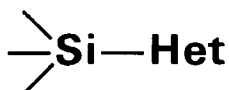


## **The silicon–heteroatom bond**

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    - Synthesis of carboxylic acids, esters and their derivatives
    - The silicon–heteroatom bond



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# The silicon–heteroatom bond

by

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Updates from the Chemistry of Functional Groups

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1991

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# Foreword

The present 'Update' volume contains five chapters from *The chemistry of organic silicon compounds*, published in 1989. The authors of each of these chapters prepared an Appendix with material published in the last few years and not covered in the original chapters. In addition, the volume contains an unpublished chapter on organosilicon–nitrogen compounds, which materialized too late to be included in the main volume, and an appendix to this chapter, again with material covering publications on the subject in the last few years.

We believe that this 'Update' volume, as its predecessors, will be useful to readers who are interested in compounds containing silicon–heteroatom bonds, and wish to have in their libraries such a volume, updated to the beginning of 1991.

The editors will appreciate all comments and suggestions regarding this volume as well as the other volumes in the main series and their updates.

Jerusalem  
August 1991

SAUL PATAI  
ZVI RAPPOPORT

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# Hypervalent silicon compounds

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## I. INTRODUCTION

Relative to carbon, silicon has a much smaller tendency to form compounds of coordination number less than four, such as silenes, silanones or silicenium ions, but a pronounced capacity for the enlargement of the coordination sphere. Complex formation by silicon tetrafluoride was first observed<sup>1</sup> early in the nineteenth century, when Gay-Lussac and Davy reported the formation of the adduct  $\text{SiF}_4 \cdot 2\text{NH}_3$ . A hexacoordinate cationic complex,  $\text{Si}(\text{acac})_3^+ \text{HCl}_2^-$  was described by Diltney<sup>2</sup> in 1903, and represented a new structural type for the element.

Isolable organosilicon compounds with coordination number greater than four generally contain halogen, oxygen or nitrogen ligands, although recently the formation of the ion  $\text{C}_3\text{H}_5(\text{CH}_3)_2\overline{\text{SiCH}_2\text{CH}_2\text{CH}_2^-}$  in the gas phase has been reported<sup>3</sup>. In the last twenty years interest in hypervalent silicon compounds has grown considerably as the scope for additional coordination has been explored. New structural types, particularly those in which intramolecular coordination is favoured, have been developed, and studies of permutational isomerization in pentacoordinate species have been vigorously pursued. Such studies are particularly relevant to the understanding of the stereospecificity generally observed in nucleophilic substitution reactions at silicon, in which pentacoordinated intermediates are usually involved.

## II. FORMATION

### A. Pentacoordinate Silicon Compounds

#### 1. Anionic complexes

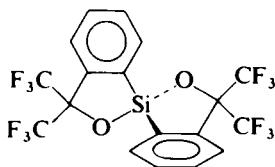
A series of pentacoordinate organofluorosilicate ions,  $\text{R}_n\text{SiF}_5^-$ ,  $n = 1$  to 3, has been described<sup>4-6</sup>, formally derived from the  $\text{SiF}_5^-$  ion by substitution of alkyl and aryl groups for fluorine. They are usually prepared from a fluorosilane,  $\text{R}_n\text{SiF}_4$ , or directly from some precursor to it, by reaction with a quaternary ammonium fluoride<sup>4,6</sup>, or more recently with potassium fluoride in the presence of 18-crown-6 ether<sup>5</sup>, in the stoichiometric ratio. Reaction in the presence of an excess of potassium fluoride leads to the formation<sup>7</sup> of the hexacoordinate  $\text{RSiF}_6^-$  complexes from  $\text{RSiF}_3$  (or  $\text{RSiCl}_3$ ), and other Lewis bases may also coordinate<sup>8</sup> thus increasing the coordination number at silicon from five to six. Crystal structures of several of the pentacoordinate complexes have now been determined and extensive studies of their dynamic behaviour in solution have been made by means of <sup>19</sup>F and <sup>1</sup>H NMR spectroscopy. These aspects are further discussed in Sections III and IV.

Analogous anionic complexes with other monodentate ligands replacing fluorine are not formed so readily. Thus matrix isolation studies<sup>9</sup> failed to result in the formation from methyltrifluorosilane and caesium chloride of the complex  $\text{Cs}^+[\text{MeSiF}_3\text{Cl}]^-$  under conditions where a similar reaction of the fluorosilane with caesium fluoride allowed

the characterization of  $\text{Cs}^+ [\text{MeSiF}_4]^-$ . No evidence for adduct formation was obtained either in the co-condensation of caesium fluoride with methyltrichlorosilane.

Oxygen donors such as ethers coordinate to tetrafluorosilane much less strongly than do amines<sup>10</sup>, and tetraalkoxysilanes were until recently thought to be without Lewis acid properties. It has now been established however that methoxide ion will coordinate to tetramethoxysilane and the phenylmethoxysilanes  $\text{Ph}_n\text{Si}(\text{OMe})_{4-n}$  ( $n=1,2$ ) to give the pentacoordinate silicates  $\text{Ph}_m\text{Si}(\text{OMe})_{5-m}$  ( $m=0-2$ ), on treatment with potassium methoxide in the presence of 18-crown-6 ether<sup>11</sup>.

Complexes in which oxygen is directly bound to silicon within a cyclic bidentate ligand are formed more readily, and have been extensively studied. Pentacoordinate organosilicon anions of composition  $\text{R}-\text{Si}(\overline{\text{O}-\text{C}-\text{C}-\text{O}})_2^-$  result from the reaction of organotrialkoxysilanes with 1,2-diols, both aromatic<sup>12</sup> and aliphatic<sup>13</sup>, and with 2-hydroxycarboxylic acids<sup>13</sup>. Several bis(benzene-1,2-diolato) silicates  $\text{M}^+ \text{RSi}(\overline{\text{OC}_6\text{H}_4\text{O}})_2^-$  have been described<sup>12, 14, 15</sup>, in which the ligand R may carry a functional group. Fast atom bombardment mass spectroscopy provides<sup>15</sup> an unambiguous method of confirming the composition of the anion. Detailed structural studies of these and related arenediolato species have been made<sup>14, 16</sup>, with a view to determining the principles governing the topology of pentacoordinate silicon species.



(1)

The spiro-silane **1**<sup>17</sup> has an exceptional ability to coordinate a further ligand, including organic, fluoride and other inorganic anions, and neutral donors. It has been much utilized in studies of the reactivity and dynamic stereochemistry of pentacoordinate silicon.

Although the capacity of organosilicon compounds to act as electron-pair acceptors in solution seems to be restricted, such limitations do not apply to the same extent in the gas phase. Damrauer and his collaborators have shown<sup>3</sup> by using a flowing afterglow system that pentacoordinate adducts, e.g. **2**, **3** and **4**, of a number of cyclic and acyclic silanes, are formed with fluoride ion, generated by dissociative electron attachment to nitrogen trifluoride. Fluorotrimethylsilane and 1,1-dimethylsilacyclobutane were also shown to form adducts **5** and **6** respectively with allyl ion, **6** providing the first example of a pentacoordinate siliconate ion in which all five substituents bind directly through carbon.



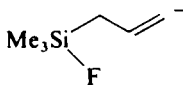
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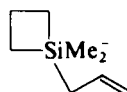
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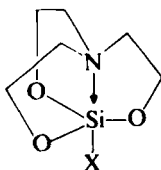
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These systems permit studies of the intrinsic properties of pentacoordinate silicon in the absence of solvation. The fluoride ion affinity of fluorotrimethylsilane is estimated to be  $40.5 \pm 5 \text{ kcal mol}^{-1}$ , whereas that of tetramethylsilane is evaluated at less than  $23 \text{ kcal mol}^{-1}$ .

## 2. Neutral complexes

Neutral complexes of silicon can be formed from the tetravalent molecules by coordination of uncharged group V and group VI donors. Indeed much of the work which established the propensity of silicon to expand its coordination sphere concerned the interaction of halogenosilanes with amines<sup>18</sup>. In these reactions, nucleophilic displacement of halide ion by the amine often occurs, with the formation of ionic adducts rather than hypervalent derivatives of silicon. Thus fluoro- and chlorotrimethylsilanes are coordinated only weakly by pyridine<sup>19, 20</sup>, whereas bromo- and iodotrimethylsilanes give the salts  $(\text{CH}_3)_3\text{SiPy}^+\text{X}^-$  ( $\text{X} = \text{Br}, \text{I}$ )<sup>21</sup>.

As is commonly observed in coordination chemistry however, chelating bidentate ligands, or intramolecular chelation by a strategically placed donor group, lead to the formation of stable hypervalent species where monodentate donors do not. The study of complexes carrying a much wider range of substituents, including organic groups, is thus rendered possible. One of the first intramolecularly coordinated systems to be studied extensively was that of the silatranes, 7.



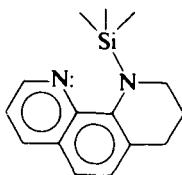
(7)

This very constrained system was first described by Frye<sup>22</sup>, and subsequently studied particularly by Voronkov<sup>23</sup> and his collaborators. Work was stimulated by the discovery of significant biological activity for these and related compounds. Structural studies showed that the Si-N distance most commonly lies in the range 2.0–2.4 Å, with a dependence of this distance and of the detailed geometry of the molecule on the electronic character of the substituent X. The more electronegative groups in general lead both to a diminution in the N-Si separation, and a more acute O-Si-X angle although the internal coordination appears exceptionally to be somewhat less strong with  $\text{X} = \text{F}$  than with  $\text{X} = \text{Cl}$ <sup>24</sup>. The geometry at the silicon atom thus tends from tetrahedral towards trigonal bipyramidal, with the nitrogen atom and the group X occupying axial positions, as the strength of the N-Si interaction increases.

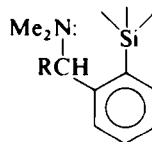
In potential bicyclic or monocyclic systems, the ligand geometry may be designed either to impose intramolecular coordination, or to allow the opportunity for donor-acceptor interaction to occur only in the more favoured cases, depending on the remaining substituents on the silicon atom. Thus structures 8<sup>25, 26</sup> and 9<sup>27</sup>, for example, hold the silicon and nitrogen atoms in close proximity, due to the rigidity of the planar aromatic systems. Structures 10<sup>28-30</sup>, 11<sup>31</sup>, 12<sup>32</sup> however, and the heterocyclic structure 13<sup>33</sup>, have accessible conformations in which the silicon atom and the potential donor may be positioned beyond a reasonable bonding distance apart. The extent of any coordinative interaction may then be inferred in the solid from crystallographic data which give donor



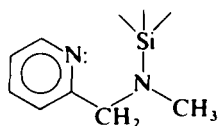
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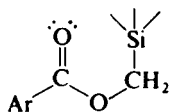
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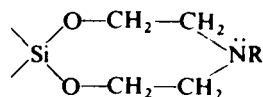
(10) R = H, Me



(11)



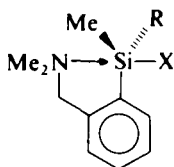
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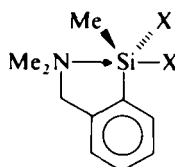
atom-silicon distances, and in solution from IR and especially NMR data.  $^{29}\text{Si}$  NMR absorbances have been shown<sup>34</sup> to be displaced to a much higher field on increase in coordination number, and  $^{19}\text{F}$  and  $^1\text{H}$  signals may also split as a consequence of the changes in geometry induced by chelation.

Variable-temperature  $^1\text{H}$  NMR studies<sup>29</sup> of the monofunctional derivatives **14** and **15**, and the bifunctional derivatives **16**, revealed intramolecular coordination at low temperatures by the presence of two signals from diastereotopic *N*-methyl groups.



(14) R = H

(15) R = 1-Naph



(16)

From the coalescence of these signals, derived free energies of activation for ring opening in the range 8–15 kcal mol<sup>-1</sup> showed the stability of the chelated form to depend on X in order.

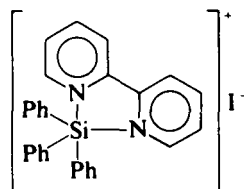
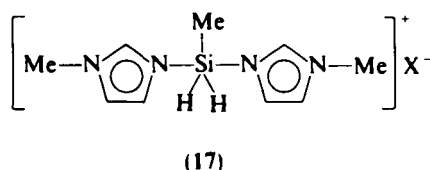


In these systems therefore it may be concluded that the major factor determining the aptitude for pentacoordination is the capacity of the Si-X bond to be stretched under the influence of the donor atom. The stronger N → Si coordination in chlorosilatrane compared with fluorosilatrane<sup>24</sup>, and the exceptional increase in length of some Si-Cl bonds *trans* to the donor atom in pentacoordinate systems, as revealed by X-ray analysis and discussed in Section III.B, are in agreement with this interpretation. The sequence above parallels the tendency to inversion in nucleophilic substitution of X at a chiral silicon centre, and the susceptibility to racemization in nucleophilic solvents.

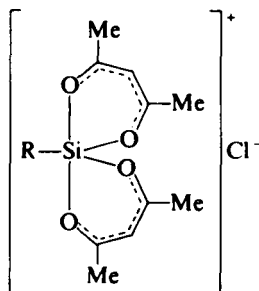
In these studies<sup>29</sup> coordination was not apparent when hydrogen was the only functional group attached to silicon. However the dihydrogenosilane 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>SiH<sub>2</sub>-1-Naph was subsequently shown<sup>35</sup> by its <sup>29</sup>Si NMR chemical shift to be chelated in solution, and N → Si coordinative interaction was established for two derivatives of ligand **8**, 8-Me<sub>2</sub>NC<sub>10</sub>H<sub>6</sub>SiH<sub>2</sub>Ph<sup>36</sup> and 8-Me<sub>2</sub>NC<sub>10</sub>H<sub>6</sub>SiH(Me)Ph<sup>26</sup>.

### 3. Cationic complexes

Cationic pentacoordinate organosilicon species have often been considered<sup>37</sup> as possible intermediates in the racemization or solvent-assisted substitution of halogenosilanes, but well-characterized examples are few in number. Some years ago, the 1:2 adducts of the compounds SiH<sub>3</sub>X and MeSiH<sub>2</sub>X (X = Br, I) with pyridine were assigned<sup>38</sup> ionic structures [RSiH<sub>2</sub>·py<sub>2</sub>]<sup>+</sup> X<sup>-</sup> (R = H, Me): (X = Br, I). More recently the reaction of Me<sub>2</sub>SiHX (X = Cl, I, OSO<sub>2</sub>CF<sub>3</sub>) with *N*-methylimidazole and 4-dimethylaminopyridine has been shown<sup>39</sup> to give 1:1 and 1:2 adducts both of which are ionic according to conductivity measurements. <sup>29</sup>Si chemical shifts are consistent with the presence of pentacoordinate silicon in the 1:2 adducts, for which the constitution **17** was proposed. An ionic structure **18** was also suggested<sup>40</sup> for the adduct of iodotriphenylsilane with bipyridyl.



With oxygen donors, the complexes derived from monoorganosilicon halides by reaction with two moles of tropolone<sup>41</sup> or of a 1,3-diketone<sup>42</sup> were assigned cationic pentacoordinate structures such as **19**, on the basis of NMR, IR, UV and chemical evidence. The acac complexes of this composition however have also been formulated as neutral hexacoordinate molecules<sup>43</sup>, and it has been suggested that the constitution depends on the method of preparation<sup>44</sup>.



## B. Hexacoordinate Silicon Compounds

Known hexacoordinate silicon complexes range from dianions to quadruply charged cations, but the majority of these compounds are formed with ligands in which electronegative groups only are directly bound to silicon. Such behaviour is to be expected in view of the accumulation of negative charge at silicon implied by an increase in coordination number to six; as a consequence hexacoordinate species with more than one direct carbon-silicon bond are less common than amongst the pentacoordinate complexes.

### 1. Anionic complexes

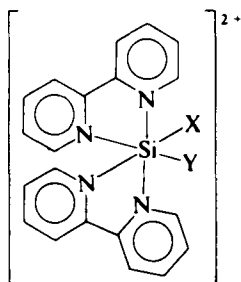
The hexafluorosilicate ion  $\text{SiF}_6^{2-}$ , known<sup>45</sup> since the beginning of the 19th century, is the parent of the anionic complexes  $\text{RSiF}_5^{2-}$ . The latter crystallize readily as their potassium salts when  $\text{RSiCl}_3$  reacts with an excess of potassium fluoride in aqueous or aqueous/alcoholic solution<sup>46</sup>. High yields are obtained when R is either aromatic or aliphatic, even in the presence of certain functional groups, which may conveniently be introduced by hydrosilation with trichlorosilane of alkenes and alkynes, appropriately substituted. The application of these pentafluorosilicates in organic synthesis is discussed in Section V.B. The corresponding salts of many other inorganic cations may be obtained<sup>47, 48</sup> but only the pentacoordinate phenyltetrafluorosilicate salt  $i\text{-Pr}_4\text{N}^+\text{SiF}_4\text{Ph}^-$  separates by crystallization from a solution made up from  $\text{SiF}_4\text{Ph}^-$  to which an excess of  $i\text{-Pr}_4\text{N}^+\text{F}^-$  has been added, despite the fact that the solution contains only the  $\text{PhSiF}_5^{2-}$  ion, as shown by  $^{19}\text{F}$  NMR spectroscopy<sup>49</sup>.

Hexacoordinate anionic complexes with oxygen donors have been described only with chelating ligands. Most are salts of tris-chelate dianions which may be formed from both aromatic<sup>12</sup> and aliphatic<sup>50</sup> 1,2-diols.  $\text{K}_2\text{Si}(\overline{\text{OC}_6\text{H}_4\text{O}})_3$  is a typical example, and it may readily be obtained from the reaction of catechol with silica gel<sup>51, 52</sup>, as well as with a tetraalkoxysilane. Similar complexes may be formed with dibasic acids<sup>53</sup>. Organosilicate complexes with direct carbon-silicon bonds, formally derived from these tris-chelate anions, clearly require the replacement of one bidentate ligand by two organic groups, to give compounds of composition  $\text{M}_2\text{R}_2\text{Si}(\text{diolato})_2$ . Insofar as they may be prepared however, such compounds appear generally not to be chelated, and to contain tetracoordinated silicon only. In his early investigations of compounds of this type, Frye reported<sup>12</sup> that the reaction of diphenyldimethoxysilane with catechol resulted in cleavage of one of the phenyl groups and formation of the pentacoordinate complex  $\text{PhSi}(\overline{\text{OC}_6\text{H}_4\text{O}})_2^-$  only.

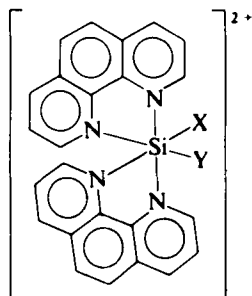
### 2. Neutral and cationic complexes

Many hexacoordinate complexes with neutral monodentate and bidentate nitrogen donors, and some with oxygen donors, have been described. As for the pentacoordinate complexes considered earlier, the heavier halogens tend to suffer nucleophilic displacement by these ligands with the formation of cationic species. A significant study of complexes formed with 2,2'-bipyridyl or 1,10-phenanthroline has resulted in the characterisation of bis-chelate dications of types **20**<sup>54</sup> and **21**<sup>55</sup> respectively. Groups X and Y range from hydroxyl, methoxyl and halogen, to hydrogen, methyl and phenyl.

The formation of cationic complexes with two organic groups bonded to silicon would thus appear to occur more readily than with the analogous anionic complexes. It is also of interest that the complexes  $\text{Si}(\text{bipy})_3\text{I}_4$ <sup>54</sup>,  $\text{Si}(\text{phen})_3\text{I}_4$ <sup>56</sup> and also  $\text{Si}(\text{pyO})_6\text{I}_4$ <sup>57</sup> (pyO = pyridine-*N*-oxide) have been prepared in which silicon cations of charge +4 are present. Complexes of bipyridyl(bipy) and phenanthroline(phen) with perhalogenodisil-

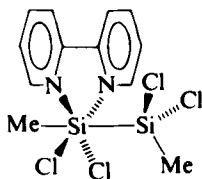


(20)

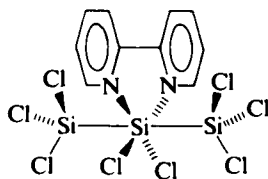


(21)

anes,  $\text{Si}_2\text{F}_6$ ,  $\text{Si}_2\text{Cl}_6$  and  $\text{Si}_2\text{Br}_6$ , with the methylchlorosilanes,  $\text{Si}_2\text{Me}_n\text{Cl}_{6-n}$  ( $n=2,3$ ), and with octachlorotrisilane form another group<sup>58</sup>. In all cases only 1:1 adducts are obtained, in which the plane of the ligand is normal to the Si-Si axis. Where isomeric adducts may be formed, the ligand is bound to the more acidic silicon atom which, for  $\text{Si}_3\text{Cl}_8$ , is the central one. Representative structures are **22**<sup>59</sup> and **23**. 1,10-phenanthroline coordinates<sup>60</sup> with the spirocyclic compound **1**, providing the sole example in which adduct formation from **1** produces hexacoordinate rather than pentacoordinate silicon.



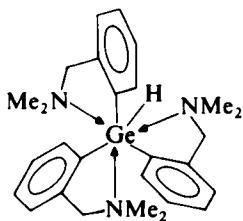
(22)



(23)

Anionic ligands like acac, tropolonate or oxinate give rise to cationic tris-chelate complexes of charge +1, such as the classic<sup>2</sup>  $\text{Si}(\text{acac})_3^+$ . Neutral complexes of composition  $\text{Si}(\text{chel})_2\text{X}_2$ ,  $\text{RSi}(\text{chel})_2\text{X}$  and  $\text{R}_2\text{Si}(\text{chel})_2$  (chel = uninegative, potentially chelating ligand) are thus possible. Several examples have been described, including  $\text{Si}(\text{acac})_2\text{X}_2$  ( $\text{X}=\text{Cl}$ <sup>61</sup>,  $\text{OAc}$ <sup>62</sup>) and  $\text{Ph}_2\text{Si}(\text{acac})_2$ <sup>63</sup>, which are apparently hexacoordinate, and  $\text{Me}_2\text{Si}(\text{acac})_2$ <sup>43</sup>, which is only tetracoordinate. In the series<sup>64</sup>  $\text{Ph}_2\text{Si}(\text{oxine})_2$ ,  $\text{PhMeSi}(\text{oxine})_2$  and  $\text{Me}_2\text{Si}(\text{oxine})_2$ , the first compound appears to be hexacoordinate, the second pentacoordinate and the last tetracoordinate. Aryl groups therefore appear less unfavourable to hypercoordination than alkyl groups.

Neutral compounds containing two ligands of types **8** or **10**, which need not be identical in a given molecule, are also potentially hexacoordinate. A number of such compounds  $\text{H}_2\text{Si}(\text{C}_{10}\text{H}_6\text{NMe}_2)_2$ ,  $\text{HFSi}(\text{C}_{10}\text{H}_6\text{NMe}_2)_2$  and  $\text{F}_2\text{Si}(\text{C}_{10}\text{H}_6\text{NMe}_2)_2$  have recently been prepared<sup>65</sup>, and their crystal structures (to be discussed in the next section) show that the silicon atom in each of these molecules is indeed coordinated by both nitrogen atoms. The compound  $\text{HSi}(\text{C}_7\text{H}_6\text{NMe}_2)_3$  has also been prepared and could be considered heptacoordinate, like its germanium analogue **24**, in which X-ray diffraction shows<sup>66</sup> entry of nitrogen at each face containing the H(-Ge) atom. The overall geometry corresponds to a tetrahedron which has suffered threefold nucleophilic coordination. Hydride abstraction from the silicon compound seems to give the cation  $^+\text{Si}(\text{C}_7\text{H}_6\text{NMe}_2)_3$ <sup>67</sup>.



(24)

### III. STRUCTURE

There is now a considerable body of crystal structure data on hypervalent silicon derivatives. A comprehensive review<sup>68</sup> was published in 1986. Much interesting information is thus available on their topology, together with details of variations in bond lengths. As expected the geometry about pentacoordinate silicon atoms is generally trigonal bipyramidal, but deviations in the direction of the square pyramid are especially significant for some of the bis(diolato) complexes.

Solution NMR studies are more plentiful still, and underpinned by knowledge of the crystal structures, basic geometries and axial or equatorial site preferences may often be deduced. Many pentacoordinated species are stereochemically non-rigid; in view of the significance of this topic a separate section is devoted to it.

#### A. Topology of Pentacoordinate Complexes

The compound  $\text{PhCH}_2\text{NMe}_3^+\text{SiF}_5^-$  and several of the related organofluorosilicates have been the subjects of single crystal X-ray diffraction analysis<sup>6, 69, 70</sup>. These have established that the structures of the complex ions are close to trigonal bipyramidal with organic groups occupying the equatorial positions (Figure 1). Observed Si-F bond lengths are summarized in Table 1. As with phosphorus fluorides the greater length of axial compared with equatorial bonds is evident, but for the silicon compounds the disparity appears to be less sensitive to increasing organic substitution. These changes and concomitant small distortions of the regular geometry are attributed<sup>6</sup> to a combination of steric and electronic effects.

TABLE 1. Summary of observed Si-F bond lengths

Ion	Si-F distances/Å		Reference
	Axial	Equatorial	
$\text{SiF}_5^-$	1.646	1.591 (av)	70
$\text{PhSiF}_4^-$	1.669 (av)	1.601 (av)	69
$\text{MePhSiF}_3^-$	1.695 (av)	1.621	6
$t\text{-BuPhSiF}_3^-$	1.700 (av)	1.639	6
$\text{Ph}_2\text{SiF}_3^-$	1.688	1.648	70
$\text{Xyl}_2\text{SiF}_3^-$	1.714 (av)	1.652	6
$\text{NaphPh}_2\text{SiF}_2^-$	1.720	—	6





FIGURE 1. Trigonal bipyramidal structures of pentafluorosilicate ion and of organofluorosilicates

In solution, the complexes with less than three organic substituents are fluxional, so that only a single averaged resonance is observed in the  $^{19}\text{F}$  NMR spectrum at ambient temperature. However the region of relatively slow exchange is readily accessible for the trifluorodiorganosilicates, and at temperatures around  $-50^\circ\text{C}$  two separate signals characteristic of axial and equatorial fluorine substituents are clearly distinguished<sup>5</sup>. The relative intensities and coupling patterns of these signals are consistent with the crystal structures (Table 2).

TABLE 2.  $^{19}\text{F}$  NMR absorptions in pentacoordinate silicon complexes at the slow exchange limit<sup>a</sup>

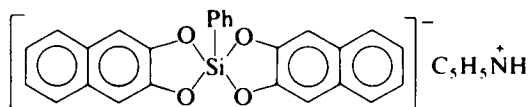
Ion		$\delta^{19}\text{F}$	$J_{\text{Si-F/Hz}}$	$^2J_{\text{F-F/Hz}}$	$^3J_{\text{H-CSiF/Hz}}$
$\text{Ph}_2\text{SiF}_3^-$	(ax)	-100.5 (2F)	252.7	2.58 (d)	—
	(eq)	-133.9 (1F)	204.6	2.58 (t)	—
$\text{MePhSiF}_3^-$	(ax)	-83.5 (2F)	251	2.6 (d)	9 (q)
	(eq)	-133.3 (1F)	210	not resolved	

<sup>a</sup> Values of  $\delta$  are in p.p.m. relative to  $\text{CFCl}_3$ ; data are taken from Reference 5.

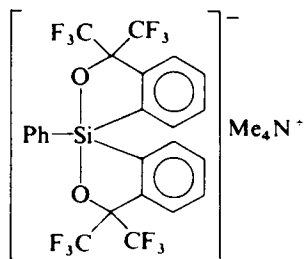
Absorptions due to axial fluorine atoms are found at a relatively low field, and those due to equatorial fluorine atoms at a relatively high field. This correlation is again the same as that for the phosphorus fluorides<sup>71</sup>, and may be used with confidence to obtain structural information for compounds for which crystal data are not available.

Although it has not been possible to establish the geometry of the  $\text{MeSiF}_4^-$  ion by NMR spectroscopy, nor has a crystal structure been determined, the IR spectrum of the matrix-isolated species supports the equatorial placement of the methyl group in a trigonal bipyramid<sup>9</sup>.

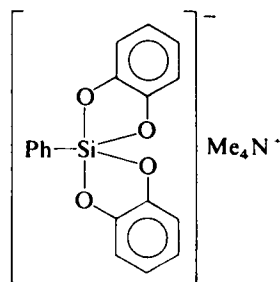
Much more structural variety is displayed by pentacoordinate silicates in which cyclic ligands are present. Holmes<sup>14</sup> in particular has explored the structures of the ions  $\text{RSi}(\text{diolato})_2^-$  as a function of both the group R and the nature of the chelate, and has shown that a wide range of geometries may exist, extending from the trigonal bipyramid to the square pyramid, and distributed along the Berry pseudorotational coordinate<sup>72</sup>. The structural feature which favours the adoption of the square pyramidal structure is the presence of two five-membered cyclic systems, with like atoms in any one ring bonded to silicon. The cyclic systems should also preferably be unsaturated and large. As the extreme example, pyridinium bis(2,3-naphthalenediolato) phenylsilicate **25**<sup>14</sup> has close to ideal square pyramidal coordination about the silicon atom. Compounds **26**<sup>73</sup> and **27**<sup>74</sup> however are closer to the trigonal bipyramidal geometry, being some 27% and 30% respectively displaced towards the square (or rectangular) pyramid<sup>14</sup>. This conformation is to be expected for **26**, since the electronegativities of the ring carbon and oxygen atoms attached to the silicon atom are substantially different, but it is surprising that the conformation of **27** differs so much from that of **25**.



(25)



(26)

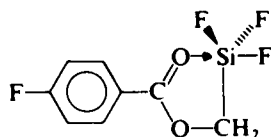


(27)

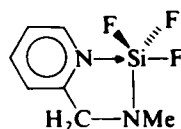
### B. Site Preferences in Trigonal Bipyramidal Complexes

Complexes in which an increase in the coordination number at silicon is achieved by intramolecular ring closure of chelating groups are particularly interesting in relation to the stereochemistry of nucleophilic substitution at silicon. In these compounds the donor atom may play the role of a 'captive nucleophile', and the nature and behaviour of the intramolecularly coordinated species serve as models for the properties of the intermediates or transition states participating in the substitution processes.

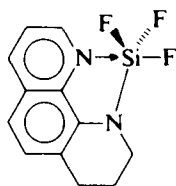
Molecular structures have been determined for compounds **28–39**, and some significant examples of association in the solid state are seen in the dimers **40** and **41** and in the pentamer **42**. In all these structures the geometry about the silicon atom is that of a somewhat distorted trigonal bipyramid, in which the donor atom occupies an axial site. The rings formed in the chelated systems thus span axial and equatorial sites, a conformation which is favoured for four- and five-membered rings because of the relief from ring strain which it affords<sup>71</sup>. The second axial site, *trans* to the donor atom, is occupied by an electronegative atom (F, Cl, O, N), except in the cases of the organosilicon hydrides, discussed below.

(28)<sup>75</sup>

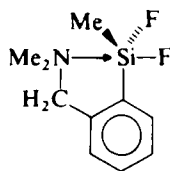
O → Si	2.029 Å
F <sub>(ax)</sub> → Si	1.602 Å
F <sub>(eq)</sub> → Si	1.583 Å

(29)<sup>31</sup>

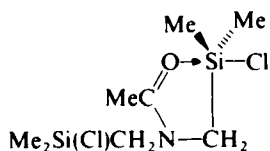
N → Si	1.974 Å
F <sub>(ax)</sub> → Si	1.621 Å
F <sub>(eq)</sub> → Si	1.603 Å

(30)<sup>27</sup>

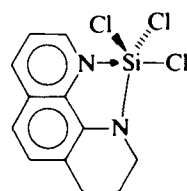
N → Si	1.969 Å
F <sub>(ax)</sub> -Si	1.621 Å
F <sub>(eq)</sub> -Si	1.590 Å

(31)<sup>76</sup>

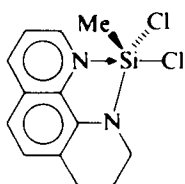
N → Si	2.346 Å
F <sub>(ax)</sub> -Si	1.627 Å
F <sub>(eq)</sub> -Si	1.590 Å

(32)<sup>77</sup>

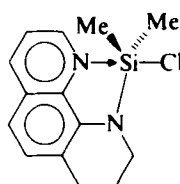
O → Si	1.918 Å
Cl <sub>(ax)</sub> -Si	2.348 Å
extracyclic Cl-Si	2.050 Å

(33)<sup>78</sup>

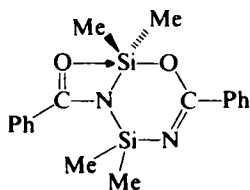
N → Si	1.984 Å
Cl <sub>(ax)</sub> -Si	2.150 Å
Cl <sub>(eq)</sub> -Si	2.094 Å

(34)<sup>79</sup>

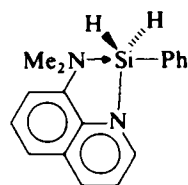
N → Si	2.027 Å
Cl <sub>(ax)</sub> -Si	2.207 Å
Cl <sub>(eq)</sub> -Si	2.049 Å

(35)<sup>79</sup>

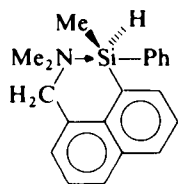
N → Si	2.028 Å
Cl <sub>(ax)</sub> -Si	2.269 Å
N <sub>(eq)</sub> -Si	1.770 Å

(36)<sup>80</sup>

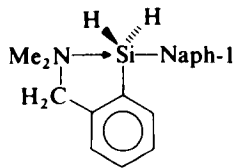
O → Si	2.613 Å
O <sub>(ax)</sub> -Si	1.670 Å

(37)<sup>36</sup>

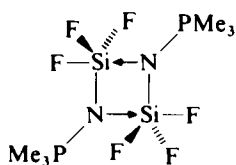
N → Si	2.584 Å
H <sub>(eq)</sub> -Si	1.44 Å
Ph <sub>(ax)</sub> -Si	1.893 Å

(38)<sup>36</sup>

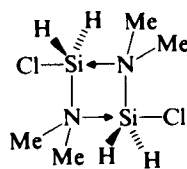
N→Si	2.66 Å
H atom	not located
Ph <sub>(ax)</sub> -Si	1.91 Å

(39)<sup>81</sup>

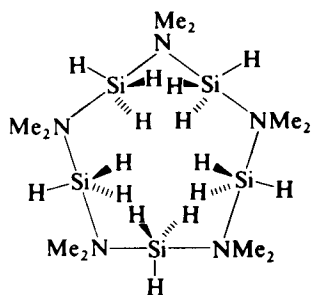
N→Si	2.44 Å
H <sub>(eq)</sub> -Si	1.46 Å (av)
1-Naph <sub>(ax)</sub> -Si	1.92 Å

(40)<sup>82</sup>

N→Si	1.857 Å
N <sub>(eq)</sub> -Si	1.736 Å
F <sub>(ax)</sub> -Si	1.668 Å
F <sub>(eq)</sub> -Si	1.606 Å

(41)<sup>83</sup>

	Dimer	Monomer
N→Si	2.054 Å	
N—Si	1.814 Å	1.689 Å
Cl—Si	2.231 Å	2.070 Å
H—Si	1.491 Å	1.47 Å

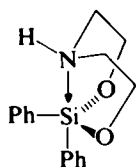
(42)<sup>84</sup>

	Pentamer	Monomer
(all)N—Si	1.98 Å	1.713 Å
H—Si	1.25–1.44 Å	

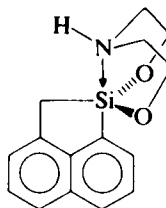
Donor–acceptor distances are significantly longer than normal single bond lengths for the pairs of elements involved but shorter than the sums of van der Waals radii, and in some instances indicate a substantial bonding interaction. The covalently bonded nitrogen atom in compound 35<sup>79</sup>, for example, is situated 1.77 Å from the silicon atom, whereas the donor nitrogen atom is at 2.03 Å, which may be compared with the sum of the

van der Waals radii of  $3.6 \text{ \AA}$ <sup>85</sup>. Bonds from silicon to other substituents are lengthened by comparison with the normal tetracoordinate distances. Direct comparisons can be made in the associated monomers, and also in compound **32**<sup>77</sup>, where there is a particularly striking increase in the length of the Si–Cl bond in the axial position to  $2.35 \text{ \AA}$ , compared to the  $2.05 \text{ \AA}$  of the otherwise structurally similar extracyclic Si–Cl bond. The increase in length of the axial bond is always greater than that of the equatorial bonds, following the structural principles noted for the acyclic complexes. Comparison of the bond lengths in the fluorosilanes with those tabulated earlier (Table 1) however shows that the disparity is less in the chelated derivatives than in the acyclic anions.

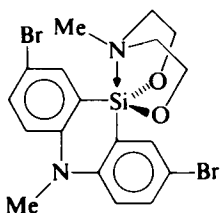
The preference for axial attack receives further confirmation from an examination of the molecular structures of some diptychoxazasilolidines **43**. In most of the compounds studied, the geometry is similar to that shown for compound **43**<sup>86</sup>. The N–Si separation in this molecule is  $2.30 \text{ \AA}$ , but this distance increases rapidly with substitution of alkyl or aryl groups for hydrogen at the nitrogen atom, due to steric interaction between this group and the equatorial phenyl substituent at silicon<sup>87</sup>. In the spirocyclic compound **44**<sup>88</sup> the N–Si distance is again  $2.30 \text{ \AA}$ ; in compound **45**<sup>89</sup> it has lengthened to  $2.95 \text{ \AA}$ , but the trigonal bipyramidal geometry with axial entry is preserved. In the latter compound it had been thought possible that the steric bulk of the brominated phenazasiline unit, with the silicon atom in a six-membered ring and the two electronegative oxygen atoms in apical positions, might lead to equatorial coordination by the nitrogen atom from the eight-membered ring. This conformation has been observed in the di-*t*-butyldiptychoxazstanolidine **46**<sup>90</sup>.



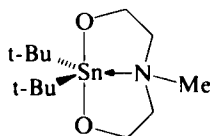
(43)



(44)



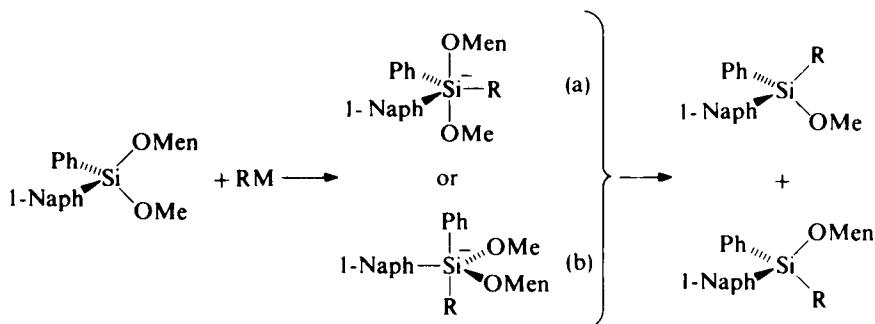
(45)



(46)

It should also be noted in support of the preference for axial entry that this geometry of interaction is usually characteristic of intermolecular interactions in the solid state in organotin<sup>91</sup> and organosilicon<sup>92</sup> compounds. The observation of axial entry only, irrespective of the nature of the substituents at silicon (halogen, oxygen or hydrogen), is supported by calculations<sup>93</sup> which show this geometry of attack to be preferred, even for the process corresponding to retention of configuration at silicon in nucleophilic substitutions. For the latter process<sup>94,95</sup>, and for nucleophilic attack on **1** leading to stereochemical mutation<sup>96</sup>, equatorial entry has been suggested as a possible route, as

for example in the cleavage with retention of one or other of the alkoxy groups in menthoxymenthoxy-naphthylphenylsilane<sup>97</sup>. This outcome may however be rationalized by the formation of either of the two intermediates shown (Scheme 1).

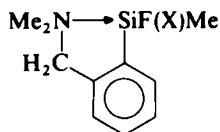


OMen = menthoxy

SCHEME 1

The formation of intermediate (a) would be expected if the stability of the intermediate were determined by the electronegativity of the substituents at silicon, the factor commonly accepted as governing the relative stabilities of trigonal bipyramidal isomers in phosphorus chemistry. This structure would be produced by direct equatorial entry by the nucleophile. The alternative axial attack, leading to intermediate (b) with the alkoxy groups initially occupying the equatorial sites, is however strongly supported by the structural information now available.

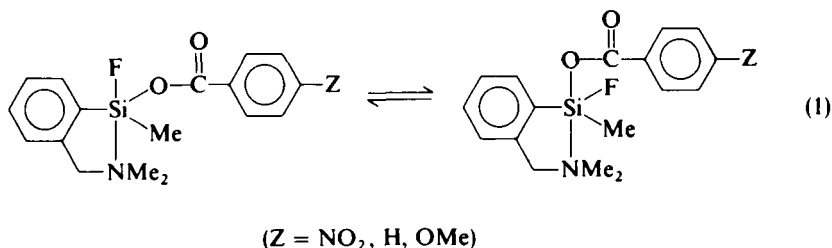
The occurrence of significant donor-acceptor interactions in the hydrogenosilanes 37-39 is particularly interesting. Earlier examples in the literature involved compounds containing hydrogen and other electronegative groups, e.g.  $CHF_2CF_2SiH_3 \cdot NMe_3$ <sup>98</sup>, amine complexes of halogenosilanes  $SiH_nX_{4-n}$  ( $n=0-3$ )<sup>19</sup> and compound 41<sup>83</sup>. It was however noted by Ebsworth<sup>38</sup> at the time that substitution of methyl for hydrogen weakened the acceptor properties, implying that hydrogen conferred significant Lewis acidity on silicon, and attention was also drawn to the occupation by hydrogen of equatorial positions in the trigonal bipyramidal structures. These conclusions have now received confirmation from a redetermination<sup>84</sup> of the structure of compound 42, actually the first compound in which the presence of pentacoordinated silicon was established<sup>99</sup> by X-ray analysis, and from the structures of 37-39, which have further shown that hydrogen atoms occupy preferentially the equatorial sites even in the absence of electronegative substituents. The donor nitrogen itself enters axially, as it does in the cases where the silicon bears an electron-withdrawing group in the opposite axial site. Consideration of the available information on the preferred disposition of substituents permits the tentative assignment of a relative apicophilicity to groups attached to pentacoordinate silicon, analogous to the apicophilicity series<sup>100</sup> for trigonal bipyramidal phosphorus. NMR data on bifunctional organosilanes, 47, containing fluorine and a



(47)

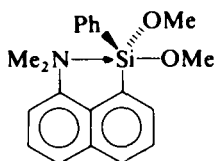
range of other groups establish the apicophilicity of X relative to fluorine according to the direction in which the fluorine resonance shifts as the temperature is lowered.<sup>101</sup>

A downfield shift indicates preferential occupation by fluorine of an axial site; an upfield shift correspondingly indicates occupation of an equatorial site. These experiments showed that fluorine was more apicophilic than hydrogen, alkoxy or dialkylamino, but less apicophilic than chlorine. In cases where X = benzoyloxy (equation 1), a slow equilibrium was apparent at  $-95^{\circ}\text{C}$  in which both topomers could be distinguished. Although that with F equatorial was always present in greater amount, the proportion was enhanced as electron-withdrawing substituents Z on the phenyl group increased the apicophilicity of the benzoyloxy moiety.

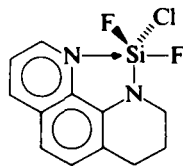


In combination with the preferred conformation found<sup>26</sup> by  $^1\text{H}$  NMR for compound **48**, and the data from the crystal structures discussed earlier, the apicophilicity of substituents in these intramolecularly coordinated compounds is ( $\text{H} < \text{Csp}^2 < \text{OR}, \text{NR}_2 < \text{F} < \text{Cl}, \text{OCOR}, \text{Br}$ ).

This series shows a number of differences from the oft-quoted series for phosphorus established by Trippett<sup>102</sup>, which leans heavily on results obtained in a system containing a highly strained four-membered ring. It is however more nearly consistent with the data of Cavell<sup>100</sup> on acyclic fluorophosphoranes, and also with observations on the preferential displacement with inversion of chlorine rather than fluorine in reactions of compounds such as 1-naphthylferrocenylchlorofluorosilane<sup>102</sup>. Somewhat surprisingly fluorine appears<sup>104</sup> nevertheless to be more apicophilic than chlorine in compound **49**, which suggests that the factors determining the relative positions of these two elements are finely balanced.

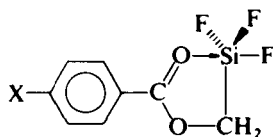


(48)



(49)

Interestingly the *trans* influence of substituents in apical positions has been illustrated<sup>105</sup> in the case of the aryl-substituted trifluoro compounds **50**. Table 3 illustrates the influence of the substituent X on the  $^{19}\text{F}$  NMR chemical shift of apical fluorine, the equatorial fluorine shift being relatively insensitive to the coordination of the carbonyl group at silicon. An electron-donating group increases the apicophilicity of the opposite fluorine while electron-withdrawing groups have the opposite effect.



(50)

TABLE 3.  $^{19}\text{F}$  NMR chemical shifts of the axial fluorine atom for different substituent groups X in the *para* position in compound 50<sup>a</sup>

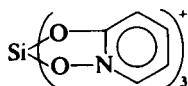
X	$\delta\text{F(a)}$
<i>p</i> -MeO	-126.74
<i>p</i> -Me	-127.16
<i>p</i> -H	-127.43
<i>p</i> -F	-128.19
<i>p</i> -NO <sub>2</sub>	-129.10

<sup>a</sup> Data are taken from Reference 105.

### C. Hexacoordinate Complexes

All available structural data are consistent with the octahedral geometry expected for hexacoordinate main group elements. Many examples of both geometric and optical isomerism have been recognized, and some interest attaches to the factors determining the relative stability of geometric isomers.

The structure of the dianion  $\text{SiF}_6^{2-}$  was first confirmed<sup>106</sup> by X-ray diffraction in 1935, and has since been re-examined with a variety of counteranions; that of  $\text{Si}(\overline{\text{OC}_6\text{H}_4\text{O}})_3^{2-}$  was determined<sup>107</sup> in 1969. The tris-chelate cations  $\text{Si}(\text{acac})_3^+$ <sup>108</sup>  $\text{Si}(\text{tropolonato})_3^+$ <sup>109</sup> and 51<sup>110</sup> have been resolved for use in mechanistic studies.



