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The tris(trimethylsilyl)silyl group in organic, coordination and organometallic chemistry

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Abstract. The published data on the synthesis, reactivities and applications of organic, coordination and organometallic compounds containing a $(Me_3Si)_3Si$ group are generalised and systematised. The bibliography includes 230 references.

I. Introduction

Among diverse organosilicon substituents of the type R_3Si, trialkylsilyl (Me_3Si, Et_3Si, Pr^i_3Si, Bu^t_3Si), triphenylsilyl (Ph_3Si) and tris(trimethylsilyl)silyl [$(Me_3Si)_3Si$] groups (hereinafter referred to as the TTS group)† attract the greatest attention of researchers. The choice of a particular group is usually determined not only by physicochemical characteristics of compounds that are essential for a specific goal, but also by commercial availability of their precursors. Until recently, compounds containing a TTS group were considered to be exotic. Significant progress has been achieved over the past decade in the development of methods for the synthesis and investigation of properties of TTS derivatives and their practical applications. Abundant experimental material accumulated thus far demands systematisation and generalisation. Yet another aim of this review is the discussion of specific characteristics of the TTS group, which differs markedly from other bulky substituents, such as [Bu^t_3Si (see Ref. 1), Pr^i_3Si (see Ref. 2) and Ph_3Si (see Ref. 3)], in its reactivity. This is due, first of all, to the high sensitivity of the highly polarisable Si – Si bond to nucleophilic and electrophilic reagents and to oxidation. In some cases, it can be activated by transition metals. In addition, molecules containing a system of Si – Si bonds can serve as precursors for silylenes when undergoing thermolysis or UV irradiation. Thus, the properties of the $(Me_3Si)_3Si$ group are rather specific and its functions are not confined solely to its use as a bulky substituent or a protecting group.

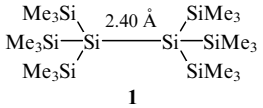
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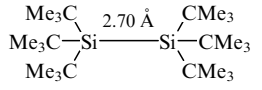
II. Steric and electronic effects of the $(Me_3Si)_3Si$ group

1. Steric effect

The tris(trimethylsilyl)silyl group possesses a pronounced steric effect which is nevertheless weaker than that of its closest analogue, *viz*., the tris(*tert*-butyl)silyl group. A comparison of the structures of $(Me_3Si)_6Si_2$ (**1**) and $(Bu^t_3Si)_2$ (**2**) molecules shows that the distance between the central silicon atoms in compound **1** (2.40 Å) does not differ substantially from the average normal value (2.35 Å), whereas that in molecule **2** is 2.70 Å. Nevertheless, the conclusion that molecule **1** is sterically overcrowded can be drawn from the fact that some distances between the carbon atoms belonging to different $(Me_3Si)_3Si$ groups are as small as 3.52 Å, which is 12% smaller than the sum of the van der Waals radii of two methyl groups, 2.00 Å each.[3, 4]



1



2

The steric effect of the TTS group was estimated using various methods including computation.[5] Thus the dynamic NMR method allowed determination of the barrier to rotation of the mesityl groups around the Mes – C bond in compounds $Mes_2C = C(OH)R$ [R = H, Me, Et, Pr^i, Bu^t, $(Me_3Si)_3Si$]. It was found that the steric effect of the TTS group on the coalescence of aromatic protons differs little from that of the *tert*-butyl group. Correlation and computational data suggest that the steric constant (E_s) of the TTS group varies from −1.46 to −1.6 (see Ref. 5), which is close to the E_s value for the Me_3C group (−1.54), but is significantly smaller than the corresponding value for the tris(trimethylsilyl)methyl group (−3.8) the van der Waals radius of which is close to that of the TTS group.[5] Such a pronounced difference in the steric constants is due to the greater distance between the TTS fragment and the reaction centre in comparison with the $(Me_3Si)_3C$ group owing to the difference in the lengths of the Si – Si and Si – C bonds.

† The term 'hypersilyl group' is generally accepted in the literature, this is also used in the present review.

2. Electronic effects of the $(Me_3Si)_3Si$ group

The tris(trimethylsilyl)silyl substituent can significantly stabilise the ground state of molecular ions. As can be seen from Table 1, the ionisation potentials of compounds containing a TTS group are much lower than those of their analogues due to significant delocalisation of the positive charge in the radical cations formed.

Table 1. The first ionisation potentials (I) of certain disilanes and benzene 1,4-derivatives.[6]

Compound	I /eV	Compound	I /eV
$F_3Si-SiF_3$	13.20	$H-C_6H_4-H$	9.24
$H_3Si-SiH_3$	10.53	$Me_3C-C_6H_4-CMe_3$	8.30
$Me_3Si-SiMe_3$	8.69	$(Me_3C)_3Si-C_6H_4-Si(CMe_3)_3$	7.45
$(Me_3Si)_4Si$	8.24	$(Me_3Si)_3Si-C_6H_4-Si(SiMe_3)_3$	7.37
$(Me_3Si)_3Si-Si(SiMe_3)_3$	7.79		

The changes in the ionisation potentials also agree with a decrease in the reduction half-wave potentials for Me_6Si_2 and $(Me_3Si)_4Si$ ($+1.400$ and $+1.320 \pm 0.005$ V, respectively),[7] which also suggests the somewhat greater proneness of tetrakis(trimethylsilyl)silane to oxidation.

A comparison of dissociation constants of carboxylic acids measured in 76% ethanol has shown[8] that tris(trimethylsilyl)silanecarboxylic acid [hypersilylcarboxylic acid, $(Me_3Si)_3SiCO_2H$] is weaker ($pK_a = 9.33$) than its closest analogues, *viz*., Me_3CCO_2H ($pK_a = 7.96$) and Ph_3SiCO_2H ($pK_a = 6.10$), which testifies to the σ-donor nature of the TTS group.

The tris(trimethylsilyl)silyl substituent can also stabilise the negative charge: more than half of the π-spin density in the 1,4-bis[tris(trimethylsilyl)silyl]benzene radical anion is localised on the $(Me_3Si)_3Si$ groups.[4] Studies on the phenyltris(trimethylsilyl)silane, $[(Me_3Si)_3SiPh]^{\bullet -}$ radical anion revealed that the TTS group behaves as a π-acceptor.[9]

Studies of electron affinities (EA) of a series of silyl radicals revealed that the radical $(Me_3Si)_3Si^{\bullet}$ has the highest value of EA (Table 2). The stability of silicenium anions increases significantly with an increase in the number of trimethylsilyl substituents at the central silicon atom.

Table 2. Electron affinities of silyl radicals.

Radical	EA /kcal mol^{-1}	Ref.
$(Me_3Si)_3Si^{\bullet}$	46.8	10
$(Me_3Si)_2HSi^{\bullet}$	44.7	10
$Me_2HSiMe_2Si^{\bullet}$	32.3	10
$Me_2HSi^{\bullet}$	24.7	11
$Me_3Si^{\bullet}$	22.4	11

It is known that silyl radicals exist predominantly in the pyramidal form with high configurational stability.[12] The rates of subsequent reactions of these radicals exceed their inversion rates. However, the fact that silyl radicals containing a Si–Si group yield racemic products[13] is in accord with an increasing deviation from planarity in the series:[14] $(Me_3Si)_3Si^{\bullet} < (Me_3Si)_2MeSi^{\bullet} < Me_3SiMe_2Si^{\bullet} < Me_3Si^{\bullet}$. The constants of the hyperfine coupling a (^{29}Si) in the ESR spectra change in the same order (Table 3).

Presumably, the stabilities of silyl radicals increase in the following order: $Me_3Si^{\bullet} < Me_3SiMe_2Si^{\bullet} < (Me_3Si)_2MeSi^{\bullet} < (Me_3Si)_3Si^{\bullet}$, mainly due to hyperconjugation with the β-Si–C bond.[21]

^{29}Si NMR spectroscopy has proved to be the most efficient method for obtaining information about the nature of the fragment linked to the TTS group and, correspondingly, about the electronic state of the TTS group itself. The values of experimentally determined chemical shifts vary in the range of more than 300 ppm (Table 4).

Table 3. Some parameters of the ESR spectra of silyl radicals.

Radical	a (^{29}Si) /Gauss	g	Ref.
$(Me_3Si)_3Si^{\bullet}$	64	2.0053	15, 16, 17
$(Me_3Si)_2MeSi^{\bullet}$	90	2.0045	18
$Me_3SiMe_2Si^{\bullet}$	137	2.0037	15, 16
$Me_3Si^{\bullet}$	181	2.0031	15, 16, 19, 20

Table 4. The chemical shifts (δ) in the ^{29}Si NMR spectra of central silicon atoms of some TTS derivatives.

Compound	δ (Si–$SiMe_3$)	Ref.
$(Me_3Si)_3SiK$	−195.8	22
$(Me_3Si)_3SiLi(THF)_3$	−185.4	23
$(Me_3Si)_3SiSnMe_3$	−136.6	24
$(Me_3Si)_3SiSiMe_3$	−135.6	22
$(Me_3Si)_3SiSi(SiMe_3)_3$	−129.5	22
$(Me_3Si)_3SiH$	−115.4	22
$(Me_3Si)_3SiEt$	−78.6	22
$(Me_3Si)_3SiHfCp^*Cl_2$ (see [a])	−49.77	25
Me_3SiK	−34.4	22, 26
$Me_3SiSiMe_3$	−20.5	22
$(Me_3Si)_3Si[B(C_6F_5)_4]$	+111.1	27
$[(Me_3Si)_3SiPh]^+$ (see [b])	+205.8	28
$(Me_3Si)_3Si^+$ (see [b])	+920.4	28

[a] Cp* is Me_5C_5; [b] calculated data.

The largest negative values of the chemical shifts (the high field) are characteristic of alkali metal hypersilanides where a considerable negative charge is localised on the central silicon atom. Contrariwise, the chemical shifts of the silicenium cations lie in the low field. The complex ion $[(Me_3Si)_3SiPh]^+$ formed upon dissolution of $(Me_3Si)_3Si[B(C_6F_5)_4]$ in benzene has the highest chemical shift for the TTS group hitherto known ($\delta = +111.1$). The calculated values of chemical shifts for the free ions $(Me_3Si)_3Si^+$ (in the gas phase) and $[(Me_3Si)_3SiPh]^+$, δ, are $+920.4$ and $+205.8$, respectively. It is suggested that the tris(trimethylsilyl)silicenium ion in benzene exists as a σ-complex $R_3Si-C_6H_6^+$ with a weak Si–C bond (13.6 kcal mol^{-1}).[28]

Quite naturally, the increasing applications of the Me_3Si group account for the progress in the chemistry of tris(trimethylsilyl)silane derivatives. By the time of the first synthesis of TTS derivatives, this group had widely been used in organic synthesis for protection of alcohols and enols.[29–32] Tetrakis(trimethylsilyl)silane and tris(trimethylsilyl)silane are the key compounds in the synthesis of numerous organometallic and organoelement compounds containing a TTS group; therefore, it seems expedient to begin with the consideration of methods for their synthesis and their reactivities.

III. Tetrakis(trimethylsilyl)silane and its reactions

The pioneering studies of the tris(trimethylsilyl)silyl group date back to 1964 when Gilman and Smith[33] synthesised tetrakis(trimethylsilyl)silane (**3**) by the reaction of chlorotrimethylsilane with $SiCl_4$ in the presence of metallic lithium in tetrahydrofuran.

$$4\ Me_3SiCl + SiCl_4 \xrightarrow[THF]{Li} (Me_3Si)_4Si$$

3 (70%)

In addition to compound **3**, this reaction yields an insoluble organosilicon polymer, which hampers the isolation of the target product.

It is known that tetrakis(trimethylsilyl)silane (**3**) is a side product in the preparation of tris(trimethylsilyl)silane (**4**);[34] however, it is often formed in substantial amounts due to exchange nucleophilic processes (see Section V.1.b).

$$Me_3SiCl\ (excess) + HSiCl_3 \xrightarrow[-10\ ^\circ C]{Li} \underset{\mathbf{4}\ (\sim 70\%)}{(Me_3Si)_3SiH} + \underset{\mathbf{3}\ (\sim 30\%)}{(Me_3Si)_4Si}$$

If this reaction is carried out at 20 °C, $(Me_3Si)_4Si$ is formed as the major product.

Compound **3** is stable in air and manifests high thermostability (m.p. 319–321 °C) (in a sealed capillary), sublimation temperature > 265 °C (at atmospheric pressure) and is easily sublimed *in vacuo*. The $(Me_3Si)_4Si$ molecule represents a virtually ideal sphere and has a rigid backbone with a tetrahedral symmetry.[35]

Tetrakis(trimethylsilyl)silane and other molecules containing a TTS fragment are easily obtained upon catalytic electrophilic rearrangements of linear polysilanes.[36]

$$Me(Me_2Si)_5Me \xrightarrow{AlCl_3,\ 1\%\ FeCl_3} \mathbf{3}\ (\sim 100\%)$$

Studies into the reactivity of $(Me_3Si)_4Si$ have shown that this is sensitive to both nucleophilic and electrophilic reagents. Treatment of compound **3** with methyllithium in THF results in elimination of the trimethylsilyl group in the form of tetramethylsilane and formation of a tris(trimethylsilyl)silyllithium–THF complex (**5**).[37]

$$\underset{\mathbf{3}}{(Me_3Si)_4Si} + MeLi \xrightarrow{THF-Et_2O} \underset{\mathbf{5}}{(Me_3Si)_3SiLi(THF)_3} + Me_4Si$$

The lithium derivative **5** is readily soluble in saturated and aromatic hydrocarbons, which is a prerequisite for subsequent syntheses.

Marschner[22] has prepared tris(trimethylsilyl)silylpotassium (**6**) in 80% yield by splitting the Si–Si bond with yet another strong nucleophile, *viz*., potassium *tert*-butoxide, in THF or dimethoxyethane (DME).[22]

$$\underset{\mathbf{3}}{(Me_3Si)_4Si} + Bu^tOK \longrightarrow \underset{\mathbf{6}}{(Me_3Si)_3SiK} + Bu^tOSiMe_3$$

Depending on the nature of the electrophile, treatment of silane **3** with strong electrophilic reagents results in cleavage of either Si–Si or Si–C bonds. Thus acetyl chloride reacts with compound **3** to eliminate four terminal methyl groups, which yields tetrakis(chlorodimethylsilyl)silane (**7**).[38]

$$\underset{\mathbf{3}}{(Me_3Si)_4Si} + 4\ MeC(O)Cl \xrightarrow{AlCl_3} \underset{\mathbf{7}}{(Me_2ClSi)_4Si} + 4\ Me_2CO$$

This reaction occurs in a stepwise manner in several steps, but the isolation and purification of the intermediate products present a considerable problem.

The reactions of halogens with silane **3** result in cleavage of the Si–Si bond.

$$\underset{\mathbf{3}}{(Me_3Si)_4Si} + 4\ Hal_2 \longrightarrow 4\ Me_3SiHal + SiHal_4$$

Hal = Cl, Br, I.

Compounds containing a $(Me_3Si)_3Si$ group and related compounds containing a $(Me_3Si)_3C$ group react with trifluoroacetic acid to yield different products.[39]

$$(Me_3Si)_3SiSiMe_2OMe + CF_3CO_2H \xrightarrow[-MeOH]{} (Me_3Si)_3SiSiMe_2O_2CCF_3,$$

$$(Me_3Si)_2C(SiMe_3)(SiMe_2OMe) \xrightarrow[-MeOH]{CF_3CO_2H} \underset{\mathbf{A}}{(Me_3Si)_2C^+(Me)(SiMe_2)_2\ CF_3CO_2^-} \xrightarrow[-CH_4]{CF_3CO_2H} (Me_3Si)_2C[SiMe_2OC(O)CF_3]_2.$$

Such a drastic difference is due to the formation, in the latter case, of intermediate cyclic silicenium cations **A** where elimination of methane occurs smoothly with simultaneous demethoxylation.[39]

IV. Tris(trimethylsilyl)silane and its reactions

Tris(trimethylsilyl)silane can be prepared by either direct synthesis from $HSiCl_3$ and Me_3SiCl or by acid hydrolysis of alkali metal silanides.[40]

$$(Me_3Si)_3SiLi + H_3O^+ \longrightarrow \underset{\mathbf{4}}{(Me_3Si)_3SiH} + Li^+ + H_2O$$

Despite its high cost, tris(trimethylsilyl)silane (TTSH, **4**) is becoming more and more popular as a versatile, mild and selective reducing agent for organic compounds.[41] Its efficiency exceeds those of other silicon hydrides. Presumably,[41] this can be attributed to the low dissociation energy of the Si–H bond in this compound in comparison with other organosilanes (Table 5).

Table 5. Dissociation energies (E_D) of the Si–H bond of some organosilanes.

$R-H \longrightarrow R^\bullet + H^\bullet$

Compound	E_D /kcal mol^{-1}	Ref.
$(Me_3Si)_3SiH$ (**4**)	79.0	10, 42
$Me_3SiSiMe_2H$	85.3	10, 42
Et_3SiH	90.1	10, 42
Me_3SiH	91.0	43, 44
F_3SiH	100.1	43, 44

1. Reduction of functional groups in organic compounds

Reduction with $(Me_3Si)_3SiH$ (**4**) is a radical-chain process. Di-*tert*-butyl peroxide and azobisisobutyronitrile (AIBN) are used as initiators. The mechanism of the Bu^tOOBu^t-induced reaction can be represented by the following scheme:

$$Bu^tOOBu^t \longrightarrow 2\ Bu^tO^\bullet,$$

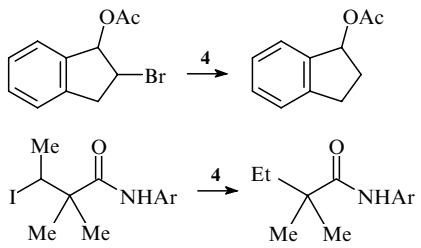
$$Bu^tO^\bullet + \underset{\mathbf{4}}{(Me_3Si)_3SiH} \longrightarrow Bu^tOH + (Me_3Si)_3Si^\bullet,$$

$$(Me_3Si)_3Si^\bullet + RX \longrightarrow (Me_3Si)_3SiX + R^\bullet,$$

$$(Me_3Si)_3SiH + R^\bullet \longrightarrow RH + (Me_3Si)_3Si^\bullet.$$

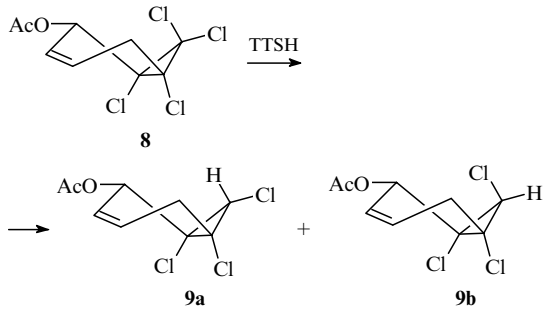
The rate ratios of individual steps make it possible to maintain the chain of radical reactions in an optimum regime for the majority of substrates. The use of other silicon hydrides (trialkyl, aryl and chlorosilanes) for the reduction of functional groups is limited due to the high dissociation energies of their Si–H bonds, which prevent the formation of extended radical chains.

The reduction of organic halides takes place upon heating equimolar amounts of $(Me_3Si)_3SiH$ and a substrate in a solvent in the presence of ~5%–10% of the initiator at the temperature of its decomposition. In these reactions, the product yields are usually high for the majority of RX substrates (R = Alk; X = Cl, Br, I).[45–47]



The selectivity of $(Me_3Si)_3SiH$ was found to be extremely high.

