Translated from *Uspekhi Khimii*, 48, 1804-1832 (1979) U.D.C. 547.245.254.9

Mixed Organic Derivatives of Mercury and Silicon

M.G.Voronkov and N.F.Chernov

The methods of synthesis and properties of all types of mixed organic derivatives of mercury and silicon are examined and certain examples of these compounds are quoted.
The bibliography includes 224 references.

CONTENTS

I. Introduction 964
II. Compounds containing the Si—Hg bond 964
III. Compounds containing the Si–(–C–)$_n$–Hg group 968
IV. Compounds containing the Si–X–Hg (X = O, S, Se, Te, or N) group 972
V. Compounds containing the Si–(–C–)$_n$–X–Hg group 973
VI. Complexes of organosilicon compounds with mercury salts 974

I. INTRODUCTION

Among the numerous classes of organosilicon derivatives incorporating other elements [1], organosilicon derivatives of mercury are of particular interest owing to the unusual nature of their structure and reactivity and because of definite prospects for their practical applications.

The chemistry of organosilicon derivatives of mercury was first surveyed in 1966 in a monograph [1]. This book was followed by reviews in which organosilicon derivatives of mercury containing an Si–Hg bond were examined [2-6]. In the last twelve years the chemistry of organosilicon derivatives of mercury has developed so vigorously that it has become necessary to carry out another survey of the extensive structural data accumulated in the world literature. This is in fact the aim of the present review, which deals with studies published up to the middle of 1977.

II. COMPOUNDS CONTAINING THE Si–Hg BOND

Compounds containing an Si–Hg bond constitute the class of organosilicon derivatives of mercury which has been most thoroughly investigated. The presence of these compounds was founded mainly as a result of the investigations of Razuvaev, Vyazankin, Wiberg, and Neuman [2,4-7].

1. Methods of Preparation

The first attempt at the synthesis of organosilicon derivatives of mercury containing the Si–Hg bond was unsuccessful [8]. The reaction of triphenylsilyl-lithium with mercury halides, phenylmercury halides, or diphenylmercury was used for this purpose.

The reaction involving $HgCl_2$ leads to the formation of chlorotriphenylsilane, mercury, Hg_2Cl_2, and hexaphenyldisilane (in 45% yield). When $HgBr_2$ is used, the yield of hexaphenyldisilane increases to 63%. Hg_2Cl_2 reacts similarly. The results have been explained by the exchange reaction

$$R_3SiLi + HgX_2 \rightarrow R_3SiX + [LiHgX] \rightarrow LiX + Hg ,$$
$$R_3SiLi + R_3SiX \rightarrow R_3SiSiR_3 + LiX .$$

When triphenylsilyl-lithium reacts with phenylmercury bromide or diphenylmercury, the main product is tetraphenylsilane:

$$Ph_3SiLi + PhHgX \rightarrow Ph_4Si + Hg + LiX ;$$
X = Br, or Ph.

In this case it was necessary to postulate that an unstable phenyl(triphenylsilyl)mercury salt is formed as an intermediate:

$$Ph_3SiLi + PhHgX \rightarrow Ph_3SiHgPh + LiX ,$$
$$Ph_3SiHgPh \rightarrow Ph_4Si + Hg .$$

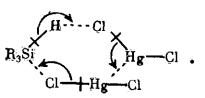
The most convenient method for the synthesis of organosilicon derivatives of mercury containing the Si–Hg bond was discovered in 1964 by Vyazankin and Razuvaev [9]. It is based on the interaction of triorganylsilanes with dialkylmercury derivatives. It had been known previously that the reaction of triorganylsilanes with mercury salts proceeds as a reduction process [9,10-19]:

$$R_3SiH + 2HgX_2 \rightarrow R_3SiX + Hg_2X_2 + HX$$

or

$$R_3SiH + HgX_2 \rightarrow R_3SiX + Hg + HX .$$

The intermediate formation of a six-membered cyclic complex in this reaction was postulated:



The reduction to univalent or metallic mercury is determined by the nature of the anion X and the solvent employed. In the reaction of triorganylsilanes with organylmercury halides the latter are also reduced [20]:

$$R_3SiH + R'HgCl \rightarrow R_3SiX + HR' + Hg .$$

In contrast to this, in the course of the slow reaction of triethylsilane with diethylmercury (117 h at 130–140°C) the products are compounds with the Si–Hg bond [9,21]:

$$Et_3SiH + Et_2Hg \rightarrow Et_3SiHgEt + C_6H_6 , \quad (1)$$

$$2Et_3SiH + Et_2Hg \rightarrow (Et_3Si)_2Hg + 2C_6H_6 . \quad (2)$$

Together with ethyl(triethylsilyl)mercury, one obtains bis(triethylsilyl)mercury, albeit in a low yield (~ 3%), possibly as a result of symmetrisation (disproportionation):

$$2Et_3SiHgEt \rightarrow (Et_3)_2Hg + HgEt_2 .$$

Indeed, when ethyl(triethylsilyl)mercury is heated for 11 h at 170°C, it is converted to a fairly large extent (70%) into bis(triethylsilyl)mercury. The low yields of triethylsilyl derivatives of mercury in reactions (1) and (2) can be explained by their secondary decomposition processes, which is indicated by the high content of metallic mercury in the reaction products[9].

Trichlorosilane reacts slowly with diethylmercury at 20°C for several days, forming ethyl(trichlorosilyl)mercury in 71.8% yield[22,23]. Bis(trichlorosilyl)mercury, which is also formed in this reaction, is a product of the symmetrisation of $EtHgSiCl_3$. Very pure $(Cl_3Si_2)Hg$ can be obtained by the ultraviolet irradiation of a mixture of bis(trimethylsilylmethyl)mercury and trichlorosilane[23]:

$$(Me_3SiCH_2)_2Hg + 2HSiCl_3 \rightarrow 2Me_4Si + Cl_3SiHgSiCl_3 .$$

In the analogous reaction of Me_3SiHCl_2 or $(Me_3)_2SiHCl$ the products are $(Cl_2MeSi)_2Hg$ and $(ClMe_2Si)_2Hg$ respectively, which decompose spontaneously above −79°C with liberation of mercury and substituted disilanes[23]. However, the reactions of $ClMe_2SiH$ and Cl_2MeSiH with di-(t-butyl)mercury at 85°C gave rise to bis(chlorodimethylsilyl)- and bis(dichloromethylsilyl)mercury, which are thermally stable (they sublime *in vacuo* at 80°C).[24] The difficulties experienced by earlier workers[23] can probably be accounted for by the use of radiation, which decomposes these compounds.

When triorganylsilanes interact with di-(t-butyl)mercury[25] or dibenzylmercury[26], the corresponding organosilicon derivatives of mercury, containing the Si–Hg bonds, are formed under mild conditions and in high yields.

The nature of the substituents at the silicon atom in triorganylsilanes affects not only the reactivity of the latter, but also the stability of the organosilicon derivatives of mercury obtained from them. Thus pentaethyldisilane reacts with diethylmercury more vigorously than does triethylsilane[27]. The yield of mono- and di-substituted pentaethyldisilyl derivatives of mercury is higher than that of the analogous triethylsilyl derivatives.

The reaction of triorganylsilanes with diorganylmercury makes it possible to obtain a wide assortment of compounds containing the Si–Hg bond with various substituents at the silicon atom. $[Me_2(n\text{-}Pr)Si]_2Hg$, $(MeEt_2Si)_2Hg$,[28] $(PhMe_2Si)_2Hg$, $(Ph_2MeSi)_2Hg$, $(Ph_3Si)_2Hg$,[29] $[(Me_3SiCH_2)\cdot Me_2Si]_2Hg$, $[(Me_3Si)_3Si]_2Hg$, $[Me_2(PhCH_2)Si]_2Hg$, and optically active bis(methylphenylsilyl-1-naphthyl)mercury were synthesised by this method. When a 2 : 1 mixture of ethylbis(triethylgermyl)silane and diethylmercury was heated in an evacuated sealed tube (14 h at 150°C), bis[ethylbis(triethylgermyl)silyl]mercury was obtained in 65.9% yield together with ethane[30]. Bis[diethyl(triethylgermyl)silyl]mercury, bis[tris(triethylgermyl)silyl]mercury, and bis[ethylbis(triethylsilyl)]mercury were synthesised under analogous conditions but after more prolonged heating (21–35 h)[30]:

$$2Et_{3-n}(Et_3\Theta)_nSiH + Et_2Hg \rightarrow [Et_{3-n}(Et_3\Theta)_nSi]_2Hg + 2EtH ;$$
$$\Theta = Si \text{ or } Ge;\ n = 1-3 .$$

Ethyltriethylsilylmercury[31] and bis-(*N*-hexamethyldisilazanyl)mercury can be used instead of diorganylmercury[32,33]:

$$Ph_3SiH + EtHgSiEt_3 \rightarrow Ph_3SiHgSiEt_3 + EtH$$
$$\downarrow$$
$$^1/_2(Ph_3Si)_2Hg + ^1/_2(Et_3Si)_2Hg ,$$
$$2(C_6F_5)_3SiH + [(Me_3Si)_2N]_2Hg \xrightarrow{150-170^\circ} 2[(C_6F_5)_3Si]_2Hg + 2(Me_3Si)_2NH .$$

The attempt to use the Wurtz reaction for the synthesis of disilane derivatives by treating halogenotrimethylsilanes with liquid sodium amalgam led to the formation of bis(trimethylsilyl)mercury[7]:

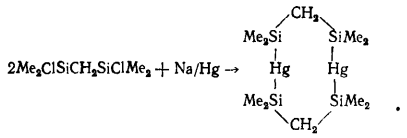
$$2Me_3SiX + 2Na + Hg \rightarrow (Me_3Si)_2Hg + 2NaX ;$$
$$X = Cl \text{ or } Br.$$

The analogous reaction with bromodimethylsilane apparently leads to the formation of $Hg(SiMe_2H)_2$, but this compound could not be isolated because of its instability[7].

Chlorodimethyl(pent-4-en-1-yl)silane gives rise to the corresponding mercury derivative[34]:

$$2H_2C{=}CH(CH_2)_3Me_2SiCl + Na/Hg \rightarrow Hg[SiMe_2(CH_2)_3CH{=}CH_2]_2 .$$

$[CH_2 = CHCH_2Me_2Si]_2Hg$, $(EtMe_2Si)_2Hg$, and $(Et_3Si)_2Hg$ were obtained similarly[28]. The interesting heterocyclic compound 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclo-octane is formed from 2,4-dichloro-2,4-dimethyl-2,4-disilapentane (20°C, 1 month)[35]:



Bis(triphenylsilyl)mercury has been obtained in a yield up to 70% by treating with mercury acetate the ternary complex of ethylbis(triphenylsilyl)aluminium with lithium bromide and tetrahydrofuran (THF)[36]:

$$2Ph_3SiAl(Et)SiPh_3 \cdot 2LiBr \cdot 2THF + 3Hg(OAc)_2 \rightarrow 2(Ph_3Si)_2Hg + Et_2Hg + 2Al(OAc)_3 +$$
$$+ 4LiBr + 4THF.$$

The reaction of bis(trimethylsilyl)mercury with bromosilane (SiH_3Br) makes it possible to obtain silyl(trimethylsilyl)mercury[37]:

$$(Me_3Si)_2Hg + BrSiH_3 \rightarrow Me_3SiHgSiH_3 + Me_3SiBr .$$

$(SiH_3)_2Hg$ and $Me_3SiHgGeH_3$ have been obtained similarly.

2. Physical Properties

According to X-ray diffraction, the $(R_3Si)_2Hg$ molecule has a linear structure, the Si–Hg bond length amounting to 2.500 ± 0.005 Å.[38] The infrared spectra of compounds of this type show an intense absorption band with $\nu_{as}(Hg\text{–}Si)$ = 318 cm^{-1} and $\nu_s(Hg\text{–}Si)$ = 312 cm^{-1}.[7,38] The 474 cm^{-1} frequency corresponds to the stretching vibration of the Hg–C bond in the spectra of compounds of the type $R_3SiHg\text{–}R'$.[39]

The presence of a mercury atom at the silicon atom increases the $\nu(Si\text{–}C)$ frequency[40,41]. Thus $\nu_s(Si\text{–}C)$ = 569 cm^{-1} for hexamethyldisilane and 583 cm^{-1} for bis(triethylsilyl)mercury. This is apparently associated with the greater electronegativity of the $-Hg\text{–}Si(Et)_3$ fragment compared with $-SiEt_3$. When $(Et_3Si)_2$ is replaced by $(Et_3Si)_2Hg$, a new long-wavelength maximum (335 nm) appears in the electronic absorption spectra[42].

The ^1H NMR[43–46] and ^{199}Hg NMR[46] spectra of organosilicon derivatives of mercury of the type R_3SiHgR' and $(R_3Si)_2Hg$ have been investigated. The chemical shift of the protons in the Me_3SiHg group is τ = 9.83 p.p.m. and the spin–spin coupling constant $J(^{199}Hg\text{–}Si\text{–}C\text{–}^1H) = 40.8$ Hz for $(Me_3Si)_2Hg$;[43] τ_{CH_2} = 9.23 p.p.m. and τ_{CH_3} = 8.94 p.p.m. for the Et_3SiHg group in $(Et_3Si)_2Hg$.[44] For asymmetric organosilicon derivatives of mercury of the type Me_3SiHgR,

where R = Me, $CH=CH_2$, $\overline{CH-CH_2-CH_2}$, Ph, or CH_2Ph, the long-range spin–spin coupling constants $J(^{199}Hg-Si-C-^{1}H)$ increase with increasing electronegativity of the substituent R.[45] They are related to the spin–spin coupling constants for the corresponding organomercury compounds of the MeHgR series by the linear expression $0.453\,J(^{199}Hg-C-^{1}H) + 6.0 = J(^{199}Hg-Si-C-^{1}H)$. The existence of this relation shows that the nature of the spin–spin coupling in the two series of compounds is the same.

According to calorimetric data[47], the enthalpy of the Si–Hg bond is $\Delta H^{\circ}_{S}(liq.) = 42 \pm 1$ kcal mole^{-1} and its average dissociation energy is $\bar{D} = 20 \pm 3$ kcal mole^{-1}.

