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Organosilathianes

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Published data on the synthesis and physical and chemical properties of organosilathianes have been summarised and systematised, and the possibilities for their practical application examined and evaluated.
The bibliography contains 215 references.

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I. INTRODUCTION

The methods of synthesis and the physical and chemical properties of organosilathianes, and the possibility of their practical application, have been the subject of a large number of papers, which have not yet been reviewed. The increasing use of organosilathianes in polymer chemistry and in preparative synthesis, and the accumulation of experimental data on their methods of synthesis and properties, make it necessary to systematise the available material. The present review examines published work on the synthesis, properties, and applications of organosilathianes, published up to 1986.

II. METHODS OF PREPARATION

1. The Reaction of Organosilicon Compounds with Sulphur

A simple and convenient method for obtaining organosilathianes is by the insertion of sulphur at an Si—H bond.[1-5] The resulting organosilane thiols, when left to stand,[6] heated,[5] or treated with organochlorosilanes[7,8] or organoaminosilanes,[9] are converted into organosilathianes:

$$2Ar_nR_{3-n}Si{-}H + S \xrightarrow[\text{decalin, } 10\text{-}20\text{ h}]{180\text{-}200^\circ} 2Ar_nR_{3-n}SiSH \xrightarrow{-H_2S} (Ar_nR_{3-n}Si)_2S \quad (1)$$

$Ar = Ph$; $R = Me$, Et, Pr, Ph

$$3Ph_2SiH_2 + 6S \xrightarrow{-3H_2S} (Ph_2SiS)_3$$

$$4PhSiH_3 + 12S \xrightarrow{-6H_2S} PhSi\langle S\text{-}SiPh\rangle_3$$

$$R_3SiSH + ClSiR'_3 + R''_3N \xrightarrow[-R''_3N\cdot HCl]{} R_3SiSSiR'_3 \quad (2)$$

$$(RO)_3SiSH \xrightarrow{(R'O)_3SiNH_2,\ -(RO)_3SiSiNH_4} (RO)_3SiSSi(OR')_3$$

$$(RO)_3SiSH \xrightarrow{Me_3SiNR''_2,\ -(RO)_3SiSH_3NR''_2} (RO)_3SiSSiMe_3$$

$NR''_2 = NEt_2$, $NHSiMe_3$.

In reaction (2), instead of organosilane thiols, it is possible to use alkali and alkaline earth metal triorganosilanethiolates:[2,10]

$$(R_3SiS)_nM + nClSiR'_3 \rightarrow nR_3SiSSiR'_3 + MCl_n$$

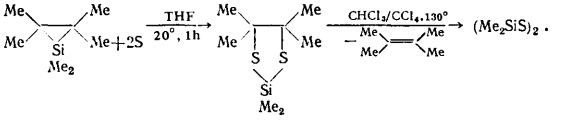
$M = Li, Na, K\ (n=1)$ [2]; $Ca, Sr, Ba\ (n=2)$ [10] .

At a high temperature, sulphur is also inserted into the Si—C bond. For example, tetrabutylsilane at 240° gives hexabutyldisilathiane:[11]

$$Bu_4Si + S \rightarrow [Bu_3SiSBu] \rightarrow (Bu_3Si)_2S + Bu_2S \ .$$

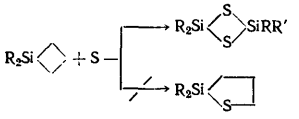
A similar reaction is observed with disilylhydronaphthalenes.[12]

The introduction of sulphur into strained silicon-containing rings takes place under much milder conditions (20°, 1—3 h), for example:[13]



With increase in temperature, the insertion product decomposes to a cyclic silathiane and an unsaturated hydrocarbon.

Cyclosilathianes are also obtained by the reaction of sulphur with dialkylsilacyclobutane[14] and with compounds containing Si—Si bonds:[15]



$$R_2HSiSiHR_2 + S \rightarrow (R_2SiS)_2 + R_2SiH_2 + R_2SiH + R_2Si\langle S\text{-}S\text{-}Si(H)R$$

$$R_3SiSiR_3 + S \rightarrow (R_2SiS)_2$$

$$(Me_2Si)_5 + S \xrightarrow{180^\circ} (Me_2Si)_5S$$

$R = Me$, i-Pr, t-Bu, cyclohexyl .

Sulphur is very easily inserted at an Si—Hg bond; the resulting unstable insertion product decomposes under the influence of ultraviolet radiation[16-18] or when heated:[19]

$$(Et_3Si)_2Hg + S \xrightarrow{20^\circ} Et_3SiSHgSiEt_3 \rightarrow (Et_3Si)_2S + Hg$$

$$(Et_3SiS)_2Hg \xrightarrow{\Delta} (Et_3Si)_2S + HgS \ .$$

Finally, sulphur can be inserted directly at an Si—S bond, forming organosilylsulphanes:[20]

$$R_3SiSSiR_3 + nS \xrightarrow{200^\circ} R_3SiS_{n+1}SiR_3$$

$R = Me$, Et; $n = 1-8$.

2. Reactions with Hydrogen Sulphide

The most widely used method for synthesising organosilathianes is by the thiolysis of organochlorosilanes in a solvent in the presence of tertiary amines. This method was used to obtain the first linear[21–23] and cyclic[24–26] silathianes:

$$2R_3SiCl + H_2S + 2R'_3N \xrightarrow[-2R'_3N\cdot HCl]{} (R_3Si)_2S \ .$$

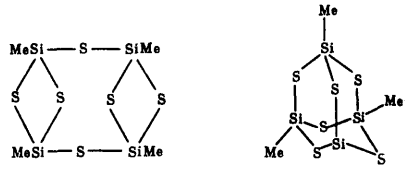
With triorganohalogenosilanes, this reaction gives hexaorganodisilathianes:[21,22,27–32] when the silicon atom has a substituent with a high electronegativity or a large volume, triorganosilane thiols are obtained in addition to disilathianes. The conversion of silane thiols or their salts to disilathianes is readily carried out by reactions (1)–(3).

The reaction of diorganodihalogenosilanes with hydrogen sulphide gives cyclic silathianes:[33–36]

$$nR_2SiCl_2 + nH_2S \xrightarrow[-2nR_3N\cdot HCl]{2nR_3N} (R_2SiS)_n \ . \quad (4)$$
$$n = 2, 3$$

With methyldichlorosilane, the reaction products, in addition to trimethylcyclotrisilathiane, also contain crystalline $[(MeSi)_2S_3]_2$,[33] which is assigned the structure (I)[31] or (II):[34,38]

$$MeHSiCl_2 + H_2S \xrightarrow[-R_3N\ HCl]{R_3N} (MeHSiS)_3 + \left[(MeSi)_2S_3\right]_2$$



(I)

(II)

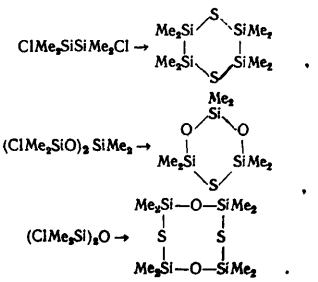
Products of this type are obtained by the reaction of H_2S with methyl(methoxy)dichlorosilane or organotrichlorosilanes in the presence of a hydrogen chloride acceptor:[24,31,37,39]

$$RSiCl_3 + H_2S \xrightarrow[-R_3N\cdot HCl]{R_3N} [(RSi)_2S_3]_2 \xleftarrow[-MeOH]{R_3N} Me(MeO)SiCl_2 + H_2S \ .$$

With a deficit of the tertiary amine, 1,3-dichloro-1-3-dialkylcyclodisilathianes (III) can be isolated from the reaction mixture;[24] compounds (III) react further with hydrogen sulphide and the amine to give $[(RSi)_2S_3]_2$, confirming structure (I):

$$2PrSiCl_3 + 2H_2S + 4C_5H_5N \rightarrow \underset{\text{(IiI)}}{\text{Pr(Cl)Si(S)Si(Cl)Pr}} \xrightarrow{2H_2S,\ 4C_5H_5N} (I) \ .$$

Various organochlorosilanes and organosiloxanes also undergo thiolysis and cothiolysis. This makes it possible to obtain a wide range of cyclic products,[40–43] for example:



The reaction of triethyl- and tripropylsilylamines and triethyl-N-(2-phenylethyl)silylamine with hydrogen sulphide gives the disilathiane and a small quantity of the silane thiol:[21,44]

$$Et_3SiNH_2 + H_2S \rightarrow (Et_3Si)_2S + Et_3SiSH \ .$$

Tris-silylamine and N-methyldisilylamine absorb H_2S at room temperature and under pressure to give disilathianes and ammonium salts of silane thiols:[45,46]

$$(H_3Si)_3N + 2H_2S \rightarrow H_3SiS^-NH_4^+ + (H_3Si)_2S$$
$$(H_3Si)_3NMe + 3H_2S \rightarrow (H_3Si)_2S + 2H_2SiS^-MeNH_3^+ \ .$$

Treatment of these salts with trimethylchlorosilane gives unsymmetrical trimethyldisilathiane,[45] and the reaction with BCl_3 gives disilyl sulphide:[46]

$$H_3SiSH\cdot NH_3 + Me_3SiCl \xrightarrow{-NH_4Cl} H_3SiSSiMe_3$$
$$H_3SiSH\cdot MeNH_2 + BCl_3 \xrightarrow[-MeNH_2\cdot HCl]{} [(H_3SiS)_3B] \xrightarrow[-B_2S_3]{} (H_3Si)_2S \ .$$

