diketones, and metal (III) chlorides [463], and fully methylated silylamide derivative 589 and related compounds from halotitanium species [464]. The first chiral zirconocene compound, 590, was prepared from chiral α-phenethylcyclopentadiene, 591, and methyllithium [465].



$$\left[Cp_2\overset{Me}{Ti}-O\right]_2$$

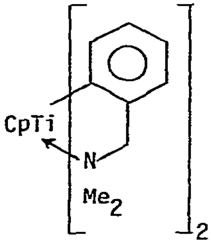
583



584

$$Cp_2TiPh_2$$

585



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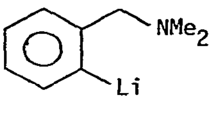

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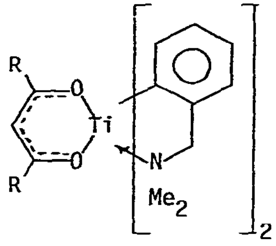

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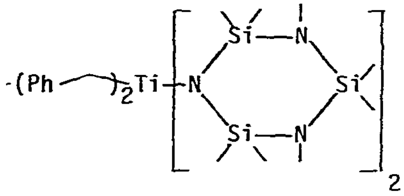

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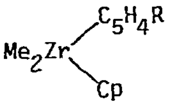


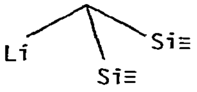
$Me_2Zr(C_5H_4R)(Cp)$

590

$CpZrCl_3$

591

A full paper described the details of the preparation, properties, and structures of tris[bis(trimethylsilyl)methyl] derivatives of titanium(III), zirconium(IV), hafnium(IV), vanadium(III), and chromium(III) [466]. Each of the compounds was synthesized from 592 and appropriate metal chlorides.

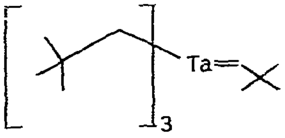


592

Niobium-containing compounds 593 and 594 have been obtained from 595 and 596 [467] and various cyclopentadienyl anions and niobium(V) and (IV) chlorides [468], respectively.

$Cp_2NbC_9H_9$	$(RC_5H_4)_2NbCl_2$	Cp_2NbCl_2	LiC_9H_9
593	594	595	596

Neopentylidene complex 597 has been prepared from 598 and two equivalents of lithio-2,2-dimethylpropane apparently via 599 [469]. The corresponding niobium compound is also described. Additional chemistry of 597 and a related cyclopentadiene derivative is described [470,471].



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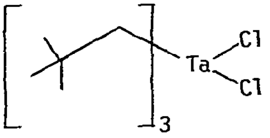

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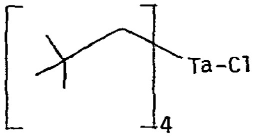
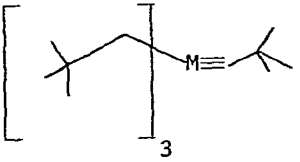


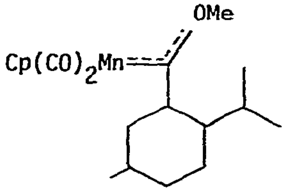
599

Chemistry similar to the above has been employed to synthesize tungsten and molybdenum complexes 600 [472].



600

Several optically active carbene and carbyne complexes have been prepared using (+)-menthyllithium and metal carbonyls and then characterized by IR, ^{1}H-, and ^{13}C-NMR spectroscopy, and by polarimetry [473,474]. The compounds listed include 601 [473], 602 [M = Cr,W) [474], and 603 (M = Cr,W) [473].



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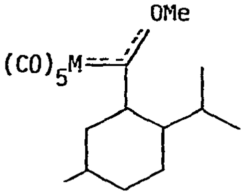

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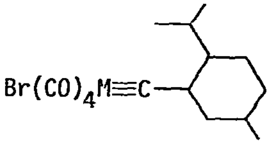
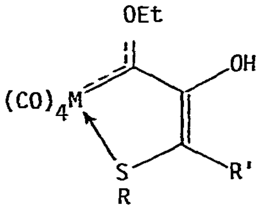
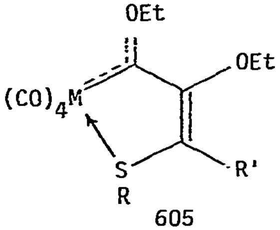


603

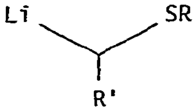
Carbene complexes 604 and 605 (M = Cr,W) have been synthesized from the metal hexacarbonyls and 606 [475]. The R groups of 606 were Me, Ph, SPh, and $(CH_2)_3S$. Another paper presented a full disclosure about the preparation and reactions of alkyl- and arylpentacarbonyltungsten anions [476].



604



605



606

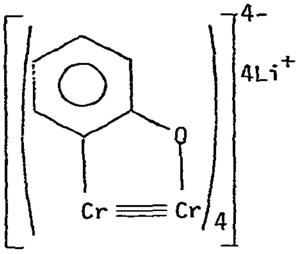
In an effort to determine if metal-metal metathesis in the chemistry of triple bonds between molybdenum and tungsten were possible, a mixture of WCl_6 and $MoCl_5$ was treated with lithium dimethylamide [477]. That only 607-609 but not 610 were formed along with other experiments suggested that such metal-metal triple bonds are not ruptured.

$MO_2(NMe_2)_6$	$W_2(NMe_2)_6$	$W(NMe_2)_6$	$MoW(NMe_2)_6$
607	608	609	610

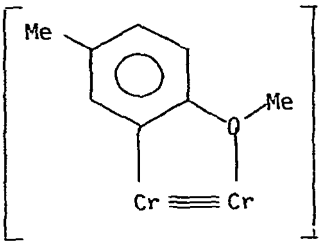
Now σ-alkyl systems 611 [478] and 612 [479] have been prepared by treatment of 613 with methyl- and ethyllithium, respectively.

$Me_2Mo_2(NMe_2)_4$	$(CH_3CH_2)_2Mo_2(NMe_2)_4$	$Cl_2Mo_2(NMe_2)_4$
611	612	613

Several new species containing chromium-chromium and molybdenum-molybdenum quadruple bonds have been prepared from o-lithiophenyl ethers or phenoxides and dichromium and dimolybdenum tetraacetates [480-482]. The compounds are illustrated by 614 and 615. Similar compounds have been obtained from lithio-2-amino-6-methylpyridine [483].

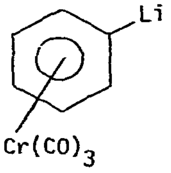


614

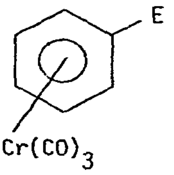


615

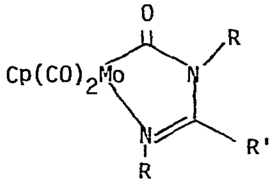
Finally, in this family, novel lithium derivative 616 has been prepared from the corresponding organomercurial, then combined with a variety of electrophiles to afford 617 [484]. An unrelated paper describes the preparation of 618 (R,R' = alkyl, aryl) from the chloromolybdenum tricarbonyl and lithioamidines [485].



616

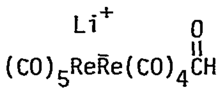


617



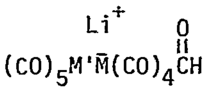
618

Binuclear formyl complex 619 has been obtained by reaction of lithium triethylborohydride with dirhenium decacarbonyl [486]. The kinetically less stable 620 (M,M' = Re,Mn) has been similarly prepared from 621. Both 619 and 620 are potent hydride donors.



$Li^+ \; (CO)_5Re\bar{R}e(CO)_4\overset{\overset{O}{\|}}{C}H$

619



$Li^+ \; (CO)_5M'\bar{M}(CO)_4\overset{\overset{O}{\|}}{C}H$

620

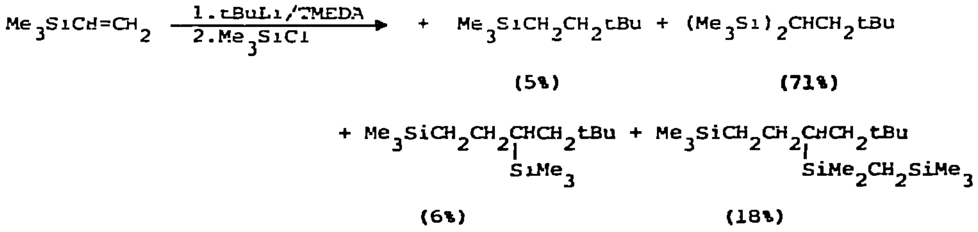
$ReMn(CO)_{10}$

621

Manganese derivative 622 has been prepared from lithiopentamethylcyclopentadiene and manganese(II) chloride [487]. Compound 622 was converted to the first isolable metallocene anion by sodium naphthalenide. Manganese derivative 623 has been converted to alkyldiazene complex 624 by methyllithium which was then methylated to give azo derivative 625 [488].

IV. CARBOFUNCTIONAL SILANES

Treatment of vinyltrimethylsilane with t-butyllithium-TMEDA followed by derivatization with trimethylchlorosilane affords only products arising from addition of the organolithium reagent to the double bond. In contrast, the sterically hindered trans- and cis-1-trimethylsilyl-3,3-dimethyl-1-butenes were metalated by organolithium - TMEDA systems at the silicon-methyl groups and (for the latter) at the α-silylvinyl position.[47]



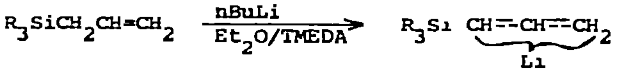
$$Me_3SiCH{=}CH_2 \xrightarrow[2.Me_3SiCl]{1.tBuLi/TMEDA} + Me_3SiCH_2CH_2tBu\ (5\%) + (Me_3Si)_2CHCH_2tBu\ (71\%)$$

$$+ Me_3SiCH_2CH_2\underset{SiMe_3}{CH}CH_2tBu\ (6\%) + Me_3SiCH_2CH_2\underset{SiMe_2CH_2SiMe_3}{CH}CH_2tBu\ (18\%)$$

$$Me_3CCH{=}CHSiMe_3 \xrightarrow[R=tBu,nBu]{RLi/TMEDA} Me_3CCH{=}CHSiMe_2CH_2Li + Me_3CCH{=}CLiSiMe_3$$

(from cis substrate only)

Allylsilanes are metalated by n-butyllithium-TMEDA to form organolithium compounds which preferentially derivatize at the position γ to silicon. The corresponding Grignard reagent undergoes similar reactions, but with a preference, in some cases, for α-derivatization.

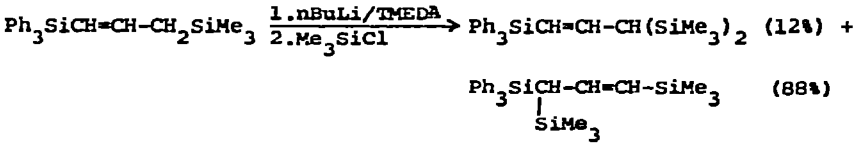


$$R_3SiCH_2CH{=}CH_2 \xrightarrow[Et_2O/TMEDA]{nBuLi} R_3Si\ \underbrace{CH{=}CH{=}CH_2}_{Li}$$

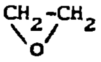
R = Me, Ph

$$Ph_3SiCH{=}CH{-}CH_2Br \xrightarrow{Mg} Ph_3SiCH{=}CH_2{-}CH_2MgBr$$

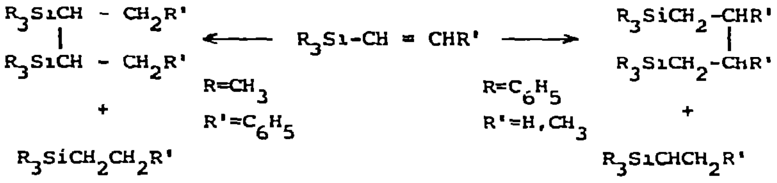
A γ-silyl product was further lithiated and treated with trimethylchlorosilane to yield both α- and γ-silylated compounds.[48]

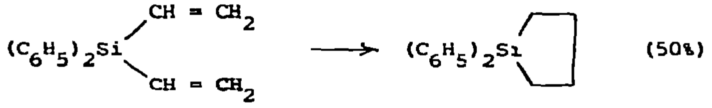


$$Ph_3SiCH{=}CH{-}CH_2SiMe_3 \xrightarrow[2.Me_3SiCl]{1.nBuLi/TMEDA} Ph_3SiCH{=}CH{-}CH(SiMe_3)_2\ (12\%) + Ph_3Si\underset{SiMe_3}{CH}{-}CH{=}CH{-}SiMe_3\ (88\%)$$

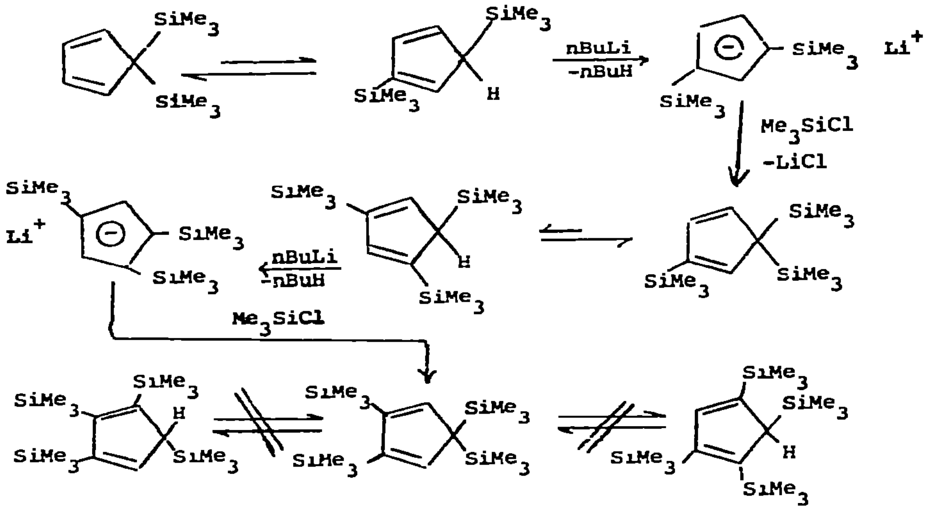
	Organolithium Reagent			Grignard Reagent		
Derivatizing Agents	Yield (%)	Derivatization α (%)	Derivatization γ (%)	Yield (%)	Derivatization α (%)	Derivatization γ (%)
H_3O^+	>80	30-40	60-70	80	>95	
CO_2	60	20	80	60	85	
$Ph_2C{=}O$	90		>95	65		>60
	70	40	60	70	90	10
CH_3I	80		100	no reaction		
Me_3SiCl	70		100	50		>95

Vinylsilanes were effectively coupled with Li/THF in the presence of t-butyl alcohol to give products expected from intermediate radical anions.[49]

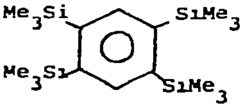




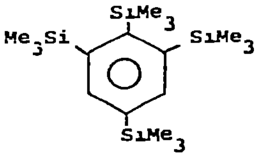
Tris- and tetrakis(trimethylsilyl)cyclopentadienes have been prepared. The tetrakis compound does not undergo isomerization by silyl group migration.[50]



Photolysis of 1,2,4,5-tetrakis(trimethylsilyl)benzene yields a number of rearranged products which include either 6a or 6b, but not 7.



1



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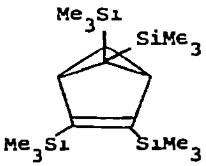

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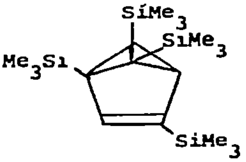

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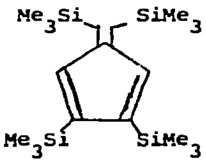

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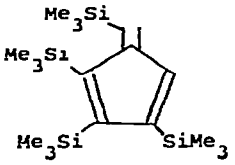
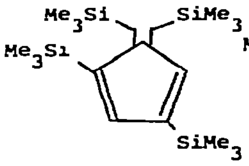
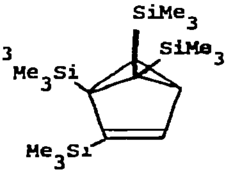


6a



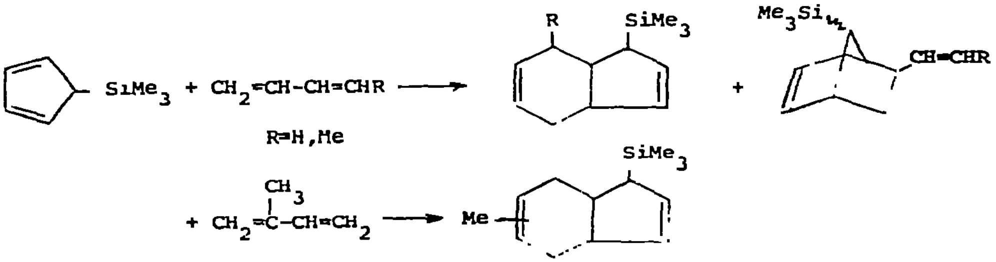
6b



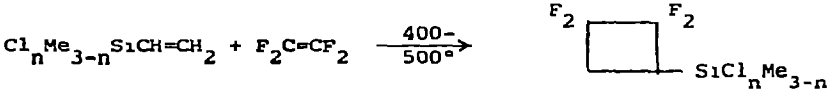
7

Heating 1 at 90° readily converts it into 2, while 3 can be photolyzed to produce 1, 2, 4, and 5.[51]

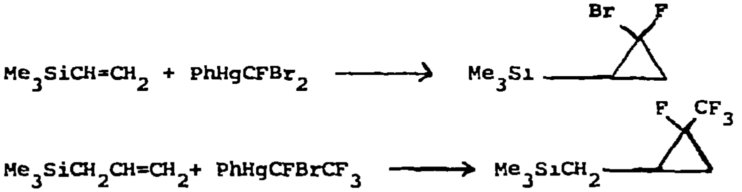
The following cycloaddition chemistry of trimethylsilylcyclopentadiene has been reported.[52]



Vinylsilanes and tetrafluoroethylene afford tetrafluorocyclobutylsilane; yields are best with trimethylvinylsilane.[53]



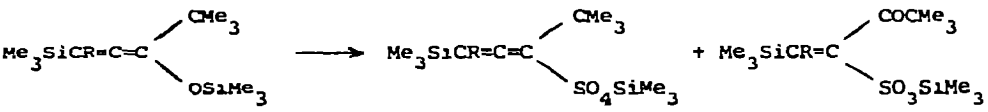
The reaction of organomercurial carbene precursors with unsaturated silanes gave substituted cyclopropanes[32,33].



Treatment of acetylenes and allenic silanes with $ClSO_2(OSiMe_3)$ or SO_3-dioxane yielded products of SO_3 insertion into Si-C≡ and Si-O bonds.[54]

$$RCH_2C{\equiv}CSiMe_3 \xrightarrow{SO_3} RCH_2C{\equiv}CSO_3SiMe_3 \quad (R = H, Ph, Me_3C, Me_3Si) \quad +$$

$$Me_3SiOSO_2CH_2C{\equiv}CSiMe_3 \quad (R = Me_3SiO)$$



$$Me_3SiCR{=}C{=}C{<}^{CMe_3}_{OSiMe_3} \longrightarrow Me_3SiCR{=}C{=}C{<}^{CMe_3}_{SO_4SiMe_3} + Me_3SiCR{=}C{<}^{COCMe_3}_{SO_3SiMe_3}$$

(R = Me_3Si,nBu)

Silyl ketenes have been prepared under both thermolytic and basic conditions in 30-80% yields.[55]

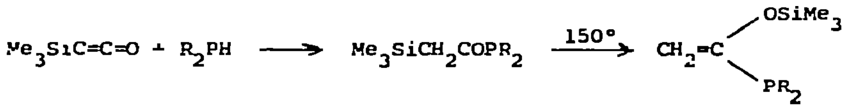
$$R_3SiCH_2CO_2H \xrightarrow{CH_2=C=O} R_3SiCH_2CO_2\overset{O}{\overset{\|}{C}}Me \xrightarrow[\Delta]{} R_3SiC{=}C{=}O$$

(R=Me,Et,)

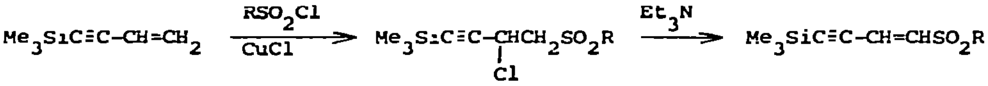
$$R_3SiCH_2COCl \xrightarrow[\Delta]{R'_3N} R_3SiC{=}C{=}O$$

(R=Et,Ph)

Trimethylsilylketenes undergo reaction with phosphines to give adducts which rearrange upon heating[56]

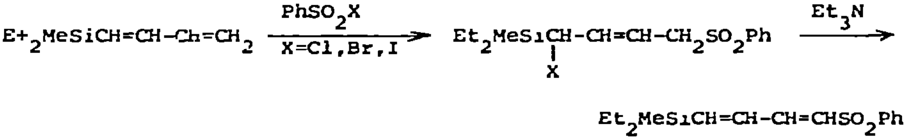


Arene- and alkyl- sulfonyl chlorides reacted with 3-buten-1-ynyltrimethylsilane in the presence of cuprous chloride to give products of 1,2- addition across the double bond. These were easily dehydrohalogenated by triethylamine.[57] Benzenesulfonyl halides add in a 1,4 fashion



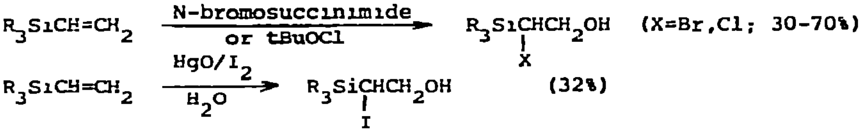
$$Me_3SiC{\equiv}C{-}CH{=}CH_2 \xrightarrow[CuCl]{RSO_2Cl} Me_3SiC{\equiv}C{-}\underset{\displaystyle Cl}{CH}CH_2SO_2R \xrightarrow{Et_3N} Me_3SiC{\equiv}C{-}CH{=}CHSO_2R$$

to 1,3-butadienyldiethylmethylsilane; these products are also dehydrohalogenated by triethylamine.[58]



$$E{+}_2MeSiCH{=}CH{-}Ch{=}CH_2 \xrightarrow[X=Cl,Br,I]{PhSO_2X} Et_2MeSi\underset{\displaystyle X}{CH}{-}CH{=}CH{-}CH_2SO_2Ph \xrightarrow{Et_3N} Et_2MeSiCH{=}CH{-}CH{=}CHSO_2Ph$$

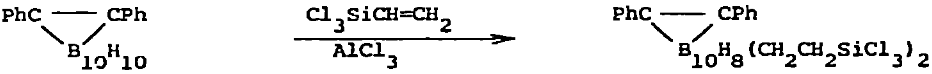
Halohydrins may be prepared in good to moderate yields from the reaction of trialkylvinylsilanes with N- or O-halo compounds in an acidic aqueous medium.[59]



$$R_3SiCH{=}CH_2 \xrightarrow[\text{or tBuOCl}]{\text{N-bromosuccinimide}} R_3Si\underset{\displaystyle X}{CH}CH_2OH \quad (X=Br,Cl;\ 30\text{-}70\%)$$

$$R_3SiCH{=}CH_2 \xrightarrow[H_2O]{HgO/I_2} R_3Si\underset{\displaystyle I}{CH}CH_2OH \quad (32\%)$$

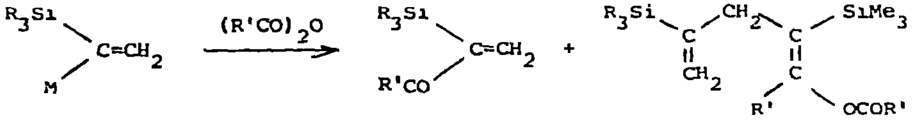
The reaction of trichlorovinylsilane, $AlCl_3$ and o-, m- or p-carborane leads to the corresponding mono- or bis-B-(β-trichlorosilylethyl) carboranes. 1,2-Diphenyl-o-carborane underwent a similar reaction. All products could be trimethylated at silicon with methylmagnesium iodide.[60]



Triethylsilylacrylic acids may be prepared by oxidation of the corresponding aldehydes without Si-C bond cleavage.[61]

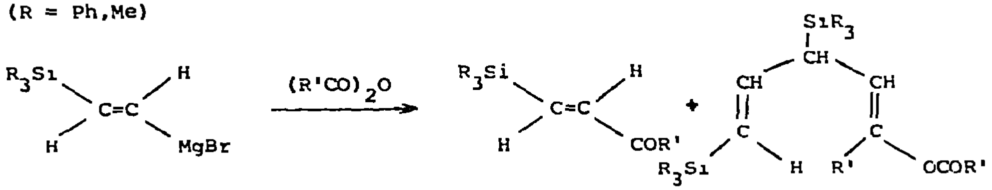
$$Et_3SiCH{=}CHCHO \xrightarrow[H_2SO_4]{CrO_3} Et_3SiCH{=}CHCO_2H \quad (70\%)$$

A series of α-lithio and α- and β-bromomagnesium vinylsilanes was treated at low temperatures with acetic and benzoic anhydrides in order to prepare silyl α,β-unsaturated ketones. Best results were obtained with acetic anhydride, but higher condensation products were always present and led to reduced yields.[62]



(M = Li,MgBr)

(R = Ph,Me)