In the study of compounds containing the Si–Hg bond mass-spectrometry was used to determine their molecular weights[26,34,48] and only a few communications[28,35,49] have been devoted to their fragmentation. Under electron impact, all the compounds investigated give rise to a molecular ion and subsequently undergo fragmentation with ejection of mercury either as a result of electron impact or in consequence of pyrolytic decomposition[28]. Between 1 and 6% of the overall ionic current corresponds to the molecular ion, amounting to 15.6% only for bis(trimethylsilyl)mercury. The mass spectrum of the latter involves a considerable contribution of three ions containing mercury and silicon: $Me_5Si_2Hg^+$ (5.5%), Me_3SiHg^+ (2.16%), and Me_2SiHg^+ (0.38%). On partial or complete replacement of methyl groups by higher alkyl groups (ethyl and n-propyl), the concentration of ions containing the Si–Hg bond decreases significantly. This is also observed on passing from $(Me_3Si)_2Hg$ to $(Me_2PhSi)_2Hg$. The $(MePh_2Si)_2Hg$ and $(Ph_3Si)_2Hg$ ions, which contain the Si–Hg bond, have not been detected in the mass spectra with the exception of the molecular ions. The replacement by the alkenyl groups $CH_2=CH(CH_2)_n$ ($n = 1-3$) leads to a decrease of the concentration of the molecular ions and to the absence of other ions with the Si–Hg bond, which indicates a destabilising effect of the alkenyl groups on this bond.

Successive substitution of the methyl groups in $(Me_3Si)_2Hg$ by chlorine atoms entails an increase of the concentration of ions with the Si–Hg bond, which shows that the presence of chlorine atoms at the silicon atom stabilises the Si–Hg bond[28].

Under electron impact, 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclo-octane gives rise to a molecular ion and ions corresponding to the successive loss of one or two mercury atoms[28,35].

3. Chemical Properties

Organosilicon derivatives of mercury containing the Si–Hg bond are highly reactive. The vast majority of the chemical reactions lead to the cleavage of the covalent Si–Hg bond with preservation of the R_3Si- fragments. On the other hand, these compounds are fairly stable and usually can be vacuum distilled in the absence of atmospheric oxygen without appreciable decomposition. The thermal stability of pentaethyldisilyl derivatives of mercury is higher than that of the analogous triethylsilyl derivatives[27]. Bis(tribenzylsilyl)mercury is also very stable[50,51]. Metallic mercury and the corresponding hexaorganyldisilane are formed quantitatively in the thermal decomposition of bis(triorganylsilyl)mercury[7,22,23]:

$$(R_3Si)_2Hg \rightarrow (R_3Si)_2 + Hg .$$

The thermal decomposition of bis(trimethylsilyl)mercury in solution proceeds via a free-radical mechanism[26,52-55]. The $Me_3Si^{\cdot}$ radicals formed can not only dimerise to hexamethyldisilane but can also react with the solvent. In aromatic solvents (benzene, toluene, and anisole) this leads to aromaric homolytic substitution products[56-59].

All the compounds containing the Si–Hg bond are sensitive to light. Photolysis of bis(trimethylsilyl)mercury leads to the formation of mercury and $Me_3Si^{\cdot}$ radicals. The very short-lived $Me_3SiHg^{\cdot}$ radicals have been identified together with the above species[9,60-62]:

$$(Me_3Si)_2Hg \rightarrow Me_3Si^{\cdot} + {}^{\cdot}Hg{-}SiMe_3 \rightarrow Hg + 2Me_3Si^{\cdot}$$
$$Me_3Si^{\cdot} + Hg(SiMe_3)_2 \rightarrow Hg + (Me_3Si)_2 + {}^{\cdot}SiMe_3 .$$

Compounds with the Si–Hg bond are very readily oxidised by atmospheric oxygen. Oxidation of ethyl(triethylsilyl)mercury is a free-radical chain process initiated at the beginning by the $Et_3SiHg^{\cdot}$ and $Et_3Si^{\cdot}$ radicals formed[9,25,63,64]:

$$2R_3SiHgR \rightarrow R_2Hg + R_3SiHg^{\cdot} + R_3Si^{\cdot},$$
$$R_3Si^{\cdot} + O_2 \rightarrow R_3SiOO^{\cdot},$$
$$R_3SiHg^{\cdot} \rightarrow R_3Si^{\cdot} + Hg,$$
$$R_3SiOO^{\cdot} + R_3SiHgR \begin{cases} \rightarrow R_3SiOHgR + R_3SiO^{\cdot} \\ \rightarrow (R_3SiO)_2 + RHg^{\cdot} \end{cases},$$
$$R_3SiO^{\cdot} + R_3SiHgR \rightarrow (R_3Si)_2O + RHg^{\cdot},$$
$$RHg^{\cdot} + O_2 \rightarrow CH_3CHO + {}^{\cdot}HgOH,$$
$$^{\cdot}HgOH + R_3SiHgR \rightarrow R_3SiOH + RHg^{\cdot} + Hg^{\cdot},$$
$$2R_3SiOH \xrightarrow[-H_2O]{} (R_3Si)_2O;$$
$$R=Et .$$

The oxidation is accelerated severalfold in the presence of traces of Lewis bases capable of forming complexes with organomercury compounds, (ammonia, amines, triphenylphosphine, etc.)[64-66].

Under the usual conditions, bis(triorganylsilyl)mercuranes $(R_3Si)_2Hg$ are resistant to hydrolysis and alcoholysis, but these reactions take place readily in a homogenising solvent. Thus, when bis(triphenylsilyl)mercury is acted upon by moist benzene, there is very rapid formation of mercury (quantitative), triphenylsilanol, and hydrogen[26]:

$$\begin{array}{l} Ph_3Si{-}Hg{-}SiPh_3 \\ \vdots\quad\vdots \\ HO{-}H \end{array} \rightarrow Ph_3SiOH + HHgSiPh_3 ,$$
$$HHgSiPh_3 + H_2O \rightarrow Ph_3SiOH + [H_2Hg] \rightarrow H_2 + Hg + Ph_3SiOH .$$

In addition, small amounts of triphenylsilane, hexaphenyldisiloxane, and hexaphenyldisilane are produced. The alcoholysis of $(R_3Si)_2Hg$ can proceed via two pathways[67]:

$$\begin{array}{l} Ph_3Si{-}Hg{-}SiPh_3 \\ \vdots\quad\vdots \\ RO{-}H \end{array} \rightarrow Ph_3SiOR + HHgSiPh_3 \rightarrow Ph_3SiOR + Hg + HSiPh_3 ,$$
$$\begin{array}{l} HHg{-}SiPh_3 \\ \vdots\quad\vdots \\ H\ {-}OR \end{array} \rightarrow Ph_3SiOR + [H_2Hg] \rightarrow Ph_3SiOR + H_2 + Hg ,$$
$$\begin{array}{l} Ph_3Si{-}Hg{-}SiPh_3 \\ \vdots\quad\vdots \\ HO{-}R \end{array} \rightarrow Ph_3SiOH + RHgSiPh_3 .$$

The interaction of organosilicon derivatives of mercury containing the Si–Hg bond with acids leads to the quantitative formation of mercury and can serve as a method for the analysis of these compounds[7,25,50]:

$$(R_3Si)_2Hg + HX \rightarrow R_3SiH + Hg + R_3SiX ;$$
$$R=Me,\ Et\ or\ Ph;\ X=Cl\ or\ OAc .$$

Bis(trimethylsilyl)mercury reacts with CO_2 only in hexamethylphosphoramide (HMPT) to form CO and hexamethyldisiloxane[68]:

$$(Me_3Si)_2Hg + CO_2 \xrightarrow[-Hg]{} \begin{array}{l} SiMe_3 \\ | \\ O{=}C{-}OSiMe_3 \end{array} \rightarrow (Me_3Si)_2O + CO .$$

The reaction with carbon disulphide proceeds via a similar mechanism:

$$(Me_3Si)_2Hg + CS_2 \xrightarrow{-Hg} S{=}C(SiMe_3){-}SSiMe_3 \rightarrow (Me_3Si)_2S + 1/n\,(CS)_n .$$

The interaction of SO_2 with bis(trimethylsilyl)mercury at 20°C proceeds via the mechanism[68]

$$(Me_3Si)_2Hg + SO_2 \xrightarrow{-Hg} Me_3Si{-}O{-}S{-}O{-}SiMe_3 .$$

The bis(trimethylsilyl)sulphoxylate formed decomposes at room temperature into hexamethyldisiloxane and sulphur, which reacts with mercury to form HgS.

Acyl peroxides (but not t-butyl peroxide[2]) react vigorously with compounds containing the Si–Hg–Si[2,25,69] or Si–Hg–C[9] groups:

$$(Et_3Si)_2Hg + (PhCOO)_2 \rightarrow Hg + 2Et_3SiOCOPh ,$$
$$2Et_3SiHgEt + (PhCOO)_2 \rightarrow Et_2Hg + 2PhCOOSiEt_3 + Hg .$$

Aliphatic aldehydes interact with bis(trimethylsilyl)mercury very slowly in benzene. On the other hand, aromatic aldehydes interact rapidly even at 20°C, forming bis(trimethylsiloxy)hydrobenzoin[70,71]:

$$(Me_3Si)_2Hg + 2RCHO \xrightarrow{-Hg} R{-}CH(OSiMe_3){-}CH(OSiMe_3){-}R ,$$

where R = aryl.

2,2-Dichlorovinyloxytrimethylsilane is formed from chloral via an exothermic reaction[71]:

$$(Me_3Si)_2Hg + CCl_3CHO \xrightarrow{-Hg} Me_3SiOCHCCl_3(SiMe_3) \rightarrow Me_3SiCl + Me_3SiOCH{=}CCl_2 .$$

Bis(trimethylsilyl)mercury reacts vigorously at room temperature with ketones and quinones such as acetone[72-74], hexafluoroacetone[75], cyclohexanone[72,73], 9-fluorenone[76], acetophenone[70,72,73], benzophenone[72,73], 1,4-naphthoquinone, 1,2-naphthoquinone, and anthraquinone[70], forming the intermediate $R_2COSiMe_3$ radical, which then dimerises or disproportionates:

$$(Me_3Si)_2Hg + R_2CO \xrightarrow{-Hg} R{-}C(R)(OSiMe_3){-}C(R)_2{-}OSiMe_3 + R{-}C(R){=}C(R){-}OSiMe_3 .$$

1,2-Diketones react via the mechanism[71]

$$(Me_3Si)_2Hg + RCOCOR \xrightarrow{-Hg} R{-}C(OSiMe_3){=}C(OSiMe_3){-}R ,$$

where R = Me or Ph.

The following reactions occur when bis(trimethylsilyl)-mercury interacts with diorganylketones[68,70]:

$$(Me_3Si)_2Hg + 2R_2C{=}C{=}O \xrightarrow{-Hg} R_2C(SiMe_3){-}CO{-}C(OSiMe_3){=}CR_2 + R_2C{=}C(OSiMe_3){-}CR_2{-}COSiMe_3 + R_2C{=}C(OSiMe_3){-}C(OSiMe_3){=}CR_2 ,$$

where R = Me or Ph.

The reaction with aryl isocyanates in HMPT leads to the formation of *N*,*N'*-diaryl-*N*,*N'*-bis(trimethylsilyl)urea and carbon monoxide[68,70]:

$$(Me_3Si)_2Hg + 2R{-}N{=}C{=}O \xrightarrow[-Hg]{-CO} R{-}N(Me_3Si){-}C(=O){-}N(SiMe_3){-}R ,$$

where R = Ph, 4-$CH_3C_6H_4$, or 1-$C_{10}H_7$.

Diphenylcarbodiimide reacts rapidly[68] with bis(trimethylsilyl)mercury in HMPT via the mechanism

$$(Me_3Si)_2Hg + PhN{=}C{=}NPh \xrightarrow{-Hg} Ph{-}N(SiMe_3){-}C{=}NPh .$$

1,4- and 1,6-additions take place in the reaction of bis(trimethylsilyl)mercury with maleate or fumarate esters[71,78]:

$$(Me_3Si)_2Hg + HC(COOEt){=}HC(COOEt) \xrightarrow{-Hg} HC(OSiMe_3){=}C(OEt){-}HC(SiMe_3)(COOEt) + HC(OSiMe_3){=}C(OEt){-}HC(OSiMe_3){=}C(OEt) .$$

On heating or under ultraviolet irradiation, bis(trimethylsilyl)mercury cleaves the isoxazole ring[79]:

$$6\,(Me_3Si)_2Hg + 2N{=}CRCH{=}CR'O \xrightarrow{-3Hg} [(Me_3Si)_2NCR{=}CHCR'OSiMe_3]_2 ;$$
R, R' = H or Me.

The reaction of bis(trimethylsilyl)mercury with pyridine and its derivatives leads to *N*,*N'*-bis(trimethylsilyl)tetrahydro-4,4'-bipyridyls[80,81-83]:

$$(Me_3Si)_2Hg + 2N{=}C(X){-}CH{=}CH \xrightarrow{-Hg} Me_3SiN(X){-}CH{=}CH{-}C(X){=}NSiMe_3 ;$$
X = H, 2-Me, 3-Me, 3-CN, 3-COOMe, 4-COOMe, or 4-Ac.

When an equimolar mixture of $(Me_2Si)_2Hg$ and a pyridine derivative containing the carbonyl group in the 4-position is irradiated with ultraviolet light, the α-trimethylsiloxy-*N*-trimethylsilyl derivatives of 4-methylenedihydropyridines are formed[84]:

$$(Me_3Si)_2Hg + N{=}CH{-}CH{=}C(R){-}C(=O){-}R \xrightarrow{-Hg} Me_3SiN{-}CH{=}CH{-}C(OSiMe_3){=}C(R){-}R ;$$
R = H, Me, or Ac.

Bis(trimethylsilyl)mercury reacts with azo-compounds as a nucleophile, adding to the azo-group[78,82]:

$$(Me_3Si)_2Hg + R{-}N{=}N{-}R \rightarrow R{-}N(HgSiMe_3){-}N(SiMe_3){-}R \xrightarrow{-Hg} R{-}N(SiMe_3){-}N(SiMe_3){-}R ;$$
R = EtOCO, Ph, or 2-C_5H_4N.

$(Me_3Si)_2Hg$ interacts with aryl azides via a radical mechanism to form nitrogen and *N*,*N'*-bis(trimethylsilyl)-anilines[68]:

$$(Me_3Si)_2Hg + R{-}N{=}N{-}N \xrightarrow{-Hg} (Me_3Si)_2N{-}N{=}NR \xrightarrow{-N_2} (Me_3Si)_2NR ;$$
R = Ar .