Hexamethyldisilazane and N-trimethylsilylaniline reacts with hydrogen sulphide with difficulty to give trimethylsilanethiol in ~14% yield.[45]

At the boiling point, organocyclosilazanes undergo slow thiolysis with the subsequent transformation of the silazane groups into silathiane groups:[47,48]

$$[R_2SiNH]_n \xrightarrow[-NH_4SH]{2nH_2S} \left[(R_2SiNH)_{n-1}(R_2SiS)\right] \xrightarrow[-NH_4SH]{2nH_2S} \left[(R_2SiNH)_{n-2}(R_2SiS)_2\right] \cdots \rightarrow$$
$$\xrightarrow[-(n-2)NH_4SH]{2(n-2)H_2S} [R_2SiS]_m \quad (5)$$
$$R = Alk,\ m = 2, 3;\ n = 3, 4 \ .$$

Imidazole is an effective catalyst for the thiolysis of hexamethyldisilazane.[49–51] Its catalytic action involves the ready formation of N-trimethylsilylimidazole, which subsequently silylates hydrogen sulphide:[51]

$$(Me_3Si)_2NH + 2HN\langle\rangle \xrightarrow{-NH_3} 2Me_3SiN\langle\rangle \xrightarrow[-2HN\langle\rangle]{H_2S} (Me_3Si)_2S \ .$$

Another method of improving reaction (5) is by the combined thiolysis of SiN- and SiCl-containing compounds:[52,53]

$$2(Me_3Si)_2NH + 3H_2S + 2Me_3SiCl \rightarrow 3(Me_3Si)_2S + 2NH_4Cl \ , \quad (6)$$

$$(R_2SiNH)_n + R_2SiCl_2 + H_2S \xrightarrow{-NH_4Cl} (R_2SiS)_m \ , \quad (7)$$
$$n = 3, 4;\ m = 2, 3$$

$$Me_3SiNR_2 + H_2S + Me_3SiCl \rightarrow (Me_3Si)_2S + R_2NH\cdot HCl \ . \quad (8)$$

Carboxylic acid silylamides[54] and trimethylcyanosilane[55] react readily with hydrogen sulphide to give hexamethyldisilathiane in high yield (86%):

$$\left.\begin{array}{l} MeC(OSiMe_3)=NSiMe_3 \xrightarrow[-MeCONHSiMe_3]{H_2S} \\ Me_3SiCN \xrightarrow[-HCN]{H_2S} \end{array}\right\} \rightarrow (Me_3Si)_2S \ .$$

To conclude this section, mention must be made of a method for obtaining disilathiane by the action of an electric discharge on an equimolar mixture of SiH_4 and H_2S.[56]

3. Reactions of Hexamethyldisilathiane

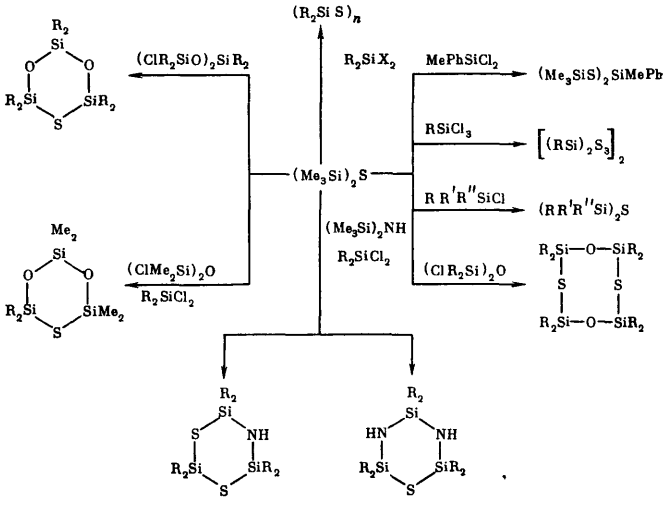
Reactions (6) and (8) have proved extremely promising for the synthesis of linear organosilathianes, in particular hexamethyldisilathiane, which has been obtained chromatographically pure in almost quantitative yield. The synthesis of cyclic silathianes by reaction (7), however, in spite of the high activity of the starting materials, has a significant disadvantage, namely the formation in a number of cases of a mixture of cyclosilathianes and cyclosilathiazanes, difficult to separate.

An effective method for the synthesis of linear and cyclic organosilathianes, organosilathiaoxanes, and organosilathiazanes is based on the trans-silylation of hexamethyldisilathiane by organochlorosilanes:[57]

$$n/2\ (Me_3Si)_2S + R_{n-4}SiCl_n \rightleftarrows nMe_3SiCl + R_{4-n}SiS_{n/2} \quad (9)$$
$$R = Alk, Ar;\ n = 1-3$$

This equilibrium reaction takes place with difficulty even on prolonged heating (200–250 °C). In the presence of catalytic quantities of amines or DMF, however, its rate increases markedly, and the reaction is quantitative when the trimethylchlorosilane is continuously removed.

The extensive synthetic possibilities of reaction (9) can be illustrated by the following examples:[57–62]



These examples show that this method can be used to obtain organosilicon compounds containing Si–S–Si bonds with practically any specified structure.

The splitting of cyclosilathianes by bifunctional organosilanes has been proposed as a method of obtaining polymeric organosilathianes.[63] An NMR study of the equilibrium of the reaction between $(Me_2SiS)_3$ and Me_2SiX_2, where X = Cl, Br, OMe, SMe, at 150 °C and 200 °C showed that the reaction is displaced towards the formation of the cyclic dimers and trimers, and also short chain molecules.[64,65]

4. Reaction with Inorganic Sulphides

A general method for synthesising organosilathianes is by the reaction of organo-iodosilanes with the sulphides of silver[23,24,66–68] and mercury:[68–77]

$$2nR_3SiI + M_nS \rightarrow (R_3Si)_2S + MI_n$$
$$R = Alk, Ar;\ M = Hg, Ag;\ n = 1, 2$$

The same reaction can be used to obtain Si–H-containing organosilathianes:[76,77]

$$Me_nH_{3-n}SiI + HgS \xrightarrow[-HgI]{35^\circ} (Me_nH_{3-n}Si)_2S$$

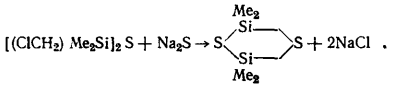
The reaction of mercury sulphide with di-iodosilane gives a mixture of oligomers $(H_2SiS)_x$, containing as the principal component $(H_2SiS)_3$, which cannot be isolated from the mixture, because of its low thermal stability. When kept in the light (20°, 8 d), the oligomers are converted into a resinous polymer, which when heated in a vacuum is depolymerised to give trisilathiane. Unlike its alkyl homologues, trisilathiane is unstable, and polymerises at room temperature. In contact with pumice or aluminium sulphide, its stability is increased, and decomposition begins only at 250 °C:[77]

$$HgS + H_2SiI_2 \xrightarrow[benzene]{80^\circ} (H_2SiS)_n \xrightarrow[10^{-3}\ mmHg]{210^\circ} (H_2SiS)_3 \xrightarrow[[Al_2S_3]]{250^\circ} H_3SiSH + (H_3Si)_2S + H_2S$$

The passage of trimethylchlorosilane vapour (400°) through a molten eutectic LiCl/KCl mixture containing 25% potassium sulphide gave hexamethyldisilathiane in 81% yield.[78,79]

Hexamethyldisilathiane is also formed when trimethylchlorosilane is heated with anhydrous sodium sulphide in a sealed tube.[80]

Sodium sulphide can also be used to obtain cyclic silathianes, for example:[81]

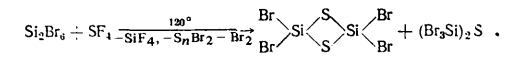


Organochlorosilanes react vigorously with ammonium hydrogen sulphide even in the cold, to give organosilathianes in high yield (up to 90%):[82]

$$2R_3SiCl + 2NH_4SH \xrightarrow[-H_2S]{-2NH_4Cl,} (R_3Si)_2S$$

In addition to the desired compounds, the reaction products also include Si–N-containing compounds, formed by an ammonolysis side reaction.

The reaction of disilanes with sulphur tetrafluoride can in principle be used to synthesise various organosilathianes:[83]



Hexamethyldisilathiane has been isolated as one of the products of the reaction of trimethyl(dimethylamino)silane with phosphorus pentasulphide:[84]

$$8Me_3SiNMe_2 + P_4S_{10} \rightarrow 2\ (Me_3Si)_2S + 4\ (Me_2N)_2P(S)SSiMe_3$$

5. Thermal Rearrangements of Sulphur-Containing Organosilicon Compounds

When distilled at atmospheric pressure, hexamethylcyclotrisilathiane undergoes rearrangement to give the cyclic dimer:[36,64,85]

$$2(Me_2SiS)_3 \rightleftarrows 3(Me_2SiS)_2 \quad (10)$$

A ^1H NMR study of this equilibrium in solution showed that high temperatures and high dilution facilitate the formation of small rings. The ring strain energy in the cyclic dimer is ~3 kcal per monomer unit.[86]

2,4,6-Trimethyl-2,4,6-triphenylcyclotrisilathiane[36] and hexaphenylcyclotrisilathiane[35] behave similarly.