Homologation of α-silyl-α,β-unsaturated esters has been observed to occur in a stereospecific fashion upon reaction with diazomethane.[63]

$$\underset{(\underline{cis}\text{ or }\underline{trans})}{Me_3SiCH{=}CHCO_2Me} \xrightarrow{CH_2N_2} \underset{(\underline{cis}\text{ or }\underline{trans})}{Me_3SiCH_2CH{=}CHCO_2Me} \qquad (70\text{-}80\%)$$

Based upon product mixtures obtained by hydrolysis and trimethylchlorosilane treatment of reaction mixtures, the reaction of trans-2-bromovinyltrimethylsilane with lithium appears to produce the following compounds in the ratios shown.[64]

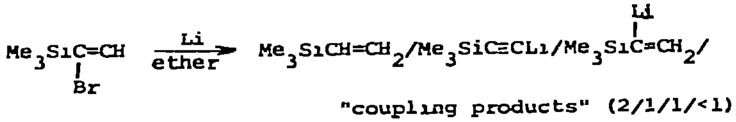
$$Me_3SiCH{=}CHBr \xrightarrow[ether]{Li} Me_3SiCH{=}CH_2/Me_3SiC{\equiv}CLi/Me_3SiCH{=}CHLi/$$

$$\text{"coupling products"} \quad (2/1/3/3)$$

The yield of utilizable 2-lithiovinyltrimethylsilane is thus low, although *in situ* reaction of trans-2-bromovinyltrimethylsilane, trimethylchlorosilane and lithium affords trans-bis(trimethylsilyl)ethylene in 82% yield. Longer contact times lead to reductive silylation of this product.

$$\mathrm{Me_3SiCH{=}CHBr \xrightarrow[Li]{Me_3SiCl} Me_3SiCH{=}CHSiMe_3 \xrightarrow[Li]{Me_3SiCl} (Me_3Si)_2CHCH_2SiMe_2CH_2SiMe_3}$$

The reaction of (1-bromovinyl)trimethylsilane with lithium gave similar results.



$$\mathrm{Me_3Si\underset{\underset{Br}{|}}{C}{=}CH \xrightarrow[ether]{Li} Me_3SiCH{=}CH_2/Me_3SiC{\equiv}CLi/Me_3Si\overset{\overset{Li}{|}}{C}{=}CH_2/}$$

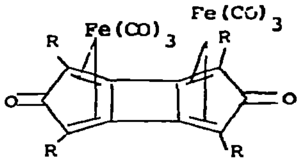
"coupling products" (2/1/1/<1)

Characterizable complexes are formed between bis-(trimethylsilyl) acetylene and bis-(trimethylsilyl) butadiyne with iron, cobalt and manganese carbonyls.[65]

$$\begin{aligned}
&\mathrm{Me_3SiC{\equiv}CSiMe_3 + Fe_3(CO)_{12} \longrightarrow (Me_3SiC_2SiMe_3)Fe(CO)_4}\\
&\qquad\text{"}\quad\mathrm{+ Co_2(CO)_8 \longrightarrow (Me_3SiC_2SiMe_3)Co_2(CO)_6}\\
&\qquad\text{"}\quad\mathrm{+ CpMn(CO)_3 \longrightarrow (Me_3SiC_2SiMe_3)CpMn(CO)_2}
\end{aligned}$$

(Cp = cyclopentadienyl)

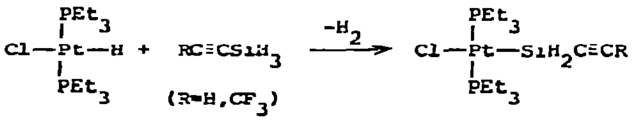
$$\mathrm{Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3 + Fe_3(CO)_{12} \longrightarrow}$$



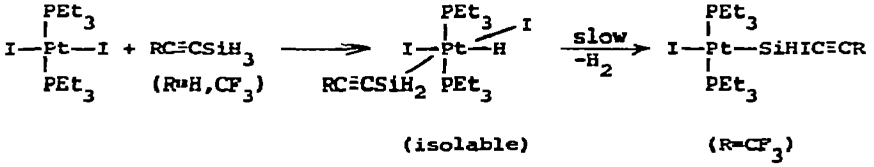
(R=$\mathrm{Me_3Si}$)

$$\begin{aligned}
&\text{"}\quad\mathrm{+ Co_2(CO)_8 \longrightarrow (Me_3SiC_4SiMe_3)Co_2(CO)_6}\\
&\qquad\qquad\qquad\qquad\quad\mathrm{(Me_3SiC_4SiMe_3)Co_4(CO)_{12}}
\end{aligned}$$

Platinum complexes are formed by the reaction of acetylenic silanes with trans-$\mathrm{HPt(PEt_3)_2Cl}$ and trans-$\mathrm{I_2Pt(PEt_3)_2}$.[66]

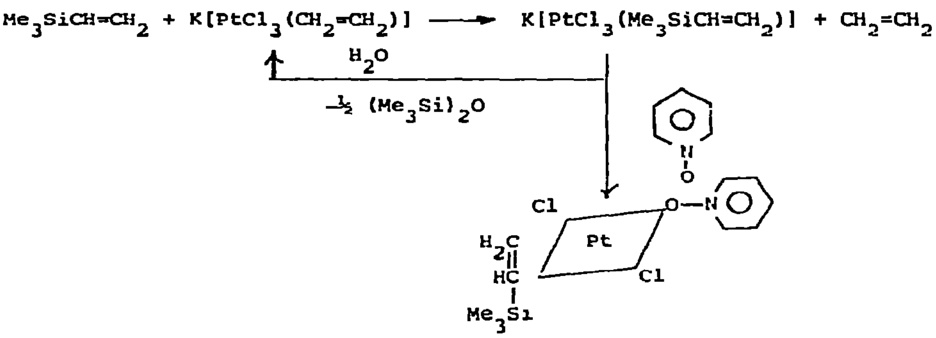


$$\mathrm{Cl{-}\overset{\overset{PEt_3}{|}}{\underset{\underset{PEt_3}{|}}{Pt}}{-}H + \underset{(R=H,CF_3)}{RC{\equiv}CSiH_3} \xrightarrow{-H_2} Cl{-}\overset{\overset{PEt_3}{|}}{\underset{\underset{PEt_3}{|}}{Pt}}{-}SiH_2C{\equiv}CR}$$

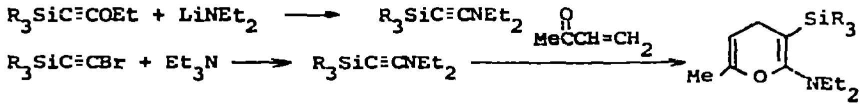


$$\mathrm{I{-}\overset{\overset{PEt_3}{|}}{\underset{\underset{PEt_3}{|}}{Pt}}{-}I + \underset{(R=H,CF_3)}{RC{\equiv}CSiH_3} \longrightarrow \underset{\text{(isolable)}}{\underset{RC\equiv CSiH_2\ \ PEt_3}{I{-}\overset{\overset{PEt_3\ \ I}{|}}{Pt}{-}H}} \xrightarrow[-H_2]{slow} \underset{(R=CF_3)}{I{-}\overset{\overset{PEt_3}{|}}{\underset{\underset{PEt_3}{|}}{Pt}}{-}SiHIC{\equiv}CR}}$$

Potassium trichloro(trimethylvinylsilane)platinate(II) was prepared by a metathesis reaction in acetone. The complex underwent cleavage with water and replacement of chloride with pyridine N-oxide.[67]



The following reactions of β-functional acetylenic silanes have been reported.[68]

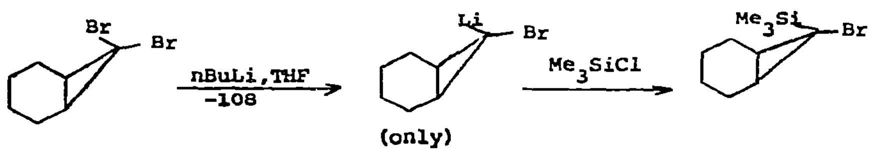


(R = Me,Et)

Chlorine added to a number of aromatic silanes to form hexachloro-derivatives which could be dehydrochlorinated thermally. For example, phenyltrichlorosilane gave trichloro(trichlorophenyl)silane.[69]

$$C_6H_5SiCl_3 \xrightarrow[h\nu]{3Cl_2} C_6H_5Cl_6SiCl_3 \xrightarrow{550^\circ} C_6H_2Cl_3SiCl_3$$

Organohalolithium compounds have been employed to prepare α-haloalkylsilanes.



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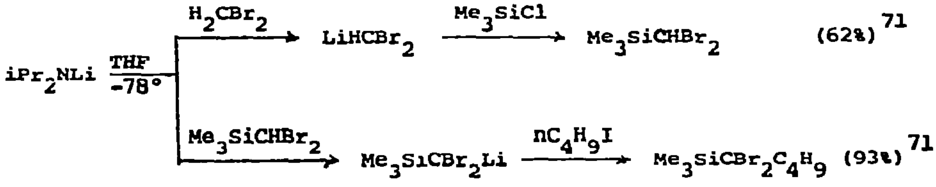
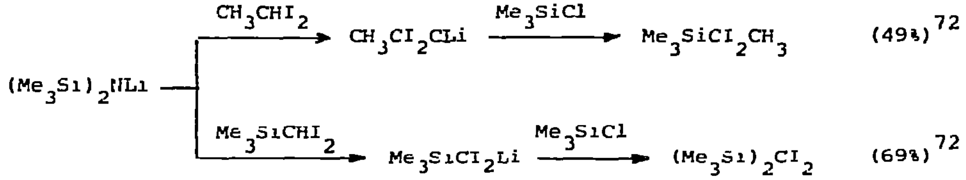
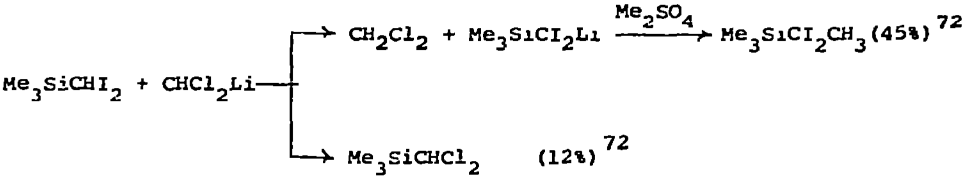




$(Me_3Si)_2NLi \xrightarrow{CH_3CHI_2} CH_3CI_2CLi \xrightarrow{Me_3SiCl} Me_3SiCI_2CH_3$ (49%)[72]

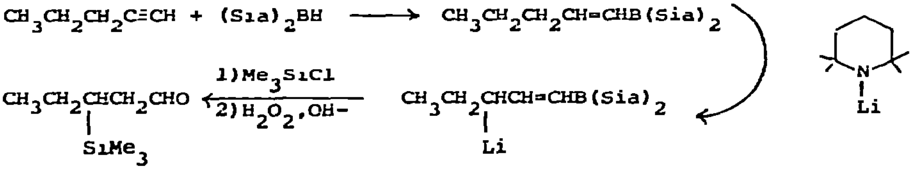
$(Me_3Si)_2NLi \xrightarrow{Me_3SiCHI_2} Me_3SiCI_2Li \xrightarrow{Me_3SiCl} (Me_3Si)_2CI_2$ (69%)[72]



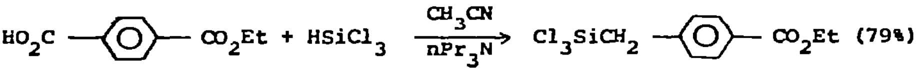
$Me_3SiCHI_2 + CHCl_2Li \rightarrow CH_2Cl_2 + Me_3SiCI_2Li \xrightarrow{Me_2SO_4} Me_3SiCI_2CH_3$ (45%)[72]

$Me_3SiCHI_2 + CHCl_2Li \rightarrow Me_3SiCHCl_2$ (12%)[72]

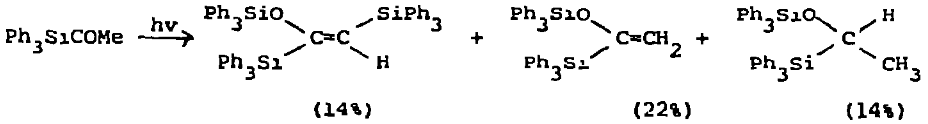
The monohydroboration of acetylenes with disiamylborane $[HB(Sia)_2]$ gives vinylboranes which may be metalated at the allylic position. Subsequent reaction of the organolithium reagent thus formed with trimethylchlorosilane followed by oxidation affords 3-trimethylsilyl-substituted aldehydes. In addition to the example shown below, the following acetylenes gave similar products in the yields shown: 1-hexyne (66%), 1-octyne (75%) and 3-hexyne (90%).[73]

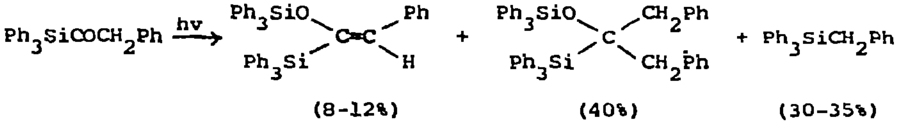


Ester-containing organotrichlorosilanes can be obtained by the following procedure.[74] Base treatment cleaves the Si-C bond.

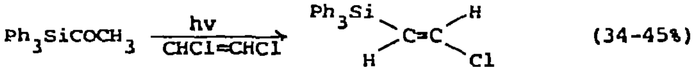


Several acylsilanes have been photolyzed in cyclohexane solvent.[75] Products arise whose appearance may be rationalized by silyl radical formation, followed by subsequent attack of these species on original substrate or some of the products subsequently formed. Triphenylsilylbenzyl ketone is thought to give rise to triphenylbenzylsilane by an intramolecular process.



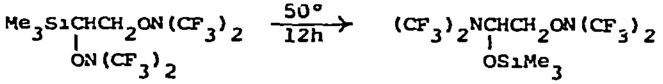


When the photolysis of acetyltriphenylsilane was carried out in di- or trichloroethylene, products of reaction with the solvent were isolated.

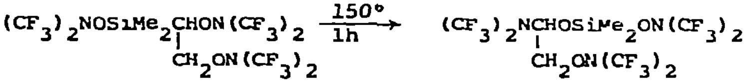


$\mathrm{Ph_3SiCOCH_3} \xrightarrow[\mathrm{CHCl=CCl_2}]{hv} \mathrm{Ph_3SiCH{=}CCl_2}$ (28%)

A rearrangement of the type Si-C-O-N ⟶ N-C-O-Si has been reported in which migration of silicon to oxygen is accompanied by migration of nitrogen to carbon.



$\mathrm{Me_3Si\underset{ON(CF_3)_2}{\underset{|}{C}}HCH_2ON(CF_3)_2} \xrightarrow[12h]{50°} \mathrm{(CF_3)_2N\underset{OSiMe_3}{\underset{|}{C}}HCH_2ON(CF_3)_2}$ (100%)



$\mathrm{(CF_3)_2NOSiMe_2\underset{CH_2ON(CF_3)_2}{\underset{|}{C}}HON(CF_3)_2} \xrightarrow[1h]{150°} \mathrm{(CF_3)_2N\underset{CH_2ON(CF_3)_2}{\underset{|}{C}}HOSiMe_2ON(CF_3)_2}$ (100%)

$\mathrm{Me_3SiCH_2ON(CF_3)_2} \xrightarrow{150°}$ No Rearrangement

$\mathrm{Cl_3SiCMe_2ON(CF_3)_2} \xrightarrow[2h]{100°} \mathrm{(CF_3)_2NCMe_2OSiCl_3}$ (98%)

In compounds of the last type, the ease of rearrangement was found to be $\mathrm{Cl_3SiCRR'ON(CF_3)_2} > \mathrm{Cl_3SiCHRON(CF_3)_2} > \mathrm{Cl_3SiCH_2ON(CF_3)_2}$.[76]

The carbinols $\mathrm{R_{3-n}CPh_nOH}$ ($\mathrm{R = p\text{-}Me_3SiC_6H_4}$; n=1,2) have been prepared by way of $\mathrm{p\text{-}Me_3SiC_6H_4MgBr}$ and the appropriate ketone or ester.[77]

Bischloroformates may be synthesized from certain organosilicon diols.[78]

$$O(SiMe_2ROH)_2 \xrightarrow[THF]{COCl_2} O(SiMe_2ROCOCl)_2$$

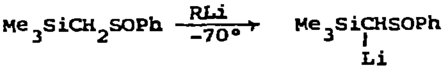
$$R = CH_2, (CH_2)_3, CH_2OCH_2CH_2$$

Silicon-carbon bond cleavage has been observed during treatment of trialkylsilylalkyl sulfides and tetraethylsilane with 30% H_2O_2 in acetic acid.[79]

$$\underset{}{EtSCH_2SiEt_3} \xrightarrow[HOAc]{H_2O_2} \underset{(56\%)}{EtSO_2CH_2SiEt_3} + \underset{(10\%)}{(EtSi)_2O} + "C_3H_6O_3Si"$$

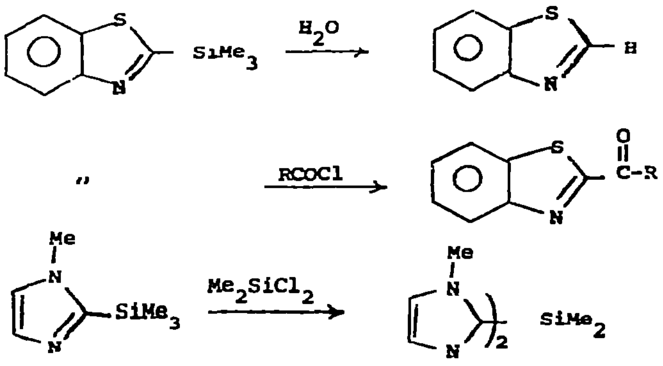
$$Et_4Si \xrightarrow[HOAc]{H_2O_2} \underset{(14\%)}{(Et_3Si)_2O} + "C_3H_6O_3Si"$$

1-Trimethylsilyl-1-(phenylsulfinyl)methyllithium can be generated in high yield from the n- or t-butyllithium metalation of phenyl trimethylsilylmethyl sulfoxide. The reagent reacts normally with carbonyl containing compounds, to give, ultimately, olefinic products by way of β-elimination.[80]



$$Me_3SiCH_2SOPh \xrightarrow[-70°]{RLi} Me_3Si\underset{\displaystyle Li}{\underset{|}{C}}HSOPh$$

A variety of 2-benzothiazolylsilanes[81] and 2-imidazoylsilanes,[82] have been found to be very susceptible to transsilylation and Si-C bond cleavage in the presence of weak electrophiles.



The stability of some β-aminoethylsilanes to a variety of reaction conditions was examined.[83]

$$Me_3SiCH_2CH_2NR_2 \xrightarrow{300°} \text{No Reaction}$$

$$Me_3SiCH_2CH_2NHR \xrightarrow[10h]{300°} Me_3SiNHR + CH_2{=}CH_2\ .$$

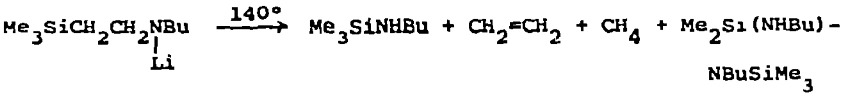
$$(30\%)$$

$$Me_3SiCH_2CH_2\overset{+}{N}Et_2Me\ \ I^- \xrightarrow{250°} Me_3SiI + CH_2{=}CH_2 + Et_2NMe$$

$$Me_3SiCH_2CH_2\overset{+}{N}Et_2Me\ OH^- \xrightarrow[reflux]{H_2O} (Me_3Si)_2O + CH_2{=}CH_2 + Et_2NMe$$

$$Me_3SiCH_2CH_2\overset{+}{N}Et_2Me\ \ I^- \xrightarrow{nBuLi} Me_3SiBu + Et_2NMe + CH_2{=}CH_2$$

$$Me_3SiCH_2CH_2NR_2 \xrightarrow[140°]{nBuLi} \text{No Reaction}$$



$$Me_3SiCH_2CH_2\underset{\displaystyle Li}{\underset{|}{N}}Bu \xrightarrow{140°} Me_3SiNHBu + CH_2{=}CH_2 + CH_4 + Me_2Si(NHBu)\text{-}NBuSiMe_3$$

A variety of silicon-containing tertiary amines have been prepared utilizing tris(chloromethyl)amine.[84] The compound with X=O, R=Ph, R'=Me polymerizes at 25° with loss of $MePh_2SiOH$ to give a C,H,N-containing polymer.

$$N(CH_2Cl)_3 + 3R_2R'Si\text{-}X\text{-}Na \xrightarrow{-3NaCl} N(CH_2\text{-}X\text{-}SiR_2R')_3$$

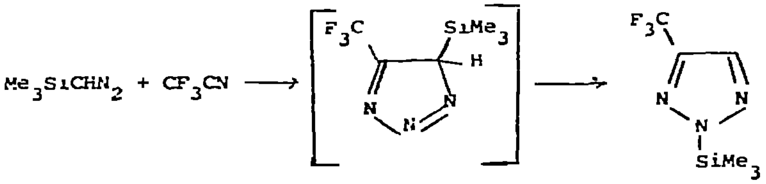
X	R	R'
O	Me	Me
O	Ph	Me
S	Ph	Ph
CH_2O	Me	Me
CH_2	Me	Me (*via* Me_3SiCH_2Li)

Reaction of tris(chloromethyl)amine with silyllithium reagents led to tris(silylmethyl)amines which could be isolated (except for the dimethylphenylsilyl compound), but which were thermally labile towards polymerization at 40°.

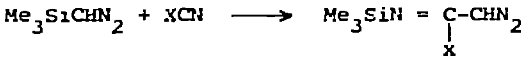
$$N(CH_2Cl)_3 + 3R_2R'SiLi \xrightarrow{-3LiCl} N(CH_2SiR_2R')_3$$

R	R
Ph	Ph
Ph	Me
Me	Ph

The reaction of trimethylsilyldiazomethane with trifluoroacetonitrile gives triazoles *via* preferential (over H) trimethylsilyl group migration in the original adduct.



Reaction of the diazo compound with cyanogen chloride or bromide affords open-chain 1:1 adducts.[85]



$$Me_3SiCHN_2 + XCN \longrightarrow Me_3SiN=C(X)-CHN_2$$

Silyl-containing ylids are found to form salts with certain transition metal complexes[86]

$$Me_3P{=}CRR' + HM(CO)_3C_5H_5 \longrightarrow [Me_3PCH_2RR']^+ \; [M(CO)_3 \; C_5H_5]^-$$

(R = $SiMe_3$, R' = H or $SiMe_3$; M = Mo,W)

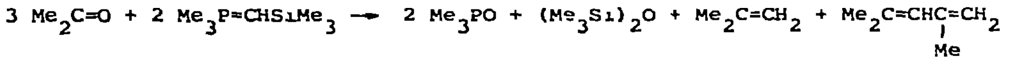
These salts can be deprotonated with $Me_3P{=}CH_2$ or nBuLi. Anions of these salts react with chlorosilanes to give compounds containing silyl-metal bonds.

$$Na^+[Cr(CO)_3C_5H_5]^- + Me_3SiBr \longrightarrow Me_3SiCr(CO)_3C_5H_5$$

The reaction of silylated ylids with ketones is known to give complicated sets of products, but the course of this reaction is explainable in a straightforward manner if the ylid and carbonyl compound are taken in a 2:3 molar ratio.[87]

$$3\ Ph_2C{=}O + 2\ Ph_3P{=}CHSiMe_3 \longrightarrow 2\ Ph_3PO + (Me_3Si)_2O + Ph_2C{=}CH_2 + Ph_2C{=}C{=}CPh_2$$

$$3\ Ph_2C{=}O + 2\ Me_3P{=}CHSiMe_3 \longrightarrow Me_3PO + (Me_3Si)_2O + 2\ Ph_2C{=}CH_2 + Me_2P(O)CH{=}CPh_2$$



$$3\ Me_2C{=}O + 2\ Me_3P{=}CHSiMe_3 \longrightarrow 2\ Me_3PO + (Me_3Si)_2O + Me_2C{=}CH_2 + Me_2C{=}CH\underset{Me}{C}{=}CH_2$$

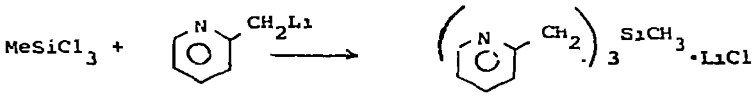
Silylated ylids have been used as starting materials for the synthesis of the novel tetraorganofluorophosphoranes.[88]

$R_3P{=}CHSiMe_3 + 2HF \longrightarrow R_3(CH_3)PF + Me_3SiF$ (R = Me,Ph)

The analogous tetraorgano(trimethylsilyloxy)phosphorane can be prepared, but decomposes above 0°.[89]

$Me_3P{=}CH_2 + Me_3SiOH \longrightarrow Me_4POSiMe_3 \longrightarrow (Me_3Si)_2O + Me_3P{=}CH_2 + Me_3P{=}O + CH_4$

The synthesis of tris-(2-picolyl)-methylsilane (TPMS) and preliminary results concerning its use as a chelating agent for transition metals has appeared.[90]

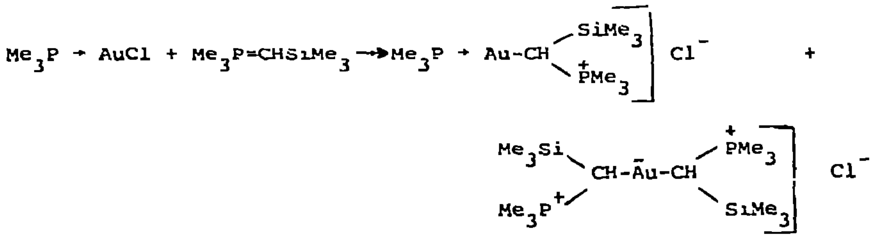


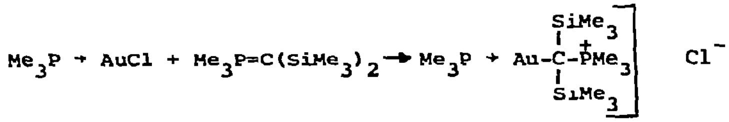
$TPMS{\cdot}LiCl + AgClO_4 \xrightarrow{EtOH} TPMS{\cdot}LiClO_4 + AgCl$

$TPMS{\cdot}LiClO_4 + M(ClO_4)_2 \longrightarrow TPMS{\cdot}M(ClO_4)_2 + LiClO_4$

(M=Ni,Cu,CO)

Silyl ylids have been found useful in stabilizing gold(I) compounds by establishing a neighboring onium center.[91]





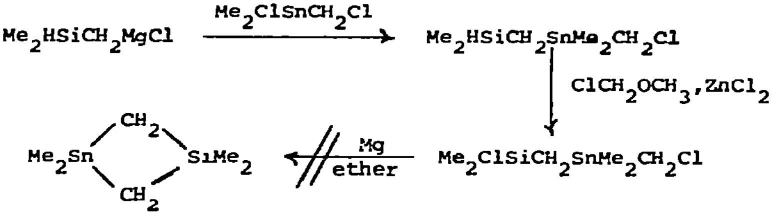
Treating 1-phenyl-10-lithio-1,10-dicarba-closo-decaborane(10) with trimethylchlorosilane gave the corresponding 1-phenyl-10-trimethylsilyl-1,10-dicarba-closo-decaborane(10).[92]

Some silylmethylgermanium compounds have been prepared by direct synthesis.[93]

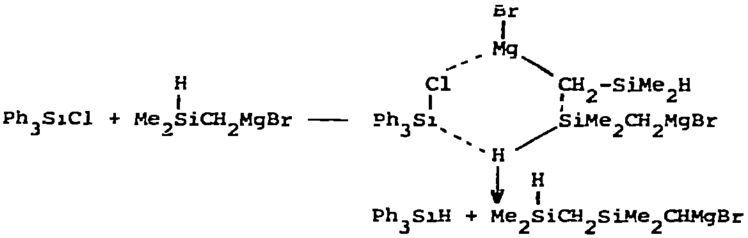
$$XMe_2SiCH_2Cl \xrightarrow{Ge/Cu} \underset{(5-8\%)}{XMe_2SiCH_2GeCl_3} + \underset{(26-47\%)}{[XMe_2SiCH_2]_2GeCl_2}$$

X = F, OCH_3, $OSiMe_3$

Hydrosilylmethyl Grignard reagents were used to synthesize the silylmethyltin compound shown. This did not give the expected cyclic product upon attempted ring closure.[94]



A number of (hydrosilyl)alkyl Grignard reagents have been found to reduce chlorosilanes. Two equivalents of Grignard are involved in hydrosilane formation.