(51)

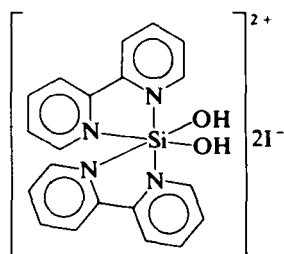
The  $^{19}\text{F}$  NMR spectrum of the phenylpentafluorosilicate ion supports the octahedral geometry, the low-temperature ( $-28^\circ\text{C}$ ) spectrum showing signals for one apical (high field) and four basal (low field) fluorine atoms with the expected F-F coupling patterns. The neutral adducts  $\text{SiF}_4\cdot 2\text{py}$ <sup>111</sup> and  $\text{SiCl}_4\cdot 2\text{PMe}_3$ <sup>112</sup> have been shown by X-ray diffraction to have the *trans* arrangement of the two donor ligands, whereas the *cis* geometry is suggested by vibrational and NMR spectroscopy for the complex  $\text{SiF}_4\cdot 2\text{NH}_3$ <sup>113</sup>. In  $\text{SiF}_4\cdot \text{bipy}$ <sup>114</sup> and in complexes such as 22 and 23 with the same ligand, *cis* entry of the donor atoms is of course imposed by the structure of the ligand.

Complexes with two chelating ligands again have the potential to display geometric isomerism. NMR studies suggest that the neutral complexes,  $\text{Ph}_2\text{Si}(\text{acac})_2$ <sup>64</sup>,

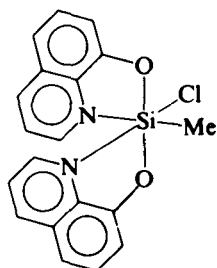


$\text{Si}(\text{acac})_2\text{Cl}_2$ <sup>62</sup> and  $\text{Si}(\text{acac})_2(\text{OAc})_2$ <sup>115</sup> have *trans* configurations, the latter at least in the solid state though it isomerizes in solution to a rapidly equilibrating mixture of the *cis* and *trans* forms. Here the *cis* form predominates, though the exact ratio is solvent dependent.

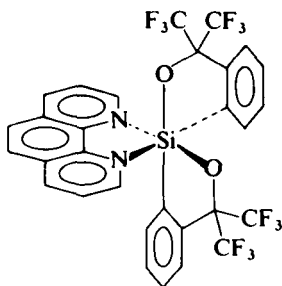
The series of cationic compounds **20** and **21** have been assigned *cis* geometries on the basis of spectroscopic studies, and this configuration has been confirmed for the dihydroxy compound **52** by X-ray single crystal analysis<sup>116</sup>. The chiral nature of the molecules evident in crystalline **53** has been discussed<sup>117</sup>; the *trans* relationship of the donor nitrogen atoms to the chlorine and the methyl group respectively is accompanied by lengthening of the bonds to silicon. The Si-Cl separation of 2.2 Å is comparable with the lengths of Si-Cl bonds in the pentacoordinate intramolecular chelates **33-35**. Compound **54** has the all-*cis* configuration in the solid state, as shown by X-ray crystallography<sup>60</sup>. In solution, minor amounts of the two other possible diastereomers are also present; the interconversion of all three forms, and the enantiomerization of each which also occurs, can be followed by the <sup>19</sup>F NMR signals of the diastereotopic trifluoromethyl groups. These processes are all believed to take place by dissociation of the phenanthroline ligand (cf. Section IV).



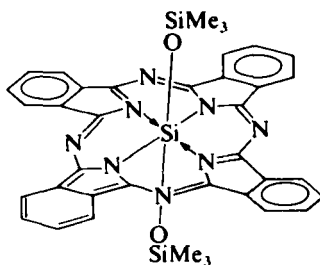
(52)



(53)



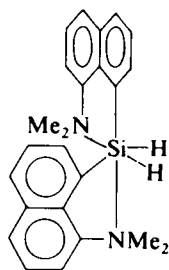
(54)



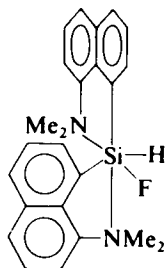
(55)

Several monomeric and polymeric hexacoordinate siloxane complexes with phthalocyanine as a planar tetradentate ligand have been the subjects of X-ray structure determination, for example the bis-trimethylsiloxy compound **55**<sup>118</sup>.

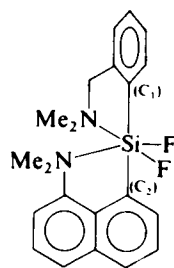
Molecular and crystal structures have recently been determined for compounds **56**, **57** and **58**. The hydrogen and/or fluorine atoms are in each case *cis* to each other, and the placement of the ligands appears to be influenced by the same factors as in the pentacoordinate complexes with the same ligands. Thus, consistent also with a *cis*



(56)



(57)



(58)

arrangement of the donor nitrogen atoms, these nitrogen atoms are as far as possible *cis* to hydrogen and *trans* to fluorine.

The most interesting feature of the structures of compounds **56**, **57** and **58** is that the covalent tetrahedral structure is largely preserved. The best picture for this geometry is that of a bicapped tetrahedron resulting from twofold nucleophilic coordination. The  $C_{(1)}SiC_{(2)}$  angle of  $135.5^\circ$  for instance is very far from the  $180^\circ$  of a regular octahedron. The same phenomenon is evident in the heptacoordinate compound (**24**) which, like (**56**), does not include any electronegative groups at the central atom. Following the suggestions of Dunitz<sup>91</sup>, these compounds can be considered as good models for hexacoordinate intermediates (or transition states). They thus lend credence to the possible formation of these species in the course of reactions such as nucleophilic displacement at silicon with nucleophilic activation. This process is controlled by the entropy of activation, and so any feature of the geometry of the intermediate which minimizes the entropic factor associated with its formation will be of significance.

#### IV. DYNAMIC STEREOCHEMISTRY

The discovery of stereochemical non-rigidity in fluorophosphoranes<sup>71</sup> was quickly followed by studies of pentacoordinate fluorosilicates<sup>4</sup>. The silicon systems, however, proved to be more complex, in that impurity-catalysed intermolecular exchange competed with intramolecular rearrangement in averaging the environments of the fluorine atoms on the NMR time scale.

Recently, a new investigation of the dynamic behaviour of phenyl-, diphenyl- and phenylmethylfluorosilicates has been carried out with their dibenzo-18-crown-6 ether complexed potassium salts by Damrauer and Danahey<sup>5</sup>. In these systems interference from water and other adventitious impurities, which had rendered the pioneering studies of Klanberg and Muetterties<sup>4</sup> so difficult, was absent. Indeed the presence of trace amounts of water was often evident from the  $^1H$  NMR spectrum but appeared to have no adverse effect. In accordance with the earlier observations, the  $^{19}F$  absorbance of the phenyltetrafluorosilicate ion remained a singlet over the accessible temperature range, down to  $-100^\circ C$ . The diorganotrifluorosilicates on the other hand displayed broad singlets in their  $^{19}F$  NMR spectra which split into two as the temperature was lowered. Further cooling resulted in the appearance of  $^{29}Si-^{19}F$  coupling and then  $F_{ax}-F_{eq}$  coupling, which however is very small at 2.6 Hz.  $^{19}F$  NMR spectral data at the low temperature limit have been given in Table 2. Intramolecular exchange of fluorine atoms between axial and equatorial sites in a trigonal bipyramid is thus confirmed at the lower temperatures. A complete line shape analysis strongly suggests that a single mechanism is operative throughout the temperature range studied, since plots of  $\log(k/T)$  against  $1/T$

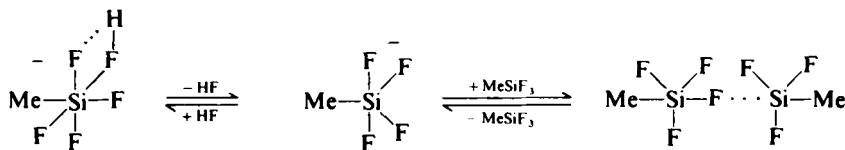
are linear in this range ( $-77^{\circ}\text{C}$  to  $+38^{\circ}\text{C}$ ). The activation parameters derived from these plots are shown in Table 4. The small values obtained for  $\Delta S^{\ddagger}$  clearly support a unimolecular mechanism.

TABLE 4. Activation parameters for intramolecular rearrangement of acyclic organofluorosilicates<sup>a</sup>

Ion	$\Delta G^{\ddagger}/\text{kcal mol}^{-1}$	$\Delta H^{\ddagger}/\text{kcal mol}^{-1}$	$\Delta S^{\ddagger}/\text{cal K}^{-1} \text{mol}^{-1}$
$\text{Ph}_2\text{SiF}_3^-$	11.7	11.2	2.5
$\text{PhMeSiF}_3^-$	9.9	9.4	-4.4

<sup>a</sup> Data are taken from Reference 5.

In the meantime, intermolecular exchange phenomena had been extensively studied by Janzen and his collaborators. They showed<sup>8</sup> that in the methyltetrafluorosilicate ion for example, intermolecular fluoride exchange was catalysed by hydrogen fluoride, and to a lesser extent by water or methanol, through their reaction with the substrate to produce hydrogen fluoride. Hexamethyldisilazane on the other hand inhibited such exchange by removal of the hydrogen fluoride as trimethylfluorosilane. Methyltetrafluorosilicate ion was also found<sup>119</sup> to exchange fluoride ion rapidly with methyltrifluorosilane. These reactions were explained by coordination of hydrogen fluoride to methyltetrafluorosilicate and of methyltetrafluorosilicate to methyltrifluorosilane respectively, to give intermediates with expanded coordination (Scheme 2).



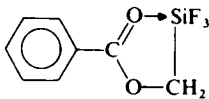
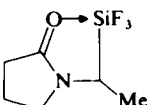

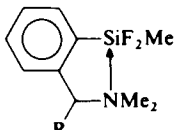
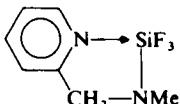
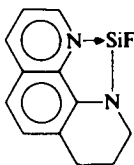
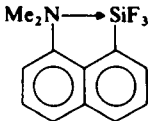
SCHEME 2

Amongst other systems in which exchange was found<sup>119</sup> to occur were  $\text{SiF}_6^{2-}/\text{SiF}_5^-$  and  $\text{SiF}_6^{2-}/\text{MeSiF}_3$ ; in the latter case the equilibrated mixture contains  $\text{SiF}_5^-/\text{MeSiF}_4^-$ . These experiments show that intermolecular exchange of fluorine is rapid between species of dissimilar coordination number, and may therefore possibly be promoted by any donor atom or molecule, capable of coordinating to a silicon atom which is not already hexacoordinate. The disproportionation of other silicon halides induced by pyridine is well known<sup>19</sup>. It is thus important to bear in mind the range of both intermolecular and intramolecular mechanisms by which positional exchange in hypervalent silicon compounds can occur.

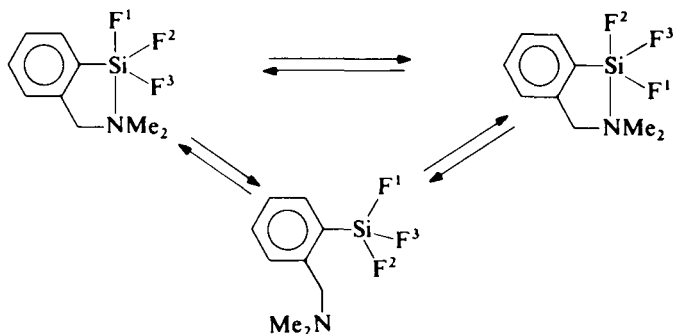
Other recent investigations of stereochemical mutation at pentacoordinate silicon have centred on a variety of cyclic systems. These include those formed by intramolecular chelation, as in ligands of types 8-12, and compounds related to the spirosilane, 1. Trifluorosilyl and methyldifluorosilyl derivatives have been studied for the widest range of ligands from the first group, and  $^{19}\text{F}$  NMR spectra for these compounds, like those of the acyclic anions, show at low temperature the presence of axial and equatorial fluorine atoms, with the methyl group occupying an axial site when present. Coalescence of the  $^{19}\text{F}$  signals is generally observed at or below room temperature, often as low as  $-60^{\circ}\text{C}$ .

From this, and in some cases from a complete line-shape analysis, free energies or enthalpies of activation have been derived for the processes equilibrating the fluorine atoms between axial and equatorial sites. Data for a representative range of ligands are summarized in Table 5.

TABLE 5. Activation parameters for intramolecular site exchange of fluorine atoms in chelated fluorosilanes

Compound	$\Delta G^\ddagger/\text{kcal mol}^{-1}$	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	Ref.
(59) 	8.4		105
(60) 	9.5		120
(61) (R = H) (62) (R = Me) 	11.7 (R = H) 13.1 (R = Me)	18.6 (R = H)	121, 122
(31) (R = H) (63) (R = Me) 	9.0 (R = H) 9.3 (R = Me)	13.3 (R = H)	121, 122
(29) 		13.2	31
(30) 		7.5	104
(64) 	12.0		26

Since  $^{29}\text{Si}$ - $^{19}\text{F}$  coupling is maintained throughout the temperature range, including temperatures higher than that at which coalescence is observed, intramolecular processes are indicated. Both 'regular' and 'irregular' mechanisms have been proposed to explain this behaviour; in a regular process the silicon atom remains pentacoordinate throughout while in an irregular process the donor-acceptor bond is broken, and the silicon atom becomes, at least momentarily, tetravalent<sup>1,2,3</sup>, e.g. Scheme 3.



SCHEME 3

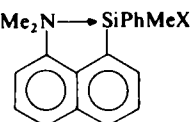
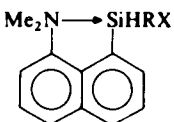
The simultaneous involvement of the dimethylamino group is indicated by the dynamic  $^1\text{H}$  NMR spectrum<sup>122</sup> for compound **31**. The diastereotopy of the methyl groups attached to the donor nitrogen, and of the benzylic protons, is eliminated in a process which has the same free energy of activation as that rendering the fluorine atoms equivalent on the NMR time scale. This equivalence could result simply from rotation of the non-chelated  $-\text{SiF}_2\text{Me}$  group, possibly accompanied by rotation and inversion of the dimethylamino group as the chelate ring is re-established. If inversion of the dimethylamino group does not occur, then the process at silicon can be assimilated into the description of a regular isomerization by turnstile rotation or Berry pseudorotation.

Further evidence on the possible dichotomy of mechanism is provided by study<sup>122</sup> of the compounds **62** and **63**, in which an additional chiral centre is present at the carbon atom adjacent to the dimethylamino group. At low temperature the  $^{19}\text{F}$  NMR spectrum of **62** shows the three absorptions expected for one axial and two diastereotopic fluorine atoms, and the  $^1\text{H}$  NMR spectrum the absorptions of two diastereotopic *N*-methyl groups.

As the temperature is raised equivalence of the fluorine atoms results from a process with a free energy of activation of  $13.1 \text{ kcal mol}^{-1}$ , significantly lower than that responsible for equivalence of the *N*-methyl groups ( $\Delta G^\ddagger = 15.8 \text{ kcal mol}^{-1}$ ). Similarly for compound **63**, both the  $^{19}\text{F}$  and  $^1\text{H}$  NMR signals permit discrimination between the regular and irregular mechanisms and the evaluation of  $\Delta G^\ddagger$  for each process. At low temperature, because of the two chiralities at carbon and at silicon, two diastereomers are visible. Each displays diastereotopy of the  $\text{NMe}_2$  groups and each has one equatorial and one apical fluorine atom. The regular mechanism eliminates the chirality at Si with  $\Delta G^\ddagger = 9.3 \text{ kcal mol}^{-1}$ , the same value being obtained from the coalescence of the  $\text{NMe}_2$  and F signals. The irregular mechanism ensues when the  $\text{NMe}_2$  is free to invert its configuration;  $\Delta G^\ddagger = 11.8 \text{ kcal mol}^{-1}$ . The existence of a mechanism for permuting fluorine atoms between sites on silicon, without inversion occurring at the adjacent dimethylamino group, is thus established.

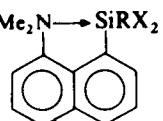
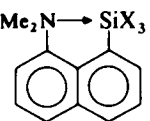
This conclusion is supported and amplified by studies<sup>26</sup> of a wide range of silyl derivatives of ligand **8**, where the nitrogen atom is held in a position suitable for bonding to silicon by the rigidity of the bicyclic system. In appropriate monofunctional compounds of this series **65**, and also those bifunctional compounds with dissimilar functional groups **66**, non-equivalence of the *N*-methyl groups is always observed in the <sup>1</sup>H NMR spectrum at room temperature. The diastereotopy is only eliminated at elevated temperatures, with free energies of activation for this process of at least 20 kcal mol<sup>-1</sup> (Table 6).

TABLE 6. Free energies of activation for equivalence of NMe<sub>2</sub> groups in monofunctional and heterobifunctional derivatives (data taken from Reference 26)

 (65)		 (66)	
Compound	$\Delta G^\ddagger/\text{kcal mol}^{-1}$	Compound	$\Delta G^\ddagger/\text{kcal mol}^{-1}$
X = H	22	RX = MeCl	22
X = Cl	20	RX = PhCl	> 22
X = F	23	RX = PhBr	> 21
X = OMe	22		

By contrast, compounds with two or three identical functional groups attached to silicon **67** and **68** always display at room temperature equivalence of the methyl groups attached to nitrogen. Diastereotopy of these groups, where expected for the more stable configuration of the trigonal bipyramid, is only apparent at low temperatures, and the differences in chemical shifts expected for groups occupying respectively axial and

TABLE 7. Free energies of activation for equivalence of NMe<sub>2</sub> groups in homobifunctional and of X<sub>3</sub> groups in homotrifunctional derivatives<sup>a</sup>

 (67)		 (68)	
Compound	$\Delta G^\ddagger/\text{kcal mol}^{-1}$	Compound	$\Delta G^\ddagger/\text{kcal mol}^{-1}$
RX <sub>2</sub> = PhCl <sub>2</sub>	11	X <sub>3</sub> = F <sub>3</sub>	12
RX <sub>2</sub> = PhF <sub>2</sub>	12	X <sub>3</sub> = H <sub>3</sub>	< 7 <sup>b</sup>
RX <sub>2</sub> = Ph(OMe) <sub>2</sub>	9	X <sub>3</sub> = (OMe) <sub>3</sub>	< 7
RX <sub>2</sub> = MeCl <sub>2</sub>	9	X <sub>3</sub> = (OEt) <sub>3</sub>	< 7

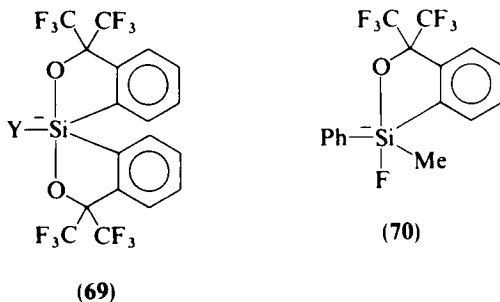
<sup>a</sup> Data taken from Reference 26.

<sup>b</sup> From Reference 124.

equatorial sites is only realized at low temperature if at all. Free energies of activation for the dynamic process occurring are given in Table 7.

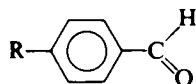
The two distinct sets of energies shown in Tables 6 and 7, respectively, probably reflect the operation of two quite different dynamic processes. The first, higher, values may be attributed to the energy required to sever the N  $\rightarrow$  Si coordinate bond and permit inversion at the nitrogen atom, in order to equilibrate the methyl group environments, whereas the second, lower, set corresponds to pseudorotation at the pentacoordinate silicon atom.

Extensive studies have been made of the isomerization of the spiroasilane **1**, induced by weak nucleophiles<sup>96</sup>, of that of siliconate anions **69** (cf. **26**)<sup>73</sup>, and that of the monocyclic anion **70**<sup>125</sup>.



In these compounds the geminal CF<sub>3</sub> groups provide by their <sup>19</sup>F NMR absorbances a sensitive probe of the isomerization processes which may occur at the silicon atom. A variety of behaviour has been revealed, and considerable uncertainty remains in the mechanistic interpretation. The monocyclic anion **70** seems to resemble the simple fluorosilicates most closely, in that the Si-bonded fluorine atom is not coupled in the <sup>19</sup>F NMR spectrum to the diastereotopic CF<sub>3</sub> groups, which themselves show the expected A<sub>3</sub>B<sub>3</sub> absorption pattern<sup>125</sup>. Rapid intermolecular exchange of the lone fluorine atom is thus indicated, which cannot be arrested by the addition of hexamethyldisilazane, even at -30°C. At higher temperatures stereomutation of the CF<sub>3</sub> groups can be observed. The free energy of activation is evaluated at approximately 17 kcal mol<sup>-1</sup>, but this parameter is sensitive to the addition of hexamethyldisilazane, and the curvature of the plot of ln *k* vs 1/*T* suggests that more than one process is involved in this stereoisomerization.

The spiroasilane **1** also shows an A<sub>3</sub>B<sub>3</sub> pattern for the -CF<sub>3</sub> absorptions in the <sup>19</sup>F NMR spectrum in non-coordinating solvents, but the addition of a weak nucleophile, such as methanol, THF or benzaldehyde, results in coalescence of these peaks at, or somewhat above, room temperature. Kinetic studies showed the reaction to be first-order in nucleophile, and at lower temperatures NMR signals corresponding to the formation of a 1:1 adduct of nucleophile and spiroasilane, with a structure analogous to that of the siliconate anions, **69**, could be observed. Experiments with a series of substituted



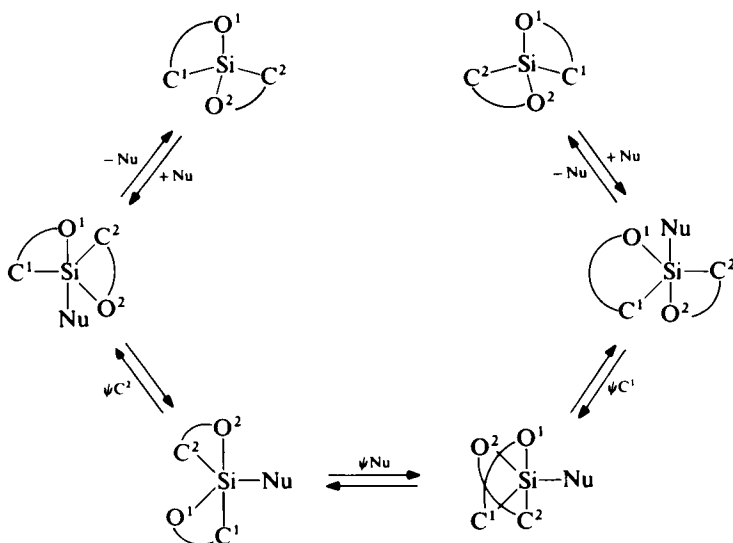
R = NMe<sub>2</sub>, OMe, Me, H, Cl or NO<sub>2</sub>

(71)

benzaldehydes, **71**, showed<sup>96</sup> that electron-releasing groups in the *para* position accelerated the rate of inversion: a value of  $10.2 \text{ kcal mol}^{-1}$  was obtained for the free energy of activation of the inversion at  $-90^\circ\text{C}$ , with *p*-dimethylaminobenzaldehyde as nucleophile.

This value was not significantly affected by solvent polarity or concentration of the reacting species, and a non-dissociative intramolecular pseudorotation was proposed to account for the enantiomerization.

Several mechanistic pathways were considered, including both edge-attack and face-attack of the nucleophile on the spirosilane. In the light of the recent results on the preferred direction of attack by nucleophiles, and on the propensity of pentacoordinate adducts to pseudorotation, that first proposed<sup>126</sup>, in which initial attack of the nucleophile occurs at a face opposite to an oxygen atom rather than at an edge, would appear most reasonable (Scheme 4).



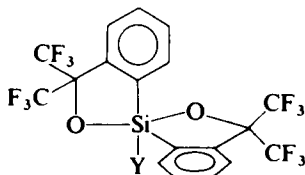
SCHEME 4

This kinetically controlled step gives rise to a relatively high-energy intermediate with a cyclic ligand spanning equatorial sites: pseudorotation about the carbon of this ligand places the nucleophile in an equatorial site, and the two cyclic ligands spanning equatorial and axial positions, albeit with one of them having the oxygen atom in the equatorial rather than the axial site. The equilibration of this intermediate with its enantiomorph, by pseudorotation about the nucleophile as pivot, is then expected to be rapid.

The siliconate anions (**69**) are inherently more stable than the adducts of **1** with weak nucleophiles, and maintain their pentacoordinated form in solution without rapid intermolecular ligand exchange (as shown, for example, by the persistence in the  $^{19}\text{F}$  NMR spectrum of coupling between the  $\text{CF}_3$  groups and the acyclic ligand in the compound with  $\text{Y}=\text{F}$ ) to temperatures above  $100^\circ\text{C}$ <sup>73</sup>. At elevated temperatures equilibration of the environment of the geminal  $\text{CF}_3$  groups is again observed. By comparison with the process involving weak nucleophiles however, free energies of activation are higher, and the enantiomerization is accelerated rather than retarded by electron withdrawal by ligand Y. Although a mechanism involving heterolytic fission of



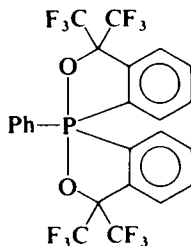
an Si-O bond, with isomerization resulting as this bond is re-established, cannot be rigorously excluded, it is most probable that pseudorotation of the pentacoordinate anion is again responsible for the stereochemical inversion. The higher activation energy is consistent with the need to attain in a first Berry process the high-energy intermediate **72**.



(72)

The reduction of the barrier to inversion represented by this intermediate, as the electron-withdrawing character of the ligand Y increases, is in accord with the greater electron density associated with the axial sites in the trigonal bipyramid. This effect is analogous to that observed in the case of the substituted benzyloxyfluorosilanes<sup>101</sup> discussed in Section III.B, where it was noted that an increase in the electron-withdrawing power of the substituted aryloxy group increased the relative stability of the isomer with that group in the axial position.

The results now available leave little doubt as to the prevalence of stereochemical non-rigidity in the behaviour of pentacoordinate derivatives of silicon. The quantitative evidence suggests furthermore that stereomutation in the silicon systems is in fact subject to lower energy barriers than those determined for isostructural phosphoranes. The free energy of activation for the equivalence of the fluorine atoms in the diphenyltrifluorosilicate ion,  $11.7 \text{ kcal mol}^{-1}$  (Table 4), is less than that<sup>127</sup> for diphenyltrifluorophosphorane,  $18.7 \text{ kcal mol}^{-1}$ , and the values for silicate ion **26** and the analogous phosphorane **73** are  $26.0$  and  $28.3 \text{ kcal mol}^{-1}$ , respectively<sup>73</sup>.



(73)

This pattern was anticipated by Holmes<sup>14</sup> on the basis of the tendency to structural distortion in the solid state displayed by the spiro-silicates **25-27** and related compounds, compared with the corresponding phosphoranes, and may be attributed to the greater effective radius of  $\text{Si}^-$  over P, typically<sup>73</sup> some  $0.07\text{-}0.15 \text{ \AA}$ .

## V. REACTIONS OF HYPERVALENT SILICON COMPOUNDS

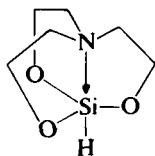
In spite of the long history of hypervalent silicon compounds, and the considerable amount of structural investigation devoted to them, relatively little of their chemistry has

been explored. There are now however indications that they have a varied chemistry, significantly different from that of their tetravalent counterparts.

Some of the hexacoordinate complexes show a striking resistance to hydrolysis, including the complex  $\text{SiF}_4 \cdot \text{bipy}^{114}$  and certain of the cationic complexes **20**<sup>54</sup> and **21**<sup>55</sup>. This no doubt arises from the coordinative saturation in complexes with strong bonding. Mechanistic studies of nucleophilic substitution<sup>108</sup> and racemization reactions<sup>60, 128</sup> in hexacoordinate silicon complexes support dissociative processes for these reactions, in contrast to the associative mechanisms characteristic of tetravalent silicon compounds.

One of the few types of organosilicon complexes to have been the subject of a systematic development of its chemistry is the organopentafluorosilicate,  $\text{RSiF}_5^{2-}$ , which has been shown by Kumada<sup>46, 129</sup> to be subject to electrophilic attack at carbon. It has been suggested that pentacoordinate compounds will show similar reactivity, particularly where an organic group occupies the more electronegative apical site in the trigonal bipyramidal geometry<sup>73</sup>.

The tris(benzene-1,2-diolato)silicon complex<sup>52</sup>,  $\text{Si}(\overline{\text{OC}_6\text{H}_4\text{O}})_3^{2-}$ , and organo-bis(benzene-1,2-diolato)silicon complexes<sup>130</sup>,  $\text{RSi}(\overline{\text{OC}_6\text{H}_4\text{O}})_2^-$ , have recently been shown to be useful starting materials for the preparation of organosilicon compounds. Evidence has also been presented<sup>131</sup> for the presence of the related hydridocomplex,  $\text{HSi}(\overline{\text{OC}_6\text{H}_4\text{O}})_2^-$  as the active agent responsible for reducing properties in solutions derived from the reaction of trichlorosilane with lithium catecholate, and the hydridosilatranes, **74**, also has significant reducing action<sup>132</sup> towards some carbonyl compounds and halides.

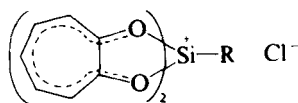


(74)

In addition to these stoichiometric reagents, many of the reactions of organosilicon compounds which are catalysed by nucleophiles, including those now commonly used in organic synthesis, involve hypervalent silicon intermediates. These systems are discussed in the last section of this chapter.

### A. Protonolysis of Hypervalent Silicon Compounds

Although the data are somewhat fragmentary, there are clear indications that hypervalent silicon derivatives are more sensitive to protonolysis than analogous tetravalent compounds. The hydridosilatranes **74** immediately evolves hydrogen on treatment with hydrogen chloride or hydrogen bromide in chloroform<sup>133</sup>, and the ammonium salt,  $(\text{NH}_4)_2\text{SiF}_5\text{CH}_3$ , was observed<sup>4</sup> to react violently with acid with the liberation of copious amounts of gas, although this compound like other  $\text{RSiF}_5^{2-}$  salts may be recrystallised from aqueous alcohol.  $\text{PhSiF}_5^{2-}$  is less reactive, but is still destroyed by a 10% excess of aqueous HF, with liberation of benzene, in less than two weeks at room temperature<sup>49</sup>. The pentacoordinate tropolonates, **75**, also suffer carbon-silicon bond cleavage, decomposing partially as they are prepared in DMSO solution to give the tris(tropolonato)silicon cation. The reactivity depends on the nature of R in the order  $\text{H} \sim \text{PhC}\equiv\text{C} > \text{vinyl} \sim \text{phenyl} > \text{alkyl}$ <sup>41</sup>.



(75)

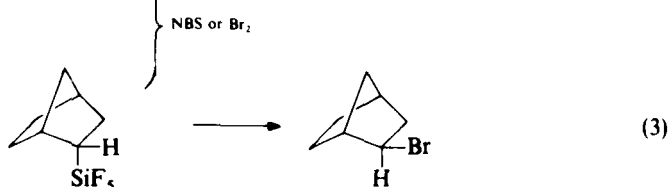
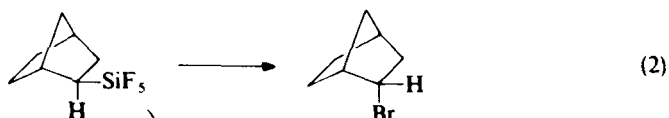
It has also been noted that hexacoordinate diphenyl derivatives are even more prone to lose an organic group; thus reaction of diphenyldifluorosilane with a primary ammonium fluoride apparently gives the  $\text{Ph}_2\text{SiF}_4^{2-}$  anion, which however rapidly decomposes to give  $\text{PhSiF}_5^{2-}$ <sup>47</sup>. The similar formation of  $\text{PhSi}(\text{-OC}_6\text{H}_4\text{O})_2^-$  in the reaction of catechol with diphenyldimethoxysilane has already been mentioned<sup>12</sup>.

## B. Organopentafluorosilicates in Organic Synthesis

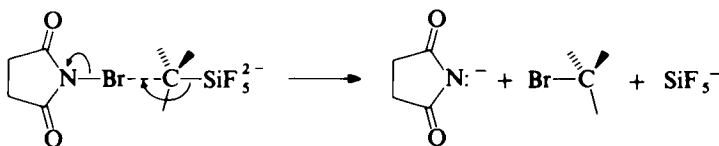
The exploitation in organic synthesis of the potassium salts,  $\text{K}_2\text{SiF}_5\text{R}$ , which are air-stable compounds easily isolated in a pure state, has given rise to a number of interesting mechanistic studies concerning the reactivity of these hexacoordinate anions. Protonolysis is of no great synthetic value, but reactions with other electrophiles are more useful.

### 1. Halogenation

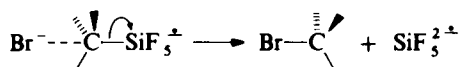
*N*-Bromosuccinimide, elemental halogen or copper(II) halides induce cleavage of the carbon-silicon bond with formation of the corresponding organic halide. Information on the stereochemistry of the cleavage of alkylpentafluorosilicates was obtained from a study of the stereospecificity of the reactions of *exo*- and *endo*-2-norbornylpentafluorosilicates<sup>129</sup>. In polar solvents both *N*-bromosuccinimide and elemental bromine gave products in which inversion of configuration had occurred at the carbon atom, with a high degree of selectivity (equations 2 and 3).



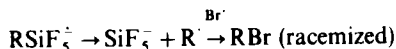
In non-polar solvents a decrease in yield was observed in the reactions with *N*-bromosuccinimide, and a loss of stereoselectivity in the reaction of the *exo*-isomer with bromine. The inversion of configuration in the reaction with *N*-bromosuccinimide was explained by direct electrophilic displacement (Scheme 5), but the reaction with bromine was considered to proceed by an initial electron-transfer step, followed by nucleophilic attack of bromide ion on the resulting organopentafluorosilicate radical-ion (Scheme 6). Steric constraints or a reduction in the polarity of the solvent would allow dissociation of the radical ion to a free alkyl radical, and loss of stereoselectivity, as observed (Scheme 7).



SCHEME 5

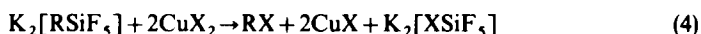


SCHEME 6

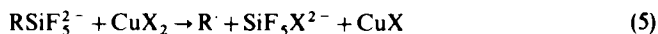


SCHEME 7

The reaction with copper(II) salts follows strictly the stoichiometry shown in equation 4, and proceeds with complete loss of stereochemistry<sup>134</sup>.

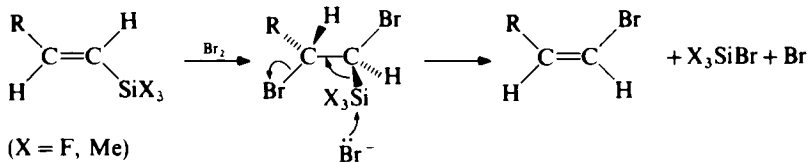


Again an initial one-electron oxidation is postulated, with liberation of a free alkyl radical which undergoes racemisation before conversion to halide (equations 5 and 6).

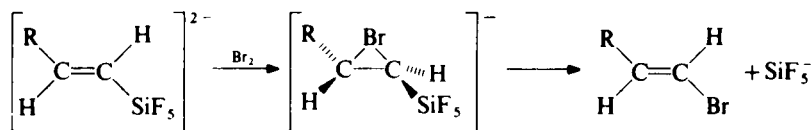


The formation of the radical is supported by the observations that, in the presence of oxygen, aldehyde is produced at the expense of the halide, and that a characteristic ESR spectrum is obtained in the presence of a nitroso radical trap.

Cleavage of alkenylpentafluorosilicates by halogen or *N*-bromosuccinimide proceeds with retention of configuration, in contrast to the inversion observed under similar conditions in the reaction of alkenyltrimethylsilanes, in which the silicon is but tetracoordinate. Alkenyltrifluorosilanes react with inversion in carbon tetrachloride, and with retention in polar solvents<sup>135</sup>. Inversion is a consequence of the accepted *trans*-addition *anti*-elimination mechanism (Scheme 8), whereas retention is explained by direct electrophilic displacement of silicon by attack at the  $\alpha$ -carbon atom (Scheme 9).



SCHEME 8

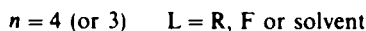
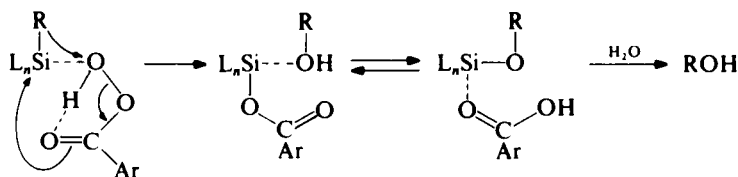


SCHEME 9

In polar solvents the change in stereochemistry observed in the case of trifluorosilyl alkenes reflects an increase in the coordination number at the silicon atom by donation from the solvent.

### 2. Oxidation by *m*-chloroperbenzoic acid

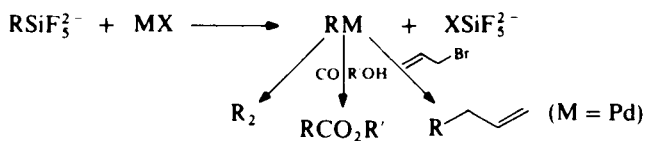
Alcohols are produced in high yield by oxidative cleavage of the carbon-silicon bond by this reagent<sup>136</sup>. The reaction is again stereospecific, but proceeds with retention of configuration. The rate of the reaction is depressed by addition of an excess of potassium fluoride, and suggests that prior dissociation of the organopentafluorosilicate is necessary, probably to the organotetrafluorosilicate, since organofluorosilanes,  $R_2SiF_2$  and  $R_3SiF$  may also be oxidised, but only in the presence of increasing amounts of potassium fluoride. The mechanism proposed is shown in Scheme 10.



SCHEME 10

### 3. Alkyl transfer

In addition to the reactions with copper(II) salts already noted, organopentafluorosilicates react with many other metal salts [e.g. of Ag(I), Cu(I) and Pd(II)]<sup>48</sup>. The reaction appears to involve alkylation of the metal, and may be followed by reductive coupling of the alkyl groups, or other established reactions, such as carbonylation in the case of palladium (Scheme 11). Similar reactions with alkenylsilicates are highly stereoselective, and often give better yields<sup>137</sup>.



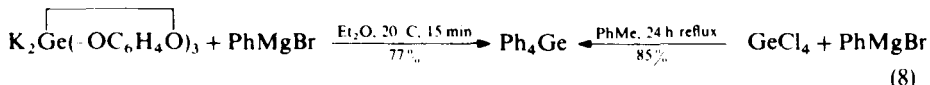
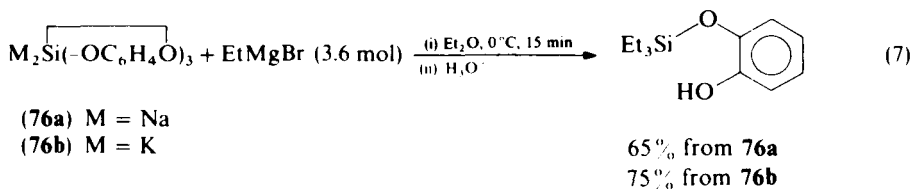
SCHEME 11

## 4. Reactions with organometallic reagents

There have been few reports of the reactions of  $\text{RSiF}_5^{2-}$  (or  $\text{SiF}_6^{2-}$ ) ions with organometallic reagents. In general further alkylation by Grignard reagents appears to be difficult, occurring only at high temperatures after Grignard of solvent, or after long periods, and in low yield<sup>138</sup>. The conversion of the norbornenylpentafluorosilicate to the norbornenyltrimethylsilane was however reported by Kumada to take place in 60% yield<sup>139</sup>.

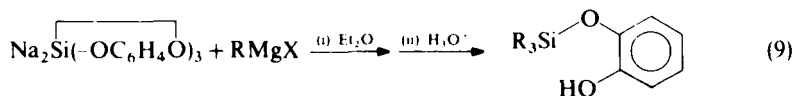
## C. Reactivity of Tris(benzene-1,2-diolato) Complexes of Silicon

The salts  $\text{Si}(\overline{\text{OC}_6\text{H}_4\text{O}})_3^{2-} \cdot 2\text{M}^+$  [ $\text{M} = \text{Na}$  or  $\text{K}$ ] were found to react very rapidly with Grignard or organolithium reagents. The high reactivity of these hypervalent species towards nucleophiles is illustrated by the examples in equations 7 and 8<sup>52, 140</sup>.

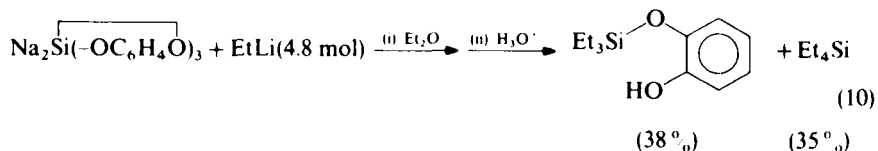


The extent of alkylation, etc., varies with the organometallic reagent as follows.

(1) When  $\text{RM}$  is an alkyl (except  $\text{MeMgBr}$ ) or benzyl Grignard reagent, three silicon-carbon bonds are formed whatever the ratio **76a**/ $\text{RM}$  (equation 9). ( $\text{MeMgBr}$  leads only to the formation of  $\text{Me}_4\text{Si}$  in good yield.)

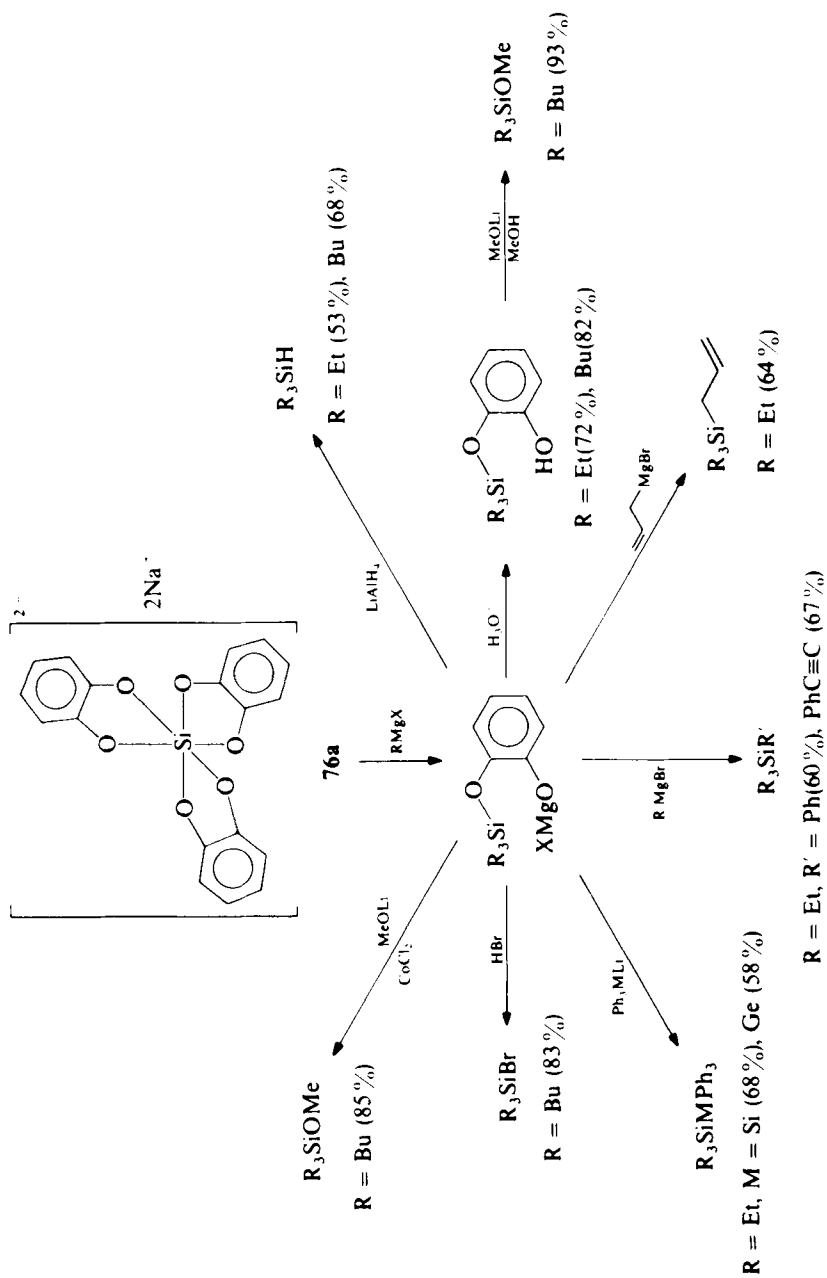


(2) When  $\text{RM}$  is an alkyllithium reagent, a mixture of tri- and tetra-organosilanes is obtained. An example is shown in equation 10.



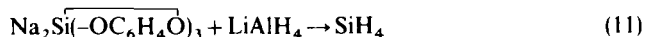
(3) When  $\text{RM}$  is an allyl, vinyl, phenyl or alkynyl Grignard reagent,  $\text{R}_4\text{Si}$  is formed directly whatever the ratio **76a**/ $\text{RM}$ .

The intermediate  $\text{R}_3\text{Si-OC}_6\text{H}_4\text{OMgX}$  obtained in the reaction of an alkyl Grignard reagent with **76a** can react with nucleophiles to give further monofunctional organosilicon compounds (Scheme 12).

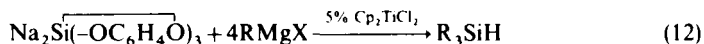


SCHEME 12

These reactions are useful for the preparation of functional organosilicon compounds, since  $\text{Na}_2\text{Si}(\overline{\text{OC}_6\text{H}_4\text{O}})_3$  can be obtained directly from silica in very mild conditions<sup>52</sup>, avoiding the route through elemental silicon. Complex **76** can also be treated with a reducing agent such as  $\text{LiAlH}_4$  to give  $\text{SiH}_4$  in quantitative yield (equation 11).

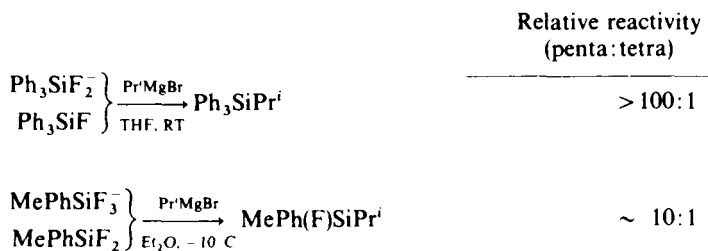


The reaction of  $\beta$ -hydrogenated Grignard reagents activated by  $\text{Cp}_2\text{TiCl}_2$  (Cp = cyclopentadienyl) was also investigated. This system, known<sup>141</sup> to be a very efficient reducing agent, produces in one step the trisubstituted hydrogenosilanes (equation 12). This is an excellent way to obtain hydrogenosilanes from silica in two steps.