The reaction of t-butyl(trimethylsilyl)mercury with substituted benzylidenemalonodinitriles leads to *N*-trimethylsilylketenimines[85]:

$$Me_3SiHgCMe_3 + XC_6H_4CH{=}C(CN)_2 \rightarrow XC_6H_4CH(CMe_3)C(CN){=}C{=}NSiMe_3 ;$$
X=H, Me, MeO, Cl, or NO_2.

t-Butyl(trimethylsilyl)mercury adds to 4-$MeOC_6H_4CH{=}C(CN)COOEt$ to form *O*-silylketen acetal[85].

In the interaction of bis(trimethylsilyl)mercury with an olefin under the conditions of photolysis trimethylsilyl radicals add to the double bond[86]:

$$(Me_3Si)_2Hg + CH_3CH(CH_3)CH{=}CHCH_3 \xrightarrow{-Hg} CH_3CH(CH_3)\underset{Me_3Si}{CH}{-}\underset{SiMe_3}{CHCH_3} .$$

The attempts to achieve the transfer of the trimethylsilyl radical from $(Me_3Si)_2Hg$ to zinc or aluminium were unsuccessful[7]. Bis(trimethylsilyl)mercury interacts with zinc only at a high temperature, liberating dimethylmercury. The interaction with aluminium results in the liberation of metallic mercury and the formation of a mixture of compounds not containing the Si–Al bond. On the other hand, lithium reacts with bis(triethylsilyl)mercury and ethyl(triethylsilyl)mercury in THF with formation of triethylsilyl-lithium[87,88]:

$$(Et_3Si)_2Hg + 2Li \rightarrow Hg + 2Et_3SiLi ,$$
$$Et_3SiHgEt + 2Li \rightarrow Hg + Et_3SiLi + EtLi .$$

This reaction is convenient for the synthesis of Alk_3SiLi.

Bis dimethyl(pent-4-en-1-yl)silyl mercury reacts with lithium to form the corresponding lithio-derivative which cyclises and gives rise to 1,1,2-trimethyl-1-silacyclopentane after hydrolysis[34]:

$$(CH_2{=}CHCH_2CH_2CH_2Me_2Si)_2Hg + Li \xrightarrow{-Hg} 2CH_2{=}CHCH_2CH_2CH_2Me_2SiLi \rightarrow$$
$$\rightarrow \underset{Me\ \ Me}{\overset{}{Si}}{-}CH_2Li \xrightarrow{H_2O} \underset{Me\ \ Me}{\overset{}{Si}}{-}CH_3 .$$

The reaction of $(Et_3Si)_2Hg$ with metallic potassium or sodium in an aromatic solvent results in the formation of triethylsilylpotassium and triethylsilylsodium, but the reaction with the solvent predominates in this case[89]: it may be that Et_3SiM is a reaction intermediate, which interacts with the solvent to form Et_3SiPh and MH:

$$(Et_3Si)_2Hg + 2M \xrightarrow{C_6H_6} 2Et_3SiM + Hg ,$$
$$Et_3SiM + C_6H_6 \rightarrow Et_3SiH + PhM ,$$
$$PhM + Et_3SiH \rightarrow PhSiEt + M ;$$
M = K or Na.

Triethylsilylpotassium can be obtained by treating $(Et_3Si)_2Hg$ with potassium using triethylsilane as a solvent[89].

Bis(trimethylsilyl)mercury interacts with alkali metals in 1,2-dimethoxyethane, forming dimetallo-organosilicon complexes[90,91]:

$$2(Me_3Si)_2Hg + 2M \rightarrow (Me_3Si)_4HgM_2 + Hg ;$$
M = K or Na.

The analogous lithium compounds have been obtained by the direct interaction of bis(trimethylsilyl)mercury with Me_3SiLi:

$$(Me_3Si)_2Hg + Me_3SiLi \rightarrow (Me_3Si)_3HgLi ,$$
$$(Me_3Si)_2Hg + 2Me_3SiLi \rightarrow (Me_3Si)_4HgLi_2 .$$

The formation of $K_2Hg(SiEt_3)_4$ has been observed in the reaction of bis(triethylsilyl)mercury with potassium cyanide in THF in the presence of a crown-ether[92]:

$$3(Et_3Si)_2Hg + 2KCN \rightarrow (Et_3Si)_4HgK_2 + 2Hg + 2Et_3SiCN .$$

Organosilicon derivatives of mercury containing the Si–Hg bond are capable of exchanging the trialkylsilyl fragment for the anions of a number of metal salts. For example, the interaction with mercury salts proceeds via the general mechanism[92–96]

$$(R_3Si)_2Hg + HgX_2 \rightarrow 2R_3SiX + 2Hg ;$$
X=Cl, Br, I, CN, $Co(CO)_3$, $Cr(CO)_3C_6H_5$, $W(CO)_3C_6H_5$, or $Mo(CO)_3C_5H_5$.

The intermediates in this reaction are probably compounds of the type R_3SiHgX, which immediately decompose to mercury and R_3SiX.

The products of the reaction of bis(triethylsilyl)mercury with alkylmercury chlorides in the absence of a solvent in atmospheric oxygen give rise to the corresponding alkyl(trialkylsilyl)mercuranes together with mercury and a trialkylchlorosilane[61,97–98]:

$$(Et_3Si)_2Hg + RHgX \rightarrow Et_3SiHgR + Et_3SiX + Hg ,$$
R=Me, Et, Pr, iso-Pr, t-Bu; X=Cl .

The reactions of $(R_3Si)_2Hg$ with organomercury compounds of the type HgR'_2, where R′ is a hydrocarbon or a polyfluoro-hydrocarbon radical [Me_2, iso-Pr, $CH{=}CH_2$, Ph,[45] $-C-C-Ph$ (bonded to $B_{10}H_{10}$),[99] CF_3, CH_2CF_3, $CHFCF_3$, CF_2CF_3, $CFClCF_3$, $CH(CF_3)_2$, and $CF(CF_3)_2$[95,100]] in aprotic solvents (benzene, toluene) lead to the corresponding trialkylsilylorganylmercuranes:

$$(Et_3Si)_2Hg + HgR'_2 \rightarrow 2Et_3SiHgR' .$$

$(R_3Si)_2Hg$ reacts via a similar mechanism with dimetallo-organic compounds of the type HgR'_2, where R = $SnMe_3$, $GeMe_3$, or $SiMeCl_2$.[43,49] Other reactions of bis(trialkylsilyl)mercuranes are listed in the Table.

Organosilicon derivatives of mercury containing the Si–Hg bond are used in the synthesis of organosilicon derivatives which are difficult to obtain otherwise and also as catalysts in the polymerisation of styrene[29,135] or ethylene[136] and in the hydroxylation of unsaturated compounds (in combination with ultraviolet irradiation)[137]. However, the considerable lability of the Si–Hg bond limits the scope of the industrial utilisation of compounds of this class.

III. COMPOUNDS CONTAINING THE Si–$(-C-)_n$–Hg GROUP

Compounds containing the Si–$(-C-)_n$–Hg group have been known much longer than those discussed above but have been investigated in much less detail.

1. Methods of Synthesis

(a) Organometallic synthesis. The first compound containing the Si–$(-C-)_n$–Hg group was obtained in 1945 by Whitmore and Sommer[138] by treating trimethylsilylmethylmagnesium chloride with mercury(II) chloride:

$$Me_3SiCH_2MgCl + HgCl_2 \rightarrow Me_3SiCH_2HgCl + MgCl_2 .$$

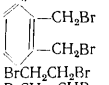
The compounds RHgCl, where R = $Me_3CSiMe_2CH_2$,[139] $PhMe_2SiCH_2$,[140–143] $Me_3SiCHMe$,[144] $Me_3SiSiMe_2CH_2$, $EtMe_2SiSiMe_2CH_2$, or $(Me_3Si)_2CH$,[139] were subsequently synthesised by a similar procedure.

The reaction of 2 moles of Me_3SiCH_2MgCl with 1 mole of $HgCl_2$ leads to the formation of bis(trimethylsilylmethyl)mercury in yields up to 50%:[145,146]

$$2Me_3SiCH_2MgCl + HgCl_2 \rightarrow (Me_3SiCH_2)_2Hg + 2MgCl_2 .$$

Symmetrical organosilicon derivatives of mercury of the type R_2Hg (for the significance of R, see above) have been obtained in the same way.

Reactions of $(R_3Si)_2Hg$ with organic and organometallic compounds.

R_3	Reagent	Reaction product	References
Et_3, $MePh_2$	$Hg[C(N_2)COCH_3]_2$	$R_3SiC(N_2)COCH_3$	101
Et_3, $MePh_2$	$Hg[C(N_2)COOE]_2$	$R_3SiC(N_2)COOEt$	102,103
Et_3	$Hg(CH_2COCH_3)_2$	$Et_3SiOC(CH_3)=CH_2$	104
Me_3	R'_3SnX (X = OMe, OEt, NEt_2, $OSnMe_3$)	$R'_3SnSnR'_3$	50,105,106
Me_3	Me_3GeOMe	$Me_3SiHgGeMe_3$	107
Me_3	$Fe(CO)_5$	$(Me_3Si)_2Fe(CO)_4$	108
Cl_3	$[Mn(CO)_5]_2$	$Cl_3SiMn(CO)_5$	23
Me_3	Me_3Tl	$(Me_3Si)_3Tl$	109
Me_3	$(Et_3P)_2PtCl_2$	$(Et_3P)_2Pt(Cl)SiMe_3$	110,111
Me_3	$[(Ph_2P)_2CH_2]PtCl_2$	$Pt(SiMe_3)_2[(PhP)_2CH_2]$	112–114
Me_3	$Ir(Et_3P)_2(CO)Cl$	$Ir(HgSiMe)(SiMe_3)_2(Et_3P)_2CO$	115
Me_3	$Pb(OAc)_4$	$Me_3SiPb(OAc)_3$	116
Me_3	$(CF_3)_2P(S)Cl$	$Me_3SiSP(CF_3)_2$	117
Me_3	$PhHgCCl_2Br$	$Me_3SiCCl=CCl_2$	118–120
Et_3, iso-Pr_3	S	$R_3SiSHgSiR_3$	50,100
Et_3, iso-Pr_3	Se	$R_3SiSeHgSiR_3$	121–123
Et_3	HSeBu	$Et_3SiSeBu$	124
Me_3	R'X (R = CCl_3, $CHCl_2$, CH_2Cl, Me, Et, iso-Pr, Bu; X = Cl, Br)	Me_3SiHgR	9,25,50, 125–127
Me_3	Ph_3CCl	$(Ph_3C)_2$	127
Me_3			126
Me_3	$BrCH_2CH_2Br$	$CH_2=CH_2$	127
Me_3	BrCH CHBr	CH≡CH	127
Me_3	$CF_3CF=CF_2$	$CF_3CF=CFSiMe_3$	129
Me_3	$CF_3C\equiv CCF_3$	$CF_3C(SiMe_3)=C(SiMe_3)CF_3$	129
Me_3	$CF_3C\equiv CF$	$CF_3C\equiv CSiMe_3+CF_3C(SiMe_3)=C(SiMe_3)F$	129
Me_3	$CF_2=CF_2$	$CF_2=CFSiMe_3$	128,129
Me_3	$CF_2CF=CFCF_2$	$CF_2CF=C(SiMe_3)CF_2+CF_2C(SiMe_3)=C(SiMe_3)CF_2$	128,129
Me_3	$CF_2=CFCl$	$CF_2=CFSiMe_3+CFCl=CFSiMe_3$	128
Me_3	$CF_2=CFBr$	$CF_2=CFSiMe_3$	130,131
Me_3	ArBr (Ar = Ph; 4-MeC_6H_4; 2, 4, 6-$Me_3C_6H_3$; 1-naphthyl)	$ArSiMe_3$ or $(Me_3Si)_2+Ar_2Hg$	55,127
Me_3	C_6F_5Br	$C_6F_5SiMe_3$ or $(Me_3Si)_2+(C_6F_5)_2Hg$	131,132
Me_3	$(CF_3)_2NCl$	$CF_3N=CF_2$	133,134

The mercuration of Me_3SiCH_3MgCl by organylmercury chlorides R'HgCl leads to compounds of the type Me_3SiCH_2HgR' [R' = Me, n-C_6H_{13}, Ph,[138] $CH_2SiMe_2CMe_3$,[139] CH_2GeMe_3,[147] $CH_2Me_2SiSiMe_3$, $CH_2Me_2SiSiMe_2Et$, or $CH(SiMe_3)_2$ [139]].

Dimethylmercury reacts with trichloromethylsilane or dichlorodimethylsilane at 450°C to form $(Cl_3SiCH_2)_2Hg$ and $(Cl_2CH_3SiCH_2)_2Hg$ respectively[148]:

$$2(CH_3)_nSiCl_{4-n} + (CH_3)_2Hg \rightarrow [(CH_3)_{n-1}Cl_{4-n}SiCH_2]_2Hg + 2CH_4 .$$

These compounds were not isolated in a pure form but were identified as their methyl derivatives, obtained by treatment with methylmagnesium bromide.

Organozinc synthesis can also be used to prepare certain organosilicon derivatives of mercury, for example[149]:

$$2Me_3SiCHIZnI + HgCl_2 \rightarrow (Me_3SiCHI)_2Hg + 2IZnCl .$$

The yield of bis[iodo(trimethylsilyl)methyl]mercury is then 45% (traces of $Me_3SiCHIHgI$ were also found).

The reaction of dichloromethyl(trimethylsilyl)lithium with mercury(II) bromide at 135°C has been used to synthesise dichlorobis(trimethylsilyl)methylmercury, which serves as a source of chlorotrimethylsilylcarbene[150–152]:

$$2Me_3SiCCl_2Li + HgBr_2 \rightarrow (Me_3SiCCl_2)_2Hg + 2LiBr .$$

For an initial reactant ratio of 1 : 1, up to 5% of Me_3SiCCl_2.HgBr is formed together with the symmetrical compound (yield 44%). When $HgBr_2$ is replaced by $HgCl_2$, the yield of $(Me_3SiCCl_2)_2Hg$ falls to 23% and up to 17% of Me_3SiCCl_2.HgCl is formed.