A detailed comparative study of the stereoselectivity of the reduction of organic *gem*-dichlorides with tris(trimethylsilyl)silane and tributylstannane has been carried out. It was found that despite numerous common features, these reagents manifest different stereoselectivities in certain cases. Thus the reduction of tetrachloride **8** with tributylstannane gives a mixture of isomers **9a** and **9b** in a ratio 1.3 : 1. At the same time, the reaction of compound **8** with tris(trimethylsilyl)silane gives a mixture of compounds **9a** and **9b** in a ratio 1.0 : 4.6.[48]



These observations are interpreted[48] as differences in the steric effects of substituents in the rigid-cage molecule $(Me_3Si)_3$. .SiH and in the molecule Bu_3SnH containing flexible mobile n-butyl groups. This hypothesis was confirmed by calculations of the geometry of the transition states.[48]

Despite the generally high reactivities of silyl radicals in halogen abstraction reactions from organic halides,[14] the radical $(Me_3Si)_3Si^{\bullet}$ manifests the lowest activity. The values of the absolute rate constants ($10^8 k$ litre mol^{-1} s^{-1}) in reactions with Me_3CBr decrease in the following order: $Et_3Si^{\bullet}$ (11.0) > $Ph_2Bu^tSi^{\bullet}$ (6.0) > $Me_3SiMe_2Si^{\bullet}$ (2.6) > $(Me_3Si)_3Si^{\bullet}$ (1.2).[14] The rate constants for each silyl radical decrease in the order: X = I > Br > Cl > F. Special mention should be made of the increasing role of electron-transfer reactions on going to polychloroalkanes; as a result, radical reactions occur spontaneously, *i.e.*, without any initiator. In the absence of exogenous radical initiators, $(Me_3Si)_3SiH$ reacts with carbon tetrachloride and bromoform. High yields of chlorotris(trimethylsilyl)silane are obtained on treatment of compound **4** with CCl_4 for 10 h at 20 °C. Trihalogenomethanes react in a similar way.[49]

$$(Me_3Si)_3SiH + CCl_4 \longrightarrow (Me_3Si)_3SiCl + CHCl_3,$$

$$(Me_3Si)_3SiH + CHX_3 \longrightarrow (Me_3Si)_3SiX + CH_2X_2$$

X = Cl, Br, I.

The spontaneous reaction of the hydride **4** with oxygen may result in its ignition in air. The mechanism of oxygen insertion into the Si–Si bond includes a series of intramolecular rearrangements.[41, 50]

$$(Me_3Si)_3Si^{\bullet} + O_2 \longrightarrow (Me_3Si)_3SiOO^{\bullet},$$

$$(Me_3Si)_3SiOO^{\bullet} \longrightarrow (Me_3Si)_2Si^{\bullet}OOSiMe_3,$$

$$(Me_3Si)_2Si^{\bullet}OOSiMe_3 \longrightarrow (Me_3Si)_2Si(O^{\bullet})OSiMe_3,$$

$$(Me_3Si)_2Si(O^{\bullet})OSiMe_3 \longrightarrow Me_3SiSi^{\bullet}(OSiMe_3)_2,$$

$$Me_3SiSi^{\bullet}(OSiMe_3)_2 + (Me_3Si)_3SiH \longrightarrow$$

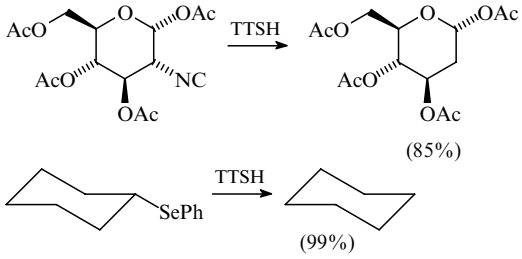
$$\longrightarrow Me_3SiSiH(OSiMe_3)_2 + (Me_3Si)_3Si^{\bullet}.$$

In the absence of other substrates and under conditions of radical initiation, recombination of the tris(trimethylsilyl)silyl radical occurs to give hexakis(trimethylsilyl)disilane in high yield.[51]

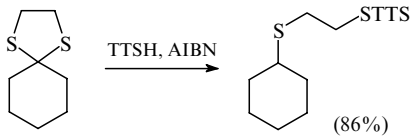
$$\underset{\mathbf{4}}{(Me_3Si)_3SiH} \xrightarrow[130\ ^{\circ}C]{(Bu^tO)_2} \underset{(92\%)}{(Me_3Si)_3SiSi(SiMe_3)_3}$$

It is noteworthy that under these conditions radical recombination products are formed in trace amounts from simpler organosilicon hydrides (Me_3SiH or Me_5Si_2H).

Tris(trimethylsilyl)silane reduces functional groups containing a heteroatom: NC, SR, SeR (R = Alk, Ar).[46, 52, 53] The yields in these reactions are rather high.



Upon treatment with 1 equiv. of $(Me_3Si)_3SiH$, 1,3-dithiolanes afford cleavage products of only one C–S bond.[54]



Under free-radical initiation conditions, carboxylic acid chlorides and phenyl selenoesters are reduced by tris(trimethylsilyl)silane to the corresponding aldehydes and alkanes.[55, 56]

$$RC(O)X + (Me_3Si)_3SiH \longrightarrow RC(O)H + RH + (Me_3Si)_3SiX$$

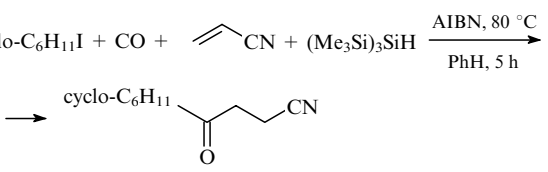
R = Alk, cyclo-Alk; X = Cl, SePh.

Tris(trimethylsilyl)silane is a convenient reagent for radical deoxygenation of alcohols following their conversion into *O*-phenoxythiocarbonyl derivatives.[57]

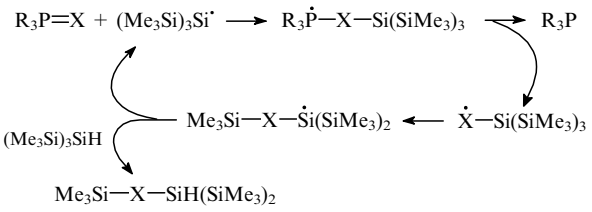
$$ROH + PhOC(S)Cl \xrightarrow[CH_2Cl_2]{Py} ROC(S)OPh \xrightarrow[AIBN]{\mathbf{4}} RH$$

The hydroxy group can also be reduced with $(Me_3Si)_3SiH$ *via* selenocarbonate derivatives.[58]

Successful application of tris(trimethylsilyl)silane as a promotor in multicomponent combination reactions of organic molecules is reported.[59, 60]



In the presence of AIBN, tris(trimethylsilyl)silane reacts with equimolar amounts of phosphine sulfides and phosphine selenides to give the corresponding phosphines in good yields.[7] Stereochemical studies with P-chiral phosphine sulfides have shown that this reduction occurs with retention of their configurations.[7]



R = Me, Bu^n, Ph; X = S, Se.

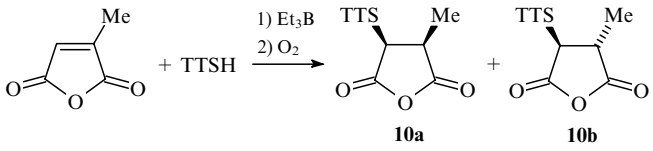
However, no reaction of tris(trimethylsilyl)silane with phosphine oxides occurs even on heating to 150 °C.

2. Hydrosilylation reactions

In the presence of radical initiators, tris(trimethylsilyl)silane easily reacts with alkenes; the addition to the double bonds occurs against the Markownikoff rule.[61, 62]

$$(MeSi)_3SiH + Bu^nOCH{=}CH_2 \longrightarrow Bu^nOCH_2CH_2Si(SiMe_3)_3 \quad (92\%)$$

The addition of $(Me_3Si)_3SiH$ to prochiral alkenes containing ester groups occurs stereoselectively. The selectivity increases with a decrease in temperature, *viz*., the **10a** : **10b** isomer ratio is 19 : 1 at 60 °C, while that at −15 °C is 99 : 1.[61]

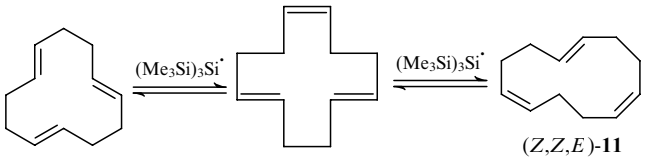


10a **10b**

The addition of $(Me_3Si)_3SiH$ to α-substituted chiral alkenes also occurs with high stereoselectivity.[63]

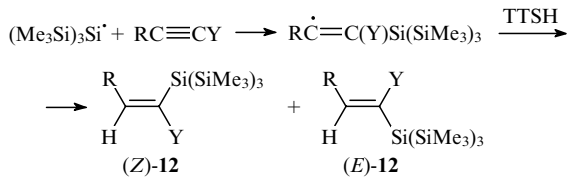
Generally, the activity of silyl radicals in addition reactions to the double bond of alkenes is high[46] (*e.g*., at 23 °C, $k = 10^6 - 10^8$ litre mol^{-1} s^{-1}), this decreases in the following order: $Et_3Si^{\bullet} > Me_3SiMe_2Si^{\bullet} > (Me_3Si)_3Si^{\bullet}$.

As a rule, the addition of trialkylsilyl radicals to alkenes is an irreversible exothermic reaction.[64] This general tendency notwithstanding, it was found that $(Me_3Si)_3Si^{\bullet}$ adds reversibly to many alkenes[65, 66] and catalyses their isomerisation. Thus treatment of each of the 1,5,9-cyclododecatriene isomers (**11**) with a $(Me_3Si)_3SiH - (Bu^tO)_2$ system at 143 °C affords a mixture of (*E*,*E*,*E*) : (*Z*,*E*,*E*) : (*Z*,*Z*,*E*) isomers in 80% yield and in a 78 : 22 : 2 ratio.



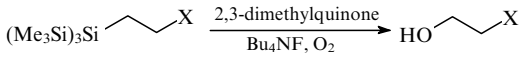
(*E*,*E*,*E*)-**11** (*Z*,*E*,*E*)-**11** (*Z*,*Z*,*E*)-**11**

Alkynes also react with tris(trimethylsilyl)silane according to a radical-chain mechanism.[61] The stereoselectivity of this reaction strongly depends on the nature of the substituents at the triple bond. For R = Ph, Y = CO_2Et or R = Bu^t, Y = H, the *Z* : *E* isomer ratio is 1 : 99. For R = Ph and Y = Alk, CN or CHO the stereoselectivity is much lower.[61]

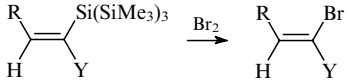


(*Z*)-**12** (*E*)-**12**

After termination of hydrosilylation reactions, the TTS group is removed using oxidative cleavage with 2,3-dimethylquinone and Bu_4NF or with bromine.[61]

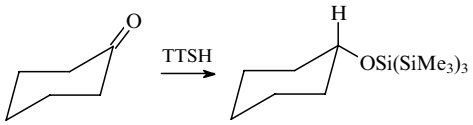


X = Ph, CN, CO_2H.

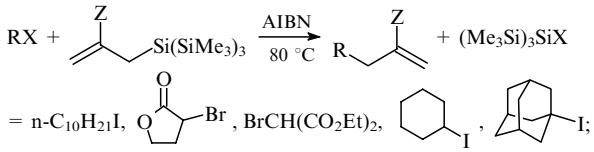


R = H, Bu^t, Ph; Y = CN, CO_2H.

The tris(trimethylsilyl)silyl radical adds easily to the carbonyl oxygen atom of aldehydes, dialkyl ketones and quinones,[67, 68] but the rate constants for these reactions were an order of magnitude lower than those of alkylsilyl radical reactions.



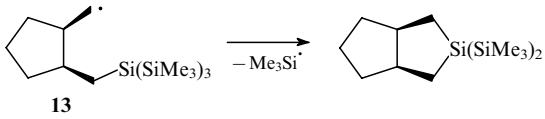
The tris(trimethylsilyl)silyl group is successfully employed in radical allylation reactions of the halogen-substituted organic compounds.[69]



Z = H, Me, Cl, CN, CO_2Et.

The use of $(Me_3Si)_3SiH$ in the synthesis of nucleosides, α-amino acids and prostaglandins[69] seems to be more preferable than that of Bu_3SnH due to high toxicity of the latter.

Some examples of radical substitution of the Me_3Si group at the silicon atom are known.[70–72] Thus the carbon-centred radical in the intermediate **13** formed from the corresponding bromide by a chain reaction displaces in an intramolecular manner the trimethylsilyl fragment of the TTS group.



13

3. Polymerisation involving $(Me_3Si)_3SiH$

Tris(trimethylsilyl)silane was found to be one of the most efficient chain transmitters in the radical polymerisation of vinylic monomers.[73] The chain transfer constants (c_s) are listed in Table 6.

Chain transmitters result in a much more narrow molecular-mass distribution, which is broadened in their absence due to the gel effect. This circumstance is of considerable practical importance because of the lack, until now, of ways to significantly

Table 6. Chain transfer constants (c_s) through silicon hydrides in the bulk polymerisation of styrene and methyl metacrylate at 60 °C.[73]

Compound	$10^3\,c_s$	
	styrene	methyl metacrylate
Et_3SiH	7.3	4.23
Me_5Si_2H	14	56
$(Me_3Si)_2SiMeH$	92	706
$(Me_3Si)_3SiH$	550	8300

decrease the polydispersity of polymers prepared by radical polymerisation.

4. Acidity of $(Me_3Si)_3SiH$

It is known that silyl anions cause metallation of weak CH-acids,[37, 74, 75] but their generation by direct deprotonation of silanes with carbanions or alkali metal amides could not be detected. Only metallation of Et_3SiH by potassium hydride in dimethoxyethane or hexamethylphosphorotriamide is known.[76] Attempts to abstract the proton from $(Me_3Si)_3SiH$ using Bu^nLi, MeLi or Ph_3CLi in THF were unsuccessful and resulted in the destruction of the substrate. Such a deprotonation could be effected only when less nucleophilic $Ph_3CLi(Et_2O)_2$ in diethyl ether was used.[77]

$$Ph_3CLi(Et_2O)_2 + (Me_3Si)_3SiH \xrightarrow{Et_2O} Ph_3CH + (Me_3Si)_3SiLi$$

The acidity of tris(trimethylsilyl)silane in solution was established in reactions of the complex $(Me_3Si)_3SiLi(THF)_3$ (**5**) with various CH-acids.[78] Thus $(Me_3Si)_3SiH$ and 9-phenylxanthyllithium ($pK = 28.7$) form an equilibrium mixture in diethyl ether with a silane : silyl anion molar ratio of 12 : 7, which corresponds to $pK = 29.4$ for $(Me_3Si)_3SiH$.

The energy of deprotonation of $(Me_3Si)_3SiH$ in the gas phase was estimated to be equal to 350.8 kcal mol^{-1}, which is by $\sim$22 kcal mol^{-1} smaller than that of SiH_4 (372.8 kcal mol^{-1}) and significantly smaller than that of methane (416.6 kcal mol^{-1}).

The use of tris(trimethylsilyl)silane as a starting reagent in the synthesis of organoelement and organometallic compounds will be considered in subsequent chapters devoted to individual groups of elements.

V. Tris(trimethylsilyl)silyl derivatives of elements of the main subgroups

1. Elements of Groups IA – IIA

a. Preparation

The synthesis of $(Me_3Si)_3SiLi$ (**5**), first developed by Gilman and Smith,[37] was modified further.[23] The reaction rate depends on the procedure used for the preparation of methyllithium. The reaction with MeLi prepared from methyl iodide or bromide proceeds at a sufficiently high rate and is significantly slower, if methyl chloride has been used. Tris(trimethylsilyl)silyllithium was isolated and characterised as a colourless crystalline adduct with THF.[23, 35] This can be stored in an atmosphere of argon for several months. It is noteworthy that if the reaction is incomplete, a crystalline compound containing one tetrakis(trimethylsilyl)silane molecule per two lithium silanide molecules, $[(Me_3Si)_4Si][(Me_3Si)_3Si.Li(THF)_3]_2$, can be isoated from the reaction mixture.[35]

Tris(trimethylsilyl)silylpotassium (**6**) is yet another popular reagent. This is highly stable, can be stored at 20 °C for a long time and is highly reactive and its synthesis from tetrakis(trimethylsilyl)silane (**3**) is rather simple and convenient.[22]

Potassium, rubidium and caesium tris(trimethylsilyl)silanides can be prepared by treatment of $(Me_3Si)_3SiLi$ with *tert*-butoxides of the corresponding alkali metals.[79]

$$(Me_3Si)_3SiLi(THF)_3 + Bu^tOM \longrightarrow (Me_3Si)_3SiM + Bu^tOLi$$

M = K, Rb, Cs.

The solid reaction products can be separated by addition of crown ethers, which also determine the formation of contact or separated ion pairs. The following ionic compounds, *e.g.*, $K(18\text{-C-}6)Si(SiMe_3)_3$, $[K(12\text{-C-}4)_2][Si(SiMe_3)_3]$, $[Rb(15\text{-C-}5)_2].[Si(SiMe_3)_3]$, $[Cs(18\text{-C-}6)_2][Si(SiMe_3)_3]$ and $[Rb(18\text{-C-}6)_2].[Si(SiMe_3)_3][Rb(18\text{-C-}6)Si(SiMe_3)_3]_2$ were prepared in this way and their structures were established.[79]

Non-solvated $(Me_3Si)_3SiLi$ was prepared by substitution of lithium for mercury in a reaction of bis[tris(trimethylsilyl)-silyl]mercury with metallic lithium in toluene.[80]

$$[(Me_3Si)_3Si]_2Hg \xrightarrow{Li,\ PhMe} 2\,(Me_3Si)_3SiLi + Hg$$

Using ^7Li NMR spectroscopy, it was found that in hydrocarbon solvents the central silicon atom in $(Me_3Si)_3SiLi$ carrying a negative charge is associated with two lithium atoms, whereas the silicon atom in Me_3SiLi is associated with three lithium atoms.[80]

Non-solvated tris(trimethylsilyl)silanides of other alkali metals were prepared using transmetallation reactions of zinc tris(trimethylsilyl)silanide with an alkali metal in saturated hydrocarbons.[81]

$$[(Me_3Si)_3Si]_2Zn \xrightarrow{M} 2\,(Me_3Si)_3SiM + Zn$$

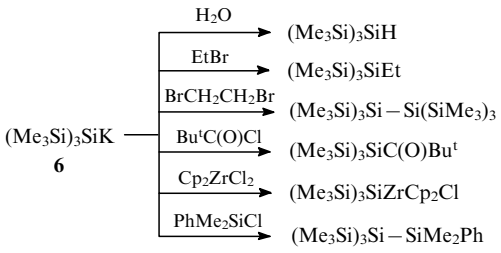
M = Na, K, Rb, Cs.