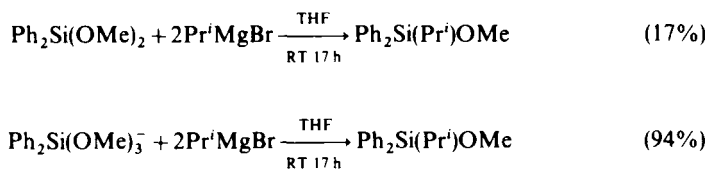


#### D. Reactivity of Pentacoordinate Organofluorosilicates and Alkoxysilicates

Recent studies<sup>142</sup> of the pentacoordinate organofluorosilicates  $\text{Ph}_3\text{SiF}_2^-$  and  $\text{MePhSiF}_3^-$ , as their 18-crown-6 ether complexed potassium salts, have shown them to be very reactive towards strong nucleophiles ( $\text{RLi}$ ,  $\text{RMgX}$ ,  $\text{RO}^-$ , complex hydrides), in contrast to the sluggish reactions of the hexacoordinated complexes  $\text{RSiF}_3^{2-}$  towards these reagents. In fact, the pentacoordinated ions react more rapidly than do the corresponding neutral tetravalent compounds (lacking an  $\text{F}^-$  ion). Semi-quantitative comparisons of the relative reactivity are shown in Scheme 13. Similar results have been obtained with pentacoordinated alkoxysilicates which also react faster than the tetracoordinated parent (Scheme 14).



SCHEME 13

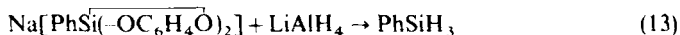


SCHEME 14

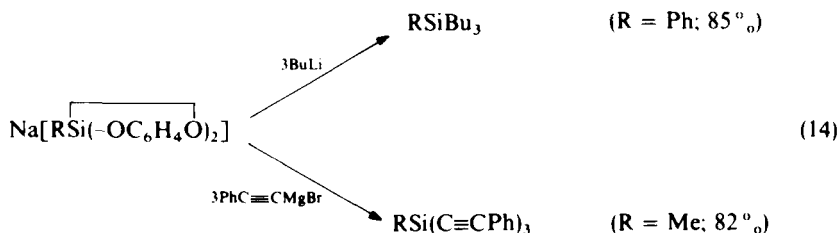


### E. Reactivity of Organobis(benzene-1,2-diolato) Complexes of Silicon

The complexes  $\text{Na}^+ \text{RSi}^-(\overline{\text{C}_6\text{H}_4\text{O}})_2^-$  ( $\text{R} = \text{Me}, \text{Ph}, 1\text{-Naphthyl}$ ) were also found<sup>130</sup> to be very reactive towards nucleophilic reagents such as organometallic reagents and hydrides. An excess of hydride leads to trihydrogenosilanes (equation 13).



Reactions with three moles of organolithium reagent or allyl and alkynylmagnesium bromide leads to the tetrasubstituted product (equation 14).



Two moles or less of an organometallic reagent react with these complexes to give as the major product the triorgano-substituted product  $\text{RR}'_2\text{SiOC}_6\text{H}_4\text{O}^- \text{Na}^+$ . This intermediate can undergo further transformation analogous to the reactions shown in Scheme 12.

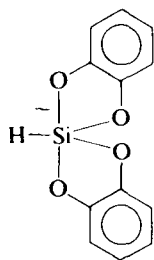
It is also notable that the spiro-silane  $\overline{\text{Si}(\text{OC}_6\text{H}_4\text{O})_2}$  is much less reactive than the salt  $\text{Na}^+ \text{PhSi}^-(\overline{\text{OC}_6\text{H}_4\text{O}})_2^-$  towards phenylmagnesium bromide implying that the latter ion is not readily formed from the tetravalent molecule in this system. Pentacoordinated anionic silicon species are seen from these results to be susceptible to nucleophilic attack and may therefore reasonably be considered as possible intermediates in nucleophilic substitutions at silicon.

### F. Pentacoordinate Silicon Hydrides as Reducing Agents

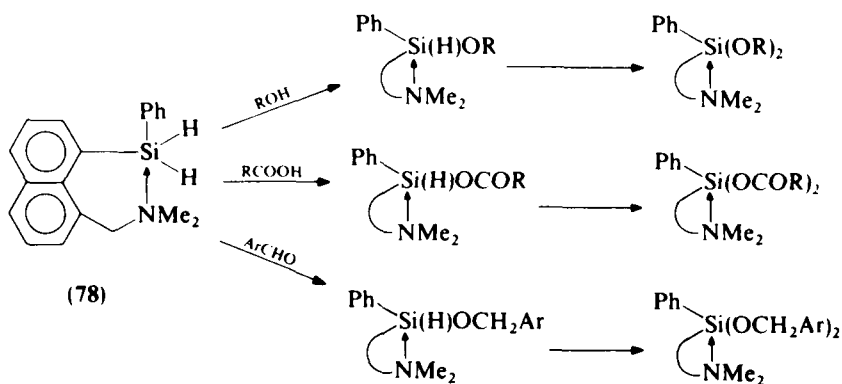
The early reports suggesting that the hydrogenosilatrane **74** might be a more powerful hydride donor and reducing agent<sup>132, 133</sup> than simple organosilicon hydrides have only recently been followed by other reports of the reducing action of hypervalent silicon hydrides. Solutions most probably containing the ion  $\text{HSi}^-(\overline{\text{OC}_6\text{H}_4\text{O}})_2^-$ , and the corresponding complex of 2,2'-dihydroxybiphenyl were found to reduce both ketones and aldehydes directly in excellent yield<sup>131</sup>. Similar reagents prepared from aliphatic 1,2-diols, especially pinacol, were also effective<sup>143</sup>, but only aldehydes were reduced by a lithium methoxide/trimethoxysilane mixture. These observations are in accord with the greater capacity of diolate ligands, to bring about hypercoordination at silicon, and strongly support the participation of the ion **77**, for example.

Hammett plots of relative reactivities of the reducing agents towards substituted benzaldehydes are in agreement with hydride transfer being the rate-controlling step<sup>143</sup>.

The intramolecularly coordinated dihydrides **37**, **39** and **78** have also been shown to possess a much more reactive hydrogen function than 1-naphthylphenylsilane. The reactions with alcohols to give alkoxides, with acids to give silyl esters, and the reduction of benzaldehydes and fluorenone were all found to proceed in usually near quantitative yield<sup>114</sup> (Scheme 15).

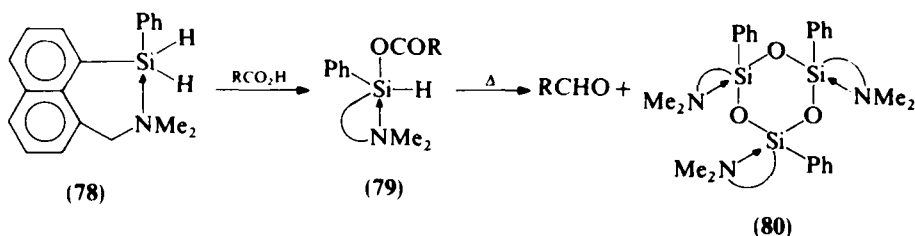


(77)



SCHEME 15

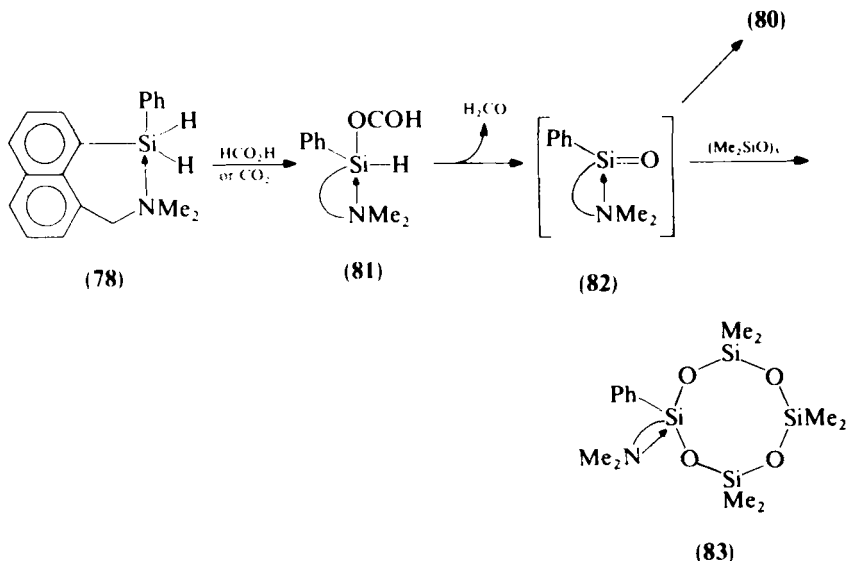
Thermal decomposition of the monocarboxylate esters (79) provides a new route<sup>145</sup> for the reduction of carboxylic acids to aldehydes (Scheme 16).



SCHEME 16

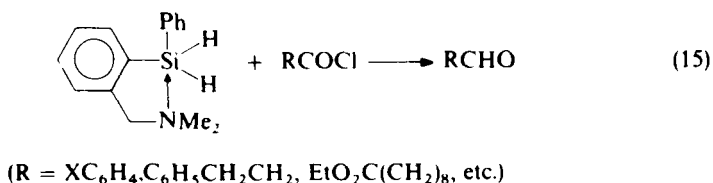
The acyclic compound 1-NaphPh(H)SiOCOPh is not significantly converted to benzaldehyde on thermolysis, even at temperatures considerably higher than those (100–160°C) which are effective with the chelate system. This reaction may proceed via the transient formation of a chelated silanone **82**, since the trisiloxane **80** is isolated as the silicon-containing product. Confirmation of this mechanism was obtained in the reaction of **78** with carbon dioxide, from which the silyl ester of formic acid **81** can be isolated and

characterized. The same compound is obtained from the reaction of **78** with formic acid. The thermal decomposition of this ester also gave **80**. When the reaction was performed in presence of hexamethyltrisiloxane ( $D_3$ ), the adduct **83** corresponding to the insertion of the silanone **82** into the Si-O bond was observed, Scheme 17. Furthermore, the formaldehyde which was released during the thermolysis was trapped and identified.



SCHEME 17

The reactivity of pentacoordinated dihydrogenosilanes towards acyl chlorides was also studied. The hydrogen/chlorine exchange takes place in very mild conditions<sup>146</sup> leading to a very general Rosenmund-type reaction. Aliphatic and aromatic acid chlorides can be reduced to aldehydes in excellent yield without any catalyst, and in the presence of other functional groups (equation 15).



## VI. HYPERVALENT INTERMEDIATES IN CATALYSED REACTIONS

### A. Solvolysis and Racemization of Organosilicon Halides

Sommer first showed that optically active halosilanes could be racemized by nucleophilic solvents, or by an excess of halide ion<sup>147</sup>. Subsequently, many instances have been discovered of nucleophiles bringing about the racemization of organosilicon (and organophosphorus) compounds, and enhancing the rates of substitution reactions, without themselves appearing in the products<sup>148, 149</sup>. The effect of amines in increasing

the rate of alcoholysis of chlorosilanes, for example, has long been known<sup>150</sup>, and has been shown to depend on the nucleophilicity, rather than the basicity of the amine<sup>151</sup>.

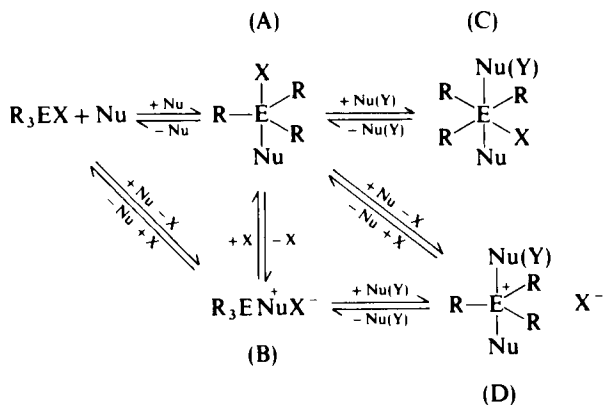
Kinetic studies<sup>37, 152</sup> have established that the rate laws for the racemization and the nucleophile-assisted substitution reactions are very similar:

$$V_{\text{rac}} = k_{\text{rac}} [\text{E-X}] [\text{Nu}]^2$$

$$V_{\text{subs}} = k_{\text{subs}} [\text{E-X}] [\text{Nu}] [\text{Y}]$$

where E-X=substrate (SiCl or PCl containing compound, etc.), Nu=nucleophilic catalyst and Y=incoming substituent.

Relative rates were found to be strongly dependent on the nature of X: Br > Cl  $\gg$  F, and within Group IV on the nature of E: Sn  $\gg$  Ge > Si. From the temperature dependence of the rates of reaction, entropies of activation were evaluated as  $\Delta S^\ddagger = -40$  to  $-60 \text{ cal K}^{-1} \text{ mol}^{-1}$ , and apparent enthalpies of activation as small,  $\Delta H^\ddagger < 3 \text{ kcal mol}^{-1}$ , or even negative. These features point to a mechanism controlled by entropy of activation in which initial reversible attack of the activating nucleophile catalyst on the substrate gives an intermediate, (A) or (B) (Scheme 18). This is followed in the rate-determining step by reaction with a second molecule of the same nucleophile in the case of racemization, and by reaction with a molecule of the incoming nucleophile which substitutes the Si-X bond in the case of the 'nucleophile-assisted' nucleophilic substitution at silicon.

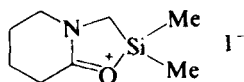


SCHEME 18

The large negative values of the entropy of activation are consistent with highly-organized transition states. In the case of racemization a symmetrical species, (C) or (D), is formed in the second step; the pathway for substitution is identical except for the nature of the nucleophile, which is then the substituting reagent. This accords with the observation that the nucleophile-assisted substitution process occurs with retention of configuration for chlorosilanes, in contrast to the inversion normally observed<sup>153</sup>.

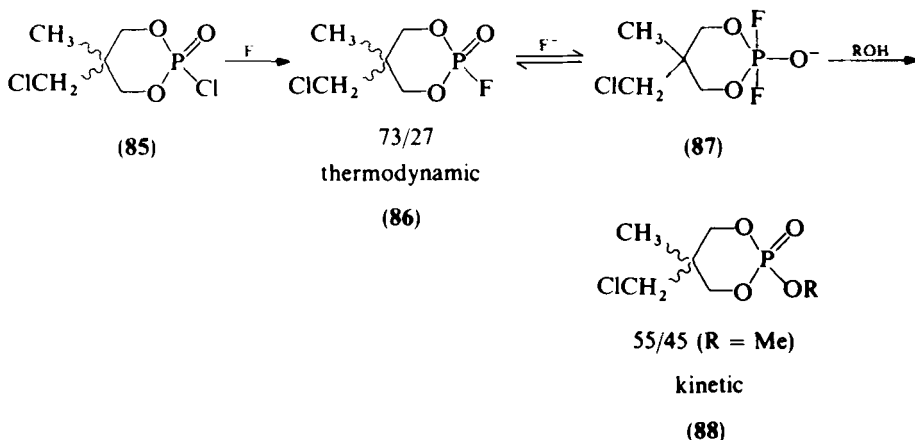
The details of the mechanistic pathways which may be followed in individual reactions have often not been elucidated, although many attempts have been made to observe as directly as possible the feasible intermediates. In particular, it has been argued that a pentacoordinate species (A) will be more negative and sterically more hindered than a tetracoordinate cation (B), so that increased rates will only be observed if (B) is the kinetically active intermediate. Observations adduced in support of this proposition

include the characterization of stable tetracoordinate complex cations such as those mentioned earlier<sup>39</sup>, the chelated cation, **84**<sup>154</sup>, and the adducts, apparently of constitution  $[(\text{Me}_2\text{N})_3\text{POSiMe}_3]^+ \text{X}^-$  ( $\text{X} = \text{Br}, \text{I}$ )<sup>155</sup>, in which the donor, HMPT, is one of the more effective catalysts for racemization of optically active halogenotriorganosilanes.



(84)

However, the analogues of these compounds where  $\text{X} = \text{Cl}$  or  $\text{F}$  are not ionic, and solvents such as acetonitrile which are not sufficiently nucleophilic to displace even  $\text{I}^-$  or  $\text{Br}^-$  in the above cases, are still efficient catalysts for racemization. Furthermore the activating nucleophile may be identical with the leaving group, as occurs in the solvolysis of *p*-nitrophenyldiphenylphosphate catalysed by *p*-nitrophenoxide ions<sup>156</sup>. In yet others, displacement of the leaving group by the catalyst gives rise to a putative intermediate which is *less* reactive than the substrate. This situation is found in the reactions of the chlorophosphorinane **85**, with catalysis by fluoride ion (Scheme 19)<sup>157</sup>. Whatever the structure of the starting compound **85** (pure *cis*, pure *trans* or a mixture), the fluoride **86** is in fact first formed rapidly as the thermodynamic mixture. However its further transformation is accelerated by an excess of fluoride ion. The isolation of the diastereomeric products, **88** in near equal amounts, significantly different from the thermodynamic equilibrium ratio, supports the formation of a quasi-symmetric penta-coordinate intermediate **87**.



SCHEME 19

There is thus good evidence that pentacoordinate intermediates of type (A), even if negatively charged, can be more reactive towards nucleophiles than their tetracoordinate precursors. Recent calculations have shown that the positive charge on the central atom actually increases on coordination by a negative ion, and that the ligands therefore acquire a correspondingly greater negative charge, especially in the axial positions of a trigonal bipyramid<sup>158</sup>. Since, as described, an increase in bond lengths also occurs on

complexation, it is not unreasonable that leaving group ability should be enhanced in the complex.

No firm evidence is available to exclude either type of the intermediates (C) and (D). Stable examples of both are now well-documented in phosphorus<sup>159</sup> as well as in silicon chemistry (Section II). The participation of pentacoordinate siliconium ions in chlorosilacyclobutane isomerization<sup>160</sup> and of analogous cationic species in the racemization of triorganotin halides<sup>161</sup> has been supported. The possible intervention of hexacoordinate intermediates in substitution reactions at phosphorus has often been considered<sup>162</sup>.

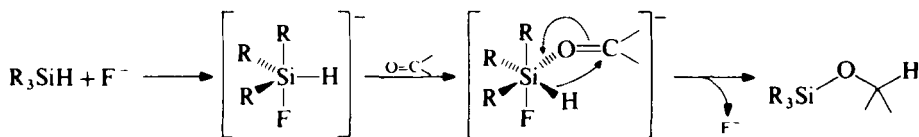
It seems clear therefore that a unique mechanistic pathway should not be sought to accommodate the whole range of observed behaviour. In particular, the intermediates involved in a given reaction will depend on the nature of the substrate (both the functional group and the remaining substituents on the central atom), of the nucleophilic reagent(s), and possibly also of the solvent<sup>163</sup>, even where it is not itself the nucleophile. The kinetic behaviour is however satisfactorily contained within the scheme outlined above<sup>164</sup>. Where the second step is the slower, rate-determining one, as is usually the case with acyclic silicon halides, third-order kinetics are observed, and values of the activation enthalpy near zero for the overall process reflect the exothermic nature of the first step. The situation in which the first step is rate-determining, and the kinetics overall are second order, may also be realized, as is the case with the ethanolysis of the cyclic chlorophosphate  $\text{Cl}(\text{O})\text{P}(\text{O})(\text{OCH}_2\text{CH}_2\text{O})$  catalysed by *N*-methylimidazole<sup>165</sup>. Intermediate cases with more complex fractional-order kinetics are also known, and are represented in silicon chemistry by the racemization and solvolysis of the chlorosilacyclobutanes studied by Cartledge<sup>166</sup>. It is also noteworthy that aryloxytriphenylsilane hydrolysis with catalysis by hydroxide ion was found<sup>167</sup> to be second order in hydroxide at low hydroxide ion concentration, although the significance of these results has been questioned<sup>168</sup>.

## B. Activation by Nucleophiles of Reactions of Silyl Derivatives in Organic Synthesis

The activation of organosilicon compounds by nucleophiles is now widely exploited in many reactions of value in synthetic organic chemistry. As discussed in the preceding section, coordination to an organosilicon compound may enhance the electronegative, potentially nucleophilic, character of the remaining substituents, whilst increasing the electrophilicity of the silicon atom. In this way heterolytic cleavage of Si–O, Si–C, Si–H and Si–N bonds may be facilitated, and exploited in the protection and deprotection of alcohols; in the use of silyl derivatives as enolate or carbanion equivalents; in the activation of organosilicon hydrides as reducing or silylating agents; and in the application of *N,N*-bis(silyl) enamines as protected vinylamines<sup>169</sup>.

### 1. Activation of the Si–H bond—reduction reactions

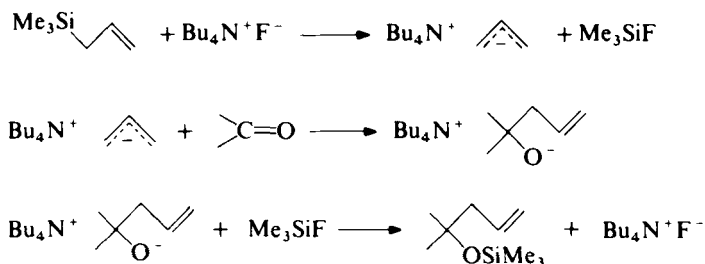
Fluoride ion is a particularly effective catalyst<sup>170</sup> and has been widely employed since Vol'pin<sup>171</sup> first reported the catalysis by caesium fluoride of the addition reactions of alkylsilanes with carbonyl compounds. This catalyst can be used either in heterogeneous ( $\text{M}^+\text{F}^-$ ) or in homogeneous ( $\text{NR}_4^+\text{F}^-$ ) conditions. Other nucleophilic catalysts have been found effective for particular reactions, especially alkoxide ions, carboxylate ion, cyanide ion and amines. The most probable mechanism involves the coordination of  $\text{F}^-$  at silicon followed by the concerted attack of carbonyl group at silicon with the formation of the alkoxy silane (Scheme 20). This mechanism is supported by the high reactivity of the pentacoordinated hydrogenosilanes towards carbonyl groups<sup>144</sup> and by kinetic studies<sup>172</sup>.



SCHEME 20

### 2. Activation of the Si-allyl bond

The reaction of allyltrimethylsilane with carbonyl compounds, catalysed by tetrabutylammonium fluoride, is also believed<sup>173</sup> to proceed by way of the allyl ion salt (Scheme 21).

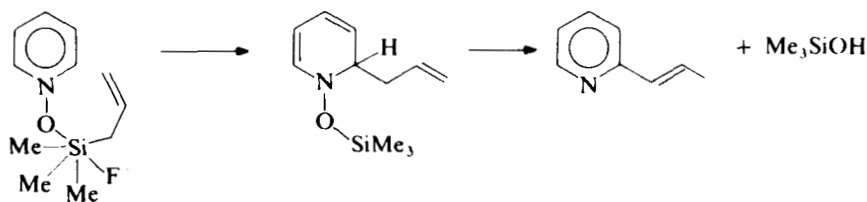


SCHEME 21

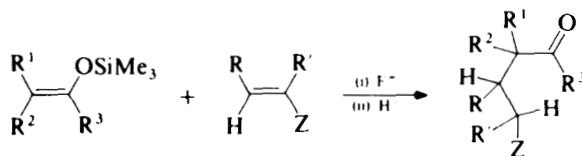
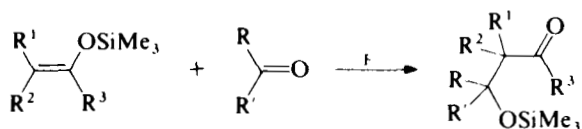
In this system the reaction of compound  $\text{Me}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$  gave reaction predominantly at the primary ( $\alpha$ ) carbon atom, and this was taken as evidence for the intermediacy of the free allyl ion. It has been noted<sup>174</sup> however that proton abstraction is rarely observed in these reactions, suggesting therefore that a non-basic hypervalent silicon intermediate is acting as the allyl transfer agent. Reaction of the allylbis(benzenediolato)silicate ion with aldehydes occurs even in protic solvents, without any added nucleophilic catalyst<sup>175</sup>, but its reactivity can apparently be increased by addition of anions and, in the presence of methoxide ion, transfer of the allyl group to ketones can also be effected<sup>176</sup>. In the non-catalysed system, reaction of  $\text{Me}_2\text{C}=\text{CHCH}_2\text{Si}(\text{OC}_6\text{H}_4\text{O})_2^-$  takes place at the remote ( $\gamma$ ) carbon atom of the substituted allyl group, and a similar regiochemistry characterises the reaction of the allyltrifluorosilane  $\text{Me}_2\text{C}=\text{CHCH}_2\text{SiF}_3$  with catalysis by caesium fluoride<sup>177</sup>. Coordination of the carbonyl group to the hypervalent silicon species and intramolecular allyl transfer is the favoured mechanism. A further instance where this mechanism is strongly indicated, is in the introduction of the allyl group into the 2-position of pyridine-*N*-oxide by allyltrimethylsilane with fluoride ion catalysis, with concomitant reduction of the heterocyclic oxide to the substituted heterocycle<sup>178</sup>. Formation of the silanol, allied to the known effectiveness of pyridine *N*-oxide as a ligand to silicon<sup>57</sup>, is particularly significant (Scheme 22).

### 3. Activation of the Si-O bond

The activation of enoxysilanes by fluoride ions provides a general method for carbon-carbon bond formation. The most extensively studied reactions are the cross-aldolization and the Michael reactions (see Scheme 23). These reactions can be activated, as noted earlier, by  $\text{CsF}$  in heterogeneous conditions or by  $\text{NR}_4^+\text{F}^-$  in homogeneous

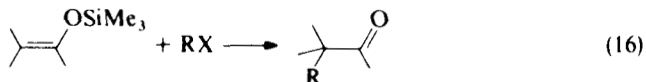


SCHEME 22

(Z = COR, CO<sub>2</sub>R, CN)

SCHEME 23

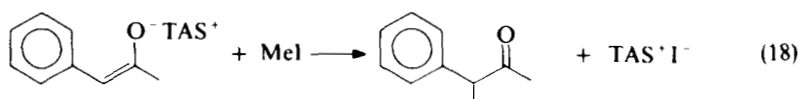
conditions. Under these last conditions only it is also possible to promote the alkylation reaction<sup>179</sup> (equation 16).



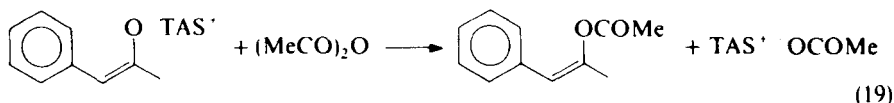
Two distinct mechanisms have been proposed. In the first, the formation of free enolates by nucleophilic attack of F<sup>-</sup> at silicon was supported by a study<sup>180</sup> of the interaction of tris(diethylamino)sulphonium (TAS) difluorotrimethylsilicate and the enol trimethylsilyl ether of benzyl methyl ketone. An equilibrium mixture appears to be produced (equation 17), which may be displaced in the direction of the TAS enolate by removal of the volatile fluorotrimethylsilane.



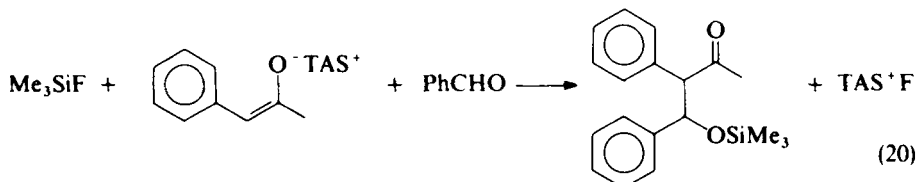
The reactions of the 'naked enolate' studied included C-alkylation and O-acylation (equations 18 and 19).





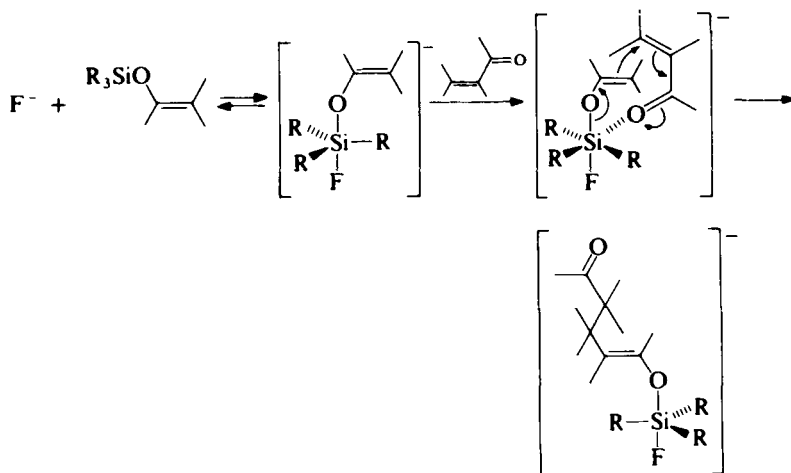


The reaction with benzaldehyde however failed to produce the expected aldol product (after hydrolysis), unless an excess of fluorotrimethylsilane (or of the original enol trimethylsilyl ether) was present to capture the adduct anion (equation 20).



The aldol products formed in these reactions were found to have predominantly *erythro* stereochemistry, in accord with reaction via the free enolate, since it was considered that in these circumstances the repulsion between negatively charged oxygen atoms in the transition state would ensure that they were widely separated. *Threo* stereochemistry is by contrast realized when a metal centre maintains the oxygen atoms close together<sup>181</sup>.

The second possible mechanism has, for example, been proposed for the Michael addition performed in heterogeneous conditions. It postulates the activation of a silyl enol ether by  $\text{F}^-$  with formation of pentacoordinated silicon in a pre-equilibrium, followed by concerted attack of the Michael acceptor in the rate-determining step giving a hexacoordinate intermediate<sup>169</sup> (Scheme 24).

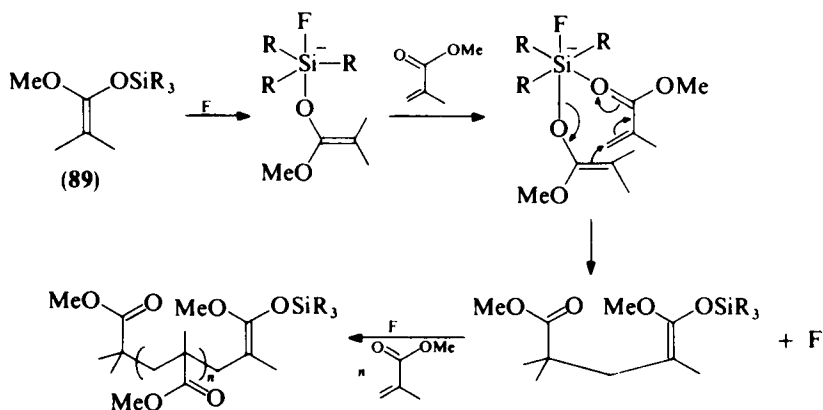


SCHEME 24

The most thorough mechanistic investigation which supports an intramolecular silyl group migration has been carried out in connection with the method known as group transfer polymerization (GTP), for the polymerization of acrylic monomers<sup>182</sup>. This involves a catalysed Michael addition of silyl ketene acetals **89** to  $\alpha,\beta$ -unsaturated esters.

for which anionic catalysts including  $\text{HF}_2^-$ ,  $\text{CN}^-$  and  $\text{Me}_3\text{SiF}_2^-$  (*vide supra*) may be employed.

An ingenious set of experiments, in which both polymer chain and silyl group were distinguished by the substituents they carried, established that the silyl group remained attached to a single polymer chain capable of growth as long as monomer was available. Free ester enolate was therefore not produced, and the mechanism shown in Scheme 25 firmly established.



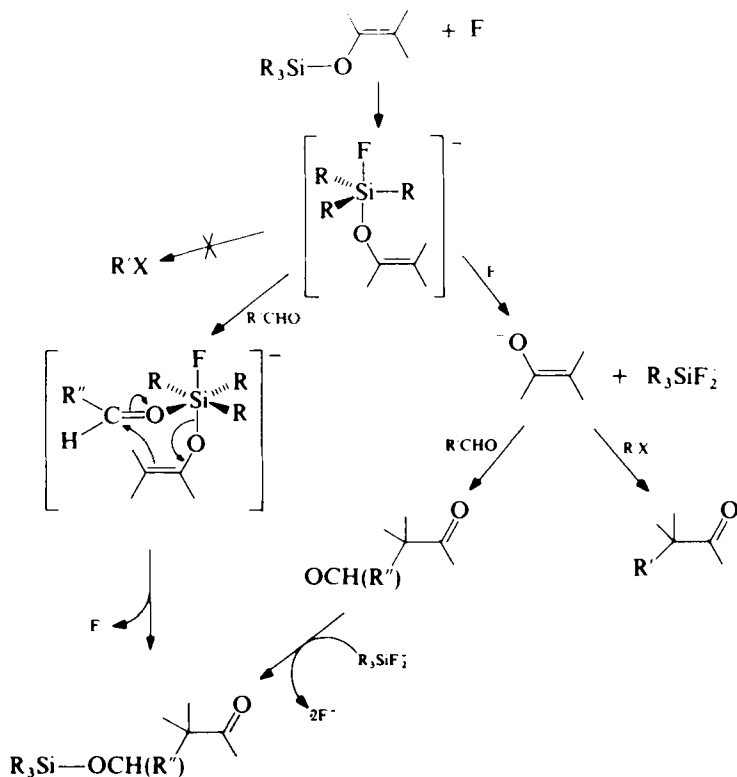
The key features of this mechanism are the activation of the silyl ketene acetal initiator by the nucleophilic catalyst, the further coordination of the monomer to the nucleophilic silicon centre, rendering the silicon hexacoordinate, and the transfer of the silyl group to the incorporated monomer, thus regenerating the reactive silicon group to continue the polymerization.

These experimental findings again suggest that a range of mechanisms may operate (Scheme 26).

The most effective sources of nucleophilic activation, complemented by substantial leaving group capability, may well bring about the dissociation of free anion. In the reaction of the very efficient fluoride donor,  $\text{TAS}^+ \text{Me}_3\text{SiF}_2^-$ , with the silyl enolate derived from benzyl methyl ketone, transfer of *two* fluoride ions may be envisaged, resulting in separation of the enolate ion and reformation of  $\text{Me}_3\text{SiF}_2^-$ . The enolate is reactive towards a wide range of electrophiles, including alkyl halides, and in its reaction with aldehydes the  $\text{Me}_3\text{SiF}_2^-$  ion is best able to capture the adduct aldolate ion, being more reactive (and less volatile) than  $\text{Me}_3\text{SiF}$ .

Where the catalyst is less nucleophilic, e.g. potassium fluoride or solid caesium fluoride, only one fluoride ion is likely to coordinate at all firmly to the silane. The nucleophilic reactant will then also be able to coordinate to the electrophilic silicon atom, itself receiving further activation in the process, and reaction ensues by intramolecular transfer about the hexacoordinate silicon atom as demonstrated in the GTP process. Less nucleophilic substrates such as alkyl halides are unreactive in these circumstances.

This rationalization of the mechanisms is fully consistent with the information now available on the enhanced reactivity of pentacoordinate organosilicon complexes such as  $\text{R}_3\text{SiF}_2^-$  towards nucleophiles, and the ample precedent which exists in the formation of



SCHEME 26

hexacoordinate complexes for the participation of similar intermediates and transition states in organosilicon chemistry.

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# Appendix to 'Hypervalent silicon compounds'<sup>†</sup>

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<sup>†</sup>The material in this Appendix is divided in the same manner as in the original chapter. The section numbers in the Appendix are preceded by an asterisk. The numbers of structures, equations, schemes, tables and references run continuously in the original chapter and in this Appendix.

## \*II. FORMATION

### \*A. Pentacoordinate Silicon Compounds

#### \*1. Anionic complexes

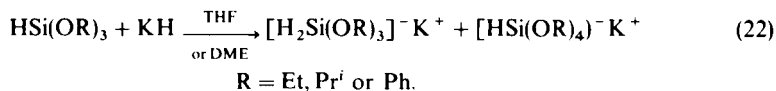
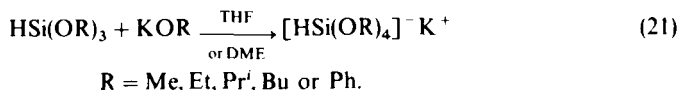
The observation that the formation and stability of pentacoordinate anionic silicates in solution is much enhanced in the presence of potassium ion complexed by 18-crown-6 ether as counterion has led to the characterization of many new fluoro-, alkoxy- and aryloxy-silicates, several of which have been obtained crystalline for X-ray diffraction studies.

The series of phenylmethoxysilicates,  $[\text{Ph}_n\text{Si}(\text{OMe})_{5-n}]^- \cdot [\text{K}^+, 18\text{-crown-6}]$  ( $n = 1-3$ ), which are formed in solution when potassium methoxide is mixed with the neutral methoxysilanes in the presence of 18-crown-6 ether, have been isolated<sup>183</sup> as white crystalline powders. They may be recrystallized from THF, but are air- and moisture-sensitive. In analogous reactions the salts of  $[\text{MeSi}(\text{OEt})_4]^-$ <sup>183</sup> and  $[\text{PhSi}(\text{OCH}_2\text{CF}_3)_4]^-$ <sup>184</sup> were similarly isolated, the former arising from aryl-silicon bond cleavage when  $\text{MePhSi}(\text{OEt})_2$  was treated with  $\text{EtO}^- \text{K}^+$  and 18-crown-6.

The formation of other acyclic pentacoordinate oxysilicates under similar conditions has generally been inferred from the upfield shift of the <sup>29</sup>Si NMR resonances. Species detected in this way include  $[\text{Si}(\text{OR})_5]^-$  ( $\text{R} = \text{Me, Et, Pr}^n, \text{Pr}^i, p\text{-Tol or CH}_2\text{CF}_3$ );  $[\text{R}'\text{Si}(\text{OR})_4]^-$  ( $\text{R}' = \text{Ph; R} = \text{Me, Et, } p\text{-Tol or CH}_2\text{CF}_3$  and  $\text{R}' = \text{vinyl; R} = \text{Et}$ );  $[\text{R}'_2\text{Si}(\text{OR})_3]^-$  ( $\text{R}' = \text{Ph; R} = \text{Et or CH}_2\text{CF}_3$ ); and  $[\text{Ph}_3\text{Si}(\text{OCH}_2\text{CF}_3)_2]^-$ . <sup>29</sup>Si chemical shifts are generally displaced to lower field as the number of alkoxy ligands decreases, but remain upfield of the corresponding resonance for the four-covalent compound. There was no evidence in these studies for the formation of hexacoordinate dianions<sup>184</sup>.

The penta-alkoxysilicates reacted readily with the diols pinacol and catechol. The latter gave only the  $[\text{Si}(\text{OC}_6\text{H}_4\text{O})_3]^{2-}$  ion but the former yielded bis(pinacolates)  $[(\text{Me}_4\text{C}_2\text{O}_2)_2\text{SiOR}]^- \cdot \text{K}^+$  (18-crown-6). The pinacolates could also be prepared from the spiro-silicate,  $(\text{Me}_4\text{C}_2\text{O}_2)_2\text{Si}$  and potassium alkoxide in the presence of 18-crown-6 ether, and as quaternary ammonium salts by the classical route<sup>13</sup> from tetra-alkoxy silane and pinacol in the presence of amine<sup>185</sup>. The molecular structures of some of these salts, the first penta-oxysilicates to be structurally characterized, are discussed in Section \*III.

Formation of potassium hydrosilicates,  $\text{K}^+ [\text{H}_n\text{Si}(\text{OR})_{5-n}]^-$  ( $n = 1, 2$ ), occurs in THF or DME, even in the absence of crown ether, from reaction of alkoxy (or aryloxy) silanes with potassium alkoxide (or aryloxy) (equation 21) or potassium hydride (equation 22) as appropriate<sup>186</sup>. The dihydrosilicates may undergo redistribution reactions which occur more readily in the order  $\text{R} = \text{Ph} > \text{Et} > \text{Pr}^i$ , and with increasing solvating power of the solvent,  $\text{THF} > \text{DME}$ .



A study<sup>187</sup> of the equilibrium (equation 23) in THF solution showed that the pentacoordinate cyanosilicate was formed to the extent of about 30% when  $\text{R} = \text{Me}$ , but was present in minimal concentration when  $\text{R} = \text{Pr}^i$  or  $\text{Bu}^i\text{O}$ . Evaporation of the



solvent in the case when R = Me gave crystalline  $\text{Bu}_4\text{N}^+[\text{Me}_3\text{Si}(\text{CN})_2]^-$ .

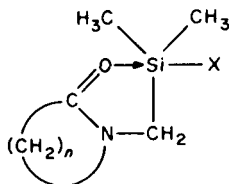


### \*III. STRUCTURE

#### \*A. Pentacoordinate Complexes

Chlorosilane has been found<sup>188</sup> to form a crystalline adduct with dimethyl ether at low temperature, in which oxygen and chlorine atoms occupy axial sites as expected. The silicon atom is displaced towards chlorine relative to the plane of the three hydrogen atoms, and the Si—Cl bond length is 2.14 Å, an increase of 0.09 Å over that of the isolated molecule in the gas phase.

The structures of an interesting series of halodimethylsilyl-piperidones and a pyrrolidone **90**–**92** related to **84**<sup>154</sup> have been published<sup>189–191</sup>. The Si—halogen and Si—O distances in these compounds (Table 8) clearly show that the heavier the halogen, the more readily is the bond lengthened on intramolecular coordination by oxygen. At the same time the Si—O separation decreases, so much so that in the iodo-derivative **84**, it is within 10% of the typical Si—O covalent bond length. The silicon–iodine distance is not far short of that expected for an ion pair involving an iodide ion and a silocation, and the constitution of the chelate is therefore best represented in this way.



(**90**)  $n = 3$  ;  $X = \text{F}$

(**91**)  $n = 4$  ;  $X = \text{Cl}$

(**92**)  $n = 4$  ;  $X = \text{Br}$

(**84**)  $n = 4$  ;  $X = \text{I}$

The above series provides a model for successive stages in bimolecular nucleophilic substitution at silicon; in the same way compound **93** shows<sup>192</sup> Si—O bond formation well advanced, and a long Si—Cl bond, whereas in compound **94**<sup>193</sup>, because of the electron-withdrawing character of the  $\text{CF}_3$  group, approach of the oxygen atom to the

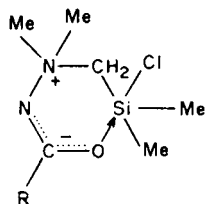
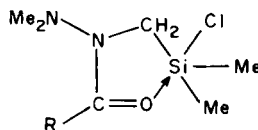
TABLE 8. Bond lengths to silicon in chelated piperidones and a pyrrolidone

Compound	Distances (Å)		Reference
	O—Si	Si—X	
<b>90</b>	2.394 (av)	1.652 (av)	189
<b>91</b>	1.954	2.307	190
<b>92</b>	1.800	3.122	191
<b>84</b>	1.749	3.734	154

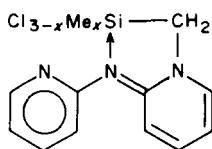
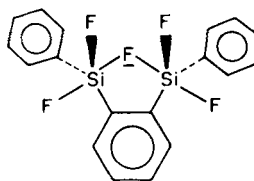
TABLE 9. Bond lengths to silicon in chelated (acylhydrazonium) methylsilanes

Compound	Distances (Å)		Reference
	O—Si	Si—Cl	
<b>93</b>	1.788	2.624	192
<b>94</b>	1.879	2.432	193

silicon is less close, and the Si—Cl bond correspondingly less stretched (Table 9). These compounds undergo isomerization on heating, forming chelates with five-membered rings (**95**).

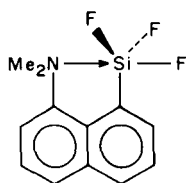
**(93)** R = 4-An**(94)** R = CF<sub>3</sub>**(95)**

In the 2-pyridone-(2'-pyridyl)imine derivatives, **96** and **97**, the Si—Cl(axial) bond of the SiMe<sub>2</sub>Cl group is considerably longer than the Si—Cl(axial) bond of the SiCl<sub>3</sub> derivative (Table 10)<sup>194</sup>. The disparity is in the same direction but considerably greater than that in the analogous derivatives of tetrahydropheanthroline, **33** and **35**.

**(96)** x = 2**(97)** x = 0**(98)**TABLE 10. Bond lengths to silicon in chelated 2-pyridone-(2'-pyridyl)imines<sup>194</sup>

Compound	Distances (Å)	
	N—Si	Si—Cl(axial)
<b>96</b>	1.898	2.598
<b>97</b>	1.901	2.238

The molecular structure of **64**<sup>195</sup> provides an interesting comparison with compounds **28–30** in that it displays a longer N–Si distance, more similar in fact to that in **31**.



(64)

N → Si	2.318 Å
F(ax) – Si	1.612 Å
F(eq) – Si	1.571 Å (av)

The crystal structures of several more organofluorosilicate ions as their  $K^+$ , 18-crown-6 salts have been determined by X-ray diffraction<sup>196–198</sup>. Mean bond lengths for the axial and equatorial Si–F bonds are shown in Table 11, and may be compared with those given in Table 1 (in most cases the axial bond lengths are unequal, due to the interaction of only one of the axial fluorine atoms with the cation). Detailed analyses of the structural data confirm that steric distortions are generally quite small, although there is a tendency for all bond lengths to increase with increasing steric bulk of the organic groups, as well as with diminishing number of electronegative atoms<sup>199</sup>. In the most extreme case of the 2,4,6-tri-*t*-butylphenyltetrafluorosilicate ion, however, the very large *ortho* substituents reduce the F(eq)–Si–F(eq) angle to only 107.1°, and the phenyl group is not rotated out of the equatorial plane as normally occurs, but is tipped up at an angle of nearly 14°.

A novel pentacoordinate complex  $[o-C_6H_4(SiPhF_2)_2F]^-$  (**98**), again as the  $K^+$ , 18-crown-6 salt, containing a fluoride ion chelated by two silyl groups, has been described<sup>200</sup>. In the crystalline solid, where the *cis* configuration only is found, the fluoride bridge is unsymmetrical and these axial Si–F distances (1.898 and 2.065 Å, respectively) are significantly longer than in the acyclic pentacoordinate silicates (Tables 1 and 11).