Trimethyl[(methylmercuri)(trimethylsilyl)methylene]-phosphorane has been obtained by the reaction of the lithium derivative of trimethyl(trimethylsilylmethylene)phosphorane with methylmercury chloride[153]:

$$Me_2P(CH_2Li)=CHSiMe_3 + Me_3HgCl \rightarrow Me_3P=C(HgMe)(SiMe_3) + LiCl .$$

(b) Mercuration of unsaturated organosilicon compounds. The addition of mercury salts to the double bonds of unsaturated organosilicon compounds was first achieved in 1959[154]:

$$Me_3SiCH=CH_2 + Hg(OAc)_2 \xrightarrow[-CH_3COOH]{H_2O} Me_3SiCH(HgOAc)CH_2OH .$$

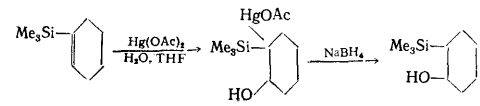
The reduction of the product with sodium amalgam led to (2-hydroxyethyl)trimethylsilane, which confirmed the above anomalous mode of reaction [the mercuration of olefins of the type $RCH=CH_2$ with mercury acetate usually proceeds in accordance with the Markovnikov rule, leading to $RCH(OH)CH_2HgOAc$ [155]]. The unusual mode of mercuration in this case is due to the interaction of the π electrons of the vinyl group with the vacant 3*d* orbitals of the silicon atom (the effect of the $d_\pi - p_\pi$ conjugation), which predominates over the opposed inductive effect of the trimethylsilyl group, which reduces the electron density at the β-carbon atom.

When trimethylallylsilane is acted upon by mercury salts, only the products of the cleavage at the $Si-CH_2$ bond are formed, which is apparently due to the β-decomposition of the adduct formed initially[156–158]. The study of the kinetics of this process showed that its mechanism does not fit within the framework of simple bimolecular electrophilic substitution[158]. The reaction proceeds in several stages, the rate of the process being determined by the cleavage of the adduct to $(CH_3)_3SiX$ and $CH_2=CHCH_2HgS$.

The addition of bis(trinitromethyl)mercury to trimethylvinylsilane in water, alcohol, benzene, and carbon tetrachloride leads to bis[(3,3,3-trinitro-1-trimethylsilyl)propyl]mercury (in 90% yield)[156,157]:

$$2Me_3SiCH=CH_2 + Hg[C(NO_2)_3]_2 \rightarrow Hg[-CH(SiMe_3)CH_2C(NO_2)_3]_2 .$$

The interaction of mercury acetate with 1-trimethylsilylcyclohexane in an aqueous medium gives rise to an addition product, whose reduction with sodium tetrahydroborate results in the formation of 1-trimethylsilyl-2-cyclohexanol[159]:



The mode of addition of the HgOAc group in the mercuration of unsaturated compounds of the type $RCH=CH(CH_2)_n.SiX_3$ (R = H, Me, or Ph; X = Me, Et, Me, Et, or Ac)

depends on the nature of the substituents at the double bond (**R**) and at the silicon atom (**X**) as well as the position of the double bond[160]. It has been established by ^{1}H NMR that, in the reaction of mercury acetate with trimethylvinylsilane in both alcoholic and acetic acid media, the HgOAc group adds only to the α-carbon atom:

$$Me_3SiCH{=}CH_2 + Hg(OAc)_2 \xrightarrow[-AcOH]{R'OH} Me_3SiCH(HgOAc)CH_2OR';$$
$$R' = Me, \text{ or } Ac.$$

The addition of mercury acetate to trimethylpropenylsilane and trimethyl-β-styrylsilane is no longer selective. In both instances the HgOAc group adds to both α- and β-carbon atoms:

$$Me_3SiCH{=}CHR + Hg(OAc)_2 \xrightarrow[-AcOH]{R'OH} \begin{cases} \rightarrow Me_3SiCH(HgOAc)CH(R)OR' \\ \rightarrow Me_3SiCH(OR')CH(R)HgOAc \end{cases}.$$

The ratio of the α- and β-adducts is 7 : 3 for **R** = Me and 1 : 1 for **R** = Ph. The breakdown of selectivity in the addition reaction is due to the enhanced electron density at the β-carbon atom owing to the $+I$ effect of the methyl group or the incorporation of the phenyl group in the conjugation chain.

Contrary to data published previously[161], the addition of mercury acetate to alkenyltrialkoxysilanes in an alcoholic medium is in all cases quantitative and vigorously selective with formation of α-mercurated adducts alone[160]:

$$(MeO)_3SiCH{=}CHR + Hg(OAc)_2 \xrightarrow{MeOH} (MeO)_3SiCH(HgOAc)CH(R)OMe + AcOH;$$
$$R = H, Me, \text{ or Ph.}$$

On the other hand, only the γ-mercuri-derivative has been obtained from trialkoxyallylsilane:

$$(EtO)_3SiCH_2CH{=}CH_2 + Hg(OAc)_2 \xrightarrow[-AcOH]{EtOH} (EtO)_3SiCH_2CH(OEt)CH_2HgOAc.$$

The adducts formed in both cases are fairly stable.

In nitromethane or chloroform mercury acylates add smoothly to vinylsilanes with formation of the corresponding α-acyloxymercuri-derivatives[160]:

$$X_3SiCH{=}CH_2 + Hg(OCOR)_2 \rightarrow X_3SiCH(HgOCOR)CH_2OCOR;$$
$$X = Et, Me, \text{ or AcO; } R = Me, \text{ or Ph.}$$

When trialkylethynylsilanes are acted upon by mercury salts, the acetylenic hydrogen atom is substituted instead of the addition to the triple bond[162]:

$$Me_3SiC{\equiv}CH + XHgOAc \rightarrow Me_3SiC{\equiv}CHgX + AcOH;$$
$$X = I, \text{ or OAc.}$$

The reaction of mercury(II) chloride with 1-triethylsilyl-2-tripropylstannylethylene leads to the cleavage of the bond between tin and the unsaturated group[163]:

$$Et_3SiCH{=}CHSnPr_3 + HgCl_2 \rightarrow Et_3SiCH{=}CHHgCl + ClSnPr_3.$$

The interaction of methylmercury chloride with trimethyl(trimethylsilylmethylene)phosphorane leads to trimethyl[(methylmercuri)(trimethylsilyl)methylene]phosphorane[153,164]:

$$MeHgCl + Me_3P{=}CHSiMe_3 \rightarrow (Me_3\overset{+}{P}{-}\underset{SiMe_3}{\underset{|}{CH}}{-}HgMe)\,Cl^- \xrightarrow{Me_3P=CHSiMe_3} \rightarrow Me_3P{=}C\begin{matrix}HgMe\\SiMe_3\end{matrix} + (Me_3\overset{+}{P}CH_2SiMe_3)\,Cl^-.$$

(c) The cleavage of sila- and 1,3-disilacyclobutanes with mercury salts. When 1,1-dialkylsilacyclobutanes are acted upon by mercury salts in an aqueous or alcoholic medium, the endocyclic Si–C bond is cleaved[165-168]. This results in the smooth formation of γ,γ'-mercurated 1,1,3,3-tetraorganyl-1,3-dipropylsiloxanes:

$$R_2Si\begin{matrix}CH_2\\CH_2\end{matrix}CHR' + HgX_2 \rightarrow XSiR_2CH_2CHR'CH_2HgX \xrightarrow{R''OH} \rightarrow R''OSiR_2CH_2CHR'CH_2HgX \rightarrow O(SiR_2CH_2CHR'CH_2HgX)_2.$$

In an alcoholic medium these compounds are apparently formed as a result of heterofunctional condensation catalysed by mercury salts:

$$\equiv SiX + R''OSi\equiv \xrightarrow{HgX_2} \equiv Si{-}O{-}Si\equiv + R''X.$$

Mercury salts cleave 1,1,3,3-tetramethyl-1,3-disilacyclobutane even more readily (the rate of its cleavage by $HgCl_2$ is four times greater than the rate of cleavage of 1,1-dimethylsilacyclobutane)[165-168]:

$$Me_2Si\begin{matrix}CH_2\\CH_2\end{matrix}SiMe_2 + HgX_2 \rightarrow XSiMe_2CH_2SiMe_2CH_2HgX \xrightarrow{R''OH} \rightarrow R''OSiMe_2CH_2SiMe_2CH_2HgX \rightarrow O[SiMe_2CH_2SiMe_2CH_2HgX]_2.$$

The homogeneous reaction of sila- and 1,3-disila-cyclobutanes with $Hg(NO_3)_2$ in an alcoholic medium proceeds in the same direction as for $HgCl_2$ or $HgAc_2$, but in a heterogeneous medium (when aqueous mercury nitrate solutions are used) oligomeric (telomeric) mercuration products are formed[169,170] probably via the mechanism

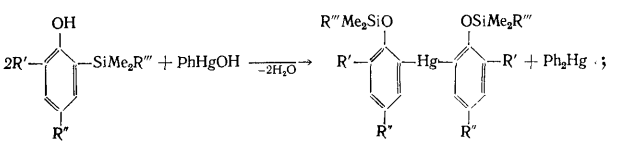
$$R_2Si\begin{matrix}CH_2\\CH_2\end{matrix}R' + Hg(NO_3)_2 \xrightarrow{H_2O} [O_3NSiR_2CH_2R'CH_2HgNO_3] \xrightarrow{nR_2Si\square R'} \rightarrow \{O_3N[SiR_2CH_2R'CH_2]_{n+1}HgNO_3\} \xrightarrow{H_2O} HO[SiR_2CH_2R'CH_2]_{n+1}HgNO_3 \rightarrow O\{[SiR_2CH_2R'CH_2]_{n+1}HgNO_3\}_2;$$
$$R = Me, \text{ or Ph; } R' = CH_2, \text{ or } SiR_2.$$

Evidently in this case the primary cleavage product, containing the labile Si–O–NO_2 group, is itself capable of breaking the sila- or 1,3-disila-cyclobutane ring, which leads to the formation of oligomeric compounds.

Five-membered heterocycles with one or two silicon atoms in the ring do not react with mercury salts[167]. It has been suggested that the rate of these reactions is controlled by the electrophilic attack by the HgX^+ cation.

(d) Mercuration of aromatic organosilicon derivatives. The reactions of mercury salts with organosilicon compounds in which the silicon atom is linked directly to an aromatic ring lead in all cases to the dissociation of the Si–Ar bond and not to the mercuration of the ring[171-176].

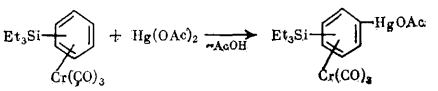
Sterically hindered *o*-trialkylsilylphenols react with PhHgOH or Ph_2Hg, forming the corresponding bis-(2-trialkylsiloxyphenyl)mercuranes[177-180]:



$R' = R'' = CMe_3$, $R''' = Me$; $R' = SiMe_3$, $R'' = CMe_3$, $R''' = Me$; $R' = CMe_3$, $R'' = SiMe_3$, $R''' = Me$; $R' = R'' = CMe_3$, $R''' = Ph$.

When PhHgOH interacts with *o*-trialkylsilylphenols containing a less hindered OH group, polymeric arylmercury oxides which do not contain silicon are formed[178]. If the trialkylsilyl group is in the *para*-position relative to the hydroxy-groups, mercuration does not occur[181] and oxidation of the organosilicon phenols is observed.

The interaction of triethylsilylbenzenechromium tricarbonyl by mercury acetate in glacial acetic acid leads to mercuration in the aromatic ring without the elimination of the triethylsilyl group [182]:



The separation of the silicon atom from the aromatic ring by the $-(CH_2)_nO$-group permits the smooth mercuration of the ring [183]:

$$X_3Si(CH_2)_nOC_6H_4Y + Hg(OAc)_2 \xrightarrow{-AcOH} X_3Si(CH_2)_nOC_6H_3Y(HgOCOCH_3);$$

X = Me, MeO, or EtO;

Y = H, OMe-*o*, Me-*p*; $n = 1, 3$.

Using an excess of mercury acetate, it is possible to convert compounds of the type $X_3Si(CH_2)_nOPh$ into [bis(acetoxymercuri)phenoxyalkyl]trialkyl- or [bis(acetoxymercuri)phenoxyalkyl]trialkoxy-silanes $X_3Si(CH_2)_nOC_6H_3.(HgOAc)_2$. [183]

2. Properties

Organomercury compounds containing the $Si-(-C-)_n-Hg$ group are fairly resistant to the action of atmospheric oxygen, moisture, and light, in contrast to compounds with the Si–Hg bond. They also exhibit a comparatively high thermal stability. Thus many compounds of the type R_3SiCH_2HgR' can be distilled *in vacuo* without appreciable decomposition and can be successfully separated by the gas–liquid chromatography (GLC) [139]. Bis(trimethylsilylmethyl)mercury decomposes slowly only at 200°C (to the extent of 5% after 100 h) [145], forming mercury, tetramethylsilane, and $Me_3SiCH_2HgCH_2SiMe_2CH_2CH_2SiMe_3$.

However, in the photolysis of $(Me_3SiCH_2)_2Hg$ vigorous decomposition is observed with formation of mercury, methane, tetramethylsilane, and small amounts of $Me_3SiCH_2HgCH_2SiMe_2CH_2CH_2SiMe_3$, $Me_3SiSiMe_3$, $(Me_3SiSiMe_2)_2$, and $(Me_3SiCH_2CH_2SiMe_2CH_2)_2$. [145] When bis[tris(trimethylsilyl)methyl]mercury is acted upon by light, the relatively stable free radicals $[(CH_3)_3Si]_3Si^{\cdot}$ are generated [184]. They are only slightly less stable than $(Ph_3C^{\cdot})$:

$$[(Me_3Si)_3C]_2Hg \rightarrow 2(Me_3Si)_3C^{\cdot} + Hg.$$

The products of the mercuration of Si-substituted alkenylsilanes and organosilicon derivatives of mercury, formed when sila- or 1,3-disila-cyclobutanes are cleaved by mercury salts, exhibit an inadequate thermal stability. They do not distill *in vacuo*, since they readily eliminate metallic mercury.

Treatment of organosilicon derivatives of mercury of the type $Me_3SiCH(HgOAc)CH_2OH$ with saturated solutions of alkali metal halides leads to the exchange of the acetoxy-group at the mercury atom for the halogen [154]:

$$Me_3SiCH(HgOAc)CH_2OH + MX \rightarrow Me_3SiCH(HgX)CH_2OH + MOAc;$$

M = K or Na; X = Cl, Br, or I.