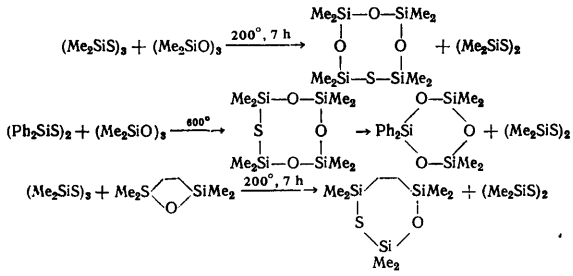
The existence of equilibrium (10) explains the lack of agreement in the physical constants given by many authors for various cyclosilathianes. For example, for hexaphenylcyclotrisilathiane, melting points 188–198° [35] and 191–193° [4] have been given; two melting points have also been given for trimethyltriphenylcyclotrisilathiane: 109° [59] and 112.5–114°.[87] It has been suggested that reaction (10) may take place with the intermediate formtion of silathiane oligomers[64,65,67] or the unstable species $[R_2Si=S]$:[88]

$$(Me_2SiS)_3 \rightleftarrows -(-Me_2SiS-)_n- \rightleftarrows (Me_2SiS)_2 \quad (11)$$

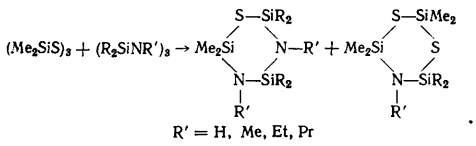
$$(Me_2SiS)_3 \rightleftarrows [Me_2Si=S] + (Me_2SiS)_2$$
$$2[Me_2Si=S] \rightleftarrows (Me_2SiS)_2 \quad (12)$$

Equilibrium (11) was proved in Refs.63, 65, and 77, and reaction (12) was confirmed by carrying out the reactions of cyclosilathianes with hexamethylcyclotrisiloxane or 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane, which act as "traps" for $[Me_2Si=S]$. Thus when

these reagents are heated, the products are the cyclosilathiaoxanes and the cyclodisilathiane:[88-90]



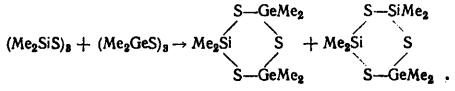
Cyclic organosilathiazanes have been obtained by heating hexamethylcyclotrisilathiane and hexaorganocyclotrisilazanes:[91,92]



R' = H, Me, Et, Pr

Depending on the group, this exchange reaction gives a mixture of the cyclotrisiladithiazane and the cyclotrisilathiadiazane or only the cyclotrisiladithiazane.

The exchange reaction between hexamethylcyclotrisilathiane and hexamethylcyclotrigermanium sulphide gives mixed heterocyclic compounds containing silicon, germanium, and sulphur atoms:[93]



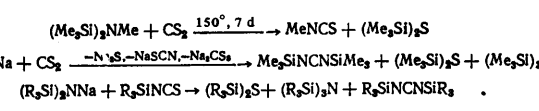
6. Other Methods

This section deals with studies whose aim was not the directed synthesis of organosilathianes.

An exception is the reaction of thiophene with the reagents usually employed for C-silylation:[94]

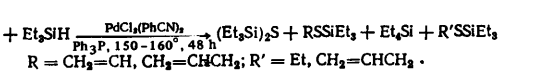


Silazanes and their N-metal derivatives react with CS_2, COS, and RNCS to give mixtures of products including hexamethyldisilathiane:[92-98]

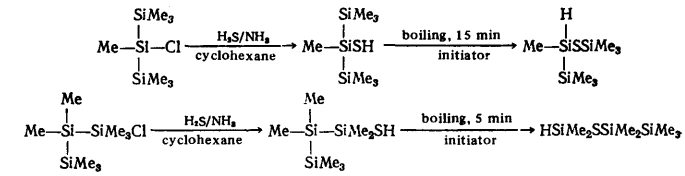


A similar result was obtained in the reaction of carbon disulphide with trimethylsilyl esters of isothiocyanatocarboxylic acids.[99]

The splitting of unsaturated sulphides by triethylsilane, in addition to other products, gives hexaethyldisilathiane:[100]

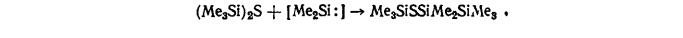


Under the influence of the radical reaction initiators benzoyl peroxide or azo-bis-isobutyronitrile, trisilanethiols undergo rearrangement to give silathianes:[101]

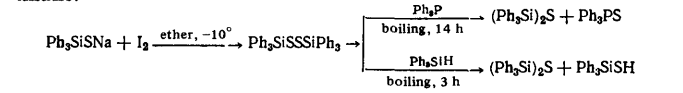


Trialkylsilanethiols do not undergo this rearrangement, even on prolonged boiling in xylene.

The insertion of dimethylsilylene, obtained by the thermal decomposition of $(Me_2Si)_6$, at an Si–S bond provides an interesting method for obtaining unsymmetrical silathianes:[102]



Hexaphenyldisilyl disulphide is obtained by the action of iodine on sodium triphenylsilanethiolate.[103] Treatment of this compound with triphenylphosphine or triphenylsilane gives hexaphenyldisilathiane:



III. PHYSICAL PROPERTIES

In spite of recent progress in the synthesis of organosilathianes, their physical properties have been comparatively little studied.

Data on the structure of various linear and cyclic organosilathianes have been obtained by electron diffraction and microwave spectroscopy:[104,105]

Compound	Bond length Si–S, Å	Si–S–Si	Angles, degrees S–Si–S	Refs.
$(Me_2SiS)_2$	2.18±0.03	75	105	[104, 105]
$(Me_2SiS)_3$	2.15±0.03	110	115	[104, 105]
$(H_3Si)_2S$	2.136±0.002	97.4±0.7	—	[6]

Comparison with the C–S–C angle in dimethyl sulphide (98°51′)[106] shows that there is no π-bonding in disilyl sulphide.

The Si–S–Si stretching bands in the infrared (IR) spectra of linear and cyclic silathianes lie in the following ranges (cm^{-1}):[107] 396–416 $[(Cl_3Si)_2S]$; 437–493 $[(Me_3Si)_2]$; 480–524 $[(H_3Si)_2S]$; 493–530 $\{[(PhCH_2)_3Si]_2S\}$; 519–556 $\{[(p\text{-}MeC_6H_4)_3Si]_2S\}$; 518–572 $[(Ph_3Si)_2S]$. The displacement of ν_{Si-S} to higher wavenumbers is attributed to the decrease in the polarity of this bond in the last three compounds. It has been suggested[107] that in view of the strong inductive effect of the phenyl group, structures $Ph_3Si^- = S^+$ with a $(p \rightarrow d)_\pi$ double bond plays a significant part in the resonance system.

The Raman and IR spectra of hexamethyldisilathiane have been used to determine the force constant (2.20×10^5 dyne cm^{-1}), The Si–S–Si angle (104°), and the bond dissociation energy (63 kcal $mole^{-1}$).[108]

An overall similarity is observed in the Raman spectra of hexamethyl- and hexachlorodisilathianes, whose molecules have C_{2v} symmetry. The comparatively small splitting of $\nu_{Si-S-Si}$ [47 cm^{-1} in $(Me_3Si)_2$ and 21 cm^{-1} in $(Cl_3Si)_2S$] shows that the Si–S–Si angle is close to 90°. The spectra of $(Me_2SiS)_2$ and $(Cl_2SiS)_2$ indicated that the Si_2S_2 ring is planar. On going from the linear to the cyclic disilathiane, the spectra show an increase in $\nu_{s(Si-S-Si)}$ and an increase in ν_{as} to approximately the same extent as on going from propane to cyclobutane.[109]

In the Raman spectrum of molten tetramethylcyclodisilathiane, the strongest lines of hexamethylcyclotrisilathiane were detected, indicating the existence of the equilibrium $3(Me_2SiS)_2 \leftrightarrows 2(Me_2SiS)_3$.[110]

The vibrational spectra indicate that $(Me_2SiS)_2$ has a planar structure with D_{2h} symmetry, in agreement with electron diffraction data and dipole moment measurements. The choice between models with symmetry C_{3v} (chair form) and C_s (boat form) for $(Me_2SiS)_3$ is not so obvious, although the combined spectroscopic data provide evidence for the latter. Comparison of data on the structure of cyclosilathianes with the magnitude of the Si–S–Si angle in $(H_3Si)_2S$ shows that the tetramethylcyclodisilathiane ring is strained as a result of a deviation from the normal valence angles.[110]

There are no unambiguous published data on the conformational transformations of cyclosilathianes. Thus according to X-ray diffraction data, *trans*-2,4,6-trimethyl-2,4,6-triphenylcyclotrisilathiane is present in the crystals in a boat form,[111] whereas in solution (according to ^{1}H NMR data) is is present as boat forms undergoing rapid interconversion, although the chair form cannot be completely excluded.[87]

Gas-phase electron diffraction showed that hexamethylcyclotrisilathiane is non-planar.[105] From a comparison of the experimentally determined value of the dipole moment with the values calculated for the chair and boat models, it was suggested[112] that $(Me_2SiS)_3$ exists chiefly in the chair form, although a small concentration of the boat form is possible. From the Raman and IR spectra, it was concluded[110] that hexamethylcyclotrisilathiane in the liquid state is present in the boat form.