The Grignards employed and the yields of triphenylsilane obtained were: Me_2SiHCH_2MgBr (90); $MeSiH_2CH_2MgBr$ (75); $PhMeSiHCH_2MgBr$ (80); Ph_2SiHCH_2MgBr (95); $Ph_2SiH(CH_2)_2MgBr$ (50); $Me_2SiH(CH_2)_3MgCl$ (80); Me_2-$SiHCH_2SiMe_2CH_2MgI$ (45); Me_2SiHCH_2MgBr (with $Ph_2MeSiCl$ gave 49% Ph_2MeSiH and 44% $Ph_2MeSiCH_2SiMe_2$; with Me_3SiCl gave 39% $Me_3SiCH_2SiMe_2H$ and 34% $Me_2SiHCH_2SiMe_2CH_2D$ after D_2O treatment).[95]

The behavior of $(Me_3Si)_3CH$ and $(Me_3Si)_4C$ toward some metalating reagents has been examined. No metalation of $(Me_3Si)_3CH$ was observed with nBuLi in ether, tetrahydrofuran (THF), or pentane-TMEDA or with tBuLi in pentane or pentane-THF. Metalation did occur with methyllithium in ether-THF to give $(Me_3Si)_3CLi$ and with tBuLi in pentane-TMEDA to give $(Me_3Si)_2CHSiMe_2CH_2Li$ only. The tBuLi-TMEDA system (but not CH_3Li) also metalated $(Me_3Si)_4C$ to give $(Me_3Si)_3CSiMe_2CH_2Li$.[96]

The use of trimethylsilylmethyl groups for the stabilization of metals in low coordination states continues to be an active area. A dialkyltin(II) compound has been prepared by the use of the bis(trimethylsilyl)methyl ligand.

$$(Me_3Si)_2CHLi + SnCl_2 \longrightarrow [(Me_3Si)_2CH]_2Sn \qquad (54\%)$$

This compound forms stannylene complexes with $Cr(CO)_5$ and $MO(CO)_5$, as well as a 1:1 adduct with α-picoline. A 3% yield of $[(Me_3Si)_2CH]_2Pb$ was also reported.[97]

In contrast to other bis(trialkylstannyl)mercury compounds, bis[tris(trimethylsilylmethyl)stannyl] mercury is stable, and undergoes expected transmetalation and exchange reactions.[98]

$$RMgCl \xrightarrow{SnCl_4} R_4Sn \xrightarrow{SnCl_4} R_3SnCl \xrightarrow{LiAlH_4} R_3SnH \xrightarrow{Et_2Hg} (R_3Sn)_2Hg$$

$(R = Me_3SiCH_2)$

$$(R_3Sn)_2Hg \xrightarrow{2\ Li} Hg + 2\ R_3SnLi$$

$$(R_3Sn)_2Hg + HgX_2 \longrightarrow 2\ Hg + 2\ R_3SnX$$

$[X{=}Cl,\ CH_2CO_2Me,\ C{\equiv}CPh,\ Co(CO)_4]$

$$(R_3Sn)_2Hg + Hg[C(CF_3)_3]_2 \longrightarrow 2\ Hg + 2\ R_3SnF + 2(CF_3)_2C{=}CF_2$$

The hydride R_3SnH also was employed to prepare a dialkyl cadmium compound.

$$2\ R_3SnH + Et_2Cd \longrightarrow CH_3CH_3 + (R_3Sn)_2Cd$$

A stable copper(I) alkyl has been prepared from Me_3SiCH_2Li and CuI. The reaction of this Me_3SiCH_2Cu with Me_3SiCl, $CH_2{=}CHCH_2Br$, PhI and $PhCH_2Br$ gave the expected alkylation products. With a 2:1 ratio of Me_3SiCH_2Li to CuI, a stable solution of $(Me_3SiCH_2)_2CuLi$ was obtainable in ether.[99]

The trimethylsilylmethyl Grignard reagent was used to prepare $(Me_3SiCH_2)_3Al{\cdot}OEt_2$ and $(Me_3SiCH_2)_2Zn$.[100] The latter formed isolable complexes with 2,2'-bipyridine, 1,10-phenanthroline, tetramethylethylenediamine, quinoline and pyridine. The first two of these were stable in air for several days. In contrast to the reaction of Me_3SiCH_2M (M=Li or MgX) with $NbCl_5$ and $TaCl_5$, which affords complexes such as $(Me_3SiCH_2)_2Nb-(\mu-SiMe_3)_2Nb(CH_2SiMe_3)_2$, the interaction of $(Me_3SiCH_2)_2Zn$ and $TaCl_5$ gives a mixture of $(Me_3SiCH_2)_2TaCl_3$ and $(Me_3SiCH_2)_3TaCl_2$. Niobium pentachloride affords mainly $(Me_3SiCH_2)_3NbCl_2$.

Tris[tris(trimethylsilylmethyl)stannyl]thallium has been prepared from triethylthallium and three equivalents of $(Me_3SiCH_2)_3SnH$. This compound underwent the following reactions in high yields.[101]

$$[(Me_3SiCH_2)_3Sn]_3Tl \xrightarrow{Hg} [(Me_3SiCH_2)_3Sn]_2Hg + Tl$$

$$'' \xrightarrow{BrCH_2CH_2Br} (Me_3SiCH_2)_3SnBr + CH_2{=}CH_2 + TlBr$$

$$'' \xrightarrow{Bz_2O_2} (Me_3SiCH_2)_2SnOBz + ThOBz$$

Stable alkyls of titanium(IV), zirconium(IV) and hafnium(IV) have been prepared which contain trimethylsilylmethyl- and trimethylgermylmethyl stabilizing groups.[102] Detailed preparative procedures, stabilities, and thermal and chemical reactivities are given for these compounds. π-Cyclopentadienyl (Cp) species were best prepared from Cp_2MCl_2 and $Me_3M'CH_2Li$ in ether, while the neutral tetrachlorides were starting materials for obtaining $(Me_3M'CH_2)_4M$ products. The thermal stabilities of the cyclopentadienyl complexes lie in the order Hf∼Zr>Ti, the stabilities of these species being greater than the methyl and ethyl analogues.

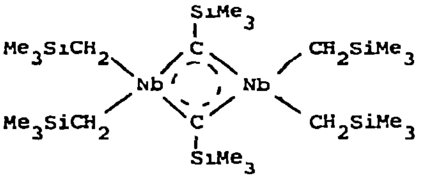
The compound $(Me_3SiCH_2)_4Zr$ exhibits a thermal stability which is close to, but somewhat less than, $(Me_3CCH_2)_4Zn$.

Compound	Starting reagent	Yield (%)
$Cp_2Ti(CH_2SiMe_3)_2$	Me_3SiCH_2Li	60
$Cp_2Ti(CH_2GeMe_3)_2$	Me_3GeCH_2Li	70
$Cp_2Zr(CH_2SiMe_3)_2$	Me_3SiCH_2Li	70
	Me_3SiCH_2MgCl	5
$Cp_2Zr(Cl)CH_2SiMe_3$	Me_3SiCH_2MgCl	38

Compound	Starting reagent	Yield (%)
$Cp_2Hf(CH_2SiMe_3)_2$	Me_3SiCH_2Li	50
$(Me_3SiCH_2)_4Ti$	Me_3SiCH_2MgCl	65
	$(Me_3SiCH_2)_2Mg$	73
	Me_3SiCH_2Li	69
$(Me_3SiCH_2)_4Zr$	Me_3SiCH_2MgCl	63
	$(Me_3SiCH_2)_2Mg$	60
	Me_3SiCH_2Li	89
$(Me_3SiCH_2)_4Hf$	Me_3SiCH_2Li	96
$(PhMe_2SiCH_2)_4Ti$	$(PhMe_2SiCH_2)_2Mg$	50-75
$(PhMe_2SiCH_2)_4Zr$	$PhMe_2SiCH_2MgCl$	66
$(Ph_2MeSiCH_2)_4Ti$	$(Ph_2MeSiCH_2)_4Mg$	60
$(PhCH_2Me_2SiCH_2)_4Ti$	$(PhCH_2Me_2SiCH_2)_2Mg$	66

In a related investigation, the preparation of the neopentyls $(Me_3CCH_2)_4M$, M = Ti, Zn or Hf is reported, and thermal stability comparisons made with the corresponding $(Me_3SiCH_2)_4M$ compounds.[103] Stability increases in the order M = Ti<Zn<Hf and for R M: $R = Me << Me_3CCH_2 \simeq Me_3SiCH_2$.

As was previously mentioned, treating niobium or tantalum pentachloride with Me_3SiCH_2MgCl affords the compounds $(\mu\text{-}CSiMe_3)_2M_2(CH_2SiMe_3)_2$, M = Nb, Ta.[104] The niobium complex has the structure



The first well-characterized binary alkyls of lanthanide elements have also been prepared *via* Me_3SiCH_2Li and the anhydrous metal chloride, MCl_3. Thus, $(Me_3SiCH_2)_3Sc\cdot 2$ THF and $(Me_3SiCH_2)_3Y\cdot 2$ THF (along with the neopentyl analogues), and the solvent-free $(\underline{o}\text{-}MeOC_6H_4SiMe_2CH_2)_3Sc$ have been reported.[105]

Carbonyl complexes of iron, cobalt and nickel with tris(trimethylsilylmethyl)phosphine (L) were synthesized and some of their chemistry explored.[106]

$$(Me_3SiCH_2)_3P + Fe_3(CO)_{12} \longrightarrow Fe(CO)_3L_2$$

$$+ Fe_2(CO)_9 \longrightarrow Fe(CO)_4L$$

$$+ Hg[Fe(CO)_3(NO)]_2 \longrightarrow Hg[Fe(CO)_2(NO)L]_2$$

$$+ Ni(CO)_4 \longrightarrow Ni(CO)_3L$$

$$+ Co_2(CO)_8 \longrightarrow [Co(CO)_3L]_2 \xrightarrow{Na(Hg)} NaCo(CO)_3L$$

$$+ Co_2(CO)_8 \longrightarrow [Co(CO)_3L_2][Co(CO)_4]$$

$$\Big\downarrow CCl_4$$

$$ClCCo_3(CO)_9 + CoCl(CO)_2L$$

$$NaCo(CO)_3L + Hg(CN)_2 \longrightarrow Hg[Co(CO)_3L]_2 \xrightarrow{HgCl_2} ClHgCo(CO)_3L$$

$$+ TlNO_3 \longrightarrow Tl[Co(CO)_3L]_3$$

The reaction of trichloromethyl compounds with dicobaltoctacarbonyl yields alkylidenetricobalt nonacarbonyl species. The use of

$$Co_2(CO)_8 + Me_3SiCCl_3 \longrightarrow Me_3SiCCo_3(CO)_9 \quad (41\%)$$

$$+ PhMe_2SiCCl_3 \longrightarrow PhMe_2SiCo_3(CO)_9 \quad (50\%)$$

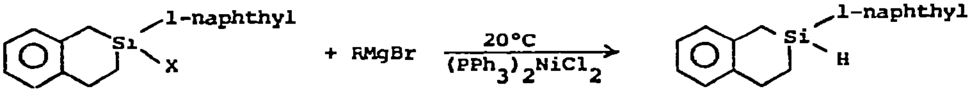
$$+ Me_3SiO_2CCCl_3 \longrightarrow Me_3SiO_2CCCo_3(CO)_9 \quad (38\%)$$

$Me_3SiOCH_2CX_3$ (X = Cl,Br) followed by hydrolysis afforded $HOCH_2CCo_3(CO)_9$ in 4-5% yields.[107]

V. SILAFUNCTIONAL COMPOUNDS

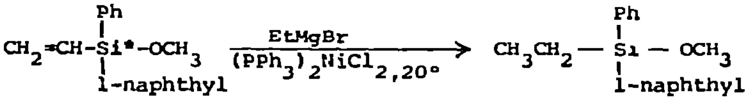
1. Si-H

In the presence of $(PPh_3)_2NiCl_2$ alkoxy-, chloro-, and fluorosilanes are reduced stereospecifically to the corresponding hydride by the action



X = OCH_3, Cl, F, D

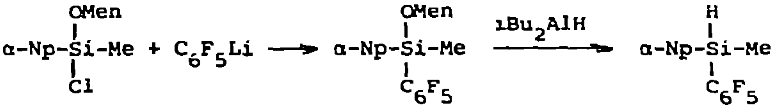
[% retention = 94-100, 0, 90, 100 (100% inversion for Cl)] of Grignard reagents possessing β-hydrogens. Reactivity of the Grignard depends markedly on structure. For example, the use of X = OCH_3, above, plus a Grignard under standardized conditions gave the following yields after 72 h (R, % SiH, % retention given): Et, 90, 100; nPr, 62, 98; iPr, 24, 94; nBu, 85, 99; iBu, 6, 97; tBu, 0, —). .Vinylsilanes are reduced at the olefinic site faster than the Si-OCH_3 bond is attacked.[108]



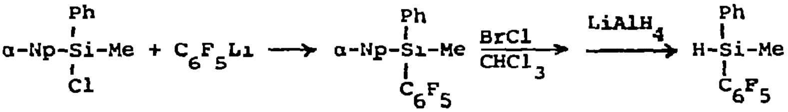
$$CH_2{=}CH\text{-}\overset{Ph}{\underset{\text{1-naphthyl}}{Si^*}}\text{-}OCH_3 \xrightarrow[(PPh_3)_2NiCl_2,20^\circ]{EtMgBr} CH_3CH_2-\overset{Ph}{\underset{\text{1-naphthyl}}{Si}}-OCH_3$$

(optical purity > 95%)

Several perfluorophenyl-containing chiral silanes were synthesized to provide an electronegative group on silicon which would not be susceptable to easy nucleophilic replacement.[109]



$$\alpha\text{-Np-}\overset{OMen}{\underset{Cl}{Si}}\text{-Me} + C_6F_5Li \longrightarrow \alpha\text{-Np-}\overset{OMen}{\underset{C_6F_5}{Si}}\text{-Me} \xrightarrow{iBu_2AlH} \alpha\text{-Np-}\overset{H}{\underset{C_6F_5}{Si}}\text{-Me}$$



$$\alpha\text{-Np-}\overset{Ph}{\underset{Cl}{Si}}\text{-Me} + C_6F_5Li \longrightarrow \alpha\text{-Np-}\overset{Ph}{\underset{C_6F_5}{Si}}\text{-Me} \xrightarrow[CHCl_3]{BrCl} \xrightarrow{LiAlH_4} H\text{-}\overset{Ph}{\underset{C_6F_5}{Si}}\text{-Me}$$

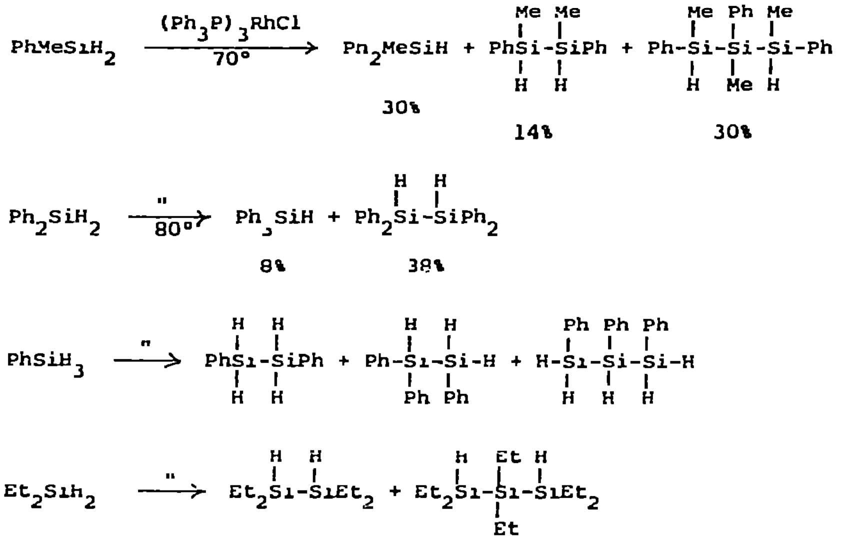
Chiral reducing agents (alkaloid-$LiAlH_4$ or alcohol-$LiAlH_4$ combinations) have been used to reduce a series of silanes [MeSi(OMe)RR'; R = 1-naphthyl, Et, $PhCH_2$, mesityl, iPr, R' = Ph and R = cyclohexyl, R' = Et] to optically active mixtures of enantiomers suitable for further stereochemical studies.[110]

Diethylfluorosilane has been reported to undergo thermal disproportionation in the absence of catalysts. Disproportionation occurs to the

$$2\ HSiEt_2F \xrightarrow{\Delta} H_2SiEt_2 + F_2SiEt_2$$

extent of 49% in 3h at 56° to give (by weight) 51% of unchanged fluorosilane, 10% diethylsilane, 33% difluorodiethylsilane and 5% of an unknown substance. In 15 h at 20°, 63% disproportionation is observed. Thus, hydrosilylation employing, e.g., diethylfluorosilane leads to products of mono- and di- substitution at silicon.[111]

Heating phenylmethylsilane with $(Ph_3P)_3RhCl$ led not only to disproportionation products, but also to higher condensation products possibly arising through a silylene-type intermediate.[112]



$$PhMeSiH_2 \xrightarrow[70°]{(Ph_3P)_3RhCl} Ph_2MeSiH + Ph\overset{Me}{\underset{H}{Si}}-\overset{Me}{\underset{H}{Si}}Ph + Ph-\overset{Me}{\underset{H}{Si}}-\overset{Ph}{\underset{Me}{Si}}-\overset{Me}{\underset{H}{Si}}-Ph$$

30% 14% 30%

$$Ph_2SiH_2 \xrightarrow[80°]{''} Ph_3SiH + Ph_2\overset{H}{Si}-\overset{H}{Si}Ph_2$$

8% 38%

$$PhSiH_3 \xrightarrow{''} Ph\overset{H}{\underset{H}{Si}}-\overset{H}{\underset{H}{Si}}Ph + Ph-\overset{H}{\underset{Ph}{Si}}-\overset{H}{\underset{Ph}{Si}}-H + H-\overset{Ph}{\underset{H}{Si}}-\overset{Ph}{\underset{H}{Si}}-\overset{Ph}{\underset{H}{Si}}-H$$

$$Et_2SiH_2 \xrightarrow{''} Et_2\overset{H}{Si}-\overset{H}{Si}Et_2 + Et_2\overset{H}{Si}-\overset{Et}{\underset{Et}{Si}}-\overset{H}{Si}Et_2$$

$$Ph_2SiH_2 + Et_3SiH\ (1:10) \xrightarrow{''} Et_3Si-SiPh_2H\ (8\%)$$

Mixtures of trimethyl- or triethylsilane with nitrogen dioxide react in the gas phase, explosively under certain conditions, to give hexaalkyldisiloxanes, nitric oxide and water as the predominant products.[113]

2. Si-Group VII

The redistribution reaction between bromofluorosilanes and $HSiI_3$ has been used to prepare the following Br/I exchange products: $SiFCl_2I$, $SiFClI_2$, $SiFBr_2I$, $SiFBrI_2$, SiF_2BrI, $SiFI_3$ and SiF_2I_2.[114]

Disproportionation occurs when trichlorosilane, α-chloromethylchlorosilanes and tertiary amines are allowed to react. This reaction is accompanied by condensation products.[115]

$$ClCH_2SiMe_2Cl + 2HSiCl_3 \xrightarrow{amine} Cl_3SiCH_2SiMe_2Cl_2 + SiCl_4 + H_2$$
$$ClCH_2SiMe_2Cl + HSiCl_3 \xrightarrow{amine} 2\ CH_3SiCl_3$$

The exchange equilibria of fluorine with the silicon substituents

Br, H, OMe, NMe$_2$ and SMe in the mono- and trimethylsilyl(substituent) series have been determined. The order of substituents in terms of their preference for the least alkylated silicon atom was given as OMe > NMe$_2$ > H > F > SMe > Cl > Br.[116]

Methods for the preparation of aryloxyfluorosilanes (R$_2$SiFOC$_4$H$_6$X; R = alkyl, aryl) have been investigated. The best preparative method involves the reaction of R$_2$SiHF with the required phenol, although significant amounts of R$_2$Si(OAr)$_2$ compounds are also produced. The synthesis of the required R$_2$SiHF starting compounds was also given.[117]

Exchange of chloro and ethoxy groups during the hydrosilylation of vinyldimethylethoxysilane by dimethylchlorosilane was found to occur both before and after addition, and was not dependent on the presence of chloroplatinic acid. Vinyl-hydrogen exchange was shown not to occur.[118]

$$Me_2SiClH + CH{=}CHSiMe_2OEt \rightleftharpoons Me_2Si(OEt)H + CH_2{=}CHSiMe_2Cl$$

$$2\ ClSiMe_2CH_2CH_2SiMe_2OEt \rightleftharpoons ClSiMe_2CH_2CH_2SiMe_2Cl + EtOSiMe_2CH_2CH_2SiMe_2OEt$$

The replacement of dimethylamino groups by iodine has proven to be the best route to pure fluoroiodosilanes.[119]

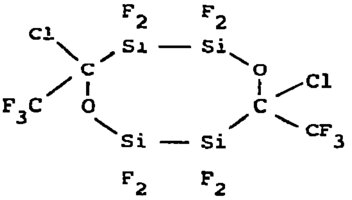
$$SiF_{4-x}(NMe_2)_x + 2xHI \longrightarrow SiF_{4-x}I_x + xNH_2Me_2I \quad (x = 1,\ 71\%;\ x = 2,\ 80\%)$$

Some chemistry of these species was reported, among which were the following:

$$\begin{aligned}
2\ F_3SiI &+ H_2O \longrightarrow F_3Si\text{-}O\text{-}SiF_3 + 2\ HI\\
&+ HgO \longrightarrow F_3Si\text{-}O\text{-}SiF_3\\
&+ HgS \longrightarrow F_3Si\text{-}S\text{-}SiF_3\\
F_3SiI &+ Hg(CN)_2 \longrightarrow F_3SiCN\\
&+ Hg(NCS) \longrightarrow F_3SiNCS\\
&+ Me_3N \longrightarrow Fe_3Si\cdot 2\ NMe_3\\
&+ Me_2NH \longrightarrow F_3SiNMe_2
\end{aligned}$$