The amorphous halogenomercuri-derivatives formed under these conditions exchange the HgX group for the halogen in reactions with the latter [154,156]:

$$Me_3SiCH(HgX)CH_2OH + X_2 \rightarrow Me_3SiCHXCH_2OH + HgX_2.$$

The reactions of $Me_3SiC{\equiv}CHgOAc$ and $Me_3SiC{\equiv}CHgI$ with iodine lead to the formation of trimethyliodoethynylsilane [162]:

$$(CH_3)_3SiC{\equiv}CHgX + I_2 \rightarrow (CH_3)_3SiC{\equiv}CI + IHgX;$$

X = OAc or I.

[(Phenyldimethylsilyl)methyl]mercury bromide is converted into the corresponding mercury acetate when acted upon by silver acetate [143]; the mercury acetate readily symmetrises under the influence of a 0.02 M perchloric acid solution:

$$PhMe_2SiCH_2HgBr \xrightarrow[-AgBr]{AgOAc} PhMe_2SiCH_2HgOAc \xrightarrow{HClO_4} (PhMe_2SiCH_2)_2Hg + Hg(OAc)_2$$

When acted upon by a saturated solution of hydrogen chloride in ethanol, compounds of the type Me_3SiCH_2HgR are cleaved [138] via the mechanism

$$Me_3SiCH_2HgR + HCl \xrightarrow{C_2H_5OH} \begin{cases} \rightarrow Me_4Si + RHgCl \ (R = Me \text{ or } n\text{-}C_6H_{13}) \\ \rightarrow Me_3SiCH_2HgCl + RH \ (R = Ph) \end{cases}.$$

This reaction made it possible to estimate the relative electronegativities of the substituent R linked to the mercury atom, which decrease in the following sequence:

$$Ph > Me_3GeCH_2 > Me_3SiCH_2 > Me > n\text{-}C_6H_{13} > Me_3CCH_2.$$

The higher electronegativity of the Me_3GeCH_2 group compared with that of the Me_3SiCH_2 group is indicated by the reaction [147]

$$2Me_3SiCH_2HgCH_2GeMe_3 + HCl \rightarrow \underset{(80\%)}{Me_4Ge} + \underset{(85\%)}{Me_3SiCH_2HgCl} + \underset{(20\%)}{Me_4Si} + Me_3GeCH_2HgCl.$$

However, all these data concerning the relative ease of elimination of substituents from the mercury atom characterise not only their electronegativity, but also their steric effect. For example, although the $Me_3SiSiMe_2$ group has stronger electron-donating properties than the Me_3Si group, it is eliminated from the mercury atom by hydrogen chloride with greater difficulty owing to steric hindrance [139]. The more bulky $Me_3CSiMe_2CH_2$ and $(Me_3Si)_2CH$ group are also split off from the mercury atom with greater difficulty than the Me_3SiCH_2 group.

Compounds of the type Me_3SiCH_2HgR' are also cleaved by mercury(II) chloride [138]:

$$Me_3SiCH_2HgC_6H_{13} + HgCl_2 \rightarrow Me_3SiCH_2HgCl + C_6H_{13}HgCl.$$

Bis(triorganylsilylmethyl)mercuranes interact with alkali metals, splitting off mercury and forming the corresponding alkali metal derivatives [140–142,185]:

$$(R_3SiCH_2)_2Hg + 2M \rightarrow 2R_3SiCH_2M + Hg,$$

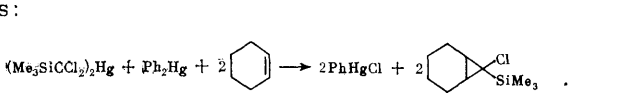
where M = Li, Na, K, Rb, or Cs.

This reaction constitutes a convenient method for the synthesis of organosilicon derivatives of alkali metals.

Tris(trimethylsilylmethyl)aluminium has been obtained similarly [186]:

$$3(Me_3SiCH_2)_2Hg + 2Al \rightarrow 2(Me_3SiCH_2)_3Al + 3Hg.$$

On heating, compounds of the type $(Me_3SiCX_2)_2Hg$ ($X_2 = Cl_2$, HBr, ClBr, or Br_2) give rise to the carbenes Me_3SiCH, Me_3SiCCl, and Me_3SiCBr, [150–152] which are capable of adding to the double bonds of unsaturated compounds:



In view of the high stability of compounds containing the $Si-(-C-)_n-Hg$ group, in contrast to compounds with the Si–Hg bond, the former can find practical applications. Thus compounds having the general formula $ROCOHgCH_2C.(OR')YA_nSi(R'')_a(X)_b$ ($R = R' = R'' =$ alkyl; Y = H or Me; A = alkylene; X = alkoxy- or acetoxy-group; $a = 0-2$; $b = 3-a$) can serve as fungicidal additives to silicone elastomers [161].

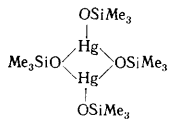
IV. COMPOUNDS CONTAINING THE Si–X–Hg (X = O, S, Se, Te, OR N) GROUP

1. Compounds Containing the Si–O–Hg Group

One of the most widely used methods for the synthesis of compounds containing the Si–O–Hg group involves the reaction of alkali metal triorganylsilanoxides with mercury salts. Mercury(II) chloride reacts with sodium trimethylsilanoxide in dioxan, forming the ether-soluble bis(trimethylsiloxy)mercury, which is extremely sensitive to moisture [187]:

$$2Me_3SiONa \xrightarrow[-2NaCl]{HgCl_2} (Me_3SiO)_2Hg \xrightarrow[-HgO]{H_2O} 2Me_3SiOH \ .$$

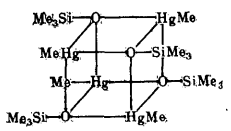
This compound sublimes in a high vacuum at 90°C, forming crystals. Determination of the molecular weight revealed its dimeric structure [188]:



At approximately 0°C bis(trimethylsiloxy)mercury slowly decomposes with dissociation of the Si–C bond:

$$(Me_3SiO)_2Hg \rightarrow Me_3SiOHgMe + 1/n\,(Me_2SiO)_n \ .$$

Methyl(trimethylsiloxy)mercury, obtained by treating Me_3SiONa with methylmercury chloride, is more stable and is readily soluble in organic solvents [188–190]. It is associated and has a tetrameric structure in the crystalline state [190,191]:



When $HgCl_2$ interacts with sodium triphenylsilanoxide (in molar proportions of 1 : 2) in ether, sodium chloride precipitates instantaneously and bis(triphenylsiloxy)mercury is formed [192]. However, even when the solvent is removed *in vacuo* (< 20°C), the decomposition of this compound begins. This results in a 34% yield of phenyl(triphenylsiloxy)mercury and a solid polymer which melts in the range 135–250°C:

$$2Ph_3SiONa + HgCl_2 \xrightarrow[-2NaCl]{} [Ph_3SiO]_2Hg \rightarrow Ph_3SiOHgPh + Ph_3SiO\,(Ph_2SiO)_n\,HgPh \ .$$

When the proportions of $HgCl_2$ and PhSiONa are 1 : 1, a similar polymer and PhHgCl are formed, which indicates an analogous process (with dissociation of the Si–C bond):

$$R_3SiONa + HgCl_2 \rightarrow R_3SiO\,(R_2SiO)_n\,HgCl + RHgCl \ .$$

Phenyl(triphenylsiloxy)mercury can be obtained also by another procedure [192]:

$$Ph_3SiOK + PhHgCl \rightarrow Ph_3SiOHgPh + KCl \ .$$

This compound is not hydrolysed by water but is cleaved on treatment with HCl, forming triphenylsilanol and PhHgCl. It is stable at room temperature, but above the melting point decomposes with formation of Ph_2Hg and $Ph_3SiO(Ph_2SiO)_nHgPh$.

Organosilicon derivatives of mercury containing the Si–O–Hg group can be obtained [193] by the reaction of RHgX (R is an organic group and X the hydroxy-group or the residue of an inorganic or acetic acid) with silicon tetrachloride, tetraethoxysilane, metal silicates, and silicic acid. After prolonged refluxing of a mixture of $SiCl_4$ and mercury(II) oxide in a polar solvent (acetonitrile, nitromethane, etc.) in the presence of mercury(II) chloride [194], perchloro-oligosiloxanes $Cl_3Si(OSiCl_2)_nCl$ (n = 1–4), boiling in the range from 190° to 262°C at 15 mmHg, and a solid having the composition $ClHgOSiCl_3$ are formed.

The attempt to obtain polyphenylmercurosiloxanes by the reaction of disodium diphenylsilanedioxide with mercury(II) chloride led only to the formation [195] of octaphenylcyclotetrasiloxane $Ph_2SiOPh_2SiOPh_2SiOPh_2SiO$, but the reaction of diphenylsilanediol with diethylmercury nevertheless made it possible to synthesise the polymeric organosilicon derivative of mercury containing the Si–O–Hg group [195].

The 885 cm^{-1} [192] and 932 cm^{-1} [188] bands in the infrared spectra of triorganylsiloxymercuranes have been assigned to the vibrations of the Si–O–Hg group [188].

2. Compounds Containing the Si–X–Hg Groups (X = chalcogen).

As stated in Section II. 3 (see Table), organosilicon derivatives of mercury containing the Si–X–Hg group are formed when bis(trialkylsilyl)mercuranes interact with sulphur or selenium [50,100,121–123]:

$$(R_3Si)_2Hg + 1/8\,X_8 \rightarrow R_3SiXHgSiR_3 \ ;$$
$$R = Et \text{ or iso-Pr};\ X = S \text{ or Se}.$$

Selective heterolytic cleavage of bis(triethylgermyl)-mercury with triethylsilaneselanol or triethylsilanetellurol leads to the corresponding germanium derivatives [100,196,197]. When the reactants are in proportions of 1 : 2, $(R_3SiX)_2Hg$ is formed together with triethylgermane:

$$(R_3Ge)_2Hg + HXSiR_3 \rightarrow R_3GeHgXSiR_3 + R_3GeH \ ,$$
$$(R_3Ge)_2Hg + 2HXSiR_3 \rightarrow 2R_3GeH + Hg\,(XSiR_3)_2 \ ,$$
$$R = Et;\ X = Se \text{ or Te} \ .$$

Asymmetric compounds containing the Si–X–Hg group readily decompose at room temperature via the mechanism [196,197]

$$R_3GeHgXSiR_3 \rightarrow R_3GeXSiR_3 + Hg \ .$$

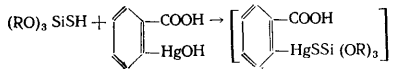
On the other hand, the symmetrical derivatives $(R_3SiX)_2Hg$ have a fairly high thermal stability and do not fully decompose in solution even under prolonged heating (7 h, 130°C). Their decomposition products are the mercury chalcogenide and $(R_3Si)_2X$:

$$(R_3SiX)_2Hg \rightarrow (R_3Si)_2X + HgX \ .$$

Trialkoxysilylthiomercuranes, which are relatively soluble in ether and tetrahydrofuran and are stable in the absence of moisture, have been obtained by the interaction of trialkoxysilanethiols with ethylmercury bromide [198]:

$$(RO)_3SiSH + EtHgBr \rightarrow (RO)_3SiSHgBr + C_2H_6 \ ;$$
$$R = \text{iso-Pr, } Me_3C, \text{ or } (CH_3)_2CHCH_2CH_2 \ .$$

The formation of a compound containing the Si–S–Hg group is observed in the reaction of trialkoxysilanethiols with *o*-hydroxymercuribenzoic acid. However, the product has not been isolated in a free form [199]:



3. Compounds Containing the Si–N–Hg Group

The exothermic reaction of sodium bis(trimethylsilyl)-amide with mercury(II) bromide in ether yielded di[bis(trimethylsilyl)amino]mercurane [153,200,201]:

$$2\,(Me_3Si)_2NNa + HgBr_2 \rightarrow [(Me_3Si)_2N]_2Hg + 2NaBr\ .$$

The reaction product is a colourless crystalline substance, which distills *in vacuo*, does not form adducts with pyridine or tetrahydrofuran, and is readily hydrolysed to $Hg(OH)_2$ and hexamethyldisilazane.

The force constant, indicating that the Hg–N bond is covalent and single, has been calculated from infrared and Raman spectroscopic data [200]. The Hg–N interatomic distance is 2.23 Å. The band at 406 cm^{-1} in the infrared spectrum was assumed to correspond to the $\nu_{as}(N–Hg–N)$ frequency. The 390 cm^{-1} line in the Raman spectrum corresponds to the $\nu_S(N–Hg–N)$ vibration.

Lithium tris(trimethylsilyl)hydrazide reacts exothermically with mercury(II) chloride or bromide in pentane [202], forming the lithium halide and mercury tris(trimethylsilyl)-hydrazide:

$$2\,(R_3Si)_2N–N(Li)–SiR_3 + HgX_2 \rightarrow 2LiX + (R_3Si)_2N–N\begin{matrix}SiR_3\\ \diagdown\\ Hg–N–N–(SiR_3)_2\\ \diagup\\ SiR_3\end{matrix}\ ;$$

$$R = Me,\ X = Cl\ or\ Br\ .$$

This hydrazide is a crystalline substance, which is readily soluble in petroleum ether, benzene, and THF and is sensitive to moisture. According to cryoscopic data, the compound is monomeric. Its infrared spectrum exhibits the intense asymmetric vibration of the N–Hg–N group with $\nu_{as} = 379\ cm^{-1}$ in the region of low frequencies. The ^1H NMR spectrum is a doublet ($\nu = 0.28,\ 0.26$). [202]

The interaction of lithium bis(trimethylsilyl)amide with alkylmercury halides gave *N*,*N'*-bis(trimethylsilyl)alkylmercuramines in yields up to 85% [203]:

$$(Me_3Si)_2NLi + RHgX \rightarrow (Me_3Si)_2NHgR + LiX\ ;$$

$$R = Me\ or\ Et;\quad X = Cl\ or\ Br\ .$$

They are colourless liquids which distill *in vacuo*. ^1H NMR spectra: $\delta(CH_3Hg) = 0.37$ p.p.m., $\delta(CH_3Si) = 0.17$ p.p.m., and $J(^{199}Hg–CH_3) = 157$ Hz were obtained for $CH_3HgN[Si(CH_3)_3]_2$; $\delta(CH_3CHg) = 1.07$ p.p.m., $\delta(CCH_2Hg) = 1.17$ p.p.m., $\delta(SiCH_3) = 0.19$ p.p.m., $J(^{199}Hg–CH_2) = 160$ Hz, and $J(^{199}Mg–CCH_3) = 195$ Hz were found for $C_2H_5HgN.[Si(CH_3)_3]_2$.