Tris(trimethylsilyl)silanides of alkali metals exist in a crystalline state as dimers with a nearly planar M_2Si_2 ring. The dimeric molecules are associated into a coordination polymer by abnormally short bonds between the alkali metal atom of one molecule and the methyl group of another molecule.[81]

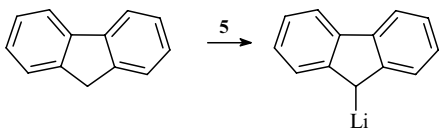
b. Reactivities of tris(trimethylsilyl)silanides

Alkali metal silanides manifest extremely high reactivities. Many of them easily react even with the solvent. Potassium triethylsilanide, for example, deprotonates weak acids such as benzene or toluene. These reactions yield potassium hydride and triethylphenylsilane or benzyltriethylsilane, respectively.[82] The main advantage of alkali metal tris(trimethylsilyl)silanides is that they maintain high reactivities with respect to electrophilic sites without affecting the molecules of aromatic solvents (*e.g.*, benzene, toluene) and ethers. This can partly be due to the steric shielding of the nucleophilic centre and the simultaneous intramolecular stabilisation of the complex by $M\cdots CH_3$ interactions.[81]

Reactions of tris(trimethylsilyl)silylpotassium (**6**) with various electrophilic reagents proceed in high yields.[22]



Tris(trimethylsilyl)silyllithium (**5**) lithiates hydrocarbons containing an active hydrogen atom.[37]



However, this reaction cannot be used for preparative purposes, since it is concomitant with side metathesis.

$$(Me_3Si)_3SiLi + (Me_3Si)_3SiH \longrightarrow (Me_3Si)_4Si + (Me_3Si)_2Si(H)Li$$

Treatment of magnesium bromide with 1 or 2 equiv. of lithium or potassium tris(trimethylsilyl)silanides in THF yielded the corresponding mono- $[(Me_3Si)_3SiMgBr(THF)_2]$ and disubstituted $\{[(Me_3Si)_3Si]_2Mg(THF)_2\}$ derivatives.[83] The crystalline complex $[(Me_3Si)_3Si]_2Mg(THF)_2$ is thermally highly stable and does not melt at temperatures up to 200 °C. However, in solution it slowly

(within 7 days) decomposes to give hexakis(trimethylsilyl)disilane and metallic magnesium.

$$[(Me_3Si)_3Si]_2Mg(THF)_2 \xrightarrow{C_6D_6} (Me_3Si)_3Si-Si(SiMe_3)_3 + Mg \quad (40\%)$$

Tris(trimethylsilyl)silylmagnesium bromide yields symmetrisation products upon addition of dioxane:

$$(Me_3Si)_3SiMgBr(THF)_2 + C_4H_8O_2 \longrightarrow [(Me_3Si)_3Si]_2Mg(THF)_2 + MgBr_2(C_4H_8O_2)$$

Since alkali metal tris(trimethylsilyl)silanides are used in the synthesis of diverse organoelement and organometallic compounds, their reactions will be considered in the appropriate sections.

2. Group IIIA elements

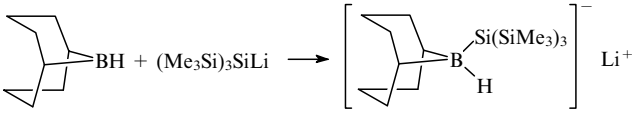
a. Boron

Silyl boranes constitute a small class of compounds due to instability of the Si–B bond. The tris(trimethylsilyl)silyl group has good potential for steric and electronic stabilisation of the electron-deficient boron atom. The reaction of lithium tris(trimethylsilyl)silanide with boron halides and alkylamides yields highly stable derivatives.[84]

$$n\,(Me_3Si)_3SiLi(THF)_3 + R_{3-n}BX_n \longrightarrow R_{3-n}B[Si(SiMe_3)_3]_n + n\,LiX$$

R = Me, Bu^t, bicyclo[3.3.1]nonane, Me_2N; X = Br, Cl.

Boron hydrides react with TTS-Li to give lithium salts:



Upon methanolysis in acidic media, boroakylamides yield methoxyboranes with retention of the Si–B bond.[84]

$$[(Me_3Si)_3Si]_2BNMe_2 + HCl + MeOH \longrightarrow [(Me_3Si)_3Si]_2BOMe + [Me_2NH_2]Cl$$

Tris(trimethylsilyl)silyllithium reacts with aminodifluoroboranes to give substitution products.[85]

$$(Me_3Si)_3SiLi + F_2BN(R)SiMe_3 \longrightarrow (Me_3Si)_3SiB(F)N(R)SiMe_3 + LiF$$
14

R = Me, Et, Pr^i, Bu^t, $SiMe_3$.

The thermolysis of hypersilylaminofluoroboranes **14** results in stable iminoboranes **15**, which proved to be highly reactive compounds. They easily add water, methanol and even sterically hindered aromatic amines.[85]

$$(Me_3Si)_3SiB(F)N(R)SiMe_3 \xrightarrow{400-500\ ^\circ C} (Me_3Si)_3SiB{\equiv}N-R\ ,$$
14 **15**

$$(Me_3Si)_3SiB{\equiv}N-R + ArNH_2 \longrightarrow (Me_3Si)_3SiB(NHR)NHAr$$
15

R = $SiMe_3$, Bu^t; Ar = 2,4,6-$Me_3C_6H_2$.

b. Aluminium

Reactions of aluminium chloride, alkyl- and arylaluminium chlorides with TTS-Li give the corresponding hypersilyl derivatives.[86]

$$(Me_3Si)_3SiLi(THF)_3 + R_{3-n}AlCl_n \longrightarrow (Me_3Si)_3SiAlR_{3-n}AlCl_{n-1}(THF)$$

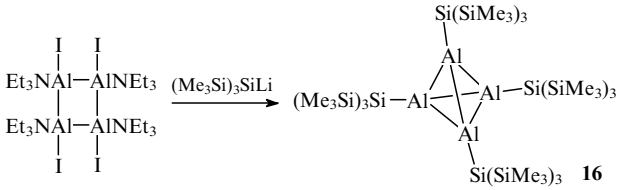
R = Me: n = 1 (81%); 3 (60%); R = Et: n = 1 (78%); 2 (83%).

It was shown that at low temperatures aluminium chloride forms a lithium adduct $[Li(THF)_4][(TTS)AlCl_3]$,[87] which decomposes at −15 °C. Trialkylaluminium gives a complex salt with TTS-Li.

$$(Me_3Si)_3SiLi(THF)_3 + R_3Al \xrightarrow{THF} [(Me_3Si)_3SiAlR_3]Li(THF)_n$$

R = Me, Et.

The reaction of lithium hypersilanide with tetrameric aluminium(I) bromide or iodide was used for the preparation of a tetranuclear complex of monovalent aluminium **16**.[88]



16

The interatomic distance Al–Al in compound **16** is equal to 2.602 Å, *i.e.*, is only slightly greater than the sum of the covalent radii (2.48 Å).

c. Gallium

In the past decade, the chemistry of silicon–gallium compounds has been developing especially intensely due to considerable interest in these compounds as precursors of materials for microelectronics.[89] In this context, much attention is being given to hypersilyl derivatives containing Si–Si and Si–Ga bonds initially.

The structurally characterised compounds with $(Me_3Si)_3SiGa$ fragments can be classified into three groups, *viz.*: (1) mononuclear gallium complexes containing a single Si–Ga bond of the type $(Me_3Si)_3Si-GaR_2$; (2) digallanes; (3) nuclear clusters containing gallium atoms surrounded by silyl substituents.

Compounds with Si–Ga bonds are prepared by reactions of the corresponding chlorides R_2GaCl with TTS-Li.

$$R_2GaCl + (Me_3Si)_3SiLi(THF)_3 \longrightarrow R_2Ga-Si(SiMe_3)_3 + LiCl$$
17

R = Me, Ph, 2,2,6,6-tetramethylpiperidine (tmpp).

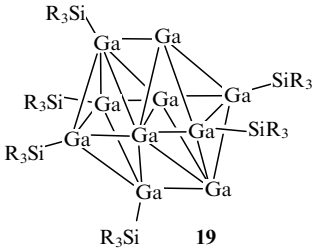
The 2,2,6,6-tetramethylpiperidine derivative, $(tmpp)_2Ga$-TTS (**17**), is easily split at the Ga–N bond by treatment with water, EtOH, PhOH or HCl to give the corresponding derivatives, *viz.*, $[(Me_3Si)_3SiGa(OH)_2]_3$, $[(Me_3Si)_3SiGa(OEt)_2]_2$, $\{[(Me_3Si)_3Si.Ga(OPh)_3]^-[(tmpp)H_2^+]\}$ or $\{[(Me_3Si)_3SiGaCl_3]^-[(tmpp)H_2^+]\}$ where the coordination number of gallium is usually equal to 4.[90]

By virtue of their high proneness to form coordination compounds, gallium halides yield products with various compositions depending on the stoichiometric ratios of the components.[90,91] Two compounds with tentative compositions $Li[(Me_3Si)_3Si-GaCl_3](THF)_4$ and $(Me_3Si)_3Si-GaCl_2(THF)$[91] are formed at the $GaCl_3:(Me_3Si)_3SiLi$ ratio of 1 : 1 that could not be isolated in the pure state. The same reaction with two moles of $(Me_3Si)_3SiLi$ gives a structurally characterised ate-complex with lithium chloride **18**.[92] The TTS-$GaCl_2(THF)$ complex was prepared in the presence of an excess $GaCl_3$.[90]

$$(Me_3Si)_3SiLi + GaCl_3 \xrightarrow{THF} [(Me_3Si)_3Si]_2Ga(\mu\text{-}Cl)_2Li(THF)_2$$
18

Gallium(I, III) chloride, $Ga[GaCl_4]$, reacts with lithium tris(trimethylsilyl)silanide and, depending on the ratio of reagents, reaction temperature and the solvent type, yields a tetranuclear

cluster $[(Me_3Si)_3SiGaCl]_4$,[93] a homoleptic gallium(I) silanide, $[(Me_3Si)_3SiGa]_4$,[94] or gallium bis(hypersilyl)chloride, $[(Me_3Si)_3Si]_2GaCl$.[95] Larger clusters have been isolated, *e.g.*, the complex $Ga_{10}[Si(SiMe_3)_3]_6$ (**19**),[96] which represents two edge-shared octahedra one of which contains four TTS substituents, while the other one contains only two substituents.



R = $SiMe_3$.

19

The reaction of Ga(I)Br with TTS-Li gives the cluster $Ga_{22}[(Me_3Si)_3Si]_8$ (**20**) which contains 22 gallium atoms;[97] the central gallium atom in this complex is surrounded by 13 different gallium atoms carrying eight $GaSi(SiMe_3)_3$ fragments on the outer side.

$$GaBr + (Me_3Si)_3SiLi(THF)_3 \longrightarrow$$
$$\longrightarrow [(Me_3Si)_3Si]_2GaBr_2 \cdot Li(THF)_2 + [(Me_3Si)_3SiGaBr]_4 +$$
$$+ Ga_{22}[(Me_3Si)_3Si]_8$$

20

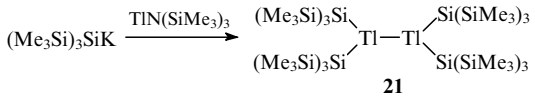
The reactions of the cluster $[(Me_3Si)_3SiGaCl]_4$ with iron carbonylates, *e.g.*, $Na_2Fe(CO)_4$, $Na_2Fe_2(CO)_8$ and $Na_2Fe_3(CO)_{11}$, have been studied.[95] The reaction products, *viz.*, $(CO)_3Fe[Ga(TTS)]_3Fe(CO)_3$ and $(CO)_3Fe[Ga(TTS)]_2(\mu\text{-}CO).Fe(CO)_3$, represent $Fe_2(CO)_9$ derivatives where the bridging CO groups are partly or completely replaced by the $GaSi(SiMe_3)_3$ fragment.

d. Indium, thallium

Indium hypersilyl derivatives are not numerous. One of them is the ate-complex of indium bis(hypersilyl)chloride with LiCl , *viz.*, $[(Me_3Si)_3Si]_2In(\mu^2\text{-}Cl)_2Li$.[92] All attempts to obtain monovalent indium derivatives by reaction of indium(I) chloride with TTS-Li gave the same product, presumably, as a result of disproportionation of indium(I) chloride by the reaction:

$$3\,InCl \longrightarrow 2\,In + InCl_3.$$

The reaction of indium trichloride with TTS-Li at −60 °C yields $[(Me_3Si)_3Si]_2$ and metallic indium; however, at lower (−100 °C) temperatures, it is the bimetallic derivative $(TTS)_2In-In(TTS)_2$ that is formed.[98] A similar thallium derivative, *viz.*, compound **21**, was isolated by treatment of the monovalent thallium silylamide with potassium hypersilanide.[99]



21

3. Group IVA elements

a. Carbon

Numerous compounds in which the hypersilyl group is bound to carbon are referred to in different sections of the present review. Let us give some additional examples.

The reaction of fullerene C_{60} with $(Me_3Si)_3SiLi$ in toluene at −78 °C and subsequent treatment of the reaction products with ethanol resulted in 1,16-bis[tris(trimethylsilyl)silyl]-C_{60}-fullerene in 69% yield. Its structure (in the form of a solvate with CS_2) was confirmed by X-ray diffraction analysis.[100]

The sterically overcrowded TTS derivatives present certain interest. Thus bis(hypersilyl)methoxymethane **22** is formed in the reaction of $(Me_3Si)_3SiLi$ with dichloromethoxymethane.[101, 102]

$$(Me_3Si)_3SiLi + Cl_2CHOMe \longrightarrow [(Me_3Si)_3Si]_2CHOMe$$

22 (35%)

The methoxy group in compound **22** is so strongly shielded that it is resistant to acid hydrolysis under drastic conditions;[101] the Si−C−Si angle is equal to 132.7°, which suggests steric overcrowding of this molecule. The reaction of TTS-Li with methyl formate afforded sterically overcrowded bis(hypersilyl)-methanol, $[(TTS)_2CHOH]$.

Treatment of hypersilyllithium with carbon dioxide and subsequent hydrolysis yielded thermally stable ($T_{decomp.}$ = 225 °C) hypersilylcarboxylic acid $(Me_3Si)_3SiCO_2H$.[8] Stable acylsilanes are formed in reactions of TTS-Li with acyl halides.[103]

$$(Me_3Si)_3SiLi + RC(O)Cl \longrightarrow (Me_3Si)_3SiC(O)R + LiCl$$

R = Bu^t, CEt_3, 1-adamantyl.

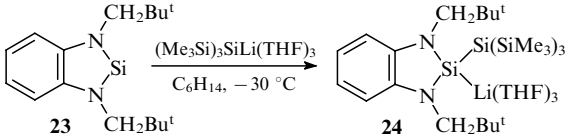
The properties of acylsilanes are considered in Section VIII. The tris(trimethylsilyl)silyl group confers stability also to the aldehyde $(Me_3Si)_3SiC(O)H$; however, this can be prepared exclusively using organometallic reagents (see Section VI.4).

b. Silicon

Treatment of $(Me_3Si)_3SiLi$ with various organosilicon halides was used for the preparation of derivatives of the type $(Me_3Si)_3SiSiR_2X$ (R = Cl, Me, Pr^i, Bu^t, Ph, X = Cl; R = $Bu^t(Me_3Si)N$, X = F)[104] as well as compounds of the type $(Me_3Si)_3SiR$, where R = $SiCl_3$, $SiMe_2H$, $SiPh_2Cl$.[39] Halogen or hydrogen atoms in the latter are fairly mobile and can easily be substituted by other functional groups, *e.g.*, OMe, I, OH, OAc, O_2CCF_3.[39]

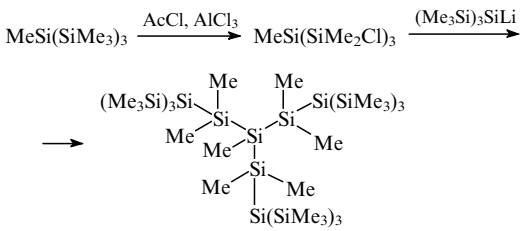
Careful hydrolysis of disilane $(Me_3Si)_3SiSiCl_3$ allowed isolation of the thermally stable (m.p. = 210–213 °C) silanetriol $(Me_3Si)_3SiSi(OH)_3$, which exists as a hexamer in the crystalline state. The core of this spherical molecule consists of six associated silanetriol groups.[105]

Under mild conditions, lithium tris(trimethylsilyl)silanide reacts with stable silylene **23** to give the addition product **24**.[106]



23 **24**

The tris(trimethylsilyl)silyl group plays a key role in the synthesis of branched polysilanes, since it allows one to elongate the chain by substitution of SiLi or SiCl for the terminal fragments SiMe.[107–109]

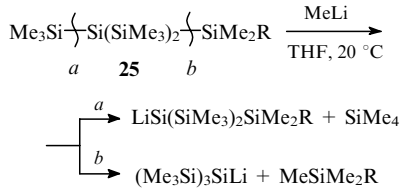


The synthesis of branched polysilanes has a number of specific features related to the steric factors and the ability of the Si−Si bond to be cleaved by nucleophilic reagents. Although some examples of Si−Si bond cleavage in disilanes[110, 111] resulting in Me_3SiM (M is an alkali metal) are known, this process never takes place in branched polysilanes. The formation of a silyl anion with a 'tertiary' silicon atom ($\equiv Si)_3Si^-$ is thermodynamically the most favourable process.

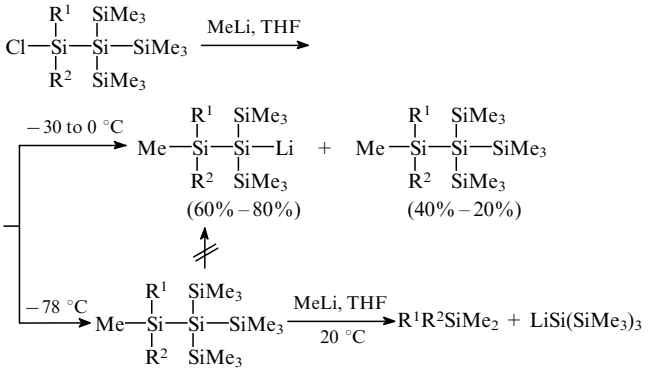
Splitting of branched polysilanes **25** under the action of methyllithium is mainly controlled by steric factors; MeLi largely attacks the least sterically hindered silicon atom (Table 7).[112]

Table 7. Relative yields (%) of the lithiation products of branched polysilanes $(Me_3Si)_3SiR$ **25**.[112, 113]

R	Route *a*	Route *b*
$SiMe_2H$	< 2	> 98
$SiMe_2Bu^t$	> 99	< 1
Si_2Me_5	70	30
$SiMe_2SiMe_2Bu^t$	98	2
$SiMe(SiMe_3)_2$	40	60
$Si(SiMe_3)_3$	< 2	> 98
$SiMeHSi(SiMe_3)_3$	< 2	> 98
$SiMe_2Si(SiMe_3)_3$	< 2	> 98



In branched chloropolysilanes, chlorine is relatively inactive; however, being an electronegative substituent, it stabilises 'tertiary' silyl anions. Therefore, at 0 – 30 °C (60% – 80%) the initial elimination of the trimethylsilyl group prevails.



R^1, R^2 = Me, $SiMe_3$, $Si(SiMe_3)_3$.

The formation of disilenes as intermediates in this reaction is not excluded.[112] With a decrease in temperature down to −78 °C, the mobility of the TTS-group seems to decrease considerably and substitution of the methyl group for the chlorine atom becomes predominant.

The use of bulkier silyllithium reagents, such as Ph_3SiLi and TTS-Li as well as of Bu^tOK,[22] results in the cleavage of one or two peripheral Si – Si bonds.[113]

$$(Me_3Si)_3SiSi(SiMe_3)_3 \xrightarrow{RLi} (Me_3Si)_3SiSi(SiMe_3)_2Li + Li(Me_3Si)_2SiSi(SiMe_3)_2Li + RSiMe_3$$

R = Ph_3Si, $(Me_3Si)_3Si$.

$$(Me_3Si)_3SiSi(SiMe_3)_3 \xrightarrow{Bu^tOK} (Me_3Si)_3SiSi(SiMe_3)_2K + Bu^tOSiMe_3$$

The reaction of the resulting silyllithium derivatives with silicon halides constitutes the second step in the synthesis of branched polysilanes.