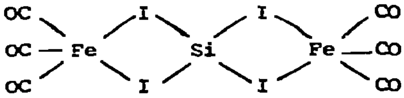
A number of chloro- and fluorophenylethynylsilanes have been prepared from phenylethynyl magnesium bromide and the appropriate mono-, or trihalosilane. Yields of partially substituted halosilanes were better when organofluorosilanes instead of organochlorosilanes were used as starting materials.[120]

The reaction of silicon difluoride with trifluoroacetyl chloride at liquid nitrogen temperatures afforded a volatile product which was characterized as 2,2,3,3,6,6,7,7-octafluoro-2,3,6,7-tetrasila-4,8-dioxa-1 5-dicnloro-1,5-bis(trifluoromethyl)cyclooctane.[121]



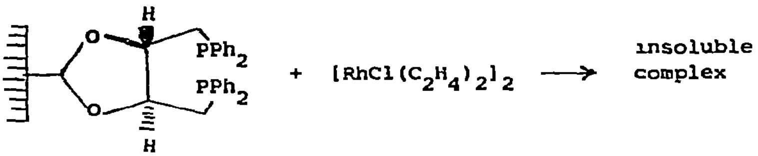
The reaction of SiF_4, Si_2F_6, $SiCl_4$, Si_2Cl_6, SiH_3I, SiH_3Br, SiF_3I and p-$ClC_6H_4SiH_3$ with various nitrogen oxides has been studied with and without U.V. irradiation. Silicon tetrafluoride is generally inert, but reacts below -60° with N_2O_3 to form a thermally labile (above 0°) adduct, probably NO^+ $(SiF_4{\cdot}NO_2)^-$; Si_2F_6 and NO or N_2O_4 produce $(F_3Si)_2O$, and Si_2Cl_2 behaves similarly. Other silanes produced siloxane mixtures, but no reaction occurred between p-$ClC_6H_4SiH_3$ and NO in the absence of irradiation. No evidence for isolable Si-nitroso compounds was obtained.[122]

The first example of a metal carbonyl complex where the halogen atoms of a metal halide serve as ligands has been reported. Thus, the irradiation of a mixture of $Fe(CO)_5$ and SiI_4 gives the compound SiI_4 - $[Fe(CO)_3]_2$ in low yield.[123] Its proposed structure is

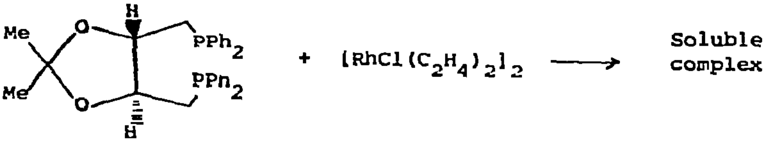


3. Si-Group VI

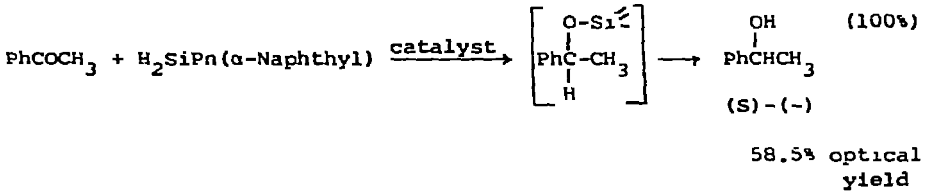
An insoluble polymer-supported chiral rhodium complex for the asymmetric hydrogenation of olefins and hydrosilylation of ketones has been prepared.[124]



The hydrogenation of olefins (2-ethyl-1-hexene, α-ethylstyrene, methyl atropate) is effectively catalyzed by this material, but optical yields are lower (0.6-2.5%) than with the soluble complex shown below (15% optical yield with α-ethylstyrene). However, use of the insoluble complex



for the hydrosilylation of acetophenone with dihydrosilanes (diphenylsilane, phenylmethylsilane, α-naphthylphenylsilane) gave high optical yields (up to 58%) which closely paralleled those obtained employing the soluble complex. Isobutyrophenone was an exception in that somewhat lower optical yields were obtained from the insoluble complex. An extremely



$$PhCOCH_3 + H_2SiPn(\alpha\text{-Naphthyl}) \xrightarrow{\text{catalyst}} \left[\begin{array}{c} O\text{-}Si\lessgtr \\ | \\ PhC\text{-}CH_3 \\ | \\ H \end{array}\right] \longrightarrow \begin{array}{c} OH \\ | \\ PhCHCH_3 \\ (S)\text{-}(-) \end{array} \quad (100\%)$$

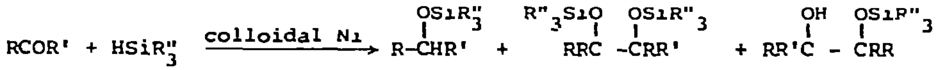
58.5% optical yield

useful observation is that with the soluble catalyst, dihydrosilanes afforded much higher optical yields, and under milder conditions, than did monohydrosilanes.

A chiral cationic complex, $[Rh\{(\underline{R})\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ ClO_4^-$ (S = solvent) has also been found effective for asymmetric hydrosilylation of a number of alkyl phenyl ketones. The silyl ethers produced were isolated and converted to carbinols by methyllithium treatment.[125]

The reaction of hydrosilanes with ketones in the presence of colloidal nickel produces both monosilylethers and silylated dimerization products.

	PhCOR R=	Silyl Ether Yield (%)	Carbinol Configuration	Optical Yield (%)
$PhMe_2SiH$	Me	97	S	31.6
	Et	94	S	43.1
	tBu	84	S	61.8
Me_3SiH	Me	100	S	5.1
	Et	92	S	6.4
	tBu	81	R	28.1



$$RCOR' + HSiR''_3 \xrightarrow{\text{colloidal Ni}} R-\overset{OSiR''_3}{\overset{|}{C}}HR' + RR\overset{R''_3SiO}{\overset{|}{C}}-\overset{OSiR''_3}{\overset{|}{C}}RR' + RR'\overset{OH}{\overset{|}{C}}-\overset{OSiR''_3}{\overset{|}{C}}RR$$

R = R' = Ph	R'' = Et	40.4%	57.0%	-----------
R = Ph; R' = Me	R'' = Et	50.3%	42.6%	-----------
"	= nBu	67.1%	14.3%	8.2%
R = Me; R'tBu	R'' = Et	47.5%	trace	-----------
"	= nBu	70.1%	8.6%	8.4%

For those ketones which are enolizable, small amounts of the corresponding silyl enol ether may have been present in the monosilylether product.[126]

A facile O-silylation of alcohols has been reported using a homogeneous system containing $ClRh(PPh_3)_3$ as catalyst. Isomerization or disproportionation is not observed. A mixture of cholesterol, diethylsilane and catalyst in hexane, for example, afforded a quantitative yield of cholesterol diethylsilyl ether. The rate of silylation is in the order phenol > MeOH > EtOH > iPrOH > tBuOH and $RSiH_3 > R_2SiH_2 > R_3SiH$.[127]

Diarylalkoxysilanes (R_2SiHOR') can be prepared by either the monoalcoholysis of diarylsilanes or the hydrosilylation of ketones with diarylsilanes, both in the presence of either rhodium or ruthenium complexes,

$$R_2SiH + R'OH \xrightarrow[\text{or } (PPh_3)_3RuCl_2]{(PPh_3)_3RhCl} R_2SiH(OR') + H_2$$

$$R_2SiH + R'R''C{=}O \xrightarrow[\text{above}]{\text{as}} R_2SiH(OCHR'R'')$$

The method appears to be general in the nature of R' and R". For both reactions, the rhodium complex was found to be the more efficient catalyst.[128]

Ionic fluorides catalyze both the alcoholysis of hydrosilanes and the addition of hydrosilanes to conjugated ketones and aldehydes. The following conversions are illustrative of the method.[129]

$$Et_3SiH + PhCH_2OH \xrightarrow[CsF]{CH_3CN} \underset{(95\%)}{Et_3SiOCH_2Ph} + H_2$$

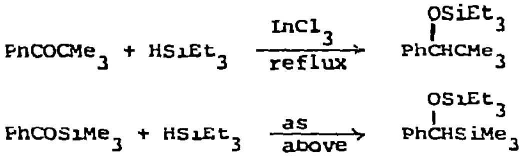
$$Et_3SiH + PhCHO \xrightarrow[CsF]{CH_3CN} \underset{(96\%)}{Et_3SiCCH_2Ph}$$

As part of an investigation concerning the mechanism of acetal formation from the photolysis of acylsilanes in alcoholic media, the photolytic behavior of acylsilanes in other protic solvents has been reported. In almost all cases, the indicated products were formed in good yields.[130]

$$Ph_3SiCOPh + HX \xrightarrow{h\nu} Ph_3SiOCHPh(X)$$

$X = OAc, CN, \text{pyrrolyl}, SPh, Cl, CH(CN)_2$

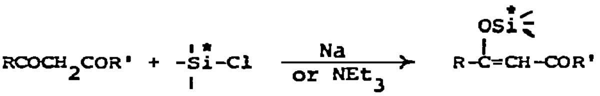
Triethylsilane adds to the carbonyl group of ketones under catalysis by indium trichloride.[131]



$$PhCOCMe_3 + HSiEt_3 \xrightarrow[reflux]{InCl_3} PhCH(OSiEt_3)CMe_3$$

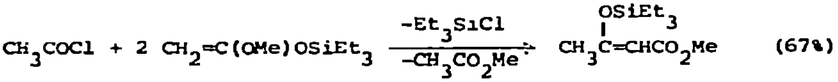
$$PhCOSiMe_3 + HSiEt_3 \xrightarrow[above]{as} PhCH(OSiEt_3)SiMe_3$$

Optically active O-silyl enol ethers are formed with inversion of configuration at silicon when optically active methylphenyl-α-napthylchlorosilane is allowed to react with an active methylene compound in the presence of base. Both β-keto esters and ketones behave similarly.[132]



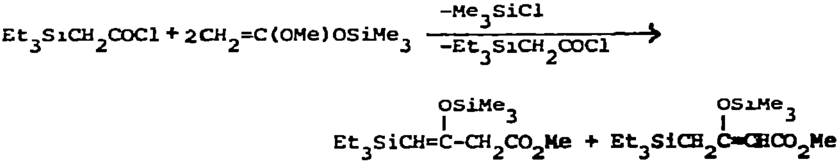
$$RCOCH_2COR' + -\overset{|*}{\underset{|}{Si}}-Cl \xrightarrow[\text{or } NEt_3]{Na} R-\overset{\overset{*}{O}Si\lessdot}{\overset{|}{C}}=CH-COR'$$

Silylated enol ethers have been prepared as follows.



$$CH_3COCl + 2\ CH_2=C(OMe)OSiEt_3 \xrightarrow[-CH_3CO_2Me]{-Et_3SiCl} CH_3\overset{OSiEt_3}{\overset{|}{C}}=CHCO_2Me \quad (67\%)$$

(cis:trans = 9:1)



$$Et_3SiCH_2COCl + 2CH_2=C(OMe)OSiMe_3 \xrightarrow[-Et_3SiCH_2COCl]{-Me_3SiCl}$$

$$Et_3SiCH=\overset{OSiMe_3}{\overset{|}{C}}-CH_2CO_2Me + Et_3SiCH_2\overset{OSiMe_3}{\overset{|}{C}}=CHCO_2Me$$

In the latter case, the principal product is the β,γ-unsaturated isomer.[133]

A number of soluble and insoluble (polymer-supported) palladium catalysts were investigated for the addition of trimethylsilanol to butadiene.

$$Me_3SiOH + CH_2=CH-CH=CH_2 \xrightarrow[Me_3SiONa]{Pd\ catalyst} Me_3SiOCH_2CH=CH(CH_2)_3CH=CH_2$$

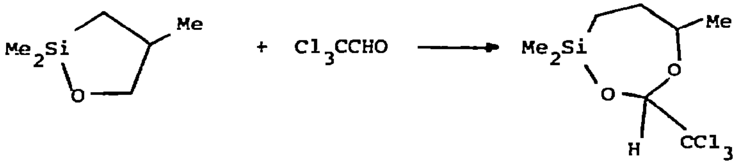
The soluble system $PdCl_2(PhCN)_2$-PPh_3-Me_3SiONa was the most advantageous. Polymeric catalysts could not be recycled and lost palladium content after one use.[134]

Lithium derivatives of the compounds H_3SiXH (X=O,S,Se) and of $(H_3Si)_2YH$ (Y=P,As) can be prepared indirectly by treating fully silylated X or Y with methyllithium.[135]

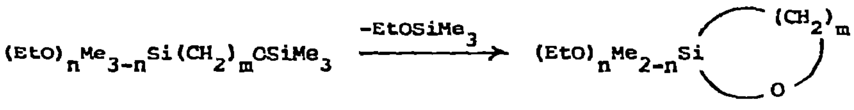
$$(H_3Si)_2X + MeLi \longrightarrow LiXSiH_3 + MeSiH_3$$

$$(H_3Si)_3Y + MeLi \longrightarrow LiY(SiH_3)_2 + MeSiH_3$$

Chloral inserts into the ring structure of a cyclic silylether to give the acetal product in quantitative yield.[136]



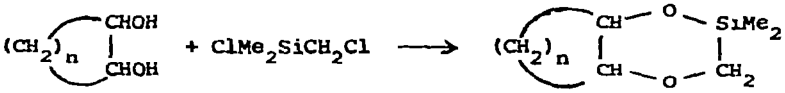
A series of (ω-ethoxysilylalkoxy)trimethylsilanes has been synthesized and their cyclization studied under basic (NaOEt) and acidic (HCl) conditions.



(n = 1-3, m = 3,4) (n = 0-2, m = 3,4)

Six-membered rings are formed faster than five-membered rings, and with base catalysis, the reactivity towards cyclization increases with increasing numbers of ethoxy groups on silicon. The latter observation is also true of acid-catalyzed cyclizations to five-membered rings, but a reversal in reactivity is observed for cyclization to the six-membered heterocycles.[137]

Cyclic vicinal diols produce heterocycles upon appropriate silylation.[138]



n = 3,4

Trimethylsilylcyanide affords functionalized silyl ethers with a number of co-reactants

$$Me_3SiCN + COCl_2 \longrightarrow Me_3SiOC(CN)_3\ ^{139}$$

$$'' \quad + ClCOCOCl \longrightarrow [Me_3SiOC(CN)_2]_2\ ^{139}$$

$$'' \quad + F_3CCOCl \longrightarrow Me_3SiOC(CN)_2CF_3\ ^{139}$$

$$'' \quad + R\,COR' \longrightarrow Me_3SiOCRR'CN\ ^{139,140}$$

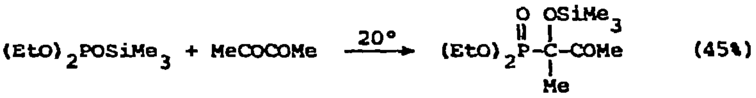
$''$ +  $\xrightarrow{AlCl_3}$ $Me_3SiOCH_2CH_2CN$ [141]

$$'' \quad + RCOCl \xrightarrow{pyridine} Me_3SiOC(CN)_2R\ ^{141}$$

$$'' \quad + RCO\text{-}G\text{-}COR \longrightarrow Me_3SiOCR(CN)GCR(CN)OSiMe_3\ ^{141}$$

(G = CMe_2, o-phenylene) + $Me_3SiOCR(CN)GCOR$

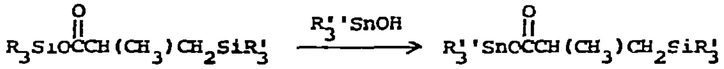
Trimethylsilyl phosphite was found to add to 2,3-butanedione.[142]



$$(EtO)_2POSiMe_3 + MeCOCOMe \xrightarrow{20°} (EtO)_2\overset{O}{\overset{\|}{P}}\text{-}\underset{Me}{\overset{OSiMe_3}{C}}\text{-}COMe \qquad (45\%)$$

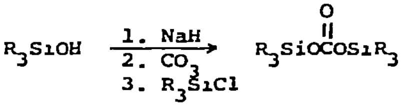
Organotrichlorosilanes react with ß-diketones to form chelate complexes of the form $[RSi(diket)_2]^+X^-$ (diket-H = acetylacetone, benzoylacetone, dibenzoylmethane, benzoylacetanilide); the complexes with X = Cl were easily converted into those with X = HCl_2, $FeCl_4$ and $SnCl_5$. Similar complexes of formula $(SiL_3)^+X^-$ were prepared from $SiCl_4$ and β-hydroxyketones and β-hydroxynitro (or nitroso) compounds. These complexes appear to be ionic and contain pentacoordinate silicon.[143]

Stannyl-silyl group transesterification has been effected in some Group IV esters.[144]

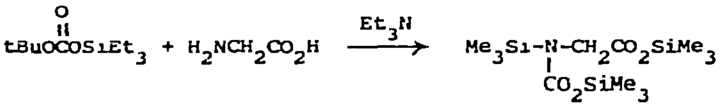


$$R_3SiO\overset{O}{\overset{\|}{C}}CH(CH_3)CH_2SiR'_3 \xrightarrow{R''_3SnOH} R''_3SnO\overset{O}{\overset{\|}{C}}CH(CH_3)CH_2SiR'_3$$

Bistrialkylsilylcarbonates have been prepared and the reaction of t-butyl trimethylsilyl carbonate with aminoacids investigated.[145]



$$R_3SiOH \xrightarrow[\substack{2.\ CO_3\\3.\ R_3SiCl}]{1.\ NaH} R_3SiO\overset{O}{\overset{\|}{C}}OSiR_3$$



$$tBuO\overset{O}{\overset{\|}{C}}OSiEt_3 + H_2NCH_2CO_2H \xrightarrow{Et_3N} Me_3Si\underset{\substack{|\\CO_2SiMe_3}}{N}CH_2CO_2SiMe_3$$

Unsymmetrical organosilicon peroxides result from the treatment of a mixture of hydroperoxide and chlorosilane with anhydrous ammonia.[146]

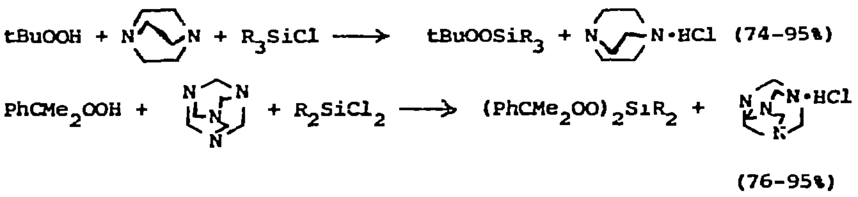
$$Ph_3SiOOH + RSiMe_2Cl \xrightarrow[Et_2O]{NH_3} Ph_3SiOOSiMe_2R$$

(R = aryl, akyl)

Heating some peroxides results in phenyl group migration.[147]

$$Ph_3SiOOSiPh_3 \xrightarrow{100°} PhO(Ph)_2SiOSiPh_3 \qquad (100\%)$$

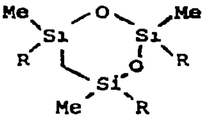
A method for the high-yield synthesis of mono- and bis-peroxysilanes has been reported.[148]



The reactivity of bis (trimethylsilyl) peroxide with a variety of nucleophilic, electrophilic, oxidizing and reducing agents has been probed.[149]

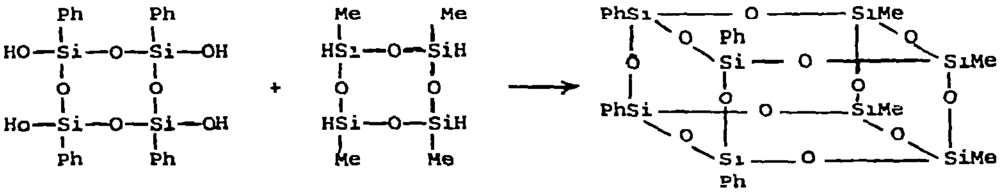
Agent	Products
	 + $Me_3SiOSiMe_3$(HMDS)
Ph_3P	Ph_3PO + HMDS
$(EtO)_3P$	$(EtO)_3PO$ + HMDS
Et_2S	$Et_2SO + Et_2SO_2$ + HMDS
PhSH	$PhSO_3H$ + HMDS
nBuLi	$nBuOSiMe_3 + Me_3SiOLi$
EtMgI	$EtOSiMe_3 + Me_3SiOMgI$"
$NaOH, H_2O$	$Me_3SiOH + H_2O_2$
NaOMe,PhH	$EtOSiMe_3 + Me_3SiOO^-Na^+$
Li,Na or K (M)	Me_3SiOM
$Ni(CO)_4$	$(Me_3SiO)_2Ni + CO$
Ph_2Cr	Cr_2O_3 + HMDS + $Ph_2 + H_2O$
$Pb(OAc)_4$	$Me_3SiOCOMe + Pb(OAc)_2 + O_2$
CrO_3,HOAc	$Cr(OAc)_3$ + HMDS + $H_2O + O_2$
Ph_3COH	$(Ph_3CO)_2$
SO_2	$Me_3SiOSO_2OSiMe_3$

The *cis*- and *trans*-isomers of a fluorine-containing diorganocyclosiloxane have been prepared and characterized.[150]

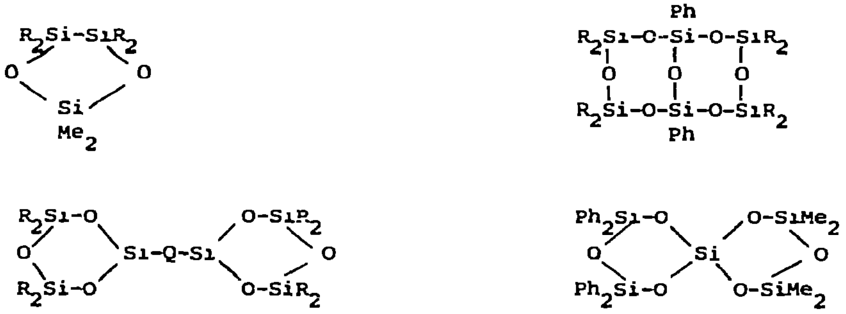


$R = CF_3(CF_2)_3CH_2CH_2$

An excellent yield of a polycyclic compound can be obtained by control of a polycondensation reaction.[151]

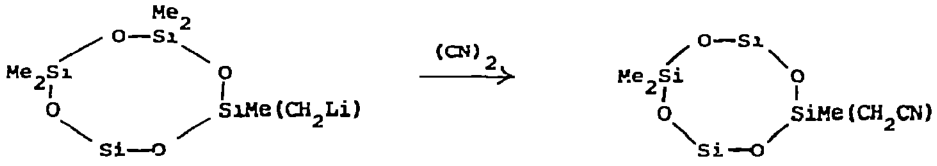


The preparation and physical properties of cyclic organopolysiloxanes having the following structures have been reported.[152]



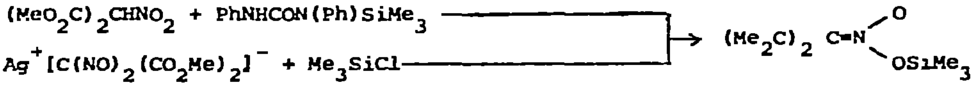
(R = Me, Ph; Q = p-C_4H_6)

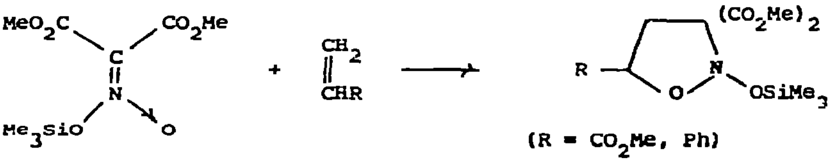
Treatment of lithium octamethylcyclotetrasiloxane with cyanogen is reported to give 80% of the cyanomethyl derivative.[153]



1-(chloromethyl)- and 1-(3-chloromethyl)- silatranes have been synthesized by standard methods.[154]

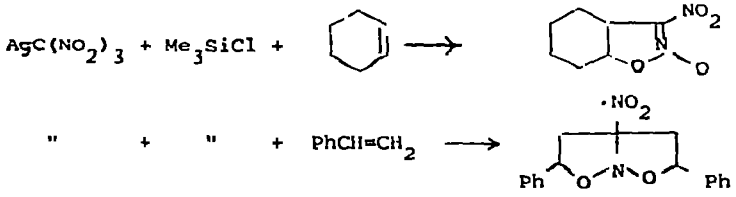
The silylation of dimethylnitromalonate occurs nearly quantitatively to afford the O-silylation product. The same product, though in lower conversion, is obtained from the silver salt of the malonate and trimethylchlorosilane. In contrast, the sodium salt of the malonate does not react with trimethylchlorosilane. The O-silylated product underwent 1,3-dipolar cycloaddition reactions with olefins.[155]





(R = CO_2Me, Ph)

Similar behavior has been reported for the nitro compounds $HC(NO_2)_3$,[156] $CH_2(NO_2)_2$[157] and $MeO_2CCH_2NO_2$.[157] Other products can arise from $AgC(NO_2)_3$.[158]

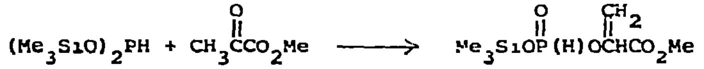


Silylation of $AgC(NO_2)_3$·p-dioxane with RPh_2SiCl (R = Me, Ph) led to isolable products (in contrast to silylation with Me_3SiCl) which underwent the expected 1,3-dipolar cycloaddition with styrene but reacted with methyl acrylate by conjugate addition.[159]