Alkyl-*N*,*N'*-bis(triorganylsilyl)mercuramines are useful reagents in the synthesis of many organomercury compounds which are otherwise difficult to obtain. Thus the interaction of $MeHgN(SiMe_3)_2$ with an equimolar amount of water in ether leads to the formation of dimethyldimercury oxide and hexamethyldisilazane in quantitative yields [203]:

$$2\,(Me_3Si)_2NHgMe + H_2O \rightarrow 2\,(Me_3Si)_2NH + MeHgOHgMe\ .$$

The reaction with HN_3 gives rise to mercury azides [203]:

$$(Me_3Si)_2NHgR + HN_3 \rightarrow (Me_3Si)_2NH + RHgN_3\ ;$$

$$R = Me\ or\ Et.$$

The reaction

$$2\,(Me_3Si)_2NHgR + H_2NCN \rightarrow 2\,(Me_3Si)_2NH + (RHg)_2NCN\ ;$$

$$R = Me\ or\ Et.$$

has been used to synthesise bis(organylmercuri)cyanamide. The interaction of *N*,*N'*-bis(trimethylsilyl)methylmercuramine with $HN=P(NMe_2)_3$ yielded tris(dimethylamino)-*N*-(methylmercuri)phosphinimide [204]:

$$(Me_3Si)_2NHgMe + HN=P(NMe_2)_3 \rightarrow (Me_3Si)_2NH + MeHgN=P(NMe_2)_3\ .$$

The reaction with nitroalkanes gives rise to organomercury derivatives of nitronic acids [205]:

$$(Me_3Si)_2NHgR + R'R''CHNO_2 \rightarrow (Me_3Si)_2NH + RHgO\overset{O}{\overset{\|}{N}}=CR'R''\ ;$$

$$R = Me\ or\ Et;\quad R',\ R'' = H\ or\ CH_3.$$

The reaction of $RHgN(SiMe_3)_2$ with diazoacetone or diazoacetophenone is used to synthesise organylmercuridiazoketones and mercuribis(diazoketones) [206]:

$$(Me_3Si)_2NHgR + HC(N_2)COR' \rightarrow (Me_3Si)_2NH + RHgC(N_2)COR'\ ,$$

$$(Me_3Si)_2NHgR + 2HC(N_2)COR' \rightarrow (Me_3Si)_2NH + Hg[C(N_2)COR']_2 + RH\ ;$$

$$R = Me\ or\ Et;\quad R' = Me\ or\ Ph.$$

$[(Me_3Si)_2N]_2Hg$ reacts analogously with 1,3-diketones [201,207,208]:

$$[(Me_3Si)_2N]_2Hg + 2HOCR=CHCOR \rightarrow (Me_3Si)_2NH + Hg(OCR=CHCOR)_2\ ;$$

$$R = Me\ or\ CMe_3.$$

Organyl-*N*,*N'*-bis(trimethylsilyl)mercuramines react with cyclopentadiene to form organylmercuricyclopentadienes [203]:

$$(Me_3Si)_2NHgR + HC_5H_5 \rightarrow (Me_3Si)_2NH + RHgC_5H_5\ ;$$

$$R = Me\ or\ Et\ .$$

Bis(cyclopentadienyl)mercury is formed similarly from $Hg[N(SiMe_3)_2]_2$ [209]:

$$[(Me_3Si)_2N]_2Hg + 2HC_5H_5 \rightarrow 2\,(Me_3Si)_2NH + Hg(C_5H_5)_2\ .$$

Mercury derivatives of tris(pentafluorophenyl)silane and tris(pentafluorophenyl)germane [21,32,210] as well as triphenylstannane [211] have been obtained with the aid of di[bis(trimethylsilyl)amino]mercury [211]:

$$[(Me_3Si)_2N]_2Hg + 2HE(C_6F_5)_3 \rightarrow 2\,(Me_3Si)_2NH + Hg[E(C_6F_5)_3]_2\ ;$$

$$E = Si\ or\ Ge.$$

$$[(Me_3Si)_2N]_2Hg + 2HSnPh_3 \rightarrow 2\,(Me_3Si)_2NH + Hg(SnPh_3)_2\ .$$

The hydrolytic instability of compounds containing the Si–X–Hg group limits their industrial manufacture and practical employment. However, they are extremely useful in the preparative synthesis of organomercury and organosilicon compounds which are otherwise difficult to obtain.

V. COMPOUNDS CONTAINING THE $Si–(–C–)_n–X–Hg$ GROUP

Among compounds of this type, only examples with X = Ge or Sn are known [212,213]. Di[tris(trimethylsilylmethyl)germyl]mercurane has been obtained by treating $(Me_3SiCH_2)_3GeH$ with diethylmercury [213]:

$$2\,(Me_3SiCH_2)_3GeH + Et_2Hg \rightarrow [(Me_3SiCH_2)_3Ge]_2Hg + 2EtH\ .$$

Di[tris(trimethylsilylmethyl)stannyl]mercurane has been synthesised by a similar mechanism [212]:

$$2\,(Me_3SiCH_2)_3SnH + Et_2Hg \rightarrow [(Me_3SiCH_2)_3Sn]_2Hg + 2EtH\ .$$

This compound is one of the products of the exchange reaction of the ester of mercurybisacetic acid with di[tris(trimethylsilylmethyl)stannyl]cadmium [213]:

$$[(Me_3SiCH_2)_3Sn]_2Cd + Hg(CH_3COOMe)_2 \rightarrow [(Me_3SiCH_2)_3Sn]_2Hg + Cd(CH_3COOMe)_2\ .$$

The asymmetric compounds $(Me_3SiCH_2)_3SnHgCH_2COOMe_3$ and $(Me_3SiCH_2)_3SnCdCH_2COOMe$ are then formed as intermediates.

Di[tris(trimethylsilylmethyl)stannyl]mercury exhibits an anomalously high thermal stability compared with its analogues $(R_3Sn)_2Hg$, where R = H, alkyl, or phenyl. This can be explained by the stabilising effect of the Me_3SiCH_2 group.

$[(Me_3SiCH_2)_3Sn]_2Hg$ is a crystalline substance which melts without decomposition. Its reactivity does not differ appreciably from that of bis(triethylsilyl)mercury and similar compounds [212,214-216]. Its solutions in hexane and THF are stable at 20°C. Thermal decomposition in the absence of solvents leads to the formation of mercury, tetrakis(trimethylsilylmethyl)stannane, and tin [221,214], probably via the intermediate formation of hexakis(trimethylsilylmethyl)distannane, which then disproportionates via the mechanism

$$2\,[(Me_3SiCH_2)_3Sn]_2 \xrightarrow{150°,\ 10\ h} 3\,(Me_3SiCH_2)_4Sn + Sn\ .$$

Oxidation with atmospheric oxygen in THF leads to the formation of mercury and hexakis(trimethylsilylmethyl)-distannoxane [218]:

$$[(Me_3SiCH_2)_3Sn]_2Hg + {}^1/_2O_2 \rightarrow [(Me_3SiCH_2)_3Sn]_2O + Hg\ .$$

The exchange reaction with $HgCl_2$ in THF at 20°C is completed after 30 min and leads to the quantitative formation of mercury and $(Me_3SiCH_2)_3SnCl$ [212,214]:

$$[(Me_3SiCH_2)_3Sn]_2Hg + HgCl_2 \rightarrow 2\,(Me_3SiCH_2)_3SnCl + 2Hg\ .$$

The interaction of di[tris(trimethylsilylmethyl)stannyl]-mercury with $Hg[C(CF_3)_3]_2$ leads to the formation of an asymmetric stannylmercury compound, which is demercurated with simultaneous β-decomposition [95,214]:

$$[(Me_3SiCH_2)_3Sn]_2Hg + Hg[C(CF_3)_3]_2 \rightarrow 2\,(Me_3SiCH_2)_3SnHgC(CF_3)_3 \rightarrow$$
$$\rightarrow 2\,(Me_3SiCH_2)_3SnF + 2Hg + 2\,(CF_3)_3C{=}CF_2\ .$$

Elemental iodine readily cleaves the Sn–Hg bond [213]:

$$[(Me_3SiCH_2)_3Sn]_2Hg + 2I_2 \rightarrow 2\,(Me_3SiCH_2)_3SnI + HgI_2\ .$$

Metallic lithium exchanges with mercury to form the corresponding stannyl-lithium derivative [213,217]:

$$[(Me_3SiCH_2)_3Sn]_2Hg + 2Li \rightarrow 2\,(Me_3SiCH_2)_3SnLi + Hg\ .$$

However, when the reaction is carried out in benzene, the main product is hexakis(trimethylsilylphenyl)distannane.

VI. COMPLEXES OF ORGANOSILICON COMPOUNDS WITH MERCURY SALTS

Triorganylsilylmethyl derivatives of phosphorus and arsenic form stable complexes with mercury halides. Thus tris(trimethylsilylmethyl)phosphine and tris(trimethylsilylmethyl)arsine react with mercury(II) chloride to form crystalline adducts [218,219]:

$$(Me_3SiCH_2)_3E + HgCl_2 \rightarrow (Me_3SiCH_2)_3E \cdot HgCl_2$$
$$E = P \text{ or } As.$$

When a solution of methyltris(trimethylsilylmethyl)arsonium iodide is refluxed with mercury(II) iodide in ethanol, methyltris(trimethylsilylmethyl)arsonium iodomercurate is formed [218]:

$$(Me_3SiCH_2)_3AsMeI + HgI_2 \rightarrow [(Me_3SiCH_2)_3AsMe]\,HgI_3\ .$$

The complexes of diphenyl-(*p*-triethylsilylphenyl)arsine with mercury(II) halides [*p*-$(Et_3Si)C_6H_4AsPh_2.HgCl_2$, *p*-$(Et_3Si)C_6H_4AsPh_2.HgBr_2$, and *p*-$(Et_3Si)C_6H_4AsPh_2.HgI_2$] are soluble in benzene and have distinct melting points (188°, 181°, and 139.5°C respectively), so that they can be used for the identification of triorganyl-silylphenylarsines [220].

The interaction of mercury(II) bromide with $[Ph_3PCH_2.SiMe_3]^+Br^-$ in methanol led to a water-soluble phosphonium complex having the composition $[Ph_3PCH_2SiMe_3]^+\,HgBr_3^-$. [221]

The reactions of mercury(II) chloride and methylmercury chloride with $Me_3P{=}CHSiMe_3$ or $Me_3P{=}C(SiMe_3)_2$ lead to the formation of mercurated silylphosphonium salts [153,164] $Me_3P{=}CHSiMe_3.HgCl_2$. When the reactant ratio is 2 : 1, the products are

$$\left[\begin{matrix} Me_3PCHHg & CHPMe_3 \\ | & | \\ Me_3Si & SiMe_3 \end{matrix}\right]^{2+} 2X^-,\ X = Cl \text{ or } Br\ .$$

In the reaction of bis(tricarbonylnitrosyliron)mercury with tris(trimethylsilylmethyl)phosphine one of the CO groups is substituted quantitatively [222]:

$$2\,(Me_3SiCH_2)_3P + Hg[Fe(CO)_3(NO)]_2 \xrightarrow[-CO]{} Hg[Fe(CO)_2(NO)P(CH_2SiMe_3)_3]_2\ .$$

On interaction with the same phosphine, bis(tetracarbonylcobalt)mercury forms a complex which undergoes an exchange or disproportionation reaction in the presence of mercury(II) halides [222]:

$$2\,(Me_3SiCH_2)_3P + Hg[Co(CO)_4]_2 \xrightarrow[-CO]{} [(Me_3SiCH_2)_3PCo(CO)_3]_2Hg \xrightarrow{+HgX_2}$$
$$\rightarrow 2\,(Me_3SiCH_2)_3PCo(CO)_3HgX\ .$$

Trialkylsilylmethanethiols react with mercury(II) chloride to form stable crystalline adducts [223]:

$$R_3SiCH_2SH + HgCl_2 \rightarrow [(R_3SiCH_2SH)_2Hg]Cl_2\ .$$

Bis(trimethylsilylmethyl) sulphide reacts with mercury(II) iodide to form $(Me_3SiCH_2)_2S.HgI_2$. [223] Compounds having the general formula $[XC_6H_4Hg]_2SiF_6$, where X = H or a halogen, are obtained by treating a phenylmercury salt with fluorosilic acid [224].

All the facts described above show that further studies in the field of organosilicon derivatives of mercury will prove extremely useful for the development of theoretical and particularly synthetic organic and organoelemental chemistry. There is also no doubt that, apart from the applications already described, new fields of the practical use of these compounds will be discovered.

REFERENCES

1. S.N. Borisov, M.G. Voronkov, and E. Lukevics, "Kremniielementoorganicheskie Soedineniya" (Organoelemental Derivatives of Silicon), Izd. Khimiya, Moscow, 1966.
2. N.S. Vyazankin and O.A. Kruglaya, Uspekhi Khim., 35, 1388 (1966) [Russ. Chem. Rev., No. 8 (1966)].
3. M.C. Baird, Prog. Inorg. Chem., 9, 2 (1968).
4. G.A. Razuvaev and N.S. Vyazankin, Pure Appl. Chem., 19, 353 (1969).
5. N.S. Vyazankin, G.A. Razuvaev, and O.A. Kruglaya, Organometallics in Chem. Synthesis, 1, 205 (1971).
6. N.S. Vyazankin, G.A. Razuvaev, and O.A. Kruglaya, Z. Chem., 11, 53 (1971).
7. E. Wiberg, O. Stecher, H.J. Andrascheck, L. Kreuzbichler, and E. Staude, Angew. Chem., 75, 516 (1963).
8. M.V. George, G.D. Lichtenwalter, and H. Gilman, J. Amer. Chem. Soc., 81, 978 (1959).
9. N.S. Vyazankin, G.A. Razuvaev, and E.N. Gladyshev, Dokl. Akad. Nauk SSSR, 155, 830 (1964).
10. A. Stock and C. Somieski, Ber., 49, 111 (1916).
11. C. Eaborn, J. Chem. Soc., 3077 (1950).
12. B.N. Dolgov, N.P. Kharitonov, and M.G. Voronkov, Zhur. Obshch. Khim., **24**, 861 (1954).
13. H. Gilman, H.G. Brooks, and M.B. Hughes, J. Org. Chem., **23**, 1398 (1958).