Crystal structures have been obtained<sup>184,185</sup> for the penta-alkoxysilicates  $[(Me_4C_2O_2)_2SiOR][BuNH_3]$ ; R = Me, Et and  $[(Me_4C_2O_2)_2SiOR']^-[K, 18-c-6]$ ; R' = Pr<sup>*i*</sup>, Bu<sup>*i*</sup>. The latter pair have structures close to the expected trigonal bipyramidal geometry, but the butylammonium salts, especially the methoxy derivative, tend more towards the square pyramid, with the acyclic group in the apical position. Such distortion is

TABLE 11. Si–F bond lengths in organofluorosilicate ions

Ion <sup>a</sup>	Si–F distances (Å)		Reference
	Axial	Equatorial	
MeSiF <sub>4</sub> <sup>–</sup>	1.672 (av)	1.606 (av)	196
TTBPSiF <sub>4</sub> <sup>–</sup>	1.676 (av)	1.622 (av)	196
( <i>o</i> -Tol) <sub>2</sub> SiF <sub>3</sub> <sup>–</sup>	1.701 (av)	1.640	197
(Mes) <sub>2</sub> SiF <sub>3</sub> <sup>–</sup>	1.703 (av)	1.641	198

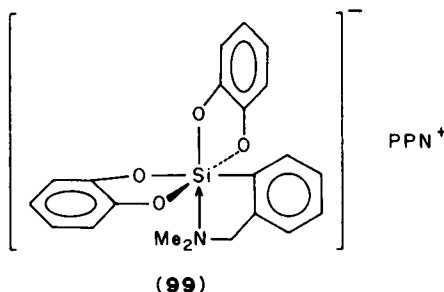
<sup>a</sup>Mes = 2,4,6-trimethylphenyl; TTBP = 2,4,6-tri-*t*-butylphenyl.

uncommon amongst *saturated* cyclic compounds of this type, and may be attributed to extensive hydrogen-bonding to the N—H containing cation.

### \*C. Hexacoordinate Complexes

Structural details for compounds **56**, **57** and **58** have now been published<sup>201</sup>. Si—N separations range from 2.6 to 2.8 Å (Table 12), somewhat longer than in the pentacoordinate complexes with the same ligands. In the fluorohydride **57**, the Si—N distances are very similar, and at the shorter end of the range. In the dihydride **56**, the Si—N distances are 2.61 and 2.80 Å, and the Si—H bonds are also of unequal length. The shorter Si—N bond is that *cis* to both hydrogens, and the shorter Si—H bond is that *cis* to both NMe<sub>2</sub> groups. In the difluoride **58** two distinct molecular conformations are revealed, both having unequal Si—N separations. In one conformation it is the NMe<sub>2</sub> group of the naphthyl ligand which is closer to the silicon atom, and in the other the NMe<sub>2</sub> group of the benzyl ligand.

The establishment of hexacoordination in these molecules has been followed by other studies to explore the relationship between 5- and 6-coordinate species. The crystal structure of compound **99** (cf. **27**) showed<sup>202</sup> the Si atom to be hexacoordinate with an almost regular octahedral geometry. The Si—N separation in this molecule at 2.15 Å is the shortest yet found for coordination of the ligand to silicon. Such a strong interaction is entirely consistent with the high reactivity towards nucleophiles found for **27**<sup>130</sup>.



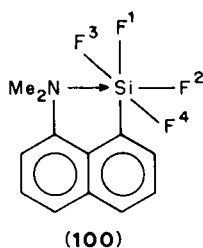
PPN<sup>+</sup> = bis(triphenylphosphoranylidene) ammonium

TABLE 12. Bond lengths to silicon in hexacoordinate chelates<sup>201</sup>

Compound	Distances (Å)		
	Si—H	Si—F	Si—N
<b>56</b>	1.44		2.61
	1.54	—	2.80
<b>57</b>			2.68
	1.55	1.63	2.65
<b>58</b> <sup>a</sup>		1.62	2.77 (Naph-N)
		1.60	2.59 (Benzyl-N)
		1.60	2.66 (Naph-N)
		1.60	2.81 (Benzyl-N)

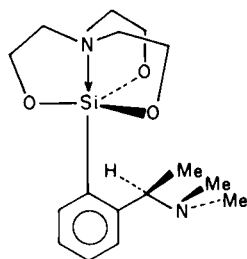
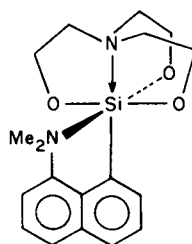
<sup>a</sup>Two distinct molecular conformations in the crystal.

The same phenomenon is apparent in the comparison of the molecular structure of **100** with that of **64**. The anion displays<sup>203</sup> a shorter Si-N distance than the neutral chelate, 2.213 Å compared with 2.303 Å (av), even though the Si-F bonds are slightly longer in the anion, as expected following an increase in coordination number<sup>92</sup>. The short Si-N distances in these anionic hexacoordinate species are thus all the more striking.



N → Si	2.213 Å
F <sup>1</sup> - Si	1.669 Å
F <sup>2</sup> - Si	1.653 Å
F <sup>3</sup> - Si	1.669 Å
F <sup>4</sup> - Si	1.682 Å

Contrasting behaviour to that described above is however shown in the silatrane series. Silatranes **101** and **102**, containing the (1-dimethylaminoethyl)phenyl and dimethylaminonaphthyl ligands, respectively, were prepared and their crystal structures elucidated<sup>204</sup>. In the first, the benzyl-bound nitrogen atom was found to be too far distant from any silicon atom for either intra- or intermolecular interaction to be present. In the second compound, the rigidity of the ligand again imposes relative proximity of the naphthylamine nitrogen atom to the silicon atom but the distance (2.95 Å) is greater than any other analogous distance yet determined, and is accompanied by severe distortion of the naphthalene nucleus and a non-classical geometry of the six nearest neighbours around the silicon atom. The <sup>1</sup>H and <sup>29</sup>Si NMR spectra of **101** gave no evidence for hexacoordination in solution, and it is therefore clear that the silatrane structure is exceptionally resistant to further coordination, in accord with the low reactivity towards nucleophiles (Section \*V.D.2).

**(101)****(102)**

## \*IV. DYNAMIC STEREOCHEMISTRY

Further studies by Damrauer and coworkers<sup>205</sup> and by Holmes and coworkers<sup>196,197</sup> have confirmed, by the persistence of  $^{29}\text{Si}$ - $^{19}\text{F}$  coupling in both the  $^{29}\text{Si}$  and  $^{19}\text{F}$  DNMR spectra, the intramolecular nature of the permutational isomerization of pentacoordinate organofluorosilicates. It appears that energy barriers for this process are more reliably represented by free energies of activation, since activation energies, and enthalpies or entropies of activation, are subject to considerable experimental uncertainty<sup>205</sup>. It is apparent from the values for  $\Delta G^\ddagger$  collected in Table 13 that energy barriers to the fluxional exchange of fluoride ligands mostly fall in the range 9–12 kcal mol<sup>-1</sup>. Steric effects are therefore generally small, and not always in the same direction; thus entries 2 and 5, or 4 and 6, where the more crowded ion has the lower energy barrier, can be contrasted with entries 5, 9 and 10, which show a definite increase in the energy barrier resulting from the presence of two *ortho* methyl substituents on the phenyl group. (One *ortho* methyl group seems to be of little consequence; see entries 3 and 5, 8 and 9.) Electronic effects as discussed previously (Section IV) are clearly responsible for the reduction of the barrier on the introduction of the *p*-nitro groups (entry 1).

Steric influences are also evident in the behaviour of the 2,4,6-tri-*t*-butylphenyl-tetrafluorosilicate ion, which is the only one in the  $\text{RSiF}_4^-$  series so far described for which fluoride exchange is sufficiently slowed at low temperatures for the resonances due to axial and equatorial fluorine atoms to be distinguished. The relatively large barrier found for this structure results both from the closing of the angle between the equatorial fluorine atoms in the ground-state structure (Section \*III.A) in the direction opposite to that involved in the Berry pseudorotational motion, and from the necessity for real rotation of the bulky organic group to accompany the pseudorotation of the fluorine substituents.

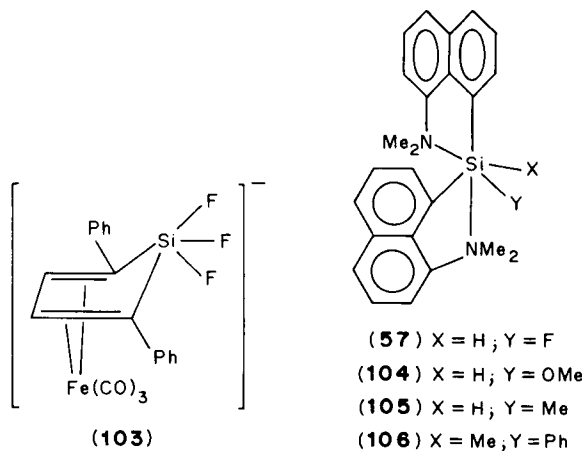
The cyclic derivatives  $(\text{CH}_2)_4\text{SiF}_3^-$  and  $(\text{CH}_2)_5\text{SiF}_3^-$  provide additional evidence that fluxional exchange in pentacoordinated silicon compounds is subject to lower activation barriers than in the analogous phosphorus compounds. Thus positional exchange in  $(\text{CH}_2)_5\text{SiF}_3^-$ , as observed in the  $^{19}\text{F}$  NMR spectrum at 282.2 MHz, is fast at  $-3^\circ\text{C}$ , but separate signals for one equatorial and two axial fluorine atoms become visible at  $-77^\circ\text{C}$ , and are sharp at  $-117^\circ\text{C}$ <sup>197</sup>. For the phosphorane  $(\text{CH}_2)_5\text{PF}_3$  only the ground-state structure, also with the ring diequatorial, is seen up to  $+100^\circ\text{C}$ <sup>71</sup>. Similarly

TABLE 13. Free energies of activation for intramolecular rearrangement of acyclic organofluorosilicates

Entry	Ion	$\Delta G^\ddagger$ (kcal mol <sup>-1</sup> )	Reference
1	(4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> SiF <sub>3</sub> <sup>-</sup>	8.8	205
2	Naph <sub>2</sub> SiF <sub>3</sub> <sup>-</sup>	9.3	205
3	2-Tol <sub>2</sub> SiF <sub>3</sub> <sup>-</sup>	9.9	205
4	PhBu <sup>t</sup> SiF <sub>3</sub> <sup>-</sup>	10.4	205
5	Ph <sub>3</sub> SiF <sub>3</sub> <sup>-</sup>	10.6	205
6	PhMeSiF <sub>3</sub> <sup>-</sup>	10.7	205
7	4-Tol <sub>2</sub> SiF <sub>3</sub> <sup>-</sup>	10.7	205
8	2-Tol-(2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> )SiF <sub>3</sub> <sup>-</sup>	11.3	205
9	Ph-(2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> )SiF <sub>3</sub> <sup>-</sup>	11.4	205
10	(2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> SiF <sub>3</sub> <sup>-</sup>	13–14	205
11	2,4,6-Bu <sub>3</sub> C <sub>6</sub> H <sub>2</sub> SiF <sub>3</sub> <sup>-</sup>	12.8 <sup>a</sup>	196

<sup>a</sup> $E_a$  value.

the fluorosilicate  $(\text{CH}_2)_4\text{SiF}_3^-$  still displays fast exchange at  $-70^\circ\text{C}$ , whereas the coalescence of the fluorine resonances occurs at this temperature for  $(\text{CH}_2)_4\text{PF}_3$ . The iron tricarbonyl complexed diphenylbutadienylene trifluorosilicate **103** also displays<sup>206</sup> a sharp singlet in the  $^{19}\text{F}$  NMR spectrum down to  $-105^\circ\text{C}$ , indicating permutational isomerization with an energy barrier of less than  $6\text{ kcal mol}^{-1}$ .



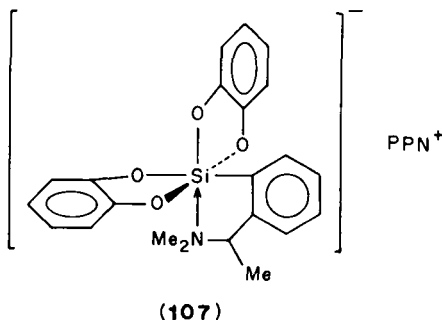
The  $^1\text{H}$  NMR spectra for the hexacoordinate compound **57** and for the related compounds **104–106** show<sup>207</sup> that they retain in solution the structure depicted, as found for **57** in the solid state<sup>201</sup>. These compounds are also fluxional; at low temperatures the two ligands appear in diastereotopic relationship for both the naphthyl and the  $\text{NMe}_2$  moieties and stereomutation is revealed at higher temperatures by coalescence of the naphthyl proton resonances, and by reduction of the four  $N$ -methyl resonances to two. Saturation transfer techniques confirm that hexacoordination is maintained, notably even when the silicon atom is bound only to carbon (apart from the coordinated nitrogen atoms) (**106**). The free energies of activation for this regular stereoisomerization range from  $9.3$  to  $15.2\text{ kcal mol}^{-1}$  (Table 14), i.e. values which are comparable with those found for some pentacoordinate complexes of the same ligand (Table 7).

The  $^1\text{H}$ DNMR spectrum of compound **99** does not display<sup>202</sup> the expected diastereotopy of the  $\text{NMe}_2$  group, even at  $-100^\circ\text{C}$ . As in the case of the pentacoordinate compounds (Section IV) this may result either from a non-dissociative stereoisomerization or from ring opening and inversion at the nitrogen atom. The introduction of the chiral carbon atom adjacent to the  $\text{NMe}_2$  group in compound **107** revealed at low temperature

TABLE 14. Free energies of activation for stereoisomerization of hexacoordinate silicon chelates<sup>207</sup>

Compound	$\Delta G^\ddagger$ (kcal mol $^{-1}$ ) (at 300 K)
<b>57</b>	14.7
<b>104</b>	15.2
<b>105</b>	9.3
<b>106</b>	12.7

diastereotopic methyl groups arising from this chirality, with a coalescence temperature of  $-58^{\circ}\text{C}$ , and a free energy of activation for Si—N bond breaking of  $10.25\text{ kcal mol}^{-1}$ . Again there was no sign of a coalescence below this temperature resulting from chirality of the hexacoordinate silicon atom, and it is clear that both **99** and **107** undergo intramolecular stereoisomerization with a very low energy of activation<sup>202</sup>.



## \*V. REACTIONS OF HYPERVALENT SILICON COMPOUNDS

### \*A. Protonolysis of Hypervalent Silicon Compounds

In an analogous reaction to the loss of the phenyl group in the formation of  $\text{MeSi}(\text{OEt})_4^-$  from  $\text{MePhSi}(\text{OEt})_2$ <sup>183</sup>, the formation of  $\text{Ph}_3\text{Si}(\text{OCH}_2\text{CF}_3)_2^-$  was found<sup>184</sup> to be accompanied always by  $\text{Ph}_2\text{Si}(\text{OCH}_2\text{CF}_3)_3^-$ . Other instances of similar Si—C bond cleavage in pentacoordinate fluorosilicates seem to be linked to steric strain in the anion. Attempted preparations of the  $\text{K}^+$ , 18-crown-6 complexes of  $\text{Bu}^t_2\text{SiF}_3^-$  and *cyclo*  $(\text{CH}_2)_3\text{SiF}_3^-$  led only to the formation of  $\text{Bu}^t\text{SiF}_4^-$ <sup>197</sup> and  $\text{PrSiF}_4^-$ <sup>196</sup>, respectively. Decomposition of  $\text{Xyl}_2\text{SiF}_3^-$ <sup>205</sup> and of  $\text{Mes}_2\text{SiF}_3^-$ <sup>198</sup> with loss of one of the organic groups also occurs on warming. This behaviour can be correlated with the relatively long bonds, as determined from the crystal structures. Other aspects of hydrolysis of dimesityltrifluorosilicate ion are discussed further in Section \*V.D.1.

### \*D. Reactivity of Pentacoordinate Organofluorosilicates and Alkoxylicates

#### 1. Acyclic anions

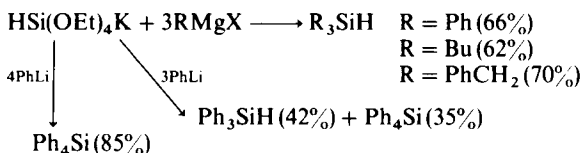
The greatly enhanced reactivity towards nucleophiles of pentacoordinate organofluorosilicates compared with neutral tetravalent fluorosilanes has been confirmed in a study of the hydrolysis of  $\text{Mes}_2\text{SiF}_2^-$ <sup>198</sup>. This compound does not react with water, even under extended reflux in acetonitrile, but rapid reaction ensues when tetraethylammonium fluoride hydrate is introduced. Hydrolysis of  $[\text{Mes}_2\text{SiF}_3^-][\text{K}, 18\text{-c-6}]$  in aqueous acetone is also extensive after five minutes. The same silicon-containing products are formed in the two hydrolytic procedures, namely the disiloxane  $(\text{Mes}_2\text{SiF})_2\text{O}$  and a bisilicate  $[\text{Mes}_2\text{Si}(\text{F})\text{O}]_2\text{H}^-$ . The tetraethylammonium salt of the latter was analysed by X-ray diffraction, which showed the presence of a hydrogen bridge between the two oxygen atoms. It was concluded that this species represented an intermediate in the hydrolysis pathway from  $\text{Mes}_2\text{SiF}_3^-$  to  $(\text{Mes}_2\text{SiF})_2\text{O}$ .

These findings complement studies<sup>208</sup> of the hydrolyses of pentacoordinate alkoxylicates and hydridoalkoxylicates which also suggest that active intermediates of this

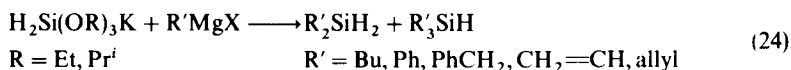


type are involved in the conversion of alkoxy silanes to siloxanes, such as occurs in the sol-gel process. In the reaction of  $[(\text{EtO})_5\text{Si}]^- [\text{K}^+, 18\text{-c-}6]$  with water, the gelation time was found to be eleven minutes, compared to the several days required for gel formation from  $\text{Si}(\text{OEt})_4$  in water. Analogous studies of the hydrolysis of the hydrosilicates,  $[\text{HSi}(\text{OR})_4]^- \text{K}^+$  ( $\text{R} = \text{Me, Et, Pr}^i, \text{Ph}$ ), showed hydrogen gas to be evolved rapidly and gelation times much shorter than for the tetravalent  $\text{HSi}(\text{OR})_3$  compounds. Reaction of the hydrosilicates with alcohol, rather than water, similarly gives rapid displacement of hydrogen, but does not proceed beyond the formation of  $\text{Si}(\text{OR})_5^-$ .

Grignard reagents readily yield the triorganosilanes; phenyllithium leads to triphenyl- and tetraphenyl-silanes (Scheme 27)<sup>186a,c</sup>. Dihydrosilicates  $\text{H}_2\text{Si}(\text{OR})_3^- \text{K}^+$  react similarly with Grignard reagents to give mainly diorganosilane, but with some triorganosilane (equation 24)<sup>186b</sup>. The formation of pure diallyl- and divinyl-silanes<sup>208</sup>, albeit in relatively modest yield (55% and 31%, respectively), is of interest in that these two diorganosilanes are difficult to obtain in a pure state by other routes.

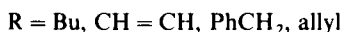
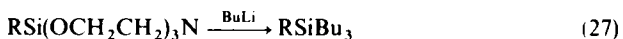
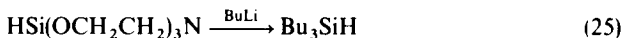


SCHEME 27



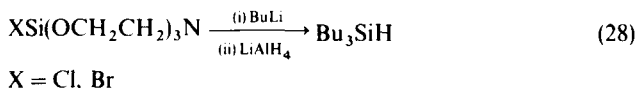
## 2. Silatranes

In contrast to the high reactivity of the derivatives described above, further investigations<sup>209</sup> of silatrane and its derivatives have confirmed the generally unreactive nature<sup>133</sup> of the compounds having this basic structure. Reaction of silatrane **74** with butyllithium gives tributylsilane only (equation 25), even with a deficiency of the organometallic reagent. The initial attack is thus rate-determining, and a silicon-oxygen bond is cleaved. In the presence of 12-crown-4 ether the reaction proceeds much more easily; direct nucleophilic attack on silicon is therefore involved, and coordination of the silatrane nitrogen atom to the lithium cation is not implicated. Aryl, but not alkyl, silatranes are reduced by lithium aluminium hydride to the arylsilane (equation 26), but butyllithium converts both aryl and alkyl silatranes to the corresponding tetraorganosilane (equation 27).



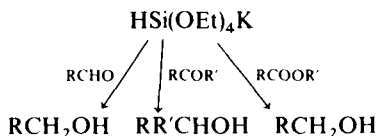
Chloro- and bromo-silatranes react with butyllithium and, after reduction with lithium aluminium hydride, tributylsilane is again obtained, even in the presence of an excess

of butyllithium (equation 28). This again implies that the initial substitution is of a silicon–oxygen bond and not the silicon–halogen bond, the reverse of the normal situation. The low reactivity of the halogenosilatrane reflects an exceptional situation in which the Si–N coordinate bond is quite short, 2.023 Å in chlorosilatrane<sup>23</sup>, while the Si–Cl bond is relatively little extended (length 2.12 Å) by comparison with other intramolecular chelates; e.g. compound **35**, Si–N, 2.028 Å, and Si–Cl, 2.269 Å<sup>79</sup>. In addition, attack of the nucleophile is necessarily *cis* to the Si–Cl bond, but *trans* to the inherently less reactive Si–O bond.

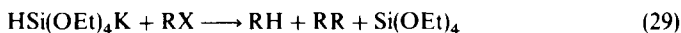


#### \*F. Pentacoordinate Silicon Hydrides as Reducing Agents

The isolated hydridoethoxysilicate  $[\text{HSi}(\text{OEt})_4]^- \text{K}^+$  was found<sup>186c,210</sup> to reduce aldehydes, ketones and esters effectively at room temperature or below (Scheme 28). No such reaction occurs with triethoxysilane; both the enhanced hydridic character of the hydrogen atom and the Lewis acidity of the silicon atom in the pentacoordinate anion account for the latter's reactivity (cf. Scheme 20). In reactions with alkyl halides, reduction to the alkane occurred in 30–50% yield, bromides being more reactive than chlorides. Benzyl or diphenylmethyl halides, however, gave predominantly the dimeric reduction product (equation 29 and Table 15). These findings suggest that a SET (single electron



SCHEME 28

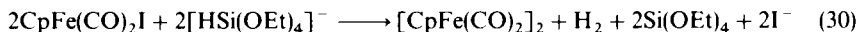


transfer) mechanism may be operating, at least in the latter cases. This interpretation is supported by the observations that reaction of the hydridosilicate with bromotriphenylmethane gave an intensely red-coloured solution, which displayed the ESR spectrum of the trityl radical. Other reactions characteristic of SET occurred with *p*-dinitrobenzene and  $\text{CpFe}(\text{CO})_2\text{I}$  (equation 30), but 6-bromo-1-hexene gave only a very small yield of methylcyclopentane, the product which is diagnostic of formation of the 5-hexen-1-yl radical<sup>186c,210</sup>.

TABLE 15. Yields of reduction products from reaction of organic halides RX with  $\text{HSi}(\text{OEt})_4^- \text{K}^+$

R	X	RH (%)	RR (%)
$\text{C}_{12}\text{H}_{25}$	Cl	33	—
$\text{C}_{12}\text{H}_{25}$	Br	47	—
$\text{PhCH}_2$	Br	20	30
$\text{Ph}_2\text{CH}$	Cl	12	40

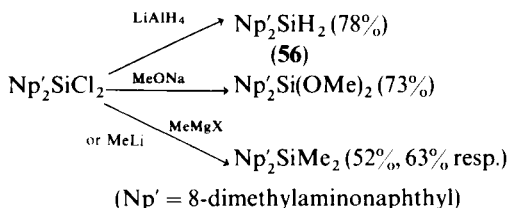
The dihydrosilicate  $[\text{H}_2\text{Si}(\text{OPr}^i)_3]^- \text{K}^+$  was also found<sup>186b</sup> to be an efficient reducing agent for aldehydes and ketones. Both hydrogen atoms are utilized, probably in two successive steps (Scheme 29).



SCHEME 29

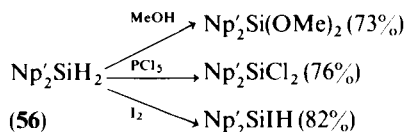
### G. Reactivity of Hexacoordinate Complexes

The chemistry of silane **56** and the analogous dichloro- and difluoro-silanes has been investigated<sup>211</sup>. The pattern of reactivity which they display is quite different from those observed for the corresponding four- or five-coordinate compounds. The difluoro compound is apparently totally inert to attack by nucleophilic reagents, but the dichloro compound is readily substituted (Scheme 30). The two halides have analogous structures, with the functional groups *cis*, and an  $\text{NMe}_2$  group *trans* to each halogen, and the pronounced difference in reactivity may possibly be due to easier dissociation of the Si—Cl bond compared to Si—F, as is observed in the pentacoordinate series. In the latter series, however, the fluorides are very reactive because of the possibility of associative substitution mechanisms.

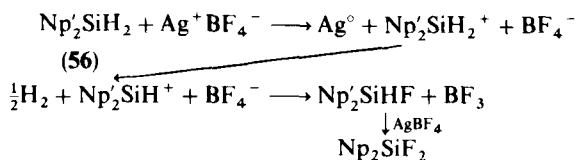


SCHEME 30

The reactivity of the dihydrogenosilane **56** is different again (Scheme 31). Reaction with hydroxyl-containing compounds is rapid and allows, for example, the synthesis of the alkoxy derivatives. Iodination occurs on treatment with iodine, and chlorination with  $\text{PCl}_5$ . These reactions probably proceed by electrophilic attack on hydrogen, since no reaction is observed for **56** with nucleophiles such as organometallic reagents, nor with carbonyl groups, both classes which react with pentacoordinate dihydrides. Alkoxide ions also do not react. **56** is susceptible to attack by oxidizing agents; in particular, reaction with  $\text{AgBF}_4$  leads to stepwise replacement of fluorine with precipitation of silver, probably via initial one-electron transfer (Scheme 32).

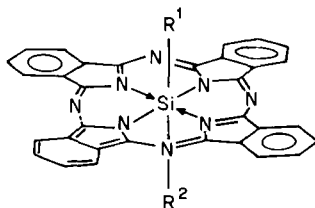


SCHEME 31



SCHEME 32

The chemistry of diorgano(phthalocyaninato)silicon compounds (**108**) has also been studied<sup>212</sup> and compared with that of the organopentafluorosilicates (Section V.B). Allyl silicon bonds in **108** are cleaved by NBS, halogens and copper(II) halides, but the aryl silicon bonds are reactive only towards the first two reagents. The sequence of reactivity with respect to NBS cleavage is  $4\text{-MeOC}_6\text{H}_4 > n\text{-C}_8\text{H}_{17} > \text{Ph} \gg 3\text{-CF}_3\text{C}_6\text{H}_4$ . One-electron transfer is again indicated as the initial step in alkyl-silicon fission, but aryl-silicon fission is probably initiated by electrophilic attack on the aryl moiety—hence the high reactivity of the  $4\text{-MeOC}_6\text{H}_4$  derivative.

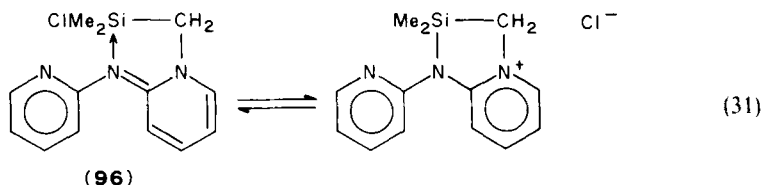


(108)

## \*VI. HYPERVALENT INTERMEDIATES IN CATALYSED REACTIONS

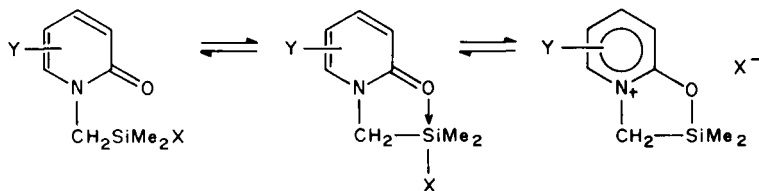
### \*A. Solvolysis and Racemization of Organosilicon Halides

A number of significant studies have been made of the behaviour in solution of compounds which may undergo intramolecular coordination leading ultimately to ionization, complementing the crystallographic studies described in Section \*III.A. Bassindale has made a systematic study<sup>213</sup> of the pyridone system **109** and, by comparison of the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  spectra of the compounds in solution with those of reference compounds **110** and **111**, has determined how the nature of X and Y influence the position of the equilibrium. Leaving group ability was found to fall in the order  $\text{X} = \text{CF}_3\text{SO}_3 > \text{Br} > \text{Cl} > \text{F} > \text{OR}$ , and the equilibrium moved to the right as Y became more electron-supplying. In a similar way compounds **96** and **97** were both found<sup>194</sup> to be pentacoordinate in  $\text{CDCl}_3$  solution at ambient temperature, but **96** only suffered reversible ionization on cooling (equation 31).

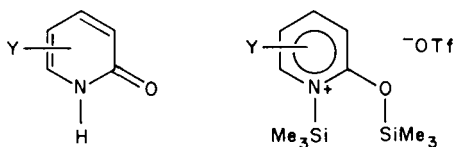


(96)

(31)



(109)



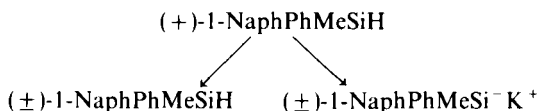
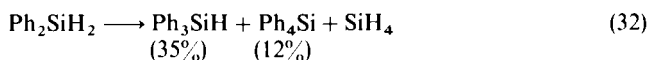
(110)

(111)

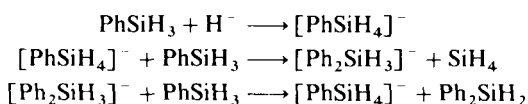
### \*B. Activation by Nucleophiles of Reactions of Silyl Derivatives in Organic Synthesis

#### \*1. Activation of the Si—H bond

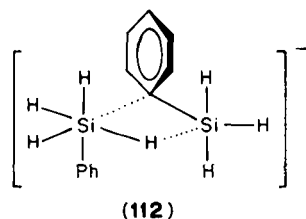
Di- and trihydrogenosilanes,  $RR'SiH_2$  and  $RSiH_3$  ( $R$  = aryl, allyl or benzyl;  $R'$  = alkyl or aryl), readily disproportionate in the presence of metallic hydrides ( $LiAlH_4$ ,  $KH$  or  $NaH$ ) as catalysts, e.g., equation 32<sup>214</sup>. This reaction is probably similar to that which results in the formation of  $[HSi(OR)_4]^-$  from  $HSi(OR)_3$  and  $KH$ , and a mechanism involving pentacoordinate hydrosilicates, rather than proton abstraction by hydride ion, is favoured. This mechanism is supported by the observation<sup>215</sup> that optically active 1-NaphPhMeSiH is rapidly racemized by hydrides at room temperature, whereas the formation of the silyl anion requires heating for a prolonged period (Scheme 33). The steps in the disproportionation of  $PhSiH_3$  are shown in Scheme 34. The migration of the phenyl group between  $[PhSiH_4]^-$  and  $PhSiH_3$  could possibly occur through a process involving a bridged dimer (112) with concerted interchange of phenyl and hydrogen.



SCHEME 33

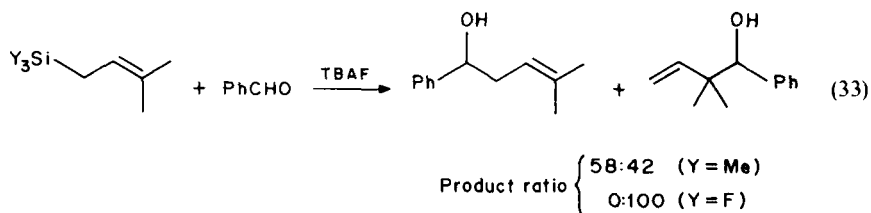


SCHEME 34

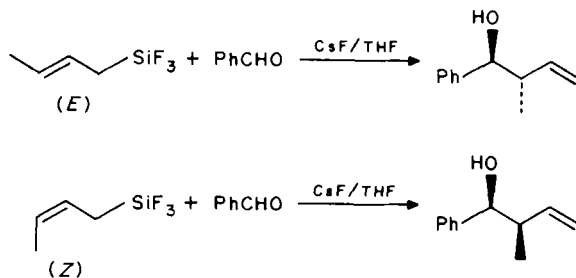


### \*2. Activation of the Si-allyl bond

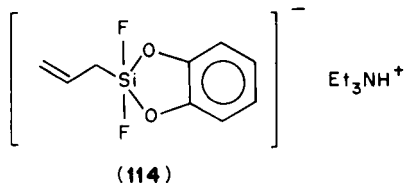
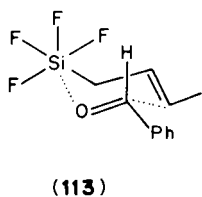
Sakurai has reviewed<sup>216</sup> his recent work on the reaction of pentacoordinate allylic silicates. It has now emerged that while the reaction of  $\text{Me}_2\text{C}=\text{CHCH}_2\text{SiF}_3$  with benzaldehyde in the presence of a catalytic amount of tetrabutylammonium fluoride (TBAF) is regiospecific, the analogous reaction of  $\text{Me}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$  is not (equation 33). The mechanisms of allyl transfer from the trimethylsilyl derivatives is thus still in doubt; indeed, further evidence<sup>217</sup> has been presented that free allyl ion is not released in the reaction with activated alkenes, catalysed by CsF (equation 34).



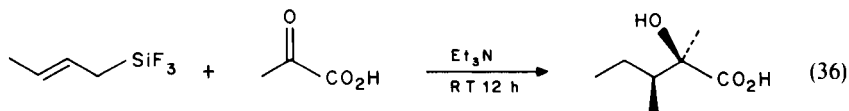
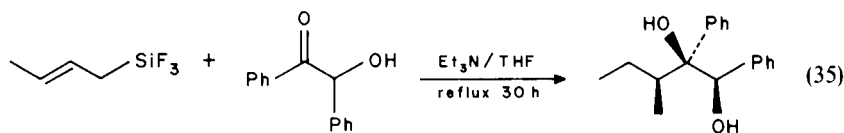
The intermediacy of pentacoordinated allylfluorosilicates in the reaction of allyltrifluorosilanes seems, however, to be firmly established, since reaction is then not only regiospecific, but in appropriate cases diastereoselective as well (Scheme 35)<sup>218</sup>. This stereospecificity may be rationalized by a cyclic transition state (113) in which the phenyl group is preferentially placed axially. The Lewis acidity of the pentacoordinated silicon atom is an essential feature of the stabilization of this transition state.



SCHEME 35



An alternative way of promoting allyl transfer to aldehydes is to treat the allyltrifluorosilane with a dihydroxy compound (e.g. catechol) and triethylamine<sup>219</sup>. A silicate of type **114** is suggested as the reactive intermediate; the system reacts with linear, but not with  $\alpha$ -branched, alkanals, and with benzaldehyde, and thus lies between allyltrifluorosilicate and allyl bis(benzene-1,2-diolato)silicate in reactivity. This reaction, which is also highly diastereoselective, may be carried out in the presence of water. Other stereoselective allylation reactions of  $\alpha$ -hydroxy ketones and  $\alpha$ -oxocarboxylic acids can be accomplished (equations 35 and 36). It should also be noted that, in the presence of nucleophiles, allylsilatrane does not react at all with carbonyl compounds<sup>176</sup>.



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# Siloxane polymers and copolymers

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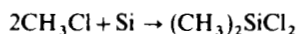
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## I. INTRODUCTION

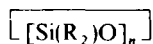
The starting materials for the manufacture of diorganopolysiloxanes are the diorganodichlorosilanes. Dimethyldichlorosilane, which is the most important one, is made industrially by the Rochow process from methyl chloride and silicon metal in the presence of a copper catalyst at 250–300 °C.



The process is run in a mode which optimises the yield of  $\text{Me}_2\text{SiCl}_2$  which is generally formed in 70–90% yield. Other primary products formed in the process are  $\text{MeSiCl}_3$ ,  $\text{Me}_3\text{SiCl}$ ,  $\text{MeHSiCl}_2$  and  $\text{Me}_2\text{HSiCl}$ . The by-products formed in the process, viz. mixed methylchlorosilanes, bis(methylchlorosilyl)methanes and a variety of hydrocarbons, are of no immediate commercial value. An extensive fractionation scheme is employed industrially to separate these methylchlorosilane fractions in high purity since the properties of the polydimethylsiloxanes (PDMS) are very sensitive to trace impurities in the chlorosilanes from which they are made. Phenylmethyldichlorosilane is manufactured from  $\text{MeSiCl}_3$  by a Grignard process. Diphenyldichlorosilane is made either directly by a

variation of the Rochow process using chlorobenzene, or as a co-product in the manufacture of phenyltrichlorosilane. Other mixed methylchlorosilanes ( $\text{MeRSiCl}_2$ ) are made from  $\text{MeHSiCl}_2$  and the appropriate alkene using a variation of Speier's Catalyst ( $\text{H}_2\text{PtCl}_6$  in isopropanol) or from (3-chloropropyl)methylchlorosilane using conventional organic reactions to convert the alkyl chloride to the required functional group.

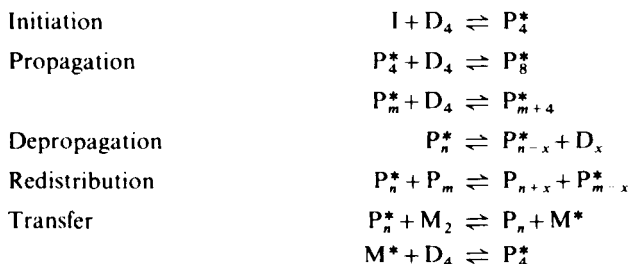
The cyclodiorganopolysiloxanes



are one of the two principal classes of siloxane intermediates used in the manufacture of siloxane polymers. The other class is that of the short chain linear  $\alpha,\omega$ -polydisiloxanols.



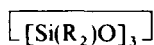
Both are formed simultaneously by hydrolysis of the appropriate diorganodichlorosilane. Ring opening polymerization of the cyclosiloxanes which can be effected by both basic and acidic catalysts produces high-molecular-weight linear polymers. Molecular weight control is obtained by the use of hexaorganodisiloxanes  $\text{R}_3\text{SiOSiR}_3$  which act as chain transfer agents. The process with both catalyst systems is a complex equilibrium polymerization and comprises a series of competing reactions involving both cyclic and linear species as represented below for octamethylcyclotetrasiloxane ( $\text{D}_4$ ) and hexamethyldisiloxane ( $\text{M}_2$ ).



Here  $\text{P}_m^*$  is the living  $m$ -meric polymer terminated in either a cationic or an anionic active centre.

The conversion of cyclosiloxanes to polysiloxanes takes place without the formation of any new type of chemical bonds and since the siloxane bond energy in the cyclic compound is generally the same as that in the polymer, the reactions are thermodynamically controlled through entropy changes. Thus, factors that control the configurational entropy of the cyclosiloxane ring, such as the size of the organic groups attached to silicon and the size of the ring itself, also influence the rate of polymerization and the position of equilibrium.

The cyclotrisiloxanes



constitute a special class of siloxane monomers. The siloxane bond in these monomers is far more reactive to both basic and acidic catalysts than that in the cyclotetrasiloxanes or in the polysiloxane. Hence polymerization conditions can be chosen so that the rates of the depolymerization and redistribution reactions are negligibly small compared to the

rate of polymerization. Under these conditions the complexity of the polymerization is much reduced.

The polydimethylsiloxanes are the most widely used siloxane polymers since they are stable and inert towards heat, chemicals and UV radiation, they have low surface tensions and their physical properties are relatively insensitive to temperature changes over the temperature range  $-50^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ . These properties result from the electronic and structural properties of the silicon-oxygen and silicon-carbon bonds which impart to the macromolecule its specific physical, chemical and mechanical properties. Keeping the siloxane backbone intact and substituting methyl groups along the chain or at the chain-end by a different inorganic or organic group generates a wide variety of new polysiloxane molecules. As a consequence the properties of the polymer change slightly and often genuinely new properties appear. Phenyl groups alter the crystallinity of the polymer, improving its mobility at low temperatures. Trifluoropropyl groups reduce the swelling of polysiloxanes in solvents. Organofunctional groups impart chemical reactivity to the polymer and alter its behaviour at interfaces.

Polysiloxanes containing both  $\text{Me}_2\text{SiO}$  and  $\text{MeRSiO}$  units are copolymers and they can be classified in several different ways depending on the structure and the microstructure of the different siloxane units<sup>1</sup>. *Linear chain copolymers*  $\text{MD}_n\text{M}$  comprise linear polymers where M and D units may be replaced wholly or partially by  $\text{M}^x$ ,  $\text{M}^{x,y}$ ,  $\text{M}^{x,y,z}$  and by  $\text{D}^x$ ,  $\text{D}^{x,y}$  units, respectively. *Branched chain copolymers* are linear chains containing T,  $\text{T}^x$  or Q units as branching centers. (M, D, T and Q represent mono, di, tri and tetra functional structural units. Those units where one or more methyl groups have been replaced by another group X, Y or Z are identified by the use of superscripts  $\text{M}^{xyz}$ ,  $\text{D}^{xy}$ ,  $\text{T}^x$  etc.) This classification based on M, D, T and Q structural units gives the macrostructure of the siloxane copolymer. The way in which the individual silicon atoms containing different substituents are arranged in the polymer describes the microstructure of the copolymer. In the simplest case of a linear chain copolymer of infinite length made up from two different siloxane units (A and B), three microstructures may be distinguished:

*Random copolymers* where the two monomers in the chain are statistically distributed:

-AAABABBABABBBABAABBBABABAABAABBABAAAABABABB-

This is the most thermodynamically favoured situation.

*Alternating copolymers* where the two monomers alternate along the chain:

-ABA-

Due to the nature of the siloxane bond this situation is rarely encountered.

*Block copolymers* where each monomer forms relatively long sequences which are linked together:

-AAAAAAAAAABBBBBBBAAAAAAAAAABBBBBBBBBBAAAAAAAAA-

Knowledge of the polymerization and copolymerization of cyclosiloxanes and the structure-property relationships of polysiloxanes. Such knowledge in the areas of polymer stability, reactivity and surface activity is of prime importance in the industrial application of polysiloxanes.

## II. RING-CHAIN EQUILIBRIA IN THE SILOXANE SYSTEM

In their pioneering work on the kinetics of the base catalysed polymerization of octamethylcyclotetrasiloxane ( $\text{D}_4$ ) Grubb and Osthoff<sup>2</sup> concluded that the rate of

polymerization of  $D_4$  was governed by competing polymerization and depolymerization reactions (equation 1).



However, it was Scott<sup>3</sup> who first measured the equilibrium concentration of  $D_4$  and  $D_5$  and postulated the participation of  $D_6$ ,  $D_7$  and  $D_8$  in the equilibrium process. Carmichael and Winger<sup>4</sup> measured the equilibrium concentrations of the cyclic species  $D_n$  for  $n=3-10$  formed in the potassium silanolate and sulfuric acid catalysed polymerizations of  $D_4$ . They found that the equilibrium concentration of cyclics was independent of the nature of the catalyst and for  $n>3$  was independent of the temperature in the range 25–178 °C. Brown and Slusarczuk<sup>5</sup> confirmed the participation of cyclic species beyond  $D_{10}$  in the equilibrium process. They isolated individual cyclic species up to  $D_{25}$  and used fractionation techniques and high resolution Gel Permeation Chromatography (GPC) to demonstrate the presence of a continuous population of cyclic species extending up to at least  $D_{400}$  at equilibrium.

The results cited above demonstrate that the equilibrium is independent of the nature of the catalyst and involves a range of cyclic species extending to very high molecular weights. Furthermore, for cyclic species other than  $D_3$  the position of equilibrium is determined by purely entropic factors. A theory for formation of cyclic compounds in such polymer systems has been developed by Jacobson and Stockmayer<sup>6</sup> from which equation (2) for the molar cyclisation constant  $K_x$  can be derived,

$$K_x = (3/\pi C_x)^{3/2} / 16l^3 x^{5.2} N_a \quad (2)$$

where  $N_a$  is Avogadro's number,  $C_x$  is the characteristic ratio for the linear  $x$ -mer which is essentially constant for values of  $x > 30$  and  $l = 1.64 \times 10^{-8}$  cm is the length of the Si–O bond.

The theory predicts independence of  $K_x$  on dilution and the dependence of  $K_x$  on  $x$  to the power of  $-5/2$ . From equation (1), equation (3) is obtained:

$$K_x = [D_x] / p^x \quad (3)$$

$$= [D_x] \quad \text{for large } n \quad (4)$$

Thus a further prediction of the theory is the existence of a critical dilution beyond which the system is composed entirely of cyclics (equation 4).

A rigorous comparison of theory with experiment in the dimethylsiloxane series has been carried out by Semlyen and Wright<sup>7</sup>. They find  $K_x$  to be independent of dilution for cyclic species  $D_x$  where  $x$  lies in the range 11–40. For cyclic species where  $x$  is 4–10,  $K_x$  does increase with dilution. There is a critical dilution beyond which only cyclics are formed but the weight fraction of cyclics as a function of dilution departs from theory due to the dependence of  $K_x$  on dilution for the smaller rings. Siloxane chains with more than 30 units obey Gaussian statistics and the plot of  $\log K_x$  against  $\log x$  for  $x > 20$  has a slope of  $-2.57$ , almost identical with that predicted by theory. However, the theory fails to account for the detailed features of the plot for values of  $x < 20$  units since the assumption implicit in the derivation of equation 2 that such chains obey Gaussian statistics is no longer valid. The cyclosiloxanes  $[R(CH_3)_2SiO]_x$  behave in a similar fashion to the dimethylcyclosiloxanes, though deviations from theory for the lower-molecular-weight cyclics are more pronounced the larger the size of the R group<sup>8</sup> (Figure 1).