The conformational transformations of methylphenyl-,[113] methylethyl-,[111] and methylvinylcyclosilathianes[111] have also been studied.

The dispole moment of hexamethyldisilathiane, measured in benzene at 25 °C, is 1.44 D. The dipole moments of $(Me_3Si)_2S$ and $(Me_3Si)_2O$ have been used to estimate the angles Si–S–Si (~97–98°) and Si–O–Si (~150°). The large difference in the angles is regarded as proof of $(p \rightarrow d)_\pi$ interaction in the Si–O bonds, and its absence in the Si–S bonds.[29]

The dipole moments of $(Me_2SiS)_2$ and $(Me_2SiS)_3$ have been calculated, assuming that the atomic polarisation of the cyclosilathianes is the same as that for the corresponding cyclosiloxanes: $\mu_{(Me_2SiS)_2}$ = 0.00; $\mu_{(Me_2SiS)_3}$ = 1.03 D.[112]

A study of compounds containing Si–S and S–Si–N bonds showed that the replacement of a C–S bond by an Si–S bond has no effect on the magnitude of the diamagnetic susceptibility;[114] similar data were obtained in Ref.115. This indicates that there is no $(p \rightarrow d)_\pi$ interaction in the Si–S bond.

Table 1. Effect of $(p \rightarrow d)_\pi$ conjugation in Si–E bonds.[40]

Physical properties	E = N		E = O		E = S	
	found	calculated	found	calculated	found	calculated
Bond length, Å	1.74±0.02; 1.72±0.03	1.81	1.63±0.04; 1.69±0.03	1.76	2.14±0.02	2.15
Force constant, mdyne Å^{-1}	4.1	3.3	4.7	3.7	2.2	2.2
Angle Si–E–Si, °	119.6±1; 131	109°28′	130±10; 145	109°28′	97.4±0.7; 104; 110	109°28′

The absence of this interaction is also indicated by ultraviolet (UV),[116] ^{1}H, ^{13}C,[117,118] and ^{29}Si NMR,[77] and Raman[119] spectroscopy.

Thus almost all studies of the physical properties of organosilathianes in one way or another deal with the problem of $(p \rightarrow d)_\pi$ conjugation. This problem is of primary importance for the chemistry of compounds containing Si–O and Si–N bonds, but it is not so important for the chemistry of organosilathianes, since the question of the existence of $(p \rightarrow d)_\pi$ conjugation in the Si–S–Si system has not yet been resolved unambiguously.

Thus from a comparison of the bond lengths, force constants, and Si–E–Si angles, it has been concluded that there is no $(p \rightarrow d)_\pi$ interaction in silathianes[40] (Table 1). This is confirmed by the physical properties of disilathianes.[6,120,121]

Nevertheless, many attempts have been made to estimate the extent of $(p \rightarrow d)_\pi$ conjugation in organosilathianes by UV, IR, and ^{1}H NMR spectroscopic studies.[122–131] It was assumed that $(p \rightarrow d)_\pi$ conjugation involves partial displacement of the p_π electrons of the S atom to the d_π orbitals of Si. As a result, the negative charge on the sulphur atom and the basic strength of the compound decrease.[129]

From an analysis of the IR spectra of substituted silicon hydrides containing Si–O and Si–S fragments, it was concluded[130] that the extent of $(p \rightarrow d)_\pi$ conjugation changes in the approximate ratio SiO : SiS = 2 : 1.

Thus $(p \rightarrow d)_\pi$ interaction (whether it exists or not) does not have the significant influence on the chemical properties of organosilathianes observed for organosiloxanes or organosilazanes. This is confirmed by a calculation of the overlap integrals of the Si–S bond,[131] where it was shown that the small magnitude of the overlap integral of the unoccupied atomic orbitals at this bond is one of the principal reasons for its high chemical activity.

IV. CHEMICAL PROPERTIES

An analysis of published data has shown that reactions involving the heterolytic splitting of Si–S–Si bonds in organosilathianes can be divided into two groups: exchange reations and insertion reactions.

The first group includes the great majority of known reactions of organisilathianes, taking place according to the general scheme:

$$\equiv Si{-}S{-}Si\equiv + X{-}Y \rightarrow \equiv Si{-}X + Y{-}S \ .$$

1) Y = H—"protic silylation" reactions (exchange between a silyl group and a mobile hydrogen atom), for example:

$$\equiv Si{-}S{-}Si\equiv + 2REH \rightarrow 2 \equiv SiER + H_2S. \qquad (13)$$

E = O, NH, S; R represents an organic or hetero-organic group.

2) Y = M—"aprotic silylation" reactions (exchange between a silyl group and a metal atom), for example:

$$\equiv Si{-}S{-}Si\equiv + HgR_2 \rightarrow 2\equiv SiR + HgS \ .$$

3) Y = Si—trans-silylation reactions (exchange between one silyl group and another), for example:

$$\equiv Si{-}S{-}Si\equiv + 2\equiv Si^*{-}E \rightleftarrows \equiv Si{-}S{-}Si^*\equiv + \equiv Si{-}E + \equiv Si^*{-}E \rightleftarrows \rightleftarrows \equiv Si^*{-}S{-}Si^*\equiv + 2\equiv Si{-}E \ .$$

4) Y = E—reactions involving the redistribution of functional groups (exchange between a silyl group and functional groups), for example:

$$X = Cl,\ \equiv Si{-}S{-}Si\equiv + 2\rangle P{-}Cl \rightarrow 2\equiv Si{-}Cl + \rangle P{-}S{-}P\langle$$

$$X = O,\ \equiv Si{-}S{-}Si\equiv + \equiv Sn{-}O{-} \rightarrow 2\equiv Si{-}O{-} + \equiv Sn{-}S{-} \ .$$

The second group includes reactions taking place according to the

$$\equiv Si{-}S{-}Si\equiv + X{-}Y \rightarrow \equiv Si{-}S{-}X{-}Y{-}Si\equiv \ . \qquad (14)$$

1) 1,1-insertion, for example:

$$\equiv Si{-}S{-}Si\equiv + [:SiR_2] \rightarrow \equiv Si{-}S{-}SiR_2{-}Si\equiv \ .$$

2) 1,2-insertion, for example:

$$\equiv Si-S-Si\equiv + (CF_3)_2CO \rightarrow \equiv SiOC(CF_3)_2S(CF_3)_2COSi\equiv .$$

3) 1,3-insertion, for example:

$$\equiv Si-S-Si\equiv + CH_2-CH_2 \rightarrow \equiv SiOCH_2CH_2SCH_2CH_2OSi\equiv ,$$

4) 1,4-insertion, for example:

$$\equiv Si-S-Si\equiv + \square \rightarrow \equiv SiOC(O)CH_2CH_2SSi\equiv .$$

5) 1,*n*-insertion, or example:

$$\equiv Si-S-Si\equiv + S_8 \rightarrow \equiv Si-S_n-Si\equiv .$$

1. Exchange Reactions

a) "Protic silylation"

The reaction of organosilathianes with proton-donor reagents involves exchange between a mobile proton of an inorganic, organic, or hetero-organic compound and a silyl group.[62] Organosilathianes silylate monohydric and polyhydric alcohols and phenols,[30,80,132–144] aminoalcohols and phosphorylated alcohols,[139,145] mineral and carboxylic acids,[70,71,90,146,149] inorganic and organic acids of phosphorus,[61,146,150,151] boron, arsenic, and sulphur,[61,151] enols,[152] aldoximes and ketoximes,[152] aromatic thiols, thioglycols,[61,153] amines and their derivatives,[80,154] and silanols and siloxanediols;[155] the silyl derivatives are formed in high yields.