14. H.H.Anderson, J.Amer.Chem.Soc., 80, 5083 (1958).
15. H.H.Anderson and H.Hendifar, J.Amer.Chem.Soc., 81, 1027 (1959).
16. Ya.I.Ryskin and M.G.Voronkov, Coll.Czech. Chem.Comm., 24, 3816 (1959).
17. H.H.Anderson, J.Amer.Chem., 82, 1323 (1960).
18. E.Lukevics and S.Hillers, Izv.Akad.Nauk Latv. SSR, Ser.Khim., 95 (1961).
19. R.Ouellette, D.Marks, D.Miller, and D.Kesatie, J.Org.Chem., 34, 1769 (1969).
20. E.Lukevics and S.Hillers, Izv.Akad.Nauk Latv. SSR, Ser.Khim., 99 (1961).
21. N.S.Vyazankin, E.N.Gladyshev, S.P.Korneva, G.A.Razuvaev, and E.A.Arkhangel'skaya, Zhur. Obshch.Khim., 38, 1803 (1968).
22. G.A.Marano and A.G.MacDiarmid, Inorg.Nuclear Chem.Letters, 5, 621 (1969).
23. C.R.Bettler, J.C.Sendra, and G.Urry, Inorg. Chem., 9, 1060 (1970).
24. T.F.Schaaf, R.R.Kao, and J.P.Oliver, Inorg. Chem., 14, 2288 (1975).
25. E.N.Gladyshev, L.O.Yuntila, G.A.Razuvaev, N.S.Vyazankin, and V.S.Sokolov, Izv.Akad.Nauk SSSR, Ser.Khim., 204 (1976).
26. C.Eaborn, R.A.Jackson, and M.T.Rahman, J.Chem.Soc., Perkin Trans. II, 55 (1972).
27. N.S.Vyazankin, G.A.Razuvaev, E.N.Gladyshev, and T.G.Gurikova, Dokl.Akad.Nauk SSSR, 155, 1108 (1964).
28. A.K.Hovland, T.F.Schaaf, and J.P.Oliver, J.Organometallic Chem., 120, 171 (1976).
29. R.A.Jackson, Chem.Comm., 827 (1966).
30. E.N.Gladyshev, N.S.Vyazankin, E.A.Arkhangel'skaya, G.A.Razuvaev, and S.R.Korneva, Dokl. Akad.Nauk SSSR, 183, 338 (1968).
31. N.S.Vyazankin, O.A.Kruglaya, G.S.Kalinina, and E.N.Gladyshev, Zhur.Obshch.Khim., 38, 1595 (1968).
32. G.S.Kalinina, B.I.Petrov, O.A.Kruglaya, and N.S.Vyazankin, Zhur.Obshch.Khim., 42, 148 (1972).
33. G.S.Kalinina, B.I.Petrov, O.A.Kruglaya, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 2158 (1970).
34. T.W.Dolzine, A.K.Hovland, and J.P.Oliver, J.Organometallic Chem., 65, C1 (1974).
35. C.R.Bettler and G.Urry, Inorg.Chem., 9, 2372 (1970).
36. G.A.Razuvaev, I.V.Lomakova, L.P.Stepovik, and V.K.Khamylov, Zhur.Obshch.Khim., 43, 1523 (1973).
37. S.Cradock, E.A.V.Ebsworth, N.S.Hosmane, and K.M.Mackay, Angew.Chem., 87, 207 (1975).
38. P.Bleckmann, M.Soliman, K.Reuter, and W.P.Neumann, J.Organometallic Chem., 108, C18 (1976).
39. A.N.Egorochkin, S.Ya.Khorshev, N.S.Vyazankin, E.N.Gladyshev, and V.T.Bychkov, Zhur.Obshch. Khim., 38, 276 (1968).
40. A.N.Egorochkin, S.Ya.Khorshev, N.S.Vyazankin, and E.N.Gladyshev, Izv.Akad.Nauk SSSR, Ser. Khim., 969 (1969).
41. A.N.Egorochkin, S.Ya.Khorshev, and N.S.Vyazankin, Dokl.Akad.Nauk SSSR, 185, 353 (1969).
42. G.A.Domrachev and V.T.Bychkov, Izv.Akad.Nauk SSSR, Ser.Khim., 237 (1977).
43. T.F.Schaaf and J.P.Oliver, J.Organometallic Chem., 32, 307 (1971).
44. A.N.Egorochkin, N.S.Vyazankin, G.A.Razuvaev, O.A.Kruglaya, and M.N.Bochkarev, Dokl.Akad. Nauk SSSR, 170, 333 (1966).
45. T.F.Schaaf and J.P.Oliver, Inorg.Chem., 10, 1521 (1971).
46. M.J.Albright, W.Butler, M.D.Glick, T.Schaaf, R.R.Kao, and J.P.Oliver, "The VIIth International Conference on Organometallic Chemistry, Venice, 1975", p.217.
47. G.M.Kol'yakova, I.V.Rabinovich, N.S.Vyazankin, and E.N.Gladyshev, Dokl.Akad.Nauk SSSR, 204, 356 (1972).
48. C.Eaborn, R.A.Jackson, and M.T.Rahman, J.Organometallic Chem., 34, 7 (1972).
49. S.W.Bennett, H.J.Clase, C.Eaborn, and R.A.Jackson, J.Organometallic Chem., 23, 403 (1970).
50. O.A.Kruglaya, L.I.Belousova, B.V.Fedot'ev, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser. Khim., 975 (1975).
51. N.S.Vyazankin, O.A.Kruglaya, L.I.Belousova, B.V.Fedot'ev, and I.B.Fedot'eva, "IV Mezhdunarodnyi Simpozium po Khimii Kremniiorganicheskikh Soedinenii" (The IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, Part 2, p.165.
52. C.Eaborn, R.A.Jackson, D.J.Tune, and D.R.M.Walton, J.Organometallic Chem., 63, 85 (1973).
53. A.G.Beaumont, C.Eaborn, R.A.Jackson, and R.W.Walsingham, J.Organometallic Chem., 5, 297 (1965).
54. C.Eaborn, R.A.Jackson, and R.Walsingham, J.Chem.Soc., Perkin Trans. II, 366 (1973).
55. R.Fields, R.N.Haszeldine, and R.E.Hutton, J.Chem.Soc., (C) 2559 (1967).
56. C.Eaborn, R.A.Jackson, and R.W.Walsingham, Chem.Comm., 300 (1965).
57. C.Eaborn, R.A.Jackson, and R.W.Walsingham, J.Chem.Soc., (C) 2188 (1967).
58. C.Eaborn, R.A.Jackson, and R.Pearce, Chem. Comm., 920 (1967).
59. S.W.Bennett, C.Eaborn, R.A.Jackson, and R.Pearce, J.Organometallic Chem., 28, 59 (1971).
60. T.N.Mitchell, Tetrahedron Letters, 2281 (1972).
61. T.N.Mitchell, J.Organometallic Chem., 71, 27 (1974).
62. M.Lehnig, F.Werner, and W.P.Neumann, J.Organometallic Chem., 97, 375 (1975).
63. V.N.Glushakova, Yu.A.Alexandrov, and G.A.Razuvaev, J.Organometallic Chem., 40, 43 (1972).
64. Yu.A.Alexandrov, J.Organometallic Chem., 55, 1 (1973).
65. Yu.A.Aleksandrov, G.A.Razuvaev, G.N.Figurova, and V.N.Glushakova, Dokl.Akad.Nauk SSSR, 185, 1293 (1969).
66. Yu.A.Alexandrov, G.A.Razuvaev, V.N.Glushakova, and V.Ya.Savukova, J.Organometallic Chem., 27, 201 (1971).
67. C.Eaborn, R.A.Jackson, and M.T.Rahman, J.Organometallic Chem., 85, 15 (1975).
68. G.Neumann and W.P.Neumann, J.Organometallic Chem., 42, 293 (1972).
69. U.Christen and W.P.Neumann, Chem.Ber., 106, 421 (1973).
70. W.P.Neumann and G.Neumann, J.Organometallic Chem., 25, C59 (1970).

71. G.Neumann and W.P.Neumann, J.Organometallic Chem., **42**, 277 (1972).
72. A.G.Beaumont, R.W.Bott, C.Eaborn, and R.A.Jackson, J.Organometallic Chem., 6, 671 (1966).
73. A.G.Beaumont, C.Eaborn, and R.A.Jackson, J.Chem.Soc.(B), 1624 (1970).
74. W.P.Neumann, K.Reuter, F.Werner, and M.Ziebarth, "IV Mezhdunarodnyi Simpozium po Khimii Kremniiorganicheskikh Soedinenii" (The IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, Part 2, p.164.
75. A.F.Janzen, P.F.Rodesiler, and C.J.Willis, Chem.Comm., 672 (1966).
76. E.J.Louis and G.Urry, Tetrahedron Letters, 3295 (1968).
77. G.A.Razuvaev, E.N.Gladyshev, P.Ya.Bayushkin, G.A.Abakumov, and E.S.Klimov, Izv.Akad.Nauk SSSR, Ser.Khim., 2762 (1976).
78. K.Kühlein, W.P.Neumann, and H.P.Becker, Angew.Chem., 79, 870 (1967).
79. T.N.Mitchell and B.Kleine, Tetrahedron Letters, 2173 (1976).
80. H.P.Becker and W.P.Neumann, J.Organometallic Chem., 20, P3 (1969).
81. B.Schroeder, W.P.Neumann, J.Hollaender, and H.P.Becker, Angew.Chem., 84, 894 (1972).
82. H.P.Becker and W.P.Neumann, J.Organometallic Chem., 37, 57 (1972).
83. T.N.Mitchell, J.Chem.Soc., Perkin Trans. II, 1149 (1976).
84. S.V.Ponomarev, H.P.Becker, W.P.Neumann, and B.Schroeder, Annalen, 1895 (1975).
85. T.N.Mitchell, J.Organometallic Chem., 71, 39 (1974).
86. S.W.Bennett, C.Eaborn, R.A.Jackson, and R.Pearce, J.Organometallic Chem., 15, P17 (1968).
87. N.S.Vyazankin, E.N.Gladyshev, S.P.Korneva, and G.A.Razuvaev, Zhur.Obshch.Khim., 36, 2025 (1966).
88. N.S.Vyazankin, G.A.Razuvaev, E.N.Gladyshev, and S.P.Korneva, J.Organometallic Chem., 7, 353 (1967).
89. E.N.Gladyshev, E.A.Fedorova, L.O.Yuntila, G.A.Razuvaev, and N.S.Vyazankin, J.Organometallic Chem., 96, 169 (1975).
90. T.F.Schaaf and J.P.Oliver, J.Amer.Chem.Soc., 91, 4327 (1969).
91. E.N.Gladyshev, G.A.Razuvaev, E.A.Fedorova, L.O.Yuntila, and N.S.Vyazankin, "IV Mezhdunarodnyi Simpozium po Khimii Kremniiorganicheskikh Soedinenii" (The IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, Part 2, p.170.
92. O.A.Kruglaya, B.A.Gostevskii, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 250 (1977).
93. A.G.Lee, J.Organometallic Chem., 16, 321 (1969).
94. O.A.Kruglaya, B.I.Petrov, and N.S.Vyazankin, Zhur.Obshch.Khim., 39, 2365 (1969).
95. B.I.Petrov, O.A.Kruglaya, G.S.Kalinina, N.S.Vyazankin, B.I.Martynov, S.R.Sterlin, and B.L.Dyatkin, Izv.Akad.Nauk SSSR, Ser.Khim., 189 (1973).
96. E.N.Gladyshev, N.S.Vyazankin, Yu.A.Sorokin, V.I.Ermolaev, G.A.Bortnikov, and G.A.Razuvaev, Dokl.Akad.Nauk SSSR, 194, 1083 (1970).
97. N.S.Vyazankin, E.N.Gladyshev, E.A.Fedorova, and G.A.Razuvaev, Dokl.Akad.Nauk SSSR, 186, 1082 (1969).
98. N.S.Vyazankin, E.N.Gladyshev, E.A.Arkhangel'skaya, and G.A.Razuvaev, J.Organometallic Chem., 17, 340 (1969).
99. O.A.Kruglaya, L.I.Zakharkin, B.I.Petrov, G.S.Kalinina, and N.S.Vyazankin, Synth.Inorg. Metalorg.Chem., 3, 63 (1973).
100. N.S.Vyazankin, O.A.Kruglaya, E.N.Gladyshev, M.N.Bochkarev, and B.I.Petrov, "V Mezhdunarodnyi Kongress po Metallorganicheskoi Khimii, Moskva, 1971" (The Vth International Congress on Organometallic Chemistry, Moscow, 1971), p.594.
101. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, I.D.Kalikhman, E.I.Brodskaya, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 1887 (1976).
102. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, and N.S.Vyazankin, "IV Mezhdunarodnyi Simpozium po Khimii Kremniiorganicheskikh Soedinenii" (The IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, Part 2, p.169.
103. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, V.V.Keiko, and N.S.Vyazankin, Zhur.Obshch. Khim., 46, 930 (1967).
104. O.A.Kruglaya, Yu.I.Baukov, B.I.Petrov, and N.S.Vyazankin, Zhur.Obshch.Khim., 41, 1408 (1971).
105. T.N.Mitchell and W.P.Neumann, J.Organometallic Chem., 22, C25 (1970).
106. T.N.Mitchell, "V Mezhdunarodnyi Kongress po Metallorganicheskoi Khimii, Moskva, 1971" (The Vth International Congress on Organometallic Chemistry, Moscow, 1971), Vol.1, p.55.
107. T.N.Mitchell, J.Organometallic Chem., 38, 17 (1972).
108. W.Jetr and W.A.G.Graham, J.Organometallic Chem., 69, 383 (1974).
109. E.A.V.Ebsworth, A.G.Lee, and G.M.Sheldrick, J.Chem.Soc.(A), 1052 (1969).
110. F.Glockling and K.A.Hooton, Chem.Comm., 218 (1966).
111. F.Glockling and K.A.Hooton, J.Chem.Soc., (A), 1066 (1967).
112. A.F.Clemmit and F.Glockling, J.Chem.Soc., 1164 (1971).
113. F.Glockling and R.J.I.Pollock, Chem.Comm., 467 (1972).
114. F.Glockling and R.J.I.Pollock, J.Chem.Soc., Dalton Trans., 2259 (1974).
115. K.A.Hooton, J.Chem.Soc., (A), 1251 (1971).
116. U.Christen and W.P.Neumann, J.Organometallic Chem., 39, C58 (1972).
117. R.G.Cavell, R.D.Leary, A.R.Sanger, and A.J.Tomlinson, Inorg.Chem., 12, 1374 (1973).
118. D.Seyferth, R.J.Cross, and B.Prokai, J.Organometallic Chem., 7, P20 (1967).
119. D.Seyferth, E.M.Hanson, B.Prokai, and R.J.Cross J.Organometallic Chem., 24, 33 (1970).
120. J.Dunogues, R.Calas, J.Malzac, N.Buffaut, and C.Biran, J.Organometallic Chem., 27, C1 (1971).
121. E.N.Gladyshev, V.S.Andreevich, N.S.Vyazankin, and G.A.Razuvaev, Zhur.Obshch.Khim., 40, 939 (1970).
122. E.N.Gladyshev, N.S.Vyazankin, V.S.Andreevichev, A.A.Klimov, and G.A.Razuvaev, J.Organometallic Chem., 28, C42 (1971).