In one of the methods for the synthesis of bis(hypersilyl) derivatives, silyl triflate $(CF_3SO_3)_2SiH_2$ formed *in situ* from Ph_2SiH_2 and CF_3SO_3H is treated with tris(trimethylsilyl)silyllithium.[114]

$$2\,LiSi(SiMe_3)_3 + (CF_3SO_3)_2SiH_2 \longrightarrow (Me_3Si)_3Si-SiH_2-Si(SiMe_3)_3 \quad (19\%)$$

c. Germanium, tin, lead

A series of organotin TTS derivatives have been obtained in satisfactory yields by the reaction of $(Me_3Si)_3SiLi(THF)_3$ with alkyltin(IV) halides.[24]

$$R_{4-n}SnCl_n + n\,(Me_3Si)_3SiLi(THF)_3 \longrightarrow [(Me_3Si)_3Si]_nSnR_{4-n} + n\,LiCl$$

R = Me, Bu^n; n = 1, 2.

The reaction of lithium tris(trimethylsilyl)silanide with silicon, germanium and tin tetrachlorides provides an illustrative example of the steric effect of the TTS group on nucleophilic substitution. Silicon tetrachloride reacts with only 1 equiv. of $(Me_3Si)_3SiLi$ to yield $(Me_3Si)_3SiSiCl_3$;[104] $GeCl_4$ gives a dimer with a Ge – Ge bond, $[Cl_2GeSi(SiMe_3)_3]_2$,[115] while the substitution of two chlorine atoms in $SnCl_4$ affords $Cl_2Sn[Si(SiMe_3)_3]_2$.[24]

The reactions of trichlorosilane and germanium(II) silylamide with TTS-Li are more complicated and give cyclic compounds **26** and **27**, which formally represent the rearrangement products of tris(trimethylsilyl)silyl derivatives of bivalent silicon and germanium.[81]

$$2\,(Me_3Si)_3SiLi \xrightarrow[C_5H_{12},\ -30\ ^\circ C]{HSiCl_3} (Me_3Si)_2Si\langle Si(SiMe_3)_2 \rangle Si(SiMe_3)_2$$

26

$$2\,(Me_3Si)_3SiLi \xrightarrow[C_5H_{12},\ -30\ ^\circ C]{Ge[N(SiMe_3)_2]_2} (Me_3Si)_2Ge\langle Si(SiMe_3)_2 \rangle Si(SiMe_3)_2$$

27

Treatment of bivalent tin chloride with TTS-Li gives the ate-complex $[(Me_3Si)_3Si]_2Sn(\mu\text{-}Cl)Li(THF)_3$.[116]

The reaction of tris(trimethylsilyl)silyllithium with $PbCl_2$ occurs as a redox process resulting in metallic lead and hexakis(trimethylsilyl)disilane.[117]

$$PbCl_2 + 2\,(Me_3Si)_3SiLi(THF)_3 \longrightarrow (Me_3Si)_3SiSi(SiMe_3)_3 + 2\,LiCl + Pb$$

Chlorotriphenylplumbane reacts with TTS-Li to give a colourless crystalline thermostable product **28** in 81% yield.[118]

$$Ph_3PbCl + (Me_3Si)_3SiLi(THF)_3 \longrightarrow Ph_3PbSi(SiMe_3)_3 + LiCl$$

28

An attempt to obtain a bis(hypersilyl) derivative $Ph_2Pb[Si(SiMe_3)_3]_2$ resulted in diplumbane **29**.[118]

$$Ph_2PbCl_2 + 2\,(Me_3Si)_3SiLi(THF)_3 \longrightarrow (Me_3Si)_3Si-Pb(Ph_2)-Pb(Ph_2)-Si(SiMe_3)_3 + Si_2(SiMe_3)_6$$

29

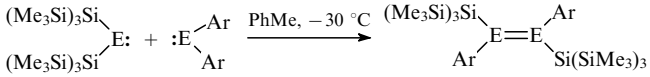
Homoleptic hypersilanides of bivalent tin and lead were prepared by reactions of the corresponding silylamides with tris(trimethylsilyl)silyl derivatives of alkali metals.[119, 120]

$$[(Me_3Si)_2N]_2E + 2\,MSi(SiMe_3)_3 \longrightarrow [(Me_3Si)_3Si]_2E + 2\,(Me_3Si)_2NM$$

E = Sn, Pb; M = Na, K, Rb, Cs.

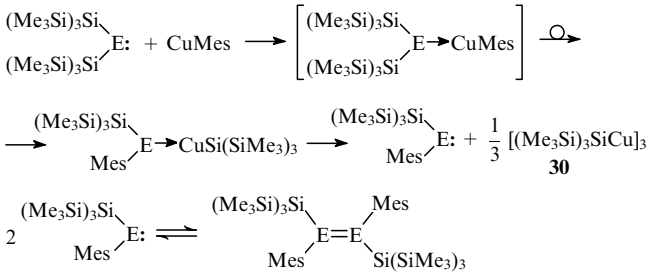
Di(hypersilyl)stannylene and -plumbene manifest amphoteric properties and behave as Lewis acids or bases. Quantum-chemical calculations of model compounds have demonstrated that the Lewis acidity of the carbenoids $(H_3Si)_2E$ (E = Sn, Pb) significantly exceeds that of the related diorganyl derivatives Me_2E, which increases their ability to form adducts (Lewis acid – base)

and dimers. The equilibrium between the monomeric and dimeric forms is more typical of di(hypersilyl)stannylene in solution, whereas in the crystalline state this compound is a dimer with an interatomic Sn–Sn distance of 2.825 Å. Di(hypersilyl)plumbene exists as a monomer both in solution and in the crystalline state, but forms adducts with other, less sterically overcrowded plumbenes. Such an interaction is also typical of di(hypersilyl)stannylene; it is of note that the formation of an adduct is accompanied by the migration of substituents.[119]



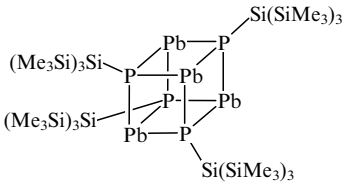
E = Sn, Pb; Ar = 2,4,6-$Me_3C_6H_2$; 2,6-$Me_2C_6H_3$.

Di(hypersilyl)stannylene and -plumbene react as Lewis bases with mesitylcopper. Hypersilylcopper **30** and mesityl(hypersilyl)-stannylene or -plumbene are the final reaction products.[121]

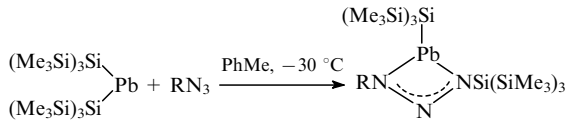


E = Sn, Pb.

In contrast to diarylstannylenes and -plumbenes, the dihypersilyl derivatives react faster with white phosphorus in toluene even at low temperatures (−30 °C).[119] Compounds containing Si–P bonds, $[(Me_3Si)_3SiP]_4Pb_4$ and $(Me_3Si)_3Si-P=P-Si(SiMe_3)_3$, are formed in the reaction of $Pb(TTS)_2$ in addition to the simple adduct $P_4[Pb(TTS)_2]_4$. $[(Me_3Si)_3SiP]_4Pb_4]$ has a cubane-like structure ($\delta\ ^{31}P = -506$).[119]

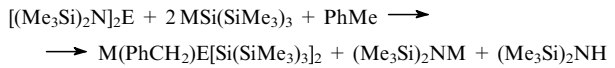


Organic azides form 1,3-addition products with di(hypersilyl)plumbene with simultaneous migration of the TTS group to the terminal nitrogen atom:[119]



R = 1-adamantyl, Me_3Si.

Numerous reactions of di(hypersilyl)stannylenes and -plumbenes with various bases, including organic and silyl derivatives of alkali metals, have been studied.[119] However, only some of them yielded stable products. Thus di(hypersilyl)stannylene reacts with $(Me_3Si)_3SiNa$ in toluene to give $[(Me_3Si)_3Si]_3SnNa(PhMe)$ in a quantitative yield. At temperatures above −30 °C, tris(trimethylsilyl)silyl derivatives of alkali metals react with tin and lead silylamides in toluene to give toluene metallation products.

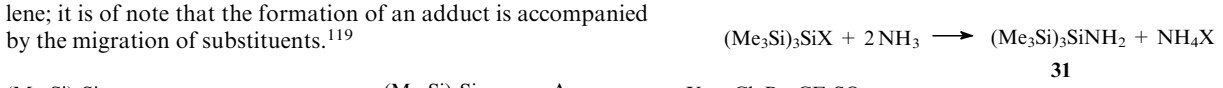


E = Sn, Pb; M = K, Rb, Cs.

4. Group VA elements

a. Nitrogen

Tris(trimethylsilyl)silyl derivatives of amines can be easily prepared by treatment of TTS halides with amines. Of particular interest in this respect is aminotris(trimethylsilyl)silane **31**, a highly stable compound which does not yield self-condensation products on heating.[122]



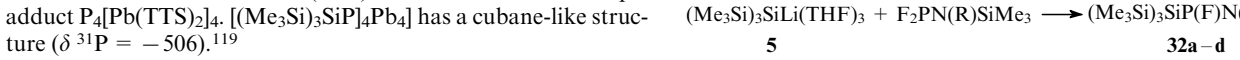
X = Cl, Br, CF_3SO_3.

b. Phosphorus

The Si–P bond is rather unstable. This has a certain effect on the chemistry of silicon–phosphorus compounds at large, on the chemistry of hypersilyl derivatives, in particular. The majority of reactions of lithium hypersilanide with phosphorus chlorides are accompanied by the formation of $(Me_3Si)_3SiCl$ (which is thermodynamically a very favourable product), and poly- or oligophosphines.[123–126]

R = 2,4,6-$Bu^t_3C_6H_2$ (see [124]), $(Me_3Si)_3C$ (see [123]).

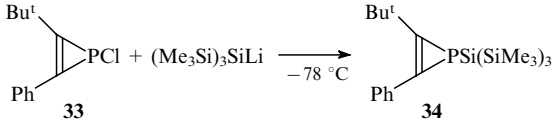
The complex of lithium tris(trimethylsilyl)silanide with THF (**5**) reacts with aminodifluorophosphines to give thermally stable derivatives **32a–d**.[127]



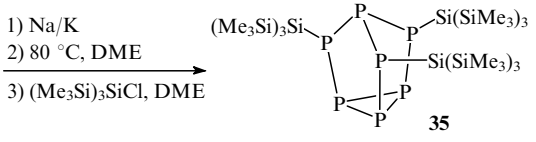
R = Bu^t (**a**), 2,4,6-$Me_3C_6H_2$ (**b**), $SiMe_3$ (**c**), 2-adamantyl (**d**).

Heating or distillation of compounds **32a–d** does not result in the elimination of Me_3SiF, whereas related tris(trimethylsilyl)-methyl derivatives are unstable and are readily converted into ylides $(Me_3Si)_2C=PN(R)SiMe_3$ (R = Bu^t, 2-adamantyl) upon elimination of fluorotrimethylsilane.[127]

The reaction of TTS-Li with 1-chloro-1*H*-phosphyrene **33** yielded the TTS-derivative **34**, which is relatively stable at 20 °C, but decomposes in light.[128]



Sodium-potassium phosphide prepared from white or red phosphorus and a Na/K alloy reacts with chloro tris(trimethylsilyl)silane to give $[(Me_3Si)_3Si]_3P_7$ (**35**), a colourless crystalline compound in which the nortricyclane cell P_7 contains three TTS substituents.[129]



The phosphanortricyclanic cell is a relatively stable structure. Compounds of an analogous structure with other silyl substituents ($SiMe_3$, $SiPh_3$, $SiBu^t_3$) can be prepared as well.[129]

5. Group VIA elements

a. Oxygen

Tris(trimethylsilyl)silanol. Tris(trimethylsilyl)silanol, $(Me_3Si)_3Si.OH$, can be prepared by hydrolysis of TTS halides.

It is known that hydrolysis of halogenosilanes usually gives disiloxanes. The bulky TTS group prevents both the hydrolysis and subsequent condensation of silanols. Of the TTS halogen derivatives, only iodo- and bromosilanes are hydrolysed at satisfactory rates. Chlorotris(trimethylsilyl)silane does not react with water in neutral media. Its hydrolysis demands long-term (7 days) stirring of a TTS chloride solution in THF with 20% KOH. During this time, the greater part of the product is lost as a result of cleavage of the Si–Si bonds in the alkaline medium. An alternative method consists of long-term intense stirring of $(Me_3Si)_3SiCl$ with aqueous triethylamine in hexane.[130] In aqueous THF, bromotris(trimethylsilyl)silane is in an equilibrium with silanol and HBr; the latter is easily titrated with 5% NaOH. The equilibrium is shifted as a result of removal of HBr and the yield of $(Me_3Si)_3SiOH$ exceeds 90%.[131] Tris(trimethylsilyl)silanol is moderately sensitive to oxygen. Upon 1-month exposure to air, its content decreases by 30% with formation of a complex mixture of oxidation products.

Tris(trimethylsilyl)silanol differs from ordinary compounds of this class in thermal stability, this does not undergo condensation to disiloxane. In acidic media, substitution reactions take place instead of self-condensation, but in the case of ordinary silanols they proceed in the opposite direction.[131]

$$(Me_3Si)_3SiOH + HCl\,(aq.) \longrightarrow (Me_3Si)_3SiCl + H_2O,$$

$$(Me_3Si)_3SiOH + Me_3SiCl \longrightarrow (Me_3Si)_3SiCl + Me_3SiOH$$

Substitution reactions with carboxylic acids and primary alcohols (MeOH, EtOH) also take place.[132]

$$(Me_3Si)_3SiOH + MeC(O)OH \longrightarrow (Me_3Si)_3SiOC(O)Me + H_2O,$$

$$(Me_3Si)_3SiOH + EtOH \longrightarrow (Me_3Si)_3SiOEt + H_2O$$

However, in the case of isopropyl alcohol no reaction occurs, presumably due to steric hindrance. The esterification of tris(trimethylsilyl)silanol by carboxylic acids easily occurs even in an aqueous medium, since the reverse reaction (hydrolysis) is impossible in neutral or weakly acidic media.[132]

The IR spectrum of $(Me_3Si)_3SiOH$ contains intense absorption bands: a narrow band at 3660 cm^{-1} and a broad band around 3240–3600 cm^{-1}, which can be associated with the free and bound hydroxy groups, respectively.[130] The bands at 3443, 1080 and 1049 cm^{-1}, which relate to the protonated OH and SiO groups, are not detected in the Raman spectra. Such a difference is explained by changes in the symmetry due to dimer formation.[130]

Hypersilanolates $[(Me_3Si)_3SiO]_nML_m$. Alkali metal triorganylsilanolates are usually synthesised by treatment of triorganylsilanols with alkali metals or their hydrides.[133] However, alkali metal tris(trimethylsilyl)silanolates cannot be prepared by this method, since they either do not react with silanol or cause its destruction under more drastic conditions.[131,134] Lithium and sodium derivatives were prepared by treatment of tris(trimethylsilyl)silanol in hexane with butyllithium or sodium isopropoxide.[131]

$$(Me_3Si)_3SiOH + Bu^nLi \longrightarrow (Me_3Si)_3SiOLi + Bu^nH,$$

$$(Me_3Si)_3SiOH + Pr^iONa \longrightarrow (Me_3Si)_3SiONa + Pr^iOH$$

The thermal stabilities and reactivities of compounds containing $R_3Si-SiR_2OM$ groups depend on several factors, *viz*., the redox potential of a metal, its oxidation state, electron-donor properties of the polysilyl substituent, the degree of ionicity of the M–O bond and enthalpy of the rearrangement:

$$Si-Si-O-M \longrightarrow Si-O-Si-M.$$

Lanthanide derivatives with high affinities for oxygen and a moderately negative value of the standard redox potential appear to be the most stable compounds.

Thus the reaction of lanthanide silylamides with tris(trimethylsilyl)silanol gives gadolinium and lanthanum hypersilanolates **36a–f**.[135]

$$[(Me_3Si)_3N]_3Ln + 3\,(Me_3Si)_3SiOH + m\,L \longrightarrow [(Me_3Si)_3SiO]_3Ln(L_m) + 3\,(Me_3Si)_2NH$$

36a–f

Ln = Gd: L_m = $(THF)_2$ (**a**), $(MeCN)_2$ (**b**), 1,4-diazobicyclo[2.2.2]octane (**c**), (4,4′-bipiridyl)$_2$ (**d**), (4,4′-bipiridyl) (**e**);
Ln = La, L_m = $(THF)_4$ (**f**).

Homoleptic hypersilanolates, which contain no coordinating molecules, cannot be prepared because of their mobile equilibra and incomplete substitution. The bidentate ligand, 4,4′-bipyridyl, yields the coordination polymer **36e** upon coordination with the fragment $[(Me_3Si)_3SiO]_3Gd$, whereas 1,4-diazabicyclo[2.2.2]octane forms only a mononuclear complex **36c** at any ratio of the reagents due to steric hindrance. Gadolinium hypersilanolate **36a** absorbs only one mole of CO_2 to give $[(Me_3Si)_3SiO]_2Gd[OCOSi.(SiMe_3)_3](THF)_2$, whereas the analogous lanthanum complex **36f** yields the percarboxylate derivative $[(Me_3Si)_3SiOCO]_3La(THF)_2$.

Gadolinium and lanthanum hypersilanolates are stable at temperatures up to 200 °C. $(Me_3Si)_3SiOH$ and polylanthanosiloxane are the only decomposition products of compound **36a** at higher temperatures. It is noteworthy that thermolysis of more ionic lithium hypersilanolate, $(Me_3Si)_3SiOLi$, affords H_2, $(Me_3Si)_3SiH$ (55%), $Me_3SiOSi(SiMe_3)_3$ (10%) and $(Me_3Si)_3SiOH$ (13%).[131]

An increase in the redox potential on going from manganese to nickel and a simultaneous increase in the energy of the metal–silicon bond in the hypersilanolates of bivalent metals of Groups VII and VIII (Mn, Fe, Co, Ni) cause a significant decrease in their stability and increase their ability for intramolecular rearrangements eventually resulting in formation of the silicon–metal bond.

Cobalt(II) and iron(II) silanolates of the general formula **37a–k** were prepared by the reaction of tris(trimethylsilyl)silanol with the corresponding silylamides.[136] The reaction of $FeBr_2$ with $(Me_3Si)_3SiONa$ in dimethoxyethane was also used for the preparation of the ate-complex $(Me_3Si)_3SiOFe[\mu\text{-}OSi(SiMe_3)_3]_2.Na(DME)$ (**38**).[137]

$$[(Me_3Si)_2N]_2M + 2\,(Me_3Si)_3SiOH + L_n \longrightarrow [(Me_3Si)_3SiO]_2M(L_n) + 2\,(Me_3Si)_2NH$$

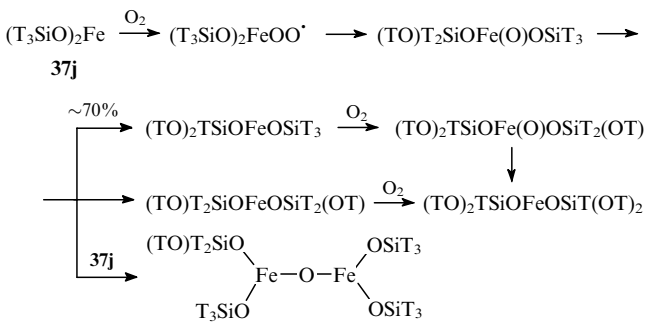
37a–l

M = Co: L_n is absent (**a**), L_n = THF (**b**), $(THF)_2$ (**c**), DME (**d**), $(MeCN)_2$ (**e**), $(PhCN)_2$ (**f**), 2,2′-bipyridyl (**g**), 4,4′-bipyridyl (**h**), $(Ph_3P)_2$ (**i**); M = Fe: L_n absent (**j**), L_n = 2,2′-bipyridyl (**k**), 4,4′-bipyridyl (**l**).