Depending on the original reagent ratio, products of complete or partial silylation may be formed. In the case of cyclic silathianes, monomeric linear and cyclic compounds, and also polymers, have been obtained:

$$(R_3Si)_2S + 2H_n^{\pm}X \xrightarrow{-H_2S} 2R_3SiXH_{n-1} \rightarrow \cdots \rightarrow \xrightarrow[-H_2S]{(R_3Si)_2S} (R_3Si)_nX$$

$$(R_2SiS)_3 + H_nX \xrightarrow{-H_2S} \begin{cases} R_2Si(X)_2SiR_2 \\ R_2Si(X)S \\ R_2Si(X)SH \\ [R_2Si(X)]_2S \\ -(-R_2Si-X-)_n- \end{cases} .$$

The following general regular features of this reaction (13) have been established: the presence of bulky or electron-donor substituents on the silicon atom leads to a decrease in the activity of organosilathianes. The introduction of alkoxy groups into the silathiane molecule leads to the same result, and this has been attributed[135,137] to an increase in the $(p \rightarrow d)_\pi$ interaction in the Si–S bond. Cyclic silathianes are more active than the linear compounds, and cyclodisilathianes have the highest activity.[135,137]

A study of the model reaction of hexamethyldisilathiane with various proton donors (REH) made it possible to arrange them in the following order of decreasing activity: ROH > RR^1NH > RSH. This order corresponds to the decrease in the energy of the ≡Si–E bond formed in reaction (13).[61] The rate of the reaction of organosilathianes with proton donors increases when the molecule of the proton donor contains electron-acceptor substituents, which increase its acidity, and also when the reaction is carried out in polar solvents and in the presence of nucleophilic catalysts (tertiary amines, DMF, acetonitrile).[61]

The synthetic possibilities provided by organosilathianes as silylating reagents have been demonstrated by the reactions of hexamethyldisilathiane and hexamethylcyclotrisilathiane with a wide range of proton donors (Tables 2 and 3).

b) Aprotic silylation

There are only a few published examples of silathiane reactions of this type: the splitting of Si–S–Si bonds by organic compounds of mercury[156–162] and phenyl-lithium.[2]

Depending on the organic group, organomercury compounds react with organosilathianes to give products containing an Si–C or an Si–O bond:

$$(Me_3Si)_2S \xrightarrow{-HgS} \begin{cases} \xrightarrow{Hg(CONEt_2)_2} Me_3SiCONEt_2 \\ \xrightarrow{Hg(COOMe)_2} Me_3SiOMe + Me_3SiCOOMe \\ \xrightarrow{Hg[C(N_2)COOEt]_2} Me_3SiCN_2COOEt \\ \xrightarrow{Hg(CH_2COOR)_2} Me_3SiCH_2COOR , \end{cases} \quad (15)$$

$$R_3SiSSiMe_3 \xrightarrow{-HgS} \begin{cases} \xrightarrow{Hg(CH_2COR')_2} R_3SiOC(R')=CH_2 + Me_3SiCH_2COR' \\ \xrightarrow[HgR_2'']{} R_3SiR'' + R''SiMe_3 , \end{cases} \quad (16)$$

$$(R_3Si)_2S + Hg(CH_2COR''')_2 \rightarrow 2R_3SiOC(R''')=CH_2 + HgS \quad (17)$$

R_3=MePhC$_{10}$H$_7$-α; R′=H, Me, OMe, Ph; R″=MeCOO, MeO; R‴=OMe, OCH=CH$_2$, OCOPh, OCOMe

Reactions (15)–(17) provide an effective method for synthesising a number of silicon compounds which are difficult to obtain; in particular, a new class of compound, carbamoylsilanes, has been synthesised in this way.[158]

In the reaction of phenyl-lithium with hexaphenyldisiladithiane, the S–S bond, and not the Si–S bond, is split first:[2]

$$Ph_3SiS-SSiPh_3 + PhLi \rightarrow Ph_3SiSLi + PhSSiPh_3 \xrightarrow[-PhSLi]{PhLi} Ph_4Si .$$

c) Trans-silylation reactions

The principal regular features and synthetic possibilities of the trans-silylation of organosilathianes by organohalogeno- and organopseudohalogenosilanes and -siloxanes were discussed in section II.

d) Reactions involving the redistribution of functional groups

Organosilathianes are split by inorganic halides to give the corresponding sulphides and organohalogenosilanes

$$\equiv Si-S-Si\equiv + M-X \rightarrow 2\equiv Si-X + M-S \quad (18)$$

MX=BCl_3 [153], PCl_3, PBr_3, $POCl_3$ [163]; PCl_5 [164]; $AsCl_3$, $SbCl_3$ [165]; $TiCl_4$ [166, 167]; $SnCl_4$, VCl_3, $CrCl_3$ [167]; $PdCl_2$ [166]; $HgCl_2$ [70]; $PbCl_2$, $CdCl_2$, AgCl, AgBr [23]; NH_4Cl, KBr [168]; HgI_2 [169]

The splitting of the Si–S bond by the ammonium, sodium, and potassium salts of inorganic and organic acids[168] and by silver salts (AgCN, AgNCS, AgNCO, AgOCOMe) [23] takes place similarly. Hexa-alkyldisilathianes do not react with silver iodide.[23]

Disilathiane[70] and 1,3-dimethyldisilathiane[71] do not react with methyl iodide, and hexamethyldisilathiane does not react with lower alkyl halides.[61] On prolonged boiling, higher alkyl halides react with organosilathianes according to the scheme:

$$\equiv Si-S-Si\equiv \xrightarrow[-\equiv SiX]{RX} \equiv SiSR \xrightarrow[-\equiv SiX]{RX} R_2S .$$

Table 2. Reactions of hexamethyldisilathiane with proton donors REH.

REH	Reagent ratio REH : $(Me_3Si)_2S$	Reaction conditions	Products (yield, %)	Refs.
ROH	1:2	Δ	Me_3SiOR, R = Et (75), Bu (94), iso-Pr (78), t-Bu (58)	[80]
			$C_{12}H_{25}$ (87.5)	[139]
$HO(CH_2)_4OH$	1:1;	100–110°, 2 h	$Me_3SiO(CH_2)_4OSiMe_3$ (97.5)	[139]
	2:1	ditto	$Me_3SiO(CH_2)_4OH$ (55)	[139]
$EtC(CH_2OH)_3$	3:2	»	$EtC(CH_2OSiMe_3)_3$ (76.5)	[139]
$HOCH_2CH(OH)CH_2OH$	3:2	»	$Me_3SiOCH_2CH(OSiMe_3)CH_2OSiMe_3$ (96)	[139]
$HO(CH_2)_2NH_2$	1:2;	20°, 0.5 h	$Me_3SiO(CH_2)_2NH_2$ (98.5)	[139]
	1:1	100°, cat. C_5H_5N	$Me_3SiO(CH_2)_2NHSiMe_3$ (82.8)	[139]
$[HO(CH_2)_2]_2NH_2$	1:1;	20°, 0.5 h	$[Me_3SiO(CH_2)_2]_2NH$ (78.5)	[139]
	2:1	ditto	$Me_3SiO(CH_2)_2NH(CH_2)_2OH$ (44)	[139]
$[HO(CH_2)_2]_3N$	3:2;	»	$[Me_3SiO(CH_2)_2]_3N$ (73.2)	[139]
	1:1	»	$[Me_3SiO(CH_2)_2]_2N(CH_2)_2OH$ (91)	[139]
PhCH(OH)COOR	1:2	70–90°, 1–2 h	PhCH(OSiMe$_3$)COOR, R=Et (93), Pr (91)	[142]
$(RO)_2P(O)CR'R''(OH)$	1:2	50–70°, 0.5–1 h	$(RO)_2P(O)CR'R''(OSiMe_3)$, R=Me, R'=H; R''=Me (92), Ph (90); R'=Me, R''=Et (80); R=Et, R'=H, R''=Me (89), Ph (97)	[145]
$RCOCH_2COMe$	1:2	50—70°, *	$RCOCH{=}C(OSiMe_3)Me$, R=Me (78), Ph (92)	[152]
CH(R)C(O)CH_2C(O)CH(R) |——CH_2——|	1:2	ditto	CH(R)C(O)CH=C(OSiMe$_3$)CH(R), |——CH_2——| R=H (86), Me (80)	[152]
RR'C=NOH	1:2	50—70°	RR'C=NOSiMe$_3$; R=R'=Ph (95); R=H, R'=Me (85), Ph (89); R=Me, R'=Me (96), Ph (94)	[152]
XC_6H_4OH	1:2	80°, 1.5 h	$XC_6H_4OSiMe_3$, X=3-Me (74.3) 2-Me_3SiO (76.3); 2-OH (75.9); 3-Me_3SiO (72.4); 4-Me_3SiO (74.3); 2,3-$(Me_3SiO)_2$ (65.9); 3-NH_2 (96); 2-C_6H_5 (77.9); 4-MeCONH (73.8); 3-OH (76.1); 4-OH (43.1); 2.3-$(OH)_2$ (48.8)	[148]
1,2,3-$(HO)_3C_6H_3$	1:1	80°, 2.5 h, toluene	3-OH-1,2-$(Me_3SiO)_2C_6H_3$ (76.5)	[148]
Bu_2NH	1:2	boiling., 3 d	Bu_2NSiMe_3 (49)	[80]
RNH_2	1:2	boiling 25 h	$RNHSiMe_3$, R=Bu (13); R=Ph (85)	[80]
$PhNH_2$	1:2	100°, 2.5 h, cat. C_5H_5N	$PhNHSiMe_3$ (94.3)	[154]
$HOC_6H_4NH_2$	1:1	ditto	$Me_3SiOC_6H_4NHSiMe_3$ (79.2)	[154]
$H_2NCH_2CH_2NH_2$	1:1	»	$Me_3SiNHCH_2CH_2NHSiMe_3$ (85.2)	[154]
H_2SO_4	1:1	18–20°, 1 h	$(Me_3SiO)_2SO_2$ (92.5)	[147]
H_3PO_4	3:2	20°, 1 h	$(Me_3SiO)_3PO$ (95.6)	[146]
H_3PO_3	3:2	120°, 4 h	$(Me_3SiO)_3P$ (81.5)	[146]
$H_2S_2O_7$	1:1	—	$(Me_3SiOSO_2)_2O$ (74)	[149]
$XC_6H_4P(OH)_2$	1:2	40—80°	$XC_6H_4P(O)(OSiMe_3)H$, X=H (93), 4-Me (91)	[150]
$PhP(OH)_2$	1:1	ditto	$PhP(OSiMe_3)_2$ (75)	[150]
$PhB(OH)_2$	1:1	100° ditto	$PhB(OSiMe_3)_2$ (72)	[151]
$PhAs(O)(OH)_2$	1:1	»	$PhAs(O)(OSiMe_3)_2$ (54)	[151]
$PhSO_2OH$	1:2	»	$PhSO_2OSiMe_3$ (96)	[151]
$(RO)_2POH$	1:2	100–120°, 2–5 h	$(RO)_2POSiMe_3$, R=Me (81); Et (72), iso-Pr (84), Ph (84)	[151]
R_2POOH	1:2	40–60°, 0.5–2 h	$R_2POOSiMe_3$, R=Me (92), Et (89), Ph (73)	[151]
R_2PSOH	1:2	ditto	$R_2PSOSiMe_3$, R=Et (95), MeO (96), EtO (97)	[151]
$(RO)_2POOH$	1:2	»	$(RO)_2POOSiMe_3$, R=Me (93), Et (92)	[151]
$(RO)_2PSSH$	1:2	»	$(RO)_2PSSSiMe_3$, R=Me (94.5), Et (92), iso-Pr (89)	[151]
Ph_2PH	1:2	cat.	no reaction	[61]
RSH	1:2	boiling, 50 h	no reaction for R = Et, Bu, C_5H_{11}, C_2 = $=CHCH_3$ [61]	[61]
PhSH	1:2	100°, 0.5 h	$PhSSiMe_3$ (88)	[61]
MeCOOH	1:2	80°, 0.5 h	$MeCOOSiMe_3$ (88.3)	[146]
$CH_2=C(CH_3)COOH$	1:2	70—80°	$CH_2=C(CH_3)COOSiMe_3$ (87.9)	[146]
$(CH_2COOH)_2$	1:1	110–140°, 4 h	$(CH_2COOSiMe_3)_2$ (98.7)	[146]
$(CH_2CH_2COOH)_2$	1:1	50–60°, 2 h	$(CH_2CH_2COOSiMe_3)_2$ (55.2)	[146]
HOC_6H_4COOH	1:1	80–90°, 1 h	$Me_3SiOC_6H_4COOSiMe_3$ (80)	[146]
$Ph_2Si(OH)_2$	1:1	120–125°, 0.5 h, cat. $(Me_3SiO)_2POH$	$Ph_2Si(OSiMe_3)_2$ (83)	[155]
$HOSiMe_2OSiMe_2OH$	1:1	90–95°, 0.5 h, cat. $(Me_3SiO)_2POH$	$Me_3SiOSiMe_2OSiMe_2OSiMe_3$ (95)	[155]