123. E.N.Gladyshev, V.S.Andreevichev, A.A.Klimov, N.S.Vyazankin, and G.A.Razuvaev, Zhur.Obshch. Khim., **42**, 1077 (1972).
124. N.S.Vyazankin, I.A.Vostokov, and V.T.Bychkov, Zhur.Obshch.Khim., 38, 2485 (1968).
125. S.W.Bennett, C.Eaborn, R.A.Jackson, and R.W.Walsingham, J.Organometallic Chem., **27**, 195 (1971).
126. S.W.Bennett, C.Eaborn, R.A.Jackson, and R.W.Walsingham, J.Organometallic Chem., **27**, 197 (1971).
127. F.Werner, W.P.Neumann, and H.P.Becker, J.Organometallic Chem., 97, 389 (1975).
128. R.Fields, R.N.Haszeldine, and A.F.Hubbard, J.Chem.Soc., (D), 647 (1970).
129. R.Fields, R.N.Haszeldine, and A.F.Hubbard, J.Chem.Soc., (C), 3838 (1971).
130. R.Fields, R.N.Haszeldine, and A.F.Hubbard, J.Chem.Soc., Perkin Trans.I, 847 (1972).
131. R.Fields, R.N.Haszeldine, and P.J.Palmer, Tetrahedron Letters, 1879 (1971).
132. R.Fields, R.N.Haszeldine, and A.F.Hubbard, J.Chem.Soc., (C), 2193 (1970).
133. H.G.Ang, J.Chem.Soc., (A), 2734 (1968).
134. H.G.Ang, Chem.Ind.(London), 863 (1969).
135. H.Ikeda, Y.Miura, and M.Kinoshita, Makromol. Chem., 177, 2647 (1976).
136. K.Kühlein and K.Clauss, Makromol.Chem., **155**, 145 (1972).
137. S.W.Bennett, C.Eaborn, and R.A.Jackson, J.Organometallic Chem., **21**, 79 (1970).
138. F.C.Whitmore and L.H.Sommer, J.Amer.Chem. Soc., 68, 481 (1946).
139. M.Kumada and M.Ishikawa, J.Organometallic Chem., 6, 451 (1966).
140. G.Fritz and H.Burdt, Z.anorg.Chem., **314**, 35 (1962).
141. G.Fritz and W.Kemmerling, Z.anorg.Chem., **322**, 34 (1963).
142. J.W.Wilt, O.Kolewe, and J.F.Kraemer, J.Amer. Chem.Soc., 91, 2624 (1969).
143. R.J.Ouellette and D.L.Marks, J.Organometallic Chem., 15, 315 (1968).
144. L.H.Sommer and F.C.Whitmore, J.Amer.Chem. Soc., 68, 485 (1946).
145. F.Glockling, S.R.Stobart, and J.J.Sweeney, J.Chem.Soc., Dalton Trans., 2029 (1973).
146. D.Seyferth and W.Freyer, J.Org.Chem., **26**, 2604 (1961).
147. V.F.Mironov and A.L.Kravchenko, Izv.Akad.Nauk SSSR, Ser.Khim., 1563 (1963).
148. J.Joklik and V.Bažant, Coll.Czech.Chem.Comm., 37, 3772 (1972).
149. D.Seyferth, S.B.Andrews, and R.L.Lambert, J.Organometallic Chem., 37, 69 (1972).
150. D.Seyferth and E.M.Hanson, J.Amer.Chem.Soc., 90, 2438 (1968).
151. D.Seyferth, E.M.Hanson, and F.M.Armbrecht, J.Organometallic Chem., **23**, 316 (1970).
152. D.Seyferth and E.M.Hanson, J.Organometallic Chem., **27**, 19 (1971).
153. H.Schmidbaur and K.H.Rathlein, Chem.Ber., 107, 102 (1974).
154. D.Seyferth and N.Kahlen, Z.Naturforsch., **14b**, 137 (1959).
155. L.G.Makarova and A.N.Nesmeyanov, "Metody Elementoorganicheskoi Khimii. Rtut'" (Methods of Organoelemental Chemistry. Mercury), Izd.Nauka, Moscow, 1965.
156. G.A.Shvekhgeimer, N.I.Sobtsova, and A.Barański, Roczniki Chem., **47**, 1243 (1973).
157. G.A.Shvekhgeimer and N.I.Sobtsova, "Trudy Moskovskogo Instituta Neftekhimicheskoi i Gazovoi Promyshlennosti" (Transactions of the Moscow Institute of the Petrochemical and Gas Industry), 1967, p.83.
158. R.M.G.Roberts, J.Organometallic Chem., **12**, 89 (1968).
159. W.K.Musker and G.L.Larson, Tetrahedron Letters, 3481 (1968).
160. M.G.Voronkov, N.F.Chernov, and I.D.Kalikhman, Dokl.Akad.Nauk SSSR, **233**, 361 (1977).
161. US.P 3532726 (1970).
162. M.F.Shostakovskii, N.V.Komarov, and O.G.Yarosh, Izv.Akad.Nauk SSSR, Ser.Khim., 908 (1968).
163. A.N.Nesmeyanov, A.E.Borisov, and Shih-Hua Wang, Izv.Akad.Nauk SSSR, Ser.Khim., 1141 (1967).
164. D.R.Mathiason and N.E.Miller, Inorg.Chem., 7, 709 (1968).
165. R.Müller and R.Köhne, Z.Chem., 9, 425 (1969).
166. R.Müller and R.Köhne, "II Symposium international sur la chimie des composes organiques du silicium, Bordeaux, 1968", p.139.
167. N.S.Nametkin, V.M.Vdovin, M.V.Pozdnyakova, E.D.Babich, and I.V.Silkina, Izv.Akad.Nauk, SSSR, Ser.Khim., 1681 (1973).
168. M.V.Pozdnyakova, E.D.Babich, N.S.Nametkin, and V.M.Vdovin, Zhur.Anal.Khim., **29**, 598 (1974).
169. N.S.Nametkin and V.M.Vdovin, Izv.Akad.Nauk SSSR, Ser.Khim., 1153 (1974).
170. E.D.Babich, M.V.Pozdnyakova, N.V.Ushakov, V.M.Vdovin, and N.S.Nametkin, Izv.Akad.Nauk SSSR, Ser.Khim., 1600 (1975).
171. F.B.Deans, C.Eaborn, and D.E.Webster, J.Chem. Soc., 3031, 3034 (1959).
172. R.A.Benkeser, D.I.Hoke, and R.A.Hickner, J.Amer.Chem.Soc., 80, 5294 (1958).
173. R.A.Benkeser, T.V.Liston, and G.M.Stanton, Tetrahedron Letters, L15, 1 (1960).
174. J.R.Chipperfield, G.D.France, and D.Webster, J.Chem.Soc., Perkin Trans.II, 405 (1972).
175. C.Eaborn, J.Organometallic Chem., 100, 43 (1975).
176. M.G.Voronkov, N.F.Chernov, and T.A.Dekina, Dokl.Akad.Nauk SSSR, **230**, 853 (1976).
177. G.A.Razuvaev, N.S.Vasileiskaya, N.N.Vavilina, and E.P.Oleinik, "IV Mezhdunarodnyi Simpozium po Khimii Kremniiorganicheskikh Soedinenii" (The IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, Part 2, p.174.
178. G.A.Razuvaev, N.S.Vasileiskaya, and N.N.Vavilina, J.Organometallic Chem., 80, 19 (1974).
179. G.A.Razuvaev, N.S.Vasileiskaya, and N.N.Vavilina, Zhur.Obshch.Khim., 44, 135 (1974).
180. G.A.Razuvaev, N.S.Vasileiskaya, E.P.Oleinik, N.N.Vavilina, and D.V.Muslin, Zhur.Obshch.Khim., 46, 2720 (1976).
181. N.N.Vavilina, N.S.Vasileiskaya, and G.A.Razuvaev, Zhur.Obshch.Khim., **42**, 548 (1972).
182. A.N.Artemov, N.I.Sirotkin, G.G.Petukhov, and G.A.Razuvaev, "Trudy po Khimii i Khimicheskoi Tekhnologii" (Papers on Chemistry and Chemical Engineering), Gorky, 1973, p.31.
183. N.F.Chernov, T.A.Dekina, and M.G.Voronkov, Zhur.Obshch.Khim., **47**, 794 (1977).

184. C.Eaborn, A.R.Bassindale, R.A.Jackson, C.L.Turpin, and R.Walsingham, U.S.Clearinghouse Fed.Sci.Techn.Inform., **40**, 1970; Chem. Abs., **75**, 19632 (1971).
185. A.J.Hart, D.H.O'Brien, and C.R.Russell, J.Organometallic Chem., **72**, C19 (1974).
186. J.Z.Ngathi, J.M.Ressner, and J.D.Smith, J.Organometallic Chem., **70**, 35 (1974).
187. W.S.Tatlock and E.G.Rochow, J.Org.Chem., **17**, 1555 (1952).
188. H.Schmidbaur, M.Bergfeld, and F.Schindler, Z.anorg.Chem., **363**, 73 (1968).
189. H.Schmidbaur and F.Schindler, Angew.Chem., **77**, 865 (1965).
190. F.Schindler and H.Schmidbaur, Angew.Chem., **79**, 697 (1967).
191. G.Dittmar and E.Hellner, Angew.Chem., **81**, 707 (1969).
192. A.K.Ghosh, C.E.Hansing, A.I.Stutz, and A.G.MacDiarmid, J.Chem.Soc., 403 (1962).
193. B.P.450256 (1936); Chem.Abs., **30**, 8532 (1936).
194. US P.2571884 (1951); Chem.Abs., **46**, 6434 (1952).
195. E.D.Hornbaker and F.Conrad, J.Org.Chem., **24**, 1858 (1959).
196. M.N.Bochkarev, L.P.Maiorova, A.I.Charov, and N.S.Vyazankin, Zhur.Obshch.Khim., **41**, 1408 (1971).
197. M.N.Bochkarev, L.P.Maiorova, A.I.Charov, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 1375 (1972).
198. W.Wojnowski and M.Wojnowska, "V Mezhdunarodnyi Kongress po Metallorganicheskoi Khimii, Moskva, 1971" (The Vth International Congress on Organometallic Chemistry, Moscow, 1971), Vol.1, p.417.
199. W.Wojnowski and M.Wojnowska, Z.anorg.Chem., **398**, 167 (1973).
200. H.Bürger, W.Sawodny, and U.Wannagat, J. Organometallic Chem., **3**, 113 (1965).
201. D.Breitinger and K.Brodersen, Angew.Chem., **82**, 379 (1970).
202. K.Seppelt and W.Sundermeyer, Chem.Ber., **103**, 3939 (1970).
203. J.Lorberth and F.Weller, J.Organometallic Chem., **32**, 145 (1971).
204. J.Lorberth, J.Organometallic Chem., **71**, 159 (1974).
205. J.Lorberth and G.Lange, J.Organometallic Chem., **54**, 165 (1973).
206. J.Lorberth, F.Schmock, and G.Lange, J.Organometallic Chem., **54**, 23 (1973).
207. K.Flatau and H.Musso, Angew.Chem., **82**, 390 (1970).
208. K.Flatau and H.Musso, Angew.Chem.Intern.Ed., **9**, 378 (1970).
209. J.Lorberth, J.Organometallic Chem., **19**, 189 (1969).
210. M.N.Bochkarev, L.P.Maiorova, L.N.Bochkarev, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser. Khim., 2353 (1971).
211. C.Eaborn, A.R.Thompson, and D.R.M.Walton, Chem.Comm., 1051 (1968).
212. G.S.Kalinina, O.A.Kruglaya, B.I.Petrov, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 2101 (1971).
213. G.S.Kalinina, O.A.Kruglaya, V.I.Petrov, E.A.Shchupak, and N.S.Vyazankin, Zhur.Obshch. Khim., **43**, 2224 (1973).
214. O.A.Kruglaya, G.S.Kalinina, B.I.Petrov, and N.S.Vyazankin, J.Organometallic Chem., **46**, 51 (1972).
215. G.A.Razuvaev, G.S.Kalinina, N.S.Vyazankin, T.A.Basalgina, and E.A.Shchupak, "IV Mezhdunarodnyi Simposium po Khimii Kremniiorganicheskikh Soedinenii, Moskva, 1975" (The IVth International Symposium on the Chemistry of Organosilicon Compounds, Moscow, 1975), Vol.1, Part 2, p.172.
216. G.S.Kalinina, E.A.Shchupak, O.A.Kruglaya, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 1186 (1973).
217. O.A.Kruglaya, T.A.Basalgina, G.S.Kalinina, and N.S.Vyazankin, Zhur.Obshch.Khim., **44**, 1068 (1974).
218. D.Seyferth, J.Amer.Chem.Soc., **80**, 1336 (1958).
219. A.T.T.Hsieh, J.D.Ruddick, and G.Wilkinson, J.Chem.Soc.Dalton Trans., 1966 (1972).
220. G.Grüttner and M.Cauer, Ber., **50**, 1559 (1917).
221. S.O.Grim and D.Seyferth, Chem.Ind.(London), 849 (1959).
222. A.T.T.Hsieh and G.Wilkinson, J.Chem.Soc., Dalton Trans., 867 (1973).
223. Q.W.Decker and H.W.Post, J.Org.Chem., **25**, 249 (1960).
224. Japanese P.6222 (1967); Ref.Zhur.Khim., 3N610 (1968).

Irkutsk Institute of Organic Chemistry,
Siberian Division of the USSR Academy
of Sciences