According to X-ray diffraction analysis, the homoleptic silanolates **37a**, **j** represent dimers in the crystalline state, but are monomers in solution (data from cryoscopic measurements in benzene). In contrast to other complexes, compound **37a** reversibly binds two THF molecules, which are easily removed *in vacuo* and upon dissolution in nonpolar solvents. 4,4′-Bipyridyl interacts with silanolates **37a**,**j** to give insoluble coordination compounds **37h**,**l**.[136]

It is of note that iron tris(trimethylsilyl)silanolates **37j**, **38** are pyrophoric in air, although they are in fact oxides. The oxidation of the Si–Si bonds proceeds at a high rate due to activation of the O_2 molecule on the coordinatively unsaturated iron atom. A detailed study of this oxidation in the example of compound **37j** revealed that oxygen is consumed in two routes, *viz*., in the

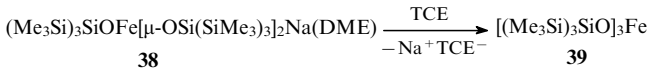
oxidation of the ligand (which is predominant) and in the oxidation of Fe(II) to Fe(III).[136]



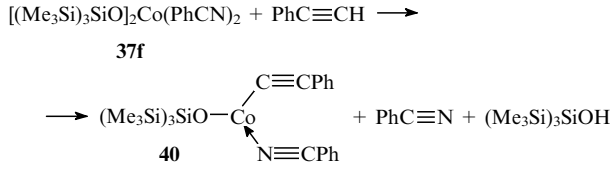
T = Me_3Si.

In the case of cobalt complexes, all of the oxygen is consumed for oxidation of the ligand.

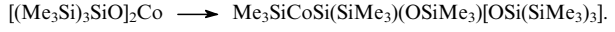
The ate-complex of bivalent iron **38** reacts smoothly with tetracyanoethylene (TCE) to give Fe(III) hypersilanolate (**39**). Compound **39** does not react with oxygen.[137]



Under ordinary conditions, homoleptic cobalt silanolate **37a** adsorbs CO to give a complex with a tentative structure $(Me_3Si)_2(Me_3SiO)SiCo_x(CO)_y$. Compounds **37** are active as catalysts in the oligomerisaton of phenylacetylene. The reaction of equimolar amounts of silanolate **37f** and PhC≡CH results in the substitution of one silanolate group. Subsequent addition of PhC≡CH to the complex **40** yields 1,3,5-triphenylbenzene and polyphenylacetylene.

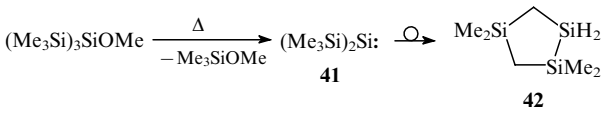


Thermal transformations of hypersilanolates have been studied. The decomposition of cobalt silanolate **37a** in solution begins at 40 °C. Acid hydrolysis of the solid thermolysis product gave Me_3SiH and $(Me_3Si)_3SiOSiH(SiMe_3)(OSiMe_3)$, which suggests a rearrangement occurs:

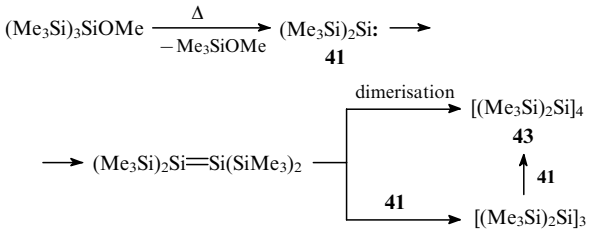


Thermolysis of $[(Me_3Si)_3SiO]_2Fe$ (**37j**) at 180–250 °C yields $(Me_3Si)_3SiOH$, $(Me_3Si)_3SiOSiMe_3$ and solid polyferro(Fe^{II})siloxane, whereas the ate-complex $(Me_3Si)_3SiOFe[\mu\text{-}OSi(SiMe_3)_3]_2.Na(DME)$ (**38**) gives silanes $[(Me_3Si)_3SiSi(SiMe_3)_3]$, $(Me_3Si)_4Si]$ and solid polyferri(Fe^{III})siloxane.[137] The reason for such a substantial difference is the presence, in the ate-complex, of sodium silanolate fragment possessing basic properties, which favours their disproportionation. Nickel hypersilanolates $LNi[OSi(SiMe_3)_3]_n$ cannot be synthesised because of smooth rearrangements leading to the formation of compounds with a Ni–Si bond.

For comparison, thermolysis of methoxytris(trimethylsilyl)silane, $(Me_3Si)_3SiOMe$, is accompanied by the formation of bis(trimethylsilyl)silylene (**41**).[138] Its further conversions depend on the reaction conditions. In the gas phase, compound **41** undergoes rearrangement into trisilylcyclopentane **42**.[139]

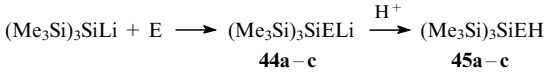


Thermolysis in the liquid phase yielded a totally different product, *viz*., octakis(trimethylsilyl)cyclotetrasilane (**43**).



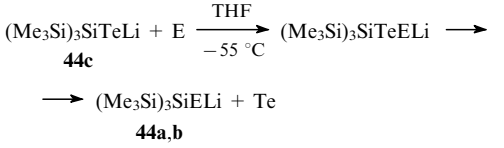
b. Chalcogens

Tris(*trimethylsilyl*)*silylchalcogenols* $(Me_3Si)_3Si-EH$ (E = S, Se, Te) *and their metal derivatives*. Chalcogens are easily inserted into the Si–Li bond of lithium hypersilanide to give the lithium derivatives **44a–c**.[140]



E = S (**a**), Se (**b**), Te (**c**).

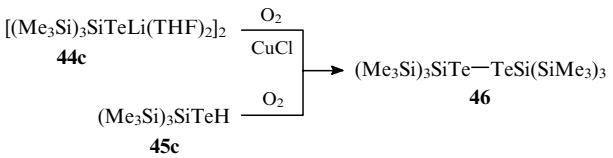
Subsitution of lighter chalcogens for tellurium is a convenient approach to the synthesis of sulfur and selenium derivatives.[140]



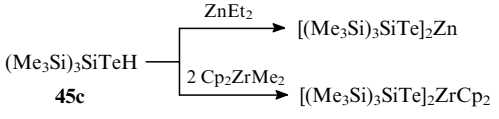
E = S, Se.

Acid hydrolysis of the lithium salts **44a–c** gives the corresponding chalcogenols **45a–c** in quantitative yields.[140,141] The acidic properties of hypersilylchalcogenols are increased, as expected, on going from sulfur to tellurium. The experimental values of pK_a for $(Me_3Si)_3SiEH$ are equal to 10.7 (**45a**, E = S), 8.3 (**45b**, E = Se) and 7.3 (**45c**, E = Te). The stretching vibration frequencies of the E–H bonds decrease significanly from sulfur to tellurium in the following order: 2557, 2294, 2017 cm^{-1}, respectively.[140]

Oxidation of the dimeric lithium hypersilyltellurolate–THF complex **44c**, like tellurol itself **45c**, gives hypersilyl ditelluride **46**.[142]



Tellurol **45c**, which possesses pronounced acidic properties, easily reacts with alkylmetal derivatives.[141]



Hypersilylselenolates and -tellurolates of bivalent lanthanides (Yb, Eu, Sm) were prepared using reactions of the corresponding silylamides with hypersilylselenol or -tellurol and characterised as complexes with donor molecules.[143]

$$(THF)_2Ln[N(SiMe_3)_2]_2 + 2\,(Me_3Si)_3SiEH + n\,L \longrightarrow$$
$$\longrightarrow [(Me_3Si)_3SiE]_2Ln(L_n) + 2\,HN(SiMe_3)_2$$

E = Se, Te; Ln = Yb, Eu, Sm;
L = TMEDA, $n = 2$; L = $(Me_2PCH_2)_2$, $n = 1.5$;
TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

The thermally induced decomposition of ytterbium(II) hypersilylselenolate and -tellurolate results in their conversion into polycrystalline metal chalcogenides with elimination of bis(hypersilyl)chalcogen at 150–200 °C.

$$[(Me_3Si)_3SiE]_2Yb(TMEDA)_2 \longrightarrow [YbE] + E[Si(SiMe_3)_3]_2 + 2\,TMEDA$$

E = Se, Te.

Hypersilylselenolates $[(Me_3Si)_3SiSe]_3Ln(THF)_2$ (Ln = La, Sm, Yb) and -tellurolates $[(Me_3Si)_3SiTe]_3Ln(dmpe)_2$ [Ln = La, Ce, Y; dmpe is 1,2-bis(dimethylphosphino)ethane] of trivalent lanthanides with coordinating ligands were prepared in a similar way.[144] The homoleptic derivatives appeared to be significantly less stable. On storage, hypersilylselenides of Sm, Eu and Yb decompose, predominantly into the bivalent complexes $[(Me_3Si)_3SiSe]_2Ln$ and bis(hypersilyl)diselenide. An attempt to isolate homoleptic hypersilyltellurides of trivalent lanthanides yielded cluster compounds, $Ce_5Te_3[TeSi(SiMe_3)_3]_9$ in particular.[144]

First attempts at the synthesis of homoleptic tellurolate derivatives of transition metals of the first row were unsuccessful. Treatment of bivalent Cr, Mn, Fe, Co and Ni halides with 2 equiv. of $(Me_3Si)_3SiTeLi(THF)_2$ yielded ditelluride $[TeSi(SiMe_3)_3]_2$ and a pyrophoric residue of an unknown nature.[145] Reactions of metal silylamides $M[N(SiMe_3)_2]_2$ with $(Me_3Si)_3SiTeH$ gave oily products, no pure compounds could be isolated. It was the use of coordinating phosphine ligands that allowed the isolation and characterisation of individual complexes.[145]

$$M[N(SiMe_3)_2]_2 + 2\,(Me_3Si)_3SiTeH + n\,dmpe \longrightarrow$$
$$\longrightarrow [(Me_3Si)_3SiTe]_2M(dmpe)_n + 2\,HN(SiMe_3)_2$$

M = Mn, $n = 1$; M = Fe, $n = 2$.

Halides of Cr, Mn and Fe afford analogous compounds in reactions with lithium hypersilyltelluride in the presence of coordinating molecules. The redox reaction of the cobalt(II) bromide diphosphine complex with TTS-TeLi is an exception.

$$CoBr_2(PMe_3)_3 + 2\,(Me_3Si)_3SiTeLi(THF)_2 \longrightarrow$$
$$\longrightarrow \underset{\mathbf{47}}{Co[TeSi(SiMe_3)_3](PMe_3)_3} + 1/2\,[(Me_3Si)_3SiTe]_2$$

The Co(I) complex (**47**) actively absorbs 2 equiv. of CO at atmospheric pressure.[145]

$$\mathbf{47} + 2\,CO \longrightarrow (CO)_2Co[TeSi(SiMe_3)_3](PMe_3) + 2\,PMe_3$$

It should be noted that the electronegative silyltellurolate ligand in compound $[(Me_3Si)_3SiTe]_2Fe(dmpe)_2$ is highly labile and can be displaced into the outer coordination sphere with acetonitrile to give the salt $[Fe\{TeSi(SiMe_3)_3\}(dmpe)_2(MeCN)].[TeSi(SiMe_3)_3]$.

Vanadium hypersilylselenides[146] and -tellurides[147] were prepared starting from vanadium(III) amidobromide **48**.

$$[(Me_3Si)_2N]_2VBr + (Me_3Si)_3SiELi(THF)_2 \longrightarrow$$
$$\underset{\mathbf{48}}{\longrightarrow} [(Me_3Si)_2N]_2VESi(SiMe_3)_3$$

E = Se, Te.

Further substitution of the hypersilylselenol group for the silylamide groups gives the disproportionation products **49** and **50**.[148]

$$[(Me_3Si)_2N]_2VSeR + 2RSeH \longrightarrow \underset{\mathbf{51}}{[V(SeR)_3]} \longrightarrow \underset{\mathbf{49}}{\tfrac{1}{2}V(SeR)_2} + \underset{\mathbf{50}}{\tfrac{1}{2}V(SeR)_4}$$

R = $Si(SiMe_3)_3$.

The trivalent vanadium derivative **51,** which is formed first, can be isolated as adducts $[(Me_3Si)_3SiSe]_3V(L)$, where L is the donor molecule (pyridine, 2,6-dimethylisocyanobenzene, pyrazine).

An attempt to substitute the hypersilyltelluride groups for the silylamide groups in $[(Me_3Si)_2N]_2V-TeR$ by treatment with hypersilyltellurol gave only the tetrasubstituted product $V[TeSi.(SiMe_3)_3]_4$ (**52**) in 20% yield.[147] A similar derivative of tetravalent molybdenum $Mo[TeSi(SiMe_3)_3]_4$ (**53**) is formed upon treatment of tetrakis(*o*-tolyl)molybdenum with hypersilyltellurol.[147] Under the action of 1,2-bis(dimethylphosphino)ethane, compounds **52** and **53** easily undergo reductive elimination to give $[TeSi(SiMe_3)_3]_2$.

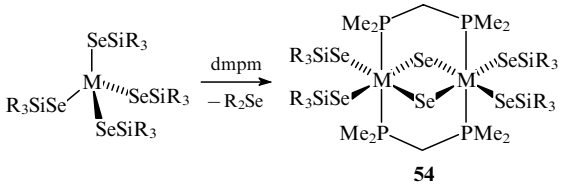
$$\underset{\mathbf{52,\ 53}}{M[TeSi(SiMe_3)_3]_4} \xrightarrow{dmpe} [TeSi(SiMe_3)_3]_2 + (dmpe)_2M[TeSi(SiMe_3)_3]_2$$

M = V (**52**), Mo (**53**).

In the presence of CO (1 atm), compound **53** readily eliminates two ditelluride molecules to give hexacarbonylmolybdenum.[147]

$$\underset{\mathbf{53}}{Mo[TeSi(SiMe_3)_3]_4} + 6\,CO \longrightarrow Mo(CO)_6 + 2\,[TeSi(SiMe_3)_3]_2$$

Homoleptic hypersilylchalcogenolates of Group IVB metals, *viz*., $M[ESi(SiMe_3)_3]_4$ (M = Ti, Zr, Hf), were prepared by treatment of the corresponding metal chlorides with TTS-ELi (E = S, Se, Te).[149] They represent thermally stable (m.p. > 220 °C) intensely coloured compounds. Treatment of zirconium and hafnium hypersilylselenides with the Lewis base bis(dimethylphosphino)methane (dmpm), yields binuclear complexes **54** the metal atoms in which are linked through selenide and phosphine bridges.[149]



54

R = $SiMe_3$; M = Zr, Hf.

With dmpm, hypersilyltellorolates $[(Me_3Si)_3SiTe]_4M$ (M = Zr, Hf) form the mononuclear complexes $(dmpm)_2.[(Me_3Si)_3SiTe]_2M$ = Te, whereas ordinary octahedral complexes $[(Me_3Si)_3SiTe]_4M(2,6\text{-}Me_2C_6H_3NC)_2$ are formed under the action of 2,6-dimethylisocyanobenzene.

6. Group VIIA elements (TTS halides)

Chloro, bromo and iodo derivatives $(Me_3Si)_3SiX$ can be prepared by the reaction of tris(trimethylsilyl)silane with polyhalohydrocarbons (see Section IV.1).[49] They cannot be prepared by selective halogenation of $(Me_3Si)_4Si$ (**3**), since the reaction rates of intermediate compounds with halogens significantly exceed those of the starting silane. Tetrahalosilane and halotrimethylsilane are formed in these reactions. However, selective substitution of bromine for lithium atoms in lithium tris(trimethylsilyl)silanide can be effected at low temperatures.[150]

$$(Me_3Si)_3SiLi \xrightarrow[-78\ °C]{Br_2} (Me_3Si)_3SiBr + LiBr$$

Fluorotris(trimethylsilyl)silane was prepared by an exchange reaction of TTS bromide with antimony trifluoride.[151]

$$(Me_3Si)_3SiBr + 1/3\,SbF_3 \longrightarrow (Me_3Si)_3SiF + 1/3\,SbBr_3$$

Careful chlorination of chlorotris(trimethylsilyl)silane has led to dichlorobis(trimethylsilyl)silane in satisfactory yields.[151]

$$(Me_3Si)_3SiCl + Cl_2 \xrightarrow[-23\ ^\circ C]{C_5H_{12},\ N_2} (Me_3Si)_2SiCl_2 + Me_3SiCl \quad (94\%)$$

Tris(trimethylsilyl)silyl halides are highly thermally stable. The decomposition of $(Me_3Si)_3SiCl$ begins at 300 °C and formally yields insertion products of silylene $(Me_3Si)_2Si$ into the Si–Cl bond. $(Me_3Si)_3SiH$ behaves in a similar way.[138]

$$(Me_3Si)_3SiX \xrightarrow{\sim 300\ ^\circ C} (Me_3Si)_3Si-Si(SiMe_3)_2X$$

X = H (1 h, 67%), Cl (4 h, 30%).

The reactivities of halides $(Me_3Si)_3SiX$ with respect to nucleophilic reagents depend substantially on the halogen and decrease in the following order: X = I > Br > Cl > F. Hydrolysis of hypersilyl halides in the presence of bases gives stable silanol $(Me_3Si)_3SiOH$ (see Section V.5.a). Bromide $(Me_3Si)_3SiBr$ is the most convenient substrate for substitution reactions. Reactions involving this compound proceed at sufficiently high rates and in good yields.[150]

$$CpH \xrightarrow{Bu^nLi} CpLi \xrightarrow[-78\ ^\circ C]{TTS\text{-}Br} CpSi(SiMe_3)_3 \quad (98\%)$$

Hypersilyl chloride is highly inert and its reactions occur under more drastic conditions and require longer times. The reaction of $(Me_3Si)_3SiCl$ with the Grignard reagent gives a TTS derivative in low yield.[4]

$$p\text{-}BrC_6H_4Br \xrightarrow[2)\ TTS\text{-}Cl]{1)\ Mg,\ THF} p\text{-}(Me_3Si)_3SiC_6H_4Si(SiMe_3)_3 \quad (5\%)$$

Other reactions of TTS halides used as starting reagents in the synthesis of organometallic and organoelement compounds are considered in the sections that follow.

VI. Tris(trimethylsilyl)silanides of d- and f-elements

The $(Me_3Si)_3Si$ group is a convenient ligand and is used in the chemistry of transition metals. It provides sufficient steric protection of the metal centre, and the products formed possess good solubilities in organic solvents. Unique electron properties of the TTS group and its electronic 'amphoteric' character allow the preparation of various types of stable transition metal complexes. It should be remembered, however, that the TTS group itself (especially in the form of a TTS anion) is a very strong reducing agent. Therefore, its interactions with transition metal ions possessing a high redox potential are complicated by redox reactions. The use of metal complexes with stabilising ligands as the starting compounds and the correct choice of reaction conditions opens up the way to the synthesis of numerous TTS derivatives of d- and f-elements endowed with unique physical and chemical characteristics.

1. Group IB elements

a Copper

Upon reaction with copper(I) chloride, TTS-Li forms a complex $Li(THF)_4[Cu_5Cl_4(TTS)_2]$, which is stable at temperatures below −30 °C.[87] This compound may conventionally be regarded as an adduct of $[Li(THF)_4][Cu(TTS)_2]$ with four CuCl molecules. The central silicon atom in its TTS groups are coordinated simultaneously by two copper atoms. Other products of this redox reaction are Cu, $CuCl_2$ and LiCl.