*Boiling until liberation of H_2S stopped.

Increase in the electron-acceptor power of the substituents on the carbon atom of the alkyl halide, the polarity of the medium, and the basic strength of the sulphur atom increases the reactivity of organosilathianes towards alkyl halides.[61]

Acyl halides are much more reactive than alkyl halides towards organosilathianes:[61,170–172]

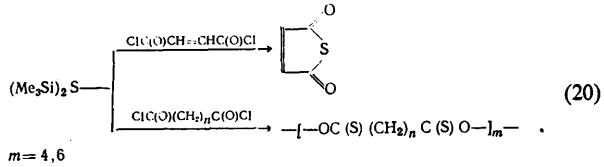
$$\equiv Si{-}S{-}Si \equiv \xrightarrow[-\equiv SiX]{RC(O)X} \equiv SiOC(S)R \xrightarrow[-\equiv SiX]{RC(O)X} [RC(O)]_2S \quad (19)$$

R=Me, Ph; X=Cl, Br

Table 3. Reactions of hexamethylcyclotristilathiane with proton donors REH.

REH	Reagent ratio $(Me_2SiS)_3$: REH	Reaction conditions	Product (yield, %)	Refs.
H_2O	2:9	alkaline hydrolysis, Δ	$HOSiMe_2OSiMe_2OH$	[26]
BuOH	1:6	70–80°, 2 h	$Me_2Si(OBu)_2$ (78)	[139]
$PhCH_2OH$	1:6	ditto	$PhCH_2OSiMe_2SH$ (49.3); $Me_2Si(OCH_2Ph)_2$ (15.2)	[139]
$HO(CH_2)_2NH_2$	1:6	20°, 0.5 h	$Me_2Si(OCH_2CH_2NH_2)_2$ (91)	[139]
$[HO(CH_2)_2]_2NH$	1:3	ditto	$Me_2SiO(CH_2)_2NH(CH_2)_2$ (82.5)	[139]
$HO(CH_2)_4OH$	1:3	100–110°, 2 h	$Me_2SiO(CH_2)_4O$ (92.5)	[139]
$HOCH_2CH(R)OH$	1:3	ditto	$Me_2SiOCH_2CH(R)OSiMe_2OCH(R)CH_2$, R=H (98), Me (81.9)	[139]
PhOH	1:6	130–140°	$Me_2Si(OPh)_2$ (89.2)	[148]
o-PhC_6H_4OH	1:6	ditto	$Me_2Si(OC_6H_4Ph\text{-}o)_2$ (93.2)	[148]
ditto	1:3	70°, 3 h, toluene	$Me_2Si(OC_6H_4Ph\text{-}o)SH$ (71.2)	[148]
p-$PhNHC_6H_4OH$	1:6	70–80°	$Me_2Si(OC_6H_4NHPh\text{-}p)_2$	[140]
RR'C=NOH	1:6	50–70° C	$Me_2Si(OC{=}CRR')_2$, R=Ph, R'=H (94); R=R'=Me (91)	[152]
MeCOOH	1:6	50–60°	$Me_2Si(OCOMe)_2$ (86.8)	[146]
»	1:3	50°, 3 h, CCl_4	$[Me_2Si(OCOMe)]_2S$ (71.2)	[146]
RCOOH	1:6	50–60°	$Me_2Si(OCOR)_2$, R=Ph (76.1), $CH_2{=}C$ (Me) (88.4)	[146]
o-HOC_6H_4COOH	1:3	175°	$Me_2Si{-}O{-}C_6H_4{-}C(O)$ (73)	[146]
HOCORZCOOH	1:3	130–140°	$-(-Me_2SiOCOZOCO-)_m-$, Z=$(CH_2)_2$, m=7(99.7); Z=$(C_2H_4)_2$, m=7(90.2); Z=C_6H_4, m=S (91.2)	[146]
H_3BO_3	1:1	Δ	$HO(Me_2SiS)_2(Me_2SiO{-}B(O){-}O{-})_n{-}H$	[146]
ditto	1:2	Δ	$HO(Me_2SiS)[(Me_2SiO{-}B(O){-}O{-})_2{-}]_n{-}H$	[146]
»	1:3	Δ	$HO(Me_2SiO{-}B(O){-}O{-})_{3n}{-}H$	[146]
$PhNH_2$	1:6	125°	$Me_2Si(NHPh)_2$ (86.2)	[154]
α-$C_{10}H_7NH_2$	1:6	»	$Me_2Si(NHC_{10}H_7\text{-}\alpha)_2$ (81.2)	[154]
p-$H_2NPhC_6H_4NH_2$	2:3	60–75°	$Me_2SiNHC_6H_4C_6H_4NHSiMe_2$ (80.6)	[154]

A study of the reaction of hexamethyldisilathiane with dicarboxylic acid halides showed that with fumaryl chloride, the cyclic sulphide is formed, whereas with the chlorides of adipic and sebacic acids, polyacyl sulphides are formed:[171]

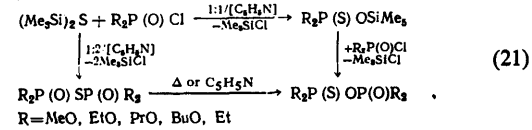


(20)

m = 4, 6

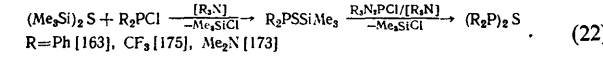
The reaction rate is increased in the presence of tertiary amines. Their catalytic action can be attributed to the formation of the N-acylammonium cation, which is more active in the exchange reaction than the original acyl halide.