Beever and Semlyen<sup>9</sup> have employed the Jacobson and Stockmayer theory without assuming Gaussian statistics to calculate  $K_x$  for the cyclics  $D_x$  where  $x=4-9$ . They find good agreement with theory for  $K_8$  and  $K_9$ . Scales and Semlyen<sup>10</sup> have extended these calculations to  $D_x$  having values of  $x$  in the range  $7 < x < 13$ . Agreement with theory is

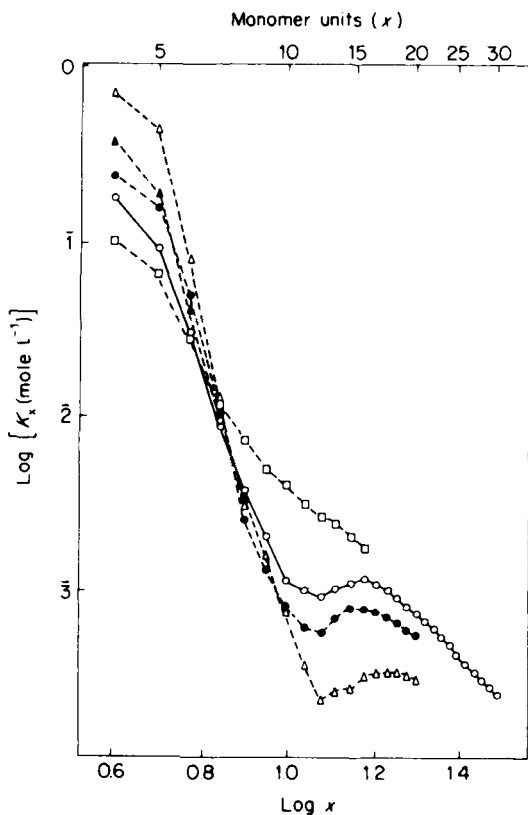


FIGURE 1. Molar cyclization constants for  $[\text{R}(\text{CH}_3)\text{SiO}]_n$ ,  $\text{R} = \text{H}$ ,  $\square$ ;  $\text{R} = \text{CH}_3$ ,  $\circ$ ;  $\text{R} = \text{CH}_2\text{CH}_2\text{CH}_3$ ,  $\bullet$ ;  $\text{R} = \text{CH}_3\text{CH}_2\text{CH}_2$ ,  $\blacktriangle$ ;  $\text{R} = \text{CF}_3\text{CH}_2\text{CH}_2$ ,  $\triangle$ . Reproduced from Wright, P. V. and Semlyen, J. A., *Polymer*, **11**, 462 (1970), by permission of the publishers, Butterworth & Co. (Publishers) Ltd.

excellent for  $K_8$ ,  $K_9$  and  $K_{10}$  but the theoretical value for  $K_{11}$  is 3 times that measured experimentally. A more detailed description of the ring-chain equilibria in the siloxane system can be found in reviews by Wright<sup>11</sup> and Wright and Beevers<sup>12</sup>.

### III. POLYMERIZATION OF CYCLOSILOXANES

#### A. Anionic Polymerization

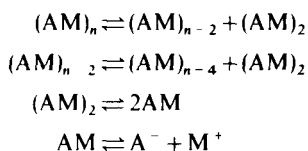
##### 1. Anionic polymerization of cyclotetrasiloxanes

The use of alkali metal hydroxides to catalyse the polymerization of cyclodiorganopolysiloxanes was first disclosed by Hyde<sup>13</sup> in 1949. He observed that initially, the metal hydroxide reacts with the cyclosiloxane to form a metal silanolate which he found to be capable of catalysing the polymerization. Grubb and Osthoff<sup>2</sup> demonstrated that the rates of polymerization of octamethylcyclotetrasiloxane ( $\text{D}_4$ ) catalysed by equimolar amounts of potassium hydroxide and potassium silanolate were

identical and concluded that the catalytic species was the metal silanolate and that the polymerization was an addition reaction where the growing polymer chain adds discrete  $D_4$  units to form high-molecular-weight polymers. In their comprehensive study of the bulk polymerization of  $D_4$  catalysed by potassium hydroxide these authors found that the rate of polymerization was first order in monomer and that the pseudo-first-order rate constant had a one-half order dependency on the catalyst concentration. These general features of the polymerization have been confirmed by several groups of workers<sup>14-16</sup>.

There is general agreement in the literature that the fractional order in catalyst arises from interchange reactions involving dormant and active catalyst species, though there is some conflict as to their nature. The half order in catalyst has been variously described as arising from ionisation of the metal silanolate<sup>2,14</sup> where the active species is the silanolate anion, or by deaggregation of a dormant ion-pair dimer to yield active ion pairs<sup>15,16</sup>. Dissociation into free ions will be significant at low concentrations or in media of very high dielectric constant<sup>17</sup>. However, there is no concrete evidence for the existence of the discrete silanolate anion under conditions where polymerization can occur. For example, conductivity measurements on sodium silanolate in the inactive (3,3,3-trifluoropropyl)methylcyclotetrasiloxane ( $D^F$ )<sub>4</sub> with and without activating solvents<sup>18</sup> confirm that free ions are absent under conditions where ( $D^F$ )<sub>3</sub> polymerization readily takes place. Conversely, there is much evidence in the literature<sup>19-21</sup> for the association of metal silanolates into aggregates in non-polar solvents. In boiling toluene the degree of aggregation for sodium trimethylsilanolate is 8.6 and that for lithium trimethylsilanolate is 4.9, both values being constant over a 0.05–0.5 mol l<sup>-1</sup> concentration range<sup>22</sup>. Similar measurements have not been carried out on the higher alkali metal silanolates, since they are less inclined to form aggregates and therefore their solubility in non-polar solvents is very low. Likewise, similar measurements on quaternary ammonium and phosphonium silanolates have not been reported despite their high solubility, high catalytic activity and industrial importance as transient catalysts for the polymerization of cyclosiloxanes.

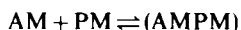
In solution the primary aggregates will exist in dynamic equilibrium with smaller aggregates and we may consider the following sequence of equilibria to be representative of the metal silanolate (AM) in non-polar solvents:



Several of the metal silanolate species involved in these equilibria have the potential to catalyse the polymerization of cyclosiloxanes. However, it is probable that the primary catalytic species is the ion pair but this is not firmly established. If the rate of reaction of the ion pair with the cyclosiloxane



is slower than the reverse reactions of the various equilibria, then equilibrium will be established and the concentration of ion pairs will be proportional to the 1/nth power of the *n*-meric catalyst species. It is possible for the polymeric siloxanolates (PM) to become involved in the aggregation-deaggregation equilibria



and this may affect the position of the various equilibria and lead to a non-steady-state concentration of ion pairs at least in the early stages of the polymerization. Induction

periods, where the rate of polymerization increases before first-order kinetics are established, have been frequently observed for the polymerization of cyclosiloxanes in non-polar solvents. If more than one catalytic species is active in the polymerization, then the rate of polymerization is given by

$$R_p = \{k_d + f(2k_m - k_d)\} [C]_0 [D] / 2$$

where  $f$  is the mole fraction of catalyst present as ion pairs,  $k_d$  is the propagation rate constant for the ion-pair dimer and  $k_m$  that for the ion pair,  $[C]_0$  the initial catalyst concentration and  $[D]$  the concentration of monomer.

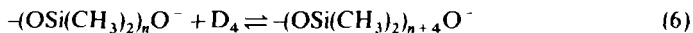
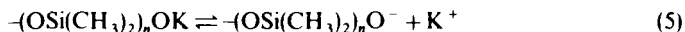
The reactivity of the metal silanolate catalyst is dependent on the nature of the metal counter-ion, the larger metal ions giving rise to more active catalysts. For example, in the metal silanolate series the order of catalyst activity<sup>23</sup> is  $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$  with quaternary ammonium and quaternary phosphonium silanolates having the same order of activity as caesium silanolate. Lithium and sodium silanolates are not very powerful catalysts for cyclosiloxane polymerization unless used in conjunction with an activating solvent such as tetrahydrofuran (THF) or dimethyl sulphoxide (DMSO).

The large dipole moment of ion pairs causes them to interact strongly with polar molecules with the result that small amounts of polar compounds profoundly affect the course of the polymerization. In polar solvents the following dynamic equilibrium will be set up involving ion pairs, solvent separated ion pairs and free ions:



The species which predominates will depend on several factors including the nature of the counter-ion, the solvating power of the solvent and the dielectric constant of the medium.

The mechanism proposed by Grubb and Osthoff<sup>2</sup> for the bulk polymerization of  $\text{D}_4$  catalysed by KOH is based on the assumption that the potassium silanolate dissociates into silanolate ions which are the active catalytic species in the polymerization.



If both the ion pair and the silanolate anion are active catalytic species in the polymerization, then the rate of polymerization of  $\text{D}_4$  is given by

$$-d[\text{D}_4]/dt = ([\text{D}_4] - [\text{D}_4]_e)(k_p[\text{SiOK}] + k_i[\text{SiO}^-]) \quad (7)$$

where  $[\text{D}_4]_e$  is the concentration of  $\text{D}_4$  at equilibrium, and

$$k/[C]_0 = k_p + (k_i - k_p)K/[C]_0^{1/2} \quad (8)$$

where  $K$  is the dissociation constant for the ion pair,  $[C]_0$  the initial catalyst concentration,  $k$  the observed first-order rate constant, and  $k_i$  and  $k_p$  are the propagation rate constants for the free ion and the ion pair respectively. Plots of  $k/[C]_0$  versus  $1/[C]_0^{1/2}$  are linear but pass through the origin signifying the participation of one species only in the propagation reaction which quite probably is the ion pair. Attempts to confirm the presence of free silanolate anions by conductivity measurements have been inconclusive<sup>22, 23</sup>. If indeed free ions are the active catalyst species in the polymerization, then increasing the dielectric constant ( $D$ ) of the polymerization medium should enhance the dissociation of the potassium silanolate and at sufficiently high  $D$ , the order in catalyst should be unity and the propagation rate constant independent of the nature of the metal counter-ion. Modest changes in the dielectric constant do significantly increase



the rate of polymerization<sup>14</sup> of  $D_4$  catalysed by KOH at 140 °C. The polymerization of mixed propylmethyl/dimethyl cyclotetrasiloxanes<sup>24</sup> in a medium where  $D$  is close to values where the concentration of free ions should be significant is first order in potassium silanolate catalyst. Furthermore, the propagation rate constants for the potassium silanolate and sodium silanolate catalysed polymerizations were of similar magnitude whilst in the absence of solvent, potassium silanolate is 40–60 times more effective a catalyst than sodium silanolate in this system<sup>24</sup>. These results suggest that the silanolate anion is an active catalyst for the polymerization of these cyclosiloxanes. However, under normal polymerization conditions the active catalyst is more probably the ion pair.

Changing the substituent on silicon has little effect on the overall kinetics of the polymerization. The orders in monomer and catalyst remain unchanged and the activation energy for the polymerization is almost identical with that for the dimethylcyclosiloxanes. The rate of polymerization though does depend on the inductive effect of the groups attached to silicon<sup>24–27</sup>. Within a single class of mixed cyclosiloxanes the introduction of electron-donating substituents reduces the rate of polymerization whilst electron-withdrawing substituents increase it.

## 2. Anionic polymerization of cyclotrisiloxanes

In the cyclotrisiloxane series the complexity of the polymerization is greatly reduced, since conditions can be chosen where the rates of the depropagation and redistribution reactions are negligible compared to the rate of propagation. The polymerization of hexamethylcyclotrisiloxane ( $D_3$ ) in toluene catalysed by bis  $\alpha,\omega$ -tetramethylammonium siloxanolate in toluene solution at 22–50 °C is first order each in monomer and catalyst<sup>28</sup>. The propagation rate constant is  $200 \text{ min}^{-1} \text{ mol}^{-1} \text{ l}$  and the activation energy for the propagation reaction is  $124 \text{ kJ mol}^{-1}$ . Similar results were reported<sup>29</sup> for the polymerization of *cis*-1,3,5-trimethyl,1,3,5-triphenyl cyclotrisiloxane catalysed by  $\alpha$ -hydroxy- $\omega$ -tetramethylammonium methylphenylsiloxanolate in benzene solution at 12–17 °C. The polymerization is first order in monomer and catalyst and the activation energy is  $103 \text{ kJ mol}^{-1}$ . The propagation rate constant at 17.5 °C is  $2500 \text{ min}^{-1} \text{ mol}^{-1} \text{ l}$ . With these quaternary ammonium silanolate catalysts the catalyst is present as a single catalytic entity, which is probably the ion pair.

The polymerization of  $D_3$  in heptane/dioxane (95/5 v/v) catalysed by potassium silanolate is half order in catalyst<sup>30</sup>, whilst the polymerization of  $D_3$  in toluene at 80 °C catalysed by sodium trimethylsilanolate is first order in catalyst<sup>31</sup>. The latter is an unusual result, though the concentration range used by these workers ( $0.05$  to  $0.2 \text{ mol l}^{-1}$ ) is higher than normal and we may assume that the polymerization is catalysed by ion-pair dimers only. In the presence of added trimethylsilanol which will aid dissociation of the aggregates into ion pairs, the order in catalyst reverts to the more commonly observed figure of 0.5 and the rate of polymerization is increased. The same authors<sup>28</sup> find that when the catalyst is quaternary ammonium siloxanolate the addition of a 15-fold excess of the silanol reduces  $k$  by a factor of 12 and the order in catalyst with and without the silanol is unity. With these metal silanolate catalysts the active catalyst is the ion pair which is in equilibrium with ion-pair dimers.

Chojnowski and Mazurek<sup>16</sup> have studied the reaction of phenyldimethyl silanolates with cyclosiloxanes under conditions where siloxane bond redistribution reactions involving the polymer and the catalyst are completely suppressed. For the reaction of sodium phenyldimethyl silanolate (I) with 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (II) they find that the rate of disappearance of I in an excess of II follows first-order kinetics. The observed first-order rate constant  $k$  varies with the initial

monomer concentration  $[M]_0$  and the initial catalyst concentration  $[C]_0$  according to the following expression:

$$k = K[M]_0/[C]_0^{1/4} \quad (9)$$

The propensity for sodium silanolates to form aggregates is well known<sup>19,21</sup> and the authors propose the following mechanism based on a series of aggregation/deaggregation equilibria between the phenyldimethylsilanolate ion pair ( $A_1$ ) and the polymeric phenyldimethylsiliconate ion pair ( $B_1$ ) formed by reaction of I with II:



They assume that the reaction of  $A_1$  with M is the rate-determining step



and derive the following expression for the rate of the reaction of I with II:

$$-dA/dt = k[M][A]/\{(nK_0)^{1/n}[A]_0^{(n-1)/n}\} \quad (14)$$

where  $[A]$  is the concentration of I at time  $t$ ,  $[A]_0$  is the initial concentration of I and  $K_0$  is the equilibrium constant for reaction 10. For  $n=2$  this is identical to the expression derived by Szwarc<sup>32</sup> for the addition of living polystyryl to 1,1-diphenylethylene. Equation 14 predicts the general features of the kinetics but does not support an order of  $\frac{1}{2}$  in initial  $[I]$ . Chojnowski and Zietera<sup>33</sup> have studied the reaction of sodium polystyryl (III) with cyclosiloxanes. The reaction does not follow simple first-order kinetics presumably because cross-aggregation of III with sodium silanolates would produce aggregates with dissociation constants intermediate in value between that for III and sodium silanolate aggregates and assumptions concerning the interrelationships of the equilibrium constants for reactions 10 through 12 which are necessary to derive equation 14 are no longer valid. However, the general features of the reaction are the same and  $k$  shows an inverse dependence on the initial concentration of III. The kinetics of the reaction of potassium phenyldimethyl silanolate (IV) has similar features<sup>30,34</sup>. Deviation from first-order kinetics is again observed and for reactions of  $D_6$  with IV the slope of  $\log k$  versus  $\log A_0$  is close to  $-0.5$ .

The observation that polar solvents increase the rate of the base catalysed polymerization of cyclosiloxanes was first reported by Hyde<sup>13</sup>. The considerable rate enhancement that can be obtained by using these dipolar aprotic solvents is well illustrated in Table 1, taken from the data of Yuzhelevskii and coworkers<sup>18</sup> for the  $(D^F)_3$ /sodium siloxanolate system.  $k_0$  is the observed first-order rate constant in the absence of an activator solvent.

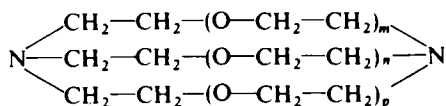
The polymerization of cyclotrisiloxanes catalysed by metal silanolates in activator solvents has been studied by several groups of workers. The metal silanolates like sodium and lithium silanolates are highly aggregated and have no catalytic activity in non-polar solvents. Thus we can reasonably conclude that these aggregates are dormant catalytic species in the polymerization of cyclosiloxanes. The polymerization of  $D_3$  in toluene/THF<sup>35</sup> at a  $[THF]$  of  $3.2 \text{ mol l}^{-1}$  is first order in monomer and of fractional order in catalyst. Yuzhelevskii, Kagan and Fedoseeva<sup>18</sup> have studied the polymerization of  $(D^F)_3$  catalysed by sodium siloxanolate at  $30^\circ\text{C}$  in the presence of DMF at concentrations varying from 1 to 10 times that of the catalyst. The polymerization is first order in monomer and the first-order rate constant  $k$  is directly proportional to the catalyst and the solvent concentrations at constant catalyst to solvent molar ratios. However, the variation of  $k$  with catalyst concentration at constant solvent concentration is complex.  $k$

TABLE 1. Relative rates of bulk polymerization of  $(D^F)_3$  in the presence of activators using sodium siloxanolate as catalyst ( $2 \times 10^{-3} \text{ mol l}^{-1}$ ) (data from Reference 18 reproduced by permission of the copyright holders, Plenum Publishing Corporation)

Solvent (complexant)	[Solvent] $\text{mol.l}^{-1}$	$^{\circ}\text{C}$	$k/k_0$
Nitrobenzene	0.1	40	2.1
Tetrahydrofuran	0.1	40	10.5
Acetonitrile	0.1	40	34
Acetone	0.1	40	95
Dimethylformamide	0.01	30	150
Dimethyl sulphoxide	0.01	30	155
Tributylphosphate	0.01	40	300
Hexamethylphosphorotriamide	0.001	30	28
Diethyleneglycol dimethyl ether	0.001	30	28

increases with increasing catalyst concentration up to a maximum and then decreases with further increase in catalyst concentration. Lee, Frye and Johannson<sup>36</sup> have studied the polymerization of  $D_3$  catalysed by BuLi ( $4 \times 10^{-3} \text{ mol l}^{-1}$ ) in *o*-xylene at  $25^{\circ}\text{C}$  and in the presence of DMSO at concentrations 50–100 times that of the catalyst. The rate of polymerization increases with the  $[\text{DMSO}]^{1.5}$ . Holle and Lehen<sup>37</sup> have polymerized  $D_3$  with lithium silanolate catalyst in the presence of HMPT and find that the observed first-order rate constant is proportional to  $[\text{HMPT}]^2$  and  $[\text{CATALYST}]^{1/2}$ .

The work of Boileau<sup>38</sup> with lithium catalysts and highly specific cation complexing compounds is particularly significant. The author describes the use of the macrobicyclic ligand or cryptate which forms multicontact complexes with the metal counter-ion of the



catalyst. The [2.1.1] cryptate where  $m = 2$  and  $n$  and  $p = 1$  is highly specific for the lithium counter-ion and polymerization of  $D_3$  with the lithium [2.1.1] cryptate is first order in catalyst. Deactivation of the living polydimethylsiloxane shows no significant change in viscosity of the polymer solution and confirms the absence of aggregates in this system. The author assumes the active catalytic species to be the lithium cryptate ion pair and estimates the ion-pair propagation rate constant to be  $78 \text{ min}^{-1} \text{ mol}^{-1}$ .

### 3. Anionic polymerization of cyclosiloxane species of more than four siloxane units

The relative rates of polymerization of the higher dimethylcyclosiloxanes have been reported by a number of groups of workers, the most complete study being that of Laita and Jelinek<sup>39</sup>. They determined the relative rates of polymerization for cyclic species up to  $D_7$  in the bulk polymerization catalysed by KOH at  $150^{\circ}\text{C}$ . Thomas<sup>40</sup> has measured the relative rates of polymerization of  $D_4$  and  $D_5$  catalysed by KOH over a range of temperatures and Yuzhelevskii and coworkers<sup>24</sup> that for  $D_3$  and  $D_4$  at  $110^{\circ}\text{C}$ . The various results, converted to a common temperature of  $150^{\circ}\text{C}$ , are quoted in Table 2. In

TABLE 2. Relative rates of polymerization of dimethylcyclosiloxanes catalysed by KOH in bulk (data from References 24, 39 and 40)

Monomer	Relative rate	Activation energy (KJ mol <sup>-1</sup> )
D <sub>3</sub>	53, 34 <sup>24</sup>	73.2, 69.4 <sup>24</sup>
D <sub>4</sub>	1	81.5, 81.9 <sup>40</sup>
D <sub>5</sub>	1.6, 1.4 <sup>40</sup>	81.5, 90.3 <sup>40</sup>
D <sub>6</sub>	11.3	81.5
D <sub>7</sub>	316	81.5

the presence of dipolar aprotic solvents this reactivity sequence is not retained. Mazurek and Chojnowski<sup>34</sup> quote relative rates for the polymerization of D<sub>4</sub> and D<sub>7</sub> catalysed by KOH in a number of solvent systems at 30°C and Boileau<sup>38</sup> for the polymerization of D<sub>3</sub>, D<sub>4</sub>, D<sub>5</sub> and D<sub>6</sub> at room temperature catalysed by lithium silanolate ([2.1.1] cryptate). The results are collected in Table 3.

TABLE 3. Relative rates of polymerization of dimethylcyclosiloxanes in various solvents (data from References 34 and 38)

Solvent (complexant)	D <sub>3</sub>	D <sub>4</sub>	D <sub>5</sub>	D <sub>6</sub>	D <sub>7</sub>
95/5 heptane/dioxane		1			432
95/5 heptane/diglyme		1			8
95/5 heptane HMPT		1			0.7
THF		1			15
THF (18-DBC-6) <sup>a</sup>		1			0.9
Li THF [2.1.1] cryptate	280	1	0.4	0.06	

<sup>a</sup> 18-DBC-6 is dibenzo-18-crown-6.

The reaction of potassium phenyldimethyl silanolate with dimethylcyclosiloxanes in the non-solvating solvent system 95/5 heptane/dioxane<sup>34</sup> gives similar results to those quoted in Table 2. The authors propose that there is an interaction between the silanolate and the cyclosiloxane which facilitates the cleavage of the siloxane. They visualize the interaction to involve the cation of the ion pair in a multipoint interaction with the cyclosiloxane similar to the polydentate interactions between cations and crown ethers. Species like crown ethers and HMPT which form stronger complexes with the cation will disrupt this multipoint interaction. Thus the relative rate of the polymerization of D<sub>4</sub>:D<sub>7</sub> is reduced from 1:161 to 1:0.7 in heptane/HMPT. It should be realized however that the relative rates are determined from observed first-order rate constants which are themselves composite terms involving the equilibrium constant for the formation of active catalytic species from the catalyst. If the higher cyclic species favour the formation of active species by some mechanism such as that proposed by Mazurek, then the relative rates for the actual propagation reaction will be more in accord with the data of Boileau where the catalyst is present as a single active species, namely the lithium cryptate/silanolate ion pair.

#### 4. Molecular weight distributions and the nature of the redistribution reactions involving the siloxane chain

The polymerization of cyclotrisiloxanes can be effected under conditions where monomer addition to the active centre occurs without termination or transfer to polymer. If the exchange between active and dormant catalytic species is fast compared to the rate of propagation, then growth of all the polymer molecules proceeds simultaneously and the polymer will have a Poisson distribution<sup>41</sup>. There have been a number of studies where polymers of narrow molecular-weight distribution have been prepared. For example, Holle and Lehen<sup>37</sup> have measured the molecular weights of polymers prepared by polymerizing  $D_3$  with lithium siloxanolate using HMPT as the activator solvent. Their results show good correspondence with theory for both the number average degree of polymerization ( $x_n$ ) and the ratio of the weight average to number average degree of polymerization ( $x_w/x_n$ ).

If the polymerization is carried out under conditions where chain transfer to polymer can occur and if the siloxane bonds in the polymer chain are of equal reactivity towards the active chain end, then the molecular-weight distribution of the polymer will be broader and at equilibrium will have the most probable distribution<sup>41</sup>, where the ratio  $x_w/x_n$  will tend to the value 2 as the extent of reaction approaches unity. Davydova and coworkers<sup>42</sup> find that the polydispersity of PDMS prepared from  $D_4$  and potassium siloxanolate becomes broader as the polymerization proceeds. Changes that do occur during the polymerization are observed in the range of high molecular weights only and number average molecular weights remain fairly constant throughout the polymerization.

Mazurek and coworkers<sup>43</sup> have studied the concentration of linear oligomers in fully equilibrated living polydimethylsiloxanes. Polymerizing  $D_3$  with potassium trimethylsilanolate should, at equilibrium, give chains with trimethylsilyl groups at each end (I), chains terminating in one trimethylsilyl group and one silanolate group (II) and chains terminated in silanolate groups only. By neutralizing the living silanolate chain ends with trimethylchlorosilane the authors found that the concentration of  $MD_nM$  oligomers exceeded that predicted from the most probable distribution by a factor of 10. By neutralizing the living polymer with ethyldimethylchlorosilane the authors were able to estimate the amounts of oligomers of type I, II and III present at equilibrium. They found that these low-molecular-weight oligomers are derived from species of type III, i.e. chains terminating in silanolate groups only. A maximum in the oligomer concentration occurs at  $n = 4-5$ . The explanation offered is that the silanolate chain ends on the same molecule aggregate to form ion-pair dimers and the ease of their doing so is probably related to the entropy change for chain closure to a ring such as that developed by Jacobson and Stockmayer<sup>6</sup>. Such phenomena might explain the broadening of the molecular weight distribution and the skewing of the distribution to high molecular weights at high conversions observed by Davydova<sup>42</sup>. The introduction of an end block molecule such as  $MD_2M$  reduces the opportunity for finding silanolate end groups on the same chain with the result that the molecular weight distribution is sharpened and the tendency to favour high molecular weights at high conversions disappears. Under conditions where aggregation does not occur Boileau<sup>38</sup> finds that the polymerization of  $D_4$  with butyllithium [2.1.1] cryptate gives a bimodal molecular weight distribution with the  $x_w/x_n$  for the high-molecular-weight peak being always equal to 2.

The polymerization of  $D_3$  with catalysts that yield narrow molecular weight distributions proceeds by successive addition of  $D_3$  units to the growing polymer chain. Zavin and his coworkers<sup>44</sup> have polymerized  $D_3$  with butyl lithium/HMPT and equimolar amounts of the chain transfer agents  $(CH_3)_nSi(OCH_3)_{4-n}$ . In the presence of dimethyldimethoxysilane, oligomers of the general formula



where  $n=3, 6, 9$  and  $12$  are formed in preference to oligomers of intermediate chain length. Such redistribution reactions as do occur in this system are specific to the terminal siloxane bond connected to the dead chain end of the oligomer. Fessler and Juliano<sup>45</sup> have studied the reaction of equimolar amounts of  $D_3$  and lithium butyldimethylsilanolate (BDLi) and characterized the oligomers formed. The principal product formed is  $BD_2Li$ , which is formed as rapidly as BDLi is consumed and faster than  $D_3$  is consumed. The  $BD_4Li$  which is formed by the primary reaction must react very rapidly with a second molecule of BDLi to give  $BD_2Li$  and  $BD_3Li$  which will react with a further molecule of BDLi to yield 2 molecules of  $BD_2Li$ . The specificity of this redistribution can be understood if one invokes a rapid exchange between ion pair and ion pair dimers such as has been used to explain the kinetics of  $D_3$  polymerization with lithium catalysts. When aggregates are not present this specificity should disappear.



### 5. Summary

The anionic polymerization of cyclosiloxanes is a complex process. For the alkali metal silanolate catalysts the weight of experimental evidence supports a mechanism based on growth from the metal silanolate ion pair. The ion pair is in dynamic equilibrium with ion-pair dimers which, for the smaller alkali metal ions like lithium and sodium, are themselves in dynamic equilibrium with ion-pair dimer aggregates. The fractional order in catalyst which is observed is a direct result of the equilibria between ion pairs, ion-pair dimers and ion-pair dimer aggregates. Polar solvents break down the aggregates and increase the concentration of ion-pair dimers and hence the concentration of ion pairs. Species like crown ethers and the [2.1.1] cryptate which form strong complexes with the metal cation increase the dissociation of ion-pair dimers into ion pairs. In the case of the lithium [2.1.1] cryptate dissociation into ion pairs is complete and the order in catalyst is unity.

Many apparent anomalies in the polymerization are explained on the basis of the equilibrium between ion-pair dimers and ion pairs. Thus the higher than anticipated concentration of cyclic oligomers observed in the polymerization of permethylcyclosiloxanes is thought to be due to the formation of internal ion-pair dimers by silanolate ion pairs on the chain ends of same polymer molecule. The wide differences in the relative rates of polymerization of permethylsiloxanes in the presence and absence of polar solvents also has its origins in this association-dissociation equilibrium. In non-polar solvents the cyclosiloxane is thought to form multicontact complexes with the metal cation which would assist the deaggregation reaction and favour the production of ion-pair dimers and ion pairs. With polar solvents or species which form complexes with the metal cation the cyclosiloxane is no longer able to impact the aggregation-deaggregation equilibria and the relative rates of polymerization reflect those for the propagation reaction itself.

The polymerization is accelerated in solvents of high dielectric constant which do not have the capability to solvate the ion pair. Under these conditions which would favour the dissociation of the ion pair into the free ions it is perhaps reasonable to conclude that the polymerization is catalysed by both the ion pair and the free silanolate anion.

## B. Cationic Polymerization of Cyclosiloxanes

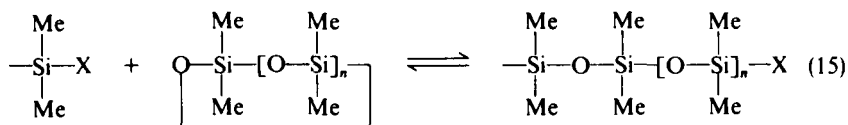
### 1. Introduction

The polymerization of cyclosiloxanes using both Bronsted and Lewis acid catalysts has been known since the earliest days of the silicone industry<sup>46</sup> and some of the first

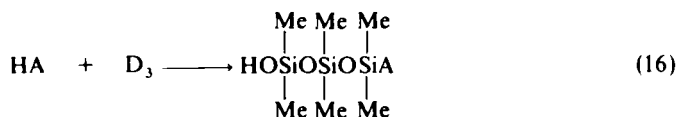
commercially available high-molecular-weight siloxane polymers were prepared in this way<sup>47</sup>. Until recently there have been few attempts to understand the fundamental chemistry and mechanisms underlying these reactions<sup>46-48</sup>, however within the last decade the cationic polymerization of cyclosiloxanes has received much attention. Catalysts that have been reported to initiate cationic polymerization of siloxanes include most strong protonic acids like  $\text{H}_2\text{SO}_4$ <sup>1, 46, 47, 49</sup> or  $\text{HClO}_4$ <sup>50</sup> and a variety of Lewis acids<sup>1, 48, 49</sup>. Other sources of exchangeable  $\text{H}^+$  are also important particularly in commercial processes. These may be cation exchange resins<sup>51</sup> such as sulphonated polystyrene, activated clays like  $\text{H}_2\text{SO}_4$  treated montmorillonite<sup>52</sup> or, more recently, graphite interchelate compounds of Lewis acids<sup>53, 54</sup>. Even the solid state polymerization of  $\text{D}_3$  using a  $^{60}\text{Co}$  source is reported to proceed via a cationic route<sup>55, 56</sup>. Many of the newer commercial processes, particularly those for the synthesis of organofunctional siloxanes<sup>57, 58</sup>, utilize strong sulphonic acids such as  $\text{CF}_3\text{SO}_3\text{H}$ . It is this catalyst that has been singled out for particular attention in the most recent kinetic and mechanistic studies<sup>59, 60</sup> and the implications of these studies on the synthesis of cyclosiloxanes have been extensively reviewed by Wright<sup>11</sup>. However, despite a great deal of effort the precise nature of the polymerization process has yet to be established.

Two general mechanisms have been proposed for the cationic polymerization of cyclosiloxanes:

*Addition polymerization*, where the growth occurs by reaction of monomer with some active propagating centre  $\equiv\text{SiX}$  which might be an oxonium ion<sup>48, 61</sup> or a discrete silicium ion<sup>49, 62</sup>.



*Acidolysis/Condensation*, in which initiation is thought to occur via decomposition of an intermediate siloxonium complex formed by electrophilic attack on the siloxane oxygen by a proton and which affords silanol ( $\text{SiOH}$ ) and silyl ester ( $\text{SiA}$ ) groups<sup>46, 63</sup>.



The acidolysis product may then undergo hetero- or homo-polycondensation and hydrolysis reactions to form oligomers and high polymer.



Recent studies have shown that the polymerization of siloxanes initiated by strong acids such as  $\text{CF}_3\text{SO}_3\text{H}$  follows a complex rate law in which it is necessary to invoke both of the mechanisms represented by equations 15 through 19 in an interrelated manner<sup>59, 60, 63</sup>.

At equilibrium cyclic oligomers coexist with both high- and low-molecular-weight linear polymers<sup>64, 65</sup>. The cyclic population, especially that obtained in the polymeriz-

ation of  $D_3$ , is discontinuous under kinetic conditions and comprises a series of cyclosiloxanes  $D_{3n}$  where  $n$  is an integer and each cyclosiloxane differs from its nearest neighbours by 3 dimethylsiloxane units. In addition small quantities of additives, particularly water, have a profound influence on the kinetics of the polymerization. For example, the reaction of  $D_3$  with  $CF_3SO_3H$  has a negative apparent activation energy under anhydrous conditions which changes to a positive value on addition of water<sup>63</sup>.

## 2. Kinetic studies of the cationic polymerization of cyclosiloxanes

The kinetics of the acid catalysed polymerization of cyclosiloxanes have been followed using dilatometry and GLC<sup>59, 63</sup> or GPC<sup>60</sup> techniques. The rate of consumption of monomer does not follow simple first-order kinetics and the addition of water not only increases the rate of polymerization of  $D_3$  and to a lesser extent  $D_4$  but also fundamentally alters the kinetics of polymerization. Thus the rate of polymerization of  $D_3$  in  $CH_2Cl_2$  in the absence of water actually decreases with increasing initial monomer concentration to the power of 0.7, but when water is present the order in monomer reverts to the expected first-order dependence. A negative activation energy was obtained for this polymerization ( $E_A = -25 \text{ KJ mol}^{-1}$ ) together with an unusually low pre-exponential factor ( $A = 10^{-8} \text{ s}^{-1}$ ). These values also change dramatically on the addition of water to yield the more conventional values of  $E_A = 50 \text{ KJ mol}^{-1}$  and  $A = 10^6 \text{ s}^{-1}$ .

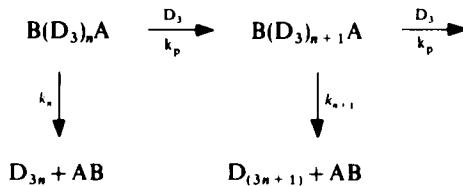
In the absence of an end-blocking species four distinct groups of products are observed by GPC<sup>60, 63</sup>; small cyclics, macrocyclic oligomers, low-molecular-weight polymer and high polymer. The oligomers and low polymer rapidly reach steady-state concentrations whilst the high-molecular-weight polymer fraction which appears at the beginning of the reaction<sup>59, 66</sup> continues to increase both its molecular weight and relative proportion at the expense of the starting monomers until equilibrium is attained. GLC analysis of the primary products from the polymerization confirms that the cyclic siloxanes initially enter the polymer as discrete monomer units<sup>59, 64, 65, 67</sup> (either  $D_3$  or  $D_4$ ). Thus in the polymerization of  $D_3$  catalysed by  $CF_3SO_3H$  the volatile fraction contains a predominance of cyclic oligomers  $D_{3n}$  where the number of dimethylsiloxane units in each oligomer is a multiple of three<sup>64, 65</sup>. Such oligomers are formed almost exclusively; small amounts of other cyclics  $D_4$ ,  $D_5$ ,  $D_7$ , etc., that are produced concurrently, are attributed to the onset of the depolymerization process. This kinetic enhancement is less obvious for similar experiments using  $D_4$ <sup>60, 68</sup> although under certain conditions cyclic siloxanes containing multiples of the  $D_4$  unit can be detected<sup>59, 67, 69</sup>. When the end blocking units MM are present, no high polymer is formed but the linear oligomers  $MD_{3n}M$  are observed and are also far in excess of their equilibrium values<sup>70</sup>. In this case the distribution of the  $MD_{3n}M$  species decreases in a highly regular manner and the molar ratio,  $u = MD_{3n}M/MD_{3(n+1)}M$ , of adjacent homologues is almost constant and independent of  $n$ . This feature is characteristic of a chain reaction in which redistribution processes play a minor role<sup>64, 70</sup>. Such a chain reaction might be ring opening of the monomer by some active centre giving chain growth and termination by reaction of the propagating centre with MM. However, the same regularity is not observed for the corresponding  $D_{3n}$  cyclic oligomer series where the ratio,  $u = [D_{3n}]/[D_{3(n+1)}]$ , is strongly dependent on the reaction conditions such as solvent and type of catalyst and on the relative thermodynamic stabilities of the cyclic products. Similar experiments using MDM as end blocking agent showed very low specificity in the distribution of oligomers<sup>70</sup>. The authors argue that a mechanism involving a five-coordinate silicon transition state is the best explanation of these results.



### 3. Mechanism of the cyclization reaction and the nature of the acidolysis/condensation equilibrium

The mechanism of formation of macrocycles in the cationic polymerization of  $D_3$  has been the subject of extensive studies mainly by GLC analysis of the volatile fraction<sup>64, 65, 69, 71</sup>. In the absence of an end blocking species condensation of chain ends effectively competes with the linear growth mechanism, the intramolecular condensation leading to the formation of cyclic species. Two possible mechanisms may be considered for the cyclisation process: linear growth of the macromolecule followed by end-to-end ring closure, or ring expansion polymerisation by insertion of monomer into the activated cyclic compound. A third possibility of ring formation by depolymerization was rejected in this case because depolymerization is a random process and therefore could not account for the characteristic distributions and the almost exclusive formation of certain  $D_{3n}$  oligomers.

Chojnowski and coworkers find that the end to end ring closure mechanism accounts for most of their experimental observations. The mechanism<sup>65</sup> assumes a linear growing species  $B(D_3)_nA$  composed of a terminal group B and an unspecified propagating centre A which can undergo competitive reactions leading either to linear propagation or cyclization.



By making the assumption that propagation is much faster than cyclization and neglecting condensation, the concentrations of intermediates at any instant during the course of the reaction become equal, i.e.  $[B(D_3)_nA] = [B(D_3)_{n+1}A]$  etc. Under these conditions the model predicts that the relative rate of formation of cyclic oligomers is independent of the instantaneous concentration of their respective linear intermediates. Thus at time  $t$

$$d[D_{3n}]/d[D_{3(n+1)}] = k_n/k_{n+1} = [D_{3n}]_t/[D_{3(n+1)}]_t$$

A logarithmic plot of the distribution of  $D_{3n}$  cyclics at different conversions should have the same shape and be parallel to one another. This is supported by experiment as shown in Figure 2. The ratio of concentrations of the  $n$ th and  $(n+1)$ th cyclic oligomers are almost the same for conversions in the range 7–90%. Additional experiments indicate that this characteristic pattern does not vary with initial monomer concentration as is anticipated.

The Jacobson and Stockmayer theory for the distribution of cyclic oligomers at equilibrium has been extended to some non-equilibrium systems by Kilb<sup>72</sup> and further developed by others<sup>73, 74, 75</sup>. Their calculations predict that for kinetically controlled reactions  $[D_x]$  should vary with  $x^{-3/2}$ . In the polymerization of  $D_3$  by  $CF_3SO_3H$  in heptane  $[D_x]$  varies as  $x^{-1.7}$  for rings of more than 18 units compared with  $x^{-2.7}$  for the equilibrium distribution as shown in Figure 3. The striking similarity between the equilibrium and kinetically controlled distributions, especially in the small cyclic region, and the difference of unity in the exponent of the limiting slopes is taken as strong evidence in favour of the end-to-end ring closure mechanism.

The processes depicted in equations 16 through 19 which give rise to silanol and silyl ester functions are well established and can be readily monitored by  $^{19}F$  and  $^1H$  NMR

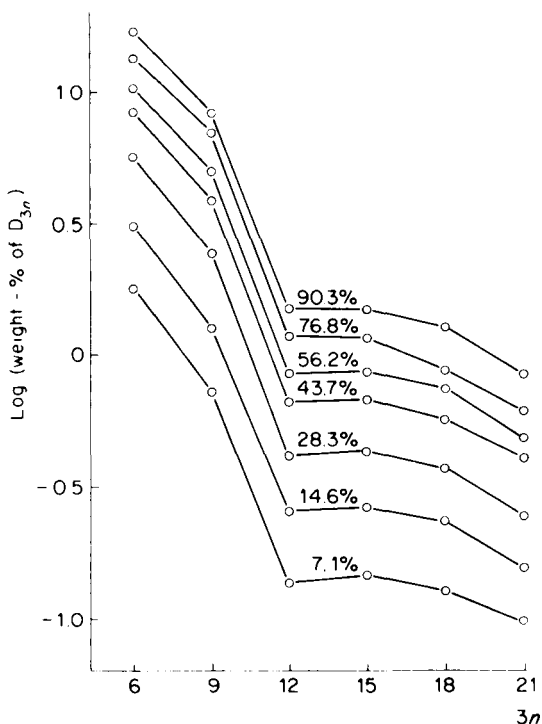
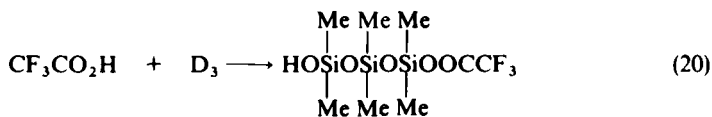


FIGURE 2. Log (weight  $D_{3n}$  oligomers) at various conversions during the polymerization of  $D_3$  with  $CF_3SO_3H$  in  $CH_2Cl_2$ . Reproduced from Reference 65 by permission of Huthig & Wepf Verlag

spectroscopy<sup>60, 63, 76</sup>. GLC techniques<sup>77</sup> and infrared spectroscopy<sup>78</sup> were employed to investigate the homocondensation reaction and to determine the effects of H-bonding. With strong protic acids such as  $CF_3SO_3H$  the acidolysis step is rate determining and the equilibria favouring the silyl ester are established very rapidly. However, the interaction of siloxanes with the moderately strong trifluoroacetic acid (TFA) is more amenable to kinetic analysis.



The reaction, followed by measuring changes in the acid or ester concentration as a function of time, gives low apparent orders in monomer (e.g.  $-1.4$  for  $D_3$  and zero for  $D_4$ ) and high apparent orders in acid (3.1–3.5). Due to H-bonding phenomena<sup>60, 63, 78</sup> the actual concentrations of uncomplexed acid and monomer are considerably less than their initial concentrations and the order in free acid and free monomer are 3 and 1 for  $D_3$  and 3.5 and 1.5 for  $D_4$ , respectively.

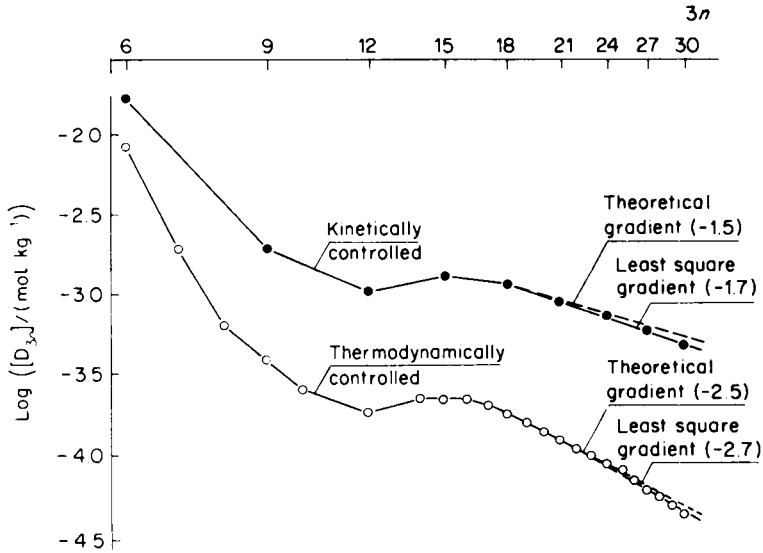
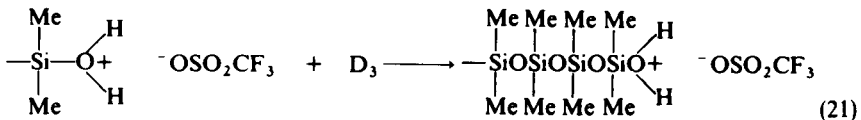


FIGURE 3. Comparison of the kinetically controlled and equilibrium distributions of oligomers in the  $D_3CF_3SO_3H$  system in heptane. Reproduced from Reference 65 by permission of Huthig & Wepf Verlag

#### 4. Summary

The preceding discussion indicates the exceedingly complex nature of the cationic process for the polymerization of cyclosiloxanes. Most workers concur that the two mechanisms, viz. addition polymerization and acidolysis/condensation, are operative and are likely to occur simultaneously. Chojnowski and Sigwalt differ in the emphasis placed on each mechanism and in their description of the precise nature of the active centre which remains the subject of much debate. The former describes activation by a silanol/acid complex (equation 21) and concludes that condensation accounts for approximately 10% of the polymerization of  $D_3$ . The latter favours initiation via the silyl ester group leading to a tertiary siloxonium ion and homoconjugate triflate complex<sup>79</sup> (equation 22) and suggests that polycondensation plays a major role in the polymerization of  $D_4$ . Both groups of workers prefer not to invoke the previously proposed<sup>49, 62</sup> discrete silicenium ion as the active species. Attempts to prove the existence of such intermediates have been numerous<sup>80</sup> but it is probably at best a fleetingly transient species in the presence of siloxane bonds. However its participation in the cationic polymerization should perhaps be reexamined in the light of the recent claims<sup>81</sup> and counterclaims<sup>82</sup> regarding the observations of stable  $Ph_3Si^+$  and  $Me_3Si^+$  species<sup>81</sup> which are known to initiate polymerization of styrene.