Reactions of alkali metal tris(trimethylsilyl)silanides with copper *tert*-butoxide yield mixtures of complex silanides.[152]

$$MSi(SiMe_3)_3 \xrightarrow{Bu^tOCu} M[(Me_3Si)_3SiCuOBu^t] + (Me_3Si)_3SiCu + M[(Me_3Si)_3SiCuSi(SiMe_3)_3]$$

M = Li, Na, K, Cs.

The best results [the yield of $(Me_3Si)_3SiCu$ is > 60%] are obtained by metathesis of lead silanide with mesitylcopper (see Section V.3.c).[121] In the crystalline state, hypersilylcopper represents a planar cyclic trimer with a short Cu–Cu distance (2.384–2.415 Å).[121] The central silicon atoms in the hypersilyl groups act as bridging groups, each being linked with two copper atoms.

b. Silver

Tris(trimethylsilyl)silyl silver derivatives, $TTS\text{-}Ag(R_3P)_n$ (n = 1, R = Ph; n = 2: $R_3P = Ph_2PMe$, $Ph_2PTol\text{-}p$), were prepared by treatment of appropriate silver phosphine halides with TTS-Li.[153] The stabilities of these compounds increase with an increase in the number of phosphine substituents.

c. Gold

Of the TTS gold derivatives, the phosphine complexes $Ph_2MeP.AuTTS$ [154] and $TTSAuPh_2PCH_2CH_2PPh_2AuTTS$ (see Ref. 155) prepared by treatment of appropriate gold chlorides with TTS-Li in THF are especially well-characterised. The Au–Si bond is easily destroyed upon treatment with halogens, but withstands hydrolysis and methanolysis.[154] Presumably, the steric requirements for the two-coordinated gold atom are not very strict (in comparison with metals with greater coordination numbers); therefore, the length of the Au–Si bond in the TTS derivatives does not differ from that of other, less sterically hindered gold silanides.[154, 155]

2. Group IIB elements (Zn, Cd, Hg)

Compounds $(TTS)_2M$ (M = Zn, Cd, Hg) were prepared by treatment of bivalent metal halides with lithium tris(trimethylsilyl)silanide in ether.[156] In contrast to their trimethylsilyl analogues, TTS derivatives are thermally stable in the absence of air over a sufficiently long period of time. These compounds were found to be rather inert and did not react with metal halides such as $TaCl_5$, $TiCl_4$, $ZrCl_4$ and VCl_3. Hydrolysis of $(TTS)_2Zn$ is complete within several hours. Cadmium iodide forms an anionic complex $[Li(THF)_4][(Me_3Si)_3SiCd(I_3)CdSi(SiMe_3)_3]$ in a reaction with TTS-Li at 20 °C.[157]

$(TTS)_2Hg$ was synthesised using the Vyazankin method.[158]

$$2\,(Me_3Si)_3SiH + Bu^t_2Hg \longrightarrow [(Me_3Si)_3Si]_2Hg + 2\,Bu^tH$$

4

It is of note that a similar reaction of Bu^t_2Hg with tris(pentamethyldisilanyl)silane (**55**) yields a binuclear complex **56** where the organosilicon ligand has an umbrella shape 'covering' the mercury atoms.[159]

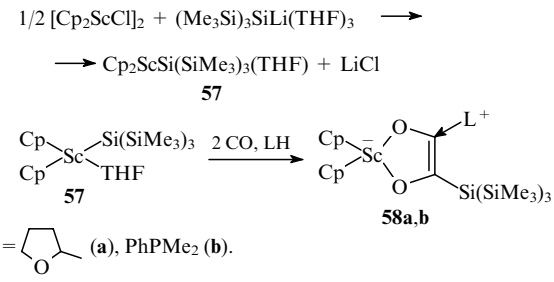
$$2\,(Me_5Si_2)_3SiH + Bu^t_2Hg \longrightarrow (Me_5Si_2)_3SiHg-HgSi(Si_2Me_5)_3 + 2\,Bu^tH$$

55 **56**

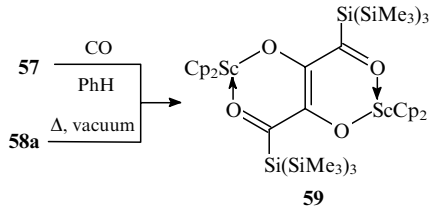
Upon heating to 180 °C, compound **56** eliminates one mercury atom to give $[(Me_5Si_2)_3Si]_2Hg$, whereas upon irradiation (λ > 330 nm) it generates a silyl radical $(Me_5Si_2)_3Si^\bullet$ stable at 20 °C.

3. Group IIIB elements, lanthanides, actinides

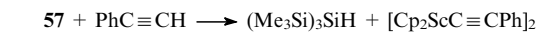
Tris(trimethylsilyl)silyl derivatives of Group IIIB elements, lanthanides and actinides are not numerous, only cyclopentadienyl complexes are known.[160] For example, the complex **57** containing a Sc–Si bond is extremely sensitive to oxygen and atmospheric moisture and easily absorbs two equivalents of CO to give the scandoxyketene derivatives **58** stabilised by donor molecules.[160]



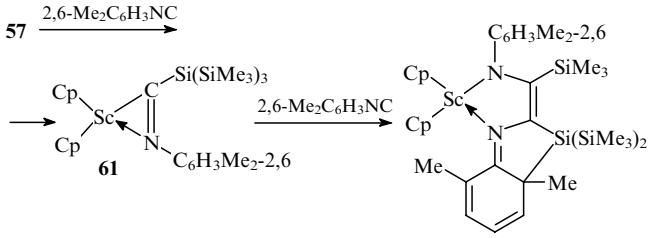
Heating of the complex **58a** *in vacuo* or carbonylation of compound **57** in a nonpolar medium gives the endione-diolate derivative **59**.



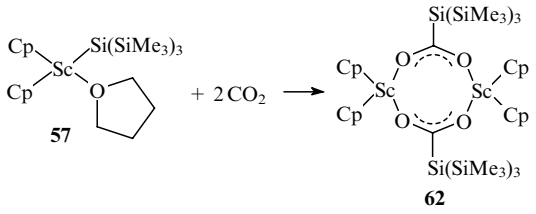
The addition of phenylacetylene to a solution of complex **57** in benzene results in the quantitative yield of $(Me_3Si)_3SiH$ and acetylenide **60**.[160]



Isocyanides are inserted into the Sc–Si bond; the primary product **61** undergoes attack by a second isocyanide molecule resulting in migration of the Me_3Si group.[160, 161]

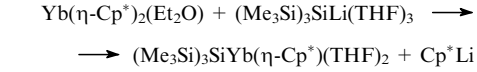


Carbon dioxide is easily incorporated into the Sc–Si bond of compound **57** to give the dimeric carboxylate **62**.[162]

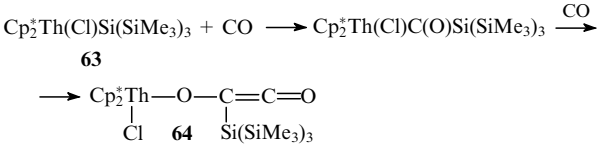


Compound **62** is unstable in solution and decomposes to the polymeric silanolate complex $[Cp_2ScOSi(SiMe_3)_3]_n$ with evolution of CO.[162]

The reaction of bis(pentamethylcyclopentadienyl)ytterbium with $(Me_3Si)_3SiLi$ in toluene results in substitution of the TTS group for one cyclopentadienyl ring.[163]



For as yet unknown reasons, silyl complexes of actinides are very difficult to isolate. The reaction of $Cp^*_2ThCl_2$ with TTS-Li yields the complex $Cp^*_2Th(TTS)Cl$ (**63**);[164] an attempt at its isolation results in its decomposition into $Cp^*_2ThCl_2$, $(Me_3Si)_3SiH$ and other products. Notwithstanding, carbonylation of compound **63** in solution with sequential insertion of two CO molecules and formation of the metalloxyketene derivative **64** takes place.[164]



4. Group IVB elements (Ti, Zr, Hf)

Numerous TTS derivatives of Group IVB elements also containing cyclopentadienyl, alkyl, alkylamide or alkoxide substituents are known. The methods for the preparation of some of them are listed in Table 8.

Attempts to synthesise TTS titanium derivatives starting from $TiCl_4$ and TTS-Li gave predominantly a complex mixture of redox reaction products among which trimethylsilane and hexamethyldisilane were isolated.[165] Mixed titanium halogenoamides were used in the synthesis of the triamide complexes TTS-Ti$(NMe_2)_3$ and TTS-Ti$(NEt_2)_3$ (see Table 8). The resulting compounds are

Table 8. Conditions of the synthesis of TTS complexes of Group IVB transition metals.

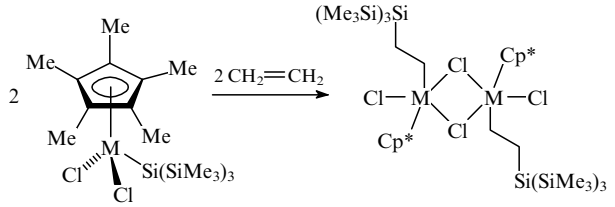
Starting compound	Reaction product	Yield (%)	Reaction conditions	Ref.
$ClTi(NMe_2)_3$, TTS-Li	TTS-Ti$(NMe_2)_3$	40	C_6H_{14}, 20 °C, 0.5 h	165
$ClTi(NEt_2)_3$, TTS-Li	TTS-Ti$(NEt_2)_3$	–	C_6H_{14}, 20 °C, 0.5 h	166
$ClTi(CH_2SiMe_3)_3$, TTS-Li	TTS-Ti$(CH_2SiMe_3)_3$	–	C_6H_{14}	167
$ClZr(NMe_2)_3$, TTS-Li	TTS-Zr$(NMe_2)_3$	–	Et_2O	168
$(Bu^tO)_3ZrCl$, TTS-Li	TTS-Zr$(OBu^t)_3$	70	Et_2O, 0 °C, 12 h	169
$(Bu^tO)_3HfCl$, TTS-Li	TTS-Hf$(OBu^t)_3$	70	Et_2O, 0 °C, 12 h	169
Cp*$ZrCl_3$, TTS-Li	TTS-ZrCp*Cl_2	–	Et_2O, −78 °C	25
Cp*CpZrCl_2, TTS-Li	TTS-ZrCp*CpCl	62	PhH, 20 °C, 12 h	170
Cp*CpHfCl_2, TTS-Li	TTS-Hf(Cl)Cp*Cp	–	Et_2O, 20 °C	171
Cp_2ZrCl_2, TTS-Li	TTS-ZrCp_2Cl	70	Et_2O, 20 °C, 2 days	172
Cp*$ZrCl_3$, TTS-Li	TTS-ZrCpCl_2	–	Et_2O	25
(TTS)ZrCp_2Cl, MeMgBr	TTS-ZrCp_2Me	71	Et_2O, −78 to 20 °C	172
(TTS)ZrCp*CpCl, MeMgBr	TTS-ZrCp*CpMe	82	Et_2O, −78 to 20 °C	170
Cp_2ZrCl_2, TTS-K	$(TTS)_2ZrCp_2$	85	C_5H_{12}, 0–20 °C, 12 h	173
$(Bu^tCH_2)_3ZrCl$, TTS-Li	TTS-Zr$(CH_2Bu^t)_3$	–	C_6H_{14}	174, 175
Cp*$HfCl_3$, TTS-Li	TTS-HfCpCl_2	–	Et_2O	25
Cp_2HfCl_2, TTS-K	$(TTS)_2HfCp_2$	81	C_5H_{12}, 0–20 °C, 12 h	173

thermally stable and chemically inert.[166, 176] The triamide and trialkoxide complexes of zirconium and hafnium possess low reactivities and are inactive as catalysts of alkene polymerisation.[168, 169]

TTS zirconium and hafnium derivatives of the type TTS-MCp_nCl_{3-n} (n = 1, 2) present special interest by reason of their high reactivities and catalytic activities.

The complexes Cp*M(TTS)Cl_2 in which M = Zr (**65**) and Hf (**66**) are stable in argon, but are rapidly decomposed in humid air. Compounds **65** and **66** in C_6D_6 are thermally rather stable as follows from the NMR spectra recorded after storage at 95 °C for 1 day in tubes protected from light. However, these compounds rapidly decompose in light.

Tris(trimethylsilyl)silylzirconium and -hafnium derivatives **65** and **66** as well as CpCp*Zr(TTS)Cl (**67**) react with ethylene with insertion into the Si–M bond.[177]

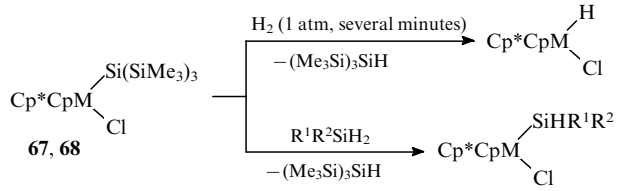


65, **66**

M = Zr, Hf.

At the same time, substituted alkenes (styrene, propene, trimethylsilylethylene) as well as diphenylacetylene do not react. The complex Cp_2Zr(TTS)Cl with non-substituted Cp ligands was found to be inert with respect to ethylene.

Compounds Cp*CpM(TTS)Cl **67** and **68** react with hydrogen and organosilanes with elimination of tris(trimethylsilyl)silane.[178]

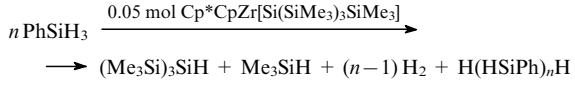


67, **68**

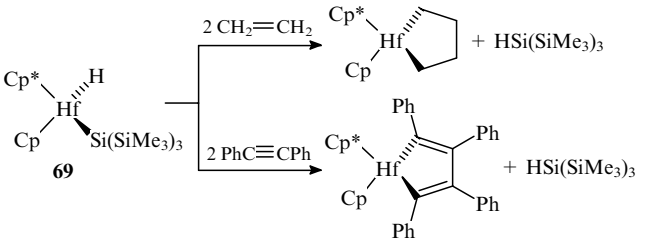
M = Zr (**67**), Hf (**68**); R^1 = H, Alk, Ar; R^2 = Alk, Ar.

The tris(trimethylsilyl)silyl group is the best leaving group for the metathesis in comparison with other R_3Si derivatives; therefore, compounds **67** and **68** are the most convenient reagents for the synthesis of novel d^0-hydridosilyl complexes in reactions with dihydrides.[171]

Dehydropolymerisation of primary silanes $RSiH_3$ in the presence of the TTS derivatives Cp*CpM(TTS)X (M = Zr, Hf; X = Me, Cl, $SiMe_3$) proceeds at a much faster rate than that with other analogous complexes.[178]

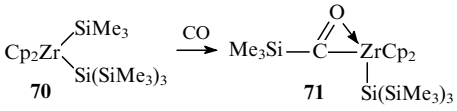


The hydride hafnocene complex **69** adds to molecules of unsaturated compounds with displacement of $(Me_3Si)_3SiH$.[179]



69

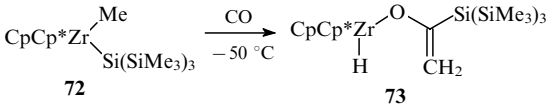
Compound **70** contains both trimethylsilyl and TTS groups, but one equivalent of CO is inserted exclusively into the Zr–$SiMe_3$ bond.[172]



70 **71**

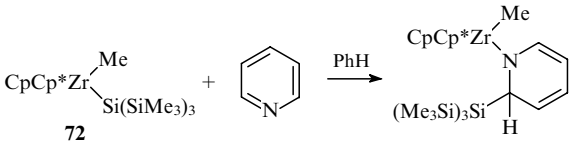
This fact is difficult to explain with account of the fact that, in the general case, CO is easily inserted into the $(Me_3Si)_3Si$–M bond, where M is a Group IVB metal. The reactivity of compound **71** is also unusual. Its treatment with HCl results in the quantitative evolution of $(Me_3Si)_3SiH$, but the use of benzoic acid causes elimination of the trimethylsilylcarbonyl group and formation of Cp_2Zr(TTS)(O_2CPh).[172] Carbon monoxide readily reacts across the Zr–Si bond of the spatially hindered CpCp*Zr(TTS)Cl molecule to give CpCp*Zr[C(O)TTS)]Cl,[170] but is not inserted into the Zr–Si bond within the Cp_2Zr(TTS)Cl complex.[172] This is attributed to the fact that the steric strains in the CpCp*Zr(TTS)Cl molecule exceed those in Cp_2Zr(TTS)Cl.[170]

The methyl derivative CpCp*Zr(TTS)Me (**72**) reacts with CO in a more complicated manner. The primary insertion product undergoes two sequential rearrangements eventually resulting in hydride-enolate **73**.[170]



72 **73**

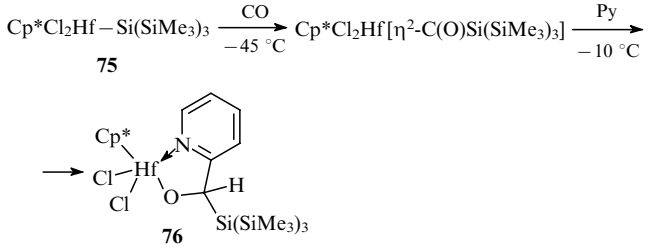
The complex **72** reacts with nitriles RCN to give the azomethine derivatives CpCp*ZrN = C(R)(TTS) (R = Me, CH = CH_2, Ph). Compound **72** reacts with pyridine to give the addition product **74**.[180]



72 **74**

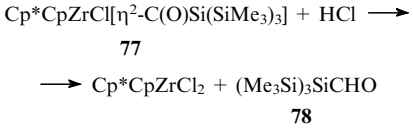
The analogous TTS zirconium complexes Cp_2Zr(TTS)Me and CpCp*Zr(TTS)Cl are significantly less reactive in reactions with nitriles and pyridine.

It was found that the insertion of CO into the Hf–Si bond of compound **75** results in an η^2-silylacyl derivative, which in turn gives rise to an insertion product **76** into the α-CH-bond of pyridine.[181]



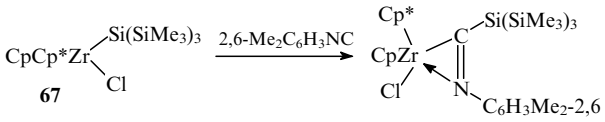
75 **76**

Protonation of the η^2-hypersilacyl zirconium complex **77** yields the organosilicon aldehyde **78**, which could not be prepared by any alternative methods.[182]



77 **78**

The insertion of isonitriles into the Zr–Si [182] bond is similar to that of carbon monoxide into the complex **70**.[175]



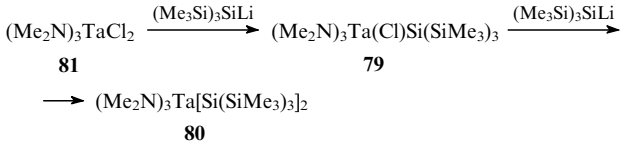
The tris(trimethylsilyl)silyl group was employed in the synthesis of 14-electron cationic complexes $[Zr(\eta\text{-}C_5H_4TTS)_2R]^+$ (R = Cl, Me), which proved to be efficient catalysts in ethylene polymerisation.[150] In the presence of a complex containing a tris(trimethylsilyl)silyl group in the cyclopentadienyl ring as a substituent, the polymerisation proceeds at a satisfactory rate. The molecular mass of the polymer (M_w = 126 000) was maximised in comparison with polymers prepared in the presence of catalysts of this series in which other substituents, *e.g.*, CH_2Ph and $CHPh_2$, were used instead of the TTS group.