The chlorides of phosphorus(V) acids react similarly with organosilathianes:[61,173]



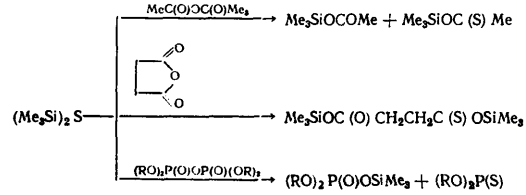
(21)

The halides of phosphorus(III) acids are more active than dialkyl phosphorochloridates towards hexamethyldisilathiane. The reaction involves the intermediate formation of silyl esters of phosphorus thio-acids:[174,175]

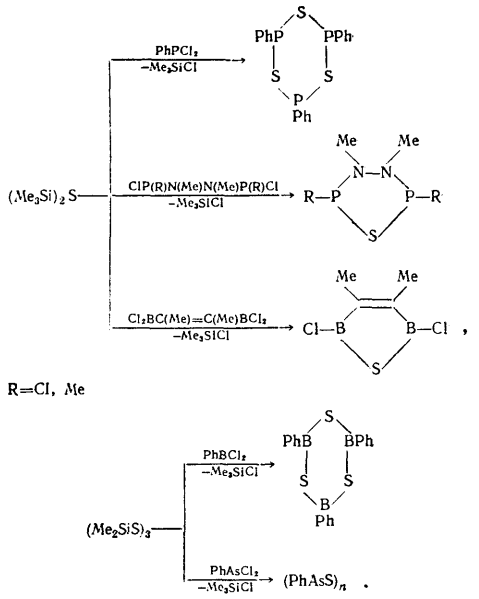


(22)

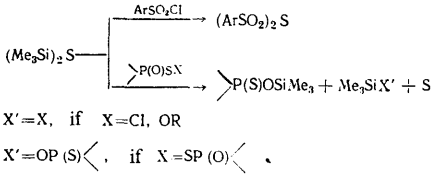
Dialkyl chlorophosphites [reaction (22)] give a mixture of products difficult to separate, formed by the thermal isomerisation of intermediate compounds and the final tetra-alkyl monothiopyrophosphites.[176,177] Carboxylic acid anhydrides and pyrophosphates undergo exchange reactions analogous to reactions (19)–(21):[61,171]



The reaction of the dichlorides of acids of phosphorus, boron, and arsenic with organosilathianes gives cyclic or polymeric products:[153,163,165]



Organosilathianes react equally readily with the halides of sulphonic acids,[61] phosphorylated sulphenyl chlorides, and their derivatives:[178]



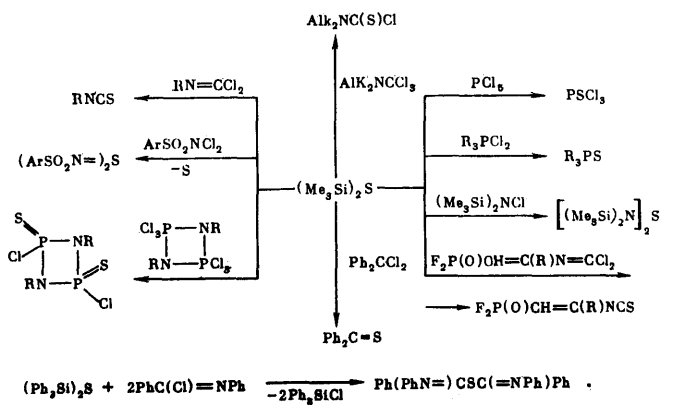
The exchange reaction of halogenogermanes with disilathiane and hexamethyldisilathiane gives mixed silyl germyl sulphides, which disproportionate when heated to give the symmetrical sulphides:[179]

$$(Me_3Si)_2S + H_3GeF \xrightarrow{-Me_3SiF} H_3GeSSiMe_3$$

$$(H_3Si)_2S + H_3GeCl \xrightarrow{-H_3SiCl} H_3GeSSiH_3$$

$$R_3SiSGeR'_3 \overset{\Delta}{\rightleftarrows} (R'_3Ge)_2S + (R_3Si)_2S \ .$$

Reactions of type (18) can be used to synthesise many sulphur compounds which are difficult to obtain:[61,103,164,180]



Thus exchange between organosilathianes and halogen-containing reagents with an E–X bond, where E is an element from groups I–VIII, and X = F, Cl, Br, I, makes reaction (18) a new general method for introducing sulphur into the molecules of inorganic, organic, and hetero-organic compounds.

Hexamethyldisilathiane reactions vigorously and exothermally with metal oxides[181] according to the scheme:

$$n\,(Me_3Si)_2S + MO_n \rightarrow n\,(Me_3Si)_2O + MS_n \qquad (23)$$
$$M=Ba,\ Pb,\ Mn,\ Zn,\ Ca$$

Cyclic silathianes are even more reactive in reactions of type (23). Thus hexamethylcyclotrisilathiane inflames spontaneously in its reaction with manganese dioxide even in a stream of nitrogen.[181]

In contrast to this, the passage of a mixture of oxides of nitrogen through a solution of hexa-alkyldisilathianes in ether does not lead to rupture of the Si–S–Si bonds, and the reaction products are bis-(trialkylsilyl) sulphones.[20]

Hexamethyldisilathiane undergoes an exchange reaction with phosphorus(V) oxide to give phosphorus(V) sulphide, tris(trimethylsilyl) phosphate, and tris(trimethylsilyl) thiophosphate:[61]

$$12(Me_3Si)_2S + 3P_4O_{10} \rightarrow 6(Me_3SiO)_3PO + 2(Me_3SiO)_3PS + P_4S_{10} \ .$$

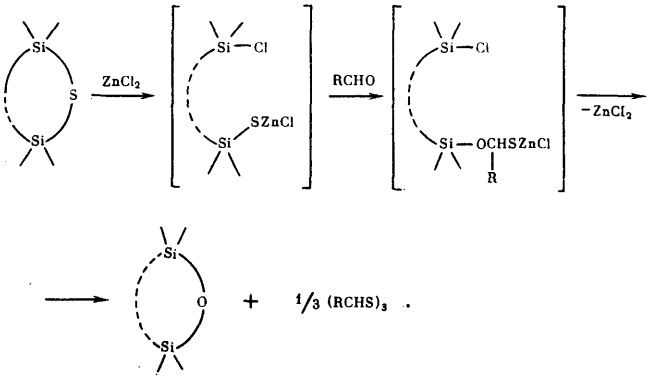
Phosphorus(V) sulphide in turn can also react with hexamethyldisilathiane to give the tris(trimethylsilyl) ester of trithiophosphoric acid.[84]

$$6(Me_3Si)_2S + P_4S_{10} \rightarrow 4(Me_3SiS)_3PS \ .$$

Organosilathianes react when heated with aldehydes and various perhalogenoketones;[183] the final products in the case of aldehydes are the products of the exchange reaction, siloxanes and thioaldehydes, and in the case of ketones the products of an insertion reaction. These data led to the proposal[182] of a general scheme for the reactions of organosilathianes with carbonyl compounds, including as an intermediate stage the formation of an unstable compound of type (IV), which subsequently decomposes to stable products by a four-centre mechanism. The introduction of halogen atoms, which have a strong electron-acceptor effect, into the molecule of the carbonyl compound stabilises the insertion product to such an extent that it can be isolated and characterised:[183]

$$(Me_3Si)_2S + RCHO \xrightarrow{50-80^\circ} \underset{(IV)}{[Me_3SiOCHRSSiMe_3]} \xrightarrow{-(Me_3Si)_2O}$$
$$\rightarrow [RCHS] \rightarrow {}^1/_3\,(RCHS)_3$$
$$R=Me,\ Et,\ Pr,\ Ph,\ p\text{-}O_2NC_6H_4,\ p\text{-}MeOC_6H_4 \qquad (24)$$
$$(Me_3Si)_2S + RR'CO \xrightarrow{70^\circ,\ 7\ d} (Me_3SiOCRR')_2S$$
$$R=CF_3,\ CF_2Cl;\ R'=CF_3.$$

In contrast to hexamethyldisilathiane, cyclic silathianes react with aldehydes at a higher temperature (140–150 °C) and in the presence of a catalyst ($ZnCl_2$) according to the scheme:[182]



The difference in the reactivities of the linear and cyclic organosilathianes towards aldehydes can be attributed to the difficulty of formation of an insertion product involving cyclosilathianes, a structure with many-membered rings is not characteristic for the insertion product.

Organosilathianes have been proposed as mild reducing agents for sulphoxides[61,184] and selenoxides.[61] The reaction apparently also takes place by the mechanism of reaction (24):

$$(Me_3Si)_2S + RR'E^+-O^- \xrightarrow[-(Me_3Si)_2O]{} RR'E + S$$
$$E = S,\ Se;\ R = Me,\ Et,\ Ph;\ R' = Me,\ Ph$$

In the reactions of hexamethyldisilathiane with various compounds of germanium, tin, and lead, exchange between the sulphur atom of the organosilathiane and an oxygen atom of the heteroorganic reagent is observed:[185]

$$(Me_3Si)_2S \xrightarrow[-Me_3SiOMe]{R_3MOMe} (R_3M)_2S$$
$$(Me_3Si)_2S \xrightarrow[-(Me_3Si)_2O]{(R_2M)_2O} (R_3M)_2S$$
$$(Me_3Si)_2S \xrightarrow[-(Me_3Si)_2O]{R_2MO} R_2MS$$

M = Ge, Sn, Pb; R = Et, Bu

Exchange between the sulphur atom of an organosilathiane and a hydrogen atom takes place as a result of reduction by metal hydrides.[23,30] Thus lithium hydride reacts with hexamethyldisilathiane in dioxan to give trimethylsilane.[23]

A study[30] of the stereochemistry of the reduction of 1,3-diphenyl-1,3-dimethyl-1,3-di-α-naphthyldisilathiane by lithium tetrahydroaluminate showed that at 20° the reduction takes place with inversion of the configuration, and at 85° racemisation takes place:

$$(+)\text{-}R_3Si^*SSi^*R_3 \xrightarrow{LiAlH_4} (+)\text{-}R_3Si^*H + [R_3Si^*S^-\ (LiAlH_3)^+] \xrightarrow{HCl}$$
(V)
$$\rightarrow [(+)\text{-}R_3Si^*SH] \xrightarrow{Et_2NH} (+)\text{-}R_3Si^*S^-\ H_2N^+Et_2$$
(VI)