Infra-red spectroscopy has been used to measure the DP of linear siloxane polymers<sup>91-94</sup>. For polymers with M<sup>H</sup> terminal units the strong and isolated Si-H stretching band at 2135 cm<sup>-1</sup> is easily measurable<sup>94</sup>. However, the overlapping peaks for CH<sub>3</sub> in M and in D siloxane units makes their respective quantitative determination extremely difficult<sup>92</sup>. The Fourier technique can be applied to enhance the observed resolution of IR spectra and it is very efficient in resolving the overlapping peaks. Using this technique chain lengths of up to 200 siloxane units in PDMS molecules can be determined<sup>92,95-97</sup>. PNMR has been used when differentiation between protons on different functional groups is possible<sup>1,83</sup> and the technique has been applied to the analysis of methyl, phenyl, vinyl, hydroxyl and hydrogen groups in polysiloxanes. However, the relatively small chemical shift for proton nuclei (10 ppm) and the increased complexity of the spectra due to scalar coupling limits the applicability of PNMR for elucidating the microstructure of siloxane copolymers. In principle carbon-13 NMR can be applied and characterization of the degree of polymerization of polydimethylsiloxanes has been reported recently<sup>87,98</sup>. However, high-resolution silicon-29 NMR allows direct observation of the silicon nuclei that form the backbone of polysiloxanes and has no rival in determining the changes in the electronic, atomic and molecular environment of silicon atoms. Excellent reviews have been published on the subject<sup>99,100</sup>. M, D, T and Q units are well separated and substitution of the methyl group is clearly differentiated. The sensitivity of chemical shift is such that the silicon nucleus screening constant is influenced by substitution at up to six bonds away from the observed nucleus thus allowing characterization of up to heptad sequences<sup>101</sup>. Furthermore, it is possible to analyse the macrostructure in terms of the number average degree of polymerization since chain and chain-end groups are simultaneously observed<sup>99-105</sup>. The only problem associated with this technique for determining the average DP is the rapidly decreasing concentration of chain ends as the molecular weight increases. Whilst Polarization Transfer Pulse Sequences might be a viable alternative<sup>106,107</sup>, FT-IR is superior in this respect<sup>92</sup>.

A typical <sup>29</sup>Si NMR spectrum of a methyl/vinyl branched fluid is shown in Figure 4. All main units can be detected. The normalized integrated intensities give the relative molar percentage of the different siloxane units. T and T<sup>vi</sup> branching as well as potential sites of branching (D<sup>OH</sup>, D<sup>vi,OH</sup>) are observed and expressed as molar percentages (Table 4). From these results an average model structure of the polysiloxane is drawn. When the structure is known, the absolute average degree of polymerization and the average number molecular weight can be calculated. The concentrations of the hydroxyl function as M<sup>OH</sup>, D<sup>OH</sup>, D<sup>vi,OH</sup> siloxane units are easily deduced and expressed as global and specific contents (Table 5). The concentration of vinyl functions as D<sup>vi,OH</sup> and T<sup>vi</sup> siloxane units can be similarly evaluated by this process.

The NMR results are certainly more accurate than any other chemical method. There are no side-reactions and there is no interference with other reactive functions as is observed in chemical analysis<sup>1,83</sup>. When a good signal-to-noise ratio is obtained the precision (relative error percentage) is 5%. For the chemical analysis of hydroxyl the relative error is 5-15%. A single NMR spectrum can yield information concerning a very complex silicone fluid that would otherwise require several different analytical methods.

Over the last ten years there has been a significant number of publications dealing with <sup>29</sup>Si NMR studies on organosilicon polymers<sup>99,100,102-105,108-119</sup>. However, there are new NMR techniques which present obvious advantages that have not yet been fully exploited for siloxane copolymer characterization. The low sensitivity of <sup>29</sup>Si nuclei can be boosted and resolution increased by the multipulse sequence techniques like Insensitive Nuclear Enhancement via Polarization Transfer (INEPT)<sup>108</sup> and Distortionless Enhancement by Polarization Transfer (DEPT)<sup>109</sup>. These pulse sequence techniques transfer the proton nuclear spin polarization to the silicon-29 spins via the <sup>1</sup>H-<sup>29</sup>Si second-order scalar coupling. Furthermore, this transfer depends only on proton relax-

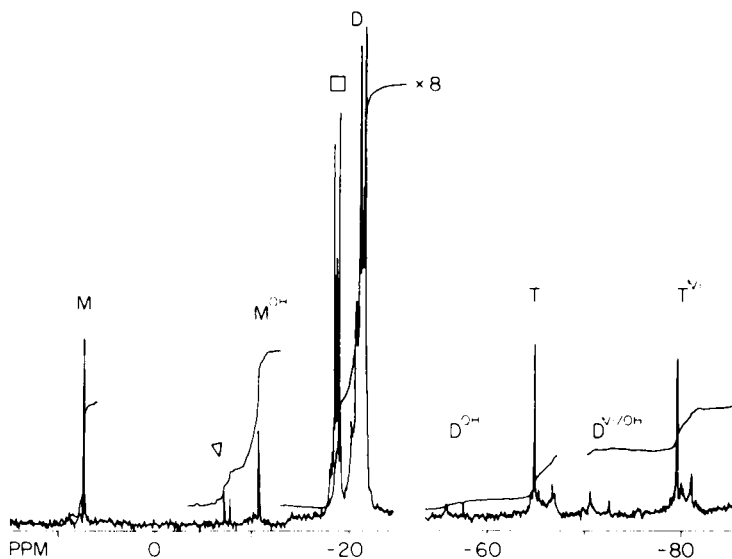


FIGURE 4.  $^{29}\text{Si}\{-^1\text{H}\}$  NMR spectrum of a methyl/vinyl T branched silicone liquid (after Reference 107);  $\nabla$  substituted cyclotrisiloxanes;  $\square$ , substituted cyclotetrasiloxanes

TABLE 4. Molar percentage of various siloxane units of a methyl/vinyl branched fluid as determined by  $^{29}\text{Si}$  NMR<sup>a</sup>

Unit	M	M <sup>OH</sup>	X	D	D <sup>OH</sup>	T	D <sup>Vi,OH</sup>	T <sup>Vi</sup>	Total
I(%)	2.7	2.8	19.1	56.2	1.5	8.1	1.8	7.8	100

<sup>a</sup> T and T<sup>Vi</sup> are the specific methyl and vinyl branching levels; X represents mixed cyclotetrasiloxanes.

TABLE 5. Specific and total hydroxyl and vinyl concentrations determined from values reported in Table 4

% OH (w/w)	M <sup>OH</sup>	0.64 ± 0.04	
	D <sup>OH</sup>	0.34 ± 0.02	
	D <sup>Vi,OH</sup>	0.34 ± 0.02	
	Total	1.32 ± 0.08	$^{29}\text{Si}$ NMR Chemical
	Total	1.7 ± 0.3	
% Vinyl (w/w)	D <sup>Vi,OH</sup>	0.54 ± 0.03	
	T <sup>Vi</sup>	2.81 ± 0.15	
	Total	3.35 ± 0.2	$^{29}\text{Si}$ NMR Chemical
	Total	3.3 ± 0.3	

ation and thus significantly decreases the experimental time<sup>110</sup>. A new technique, Recycle-Flow Fourier Transform NMR, has been recently proposed<sup>98,110-112</sup> and has been applied to the  $\langle M_n \rangle$  determination of siloxane polymers with carbon-13 and silicon-29 nuclei. This technique has several advantages. It reduces the total experimental time in getting a good signal-to-noise ratio; an improvement of 3 to 5 times is possible

with the flow technique over the conventional  $^{29}\text{Si}$  NMR enhanced by the use of  $\text{Cr}(\text{acac})_3$  relaxation reagent. Sample contamination is avoided, as is the adverse effect of the reagent on the assignment of chemical shifts and on the resolution. Furthermore, samples that cannot solubilize the chromium compound can be run.

### B. Linear Siloxane Copolymers

The description of the copolymer macrostructure requires the characterization of the chemical composition of chain and chain-end groups, the number average degree of polymerization, the molecular weight distribution and the related average molecular weights. These in turn can be related to the chemical, physical and mechanical properties of the copolymer. However, different properties are often observed for a given copolymer macrostructure and it was recognized early that the ordering of the different comonomer units in the chain, which could be non-uniform, would account for the apparently inconsistent observed properties<sup>120-128</sup>. Thus the sequence distribution in copolymers is extremely important since it may affect the copolymer properties in a subtle yet significant way. It depends on the methods of synthesis and on the reaction conditions and is governed by the kinetics and the thermodynamics of the polymerization process. Three general methods of synthesis are known, namely Sequential Polymerization, Condensation Copolymerization and Mixed Cyclic Copolymerization.

Sequential polymerization consists of first polymerizing a given cyclosiloxane to the desired chain length whereupon the comonomer cyclosiloxane is then introduced into the reaction medium and proceeds to grow from the living chain end. The reaction is terminated at the desired conversion<sup>129,130</sup>. The active reaction centre must only react with the monomer and not with the linear chains already formed. Under these conditions pure block copolymers will be produced.

Condensation polymerization requires that prepolymers are first prepared by ring opening polymerization. These homopolymers, which are generally hydroxyl end blocked, are then condensed to yield block copolymers. The concentration and the functionalities of the different prepolymers will determine the final microstructure of the copolymers. An  $A_xB_yA_x$  type copolymer, for example, will be obtained by condensing monofunctional  $A_x$  and difunctional  $B_y$  prepolymers<sup>1,49,131</sup>. Prediction of the copolymer macrostructure and of the lengths of the different blocks is straightforward. Problems only arise when redistribution reactions occur which scramble the order previously established.

The process of synthesizing high-molecular-weight copolymers by the polymerization of mixed cyclics is well established and widely used in the silicone industry. However, the microstructure which depends on several reaction parameters is not easily predictable. The way in which the sequences of the siloxane units are built up is directed by the relative reactivities of the monomers and the active chain-ends. In this process the different cyclics are mixed together and copolymerized. The reaction is initiated by basic or acidic catalysts and a stepwise addition polymerization kinetic scheme is followed. Cyclotrisiloxanes are most frequently used in these copolymerizations since the chain growth mechanism dominates the kinetics and redistribution reactions involving the polymer chain are of negligible importance. Several different copolymers may be obtained by this process. They will be monodisperse and free from cyclics and their microstructure can be varied from pure block to pure random copolymers.

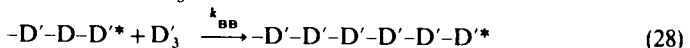
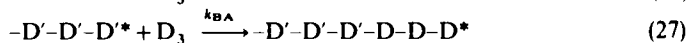
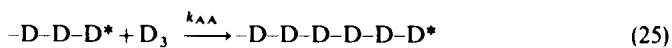
#### 1. Theoretical models<sup>120-127</sup> for mixed cyclic polymerization

Consider the copolymerization of two monomers  $D_3$  and  $D'_3$  representing two different cyclotrisiloxanes A and B. Initiation and termination bear much resemblance to those

same steps in homopolymerization, but it is the propagation step that gives copolymerization its special character by determining the composition of the copolymer. Therefore, in this treatment only the propagation step is considered and the chain lengths are assumed to be infinite. Ring opening reactions will initiate the copolymerization process by creating two active propagation centers  $D^*$  and  $D'^*$ ,



which take part in four propagation reactions,



$k_{AA}$  and  $k_{BB}$  represent the homopropagation rate constants and  $k_{AB}$  and  $k_{BA}$  represent the cross-propagation rate constants. The mechanism of the reaction is not considered as it does not influence the conclusions drawn from the model<sup>132</sup>. The rates of propagation are assumed to be dependent only on the nature and concentration of the terminal active unit regardless of the growing chain's previous history<sup>120, 127, 133</sup>. This assumption is important in the mathematical derivation since the way the chains grow may then be described by the Bernoulli trial distribution<sup>132</sup>. When the growth of the chains is affected by the nature of the monomer unit immediately preceding the active center, the first-order Markovian distribution must be applied. NMR spectroscopy can determine which theory best describes the copolymerization process<sup>129</sup>.

If A and B represent the two cyclotrisiloxanes, then the rates of consumption of monomers A and B can be expressed as

$$-d[A]/dt = k_{AA}[A^*][A] + k_{BA}[B^*][A] \quad (29)$$

$$-d[B]/dt = k_{BB}[B^*][B] + k_{AB}[A^*][B] \quad (30)$$

The ratio of these two equations yields an equation independent of the concentration of the active centres but a function of the monomer reactivity ratios  $r_1 = k_{AA}/k_{AB}$  and  $r_2 = k_{BB}/k_{BA}$ .

$$d[A]/d[B] = \{[A](r_1[A] + [B])\} / \{[B](r_2[B] + [A])\} \quad (31)$$

For the initial stages of the polymerization this equation can be rewritten in a form that relates the mole fraction of A in the copolymer ( $X_A^{cp}$ ) as a function of the mole fraction  $X_A$  and  $X_B$  of the monomers,

$$X_A^{cp} = (r_1 X_A^2 + X_A X_B) / (r_1 X_A^2 + 2X_A X_B + r_2 X_B^2) \quad (32)$$

where the mole fraction of A is given by

$$X_A^{cp} = A/(A + B) \quad (33)$$

and A and B are the amounts of the corresponding comonomers in the polymer. This equation describes the copolymer composition. The reactivity ratios can be obtained from the linear rearranged form of equation 32 or by non-linear regression analysis<sup>127, 134</sup>.

If one considers a situation where the ring opening of monomer A is easier than that of B, then  $k_{AA}$  is greater than  $k_{AB}$  and  $k_{BA}$  is greater than  $k_{BB}$ . If the active chain end is a



silanolate and the substituent on the siloxane unit is electronegative, then one can predict that  $k_{BB}$  is greater than  $k_{AB}$  and that  $k_{BA}$  is greater than  $k_{AA}$ :

$$\begin{array}{ccc} k_{BA} > k_{AA} & & \\ \vee & & \vee \\ k_{BB} > k_{AB} & & \end{array} \quad (34)$$

These qualitative comparisons of rate constants predict that in the initiation step, once  $A^*$  is formed, it will preferentially react with A. But if it reacts with B, the new  $B^*$  formed will react with A to reform an  $A^*$ . The preferential consumption of A is thus promoted both by the high rate of its homopolymerization and by the even higher rate of interaction between A and the macro-anion  $B^*$ . On the other hand, monomer B which is less active than monomer A is more inclined to interact with an active centre of its own nature ( $B^*$ ) than the macro-anion  $A^*$ . Thus further into the copolymerization a state is reached where  $[A] \ll [B]$  and reaction 25 strongly competes with reaction 26. At this stage A and B add in a random fashion to the growing copolymer chains. When A has completely reacted, the final stage is attained where only B is left and a pure B block is formed. The size of the random AB block depends on the relative reactivities of the monomers. The dual role of the electroactive substituents on silicon in the anionic copolymerization of cyclosiloxanes is well illustrated by this analysis. Electronegative substituents facilitate attack of the catalyst on the silicon atom. Once the ring is opened and the macro-anion formed, the nucleophilic activity of the anion is lowered relatively to a permethyl cyclosiloxane. Yet upon substituting a methyl group by an electronegative group, the rate of anionic polymerization still increases. Thus the nature of the cyclosiloxane which dictates the rate of the ring opening reaction has more influence on the whole process than the nature of the chain ends<sup>135</sup>.

The copolymer composition equation 32 can be used to show graphically the initial copolymer composition as a function of initial monomer composition<sup>122, 126</sup> (Figure 5). However, in the description of the copolymer, composition as a function of conversion or

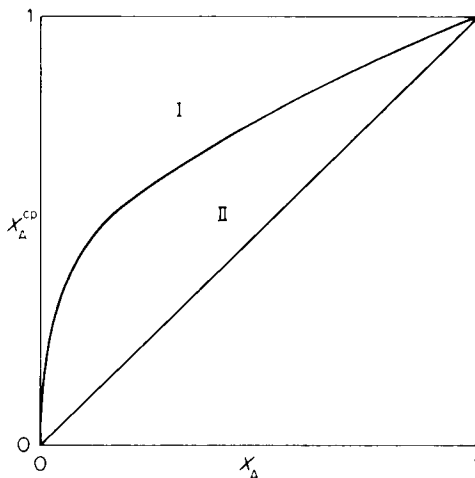


FIGURE 5. Initial mole fraction of component A in the copolymer as a function of its mole fraction in the initial comonomer mixture. Copolymerization of diphenylcyclotrisiloxane (A) and dimethylcyclotrisiloxane (B).  $r_1 = 2.14$ ,  $r_2 = 0.045$  (I);  $r_1 = r_2 = 1$  (II).

of time is of much more interest<sup>136</sup>. In the system above, if  $M$  is the total amount of A and B monomers and  $dM$  represents the number of moles of monomers that polymerize over a small time increment, then the number of moles of component A in the copolymer is  $X_A^{cp} \cdot dM$ . At the same time the number of moles of component A in the monomer has been reduced to

$$(M - dM)(X_A - dX_A) \quad (35)$$

The material balance of A is

$$X_A M - (M - dM)(X_A - dX_A) = X_A^{cp} dM \quad (36)$$

If the product of the two differentials is neglected we have

$$dM/M = dX_A/(X_A^{cp} - X_A) \quad (37)$$

which on integration gives the composition conversion equation

$$\ln(M/M_0) = \int_{X_A^0}^{X_A} dX_A/(X_A^{cp} - X_A) \quad (38)$$

This equation combined with the copolymer-composition equation 32 gives the instantaneous copolymer composition as a function of polymerization conversion. An analytical solution of equation 38 is not possible and numerical computation has to be used to solve the equation. The measured copolymer composition is the average composition from the beginning to a given conversion. The instantaneous copolymer composition must be integrated once again to provide the average copolymer composition. Figure 6 shows the variation of the instantaneous copolymer composition and the average copolymer composition as a function of the conversion for the system shown in Figure 5.

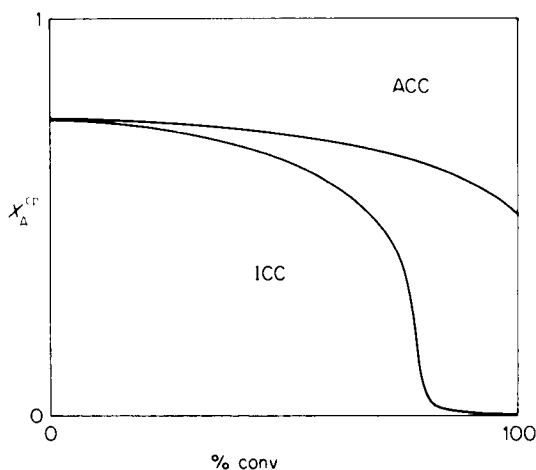


FIGURE 6. Instantaneous (ICC) and average (ACC) copolymer composition as a function of conversion for the polydiphenyl co-dimethylsiloxane. Initial monomer mixture is  $X_A^0 = 0.50$ .

### C. Copolymer Microstructure

The preceding treatment provides a description of the copolymer macrostructure as a function of the conversion. The copolymer microstructure is described by the distribution

of the different siloxane units along the macromolecular chain. Sequences of the monomer units can be considered theoretically and observed experimentally at the dyad, triad,  $n$ -ad levels. Two approaches to the microstructure determination may be considered: one derived from the kinetic scheme and the other from NMR experimental data of copolymers at equilibrium.

### 1. Analysis of kinetic chains

Price<sup>137</sup> and Bovey<sup>134</sup> were the first to develop the statistical analysis of polymers to study tacticity using Bernoullian and Markovian models. Randall and Koenig have published comprehensive surveys of the subject<sup>138, 139</sup>. In the Bernoullian trial distribution the monomer is added to the growing chain independently of the outcome of the previous addition. In the Markovian trial distribution the nature of the preceding unit does influence the chain growth. Price and Bovey have approached the problem through equivalent statistical approaches but applied different states to define the chain ends. For cyclotrisiloxanes where the siloxane units are added to the chain end in groups of 3 units the Price/Bernoulli and Bovey/Markov models do not apply. Price uses a one-state model and the preceding unit corresponds to the active chain end. The Price first-order Markovian model is described by 4 propagation reactions defined by 4 conditional probabilities:



Bovey adopts a two-state model where the preceding unit is the monomer unit immediately preceding the active chain end. The Bovey-Bernoullian model is now described at dyad levels by 4 reactions defined by the 4 probabilities of occurrence of the 4 dyads:



The correctness of each model for a given copolymer system can be tested and confirmed by experimental observation. In general, when Bernoullian statistics do not describe the sequence distribution, Markovian statistics do.

### 2. Number average sequence length

The average sequence length (ASL) is a measure of sequential homogeneity in copolymers. The basic definition of the average sequence length is the total number of siloxane units divided by the total number of sequences. It is calculated using the assumption that the chains are infinitely long<sup>140-142</sup>. Galvan and Tirrell<sup>143</sup> have developed an expression for the ASL as a function of the chain length. In their scheme they visualized finite copolymers terminated by four types of chain-ends, depending on the initial and final type of unit. Thus chains may be started and ended either by A or B units. They arrive at the following expression for the ASL of A as a function of the chain length:

$$\langle \bar{l}_A \rangle = 2 / \{ [(1 - P_{AB} - P_{BA} L^l + Y_A / T_A) / l] + P_{AB} + P_{BA} L^l \} \quad (47)$$

where  $T_A$  is the probability of finding an A unit in a chain of length  $l$ ,  $L^l = T_B/T_A$ ,  $Y_A$  is the probability that the first monomer unit in a chain is an A unit. The bar over  $l_A$  means the average and the  $\langle \rangle$  sign refers to the arithmetical mean. The expression for ASL in chains of infinite length is a particular case of equation 47 where  $l_A^x = l_A$  when  $l$  tends to  $\infty$  and  $L^{(l)}$  tends to  $P_{AB}/P_{BA}$ . This treatment will yield the instantaneous chain-length distribution, the relative population of monomer A and the ASL.

Lee and Marko<sup>144</sup> determined the sequence lengths of diphenylsiloxane units in the polydimethyl-co-diphenylsiloxane by analysing model compounds with PNMR. The differential sequence distribution and the PNMR data showed that in the first 20% of conversion, the sequence length of diphenyl and dimethyl siloxane units are mostly 6 and 3, respectively. Over the last 40% conversion the terminal segments of copolymer chains become pure dimethyl blocks.

### 3. Thermodynamic chains

The microstructure of siloxane copolymers has so far been deduced from kinetic and probabilistic considerations of the ring-opening polymerization of highly strained cyclo-siloxanes using non-rearranging anionic catalysis and under non-equilibrium conditions. The breakthrough leading to the approach where the microstructure could be obtained from a direct analysis of the copolymer regardless of its history came from Jancke, Engelhardt and Kriegsmann who combined <sup>29</sup>Si NMR data and statistical concepts<sup>145</sup>. They used the earlier concept of run number proposed by Harwood and Ritchey<sup>146</sup>. In a copolymer of infinite chain-length, the run number  $R$  is defined as the average number of monomer sequences ( $R$ ) occurring in a copolymer per 100 monomer units.  $R$  can be related to any sequence distribution sensitive physico-chemical property. The silicon-29 NMR spectrum of such copolymer will show two main groups of signals corresponding to A and B siloxane units. Each of these patterns will be a triplet since a given unit A or B is influenced in three different ways by its first A and B neighbours. These triplets correspond to three different triads. As the magnetic field increases, the influence of the second neighbours can be detected. As a result each of the signals constituting the triplet will be further split into three. The nine signals correspond to a pentad sequence (Figure 7). When the distribution of A and B siloxane units changes from pure random to pure block microstructure or when their molar concentrations are not equal, the relative intensities in the NMR pattern will gradually change from that shown in Figure 7. Furthermore, a splitting of signals can arise due to non-additivity of chemical shifts for different arrangements of neighbouring siloxane units in the pentad sequences where the central A is observed, viz. AAABB and ABAAB.

A silicon-29 NMR spectrum of a methyl phenyl silicone oil is shown in Figure 8 and illustrates the pattern described above. The first step in the determination of the microstructure is to derive the probabilities of occurrence of each signal corresponding either to a triad or to a pentad sequence centred on either an A or B monomer unit. These probabilities are directly proportional to the NMR signal intensities attributed to these sequences. In the kinetic situation  $P_{ij}$  was the instantaneous probability which could be related to the kinetic rate constants. At equilibrium,  $P_{ij}$  is the average probability of finding a dyad  $ij$  in the copolymer chain and is simply the mole fraction of an  $i$  species in a possible  $ij$  dyad sequence. According to the theory the probability of finding the triad BAB in the copolymer where the central A is observed is given by

$$P_{BAB} = P_{AB}^2 \cdot P(A) \quad (48)$$

Similarly, the pentad sequence ABABB will have a probability of occurrence given by

$$P_{ABABB} = 2P_{AB}^2 \cdot P_{BA} \cdot P_{BB} \cdot P(A) \quad (49)$$

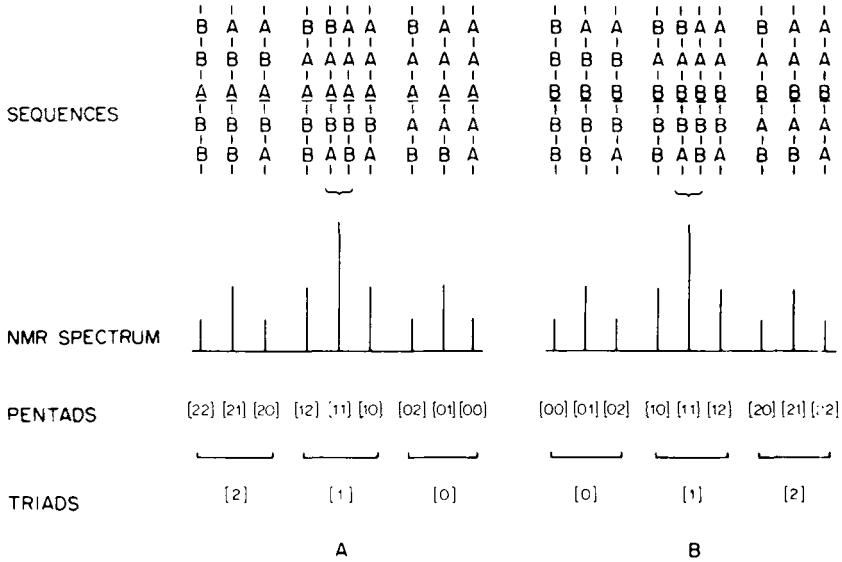


FIGURE 7. Pentad sequences and their corresponding A and B  $^{29}\text{Si}$  NMR signals for a random  $\text{A}_x\text{B}_y$  copolymer. Reproduced from Reference 145 by permission of VEB Deutscher Verlag für Grundstoffindustrie

The coefficient 2 appears as there are two ways of putting A and B at the end of the triad.  $P(\text{A})$  is the probability of finding A in the chain and is the mole fraction  $X_A$  (reported as a %). Table 6 contains the probability expressions for all triad and pentad sequences.

A consequence of the equality of A and B runs is that the percentages of various linkages can be related to the run number and to percentages of A and B units in the copolymer ( $100 \cdot X_A$ ,  $100 \cdot X_B$ ). The run number concept shows that:

$$\% \text{ A-A links} = \% \text{ A} - \% \text{ AB links} = 100 X_A - R/2 \quad (50)$$

$$\% \text{ B-B links} = \% \text{ B} - \% \text{ BA links} = 100 X_B - R/2 \quad (51)$$

$$\% (\text{AB} + \text{BA}) \text{ links} = 2(\% \text{ AB links}) = 2(\% \text{ BA links}) = R \quad (52)$$

The relative NMR intensities of triad sequences are a function of the run number and the mole fraction of the A or B siloxane units. Appropriate combinations of different NMR intensities provided expressions that lead to the run number. If the A and B units are statistically distributed along the copolymer chain, the run number will be

$$R_{\text{random}} = 200 X_A X_B \quad (53)$$

Thus the experimental run number relative to the random run number will show the average microstructure in terms of the copolymer's block, random or alternate character. Indeed when  $R > R_{\text{random}}$  the siloxane comonomer units are found to alternate, whilst when  $R < R_{\text{random}}$  they are found to agglomerate in blocks. Obviously, when  $R = R_{\text{random}}$ , the two different siloxane units are randomly distributed along the macromolecular chain. Another important microstructure parameter, the number average sequence length  $l_A$  and  $l_B$ , can be calculated from this experimental run number and the mole fraction of A and B:

$$l_A = 200 X_A/R \quad \text{and} \quad l_B = 200 X_B/R \quad (54)$$

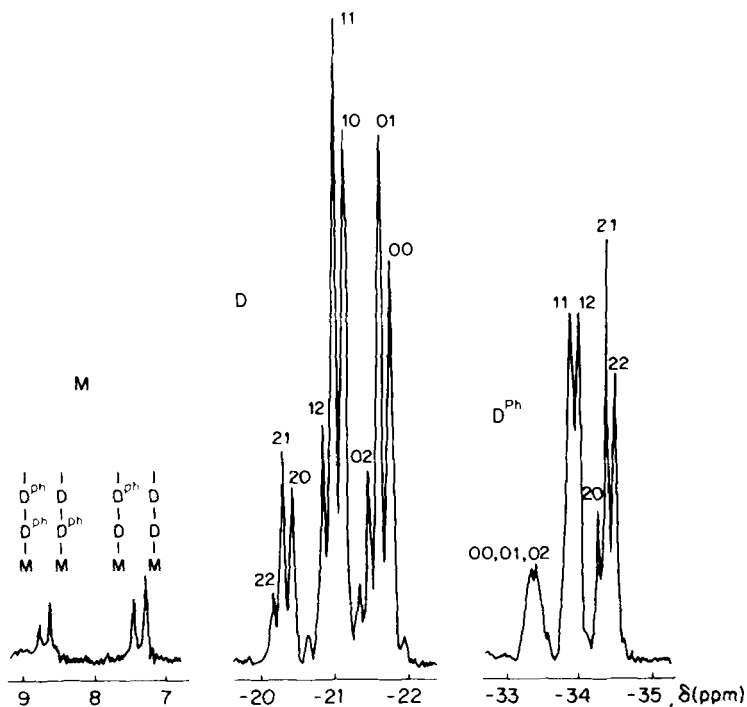


FIGURE 8. Si-29 NMR spectrum of methylphenyl silicone oil OV-7. Reproduced from Reference 121 by permission of Springer-Verlag

TABLE 6. Probabilities of occurrence of triad and pentad sequences

Triad	Probability	Intensity	Pentad	Probability	Intensity
0	$P_{AA}^2 \cdot P(A)$	$I_0$	00	$P_{AA}^4 \cdot P(A)$	$I_{00}$
			01	$2P_{AA}^3 \cdot P_{AB} \cdot P(A)$	$I_{01}$
			02	$P_{AA}^2 \cdot P_{AB}^2 \cdot P(A)$	$I_{02}$
			10	$2P_{AA}^2 \cdot P_{AB} \cdot P_{BA} \cdot P(A)$	$I_{10}$
1	$2P_{AB} \cdot P_{AA} \cdot P(A)$	$I_1$	11	$2P_{AA}^2 \cdot P_{AB} \cdot P_{BB} \cdot P(A)$	$I_{11}$
			11	$2P_{AA} \cdot P_{AB}^2 \cdot P_{BA} \cdot P(A)$	$I_{11}$
			12	$2P_{AA} \cdot P_{AB}^2 \cdot P_{BB} \cdot P(A)$	$I_{12}$
			20	$P_{AB}^2 \cdot P_{BA}^2 \cdot P(A)$	$I_{20}$
2	$P_{AB}^2 \cdot P(A)$	$I_2$	21	$2P_{AB}^2 \cdot P_{BA} \cdot P_{BB} \cdot P(A)$	$I_{21}$
			22	$P_{AB}^2 \cdot P_{BB}^2 \cdot P(A)$	$I_{22}$

The product of the reactivity ratio under non-equilibrium conditions can also be obtained:

$$r_A r_B = (l_A - 1)(l_B - 1) \quad (55)$$

Knowledge of  $X_A$ ,  $X_B$  and  $R$  thus permits one to calculate a set of microstructure parameters for a given copolymer. The Si-29 NMR analysis of the end-groups will provide a description of the 3 last siloxane units of the copolymer chain and the copolymer microstructure is fully revealed at the molecular level. The microstructure parameters for a polydimethyl co-methylphenylsiloxane are collected in Table 7.

TABLE 7. Microstructure parameters of poly(dimethyl co-methylphenyl)siloxane determined by  $^{29}\text{Si}$  NMR. Average composition  $\text{M}_2\text{D}_{58}\text{D}_{42}^{\text{h}}$

$X_A = 0.589$	$X_B = 0.411$
$l_A = 2.4$	$l_B = 1.6$
$P_{AA} = 0.585$	$P_{BB} = 0.405$
$P_{AB} = 0.415$	$P_{BA} = 0.595$
$R_{\text{exp}} = 48.9$	$R_{\text{ran}} = 48.4$

Finally, stereoisomerism of polydiorganosiloxanes  $(\text{RR}'\text{SiO})_n$  may be expected as a consequence of the pseudo-asymmetry of the silicon atoms. These polysiloxanes could be considered as configurational copolymers where the two different siloxane units adopt two different stereochemical configurations<sup>147</sup>.

#### D. Summary

In the case of copolymerization using catalysts that do not rearrange the siloxane chain and under non-equilibrium conditions a theoretical model can be developed to describe the microstructure. This same microstructure can be analysed by NMR of proton or silicon-29 nuclei. The concordance between theory and experiment enables confirmation of the correctness of either the theoretical mathematical model or the assignment of NMR signals. Quantitative information on the microstructure of copolymers as a function of time or at any conversion or for any comonomer composition can be obtained. For copolymerization under less precise conditions, the microstructure can be derived from the siloxane copolymer itself by direct observation of the magnetic resonance signals of the silicon-29 nuclei.

### V. DEGRADATION OF POLYSILOXANES

#### A. Introduction

Many industrial applications for polydimethylsiloxanes (PDMS) make use of their stability towards heat and radiation. However, under extreme conditions these macromolecules degrade and/or depolymerise and there is an ever present need for more thermally stable polymers and a better understanding of the degradation and depolymerization processes. The siloxane bond is the only bond involved in the depolymerization process whilst in the degradation process all bonds are involved. Indeed Hyde<sup>148</sup> and

Patnode<sup>46</sup> and their coworkers showed at an early date that PDMS heated at 350 to 400°C in vacuum depolymerizes to give mixtures of cyclosiloxanes of varying sizes. It is significant that the starting polymer and all the pyrolytic fractions are pure dimethylcyclosiloxanes where neither C-H nor Si-C bonds have been broken. Pyrolysis of branched polysiloxanes confirm these findings and indicate the stability of Si-CH<sub>3</sub> at temperatures up to 600°C. This result has been further confirmed by the pyrolysis of tetramethylsilane<sup>149</sup>. However, Nielsen has reported that when MD<sub>6</sub>M and MD<sub>4</sub>M fluids are heated at temperatures of 400–500°C, Si-C and C-H bonds start to break<sup>150</sup>.

In this review we first examine the degradation of silanol terminated PDMS and trimethylsilyl endblocked PDMS. This will be followed by a review of the degradation of branched polysiloxanes and of copolysiloxanes and the effect of impurities on the course of the degradation. Finally we examine the kinetics of the thermal depolymerization of PDMS.

### B. Silanol End Blocked PDMS

A silanol terminated PDMS heated under isothermal conditions at different temperatures first shows an increase in molecular weight (MW) as a function of time<sup>151</sup> (Figure 9). This process is the condensation of silanol groups on the ends the PDMS chains which leads to an increase of MW. However, the increase in MW is limited probably due to either a lowering in concentration of silanol groups or to the equilibrium nature of the silanol condensation reaction. When the temperature is further increased, a second process is observed which is the depolymerization. A mixture of cyclic oligomers

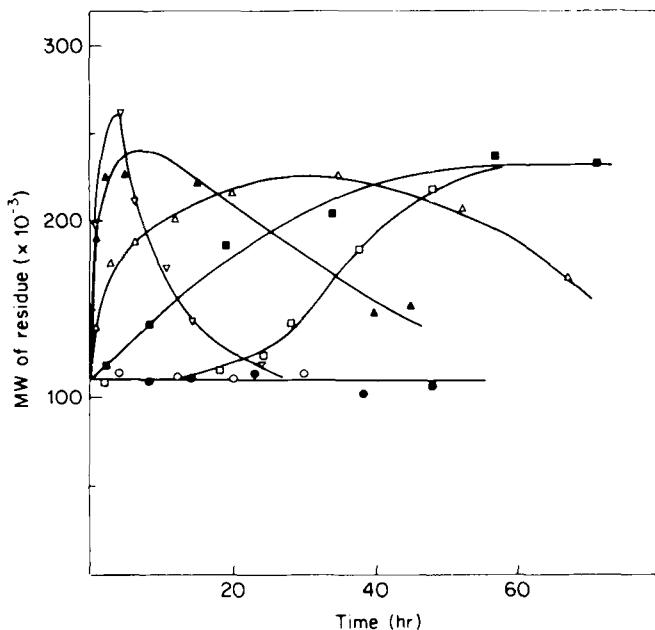


FIGURE 9. Change of molecular weight with time for silanol terminated PDMS. ○ 145°C, ● 160°C, □ 200°C, ■ 250°C, △ 300°C, ▲ 335°C, ▽ 385°C. Reproduced from Reference 151 with the permission of Pergamon Press



consisting of predominantly hexamethylcyclotrisiloxane ( $D_3$ ) and decreasing amounts of octamethylcyclotetrasiloxane ( $D_4$ ), decamethylpentacyclosiloxane ( $D_5$ ), etc., is obtained. These cyclic monomers are the only degradation products detected (Figure 10 and Table 8). Furthermore, the chemical structure of the residue is shown to be identical to that of the original polymer. The Thermal Volatilization Analysis (TVA) traces reveal that the evolution of volatile products starts at about 343 °C and reaches maximum rate at 443 °C. No evidence of methane or hydrogen was found. Trimethylsilyl (TMS) end blocked PDMS are more stable than silanol terminated PDMS though the volatile products are the same for both classes of polymer (Figure 11). Thermogravimetric analyses (TGA) confirm the TVA results (Figure 12). The TGA traces show a trend towards a higher stability with increasing MW, however the reasons for this are not clear. The MW decreases linearly as the extent of volatilization increases (Figure 13) which is interpreted as indicating a stepwise depolymerization process. The linear decrease excludes a chain scission mechanism, in which case the MW would have decreased more rapidly with the extent of volatilization. The depolymerization reaction is simply the reverse of the polymerization reaction and in a closed system the process will reach an equilibrium state. Blazso and coworkers<sup>152</sup> studied the degradation of linear PDMS terminated with -OH, -OR, -OK and -OTMS groups using Pyrolysis Gas Chromato-

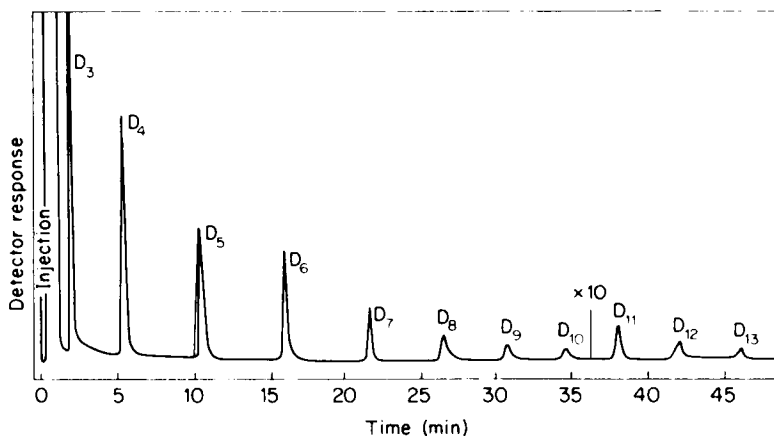


FIGURE 10. GLC trace of products of degradation of the silanol terminated PDMS heated to 500 °C. Column 1% SE 30 on Gas Chrom. Q. Programme 5° min<sup>-1</sup> ambient to 250 °C. Reproduced from Reference 151 by permission of Pergamon Press

TABLE 8. Yields of cyclic oligomers from  $\alpha,\omega$ -dihydroxy-PDMS.  $M_n = 111500$ . GLC quantitative analysis ( $T = 275\text{--}405$  °C, 0–80% degradation) (data from Reference 151 reproduced by permission of Pergamon Press)

Trimer	73%	Heptamer	1.0%
Tetramer	13%	Octamer	0.9%
Pentamer	4%	Nonamer	0.3%
Hexamer	6%	Decamer	0.2%

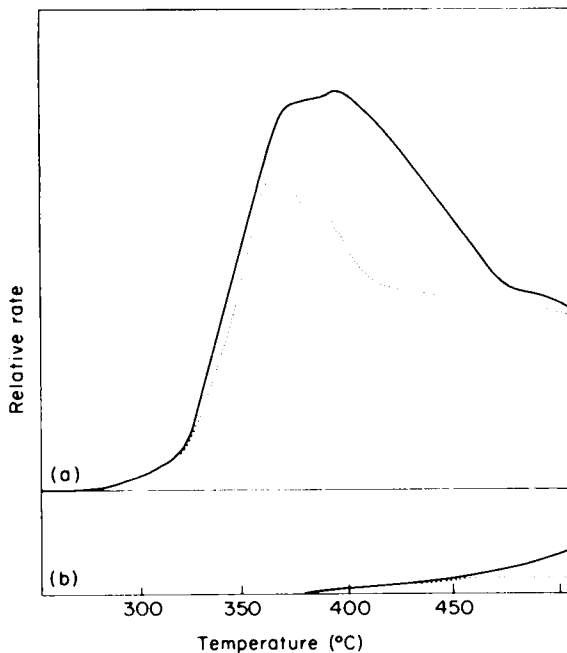


FIGURE 11. TVA traces for the silanol terminated PDMS (a) and TMS end blocked PDMS polymers (b). Trap temperatures: — 0°C, ···· 45°C. Reproduced from Reference 151 by permission of Pergamon Press

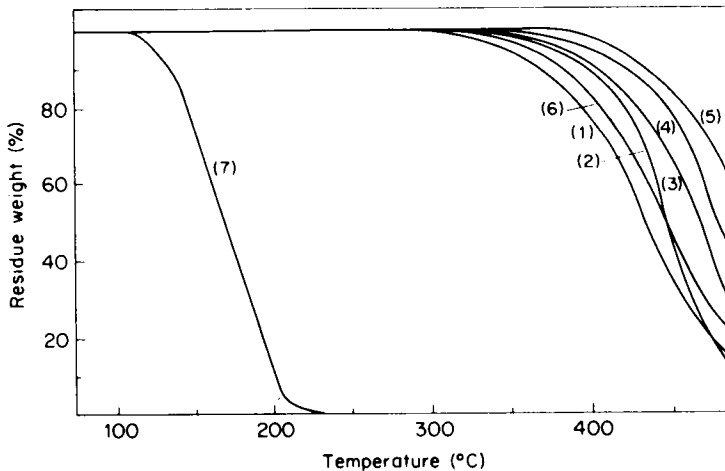


FIGURE 12. TG of polydimethylsiloxanes: 1-4 OH end blocked PDMS of various MW; 5-6 TMS end blocked PDMS; 7 Polymer 5 + 5% KOH. Reproduced from Reference 151 by permission of Pergamon Press

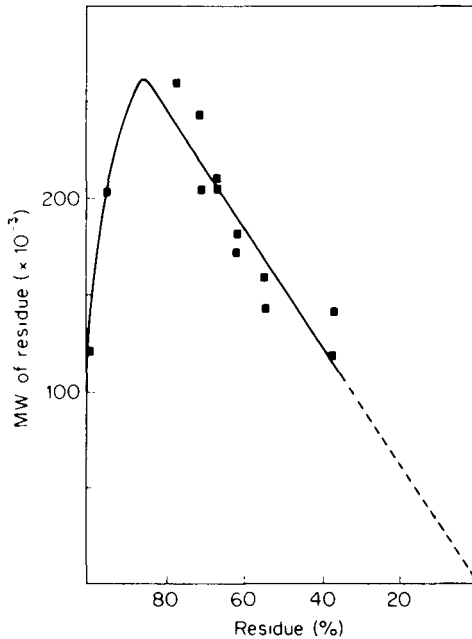
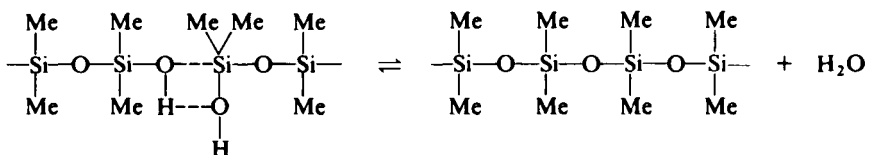


FIGURE 13. The effect of the extent of volatilization on the molecular weight of silanol end blocked PDMS heated at 385 C. Reproduced from Reference 151 by permission of Pergamon Press

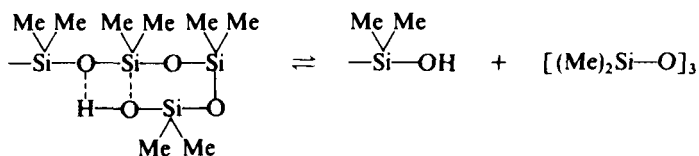
graphy (PGC), a technique which offers remarkably reproducible results. The nature and distribution of the pyrolysis products depends mainly on the chemistry of the degradation process for the particular polymer. Pyrolyses were carried out in a closed chamber in an argon atmosphere. Time ranging from 30 seconds to 5 minutes did not affect the nature and relative quantities of the volatile degradation products. Product analysis by Gas Chromatography (GC) confirmed that the degradation products were cyclic siloxanes with a relative content similar to those found by Grassie and MacFarlane<sup>151</sup> (Table 8). Andrianov<sup>153</sup> and Aleksandrova<sup>154</sup> and their coworkers found methane in the products of degradation of hydroxyl terminated PDMS. Whilst there is some disagreement on the relative proportions of the various volatile degradation products<sup>155-157</sup> the proportions of products do not vary significantly with temperature and the extent of degradation in the ranges 275-405 °C and 0-80% conversion<sup>151</sup>.

The proposed mechanisms for the condensation and depolymerization process are given below.

*Condensation:*



Depolymerization initiated by the silanol chain end:



This latter depolymerization mechanism which takes place at the chain ends was proposed by Verkhotin<sup>158</sup> and Aleksandrova<sup>154</sup> and their respective coworkers. The most complete study is that of Grassie and MacFarlane<sup>151</sup> who took into account the numerous data accumulated over the years, the importance of residual catalysts and the need of analysis by several techniques (TG, TVA, IR, GLC, GC-MS, NMR and Osmometry). They showed the necessity of a precise and reproducible method of polymerization and of precise control of the conditions under which depolymerization must be carried out in order to clearly establish mechanisms of reactions.