Tris(trimethylsilyl)silylzirconium and -hafnium derivatives containing *tert*-butoxy groups instead of cyclopentadienyl ligands were found to be inactive with respect to CO, ethylene and $PhSiH_3$. However, both zirconium and hafnium complexes react with isocyanides to give the insertion products $[(Bu^tO)_3M(\eta^2\text{-}CNC_6H_3Me_2\text{-}2,6)(TTS)]$ (M = Zr, Hf).[169]

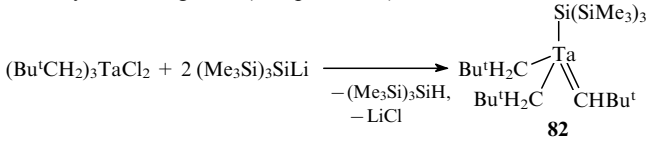
5. Elements of Groups VB – VIIIB

a. Tantalum

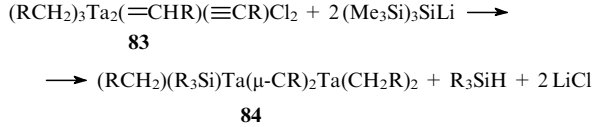
Group VB compounds are represented by tantalum complexes. The amidosilyl complexes **79** and **80** prepared from dichloride **81** are unstable and decompose even at 20 °C, which prevents their isolation.[183]



Stabilisation of neopentyl tantalum TTS complexes occurs owing to elimination of tris(trimethylsilyl)silane and formation of the alkylidene fragment (compound **82**).[175]

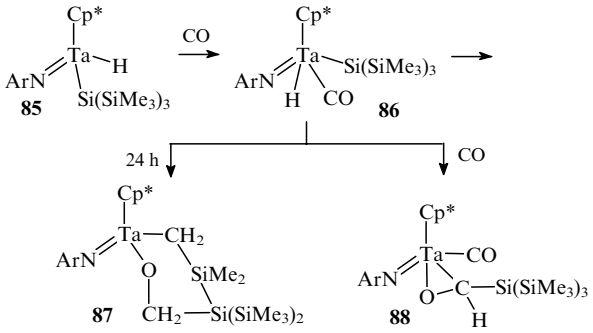


The reaction of the binuclear alkylidene – alkylidyne tantalum complex **83** with TTS-Li is also accompanied by elimination of tris(trimethylsilyl)silane. In this case, the bisalkylidyne complex **84** is formed.[184]



R = $SiMe_3$.

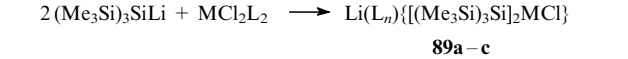
The reaction of 1 equiv. of CO with the tris(trimethylsilyl)silyl tantalum hydride complex **85** yields the addition product **86**, which isomerises within the next 24 h into the cyclic derivative **87**. This process involves the hydride, the carbonyl and the silyl groups.[185] The adduct **88** is formed in the presence of an excess of CO; its hydrolysis affords the organosilicon alcohol $(Me_3Si)_3SiCH_2OH$ in 90% yield.



Ar = 2,6-$Pr^i_2C_6H_3$.

b. Chromium, manganese, iron

The reactions of lithium tris(trimethylsilyl)silanide with chromium(II), manganese(II) and iron(II) halides in a coordinating solvent yield the bishypersilyl complexes **89a – c** of the anionic type.[186]



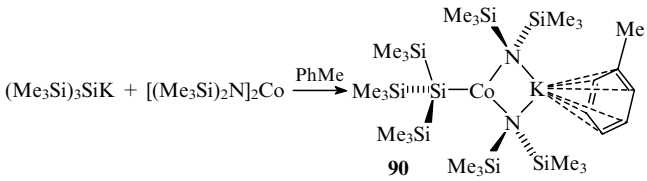
M = Cr (L = THF, *n* = 3) (**a**), Mn (L = DME, *n* = 2) (**b**), Fe (L = DME, *n* = 2) (**c**).

The iron and manganese complexes **89b,c** are rather thermally stable ($T_{decomp.}$ > 140 °C). The chromium complex **89a** was isolated and characterised only at temperatures below −20 °C.

All the low-coordination complexes obtained have high magnetic moments, which correspond to the high-spin configuration of metal atoms, but is uncommon to silyl transition-metal complexes.

c. Cobalt

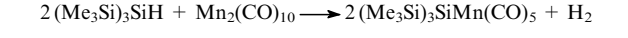
Attempts to synthesise TTS cobalt derivatives by treatment of $CoCl_2$ with potassium tris(trimethylsilyl)silanide resulted in cobalt(II) cobalt(0) reduction products. However, $(Me_3Si)_3SiK$ reacts smoothly with cobalt silylamide to give the adduct **90**.[187]



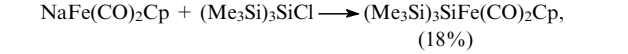
Compound **90** is stable in the crystalline state, but is rapidly decomposed in solution. The length of the Co–Si bond (2.513 Å) is the highest known value due to steric overcrowding of the complex **90**.

d. Carbonyl derivatives of Mn, Fe and Re

It is known that the reaction of metal carbonyls with silicon hydrides is one of the main approaches to the synthesis of compounds containing a silicon–metal bond [188] (see, *e.g.*, Refs 189 and 190).



However, this method is not generally employed in the synthesis of polysilyl carbonyl derivatives because of the low yields of the target products, since the side reaction (*viz.*, the cleavage of the Si–Si bond) yields siloxanes and carbonylhydride metal clusters.[188, 191] An alternative approach consists of the reaction of anionic metal carbonyl complexes with TTS halides [191] or the reaction of carbonyl halides with tris(trimethylsilyl)silyllithium.[189, 191, 192]



$$BrMn(CO)_4PPh_3 + (Me_3Si)_3SiLi \longrightarrow (Me_3Si)_3SiMn(CO)_4PPh_3, \quad (8\%)$$

$$BrM(CO)_nL + (Me_3Si)_3SiLi \longrightarrow (Me_3Si)_3SiM(CO)_nL$$

M = Mn, $(CO)_nL = (CO)_4PPh_3$; M = Re, $(CO)_nL = (CO)_5$.

d. Molybdenum, tungsten, rubidium

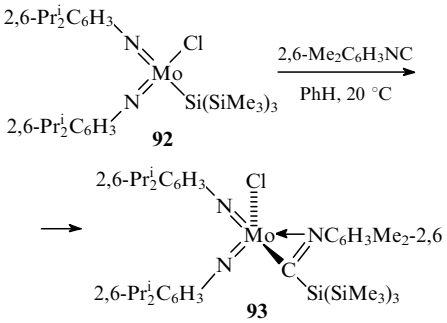
Treatment of molybdenum amidochloride, $(Me_2N)_4Mo_2Cl_2$, with TTS-Li yields the expected complex $(Me_2N)_4Mo_2(TTS)_2$, which contains a Mo≡Mo bond.[193]

Molybdenum bis(2,6-diisopropylphenylamido)dichloride (**91**) reacts with 1 equiv. of tris(trimethylsilyl)silyllithium to give the TTS derivative **92**.[194]

$$(2,6\text{-}Pr^iC_6H_3N{=})_2MoCl_2 + (Me_3Si)_3SiLi \longrightarrow$$
91

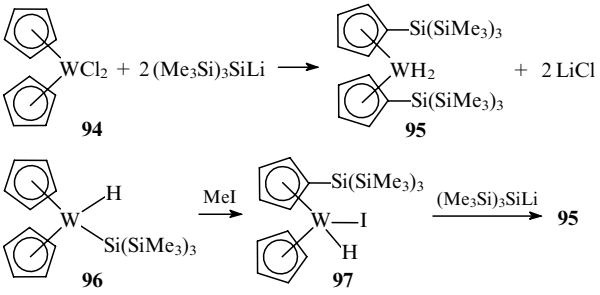
$$\longrightarrow (2,6\text{-}Pr^iC_6H_3N{=})_2Mo(Cl)Si(SiMe_3)_3 + LiCl$$
92

The complex **92** appeared to be non-reactive with respect to H_2, CO and C_2H_4, but reacted actively with 2,6-dimethylisocyanobenzene to give compound **93**, which is the isocyanide insertion product into the Mo–Si bond.[194]



The alkylidyne tungsten complex $(Bu^tCH_2)_3W(\equiv CBu^t)(TTS)$ is prepared from the corresponding chloride, $(Bu^tCH_2)_3W(\equiv CBu^t)Cl$, by treating the latter with lithium tris(trimethylsilyl)silanides.[175]

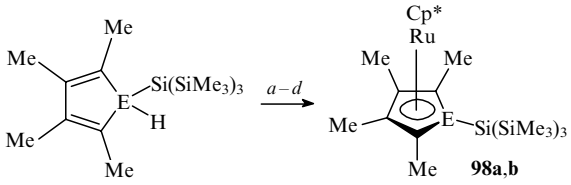
In the reaction of TTS-Li with bis(cyclopentadienyl)tungsten dichloride (**94**), substitution of the TTS group for a hydrogen atom in the cyclopentadienyl ring occurs rather than formation of the expected complex containing a W–Si bond resulting in tungsten dihydride **95**.[195,196]



The silyl complex **96** prepared from $Cp_2W(H)Cl$ and $(Me_3Si)_3SiLi$ also reacts with methyl iodide to give the substitution product of the cyclopentadienyl ring **97**. Apparently, the molecular rearrangement of the tungsten complex does not require deprotonation of the Cp ring by a base; otherwise, $(Me_3Si)_3SiH$ would be formed as a side product.

It is of note that TTS-substituted cyclopentadiene, which can also be prepared by conventional methods from CpLi and $(Me_3Si)_3SiBr$, is used in the synthesis of metal complexes, *e.g.*, $[Cp\text{-}TTS)_2Zr]$.[150]

Stable η^5-sila- and η^5-germacyclopentadienylruthenium derivatives **98a,b** were synthesised using the TTS group in the ring as a stabilising substituent.[197,198]



E = Si (**a**), Ge (**b**);
(*a*) $Cp^*Ru(OMe)_2$, (*b*) $Me_3SiOSO_2CF_3$ (2 equiv.), (*c*) 3 $NaBF_4$ (3 equiv.), (*d*) $LiSi(SiMe_3)_3$.

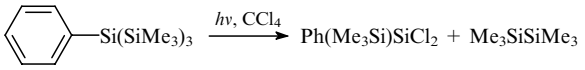
Synthesis of certain TTS derivatives of elements of Groups V–VIII is accompanied by rearrangements where the $(Me_3Si)_3Si$ fragment is destroyed, especially if the formation of metal silylene complexes is more preferable (see Section VIII).

VII. Photochemical reactions of hypersilyl derivatives

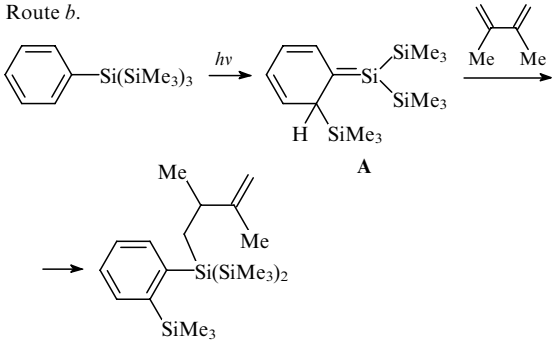
In comparison with linear derivatives, branched organooligosilanes, particularly $(Me_3Si)_4Si$, are little sensitive to UV light. However, if the TTS group is linked to a chromophore or an auxochromic group, the photoreactions involving the $(Me_3Si)_3Si$ fragment occur at noticeable rates.

Photolysis of aromatic TTS-containing compounds occurs through at least two pathways, *viz.*, with elimination of trimethylsilylphenylsilylene (route *a*) and with migration of the trimethylsilyl group into the aromatic ring (route *b*). The unstable intermediate **A** was identified following its reaction with 2,3-dimethylbuta-1,3-diene.[199,200]

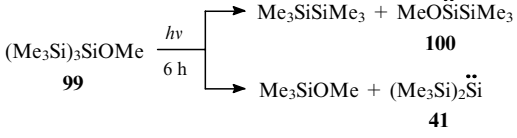
Route *a*.



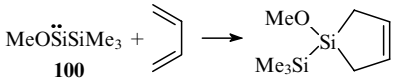
Route *b*.

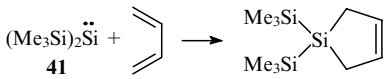


Photolysis (λ = 254 nm) of methoxytris(trimethylsilyl)silane **99** also proceeds non-selectively to yield methoxy(trimethylsilyl)silylene **100** and bis(trimethylsilyl)silylene **41** in a ~2 : 1 ratio.[201]



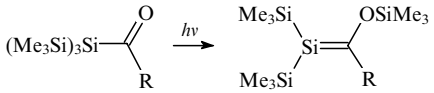
The silylenes formed were scavenged with traps, *e.g.*, buta-1,3-diene.





41

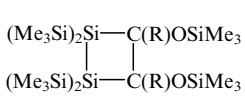
Photolysis of acyltris(trimethylsilyl)silanes is accompanied by migration of the trimethylsilyl group to the oxygen atom and the formation of silenes **101**, which undergo further conversions depending on the nature of the substituent in the acyl group and the reaction conditions.[202]



101

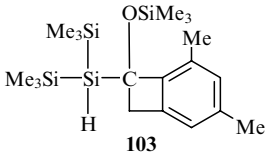
R = Me, Bu^t, 1-Ad (1-adamantyl), Ph, 2,4,6-$Me_3C_6H_2$.

The dimer **102a** of the 'head-to-head' type is formed in inert solvents for R = Ph.[203]

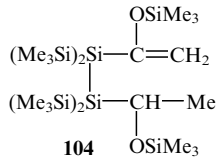


102a,**b**

R = Ph (**a**), Bu^t (**b**)



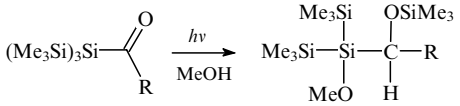
103



104

The bulkier *tert*-butyl group favours the formation of an equilibrium mixture of the dimer **102b** and the monomer **101** (R = Bu^t) in a 4 : 1 ratio.[203] The adamantyl substituent (R = 1-Ad) prevents dimerisation and a stable silene **101** is formed (R = 1-Ad).[103] However, in the case of yet another bulky substituent, *viz*., mesitylene, the sylene photochemical insertion product into the C–H-bond of one of the methyl groups (compound **103**) is formed.[202] If compound **101** contains α-protons in the substituent R (*e.g*., R = Me), the dimer undergoes disproportionation to give compound **104**.[203]

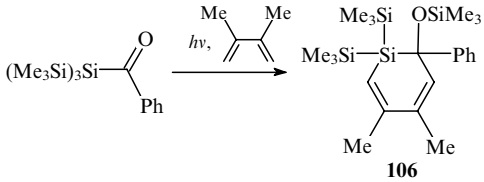
Photolysis of acylpolysilanes in the presence of methanol gives compounds **105** as the addition products to the double bond Si=C.[203]



105

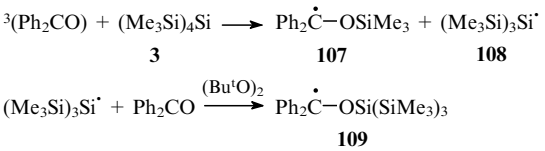
R = Me, Bu^t, Ph.

Unsaturated compounds (2,3-dimethylbutadiene, methylphenylacetylene) yield cyclic derivatives (*e.g*., compound **106**) as the addition products to the double bond Si=C of the photochemically generated silene **101**.[203]



106

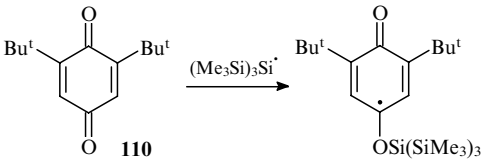
The photochemical reaction of benzophenone in a triplet state with tetrakis(trimethylsilyl)silane (**3**) affords two radical products, **107** and **108** (data from ESR spectroscopy).[203]



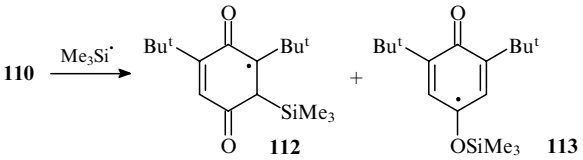
109

Photolysis of a benzophenone – tris(trimethylsilyl)silane mixture in the presence of di-*tert*-butyl peroxide yields exclusively the radical **109**. It should be noted that in contrast to $(Me_3Si)_3SiH$, $(Me_3Si)_4Si$ reacts with Bu^{t}O$^\cdot$ radicals generated upon photolysis of di-*tert*-butyl peroxide exclusively with abstraction of the hydrogen atom from the methyl groups to give the silylmethyl radicals $(Me_3Si)_3SiSiMe_2CH_2^\cdot$.

The photochemical reaction of 2,6-di-*tert*-butyl-1,4-benzoquinone **110** with tetrakis(trimethylsilyl)silane generates the radicals $(Me_3Si)_3Si^\cdot$ and $Me_3Si^\cdot$. The former adds exclusively to the oxygen atom of the quinone to give compound **111**, whereas the latter yields predominantly addition products at the carbon atom **112**. The addition product $Me_3Si^\cdot$ at the oxygen atom **113** is a minor component.[204]

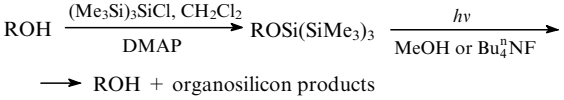


110 **111**

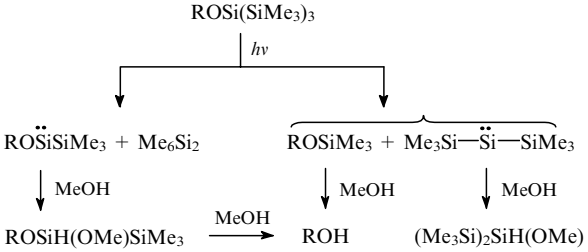


112 **113**

The tris(trimethylsilyl)silyl group can be used as a photolabile protecting group for the alcoholic function. The possibility of the use of the TTS group for this purpose was studied by Brook *et al*.[205, 206] Tris(trimethylsilyl)silyl ethers of primary and secondary alcohols were prepared in 70% to 97% yields by the reaction of tris(trimethylsilyl)silyl chloride with the corresponding alcohols in the presence of 4-dimethylaminopyridine (DMAP). The best yields are achieved in the case of more acidic alcohols. Tertiary alcohols do not react due to steric hindrance. Extremely high stability of the ethers formed with respect to aqueous bases, Grignard and Wittig reagents, butyllithium and caesium fluoride is their salient feature. Removal of the silyl protection was achieved by irradiation with UV light (254 nm; 30 min) in the presence of methanol or tetrabutylammonium fluoride



An obvious disadvantage of this silyl protection is the formation of heavy organosilicon products upon photolysis.



The use of chromatographic methods has made it possible to obtain desilylated alcohols in 80% – 90% yields.[205, 206]

VIII. Rearrangements involving the tris(trimethylsilyl)silyl fragment

The tris(trimethylsilyl)silyl group is 'milder', more mobile and more reactive in various rearrangements induced by acids, bases, light, heat and treatment with transition metals than other commonly used bulky groups (Bu^t_3C, Bu^t_3Si, Pr^i_3Si). It is of note that depending on the active site (charge) and modes of its stabilisation this group (or, to be more precise, its Si_3Si fragment) can be either destroyed or formed in different rearrrangements.