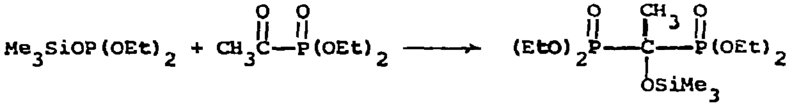
Silylation of trifluoronitrosomethane under u.v. irradiation has been reported.[160]

$$HSiX_3 + CF_3NO \xrightarrow{u.v.} CF_3NOSiX_3 \qquad X = Cl,\ 17.3\%$$
$$X = F,\ 80\%$$

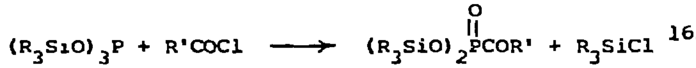
The preparative chemistry of some compounds containing Si-O-P bonding has been studied.



$$(Me_3SiO)_2PH + CH_3\overset{O}{\overset{\|}{C}}CO_2Me \longrightarrow Me_3SiO\overset{O}{\overset{\|}{P}}(H)O\overset{CH_2}{\overset{\|}{C}}HCO_2Me \qquad 161$$



$$Me_3SiOP(OEt)_2 + CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{P}}(OEt)_2 \longrightarrow (EtO)_2\overset{O}{\overset{\|}{P}}-\underset{OSiMe_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{P}}(OEt)_2 \qquad 162$$



$$(R_3SiO)_3P + R'COCl \longrightarrow (R_3SiO)_2\overset{O}{\overset{\|}{P}}COR' + R_3SiCl \qquad 163$$

$$[R = Me,\ Et;\ R' = CF_3,\ (CF_3)_2CH]$$

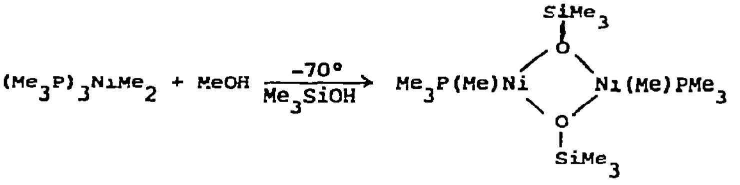
$$\left.\begin{array}{r} 3\ R_3P(X)YH + 3\ Me_3SiCl + HN(SiMe_3)_2 \\ R_3P(X)YM + Me_3SiCl \end{array}\right] \rightarrow R_2P(X)YSiMe_3 \qquad 164$$

$[R = alkyl;\ X\ and\ Y = S\ and\ O;\ M = Na,\ NH_4]$

Siloxymetallic compounds have been synthesized as shown.

$$NH_4VO_3 + 2\ HN(SiMe_3)_2 \longrightarrow (Me_3SiO)_3V{=}NSiMe_3 \qquad 165$$

$$NH_4VO_3 + 3\ nPrNHSiMe_3 \longrightarrow (Me_3SiO)_3V{=}N\text{-}nPr \qquad 165$$



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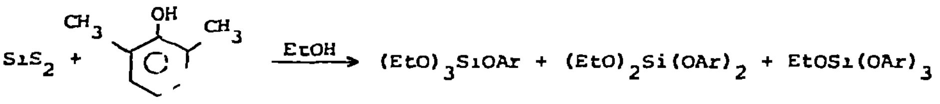
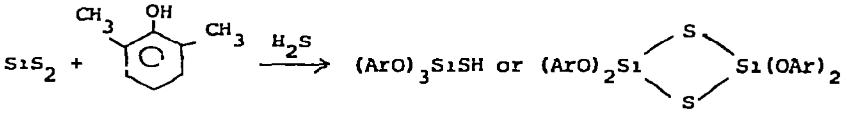
$$Ph_3SiOCdEt + O_2 \longrightarrow Ph_3SiOCdOOEt \quad ^{166}$$

$$'' + (PhCO_2)_2 \longrightarrow Ph_3SiOCdOOEt + Ph_3SiOCdOCOPh \quad ^{167}$$

Silicon disulfide reacts with 2,6-dimethylphenol (ArOH) and ethanol to form ethoxyaryloxysilanes.[168]



Substitution of H_2S for EtOH and a variation in mole ratio of reactants allows the formation of silanethiol and cyclodisilthiane.[169]



Moderate yields of silyl bis (thioethers) are obtained by the palladium-catalyzed condensation of alkyl- and aryl-thiols with diethylsilane.[170]

$$Et_2SiH_2 + HSR \xrightarrow[\Delta]{Pd} Et_2Si(SR)_2 \quad (19\text{-}41\%)$$

A highly effective catalyst for this type of transformation, however, has now been found which affords nearly quantitative yields.[171]

$$R_3SiH + R'SH \xrightarrow{(Ph_3P)_3RhCl} R_3SiSR' + H_2$$

$$R_2SiH_2 + R'SH \xrightarrow{(Ph_3P)_3RhCl} R_2Si(H)SR' + H_2$$

The known reaction of silanethiols with silver nitrate has been used to develop a potentiometric method for the determination of silanethiols.[172]

$$(RO)_3SiSH + AgNO_3 \longrightarrow (RO)_3SiSAg + HNO_3$$

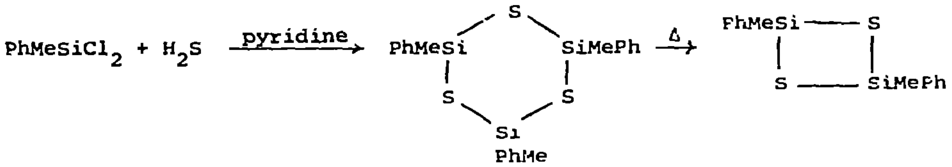
Silanethiols have been reported to undergo the following reactions:

$Ph_3SiSH + ROH \longrightarrow Ph_3SiOR + H_2S$ [173]

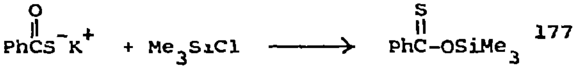
(R = 1°,2°,3° alkyl, allyl, aryl)

$Et_3SiSH + EtLi \longrightarrow Et_3SiSLi + EtH$ [174]

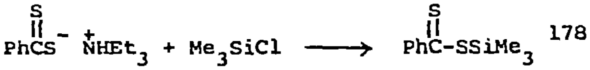
Methylphenylcyclosilthianes have been synthesized which are capable of *cis*, *trans*-isomerism, and their conformational preferences investigated.[175] A complementary investigation of the trimethyltriethylcyclotrisilthiane and the trimethyltrivinylcyclotrisilthiane systems has also appeared.[176]



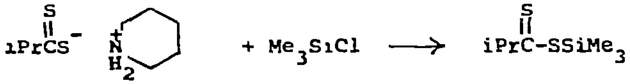
The following preparative methods for the formation of sulfur-containing silyl esters have appeared.



$Ph\overset{O}{C}S^-K^+ + Me_3SiCl \longrightarrow Ph\overset{S}{C}{-}OSiMe_3$ [177]



$Ph\overset{S}{C}S^-\ \overset{+}{N}HEt_3 + Me_3SiCl \longrightarrow Ph\overset{S}{C}{-}SSiMe_3$ [178]



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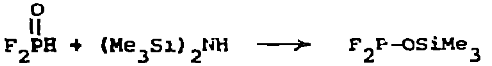
Compounds containing the P-O-Si and P-S-Si moieties have been synthesized.



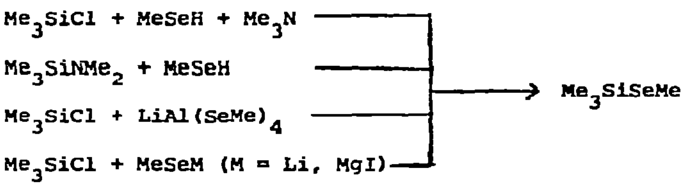
$F_2\overset{O}{P}H + (Me_3Si)_2NH \longrightarrow F_2P{-}OSiMe_3$ [179]

$(CF_3)_2PF + (Me_3Si)_2O \longrightarrow (CF_3)_2POSiMe_3$ [179]

$(CF_3)_2PCl + (Me_3Si)_2S \longrightarrow (CF_3)_2PSSiMe_3$ [179,180]

Attempts at synthesis of the P(V) isomers (e.g., $R_2P(O)SiMe_3$) gave only P(III) forms. Cleavage reactions of the P-containing silyl esters with HCl and Me_2NH as well as with HBr and $(CF_3)_2PCl$,[180] were reported.

Silicon-substituted selenium compounds have been prepared by a number of routes.[181]



Pentafluoro-orthotellurates of silicon [$Me_3SiOTeF_5$, $Si(OTeF_5)_4$] are formed by the reaction of Me_3SiCl or $SiCl_4$ with, respectively, $HOTeF_5$ and $AgOTeF_5$.[182]

Crystalline complexes are formed by mixing bis[tri(pentafluorophenyl)germyl] cadmium with silicon derivatives of Group VI elements.[183]

$$(Ph_3Ge)_2Cd + (Et_3Si)_2M \longrightarrow (Ph_3Ge)_2CdM(SiEt_3)_2$$

$$(M = S,\ Se,\ Te)$$

4. Si-Group V

The scope of aminosilane preparation by amine-silane condensations catalyzed by $(Pn_3P)_3RnCl$ has been reported. Good to excellent yields of the monoaminosilanes are obtained in all instances. Phenylsilane and triethylsilane, as well as aniline, were successfully employed in similar transformations.[184]

$$R_2SiH_2 + R'_2\,NH \xrightarrow{cat} R_2SiHNR'_2$$

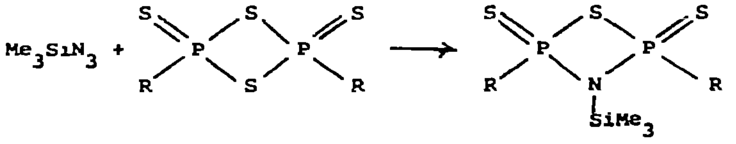
Transition metal halides are found to catalyze the fixation of molecular nitrogen by trimethylchlorosilane and lithium.[185]

$$Me_3SiCl + N_2 + Li \xrightarrow[THF]{CrCl_3} (Me_3Si)_3N$$

Syntheses of the following silylamines have appeared.

$$[(CF_3)_2N]_2Hg + H_3SiI \longrightarrow (CF_3)_2NSiH_3 \quad ^{186}$$

$$Me_3SiNH_2 + HN(CH_2)_n \longrightarrow Me_3Si\text{-}N(CH_2)_n \quad (n = 2,3) \quad ^{187}$$



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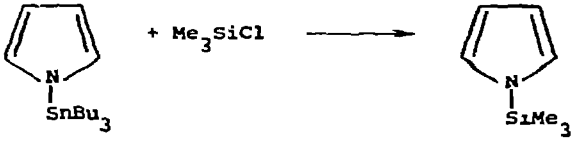

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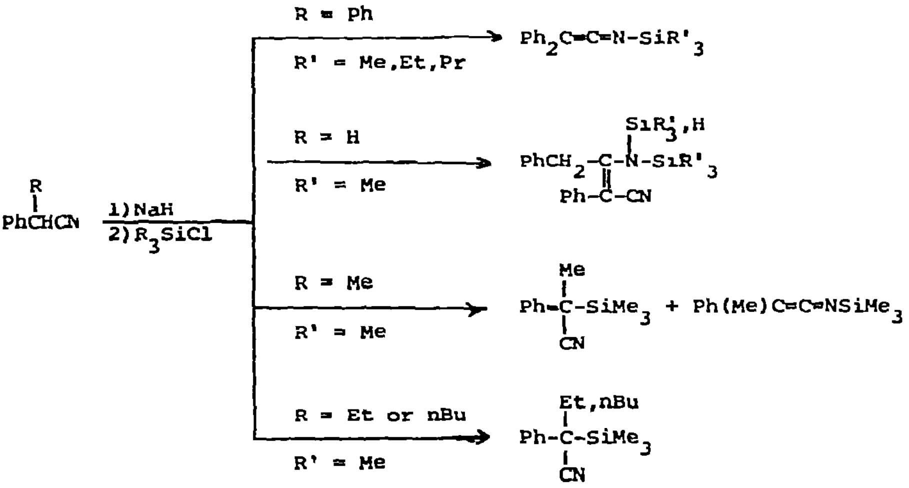
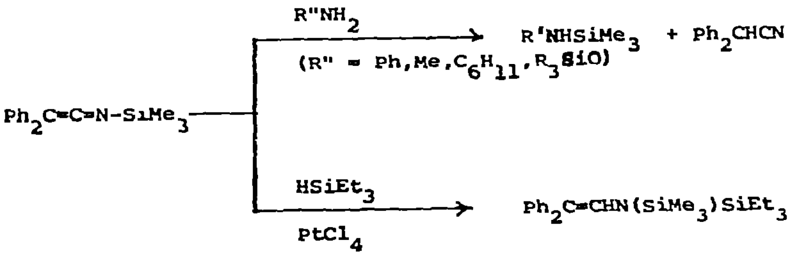
2-Trimethylsilylpyrrole has been shown to slowly isomerize into the N-silyl isomer.[189]

Silylation of substituted phenylacetonitriles by trialkylchlorosilanes varied according to substitution.[190]





Treatment of silyl amines with tetrasulfur tetranitride leads to a nitrogen exchanged product. The same product is obtained using $S_3N_2Cl_2$.[191]

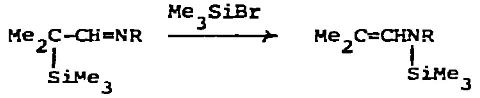
$$Me_3SiNR_2 + S_4N_4 \longrightarrow Me_3Si-N=S=N-S-NR_2$$

(R = Me,Et)

Heptasulfur imide anion and chlorotrimethylsilane afford an adduct.[192]

$$S_7NK + Me_3SiCl \longrightarrow S_7NSiMe_3$$

Under the catalytic influence of 10 mole % bromotrimethylsilane, the following carbon to nitrogen silyl group migration was effected.[193]



$$Me_2C(SiMe_3){-}CH{=}NR \xrightarrow{Me_3SiBr} Me_2C{=}CHN(SiMe_3)R$$

(R = Me, Et, nPr, iBu)

Trifluoromethyl-containing silylimines have been prepared.[194]

$$(CF_3)_2C{=}NH \xrightarrow{MeLi} (CF_3)_2C{=}NLi \xrightarrow[(n\,=\,1\text{-}4)]{Me_{4-n}SiCl} Me_{4-n}Si[N{=}C(CF_3)_2]_n$$

N-Halohexamethyldisilazanes are preparable in good yields by the use of N,N-dihalobenzenesulfonamides. Poor yields (ca. 15%) were obtained with N-bromosuccinimide.[195]

$$PhSO_2NX_2 + 2\,(Me_3Si)_2NH \xrightarrow{Bz_2O_2} PhSO_2NH_2 + 2(Me_3Si)_2NX \quad (70\%)$$

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

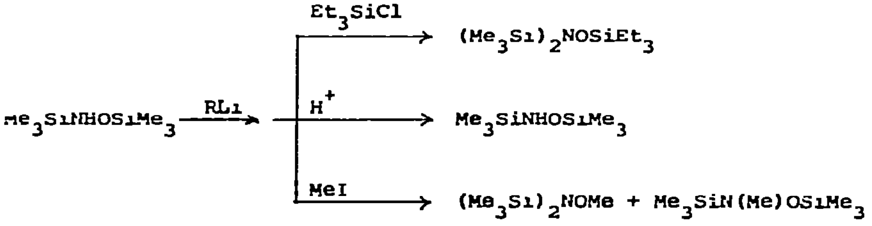
The synthesis and reactions of some silylated hydroxylamines have been reported. Equilibration (via silyl group migration) between N-lithiated and O-lithiated forms was observed.[196]

$$(Me_3Si)_2NH + HO\overset{+}{N}H_3\,Cl^- \xrightarrow[pentane]{THF-} Me_3SiNHOSiMe_3$$

$$2(Me_3Si)_2NH + 3\ HO\overset{+}{N}H_3\,Cl^- \xrightarrow{Et_3N} Me_3SiNHOSiMe_3 + 2\ H_2NOSiMe_3 \quad (1{:}1)$$

$$(Me_3Si)_2NH + HO\overset{+}{N}H_2MeCl^- \xrightarrow{Et_3N} MeNHOSiMe_3$$

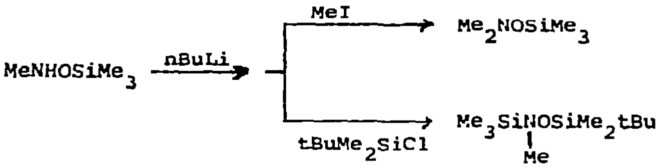
$$(Me_3Si)_2NH + MeO\overset{+}{N}H_3Cl^- \longrightarrow (Me_3Si)_2N{-}OMe$$



$$Me_3SiNHOSiMe_3 \xrightarrow{RLi} \begin{cases} \xrightarrow{Et_3SiCl} (Me_3Si)_2NOSiEt_3 \\ \xrightarrow{H^+} Me_3SiNHOSiMe_3 \\ \xrightarrow{MeI} (Me_3Si)_2NOMe + Me_3SiN(Me)OSiMe_3 \end{cases}$$

$$Me_3SiNHOSiMe_3 \xrightarrow[2)\,MeI]{1)\,2tBuLi} (Me_3Si)_2N{-}Me$$

$$H_2NOSiMe_3 \xrightarrow[2)\,tBuMe_2SiCl]{1)\,RLi} tBuMe_2SiNHOSiMe_3 + Me_3SiNHOSiMe_2tBu$$



$$\mathrm{MeNHOSiMe_3} \xrightarrow{\mathrm{nBuLi}} \begin{cases} \xrightarrow{\mathrm{MeI}} \mathrm{Me_2NOSiMe_3} \\ \xrightarrow[\mathrm{tBuMe_2SiCl}]{} \mathrm{Me_3Si\underset{Me}{N}OSiMe_2tBu} \end{cases}$$

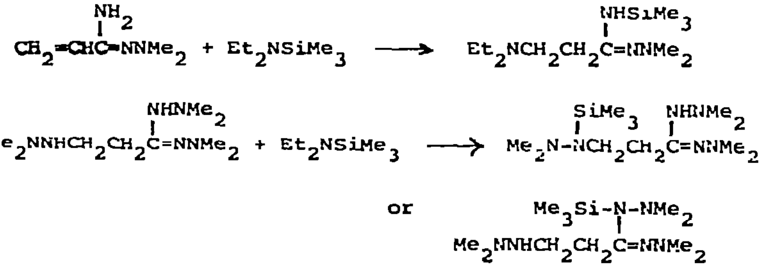
Silylated hydroxylamines have been prepared by other workers, and similar rearrangements observed.

$$\mathrm{R_3SiONH_2 + Ph_2C{=}C{=}N{-}SiR'_3 \longrightarrow R_3SiONHSiR'_3 + Ph_2CHCN}\quad{}^{197}$$

(R, R' = alkyl) (70-90%)

$$\mathrm{Me_3SiONHSiEt_3} \underset{}{\overset{120°}{\rightleftharpoons}} \mathrm{Et_3SiONHSiMe_3}\quad{}^{198}$$

Silylation of some hydrazine derivatives has been carried out.[199]



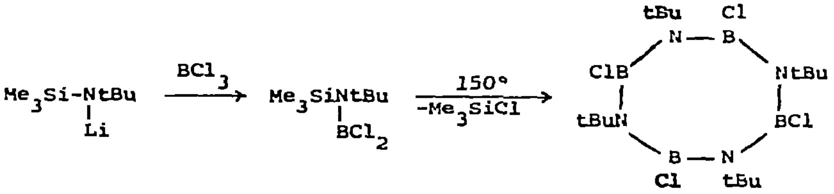
$$\mathrm{CH_2{=}CH\overset{NH_2}{C}{=}NNMe_2 + Et_2NSiMe_3 \longrightarrow Et_2NCH_2CH_2\overset{NHSiMe_3}{C}{=}NNMe_2}$$

$$\mathrm{Me_2NNHCH_2CH_2\overset{NHNMe_2}{C}{=}NNMe_2 + Et_2NSiMe_3 \longrightarrow Me_2N{-}\overset{SiMe_3}{N}CH_2CH_2\overset{NHNMe_2}{C}{=}NNMe_2}$$

$$\text{or}\quad \mathrm{Me_2NNHCH_2CH_2\overset{Me_3Si-N-NMe_2}{C}{=}NNMe_2}$$

The preparation and reactions of some silylaminoboranes have appeared.

$$\mathrm{(Me_3Si)_2NH \xrightarrow[2)\,ClB(X)Ph]{1)\,RLi} (Me_3Si)_2NB(X)Ph}\quad \mathrm{(X = Cl,\ NH_2)}\quad{}^{200}$$



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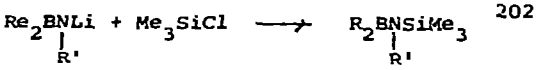
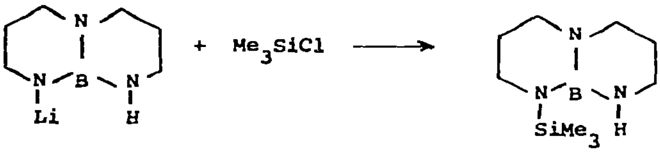


$$\mathrm{Re_2B\underset{R'}{N}Li + Me_3SiCl \longrightarrow R_2B\underset{R'}{N}SiMe_3}\quad{}^{202}$$

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



202

$$(Me_3Si)_2NMe + ClBH_2{\cdot}OEt_2 \xrightarrow{60^\circ} H_2BN(Me)SiMe_3 + Me_3SiCl \qquad 203$$

$$\text{"} \quad + ClBH_2{\cdot}OEt_2 \longrightarrow H_5B_2N(Me)SiMe_3 + Cl_2BH{\cdot}OEt_2 + Me_3SiCl \qquad 203$$

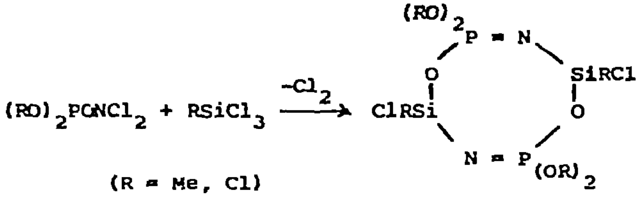
Attempted preparations of compounds containing two $-BH_2$ groups on the same nitrogen or containing the $H_2B\text{-}NH\text{-}Si$ fragment did not succeed.[203]

New chemistry of silylaminophosphorus compounds has appeared, including those containing the first example of the phosphazene structural component, $-P{=}N$.

$$(Me_3Si)_3N \ [\text{or } (Me_3Si)_2NLi] + OPF_2 \longrightarrow (Me_3Si)_2N\text{-}POF_2 \qquad 204$$

$$(Me_3Si)_3N \ [\text{or } (Me_3Si)_2NPOF_2] + P_2O_3F_4 \longrightarrow Me_3SiN(POF_2)_2 + Me_3SiOPOF_2 \qquad 204$$

$$(Me_3Si)_3N \ [\text{or } Me_3Si)_2NLi] + OPCl_3 \longrightarrow Me_3SiOP(Cl_2){=}NSiMe_3 \qquad 204$$



205

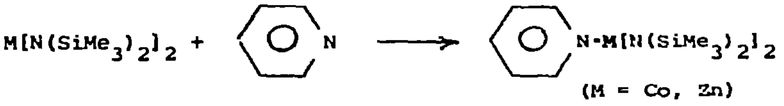
$$\begin{tikzcd}
(Me_3Si)_2NLi + (Me_3Si)_2NPF_2 \arrow[r] & (Me_3Si)_2NP{=}NSiMe_3 \arrow[d, "CCl_4"] \\
 & Me_3SiN{=}PCl(CCl_3)\ N(SiMe_3)_2
\end{tikzcd} \qquad 206$$

$$(Me_3Si)_2NLi + PCl_5 \longrightarrow Me_3SiN{=}PCl_3 \qquad 207$$

Unusual thermal stability is observed for mono N-silylated aminotellurium pentafluoride, whereas attempts to isolate the bis-silylated analogue [from $(Me_3Si)_2NLi$ and TeF_6] were unsuccessful.[208]

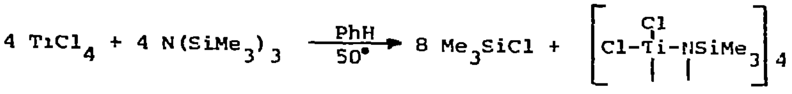
$$(Me_3Si)_2NH + TeF_6 \longrightarrow Me_3SiF + Me_3SiNHTeF_5$$

Pyridines and ring-methylated pyridines form stable adducts with diaminosilyl cobalt and zinc compounds. Triethylamine appeared to form complexes in solution, but no stable adduct was obtained, possibly due to steric factors.[209]



(M = Co, Zn)

A novel titanium-nitrogen heterocycle has been reported.[210]



$$4\ TiCl_4 + 4\ N(SiMe_3)_3 \xrightarrow[50°]{PhH} 8\ Me_3SiCl + \left[Cl{-}\overset{Cl}{Ti}{-}NSiMe_3 \right]_4$$

(65%)

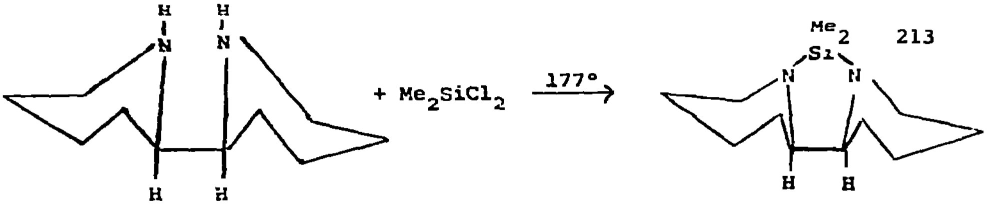
The reaction of $PdCl_2$ with silicon-containing amines affords stable complexes. For example, $[Et_3Si(CH_2)_3NH_2]_2 \cdot PdCl_2$ was characterized.[211]

A series of low-coordinate lanthanide and actinide complexes was attainable because of the large steric requirement of the bis(trimethylsilylamino) ligands.[212]

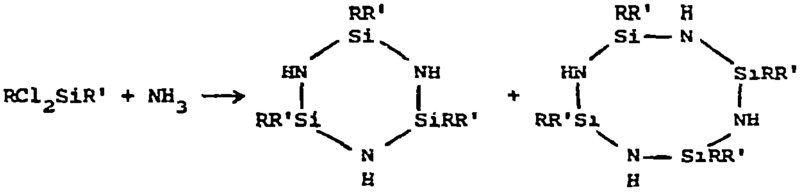
$$MCl_3 + 3\ LiN(SiMe_3)_2 \longrightarrow M[N(SiMe_3)_2]_3$$

(M = La, Ce, Pr, Nd, Sm, En, Gd, Ho, Y, Yb, Lu)

Silicon and nitrogen are heteroatoms in a variety of new cyclic compounds.