### C. Degradation of Trimethylsilyl End Blocked PDMS

From the mechanism of the depolymerization of silanol terminated PDMS it is clear that capping the silanol end groups with trimethylsilyl (TMS) groups will increase the thermal stability of PDMS in inert atmospheres. Indeed, as can be seen in Figure 11 the temperature must reach 430 °C before depolymerization starts. The problem then focuses on the nature of the products of depolymerization and how they are formed from the long polymer linear chains. Thomas and Kendrick<sup>155</sup> studied the depolymerization of TMS end blocked PDMS under non-equilibrium conditions in a catalyst-free environment. They observed that, like the silanol terminated PDMS, the main products are low MW cyclosiloxanes with D<sub>3</sub> predominating. Trace amounts of hexamethyldisiloxane (MM) and octamethyltrisiloxane (MDM) were also detected. The depolymerization process can be interpreted according to the following equilibrium:



For isothermal depolymerization where volatile products are removed from the sample as soon as they are formed, the equilibrium is constantly shifted to the right. The results of the product analysis collected in Table 9 confirm those already published by Patnode and Wilcock<sup>46</sup>. However, Tanny and St Pierre<sup>159</sup> report slightly different results for D<sub>3</sub> (61%) whilst Rode and coworkers<sup>157</sup> claim that D<sub>3</sub> is the only depolymerization product (99%). Nielsen<sup>150</sup> studied the depolymerization reaction at constant temperature and at atmospheric pressure with a nitrogen sweep for atmospheric control and to aid the removal of the volatile degradation products. At 370 ± 5 °C PDMS fluids depolymerize to produce both cyclic and linear volatile siloxane oligomers. These volatiles vary with the fluid and with the extent of the reaction. Thus a 10,000 cS fluid gives only cyclic volatiles upon depolymerization whereas PDMS of 50 to 1000 cS produce significant levels of linear oligosiloxanes throughout the depolymerization process. Blazso and coworkers<sup>152</sup> using the PGC technique confirm the product analysis results of Thomas and Kendrick<sup>155</sup>. Ballistreri<sup>160-162</sup> recently approached this problem with a new technique, viz. direct pyrolysis in the mass-spectrometer under high vacuum (DPMS). This technique, which provides information on the primary processes of the thermal decomposition of polymers, has been applied to the thermal decomposition of PDMS. The polymer sample is introduced via the direct insertion probe and the temperature is gradually increased up to the depolymerization temperature. The volatile molecules

TABLE 9. Gas chromatographic analysis of the depolymerization products of PDMS at 420 °C in vacuo (5 h) (from Reference 155 reproduced by permission of John Wiley & Sons, Inc)

Compound	% by weight
D <sub>3</sub>	43.7
D <sub>4</sub>	23.5
D <sub>5</sub>	9.7
D <sub>6</sub>	10.9
D <sub>7</sub>	7.2
D <sub>8</sub> -D <sub>12</sub>	5.0
MM	0.3 <sup>a</sup>
MDM	1.0 <sup>a</sup>

<sup>a</sup> Qualitative by peak height measurement.

formed during the depolymerization are then ionised and detected. These authors estimated the cyclic distribution by decomposing several commercial PDMS under non-equilibrium conditions. All samples yielded identical pyrolysis product distributions establishing the independence of the decomposition mechanisms on the MW and confirming the results of Thomas and Kendrick<sup>155,156</sup>. Table 10 compares the cyclics distribution they found with other published results. Grassie<sup>151</sup> pointed out that the disagreement that does occur is due mainly to the different methods of polymerization, to levels of impurities and to different experimental conditions. Lewis<sup>163,164</sup> had hitherto pointed out the importance of minute traces of acids, bases or other catalysts on the degradation of PDMS.

TABLE 10. Distribution of cyclic products generated in the thermal degradation of PDMS. Values normalized relative to D<sub>4</sub> for comparison. Peak intensities from mass spectrum at 470 °C for pure PDMS, at 350 °C for PDMS containing NaOH<sup>a</sup>

DP-MS <sup>160</sup>					
<i>n</i>	Equilibrium condition	Dynamic TGA <sup>155</sup>	Flash pyrolysis <sup>152</sup>	PDMS pure	PDMS + NaOH
3	1.7	185.9	277.8	243.9	149.2
4	100	100	100	100	100
5	61	41.1	36	35.6	28.8
6	18.5	46.3	22.2	37.6	49.1
7	3.8	30.7	16.6	13.1	15.4
8	2.5			1.1	0.5
9	1.7			0.2	0.1

Thermogravimetry has been used in many attempts to determine the mechanisms of the thermal depolymerization of silicone polymers<sup>151,155,156,163,164</sup>. A typical thermogram shows a single stage in the trace which is interpreted as the occurrence of a single

process. A second process may be observed at lower temperature which is the volatilization process of cyclics present in the polymer sample (Figure 14). The fact that in all recorded thermogravimetric traces the temperature at which depolymerization starts is greater than 350°C is strong evidence that the samples are catalyst-free. Although the activation energy derived from the Arrhenius equation is known to be empirical<sup>165</sup>, most researchers have used it to derive the main features of the depolymerization. The theories of Freeman and Carroll<sup>166</sup> and of Coats and Redfern<sup>167</sup> have been used to calculate the activation energies for the various processes operating under the different environmental conditions. Typical values are collected in Table 11. The activation energy ( $E_a$ ) for the thermal non-catalytic depolymerization process in vacuo is constant ( $177 \pm 10 \text{ kJ mol}^{-1}$ ) and independent of MW. This indicates that the same mechanism is common to all

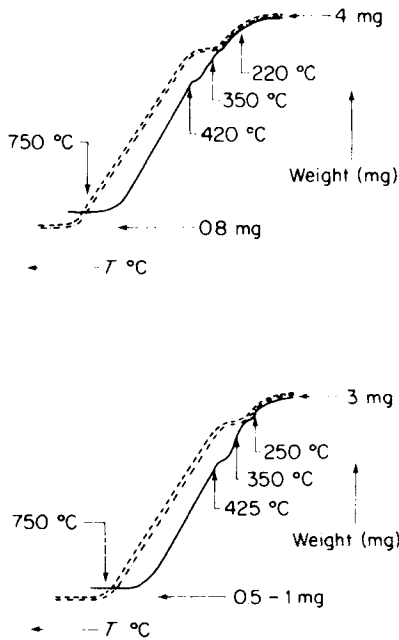
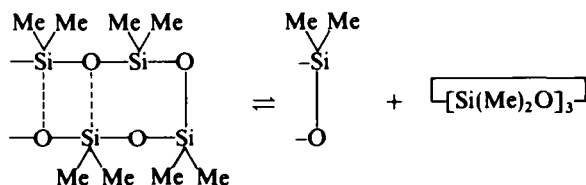


FIGURE 14. Thermogravimetric curves for two fractions of PDMS in controlled atmospheres. Reproduced from Reference 155 by permission of John Wiley & Sons, Inc

TABLE 11. Activation energies for the thermal decomposition of PDMS fractions in controlled atmospheres (from Reference 155 reproduced by permission of John Wiley & Sons, Inc)

Process	$T$ °C	$E_a$ (kJ mol <sup>-1</sup> )		
		Air	Vacuum	Argon
Cyclic volatilization	<200-300	54.3+4	48.1+4	51.8+2
Thermo-oxidation	320-420	125.4	—	—
Thermal depolymerization	420-480	188.1+8	175.6+2	152.1+8

fractions of polymer that Thomas and Kendrick<sup>155,156</sup> studied. The constancy of the first-order frequency factor ( $10^{14 \pm 0.5} \text{ min}^{-1}$ ) also supports a single mechanism of depolymerization. The value for the activation energy has been confirmed by other studies. The fact that the siloxane bond with a bond energy of  $451 \text{ kJ mol}^{-1}$  is involved in the depolymerization and that the  $E_a$  for the process ( $167 \text{ kJ mol}^{-1}$ ) is less than half of the bond energy led Thomas and Kendrick to conclude that depolymerization does not occur by direct rupture of the siloxane bond<sup>156,157,168</sup>. These authors suggest that the availability of vacant 3d orbitals on silicon allows the formation of a low-energy transition state and they propose a depolymerization mechanism based upon uncatalysed siloxane bond rearrangement which is thought to occur via an intramolecular, four-centre cyclic transition state (loop mechanism). As a result of the siloxane bond rearrangement a cyclic dimethylsiloxane is formed leaving a shorter linear chain. No scission of the main polymer chain has occurred. The transition state may not only be formed at any point along the polymer chain but also simultaneously at several points. This depolymerization process proceeds indefinitely within a chain until the residual linear structure is too short to cyclize.



The cyclization process is common to both silanol and TMS end-blocked polymers as is the relative proportion of cyclosiloxanes. The mechanism however is slightly different in the sense that, in the TMS case, a second silicon atom replaces the hydrogen atom in the four-centre cyclic transition state. Grassie<sup>151</sup> states that the mechanism implies a linear decrease of MW with extent of volatilization as in the case of silanol terminated PDMS, however this has not been shown experimentally. Further support for this mechanism comes from activation energies calculated for different substituted polysiloxanes (Table 12). A linear correlation of Taft constant  $\sigma^*$  with  $E_a$  is obtained (Figure 15). In the transition state the process leading to the release of cyclic molecules involves a nucleophilic attack by the oxygen atom on the silicon atom. Substituents with electron-donating inductive effects tend to increase the nucleophilicity of the siloxane oxygen and

TABLE 12. Taft  $\sigma^*$  constants, activation energies and first-order frequency factors ( $A$ ) for the depolymerization of substituted polysiloxanes. Major depolymerization products formed in the thermal degradation of substituted polysiloxanes are  $D_3$  and  $D_4$  (from Reference 156 reproduced by permission of John Wiley & Sons, Inc)

Polymer units	$\sigma^*$	$E_a$ $\text{kJ. mol}^{-1}$	$A$ $\text{min}^{-1}$	Ratio $D_3/D_4$
A $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{Si-O-}$	$\sim 0.10$	$146.3 \pm 12$	$10^{14 \pm 1}$	5/1
B $\text{CH}_3\text{CH}_2\text{CH}_2(\text{CH}_3)\text{Si-O-}$	$\sim 0.115$	$125.4 \pm 12$	$10^{15 \pm 1}$	10/1
C $\text{C}_6\text{H}_5(\text{CH}_3)\text{Si-O-}$	$\sim 0.10$	$179.5 \pm 8$	$10^{15 \pm 1}$	isomers
D $\text{CF}_3\text{CH}_2(\text{CH}_3)\text{Si-O-}$	$+ 0.32$	$292.6 \pm 42$	$10^{25 \pm 1}$	50/1
E $\text{CH}_3\text{CH}_2(\text{CH}_2)_2\text{Si-O-}$	$\sim 0.25$	$96.1 \pm 8$	$10^{26 \pm 1}$	20/1
$(\text{CH}_3)_2\text{Si-O-}$	0.0	$179.5 \pm 12$	$10^{14 \pm 0.5}$	2/1

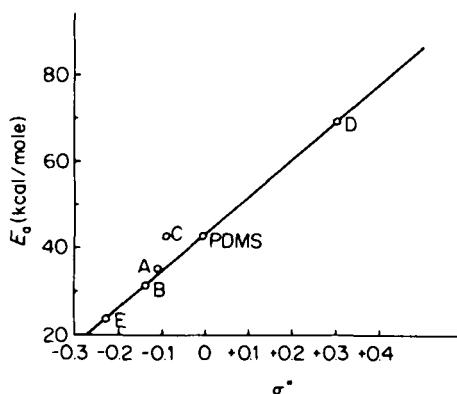
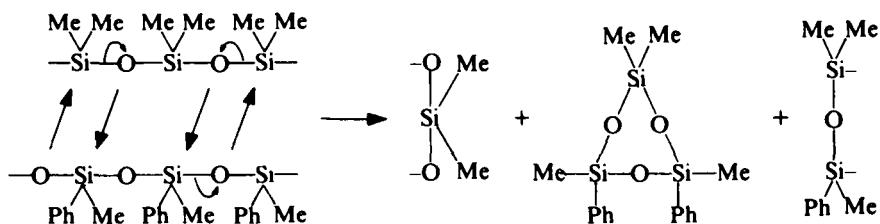


FIGURE 15. Plot of depolymerization activation energy against the Taft  $\sigma^*$  constant for the substituents on silicon. Reproduced from Reference 156 by permission of John Wiley & Sons, Inc

hence decrease the activation energy. Analysing average molecular weights and molecular weight distributions (MWD), Thomas and Kendrick<sup>155, 156</sup> showed that the mechanism corresponds to a randomly initiated depolymerization. However, the process appears to be more complex than this since intermolecular rearrangement of siloxane bonds does occur leading to a change in the MWD. The narrow MWD of the original polymer reverts to a broad Gaussian distribution (Figure 16). Perhaps the strongest support for this mechanism is found in the study of effect of heat on high MW cyclic PDMS carried out by Bannister and Semlyen<sup>169</sup>. These authors have shown that heating linear and cyclic PDMS of similar MW produces polymeric products with quite different MW and MWD (Figure 17 and 18). If a similar mechanism of bond interchange reactions is believed to operate, one would predict that the products of the thermal degradation of high-molecular-weight cyclic PDMS would be volatile cyclic oligomers and cyclic polymers of high MW (Figure 19). If the depolymerization of a large cyclic was initiated by random scission before the depolymerization (unzipping) process, a linear chain molecule with an identical MW would have been produced. The unzipping process would then take place, perhaps simultaneously, and only low MW cyclic oligomers would be detected. The results shown in Figures 17 and 18 are consistent with the mechanism involving bond interchange reactions occurring via a cyclic transition state. Further support for the cyclic transition state comes from the studies of Grassie and his coworkers<sup>170-172</sup>. Blends of TMS end blocked PDMS and polyphenylmethylsiloxane when heated produce mixed cyclics which could only be formed in the process depicted below.





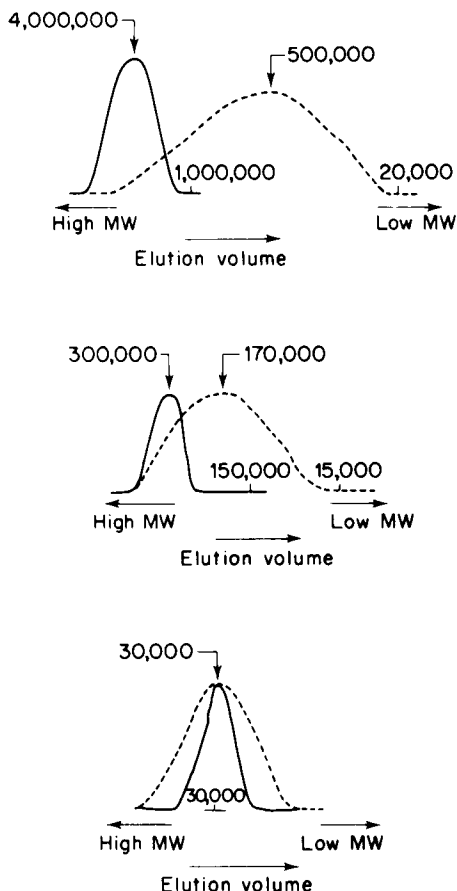


FIGURE 16. GPC MWD for three different fractions of TMS end blocked PDMS before (—) and after (---) depolymerization. Reproduced from Reference 155 by permission of John Wiley & Sons, Inc.

This also supports the intermolecular degradation mechanism. A novel investigation of PDMS degradation has been carried out by Manders and Bellama<sup>173</sup> who used a pulsed infrared CO<sub>2</sub> TEA laser. This study was aimed at determining whether the loop mechanism or the bond scission mechanism best represents the thermal depolymerization of polysiloxanes. Pulse infrared experiments are characterised by multiphoton absorption that is rapidly converted into random heat energy. A temperature jump is produced in  $10^6$ – $10^{11}$  K s<sup>-1</sup>. During the cooling period in the range of  $10^3$ – $10^6$  K s<sup>-1</sup> reactions may take place. The reactant is at the reaction temperature for a short time only and the effects of trace impurities are minimized and the effects of walls of the vessel are negligible. Different fractions of PDMS of narrow MWD and of varying viscosities (10, 50, 10000 cS), a 50 cS branched PDMS and hexamethyldisiloxane were studied. In all the experiments the degradation products were methane, ethylene, ethane and hydrogen. No low MW linear siloxanes nor cyclic siloxanes were detected.

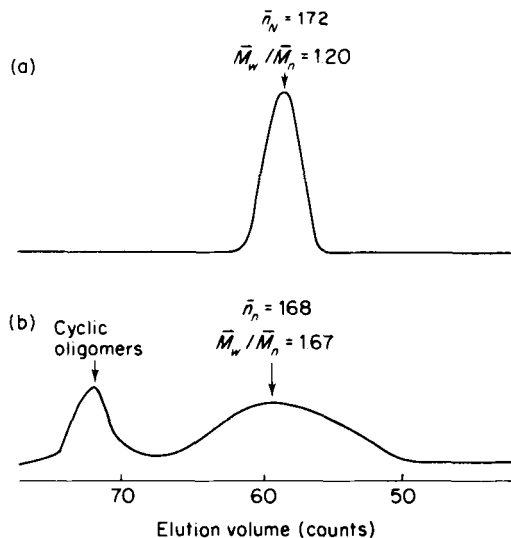


FIGURE 17. GPC traces of a linear PDMS fraction (a) before heating, and (b) the products obtained after heating at 668 K for 3 days. The scale showing the elution volumes in counts is the same for both traces. Reproduced from Bannister, D. J. and Semlyen, J. A., *Polymer* 1981, **22**, 377, by permission of the publishers, Butterworth and Co. (Publishers) Ltd.

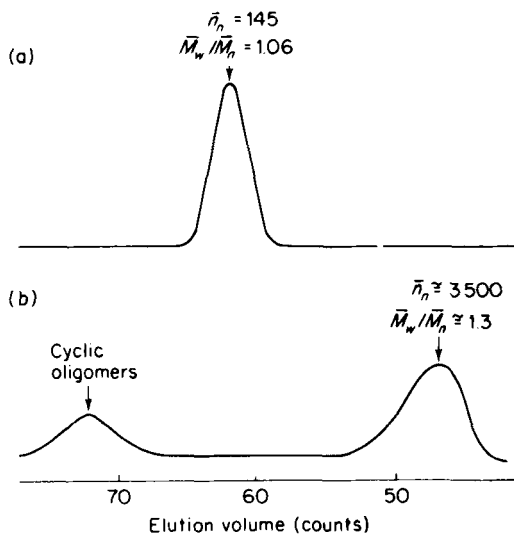


FIGURE 18. GPC traces of a cyclic PDMS fraction (a) before heating, and (b) the products obtained after heating at 668 K for 3 days. The scale showing the elution volumes in counts is the same for both traces. Reproduced from Bannister, D. J. and Semlyen, J. A., *Polymer* 1981, **22**, 377, by permission of the publishers, Butterworth and Co. (Publishers) Ltd.

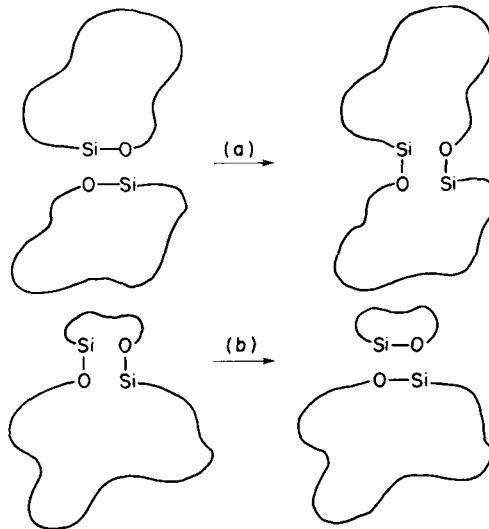
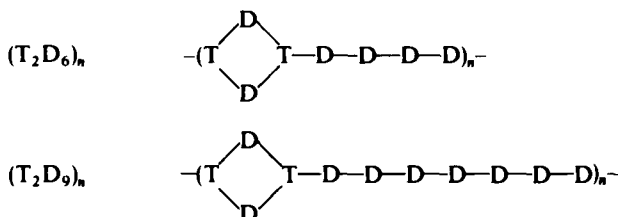


FIGURE 19. The siloxane bond interchange reaction for cyclic PDMS. The intermolecular process (a) results in a much higher molecular weight cyclic polymer than that of the starting material. The intramolecular process (b) gives a mixture of cyclic oligomers. Reproduced from Bannister, D. J. and Semlyen, J. A., *Polymer* 1981, **22**, 377, by permission of the publishers, Butterworth and Co. (Publishers) Ltd.

#### D. Degradation of Branched PDMS

The introduction of branching in linear PDMS makes the characterization of the depolymerization products more difficult. The decomposition products are more numerous and have more complex molecular structures. The thermal degradation of a T and Q branched polysiloxanes was reported by Scott<sup>174</sup> in 1946. Several linear, cyclic and polycyclic methylsiloxanes have been studied by Garzo and Alexander<sup>175-177</sup>, the products of pyrolysis are low MW dimethylsiloxanes ( $MD_mM$ ), cyclic dimethylsiloxanes ( $D_m$ ) and polycyclic methylsiloxanes ( $T_nD_m$ ). In the thermal decomposition of branched chain polysiloxanes up to seventeen different products can be identified as being either low MW methylsiloxanes with cyclic, bicyclic or polycyclic structures. Several geometric isomers are also observed in the pyrograms. These resinous materials are of irregular structure and thus do not constitute an ideal system for studying the relation between polymer structure and thermal degradation products. Blazso and coworkers<sup>178</sup> examined the thermal degradation of two well-characterized methylsiloxane cycloliner polymers:



The products of pyrolysis at 350 °C are cyclic methylsiloxane oligomers,  $D_3$  from  $(T_2D_6)_n$  and  $D_3, D_4, D_5, \dots$  from  $(T_2D_9)_n$ . The degree of conversion is low at this temperature. At 550 °C, several polycyclics ranging from 3 to 9 siloxane units are detected by GLC (Figure 20 and Table 13) and were identified by GC-MS,  $^{29}\text{Si}$  NMR and X-ray diffraction<sup>175-178</sup>. Compared to PDMS the relative amounts of the cyclic products  $D_3, D_4, D_5$  in the pyrogram of  $(T_2D_9)_n$  are similar but from  $(T_2D_6)_n$ , smaller amounts of  $D_4$  and  $D_5$  were found.

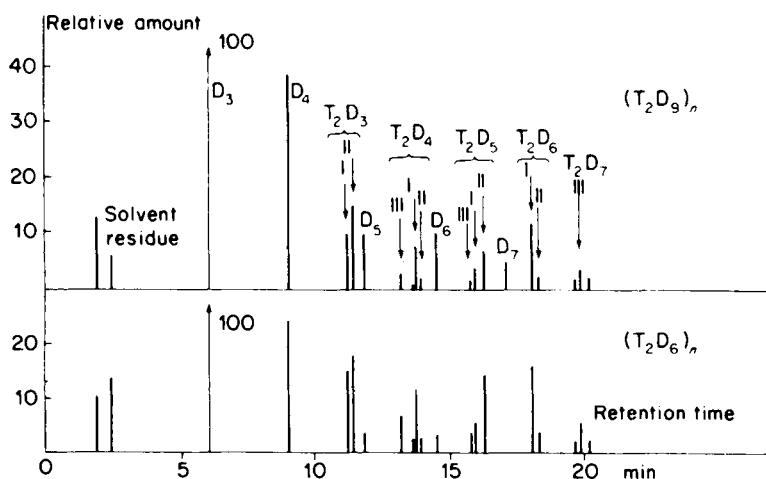
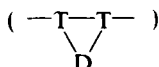


FIGURE 20. Pyrolysis products from cyclo-linear methylsiloxane polymers separated on OV-1 gas chromatographic phase. Reproduced from Reference 178 by permission of Elsevier



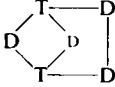
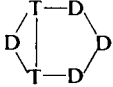
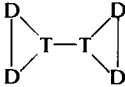
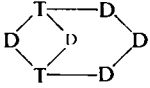
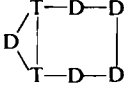
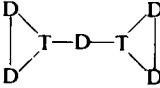
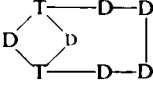
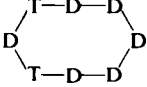
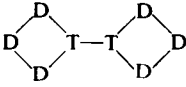
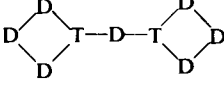
The results of the thermal decomposition of branched chain methylsiloxane polymers and polycyclics indicate that the decomposition is similar to that observed with PDMS. The structures of the degradation products from  $(T_2D_6)_n$  and  $(T_2D_9)_n$  show that they originate from the cycloliner polymers through the loop mechanism. Indeed, considering the bicyclic compounds of series I in Table 13 they can only be formed via a concerted intramolecular mechanism. Products in series II could result from three consecutive rearrangement steps which would explain the presence of the three-membered cyclic siloxane



The formation of the products in series III can be explained by a bond rearrangement process between the linear and cyclic parts of the polymer. It is clear from the results that no change occurs in functionality of siloxane units during the pyrolysis.

These studies have revealed that the molecular structure of the degradation products are closely connected with the polymer molecular microstructure. Linear segments lead to cyclic oligomers and branched fragments lead to polycyclics. The average frequency of the branching points in the polymer determine the ratio of the amounts of monocyclic to bicyclic products.

TABLE 13. The homologous series of pyrolysis products of cyclolinear methylsiloxane polymers (from Reference 178 reproduced by permission of Elsevier)

Composition	Series I	Series II	Series III
$T_2D_3$			
$T_2D_4$			
$T_2D_5$			
$T_2D_6$			
$T_2D_7$			

### E. Degradation of Copolysiloxanes

Another important class of linear polysiloxanes are the siloxane copolymers. The replacement of methyl groups by other organic groups improves the specific physicochemical properties of PDMS, and one such improvement is in the area of resistance to thermal degradation, e.g., phenyl-containing polysiloxanes have superior thermal stability compared to PDMS.

Thomas and Kendrick<sup>155, 156</sup> investigated depolymerization of variously substituted TMS end blocked linear polysiloxanes. Under the experimental conditions only the depolymerization process was observed. The activation energy associated with this process was calculated from the thermograms and the results are summarized in Table 12. Product analysis indicated cyclotrisiloxanes and cycloctetrasiloxanes as major products showing that siloxane bonds are the only bonds involved in the depolymerization process. The weight loss for all these polymers was 100% except for the trifluoropropyl polymer, in which case only 75% of the macromolecule was recovered as mixed cyclic siloxanes. The reason for this partial conversion was explained by a gamma fluoro elimination reaction where a fluorine atom migrates to the silicon atom in the chain thus

liberating 1,1-difluoropropene. A thermogravimetric study of a fluorosilicone elastomer showed that hydrogen fluoride is evolved during the degradation<sup>179</sup>.

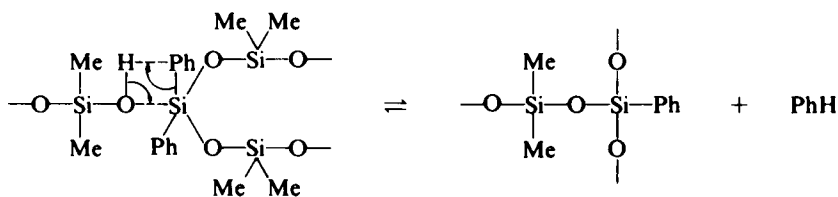
Grassie and coworkers have studied the thermal depolymerization of copolymers<sup>170-172</sup>. They prepared phenyl-containing polysiloxanes from dimethyl and methyl phenyl substituted cyclotrisiloxanes and cyclotetrasiloxanes using a transient catalyst in order to eliminate any trace of impurities. Two general approaches to the preparation of these copolymers was adopted, viz. ring opening copolymerization of dimethyl and methylphenyl cyclic oligomers and ring opening polymerization of a mixed dimethyl-/methylphenyl cyclosiloxane. In the first case a block microstructure is expected whereas in the second case a more random distribution of the different siloxane units should be obtained. Silanol and trimethylsilyl end blocked polyphenylmethylsiloxane (I), polydimethyl co-phenylmethylsiloxane (II) and polydimethyl co-diphenylsiloxane (III) were studied. TVA of I and II indicated the evolution of benzene and methane at 300 °C. Unlike PDMS, I becomes insoluble at temperatures as low as 150 °C and TVA of III revealed that the proportions of volatile products (D<sub>3</sub>, D<sub>4</sub> mainly) decrease with increasing phenyl content. The amounts of benzene formed after a long heating period (20 h at 300 °C and 10 h at 500 °C) depend on the nature of the end group. At 300 °C silanol terminated polymers evolve less benzene than theory assuming that one molecule of benzene is associated with one hydroxyl group. At 500 °C, very much more benzene is formed than predicted theoretically on this basis (Table 14). Thermogravimetry clearly demonstrates the correlation of stability and residue with molecular weight. In general higher molecular weights give lower stabilities and smaller residues. The threshold weight loss temperature and the weight of residue for silanol terminated polymers both increase with increasing phenyl content in the polymer. For the same phenyl content the stability of the silanol terminated polymers decreases with increasing molecular weight. Copolymers with very low methylphenylsiloxane to dimethylsiloxane ratios behave in a similar fashion to PDMS. For these polymers end blocking with TMS increases the stability by

TABLE 14. Evolution of benzene from polydimethyl co-phenylmethylsiloxanes; (from References 170-172)

Polymer end group	% phenyl content	Yield of benzene (mol × 10 <sup>3</sup> /g polymer)		
		300 °C	500 °C	calc. <sup>a</sup>
OH	6.25	—	0.43	0.84
TMS	6.25	—	1.02	0.00
OH	12.50	0.01	2.71	0.75
TMS	12.50	0.00	3.85	0.00
OH	37.33	0.58	28.89	3.97
TMS	37.33	0.00	44.94	0.00
OH	25.00	0.10	7.60	0.65
TMS	25.00	0.00	4.28	0.00
OH	66.70	0.60	278.20	3.87
TMS	66.70	0.00	184.04	0.00

<sup>a</sup> Calculated assuming that each terminal hydroxy group leads to the evolution of 1 benzene molecule.

preventing depolymerization centred on the silanol end groups. The silanol terminated polymers with high methylphenylsiloxane contents are more stable than their TMS end blocked counterparts. This is because branch points are formed in the polymer when the silanols react with the phenyl groups. The degradation products as observed by NMR are mainly mixtures of all possible cyclic trimers and tetramers. Neither conversion nor end blocking gives any differentiation insofar as the nature of these complex mixtures is concerned (Table 15). From the results described above it is evident that the thermal degradation of phenyl-containing copolymers differs from that observed for PDMS. Thus, benzene is formed and silanol groups confer greater stability than trimethylsilyl terminal structures. Grassie and his coworkers<sup>151, 170, 171, 172</sup> proposed that the principal effect of the silanol end group is to assist in the cleavage of Si-Ph bonds to form benzene and thereby create a T branch point in the polymer. This mechanism explains



why small amounts of benzene are formed at lower temperatures than that which would be expected from random cleavage of Si-Ph, as well as the dependency of the rate of formation of volatiles and the amount of benzene formed on the number of silanol groups in the polymer and also the introduction of branching in the residue. However, the evolution of benzene at higher temperatures is not easily explained. Possible mechanisms for its formation are random Si-Ph bond scission<sup>170</sup>, free radical reaction<sup>180</sup>, or enhanced lability of the phenyl groups adjacent to branching points<sup>181</sup>. The four-centre loop mechanism accounts for the evolution of mixed cyclics and the decreasing amount of cyclics formed as branching levels increase.

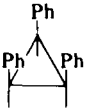
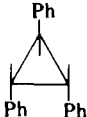
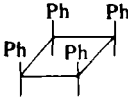
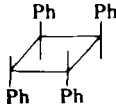
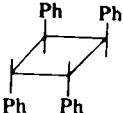
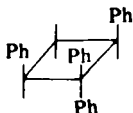
## F. The Effect of the Degradation Environment

The thermal depolymerization of PDMS in an inert atmosphere has yielded valuable information concerning the products of degradation and the mechanism of the degradation process. However, the real conditions under which silicones are used give rise to new reactions which compete with the fundamental depolymerization reaction, e.g. the presence of residual catalyst from the polymers synthesis, the nature of the degradation atmosphere and the presence or absence of water.

### 1. The effect of oxygen

The exceptional oxidation resistance of PDMS fluids is shown by the fact that their viscosities at room temperature are very little changed by heating in air. However, when heated to high temperatures or over a long period the fluids degrade by rupture of both Si-C and Si-O bonds. Cleavage of Si-C bonds gives rise to volatile organic materials. The organic group is replaced by a new siloxane bond and branching followed by cross linking occurs. Rupture of the Si-O bonds brings about the formation of low-molecular-weight siloxanes. The oxidation of methyl substituents produces carbon monoxide, carbon dioxide, hydrogen, formaldehyde and water. The oxidation of phenyl substituents produces methane, ethane, benzene, phenol, methanol, ethylene, propylene and higher molecular weight products<sup>151, 182</sup>. Despite the shortage of hard data in the literature it is

TABLE 15. Products of the depolymerization of polyphenylmethylsiloxanes (from References 170-172)

Structure	mol %
	16.5
	46.7
	5.8
	18.0
	10.3
	2.7

clear that oxygen does affect the degradation of PDMS, the production of volatiles is accelerated and cross linking occurs via oxidation of the methyl groups. The mechanism may be free radical in nature or a non-radical reaction leading to the formation of  $\equiv\text{Si}-\text{O}-\text{CH}_3$  structure.

Both oxidation and thermal depolymerization occur simultaneously. The thermogram of PDMS in a controlled air atmosphere shows an additional stage which has been attributed to the thermo-oxidation process and which occurs at a slightly lower temperature (320-420°C) than the thermal depolymerization<sup>155</sup>. During the course of the thermo-oxidation reaction the inorganic content of the polymer increases<sup>182</sup>. The activation energies calculated for this process support that calculated by Doyle<sup>183</sup> for the degradation of a silicone resin in air and by Cox and his coworkers<sup>184</sup> for the thermo-oxidation of two fluorosilicone polymers. Inhibition of the thermo-oxidation of PDMS is achieved by the use of transition metal compounds<sup>185</sup> often in the form of the oxide. The critical concentration where the oxidation is completely inhibited depends both on the temperature and the oxide concentration (Figure 21).



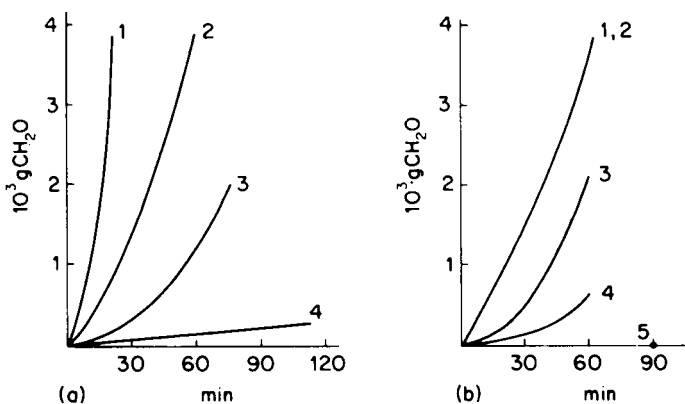


FIGURE 21. Kinetics of the formation of formaldehyde during the oxidation of PDMS in the presence of Tc oxides; (a)  $T = 305^\circ\text{C}$ , Tc concentration ( $\text{mol.l}^{-1}$ ) equal to 0 (1),  $1.1 \cdot 10^{-4}$  (2),  $1.45 \cdot 10^{-4}$  (3), and  $2.48 \cdot 10^{-4}$  (4); (b) Tc concentration equal to  $1.1 \cdot 10^{-4} \text{ mol.l}^{-1}$ ,  $T$  ( $^\circ\text{C}$ ); 305 (1), 298 (2), 290 (3), 285 (4), 280 (5). Reproduced from Reference 185 by permission of Plenum Publishing Corporation

## 2. The effect of alkaline catalysts

Traces of alkaline catalysts will simply depolymerize the high molecular PDMS. Thermogravimetry shows the effect of KOH on the stability of PDMS (Figure 22). The threshold degradation temperature is lowered by as much as  $250^\circ\text{C}$  and methane, which has been detected in the degradation products, is thought to arise from the KOH catalysed cleavage of Si-C bonds. In the presence of KOH, TMS end blocking does not effect the stability of the PDMS. Direct pyrolysis/mass spectrometry experiments showed that NaOH lowers the temperature at which polymer decomposition occurs without altering the relative amounts of pyrolysis products<sup>160-162</sup>. The mechanism that has been proposed to account for the formation of methane and bicyclic trisiloxanes is outlined in Scheme 1. A similar reaction occurring further along the same polymer chain would create a second monoalkyl substituted silicon atom in the polymer chain and further depolymerization would yield cyclodialkylsiloxanes and the bicyclic molecule: This mechanism does not involve chain ends since both silanol and TMS end blocked PDMS start to degrade at the same temperature. Kucera and his coworkers<sup>186-189</sup> showed that the weight loss could be reduced by incorporating into the polymer substances such as  $\text{Al}(\text{OH})_3$  which react with the active sites and stabilize them. Cox and coworkers<sup>190</sup> attributed differences in the thermal stability of two fluorinated siloxanes to the presence of trace impurities, including catalyst residues.

In the presence of water, alcohols or phenols at temperatures above  $200^\circ\text{C}$  PDMS undergoes cleavage to form siloxanols. The decrease in MW that occurs can be prevented by the use of bifunctional agents which react with the silanol groups as they are formed (Figure 23).

## G. Kinetics of Thermal Depolymerization

Most of the data generated on the mechanism of the thermal depolymerization of polysiloxanes has been of qualitative nature. Detailed kinetic studies have not been widely reported. Following Gordon<sup>192</sup> and Boyd<sup>193</sup>, MacCallum<sup>194</sup> has further developed the theory of the depolymerization of addition polymers to include a kinetic

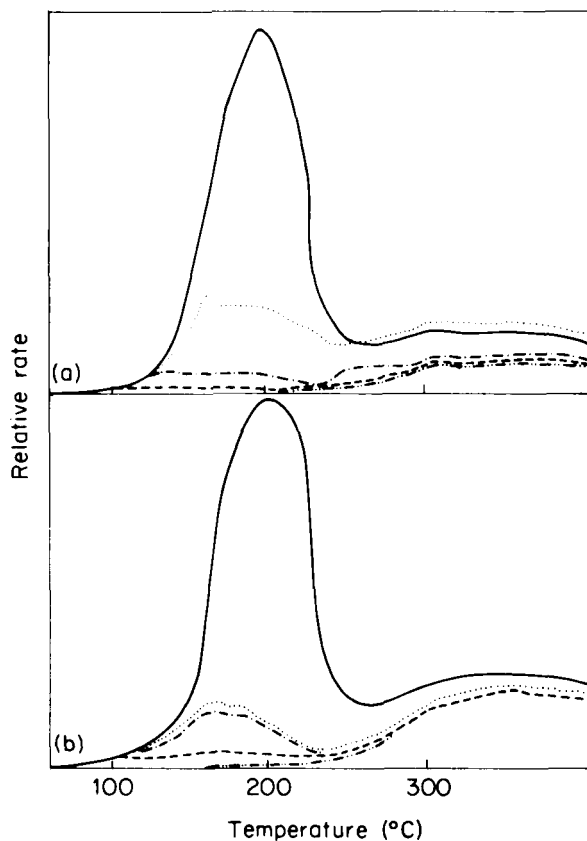


FIGURE 22. TVA traces of (a) silanol terminated polymer, and (b) TMS end blocked polymer each with 5% by weight of KOH. Trap temperatures: ( $^{\circ}\text{C}$ ) — 0,  $\cdots$  — 45,  $-\cdot-\cdot-$  — 75,  $----$  — 100,  $---$  — 196. Reproduced from Reference 151 by permission of Pergamon Press

analysis of random and chain end initiated depolymerization reactions. The overall mechanism is visualized as proceeding according to the following scheme.

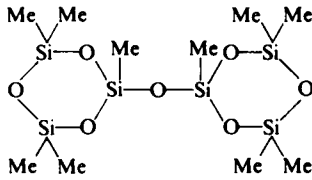
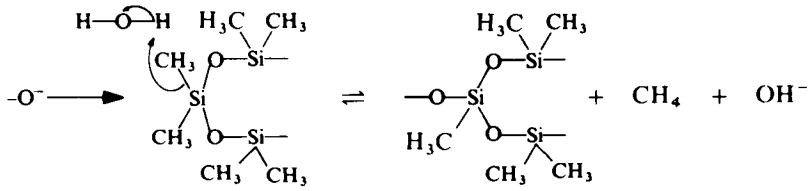
- (1) Initiation, which can take place either randomly along the polymer chain or else at the chain ends.
- (2) Depropagation, i.e. unzipping of monomer units from the chain ends created in the initiation step.
- (3) Termination by stabilization of the active chain end.

An average zip length ( $Z$ ) is defined as the average number of monomer units produced per act of initiation. For a polymer sample undergoing depolymerization the weight  $W$  is given by

$$W = N \cdot \text{DP} \cdot m \quad (56)$$

where  $N$  is the number of polymer molecules, DP the number average degree of polymerization and  $m$  the molecular weight of the monomer. The related kinetic equation is

$$dW/dt = m \cdot N \cdot d(\text{DP})/dt + m \cdot \text{DP} \cdot dN/dt \quad (57)$$



SCHEME 1

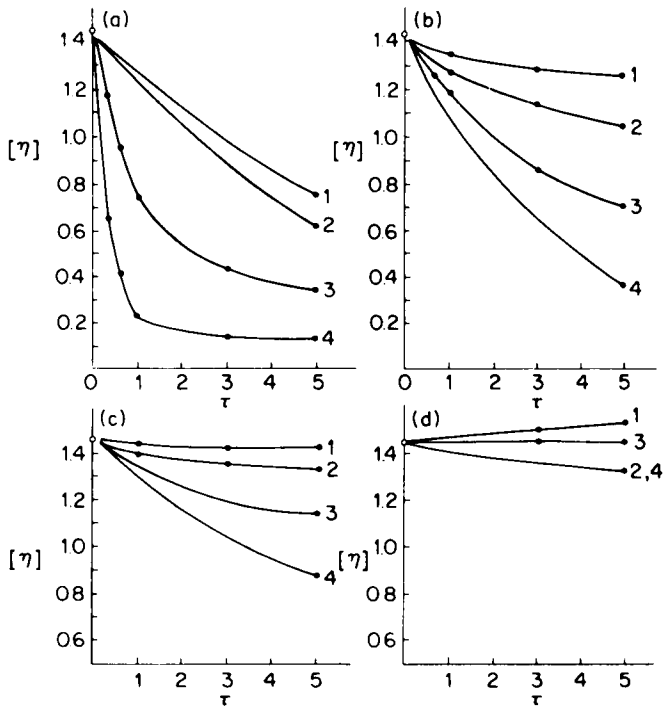


FIGURE 23. Variation of the intrinsic viscosity of PDMS with time at 300 °C (a), 260 °C (b), (c) and 200 °C (d) in an argon atmosphere: (1) PDMS + 4 wt% polycarbodiimide (PCD); (2) PDMS; (3) PDMS + 4 wt% PCD + 4 wt% H<sub>2</sub>O; (4) PDMS + 4 wt% H<sub>2</sub>O. Reproduced from Reference 191 by permission of Plenum Publishing Corporation

*Random Cleavage Initiation—Partial Unzipping:* The change in the fractional conversion ( $C$ ) is given by

$$DP/DP_0 = (1 - C)(Z/DP_0)/(C + Z/DP_0) \quad (58)$$

It can be shown that a depolymerization reaction of this type has a constant zip length. It is assumed that the depolymerization follows first-order kinetics with respect to sample weight.

*Random Cleavage Initiation—Complete Unzipping:* The average zip length will not simply be equal to the number average molecular chain length and it is necessary to postulate that  $Z = b \cdot DP$ . The parameter  $b$  is important since it is believed to be related to the type of MWD. However, a clear understanding of this relationship is not yet available for polysiloxanes. The relationship between the relative degree of polymerization and the conversion is

$$DP/DP_0 = (1 - C)^{(b-1)/b} \quad (59)$$

and the kinetic expressions depend on the parameter  $b$ .

*Chain-End Initiation—Partial Unzipping:* There is no change in the number of macromolecules and the equation is

$$DP/DP_0 = 1 - C \quad (60)$$

*Chain-End Initiation—Complete Unzipping:* The relative degree of polymerization is independent of the relative conversion:

$$DP/DP_0 = 1 \quad (61)$$

A graphical representation of equations 59 through 61 is shown in Figure 24.

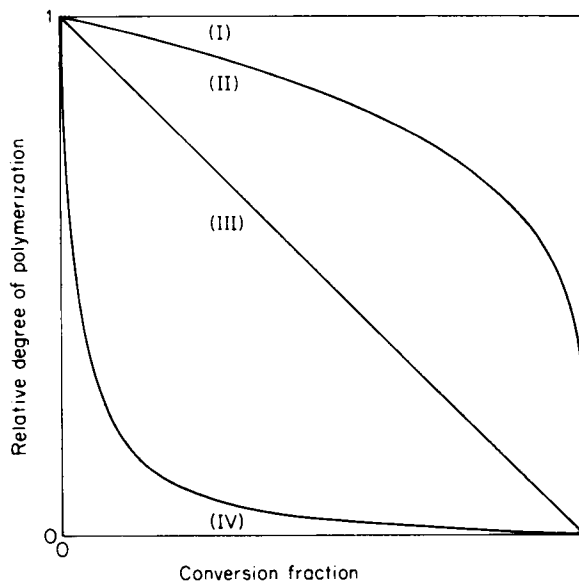


FIGURE 24. Theoretical plots of equations 58(IV), 59(II), 60(III) and 61(I). Reproduced from Reference 197 by permission of John Wiley & Sons, Inc

These equations define limiting situations within which the kinetic behaviour of intermediate cases should be found. They are valid for isothermal processes. MacCallum<sup>194</sup> has pointed out the danger of postulating mechanisms on the basis of the MW/conversion curves alone and makes the important point that the kinetics of depolymerization depend on the MWD. This model does not explicitly take into account the loop mechanism. Disagreements exist as to the interpretation of the intramolecular four-centred complex. Blazso<sup>152</sup> considers it similar to an initiation by random scission with no depropagation. According to Zeldin and coworkers<sup>195</sup> loops are formed randomly and rapid elimination of volatile cyclics should follow the chain end initiation—partial unzipping mechanism.

Zeldin and his coworkers<sup>195-198</sup> were the first to apply this kinetic approach to polysiloxanes. The fit of the data to a random chain scission followed by rapid and complete depolymerization is clearly seen (Figure 25). Zeldin suggests that the random scission is induced by trace quantities of impurities. This explains the low activation energy previously observed and which was interpreted by the loop mechanism<sup>155-156</sup>. Furthermore, the entropy of activation estimated from this model is +22 e.u. which Zeldin believes supports chain scission as the rate-determining step. According to Zeldin the loop transition state would require a negative entropy of activation. Further careful studies of both a theoretical and experimental nature are needed to resolve these apparently conflicting mechanisms for PDMS depolymerization.