1. Migrations of silyl groups

In the presence of $AlCl_3$, permethylated polysilanes, $Me(Me_2Si)_nMe$ ($n = 4-10$) undergo skeletal rearrangements to give thermodynamically more stable branched isomers in nearly quantitative yields.[36]

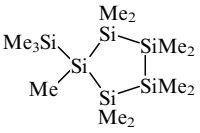
$$Me(Me_2Si)_4Me \xrightarrow{AlCl_3} (Me_3Si)_3SiMe$$

$$Me(Me_2Si)_5Me \xrightarrow{AlCl_3} (Me_3Si)_4Si$$

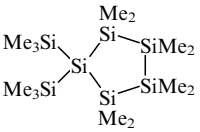
Permethylated cyclopolysilanes also yield isomeric branched cyclosilanes under the action of $AlCl_3$ containing 1% $FeCl_3$.[207]

$$(Me_2Si)_5 \xrightarrow{AlCl_3} \not\rightarrow$$

$$(Me_2Si)_6 \xrightarrow{AlCl_3}$$



$$(Me_2Si)_7 \xrightarrow{AlCl_3}$$



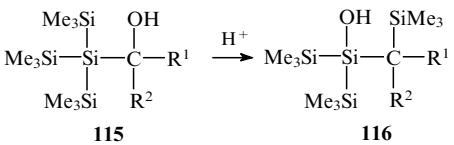
The photolytic rearrangement of the oligosilyl iron complex **114** produces the TTS fragment.[208]

$$(\eta^5\text{-Cp})Fe(CO)_2(SiMe_2)_4Me \xrightarrow{h\nu} (\eta^5\text{-Cp})Fe(CO)_2Si(SiMe_3)_3$$

114

This reaction occurs *via* the formation of silyl-silylene complexes $(\eta^5\text{-Cp})Fe(CO)(=SiMe_2)(Si_nMe_{2n+1})$ with subsequent migration of the silyl and methyl groups. The photochemical isomerisation of nonamethyltetrasilane, $H(SiMe_2)_4Me$, in the presence of catalytic amounts of $(\eta^5\text{-Cp})Fe(CO)_2SiMe_3$ or carbonyls $Fe(CO)_5$, $W(CO)_6$ initially results in $(Me_3Si)_3SiH$, which is further converted into the dimethylsilylene insertion product with insertion into the Si–H bond, $(Me_3Si)_3SiSiMe_2H$.[209] Thermal isomerisation in the presence of catalytic amounts of $(\eta^5\text{-Cp})Fe.(CO)(Ph_3P)SiMe_3$ gives exclusively tris(trimethylsilyl)silane.

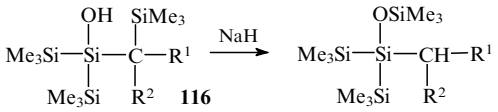
Under the action of strong acids, such as HCl or H_2SO_4, 1-hydroxyalkyltris(trimethylsilyl)silanes **115** undergo isomerisation through a 1,2-Me_3Si–OH exchange to give trimethylsilylmethylsilanols **116**.[210,211]



115 **116**

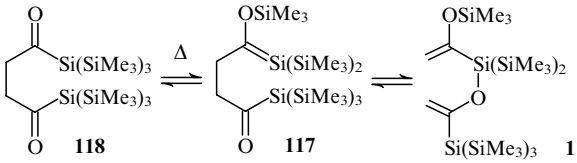
R^1 = H: R^2 = 4-MeC_6H_4, 4-$Pr^iC_6H_4$, Mes, 2-$Me_2NC_6H_4$, 2,4,6-$(MeO)_3C_6H_2$; $R^1 = R^2$ = Me.

Deprotonation of compounds **116** with sodium hydride results in migration of the trimethylsilyl group from the carbon atom to the oxygen atom.



116

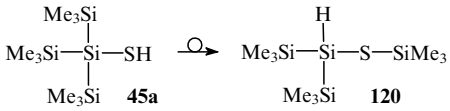
Silene **117** formed as a result of thermolysis of bis[tris(trimethylsilyl)silylcarbonyl]ethane **118** undergoes skeletal rearrangements to give the isomeric unsaturated compound **119**.[212]



118 **117** **119**

2. Rearrangements of organoelement derivatives

Tris(trimethylsilyl)silanethiol **45a** undergoes smooth radical-induced skeletal rearrangement through a 1,2-shift of the Me_3Si group from the silicon atom to the sulfur atom eventually resulting in thiohydride **120**.[213]



45a **120**

The migration of the Me_3Si group to the oxygen atom is energetically a very favourable process, this takes place in the autooxidation of tris(trimethylsilyl)silane (see Section IV.1)[50] as well as in its oxidation by alkyl nitrates.[214] The rearrangement of TTS-silanolate complexes into siloxysilyl complexes takes place in the thermolysis of transition metal hypersilylsilanolates.[136,137]

The reaction of $(Me_3Si)_3SiLi$ with *tert*-butyldichlorophosphine yields the expected product, *viz*., hypersilylphosphine **121**; however, its distillation (110–115 °C at 0.01 Torr) gives the rearrangement product **122**.[123]

$$(Me_3Si)_3SiLi + Bu^tPCl_2 \xrightarrow[-20\ ^\circ C]{THF} (Me_3Si)_3SiP(Cl)Bu^t \longrightarrow$$

121

$$\longrightarrow (Me_3Si)_2Si(Cl)P(SiMe_3)Bu^t$$

122

Alkyldichlorophosphines containing less bulky substituents, *e.g*., dichloromethylphosphine **123**, react with TTS-Li with elimination of tris(trimethylsilyl)chlorosilane.

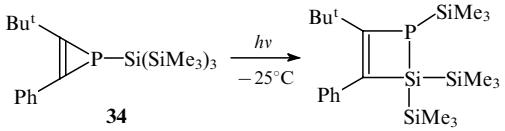
$$(Me_3Si)_3SiLi + MePCl_2 \longrightarrow [(Me_3Si)_3SiP(Cl)Me] \longrightarrow$$

123

$$\longrightarrow (Me_3Si)_3SiCl + 1/5\,(MeP)_5$$

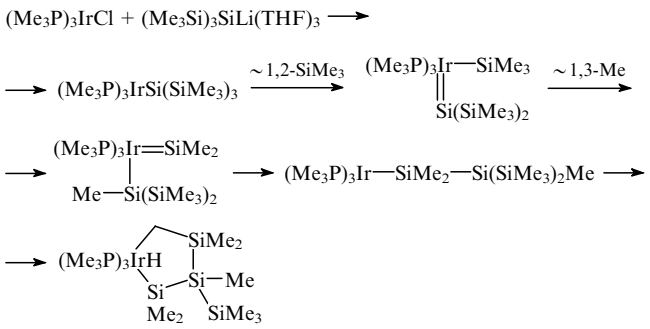
No formation of free phosphinydene took place in the presence of buta-1,3-diene in control experiments,[123] which is in favour of a bimolecular mechanism of splitting of tris(trimethylsilyl)chlorosilane.

Photochemical (λ = 280 nm) expansion of the three-membered phosphorus-containing ring **34** involving the tris(trimethylsilyl)silyl group is known.[128]

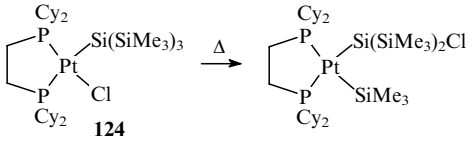


34

Low-valent transition metal complexes containing a TTS group are usually unstable; their stabilisation occurs at the expense of the migration of the silyl group.[215]

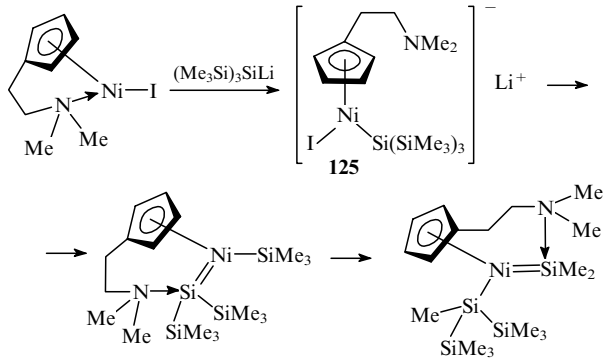


Similar migration is observed in the case of the TTS platinum complex **124**.[216, 217]



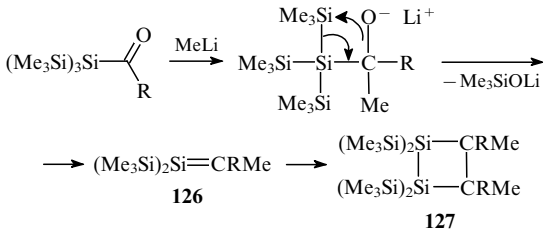
Cy is cyclohexyl.

Complex rearrangements of the TTS fragment, which first include migration of the trimethylsilyl and then of the methyl group, take place in the coordination sphere of the cyclopentadienylnickel derivative **125**.[218]



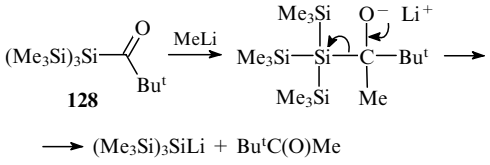
3. Migration of the trimethylsilyl group (the Peterson migration) and related processes in the series of hypersilyl derivatives

The formation of the O-nucleophilic centre in the β-position relative to the TTS group usually results in elimination of the trimethylsilanolate anion and formation of silaethenes **126**, which are further condensed to form disilacyclobutanes **127**.[219]



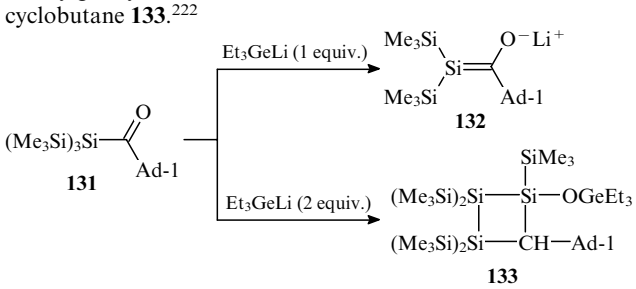
R = Me, Ph.

However, this reaction is extremely sensitive to steric factors. Under the action of methyllithium, compound **128** easily decomposes into *tert*-butyl methyl ketone and tris(trimethylsilyl)silyllithium.[219]

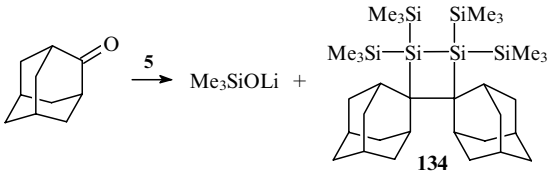


The introduction of a donor amino group that stabilises the intermediate silaethene **129** changes the direction of the dimerisation. In this case, the 'head-to-tail' dimer **130** is formed (Scheme 1).[220]

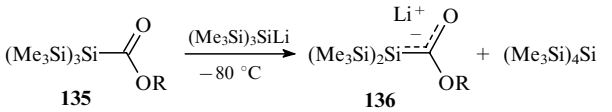
Apparently, triethylgermyllithium cannot add to the carbonyl group of 2-adamantyl tris(trimethylsilyl)silyl ketone **131** due to considerable steric hindrance. With the stoichiometric ratio of the reagents, the reaction product is silaenolate **132**; the half-conversion time is 12 h.[221, 222] In the presence of a twofold excess of triethylgermyllithium, silaenolate **132** is converted into trisilacyclobutane **133**.[222]



The Peterson elimination also occurs in the reaction of $(Me_3Si)_3SiLi(THF)_3$ with adamantanone in hexane and gives an unstable silene, which undergoes spontaneous dimerisation of the 'head-to-head' type to give disilacyclobutane **134**.[223]

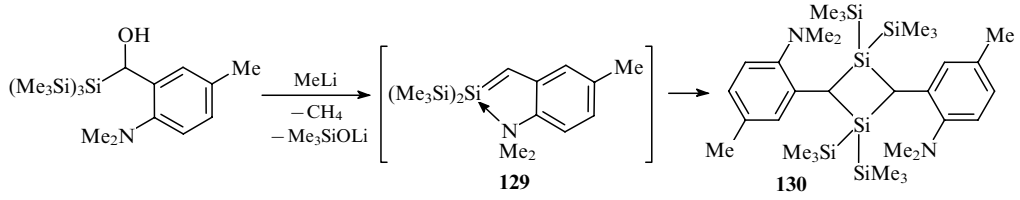


The reactions of tris(trimethylsilyl)silylcarboxylates $(Me_3Si)_3SiC(O)OR$ with lithium reagents have been studied in great detail.[224, 225] Depending on the nature of R and the reagent used, this reaction occurs through several main pathways, *viz.*: (1) formation of lithium tris(trimethylsilyl)silylcarboxylate; (2) elimination of the TTS group by a lithium reagent; (3) addition of a lithium reagent to the carbonyl group of carboxylates. In particular, the reaction of alkyl tris(trimethylsilyl)silacarboxylates **135** with $(Me_3Si)_3SiLi$ is accompanied by elimination of the Me_3Si group and formation of new silyllithium derivatives **136**.[225]

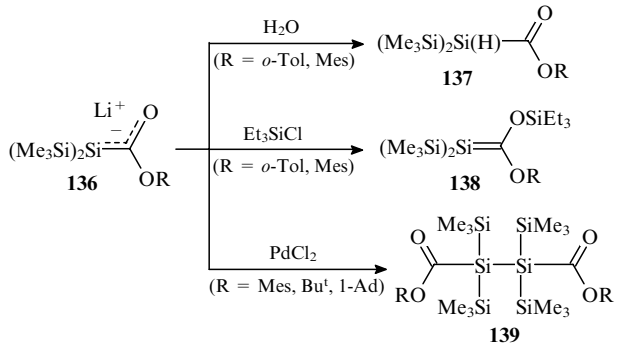


R = Cy, 1-Ad, Bn, *o*-Tol, Mes.

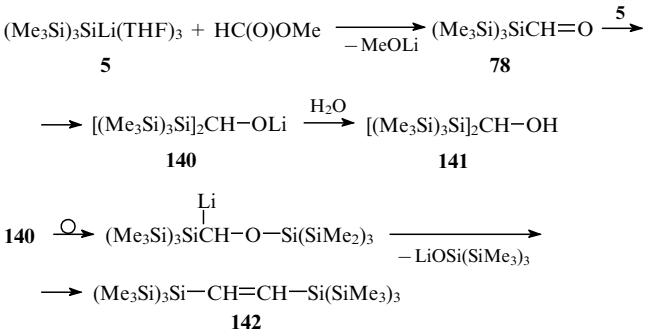
Scheme 1



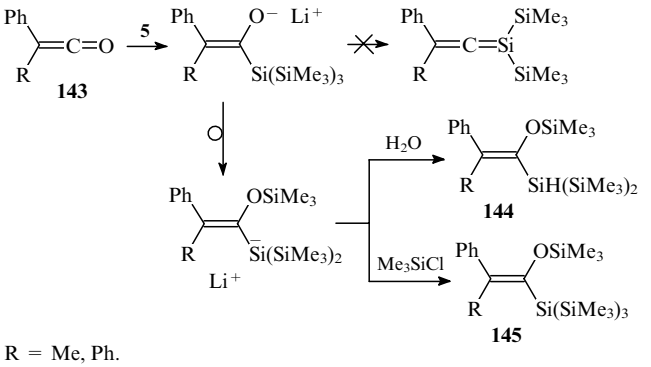
Hydrolysis, silylation and oxidation of silanoenolate **136** afford compounds **137**–**139**.



The reaction of tris(trimethylsilyl)silyllithium (**5**) with methyl formate[226] occurs *via* formylsilane **78** which adds the second molecule of $(Me_3Si)_3SiLi$. The intermediate lithium bis(trimethylsilyl)silylmethoxide **140** can be detected after hydrolysis as the corresponding bis(TTS)methanol **141**. Under the reaction conditions, compound **140** is further converted into the final product, *viz*., 1,2-bis[tris(trimethylsilyl)silyl]ethylene **142** in 60% yield.

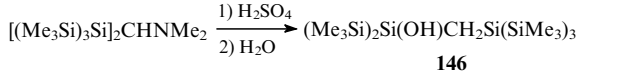


The reaction of ketenes **143** with tris(trimethylsilyl)silyllithium occurs with the migration of the anionic centre from the oxygen atom to the silicon atom, which eventually results in unexpected products **144** and **145**.[227]



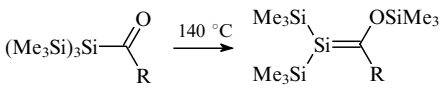
R = Me, Ph.

The synthesis of silanol **146** proceeds formally through elimination of (dimethylamino)trimethylsilane in accordance with the acid-induced Peterson reaction to give the intermediate silene $(Me_3Si)_2Si{=}CHSi(SiMe_3)_3$.[228]



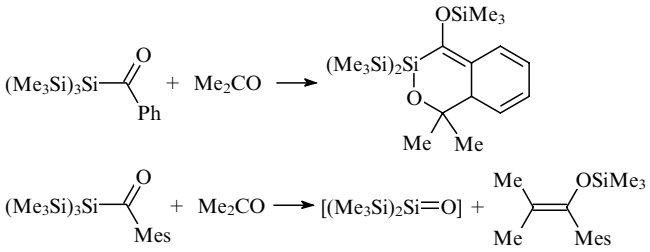
4. Thermal reactions of acylpolysilanes

Similar to photolysis, the thermolysis of acyltris(trimethylsilyl)silanes yields silaethenes.[229]



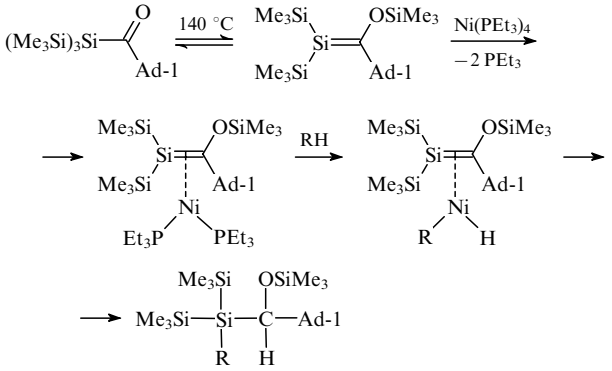
R = Me, But, 1-Ad, Ph, Mes.

Heating of acylsilanes in the presence of ketones affords products the composition of which is determined by the nature of the acyl substituent. This reaction consists of several consecutive insertion and rearrangement steps, which hinder significantly the prediction of the final products.[229]



Acetyltris(trimethylsilyl)silane, $MeC(O)Si(SiMe_3)_3$, gives no adducts when heated with ketones, presumably due to rapid dimerisation of the silaethene formed.

An unusual system $(Me_3Si)_3SiC(O)(1\text{-Ad})-Ni(PEt_3)_4$ is reported,[230] which allows activation of the C−H bonds of aromatic compounds and of the Si−H bonds of silanes. Catalytic amounts of tetrakis(triethylphosphine)nickel catalyse the addition of RH (R = Ph, $PhMe_2Si$) to the silaethenes formed upon heating 1-adamantoyltris(trimethylsilyl)silane.



R = Ph, $PhMe_2Si$.

* * *

The data on the synthesis, reactivities and applications of tris(trimethylsilyl)silyl derivatives demonstrate the high potential of the $(Me_3Si)_3Si$ ligand in organic and organometallic chemistry and testify to the uniqueness of the TTS group. The present review is an attempt to draw a 'portrait' of the TTS group from different standpoints, which may facilitate the correct choice of this ligand for concrete experimental tasks. Currently, wide application of the TTS ligand is limited due to the high cost of the starting reagents, *viz*., $(Me_3Si)_3SiH$ and $(Me_3Si)_4Si$. It remains to be hoped that the rapid development of the chemistry of TTS derivatives in the next few years will make it possible to reduce the cost and to expand the range of the reagents based on them.

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