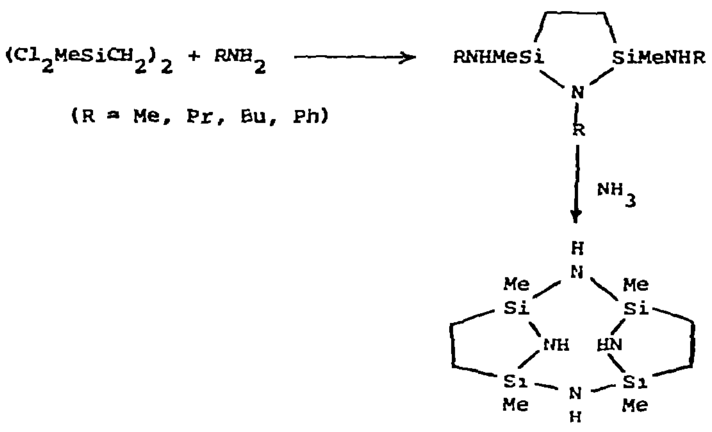


(erythro) 213 (24%)



214

(R = Me, Et; R' = $CH_2CH_2OCH{=}CH_2$)



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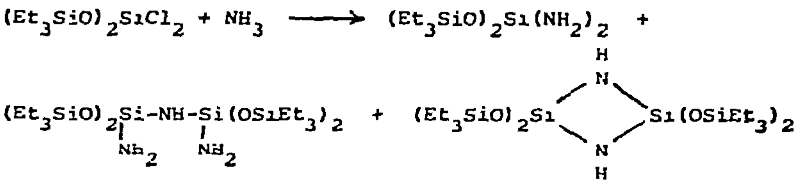

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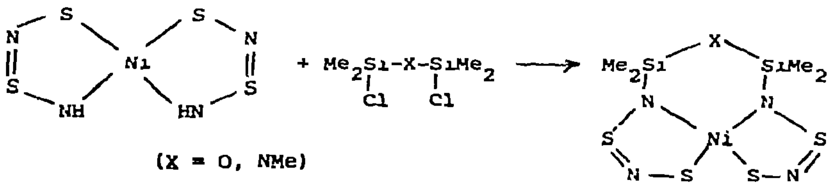

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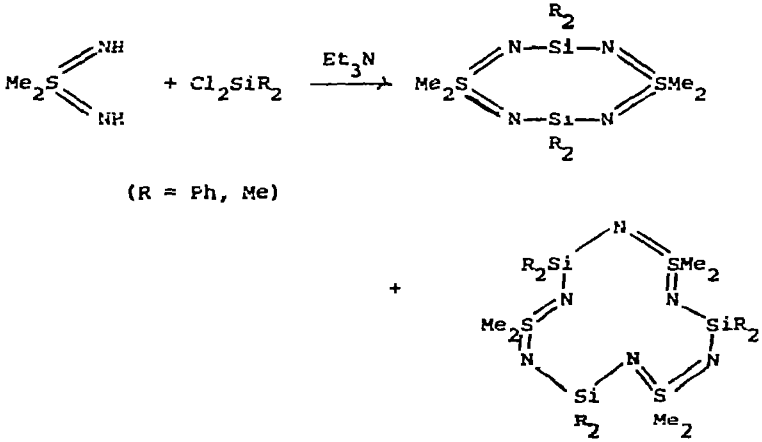

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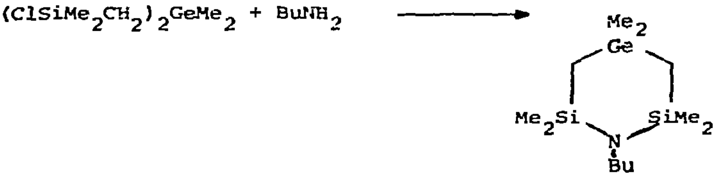
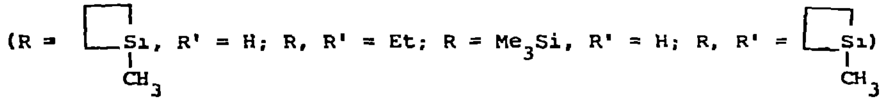


219

Complexes of aminosilanes and metal halides have been characterized.

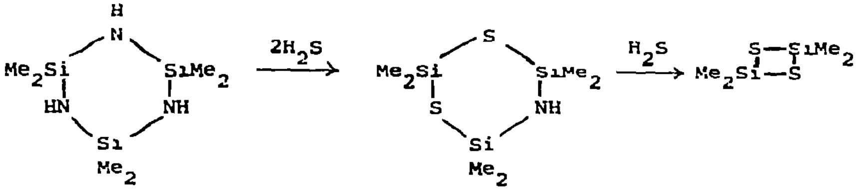
220



$(Me_2SiNH)_4 + MCl_3 \xrightarrow{L} (Me_2SiNH)_4(MCl_3)_2\cdot 2L$ 221

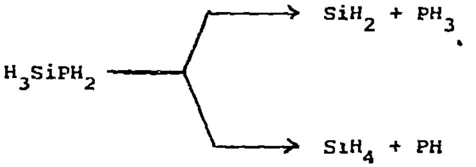
(M = Ti, V, Cr; L = THF or Me_3N)

$(Me_2SiNH)_4 + TiCl_4 \longrightarrow (Me_2SiNH)_4(TiCl_4)_2$ 221



222

Thermolytic decomposition of silylphosphine has been shown to proceed *via* two routes. The first chemical evidence for phosphylene was thus obtained.[223]

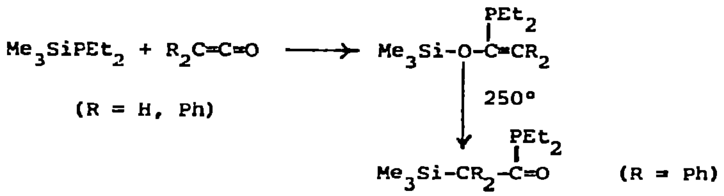


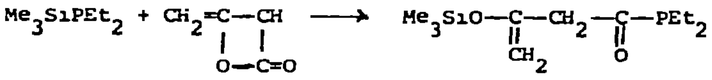
A high-yield method for the preparation of organosilylphosphines (and arsines) is now at hand.[224]

$PCl_3 + Me_3SiCl + Mg \xrightarrow{HMPT} (Me_3Si)_3P$ (76%)

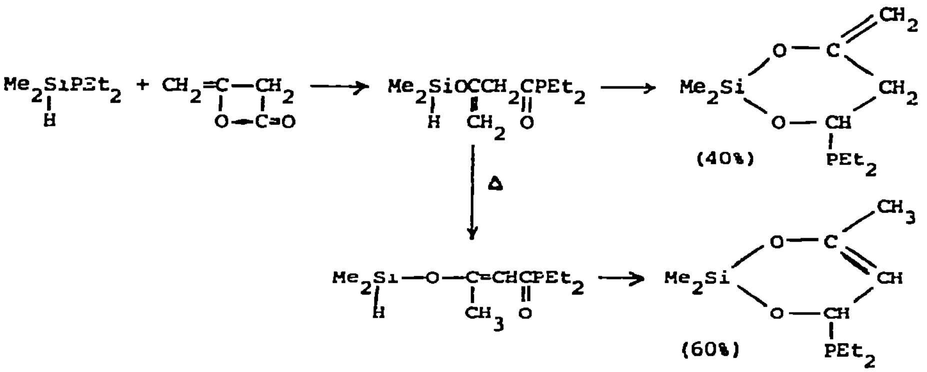
$tBu_2PCl + Me_3SiCl + Mg \xrightarrow{HMPT} Me_3SiP(tBu)_2$ (95%)

Silylphosphines add to ketenes and diketenes to form silyl enol ethers which isomerize upon heating.[225]

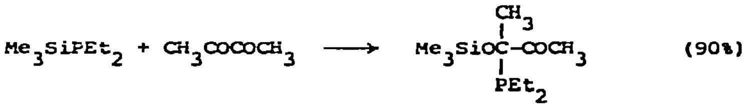


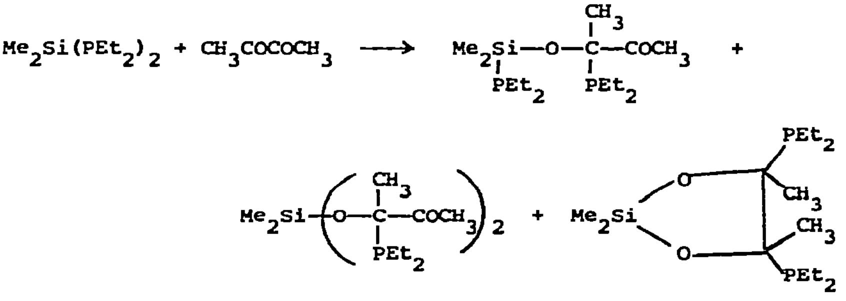


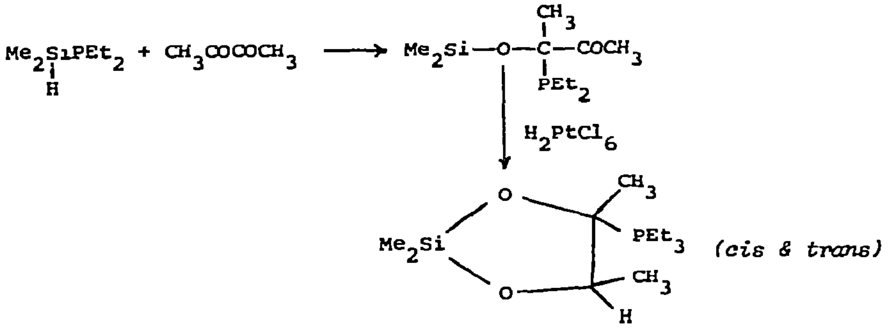
Partial isomerization and cyclization occur when the hydrosilane adduct is heated.

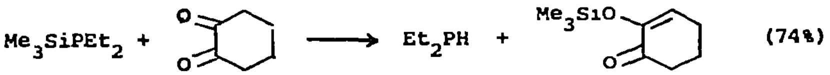


Silylphosphines undergo similar carbonyl additions to α-diketones.[226]





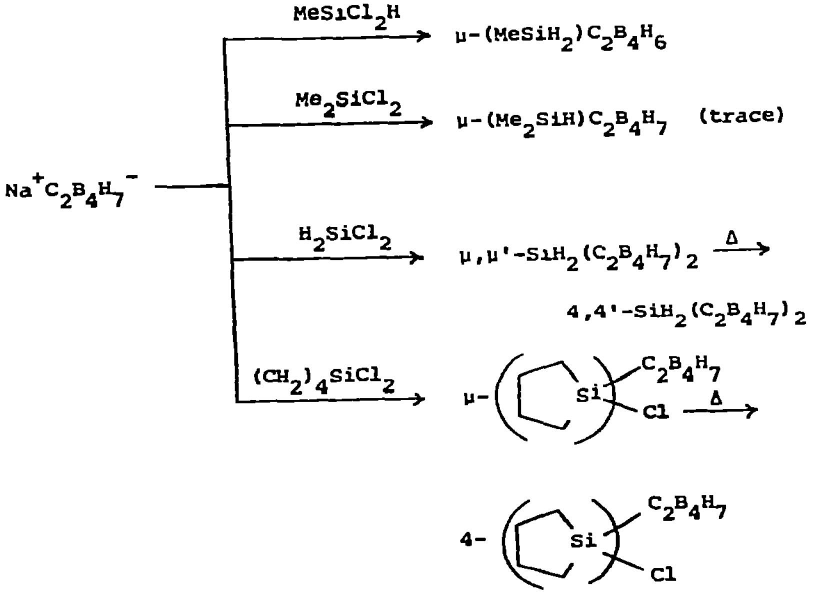




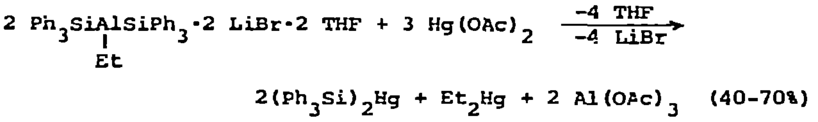
5. Si-Metal

Further chemistry of silyl-containing $C_2B_4H_8$ derivatives has been explored, including silyl migrations from bridging to terminal positions.[227]

$$\begin{tikzcd}
\mu\text{-}Me_3SiC_2B_4H_7 \arrow[r, "NaH"] & 4\text{-}Me_3SiC_2B_4H_7^-Na^+ \arrow[d, "Me_3SiCl"] \\
 & \mu,4\text{-}(Me_3Si)_2C_2B_4H_6
\end{tikzcd}$$



Ethyl bis(triphenylsilyl)aluminum has been utilized for the preparation of bis(triphenylsilyl)mercury. Results obtained upon treatment of the aluminum compound with alkyl hydroperoxides followed by hydrolysis suggests that structures with Si-O-Al bonds are formed as intermediates.[228]



$$2\ \mathrm{Ph_3Si\underset{\underset{Et}{|}}{Al}SiPh_3\cdot 2\ LiBr\cdot 2\ THF} + 3\ \mathrm{Hg(OAc)_2} \xrightarrow[-4\ \mathrm{LiBr}]{-4\ \mathrm{THF}} 2\mathrm{(Ph_3Si)_2Hg} + \mathrm{Et_2Hg} + 2\ \mathrm{Al(OAc)_3}\quad (40\text{-}70\%)$$

(Fluoroalkyl)silylmercurials may be formed by exchange reactions at mercury. Silyl β-fluoroalkylmercurials are stable but the stannyl analogues are not.[229]

$$\begin{tikzcd}
\mathrm{(Et_3Si)_2Hg + HgR_2} \arrow[r, "\mathrm{THF}"] & \mathrm{Et_3SiHgR} \arrow[d, "\mathrm{CsF}"] & \mathrm{(R = CF_3,\ CF_2CF_3)} \\
 & \mathrm{Et_3SiF + Hg + (CF_2)_n} &
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{[(Me_3SiCH_2)_3Sn]_2Hg + Hg[C(CF_3)_3]_2} \arrow[r, "\mathrm{THF}"] & 2\ \mathrm{(Me_3SiCH_2)_3SnHgC(CF_3)_3} \arrow[d, "\mathrm{in\ situ}"] \\
 & 2\ \mathrm{(Me_3SiCH_2)_3SnF + 2Hg + 2(CF_3)_2C{=}CF_2}
\end{tikzcd}$$

Onium salts containing silicon and transition metal complexes have been characterized. These undergo the normal reactions of onium halides.[230]

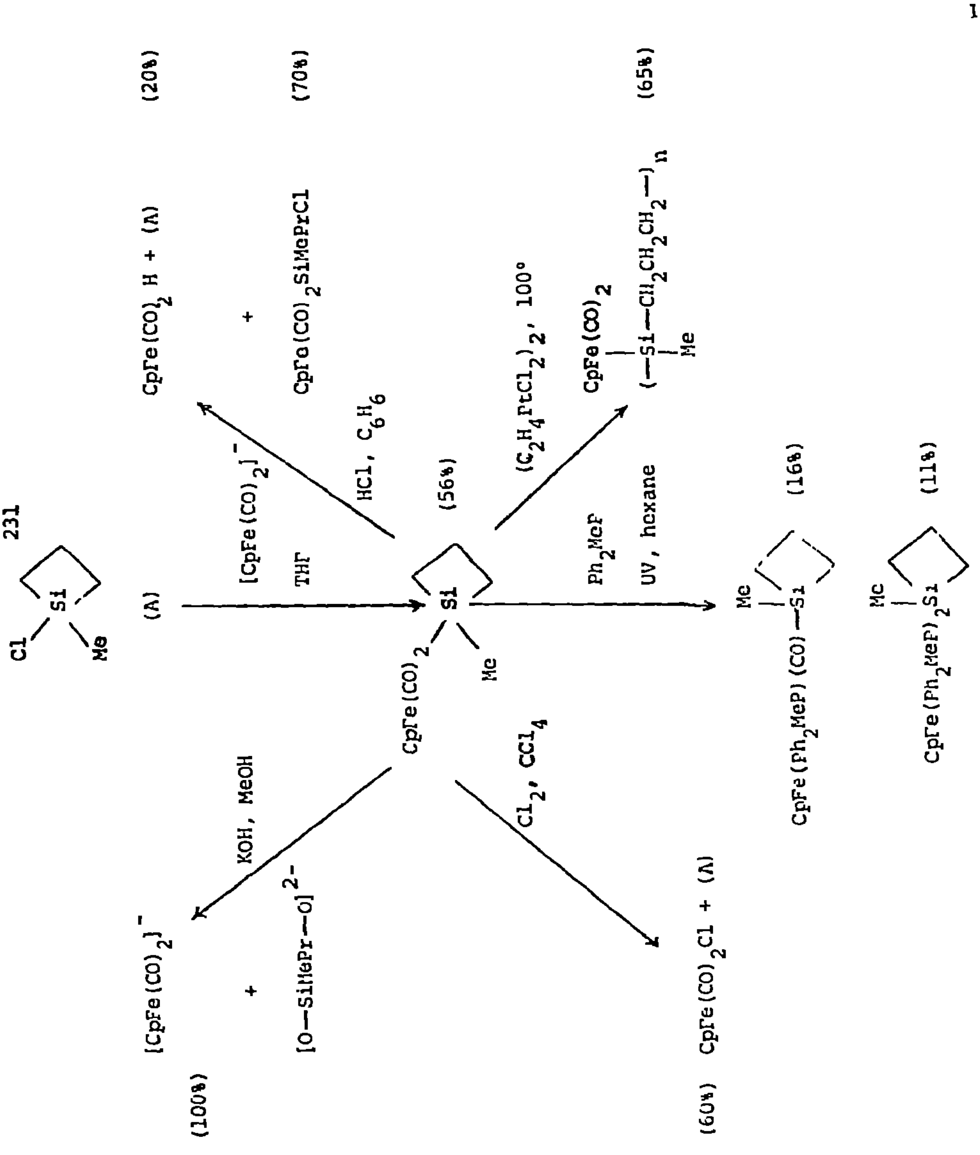
$$\mathrm{Me_3P{=}CHSiMe_3 + HM(CO)_3\text{-}\pi\text{-}C_5H_5 \longrightarrow [Me_3PCH_2SiMe_3]^+[M(CO)_3\text{-}\pi\text{-}C_5H_5]^-}$$

Iron-substituted silacyclobutanes are readily preparable and undergo reactions involving ring cleavage and demetalation.[231]

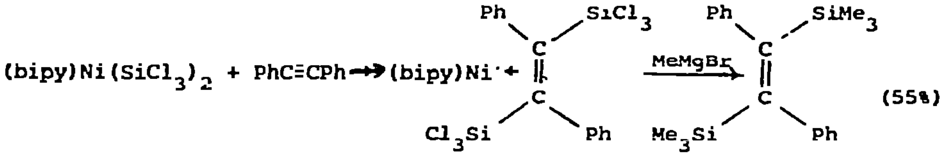
Halogen-alkoxy exchange can be effected by treating π-CpFe(CO)$_2$-SiCl$_3$ with sodium alcoholates. The species π-CpFe(CO)$_2$Si(OR)$_3$ [R = Me, Et, nPr, iPr, tBu] were thus prepared. An excess of alcoholate results in Fe-Si bond cleavage yielding the [π-CpFe(CO)$_2$]$^-$ ion.[232]

An optically active derivative of an Si-Fe compound [(-)-(π-Cp)Fe(CO)$_2$SiMePh(1-Np)] has been prepared.[233]

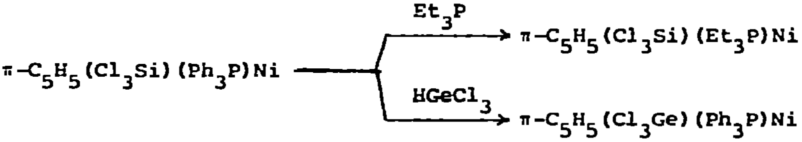
Evidence has been presented which indicates that a vicinal bis-


231
Cl
Si
Me
(A)
[CpFe(CO)2]⁻
THF
CpFe(CO)2
Si
Me
(56%)
HCl, C6H6
CpFe(CO)2H + (A)
(20%)
+
CpFe(CO)2SiMePrCl
(70%)
(C2H4PtCl2)2, 100°
CpFe(CO)2
(—Si—CH2CH2CH2—)n
Me
(65%)
Ph2MeP
UV, hexane
Me
CpFe(Ph2MeP)(CO)—Si
(16%)
Me
CpFe(Ph2MeP)2Si
(11%)
KOH, MeOH
[CpFe(CO)2]⁻
(100%)
+
[O—SiMePr—O]2-
Cl2, CCl4
CpFe(CO)2Cl + (A)
(60%)

silylation of an acetylene occurred *via* bis(trichlorosilyl)bipyridylnickel(II).[234]



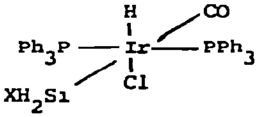
The nickel-silicon complex $\pi\text{-}C_5H_5(Cl_3Si)(Ph_3P)Ni$ was obtainable in 35% yield from $(\pi\text{-}C_5H_5)_2Ni$ and Cl_3SiH. Ligand exchange reactions were observed.[235]



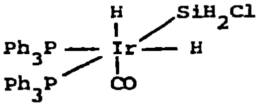
$$\pi\text{-}C_5H_5(Cl_3Si)(Ph_3P)Ni \xrightarrow{Et_3P} \pi\text{-}C_5H_5(Cl_3Si)(Et_3P)Ni$$

$$\pi\text{-}C_5H_5(Cl_3Si)(Ph_3P)Ni \xrightarrow{HGeCl_3} \pi\text{-}C_5H_5(Cl_3Ge)(Ph_3P)Ni$$

Vaska's compound [*trans*-carbonylchlorobis(triphenylphosphine)iridium(I)] added the silanes H_3SiX (X = H, Cl, Br, I), $MeSiH_2Cl$ and Si_2H_6 to afford 1:1 adducts. These appear to have the general structure



Upon several weeks standing under an equimolar excess of H_3SiCl, the 1:1 adduct from Vaska's compound and H_3SiCl formed the compound



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Low oxidation state transition metal complexes react with hexachlorodisilane to form higher oxidation state trichlorosilyl metal species.[237] In contrast to an earlier report, no reaction to form $Pt(PPh_3)(SiCl_2)_2$ was observed between $Pt(PPh_3)_2(SiCl_3)_2$ and PPh_3.