The structures of the complex (V) and the salt (VI) were proved by independent syntheses:

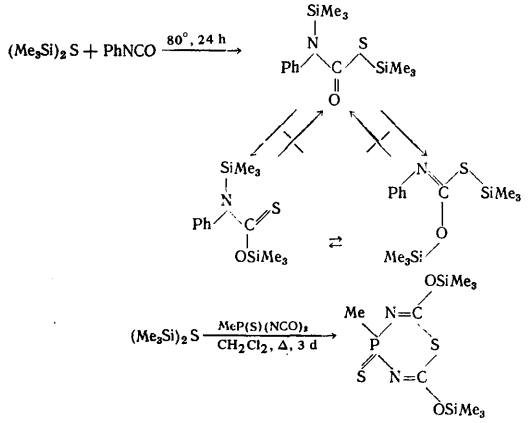
$$(+)\text{-}R_3Si^*SH + LiAlH_4 \xrightarrow[-78°]{-H_2} \ldots \xrightarrow[24\ h]{20\ °C} (V) \xrightarrow[Et_2O,\ -Bu_2O]{85°} (-)\text{-}R_3Si^*H$$
$$(+)\text{-}R_3Si^*SSi^*R_3 \xrightarrow{MeOH/Et_2NH} (VI)$$

2. Insertion Reactions

In hetero-organic chemistry, insertion reactions are usually classified according to the group being introduced, and are subdivided into 1,1-, 1,2-, ..., 1,*n*-additions to the substrate X–Y of the hetero-organic compound Z'_nM-Z, where Z'_n is the sum of the substituents, M a metal or non-metal, and Z the migrating group. In accordance with this generally accepted classification,[186] it is possible to systematise insertion reactions involving organosilathianes according to the type of addition (see start of section IV). In view of the limited number of known reactions of organosilathianes taking place by the insertion scheme (14), however, the reactions will be examined together, without breakdown into different types.

Oxygen-containing heterocyclic compounds,[187,188] organic[188] and organophosphorus[189] isocyanates, and arenesulphonyl isocyanates and arenesulphonyl isothiocyanates[190,191] split the Si–S bond in organosilathianes according to the schemes:

$$(Me_3Si)_2S + \text{cyclic-}CH_2CH_2O \xrightarrow{30°,\ 1\ d} [Me_3SiO(CH_2)_3]_2S$$
$$(Me_3Si)_2S + \text{cyclic-}CH_2CH_2CH_2O \xrightarrow{70°,\ 4\ d} [Me_3SiO(CH_2)_4]_2S$$
$$(Me_2SiS)_3 + \text{cyclic-}CH_2CH_2O \xrightarrow{70°,\ 13\ d} Me_2Si\langle O,S\rangle + -(-SiMe_2OCH_2CH_2S-)_n- ;$$



$$(Me_3Si)_2S + p\text{-}XC_6H_4SO_2N{=}C{=}Y \xrightarrow{80°,\ 24\ h} p\text{-}XC_6H_4SO_2N(SSiMe_3)C(SiMe_3){=}Y \rightarrow$$
$$\rightarrow p\text{-}XC_6H_4SO_2N(SiMe_3)_2 + CSY$$
X=H, Me, Cl; Y=O, S

Thus exchange and insertion reactions involving organosilathianes are undoubtedly related, since, as can be clearly seen from the reactions of hexamethyldisilathianes with aldehydes, ketones, and arenesulphonyl isocyanates, the exchange reactions take place with the intermediate formation of the insertion product. Depending on the stability of this product, the reaction may either stop at the insertion stage or proceed further to give the exchange products.

An analogous mechanism can be proposed, for example, for the reactions of organosilathianes with oxides:

$$\equiv Si-S-Si\equiv + M-O \rightarrow [\equiv Si-O-M-S-Si\equiv] \rightarrow$$
$$\rightarrow \equiv Si-O-Si\equiv + M-S .$$

In conclusion, mention may be made of the only reaction involving organosilathianes that does not lead to splitting of the Si–S–bonds: the reaction of hydride-containing alkylcyclosilathianes with unsaturated compounds in the presence of $H_2PtCl_6.6H_2O$:[132,192]

$$[R(H)SiS]_3 + CH_2{=}CR'R'' \longrightarrow [RSi(CH_2CR'R'')S]_3 + [RSi(CR'R'')S]_3$$
(Me)

V. POSSIBILITIES FOR THE PRACTICAL APPLICATION OF ORGANOSILATHIANES

The first mention in the patent literature of the possible use of organosilathianes appeared in 1952, when they were patented as heat-stabilisers and anti-foaming agents for mineral oils[193] and lubricating materials.[194] In 1953, a patent was published on the use of organosilathianes as fungicides, insecticides, and additives to siloxanes.[26] It has been reported[195,196] that compounds containing an Si–S bond promote the droplet condensation of steam. Because of the difficulty of obtaining organosilathianes, however, the question of their practical utilisation remained open for a long time.

The main fields of application of organosilathianes were established only after convenient and effective methods had been developed for synthesising compounds with varied structures containing the Si–S–Si fragment[52,53,57,62,197] and their principal properties had been studied.[22,40,61,197,198]

Organosilathianes are the closest structural analogues of organosiloxanes, but unlike the latter, they are extremely active in reactions involving the heterolytic splitting of the Si–S–Si bonds. Thus the possible application of polymers containing only silathiane bonds is limited. Moreover, unlike siloxanes, organosilathianes do not form homopolymers with a high molecular weight.[63–65] Thus the main efforts of research workers have been directed towards the synthesis of new heteropolymers containing Si–S–Si bonds. A method for obtaining these heteropolymers is based on the reactions of cyclic silathianes and silathiaoxanes with boric, phosphoric, and phosphorous acids and their salts.[197–200]

The synthesised bora- and phosphasilathiaoxanes are liquid products, which have the advantage over their analogues the bora- and phosphasiloxanes that they can be uniformly distributed in rubber in sufficient quantities.[197–200]

The use of borasilathiaoxanes in heat-resistant self-cross-linking resins improves the technology of the resin mixtures and their autohesion properties, and leads to milder vulcanisation conditions (a decrease in the irradiation dose).[198–200]

Siloxane sealants modified by phosphasilathiaoxanes have improved thermal stability and improved adhesion and physicomechanical properties.[198–200] Moreover, organosilathianes can be used to modify the properties of not only organosilicon polymers, but also organic polymers. Thus a study [201] of the possible use of hexa-methylcyclotrisilathiane as a stabiliser in the thermal and radiation ageing of polymethyl methacrylate showed that the stabilising effect of this cyclotrisilathiane is particularly marked at high radiation doses and at the temperature of the start of the decomposition.

The high reactivity of organosilathianes towards proton donors is responsible for their application primarily as reagents for silylating inorganic, organic, and hetero-organic compounds.[30,61,71,79,80,132–165,202–205]

A study of the silylating power of organosilathianes indicated that their efficiency is greater than that of traditional silylating agents based on compounds with a $\equiv$Si–X bond, where X = H, Cl, NR_2.[61]

One of the main advantages of organosilathianes as silylating agents is the simplicity of the silylation process, which is carried out by mixing and heating the starting materials (30–120 °C) for a short time (0.5–3 h) to give a high yield (70–98%) of the silyl derivatives. The course of the reaction is conveniently followed gas-volumetrically from the quantity of hydrogen sulphide formed. The reaction does not require a large excess of the proton donor or the use of catalysts and solvents. Moreover, organosilathianes can be used for the effective selective silylation of proton donors containing two or more active groups in the molecule.

Organosilathianes may prove to be equally useful for introducing a sulphur atom into the molecules of organic and hetero-organic reagents,[57–62,103,153,170–175,180,204] and also as mild reducing agents for a number of oxygen-containing compounds.[61,184]

Thus the progress made in the application of organosilathianes in polymer chemistry and in preparative organic synthesis show the undoubted promising possibilities provided by further studies of the practical application of organosilathianes.

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While the present manuscript was being prepared for printing, the following papers were published, and reference to these provides a valuable supplement to the material examined above: the reduction of oxides of sulphur, selenium, and tellurium by hexamethyldisilathiane, obtained *in situ*;[203] the use of the boron trichloride–hexamethyldisilathiane system for the conversion of carbonyl compounds into thiocarbonyl compounds;[204] the synthesis of cyclosilaselenosilathianes by the insertion of sulphur and selenium into octamethyltetracyclosilane;[205] the synthesis of diacetoxydisilathiane by the photochemical thiolysis of methyl(vinyl)diacetoxysilanes—the first example of the conversion of a silicon–oxygen bond into a silicon–sulphur bond;[206] the reactions of hexamethyldisilathiane with compounds containing an element–chlorine bond;[207] the synthesis of functionally substituted organosilathianes;[208] organosilathianes in organic synthesis;[209] the reaction of hexamethyldisilathiane with phosphorus(V) oxide;[210] organosilathianes as silylating agents;[211] the mass spectrometry of organocyclosilathianes;[212] the synthesis of low-coordination compounds of silicon by the thermal decomposition of cyclosilathianes;[212–214] and the molecular and crystal structure of tetramethylcyclodisilathiane.[215]

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