A series of compounds $Ir(Cl,Br)(H,D)(SiR_3)(CO)(PPh_3)_2$, where R = halogen, alkoxy, alkyl, has been prepared to assess the *trans*-influence of the silyl group in these complexes.[238]

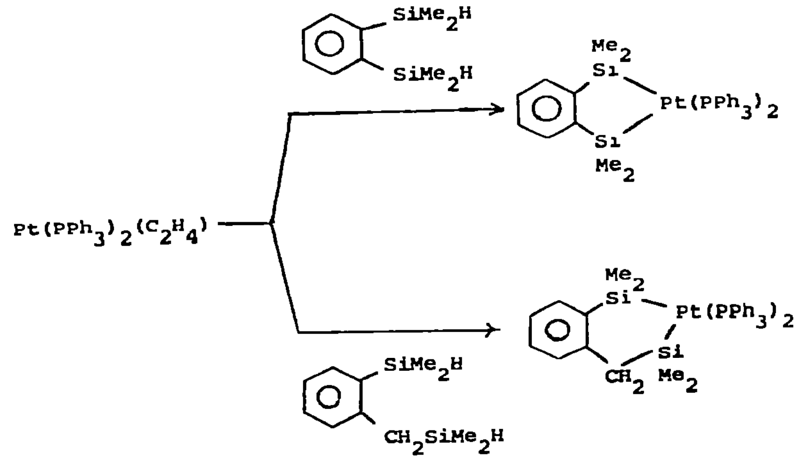
$$[\pi\text{-}C_5H_5Mo(CO)_3]_2 + Si_2Cl_6 \longrightarrow Mo(CO)_3(\pi\text{-}C_5H_5)SiCl_3$$

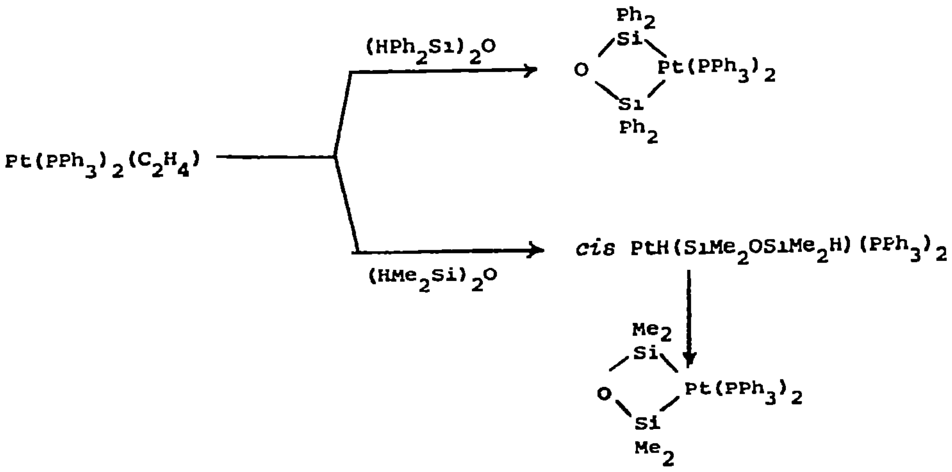
$$\begin{array}{lcl} Ir(Cl)(CO)(PPh_3)_2 + Si_2Cl_6 & \longrightarrow & Ir(Cl)(CO)(PPh_3)_2(SiCl_3)_2 \\ & & \Big\downarrow {\scriptstyle H_2O} \\ & & Ir(Cl)_2(CO)(H\ )(PPh_3)_2 \end{array}$$

$$RhCl(PPh_3)_2 + Si_2Cl_6 \longrightarrow Rh(PPh_3)SiCl_2$$

$$Fe(CO)_5 + Si_2Cl_6 \longrightarrow [Fe(CO)_4SiCl_2]_2$$

Cyclic bis-silyl chelates of platinum have been reported.[239]





The dihydrides o-$(HMe_2SiCH_2)C_6H_4$ and $HMe_2Si(CH_2)_4SiMe_2H$ do not afford cyclic products. Ligand exchange with $Ph_2PCH_2CH_2PPh_2$ and Pt-Si cleavage with bromine were both observed for the 5- and 6- membered cyclic chelate compounds.

A migration of the trimethylsilyl group from cobalt to oxygen is observed upon heating trimethylsilylcobalt tetracarbonyl. This cobalt complex also reacts with tetrahydrofuran to give silyl enol ethers.[240]

$$Me_3SiCo(CO)_4 \xrightarrow{105^\circ} Me_3SiOCCo_3(CO)_9 + (Me_3SiOC)_4Co_2(CO)_4$$

$$Me_3SiCo(CO)_4 \xrightarrow[\text{THF}]{\text{room temperature}} Me_3SiOCCo_3(CO)_9 + Me_3SiOCH{=}CHEt + Me_3SiOCH{=}CHCH_2CH_2OSiMe_3$$

Convenient syntheses have been described for a number of silyl-transition metal complexes.[241] Analogues containing the $Mn(CO)_5$ moiety

$$H_2SiCl_2 + NaCo(CO)_4 \xrightarrow{-NaCl} H_2SiClCo(CO)_4$$

$$H_2SiCl_2 + 2NaCo(CO)_4 \xrightarrow{-2NaCl} H_2Si[Co(CO)_4]_2$$

$$Me_2SiClH + NaCo(CO)_4 \xrightarrow{-NaCl} Me_2SiHCo(CO)_4$$

$$2\ H_2SiCl_2 + Co_2(CO)_8 \xrightarrow{-H_2} 2\ HSiCl_2Co(CO)_4$$

$$H_2SiCl_2 + Co_2(CO)_8 \xrightarrow[-CO]{-H_2} SiCl_2Co_2(CO)_7$$

were formed in a similar fashion. Heteropolymetallic silanes are also accessible by an extension of the method.

$$SiH_2ClMn(CO)_5 + Co_2(CO)_8 \longrightarrow SiHClMn(CO)_5Co(CO)_4 + SiClMn(CO)_5Co_2(CO)_4$$

$$SiHClMn(CO)_5Co(CO)_4 + Fe_3(CO)_{12} \longrightarrow Fe(CO)_4[SiClMn(CO)_5]_2[Co_2(CO)_7]$$

Transition metal complexes containing the trifluorosilyl group have been prepared.[242]

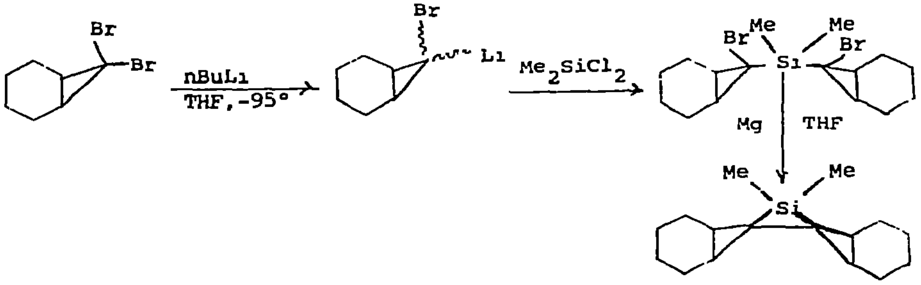
$$M_2(CO)_{10} + F_3SiH \xrightarrow[-H_2]{170^\circ} F_3SiM(CO)_5 \qquad (M = Mn, Re)$$

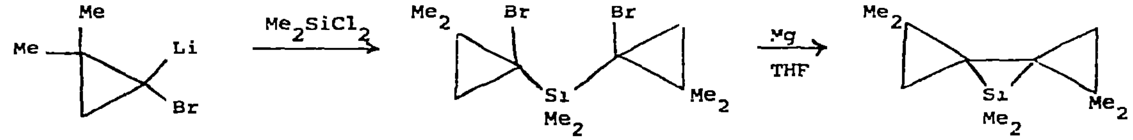
$$[\pi\text{-}C_5H_5Fe(CO)_2]_2 \text{ or } [\pi\text{-}C_5H_5M(CO)_3]_2 \xrightarrow{F_3SiH} F_3SiFe(\pi\text{-}C_5H_6)(CO)_2 \text{ or } F_3SiM(\pi\text{-}C_5H_6)(CO)_3$$

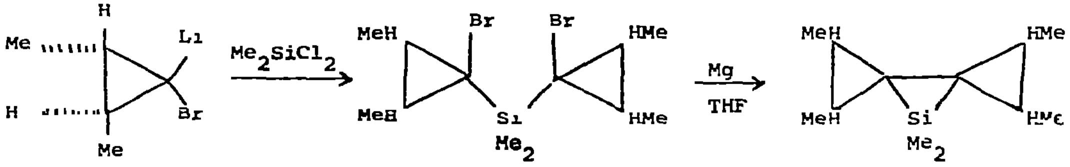
$(M = Mo, W)$

VI. SILACYCLIC COMPOUNDS

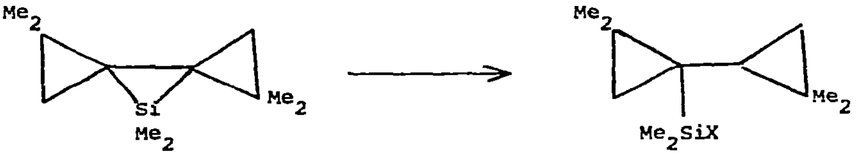
The first synthesis of the elusive silacyclopropane ring system has been reported.[243]







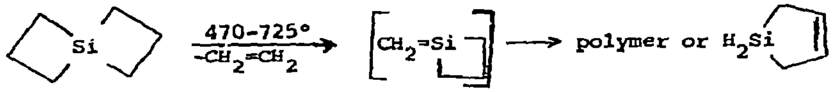
These silacyclopropanes are oxidatively unstable in air, and undergo facile ring-opening reactions with HCl, CH_3Li and $HOCH_3$, e.g.,



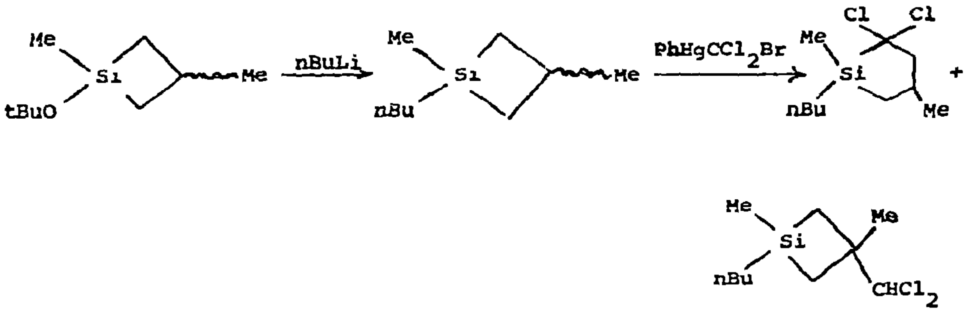
X = OCH_3, Cl, CH_3

A subsequent report indicated that this high reactivity is a general characteristic of silacyclopropanes.[244] In addition to the above, the following reagents afforded the ring-opened product with X derived from the anionic portion of the reagent: HOH, HOtBu, HOPh, $HNEt_2$, H_2NiPr, H_3N, H_2S, HStBu, HOAc and HO_2CCMe_3.

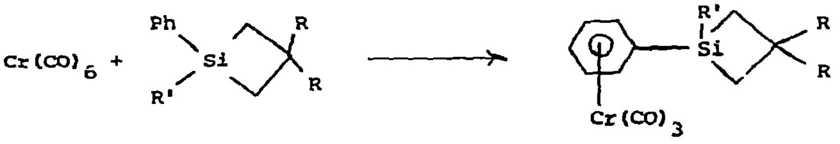
Pyrolysis of 4-silaspiro[3.3]heptane leads to polymeric, or at low pressures, monocyclic products in addition to ethylene.[245]



Mixtures of *cis*- and *trans*- 1,3-dimethyl-n-butyl-1-silacyclobutanes have been prepared and subjected to $PhHgCCl_2Br$ treatment. Both Si-C and β-C-H bond insertion products are formed with the latter predominating. The data obtained is consistant with a high degree of retention of configuration for both processes.[246]



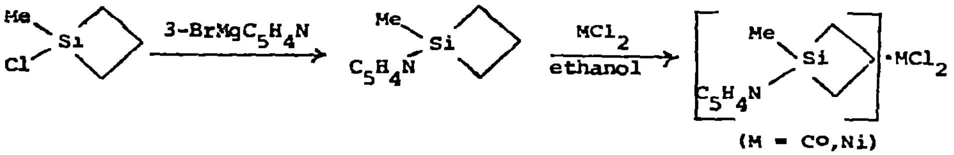
Arene complexes of chromium which contain silacyclobutane rings have been prepared. 1,1-Dimethyl-2,3-benzo-1-silacyclobutane polymerized under the reaction conditions.[247]



R' = Ph, R = H

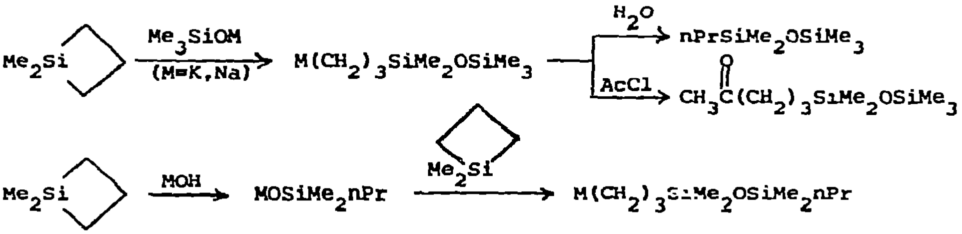
R' = Me, R = Me

Cobalt and nickel complexes containing the ligand 1-methyl-1-(3-pyridyl)-1-silacyclobutane have also been reported.[248]

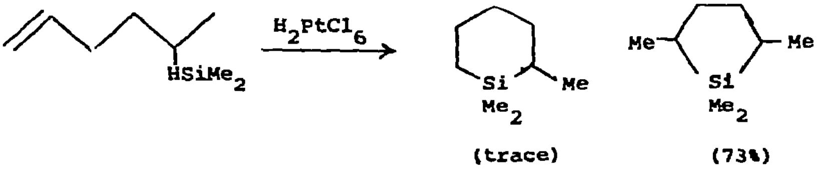


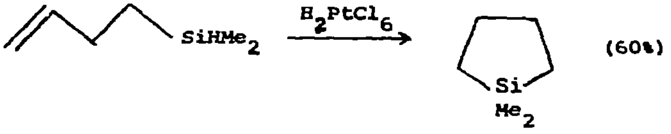
A variety of mono- and disilacyclobutanes were cleaved with $HgCl_2$ in alcohol at the Si-C bond. Products were not isolable because of thermal instability. Relative reactivity studies were carried out and compared to earlier results of HCl- and alcoholic KOH-induced ring opening. Electrophilic attack of the $[HgX]^+$ ion on the ring was indicated as the rate-controlling step.[249]

Open-chain organometallic compounds are formed when silacyclobutanes are treated with alkali metal silanoates or hydroxides.[250]

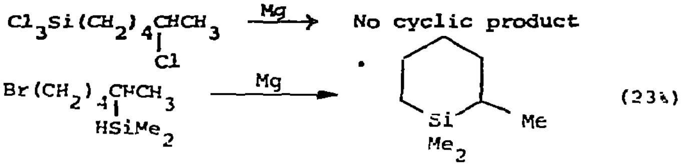


A strong ring-size effect has been observed in the attempt to form a silacyclohexane by intramolecular hydrosilylation. Although in acyclic systems, hydrosilylation leads to terminal silanes, silacyclopentanes resulting from the formation of a Si-C bond at a secondary position are the major products in this case.[251]

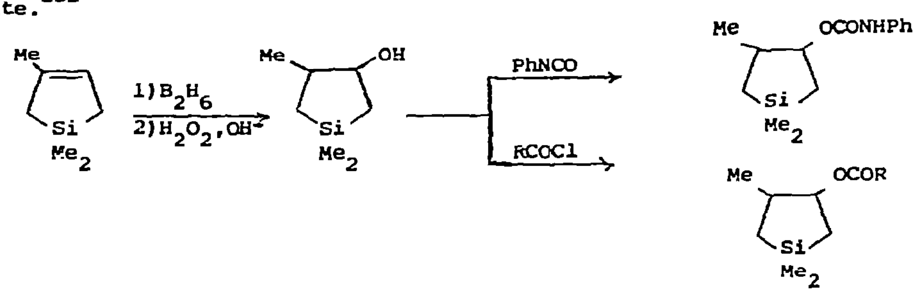




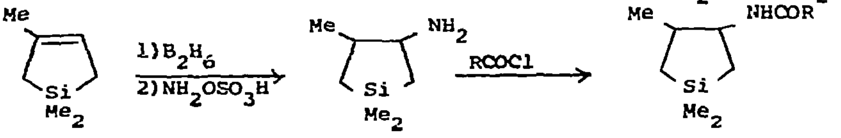
Also of synthetic interest were the following observations.



Silacyclopentanes containing hydroxyl or amino functionality *beta* to silicon underwent derivatization by acyl chlorides and phenyl isocyanate.[252]

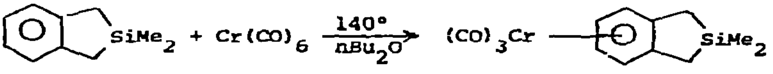


(R = Me, $CH=CH_2$, $CMe=CH_2$)

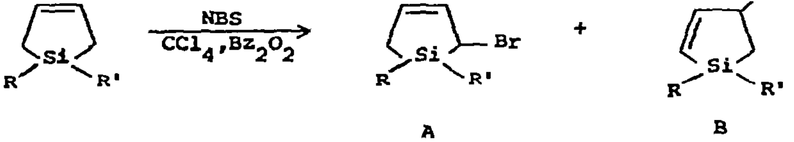


(R = Me, $CH=CH_2$, $CMe=CH_2$)

A π-complex of 2,2-dimethyl-2-silaindane has been reported.[253]

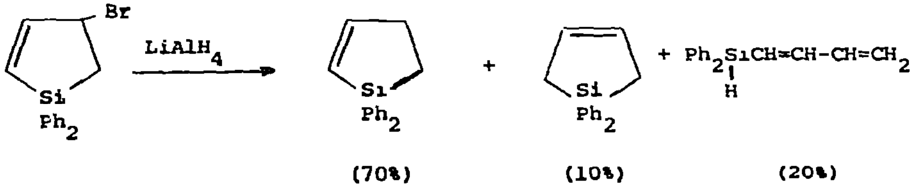


Free-radical bromination of silacyclopent-3-enes results in alpha- and/or beta-bromosilacyclopentenes. Product distribution is highly dependent on the substituents at silicon. The ring-opened product,

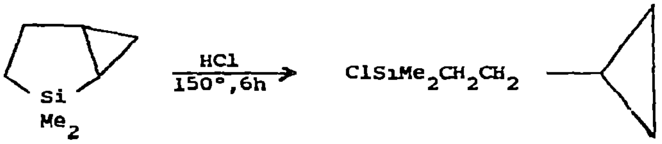


	A (%)	B (%)
R = Me; R' = Me	35	65
= Ph; = Me	25	75
= Ph; = Ph	0	100
= Ph; = $CH{=}CH_2$	0	100

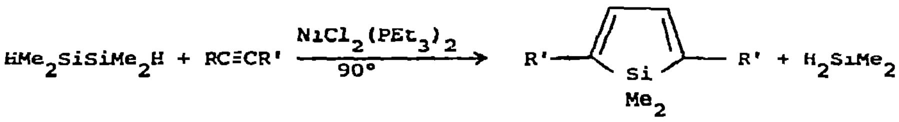
$RR'SiBrCH{=}CH{-}CH{=}CH_2$ was not observed in these reactions. Reduction of the β-bromo product affords a method for the overall conversion of a β,γ- to an α,β-silacyclopentene.[254] An unexpectedly facile ring-opening



reaction of 2,2-dimethyl-2-silabicyclo[3.1.0]hexane by anhydrous HCl has been observed. In contrast to the behavior of the isomeric 3-silabicyclo[3.1.0]hexane, in which C-C bond cleavage is observed, Si-C bond cleavage occurs in the 2-sila isomer.[255]

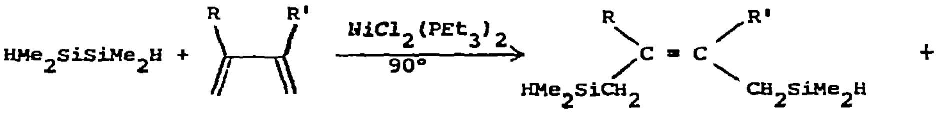


A number of new synthetic methods leading to the silacyclopentadiene system are now available. One process[256] is thought to involve



R = Ph; R' = Ph	(56%)
R = Ph; R' = Me	(44%)
R = Et; R' = Et	(95%)
R, R' = Me or nBu	(100%)

the intermediacy of "dimethylsilylene", as the omission of acetylene results in the previously observed formation of the trisilane $HMe_2SiSiMe_2SiMe_2H$. Dimethylacetylenedicarboxylate does not afford cyclic product The use of 1,3-dienes under similar conditions led to products of apparent dihydrosilylation and hydrodisilanylation. In another method,



$MeCR{=}CR'CH_2SiMe_2SiMe_2H$

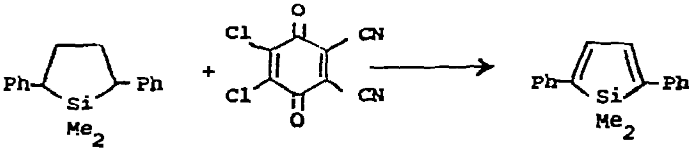
R = H; R' = H

R = H; R' = Me

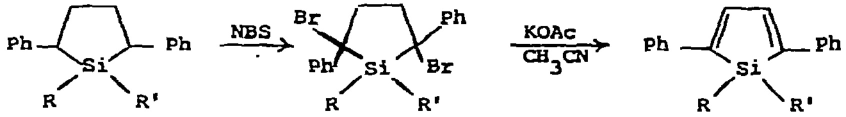
R = Me; R' = Me

R = H; R' = Ph

1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene was prepared by dehydrogenation.[257]



Similarly substituted compounds are obtainable by a three-step synthesis beginning with the silacylclopentane. Yields for each of the last two steps range from 40-65%.



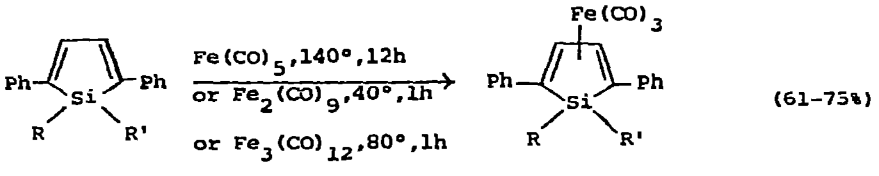
R = Et; R' = Et

R = nBu; R' = nBu

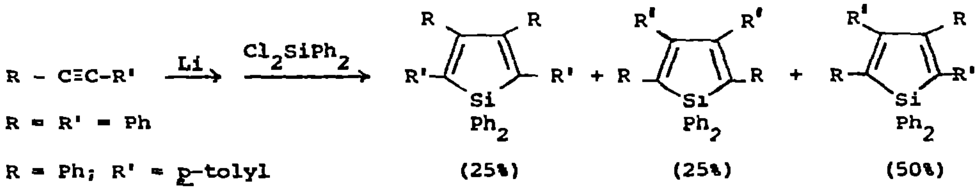
R = Me; R' = Et

R = Me; R' = Ph

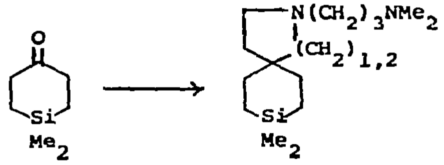
The dienes thus prepared underwent the expected cycloaddition reactions with diphenylacetylene and maleic anhydride to give 7-silabicyclic compounds. Dimethyl acetylenedicarboxylate afforded an adduct which spontaneously lost silicon to form a compound identified as a dimethyldihydrodiphenylphthalate, but may more likely be the dimethyl diphenylphthalate itself. Reaction of the silacyclopentadienes with iron carbonyls resulted in good yields of the iron complexes.[258]



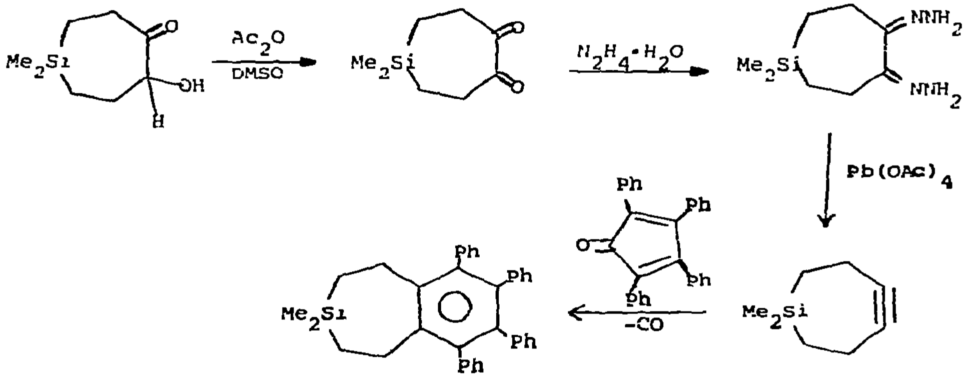
Fully arylated silacyclopentadienes have been prepared by the dimerization of diaryl acetylenes with lithium followed by reaction with diphenyldichlorosilane. The mixed acetylene, phenyl-p-tolyl acetylene, gave three isomers whose proportions were determined by NMR spectra.[259]



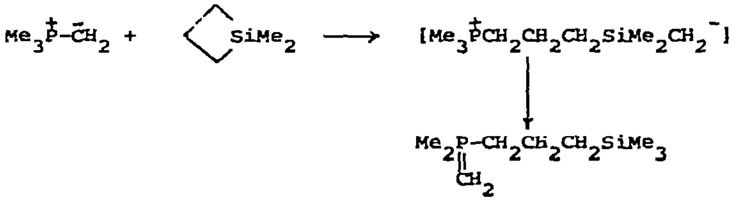
Silaazaspiro[4.5]decanes and silaazaspiro[5.5]undecanes have been synthesized from 4,4-dimethyl-4-silacyclohexanone.[260]

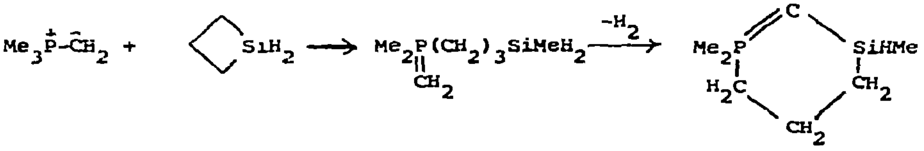


The synthesis of 1,1-dimethyl-1-sila-4-cycloheptyne was attempted in the expectation that the longer Si-C bond would render this alkyne more stable than its all-carbon counterpart. A product was obtained that had a half-life of 108 h in dilute CH_2Cl_2 solution at 4° and reacted in the expected fashion with tetraphenylcyclopentadienone.[261]

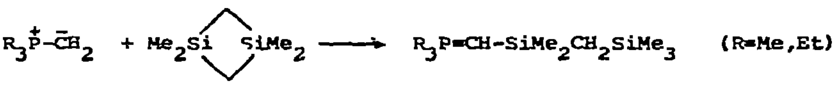


The product obtained from the reaction between trimethylmethylenephosphorane and 1,1-dimethylsilacyclobutane suggests that this may represent ring opening *via* C-C bond cleavage instead of the normal Si-C bond attack usually experienced by silacyclobutanes.[262] The use of silacyclobutane itself in the reaction leads at 0° to a cyclization of the initial product.

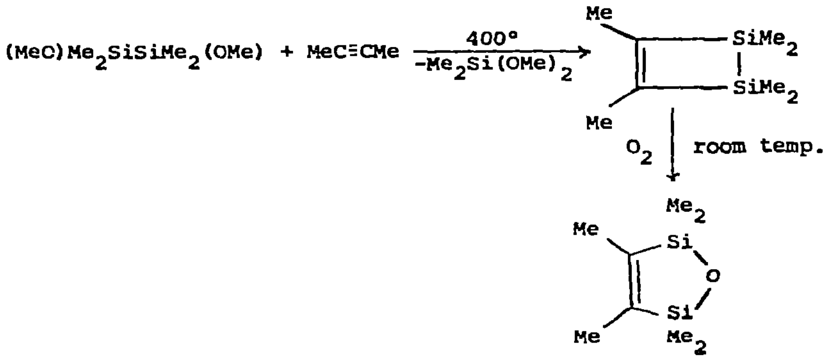




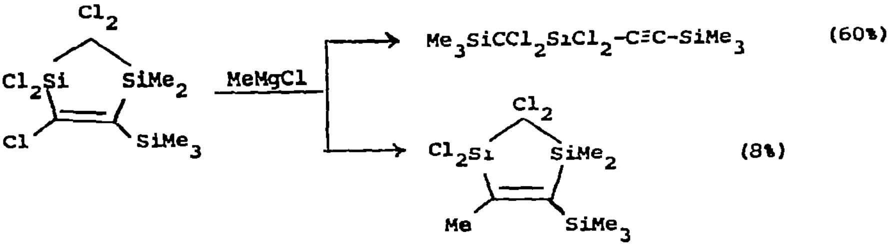
Normal Si-C bond cleavage is observed when 1,1,3,3-tetramethyldisilacyclobutane is employed.



Vapor phase thermolysis of 1,2-dimethoxytetramethyldisilane in the presence of 2-butyne afforded the novel and highly reactive hexamethyl-1,2-disila-3-cyclobutene, perhaps formed *via* a dimethylsilylene insertion into an intermediate silacyclopropene.[263]

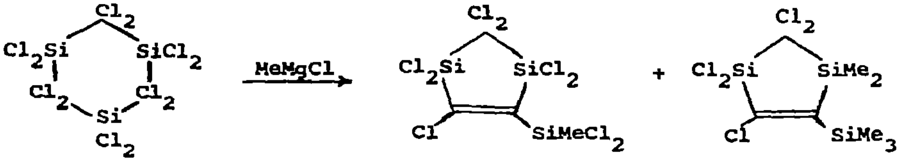


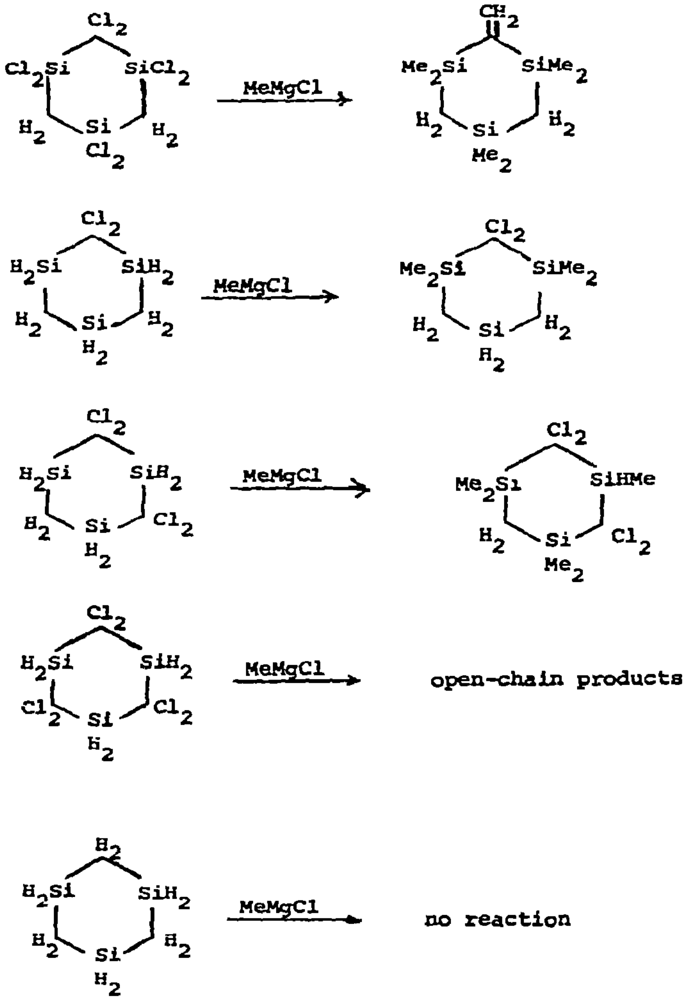
A number of partially- and extensively-methylated cyclic and acyclic derivatives of 1,3-disila-4-trimethylsilylpentene are produced upon treatment of the disilapentene with methyl magnesium chloride. Use of an



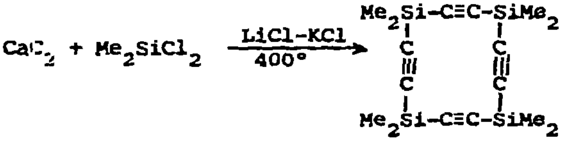
8-fold excess of methyllithium resulted in cleavage of initially-formed open-chain products to give Me_4Si, $Me_3SiCHMeSiMe_3$ and $Me_3SiCClMeSiMe_3$ as the major components of the product mixture.[264]

The disilapentene employed for the above investigations was obtained by a ring-contraction reaction of perchloro-1,3,5-trisilacyclohexane with methylmagnesium chloride. Concurrently, the behavior of other 1,3,5-trisilacyclohexanes with this Grignard reagent was also investigated.[265]

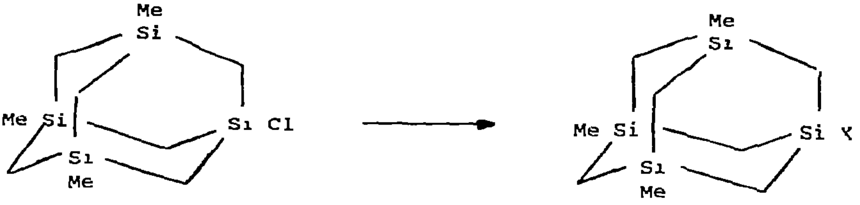




The reaction of calcium carbide with dichlorodimethylsilane in fused LiCl-KCl affords low yields of a twelve-membered tetrasilatetrayne.[266]



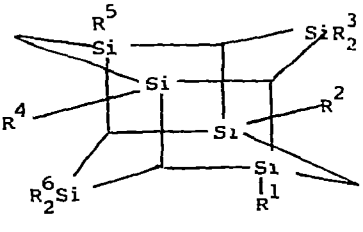
In contrast with earlier results which showed that 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (Me_3AdCl) was only sluggishly reactive with lithium aluminum hydride and water-triethylamine, this silaadamantane has been found to undergo facile reaction with various other reagents at 25°.

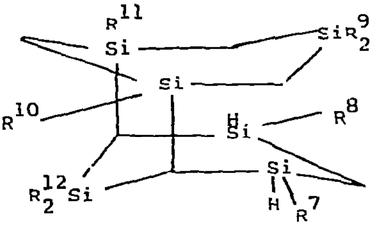


Reagent	Solvent	Rxn Time	Product (X =)	Yield (%)
NaOMe	HOMe	<15 min	OMe	86
$PhCH_2\overset{+}{N}Me_3\overset{-}{O}H$	HOMe	<15 min	OMe	92
HOMe	HOMe	24 h	no reaction	
$c\text{-}C_6H_{11}\overset{+}{N}H_3\overset{-}{F}$	HOMe	1.5 h	F	90
"	$CHCl_3$	12 h	F	89
MeLi	Et_2O-TMEDA	0.5 h	Me	70

The dichloro analogue, Me_2AdCl_2, was also found to be very reactive towards NaOMe/HOMe; $Me_2Ad(OMe)_2$ was formed in 93% yield in less than 2 minutes. In addition, Me_3AdOMe was easily reduced (25°,4h) by ethereal iBu_2AlH to Me_3AdH in 86% yield.[267]

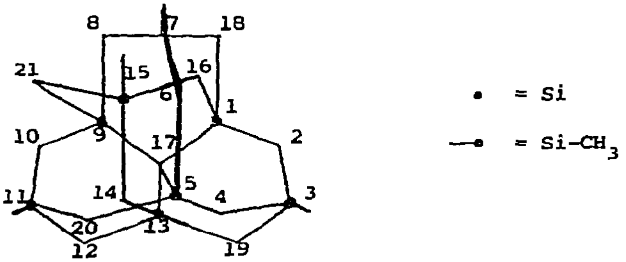
A number of transformations involving the octachlorohexasilaasterane system have been carried out. Treating the compound with R^1-R^6 = Cl with two equivalents of $LiAlH_4$ gives the products with $R^3 = R^6 = H$; R^1, R^2, R^4, R^5 = Cl and R^1-R^6 = H in a 1:5 ratio.



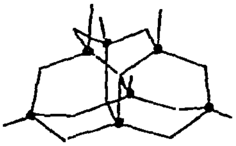


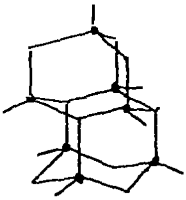
Both of these may be rechlorinated to give back the original starting material. If a 10-fold molar excess of $LiAlH_4$ is employed in the reduction step, ring cleavage occurs to give the tricyclic compound shown with R^7-R^{12} = H. Use of MeMgCl in place of $LiAlH_4$ results in the production of methylated derivatives with R^1,R^2,R^4,R^5 = Cl, R^3,R^6 = Me and R^1-R^6 = Me. No reaction of the octachloro compound with chlorine or bromine is observed, but the octamethyl derivative is cleaved by HBr to give the tricyclic product with R^7,R^8 = Br, R^9-R^{12} = Me.[268]

Separation of the products formed in the pyrolysis (700°) of tetramethylsilane has afforded a new type of carbosilane whose six-membered rings of alternating silicon and carbon atoms exist only in boat forms. A nomenclature system for this class of compounds was also proposed. For example, the product shown below is named 3,7,11,15-tetramethyl-1,-3,5,7,9,11,13,15-octasiladodecascaphane

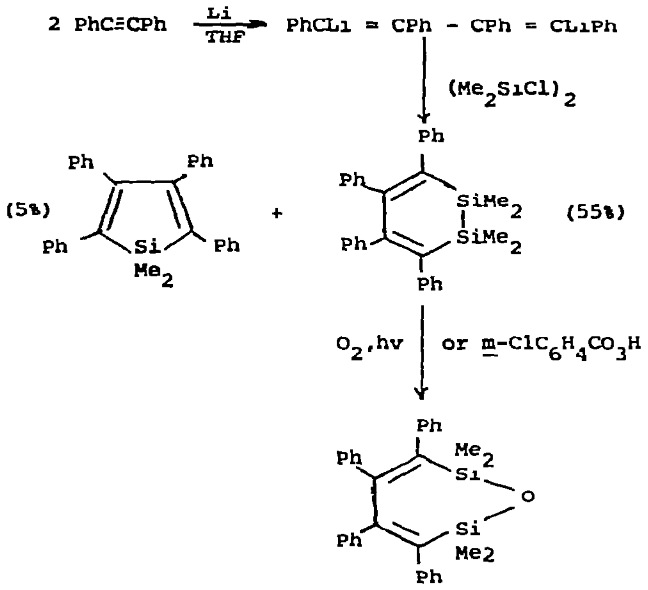


Other products characterized were as follows, the last structure representing a combination of chair (carborundane-type) and boat configurations.[269]



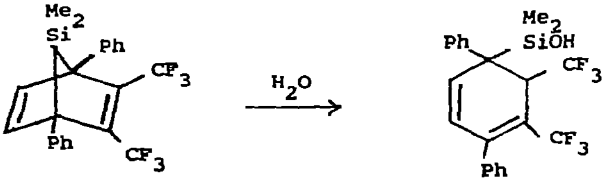


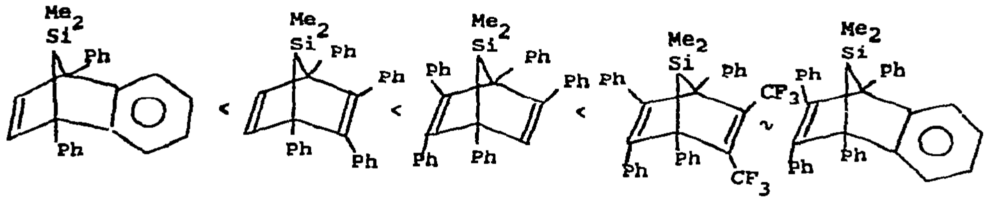
A preparation of the novel 1,2-disilacyclohexadiene system has been described. The disilane undergoes ready oxidation to the cyclic siloxane.



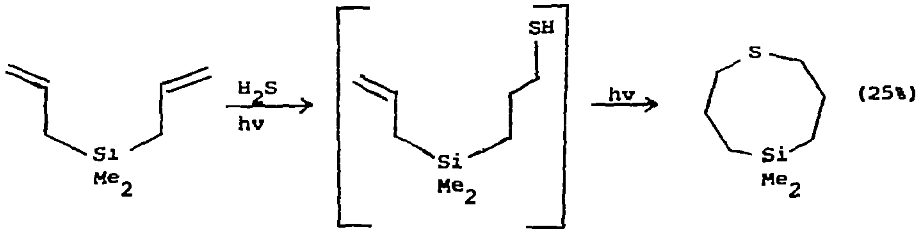
Other peroxides [(tBuO)$_2$ and tBuOOH] also led to the siloxane. Since Si-Si bonds in, e.g., 1,2-diphenyltetramethyldisilane are much less reactive towards oxidation, ring strain may be a factor in the enhanced reactivity displayed by the cyclic system.[270]

The facile reaction of 2,3-bis(trifluoromethyl)-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene with water was investigated and a ring-opened product characterized. In addition, the facility of thermal decomposition (presumably *via* expulsion of dimethylsilylene in each case) of a number of 7-silanorbornadienes was determined by mass spectrometry and compared with reported data. In general, stability towards elimination is increased by increasing numbers of substituents on the basal ring. The following order of thermal stability was indicated for the compounds shown.[271]



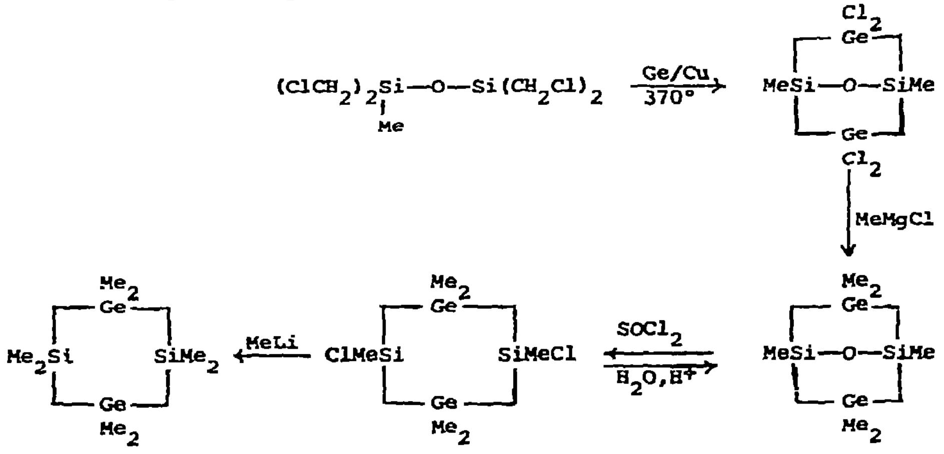


An eight-membered silicon heterocycle is formed upon irradiation of an H_2S-dimethyldialkylsilane mixture at -78°. Irradiation of an independently prepared sample of the intermediate thiol under like conditions gave



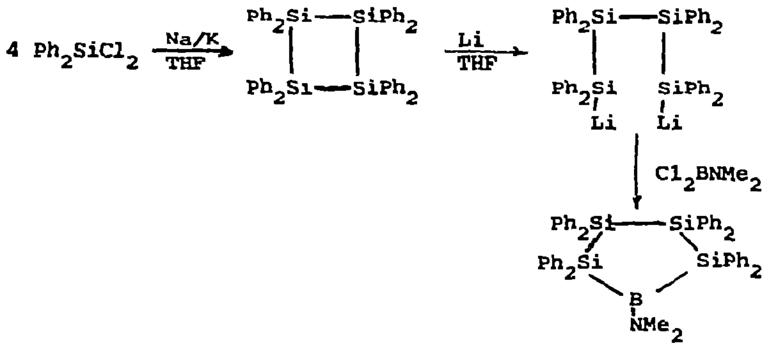
comparable yields of 1,1-dimethyl-1-sila-5-thiacyclooctane.[272]

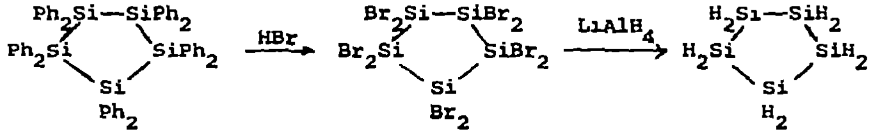
Both germanium and silicon are constituents of a novel eight-membered ring system prepared as shown.[219]



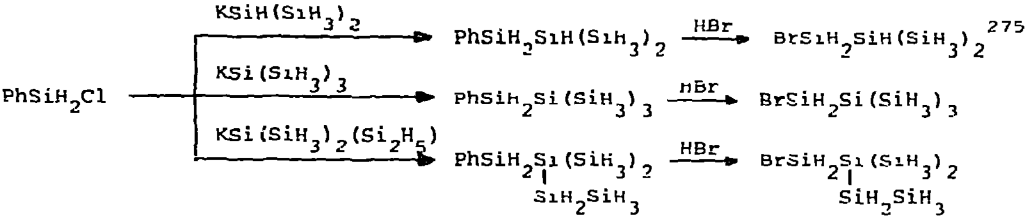
VII. POLYSILANES

The first boron-containing[273] and unsubstituted[274] cyclopentasilanes have been synthesized. The dilithium precursor to the boron heterocycle can be isolated as its tetrahydrofuran complex.





Syntheses of various polysilanes have been carried out by the methods indicated below.

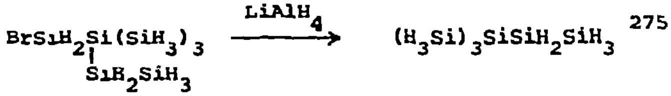


$PhSiH_2Cl \xrightarrow{KSiH(SiH_3)_2} PhSiH_2SiH(SiH_3)_2 \xrightarrow{HBr} BrSiH_2SiH(SiH_3)_2$ [275]

$PhSiH_2Cl \xrightarrow{KSi(SiH_3)_3} PhSiH_2Si(SiH_3)_3 \xrightarrow{HBr} BrSiH_2Si(SiH_3)_3$

$PhSiH_2Cl \xrightarrow{KSi(SiH_3)_2(Si_2H_5)} PhSiH_2Si(SiH_3)_2(SiH_2SiH_3) \xrightarrow{HBr} BrSiH_2Si(SiH_3)_2(SiH_2SiH_3)$

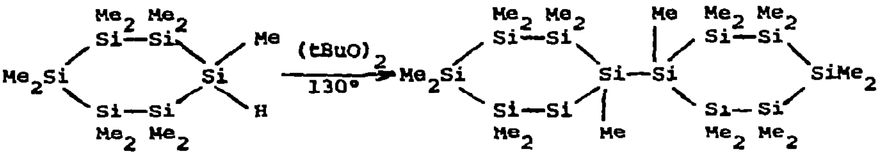
$BrSiH_2Si(SiH_3)_3 \xrightarrow{LiAlH_4} Si(SiH_3)_4$ 275



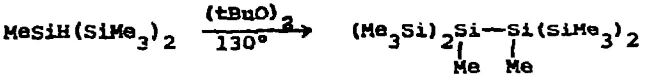
$BrSiH_2Si(SiH_3)_2(SiH_2SiH_3) \xrightarrow{LiAlH_4} (H_3Si)_3SiSiH_2SiH_3$ 275

$Si(SiCl_3)_4 \xrightarrow{LiAlH_4} SiH_4 + (H_3Si)_2SiHSiH_2SiMe_3 + Si(SiH_3)_4$ 276

$(Me_3Si)_3SiH \xrightarrow[130°]{(tBuO)_2} (Me_3Si)_3SiSi(SiMe_3)_3$ (92%) 277



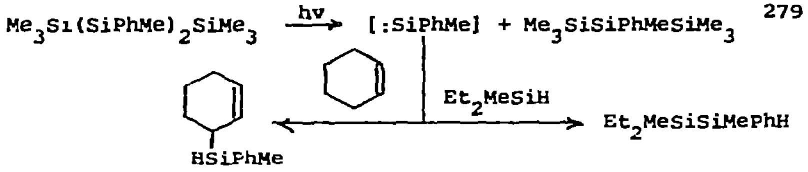
(66%) 277



$MeSiH(SiMe_3)_2 \xrightarrow[130°]{(tBuO)_2} (Me_3Si)_2Si(Me)\text{—}Si(Me)(SiMe_3)_2$ (52%) 277

$$CaSi_2(+10\%\ FeSi_2) \xrightarrow{Cl_2} Si_3Cl_8 \xrightarrow[Et_3N]{MeOH} Si_3(OMe)_8 \quad (12\text{-}15\%)$$ [278]

The following transformations are of interest in the chemistry of polysilanes.

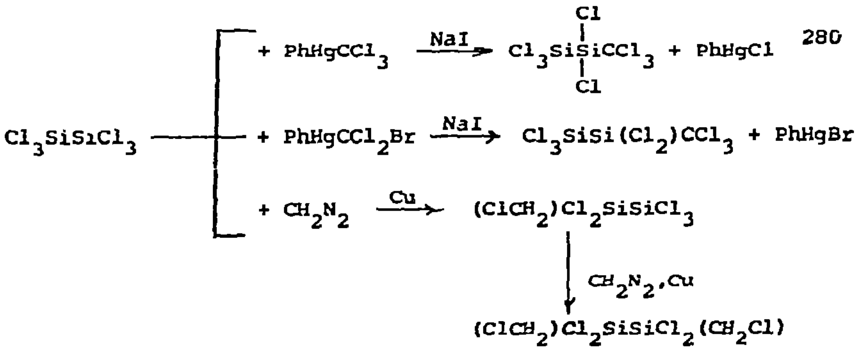


$$Me_3Si(SiPhMe)_2SiMe_3 \xrightarrow{h\nu} [:SiPhMe] + Me_3SiSiPhMeSiMe_3$$ [279]

$$[:SiPhMe] \xrightarrow{Et_2MeSiH} Et_2MeSiSiMePhH$$

HSiPhMe

(a transient silacyclopropane was postulated)



$$Cl_3SiSiCl_3 + PhHgCCl_3 \xrightarrow{NaI} Cl_3Si\overset{Cl}{\underset{Cl}{Si}}CCl_3 + PhHgCl$$ [280]

$$Cl_3SiSiCl_3 + PhHgCCl_2Br \xrightarrow{NaI} Cl_3SiSi(Cl_2)CCl_3 + PhHgBr$$

$$Cl_3SiSiCl_3 + CH_2N_2 \xrightarrow{Cu} (ClCH_2)Cl_2SiSiCl_3 \xrightarrow{CH_2N_2, Cu} (ClCH_2)Cl_2SiSiCl_2(CH_2Cl)$$

$$Me_3SiSiMe_2H + ROH \xrightarrow{(PPh_3)_3RhCl} Me_2Si(H)OR + Me_3SiH$$ [281]

$$HMe_2SiSiMe_2H + ROH \xrightarrow{''} Me_2Si(H)OR + Me_2SiH_2$$ [281]

or

$$Me_2Si(OR)_2 + Me_2SiH_2$$

$$HMe_2SiSiMe_2SiMe_2H + ROH \xrightarrow{(PPh_3)_3RhCl} Me_2SiH(OR) + (HMe_2)_2Si_2$$ [281]

or

$$Me_2Si(OR)_2 + (HMe_2)_2Si_2$$ [282]

$$PhMeSiH_2 \xrightarrow[70^\circ]{(PPh_3)_3RhCl} \underset{(30\%)}{Ph_2MeSiH} + \underset{(14\%)}{HMePhSiSiPhMeH} + \underset{(30\%)}{HMePhSiSi(MePh)SiPhMeH}$$ [282]

$$Ph_2SiH_2 \xrightarrow{''} \underset{(8\%)}{Ph_3SiH} + \underset{(38\%)}{HPh_2SiSiPh_2H}$$ [282]

$$PhSiH_3 \xrightarrow{''} (H_2PhSi)_2 + HPh_2SiSiPhH_2 + H_2PhSi(PhH)SiPhH_2$$ [282]

The formation of charge-transfer complexes between both linear and cyclic polysilanes and tetracyanoethylene has been observed.[283,284]

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