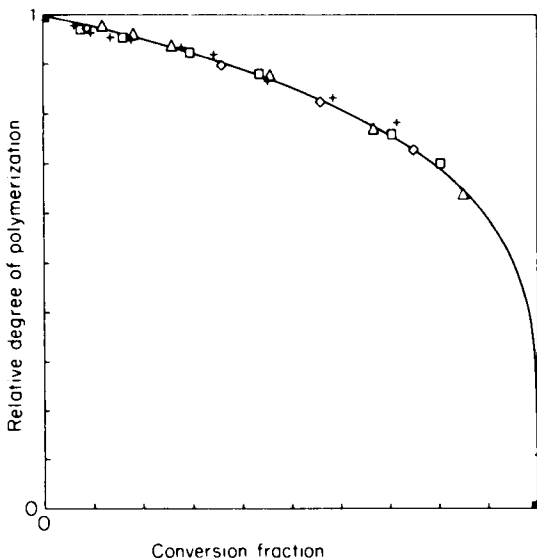


FIGURE 25. Plot of  $DP/DP_0$  vs.  $C$  for TMS end blocked PDMS ( $M_n = 68300$ ) at 450 (+), 475 (□), 490 (◇) and 510 °C (△); smooth curve corresponds to  $b = 1.30$  in equation 59. Reproduced from Reference 197 by permission of John Wiley & Sons, Inc

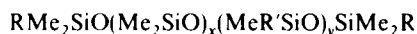
## VI. ORGANOFUNCTIONAL SILOXANES

### A. Introduction

The bulk of today's commercial applications of silicones utilise the intrinsic properties of the polydimethylsiloxanes, such as their low surface tension, thermal stability, good

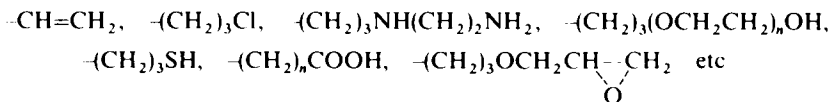
UV resistance, low glass transition temperature ( $T_g$ ) and chemical and biological inertness. Until quite recently these features have been sufficient to maintain a special position in the market place for silicones; however, with the high level of sophistication required in today's products and services the demand for chemically reactive silicones has increased. Chemists in the silicone industry have responded by preparing a plethora of organofunctional siloxane polymers many of which are just beginning to find wide application. This activity is reflected in the large proportion of recent patents which claim siloxane materials that have been modified by the incorporation of small amounts of reactive sites along the backbone.

The organofunctional siloxanes are a relatively new class of siloxane polymers which may be conveniently represented by the general formula:



The substituent  $\text{R}'$  contains a reactive organic moiety which is normally attached to silicon through a stable silicon-carbon bond and  $\text{R}$  may be  $\text{R}'$  or methyl. The propyl radical is one of the most commonly used linking groups because the separation of the organofunctional group from silicon by three carbon atoms ensures its solvolytic and thermal stability. If the substituent is attached to the carbon  $\beta$  to silicon, then in many cases unexpectedly high reactivity is observed resulting in anomalous properties and instability. This effect, has been extensively reviewed<sup>199-201</sup> and it is now generally agreed to originate from a combination of several factors. *Ab initio* calculations<sup>202</sup> on the magnitude of the  $\beta$ -silicon effect on the stabilization of carbenium ions suggest that the major contribution arises from Si-C hyperconjugation with lesser contributions from polarization and inductive effects. Silicon compounds with substituents on the  $\alpha$ -carbon are generally more stable than their  $\beta$ -substituted analogues, however, they are usually more difficult to synthesise and represent a less practical alternative than the propyl substituted species.

In principle, the range of possible substituents at silicon is limited only by the ingenuity of the silicone chemist and a huge variety of such materials is described in the open literature and in patents. In practice the commercialisation of organofunctional siloxanes has centred around a few selected groups of materials. Typical examples of the more useful reactive organic groups are:



The synthesis and properties of polymers containing these types of substituents are developed more fully in the following sections.

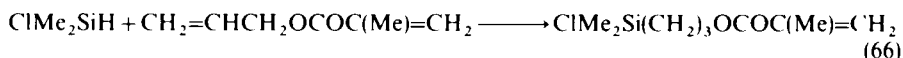
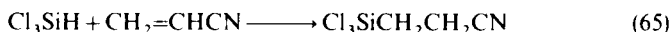
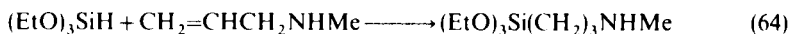
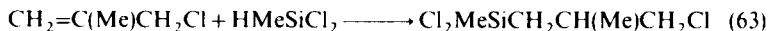
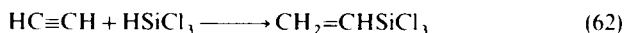
## B. Synthesis of Organofunctional Silanes

Organofunctional silanes are often the primary building blocks in the synthesis of functional polymers and several routes to such materials are known. They have many uses in their own right; for example, functional silanes are used extensively as coupling agents providing the bond between inorganic and organic systems, or surface treatments to immobilise active species such as catalysts, enzymes, biocides, ion exchangers, etc., on a given substrate and as adhesion promoters and primers for sealant applications. The chemistry, properties and applications of these materials have been thoroughly reviewed elsewhere<sup>203, 204</sup> and only the main synthetic routes will be considered here.

### 1. Hydrosilylation

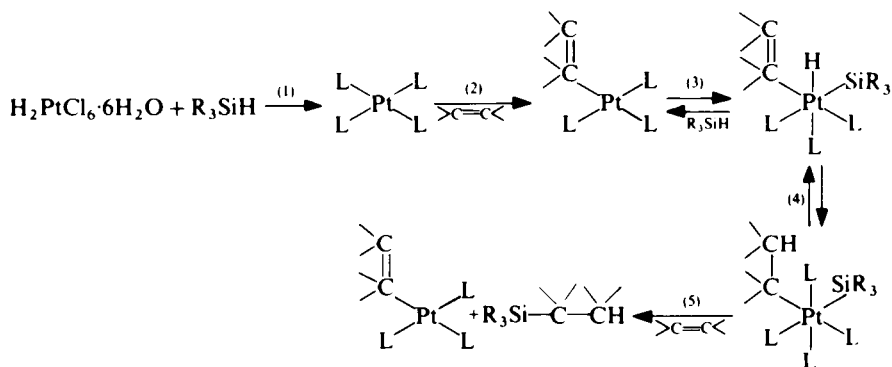
The addition reaction of a  $\equiv\text{SiH}$  moiety across an unsaturation, either photochemically or catalysed by various transition metal complexes, is known as hydrosilylation and

is one of the most frequently used methods of forming silicon-carbon bonds<sup>205-207</sup>. Some typical examples are given in equations 62-66.



The reactions depicted in these equations seldom proceed to quantitative conversion. Side-reactions, such as isomerization, elimination of alkene, non-terminal addition and disubstitution, occur giving rise to many by-products. However, a detailed treatment of these phenomena is outside the scope of this chapter and only the basic mechanism will be discussed further.

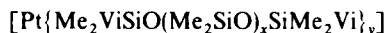
Hexachloroplatinic acid in isopropanol (Speier's catalyst) is the most commonly used hydrosilylation catalyst because of its broad applicability and effectiveness at very low concentrations. A generally accepted mechanism for homogeneous platinum catalysed hydrosilylation involves reduction of Pt(IV) to Pt(II) by the silane, ligand substitution by the alkene, oxidative addition of SiH to the metal, rearrangement to a  $\sigma$ -bonded complex and finally reductive elimination of the product and recycle of the catalyst<sup>206-208</sup>. The basic mechanism is summarised in Scheme 2.



SCHEME 2. Hydrosilylation mechanism for chloroplatinic acid. L is an unspecified ligand. Reproduced from Reference 206 by permission of Elsevier

Until quite recently this type of mechanism was thought to account for most hydrosilylations, especially since there is little doubt about the existence of some of the proposed intermediates<sup>209, 210</sup>. However, despite a great deal of research the precise nature of the active species remains the subject of much debate. For instance, in commercial applications a frequently used form of the platinum catalyst,  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ , is made by complexing it with a vinyl siloxane<sup>211</sup>. This catalyst has been recently characterised<sup>212, 213</sup> by derivatization and X-ray crystallography and been shown to

contain platinum in the zero oxidation state, with the preponderance of species containing bis chelating divinyl siloxanes in complexes of the type:



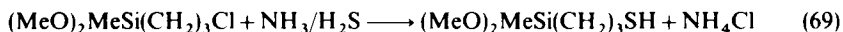
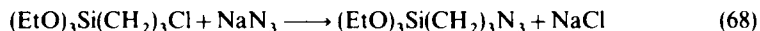
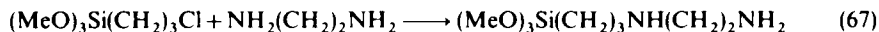
where Vi = vinyl,  $x =$  mainly 0 and  $y =$  mainly 2.

New insights into the mechanism of hydrosilylation are continually being sought and further evidence that the active species in many cases is Pt(O) has been presented in a recent paper by Lewis and Lewis<sup>214</sup>. Their observations indicate that certain highly reactive systems previously thought to be operative by an homogeneous mechanism may indeed be mediated by colloidal platinum metal in a heterogeneous process.

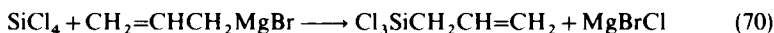
## 2. Other methods

Nucleophilic displacement reactions of chloroalkyl functional silanes (normally themselves the products of hydrosilylation) provides access to a large variety of new organofunctional silanes. Other routes include the use of organometallic species such as Grignard reagents or organic derivatives of alkali metals, further derivatization of existing silanes in which conventional organic chemistry can be utilised and direct synthesis from silicon metal and a functional chloroalkyl compound. A few representative examples<sup>1</sup> are given in equations 67–74.

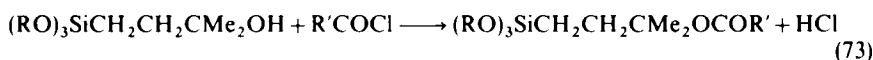
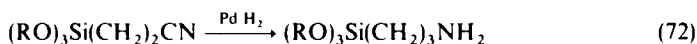
### a. Nucleophilic substitution of chloride



### b. Organometallic reagents



### c. Further derivatization



### d. Direct synthesis



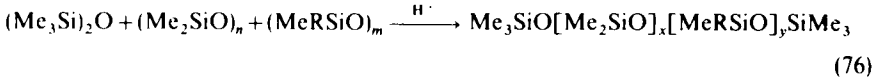
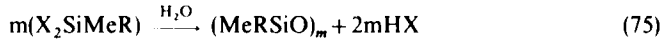
## C. Synthesis of Organofunctional Siloxanes

### 1. From organofunctional siloxane monomers

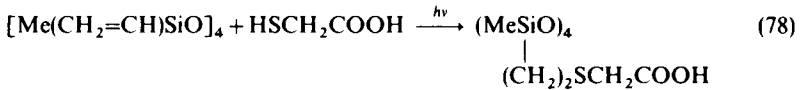
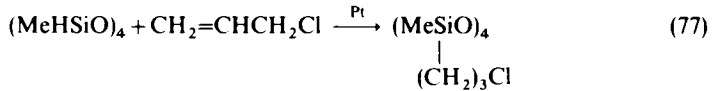
One of the best known synthetic routes to organofunctional siloxanes is ring opening copolymerization of the appropriate organofunctional monomer with dimethylcyclosiloxanes and a chain terminating agent<sup>1, 225-8, 236</sup>. The process typically utilises strongly acidic or basic catalysts which open the cyclic monomers and redistribute the siloxane bonds. Suitable organofunctional silanes can be readily converted to the siloxane



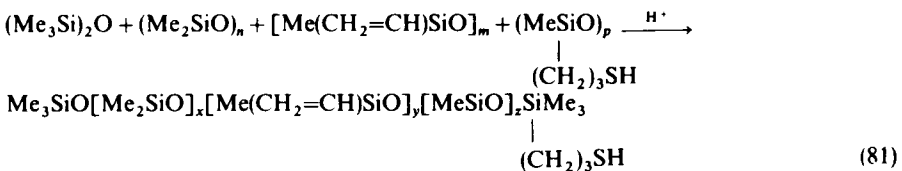
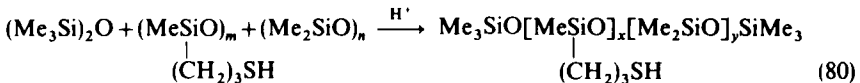
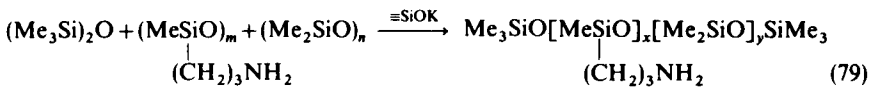
prepolymers by hydrolysis. The general reaction is:



where X is a hydrolysable halide or alkoxy group and R is the organofunctional substituent. The hydrolysis product from reaction 75 contains low-molecular-weight linear oligomers and cyclic species. Functional siloxane monomers can also be synthesized from the appropriate cyclic precursors as exemplified by equations 77 and 78.



The steps 75 and 76 are sometimes carried out in a one pot process where the water, silane, cyclic monomers, end blocker and suitable catalyst are all combined at the beginning of the reaction. Clearly in such reactions the type of catalyst is important and must be chosen to minimize interaction with the reactive group on the functional monomer. Thus, if the final copolymer contains amine groups then the catalyst would normally be a strong base such as potassium silanolate<sup>225, 227</sup> (equation 79), whereas if, for example, thiol groups are present then a strong acid is selected<sup>228</sup> (equation 80). This method is not limited to polymers containing one type of functionality and as long as the chemistry is compatible any combination of functional groups is possible. One such example is a siloxane polymer containing both vinyl and thiol groups which can be synthesised from cyclic monomers using a strong acid as the catalyst<sup>215</sup> (equation 81). The copolymers are isolated by first neutralizing or destroying the catalyst, filtering off any catalyst residues and stripping out low-molecular-weight oligomers by vacuum distillation.

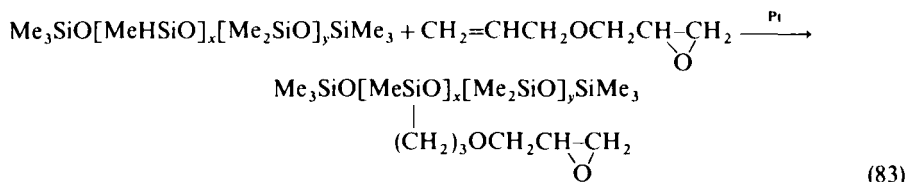
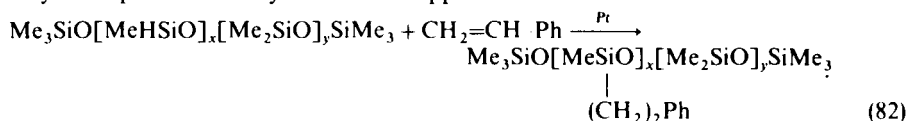


The equilibrium polymerization depicted in equation 76 gives rise to a random distribution of comonomer units in the polymer chain at thermodynamic equilibrium. If copolymers with non-random distributions are required, then alternative synthetic

routes must be sought. Anionic polymerization of strained tricyclic monomers or condensation polymerization of linear oligomers are known to give block copolymers with specific sequence distributions.

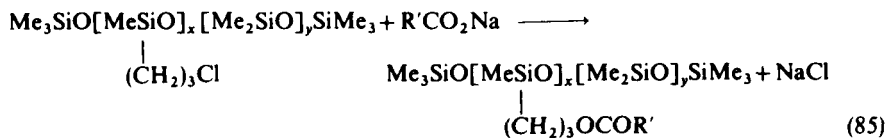
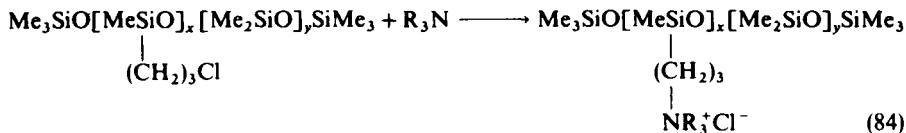
## 2. From $\equiv\text{SiH}$ containing siloxane polymers

Just as the hydrosilylation reaction is important in the synthesis of silanes, so it also serves as a useful route to functional polysiloxanes. The same variety of chemistry as previously described for silanes is available and two further examples are given in equations 82 and 83. One of the main advantages of this route is that the silicon hydride prepolymers are well characterized and readily available materials, which in turn leads to well-defined organofunctional products. A disadvantage is the low efficiency in the use of the precious metal catalyst and the difficulty of its recovery. This is particularly true for systems containing a low level of functionality but this can be partially overcome by using recyclable platinum catalysts on solid supports<sup>216, 217</sup>.



## 3. From chloroalkyl functional siloxanes

The chloroalkyl functional siloxanes provide useful starting points for further derivatization. They undergo displacement of chloride ion by a variety of nucleophiles such as amines<sup>218</sup> (equation 84) or carboxylates<sup>219</sup> (equation 85).



The 3-chloropropyl and 3-isobutyl substituted polymers are an order of magnitude less susceptible to nucleophilic displacement<sup>220</sup>, however they can be made more reactive by first converting them to the corresponding iodo compounds<sup>204</sup>.

## 4. Organic modification of functional siloxanes

Under this heading is collected a vast array of standard organic chemistry which can be routinely performed on functional polymers. The main restriction is the sensitivity of

the siloxane linkages to acidic and basic reagents, nevertheless the opportunities for further chemical reactions are large and quite complicated molecules can be built up. For instance, siloxanes containing chromophoric substituents or liquid crystalline side-chains are well known. In addition, organofunctional siloxanes have the potential to ligate metals and there are now several examples of polysiloxanes containing chemically bound transition metals<sup>221, 222</sup>.

#### **D. Properties of Organofunctional Siloxanes**

##### *1. Physical properties*

For the purposes of this discussion two types of functional polymer can be distinguished: those with <5 mol% of functional groups and those that have been highly modified, i.e. contain >5 mol% functionality. The unique physical properties of the polydimethylsiloxanes have already been emphasised and many of these characteristics are retained in the former class of organofunctional siloxane copolymers. However, the presence of small amounts of organic groups in the molecule permits new types of physical interactions to occur and such siloxanes become substantive to substrates with which they would normally have little interaction. Thus polymers containing amine groups are more strongly adsorbed on a titania surface than the corresponding dimethylsiloxanes<sup>223</sup> and just a few carboxylic acid or amine substituents, for example, dramatically change the viscosity and glass transition temperature of the polymeric system due to intermolecular H-bonding<sup>224, 225</sup>. On the other hand, if higher amounts of functional groups are present some properties can be reversed. A good example of this is that siloxanes, which are usually hydrophobic, can be made hydrophilic by the inclusion of polar groups like quaternary amines or polyethers<sup>237, 238</sup>. They can even be made totally water soluble by incorporating sufficient carboxylic or sulphonic acid groups into the polymer and converting the acid function to the sodium salt. Their surface properties can also be changed to such an extent that, instead of acting as antifoams, they behave as profoamers in certain critical industrial applications.

##### *2. Chemical properties*

In contrast to the polydimethylsiloxanes, one of the outstanding features of organofunctional siloxanes is their ability to participate in a variety of chemical reactions and experience has shown that groups attached to the silicone backbone display reactivity typical of the organic group. For example, amino functional siloxanes react with organic polymers such as urethanes, epoxides, acrylates, etc., and can permanently impart desirable silicone characteristics to them<sup>226, 227</sup>. Thiol functional silicones undergo free radical addition to alkenes<sup>228</sup> and can react with natural products containing sulphide linkages such as rubber or hair<sup>204</sup>. These and other properties are being increasingly exploited in many industrial applications.

#### **E. Applications of Organofunctional Siloxanes**

Organofunctional siloxanes are used in many applications and the following examples serve only to illustrate this diversity of application and should not be considered as a comprehensive listing.

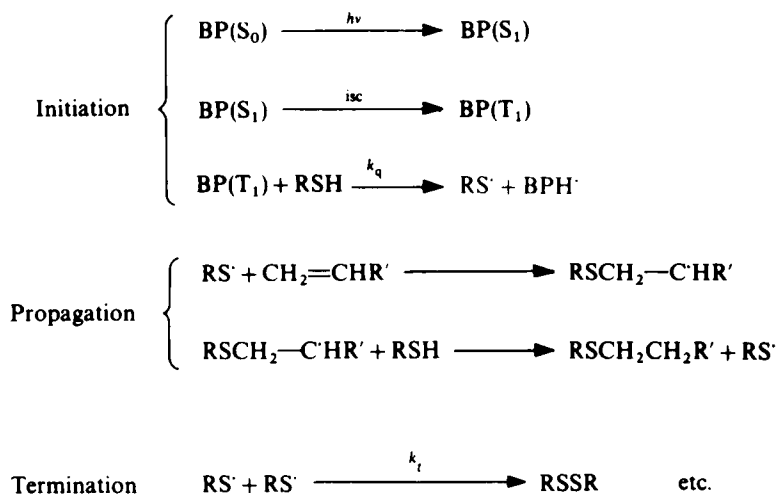
##### *1. Radiation curing siloxanes*

With the advent of new environmental legislation, the tendency to use less solvents, the drive towards lower energy consumption and the increasing costs of precious metal

TABLE 16. Functional siloxane radiation cure systems

Functional Group(s)	Catalyst	Ref.
$\equiv\text{Si}(\text{CH}_2)_3\text{SH} + \text{CHR}=\text{CH}-\text{R}'-\text{S}=\text{}$	$\text{Ph}_2\text{C}=\text{O}$	228
$\equiv\text{Si}(\text{CH}_2)_3\text{OCOCH}=\text{CH}_2$	$\text{PhCOC}(\text{OH})\text{Me}_2$	229
$\equiv\text{Si}(\text{CH}_2)_3\text{OCH}_2\text{CH}-\underset{\text{O}}{\text{C}}-\text{CH}_2$	$(\text{RC}_6\text{H}_4)_2\text{I}^+\text{SbF}_6^-$	230
$\equiv\text{Si}(\text{CH}_2)_3\text{N} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{C} \\ \parallel \\ \text{O} \end{array} \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array}$	$\text{Ph}_2\text{C}=\text{O}$	231
$\equiv\text{Si}(\text{CH}_2)_3\text{OC}(\text{O})\text{C}_6\text{H}_4\text{N}_3 + \text{CH}_2=\text{CHSi}=\text{}$		232

catalysts, the importance of alternative energy cure systems grows. It is now possible to attach a variety of radiation (usually UV or E-beam) sensitive groups to the siloxane backbone (Table 16). Some of the many different synthetic routes to such materials have already been shown and the possibility of combining two or more reactive systems in a single formulation is often cited. In the first example siloxanes containing thiol and alkenyl groups are blended in the appropriate ratio with a photoinitiator, such as benzophenone (BP), and then cured to an elastomeric or resinous film by exposure to UV light. The curing mechanism in this case is based on traditional organic chemistry which relies on the photochemically induced addition of SH across the alkene depicted in Scheme 3. In order for this process to be effective it must be fast, i.e., the rate of

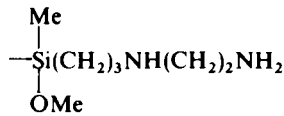


SCHEME 3

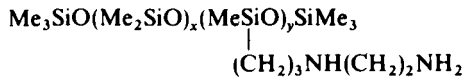
propagation relative to the rate of termination must be high and benzophenone must be rapidly and preferentially quenched by SH. Laser flash photolysis studies<sup>215</sup> indicate that the rate of quenching of the benzophenone triplet in such siloxanes is typical for an organic thiol. The quenching constant,  $k_q$ , measured in model thiol functional siloxanes is  $k_q = 1.1 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$  whereas  $k_q = 1.4 \times 10^5 \text{ s}^{-1}$  in non-reactive polydimethylsiloxanes.

## 2. Textile treatments

Silicones have been used for many years by textile manufacturers to impart water repellency to garments whilst allowing them to breathe. This feature is produced by a very thin coating of a hydrophobic polydimethylsiloxane elastomer. However, much more subtle effects can be achieved by the inclusion of reactive organic groups in the siloxane chain<sup>233-235</sup>. For example, a polymer containing less than 0.4 mol% end groups of the formula



can be made substantive to wool and prevents shrinkage in an automatic wash cycle. Treatment of polyester fibres with a polymer containing slightly more pendent diamino groups of the average structure



transforms the fibre's physical characteristics giving bounce, resilience and enhanced air entrapment. This material is widely used for the fillings of continental quilts and fashion jackets.

One of the problems with the earlier hydrophobic silicones was their tendency to attract and retain oily soil. For certain applications like polyester/cotton shirting and sheeting, a soil releasing hydrophilic silicone is preferred. This apparent contradiction may be resolved by incorporating higher levels of polar groups such as polyethers, carboxylic acids or quaternary amines into the side-chains<sup>236-238</sup>. Apart from the soil-releasing effect, these compounds also give improved wettability, softer handle and hence added comfort to the user. Functionality at silicon which facilitates crosslinking reactions can also be included in the structure.

## 3. Cosmetic applications

Functional silicones are now an accepted part of many well-known skin and hair care preparations. Typically siloxanes modified with amine or polyether substituents are employed<sup>239</sup>. Polydimethylsiloxanes are currently used in sun tan lotions in conjunction with UV-B protecting agents such as *p*-aminobenzoic acid derivatives or *p*-methoxy-cinnamates, compounds which strongly absorb the harmful wavelengths between 280-320 nm whilst allowing the tanning UV-A to pass through. However, improvements in traditional sunscreen preparations are continually being sought by the major cosmetic formulators and changing leisure-time habits coupled with a growing public awareness of the deleterious effects of the sun have increased the demand for better skin-care products. In efforts to meet these requirements attempts have been made to combine the desirable

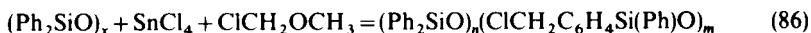
qualities of the silicone additives with the UV absorbing properties of the organic sunscreens in a single polymeric material. Ideally the polymer would be a totally inert, substantive, UV-B blocker and for ease of formulation into cosmetic preparations it should be a relatively low viscosity liquid. Organofunctional silicones with chromophores grafted along the backbone, as shown in Scheme 4, provide many of the necessary features.

	max	Reference
$(\text{Me}_2\text{SiO})_x\text{O}(\text{SiMe}_2(\text{CH}_2)_3\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4\text{OH})_2$	308 nm	240
$\text{Me}_3\text{SiO}(\text{MeSiO})_x(\text{Me}_2\text{SiO})_y\text{SiMe}_3$ $\quad \quad \quad  $ $\quad \quad \quad (\text{CH}_2)_3$ $\quad \quad \quad  $ $\quad \quad \quad \text{O}$ $\quad \quad \quad  $ $\quad \quad \quad \text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4\text{NH}_2$	288 nm	240, 241
$\text{Me}_3\text{SiO}(\text{MeSiO})_x(\text{Me}_2\text{SiO})_y\text{SiMe}_3$ $\quad \quad \quad  $ $\quad \quad \quad \text{CH}_2$ $\quad \quad \quad  $ $\quad \quad \quad \text{CH}_3\text{CHCH}_2\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CHC}_6\text{H}_4\text{OMe}$	308 nm	242

SCHEME 4

#### 4. Photolithography

Siloxanes play an important role in wafer fabrication. They are not only used for planarization and passivating purposes but are of increasing interest in the field of microlithography. The synthesis of polydiphenylsiloxane containing around 20% of chlorobenzyl groups can be achieved by chloromethylation of oligomeric diphenyl siloxanes:



It behaves as a negative photoresist in bilayer resist systems and is highly sensitive to electron beam, X-ray or UV radiation whilst being resistant to  $\text{O}_2$  reactive ion etching<sup>24,3</sup>.

#### F. Conclusions

Organofunctional siloxanes are a relatively new class of siloxane copolymers that couple the unique properties of polydimethyl siloxanes with the wide range of reactivities of carbon functional organic groups. They form the basis of a rapidly developing and diverse field of applied research. The examples given in the preceding discussion demonstrate how non-reactive polydimethylsiloxanes can be functionalized by incorporating a variety of chemically reactive groups into the polymer chain. They represent a class of materials of striking contrasts. They can be release agents or adhesives, profoamers or antifoams, hydrophilic or hydrophobic, inert or biologically active and many of the compounds mentioned are already being exploited commercially.

## VII. THE SURFACE ACTIVITY OF LINEAR SILOXANE POLYMERS AND COPOLYMERS

The unique surface properties of the polydimethylsiloxanes (PDMS) are responsible for many of their most important industrial applications. These surface properties derive from the very surface-active pendant methyl groups attached to silicon which are presented to their best effect by the several distinctive features of the siloxane backbone<sup>244</sup>. The comparatively long Si-O and Si-C bonds reduce steric conflicts between methyl groups on neighbouring silicon atoms which would otherwise occur and allow unusual freedom of rotation about the Si-O and Si-C bonds. The partial ionic character of the Si-O bond allows some distortion of the large bond angle at oxygen to relieve such steric conflicts as do occur. This freedom of rotation about the Si-O and Si-C bonds gives very effective screening of the polar Si-O-Si backbone by the non-polar methyl groups. Thus the surface tension of PDMS is significantly lower than that of the iso-electronic polyisobutylene (PIB), 20.4 dyn/cm at 20°C compared with 33.9 dyn/cm for PIB<sup>245</sup>. The low intermolecular forces which characterise PDMS, and which are the source of most of their unusual surface properties, result from the low surface energy of the methyl groups. In fact there is a close similarity between the surface parameters for PDMS and some wholly organic methyl-containing materials<sup>244</sup>. The flexibility of the Si-O-Si backbone allows PDMS to adopt various configurations at different interfaces. Thus the lower than anticipated interfacial tension of PDMS against water is thought to involve the interaction of the oxygen atoms in the backbone with the hydroxyl groups of the water phase.

Substituting the methyl groups with other higher alkyl groups increases the surface tension of the polymer<sup>246</sup>.

### A. The Behaviour of Linear Polysiloxanes at the Air/Liquid Interface

Experimental results for films of PDMS spread on water indicate that at large areas per molecule the PDMS polymer molecules are fully extended with each Si-O-Si group in contact with the water. As the PDMS monolayer is compressed the molecules are believed to assume a helical configuration with the polar Si-O-Si groups directed towards the axis of the helix<sup>246</sup>. Noll<sup>247</sup> has measured film pressure/area per molecule ( $F/A$ ) isotherms for a number of siloxane polymers including PDMS. The  $F/A$  isotherm for PDMS on water (Figure 26) is independent of chain length for DP > 14 units. The

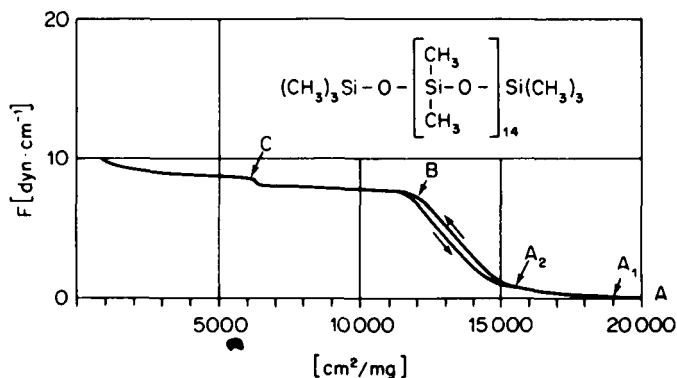


FIGURE 26. Force/area curves for PDMS on water. Reproduced from Reference 247 by permission of John Wiley & Sons, Inc

isotherm is characterised by two discontinuities at  $A_2$  and B. As the film is compressed to  $A_2$  the methyl groups approach one another until at  $A_2$  they are touching. At this point only the water molecules that are bound to the Si-O-Si chain are maintained in the interfacial film. Further compression of the film forces these water molecules out of the surface film until at B close packing of the siloxane polymers is achieved. Further compression beyond B lifts the chains out of the surface to form helices and at C the film consists of close packed helices. Further compression causes the film to collapse. Methyl/hydrogen, methyl/vinyl and methyl/trifluoropropyl siloxanes show similar behaviour to PDMS. The alkyl/methyl siloxanes where the alkyl group is  $C_4$  or greater and diethyl siloxanes give  $F/A$  isotherms that show no transitions (Figure 27). The isotherm is smooth and contains no indication of any structural transformations in the film on compression. This is believed to result from the increased steric hindrance which reduces the extent of hydrogen bonding between the Si-O-Si backbone and the water substrate thus preventing the uncoiling of the polymer molecules on the surface and denying the opportunity for structural transformations in the surface film<sup>247, 248</sup>. Siloxanes containing functional groups that interact with water, like  $CH_2CN$ ,  $CH_2NH_2$  or  $CH_2NH_2^+R$ , give  $F/A$  isotherms that continue to rise beyond B instead of reaching a plateau as does PDMS. Compression of the film beyond B lifts chain segments out of the surface, though not necessarily in the helix form, with the hydrophilic functional groups still bound to the water surface (Figure 28). Thus the effect of the functional group is to increase the coherence of the surface film, presumably by hydrogen bonding between the functional groups and water.

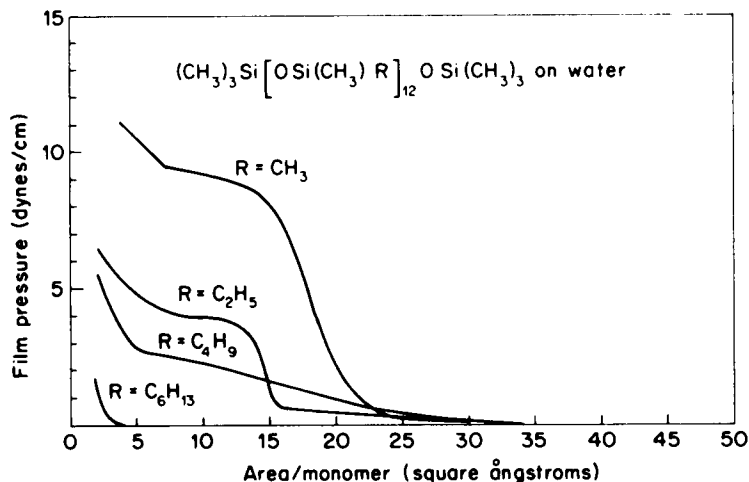


FIGURE 27. Force/area curves for alkyl substituted siloxanes on water. Reproduced from Reference 246 by permission of John Wiley & Sons, Inc

Considerably different behaviour is observed when PDMS is spread on inert organic liquids. The structural transformations that characterize the behaviour of PDMS on the water surface are not observed<sup>246</sup> (Figure 29). The substitution of ethyl for methyl in the polymer has little effect on the behaviour of the polymer at the interface. For PDMS, the film pressure begins to increase rapidly at about  $15\text{\AA}^2/\text{monomer}$  unit and this corresponds to the point at which PDMS forms the helical configuration on the water surface.



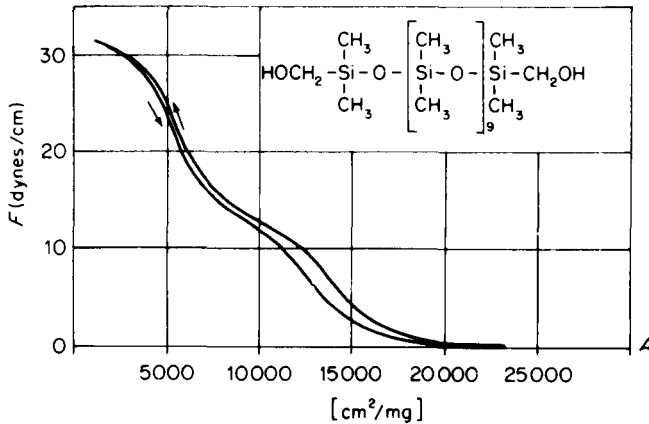


FIGURE 28. Force/area curves for a carbinol terminated PDMS on water. Reproduced from Reference 247 by permission of John Wiley & Sons, Inc

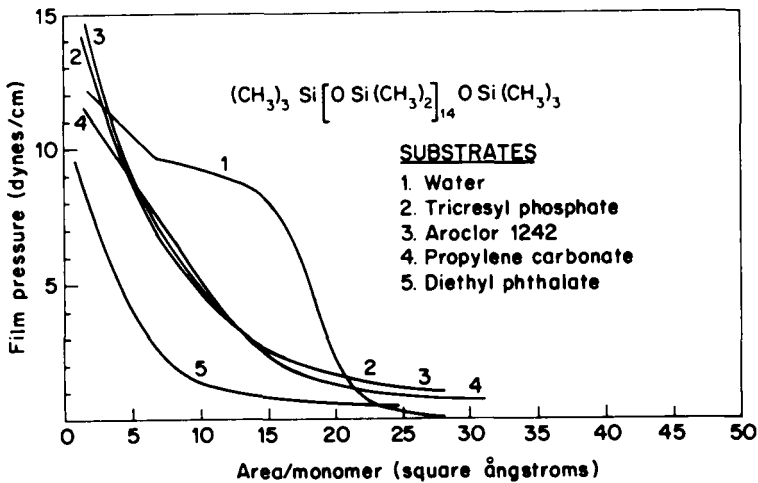


FIGURE 29. Force/area curves for PDMS on organic liquids. Reproduced from Reference 246 by permission of John Wiley & Sons, Inc

Prior to reaching this point the film pressure increases slowly with film compression<sup>246</sup> (Figure 30). In the absence of hydrogen bonding between the Si-O-Si backbone and the substrate the conformation of the polymer molecule at the surface is less sensitive to the size of the substituent on silicon and the associated steric constraints to its uncoiling on the surface.

The PDMS molecules comprising the film on the surface have low cohesive interactions. The extremely low surface shear viscosity of PDMS films ( $< 1 \mu\text{N s m}^{-1}$ ) is a direct result of the low intermolecular forces and high chain flexibility of the PDMS molecule. However, not all siloxane polymers have low surface viscosities. If the chain flexibility is

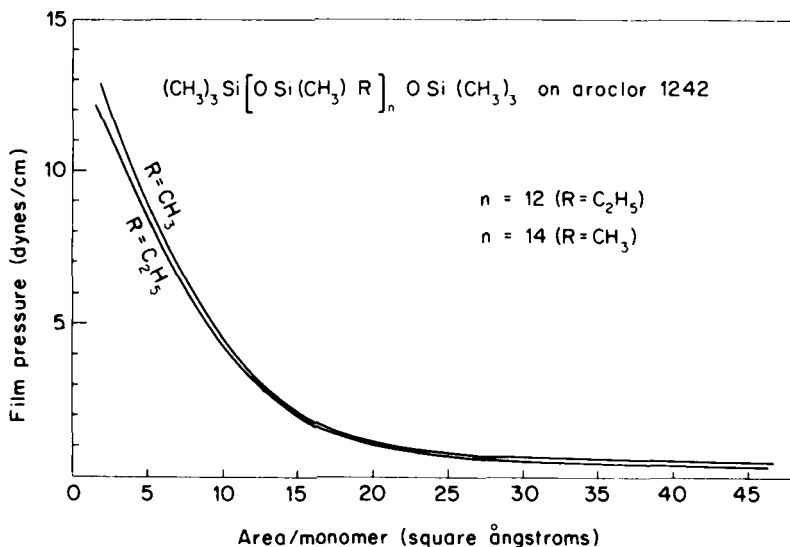


FIGURE 30. Force/area curves for polymethylethylsiloxane and PDMS on an organic liquid. Reproduced from Reference 246 by permission of John Wiley & Sons, Inc

reduced and/or the interaction with the substrate is increased, then the surface film may have a significant surface viscosity. For example, a resinous methyl siloxane containing pendant silanol groups has a surface viscosity of  $5000 \mu\text{Ns m}^{-1}$  at a 1% wt concentration in xylene<sup>244</sup>. Similarly a 1% wt solution of a polyether functional PDMS in water has a surface viscosity<sup>249</sup> of  $1400 \mu\text{Ns m}^{-1}$ . Insoluble films of PDMS copolymers containing hydrophilic groups on a water surface might be expected to show similar increases in surface viscosity.

### B. The Behaviour of Block Copolymers at the Air/Liquid Interface

Block copolymers of PDMS are amphiphiles and behave as surfactants. At low concentrations they accumulate at the surface, at intermediate concentrations they may form micelles, and at high concentrations and in the bulk they segregate into domains of one block in a continuum of the other. Thus one would expect the surface composition and morphology to be quite different from that in the bulk.

Gaines<sup>250</sup> has measured  $F/A$  isotherms of alternating PDMS/Bis-phenol polycarbonate (BPAC) block copolymers on the water surface. The copolymers exhibited monolayer characteristics and at constant low film pressure the area occupied by the surface film is proportional to the siloxane content of the copolymer. This result implies that the siloxane component of the copolymer is interacting with the water surface and that the interaction is essentially unaffected by the polycarbonate block. At chain lengths of DP greater than 20 in the siloxane segment the  $F/A$  isotherm shows similar features to that for PDMS films. Copolymers containing the same amount of PDMS (64%) but of different average PDMS block length (20 and 100) give quite different  $F/A$  isotherms. The longer PDMS blocks permit rearrangement in the 6–8 dyn/cm force range to occur in a similar fashion to that observed for PDMS homopolymer films. Gaines visualises the PDMS segments lying in the surface with the BPAC segments oriented away from the

surface. Thus the configuration of long blocks of PDMS on the surface would be unaffected by the hard polycarbonate block and would give the surface film characteristics similar to that of a PDMS monolayer. Granick and Herz<sup>251</sup> have studied the behaviour of polystyrene (PS) and poly- $\alpha$ -methylstyrene ( $\alpha$ PS) PDMS block copolymers on tricresyl phosphate which is a solvent for the organic component but not for the PDMS component. At low surface concentrations the surface pressure is indistinguishable from that for PDMS. However, at high surface concentrations the surface pressure exceeds that for PDMS, the extent being determined by the surface concentration of the PS or  $\alpha$ PS segments. The interaction between the solvent and the organic chains dangling from copolymer at the interface is a substantial contributor to the increase in surface pressure.

The surface composition of PDMS copolymers will be quite different from that of the bulk polymer because the surface-active PDMS segments will adsorb preferentially at the surface. The surface composition and morphology of BPAC/PDMS AB block copolymers has been studied using X-ray photoelectron spectroscopy (ESCA)<sup>252, 253</sup> which reveals the surface composition down to a thickness of 50 Å. The copolymers as films cast from a 1% wt solution in chloroform show an excess of PDMS in the liquid/air surface layer though the PDMS is not adsorbed exclusively in the surface, as is the case for PDMS/PS copolymers<sup>254</sup>. Depending on the copolymer composition and the solvent from which the film is cast, the block copolymer will comprise discrete domains of one segment dispersed in a continuum of the other. The ESCA results point to a similar morphology in the surface as in the bulk but with a concentration profile favouring PDMS. The authors propose a model for the surface morphology where domains of BPAC and PDMS are arranged perpendicular to the surface and extend into the sample to a depth greater than the ESCA sampling depth. Analysis of the surface composition by low-energy ion scattering spectroscopy (ISS) for BPAC/PDMS block copolymer films cast from solution on a silver substrate confirm that the PDMS segments are preferentially absorbed at the air/liquid interface<sup>255</sup>.

These PDMS block copolymers are surface active when incorporated into the organic homopolymer. For example, polyether/PDMS block copolymers are surface active in liquid polyethers and at quite low bulk concentrations reduce the surface tension of the polyether polyol to that for a PDMS surface<sup>256</sup>. Similarly, contact angle measurements on films of polymethyl methacrylate (PMMA) homopolymer containing block copolymers of (PMMA)/PDMS cast from a 6% wt solution onto a glass substrate show that the copolymer is preferentially absorbed at the air/liquid interface but not at the liquid/glass interface<sup>257-259</sup>. FT-ATR-IR shows no difference in average surface composition between the interfaces for a surface thickness of 5000 Å. ESCA data measured over a thickness of 20 Å does show significant differences between the surface concentrations of the copolymer at the two interfaces. The picture that emerges from this work is that the copolymers adsorb at the interface in such a way as to minimise the interfacial free energy of the system. Surface excess concentrations of the copolymer can only be detected down to 20 Å and it is likely that the composition at thicknesses beyond 20 Å is constant throughout the copolymer.

### C. Surface Active Siloxanes

PDMS containing hydrophilic groups or PDMS block copolymers containing hydrophilic blocks behave as surfactants in solvents where the PDMS segments are insoluble or have limited solubility. In water, for example, PDMS/Polyether block copolymers are surface active and surface saturation is achieved at quite low bulk surfactant concentrations<sup>260</sup>. The limiting surface area per molecule is controlled by the hydrophilic group and is essentially independent of the size of the PDMS segment. The relationship between

the critical micelle concentration (cmc) and the hydrophile/lipophile balance (HLB) is similar to that for organic surfactants<sup>261</sup>. Similar results have been observed for dimethylsiloxane esters of sulphonic acid<sup>262</sup> and dimethylsiloxane substituted maleates and sulphosuccinates<sup>263</sup>. All three classes of compound reduce the surface tension of water and the interfacial tension between water and siloxanes.

Gol'din and Averbakh<sup>262, 263</sup> have assessed the surface activity of these silicone surfactants in aqueous solution. They measured the decrease in the values of the surface tension at the air/water interface and the interfacial tension at the water/polydimethylsiloxane interface as a function of the surfactant concentration. The data that they obtained confirm that these silicone surfactants have a high surface activity. For example they lower the surface tension of water to 17–19 dyne cm<sup>-1</sup> and reduce the interfacial tension between water and polydimethylsiloxane from 47 dyne cm<sup>-1</sup> to 7–12 dyne cm<sup>-1</sup> at quite low bulk concentrations of the surfactant (10<sup>-3</sup> mole l<sup>-1</sup>). The critical micelle concentration (cmc) was determined from the discontinuity in the Gibbs plot of surface tension against the logarithm of the surfactant concentration (C). The values of the limiting area occupied by the silicone surfactant molecule at the interface (A) at the cmc was calculated from the modified Gibbs equation

$$A = -RT(d/d \ln C)$$

where  $d/d \ln C$  is the limiting slope of the Gibbs plot. The surface area occupied per dimethylsiloxane unit at the interface is similar in magnitude to that observed for polydimethylsiloxane/polyether block copolymers at the air/water interface. This observation suggests that the limiting area of polymeric silicone surfactants at the air/water interface is controlled by the cross sectional area of the extended dimethylsiloxane chain and the ability of these chains to close pack at the interface. These silicone surfactants are more surface active than their organic analogues.

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## CHAPTER 4

# Appendix to 'Siloxane polymers and copolymers'<sup>†</sup>

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### \*III. POLYMERIZATION OF CYCLOSILOXANES

#### \*A. Anionic Polymerization of Cyclotrisiloxanes

Wilczek and Kennedy<sup>264</sup> have carried out a careful study of the polymerization of hexamethylcyclotrisiloxane ('D<sub>3</sub>') with lithium 2,4,4-trimethyl-1-pentanoate in tetra-

<sup>†</sup>The material in this appendix is divided in the same manner as in the body of the original Chapter 21 in *The Chemistry of Organic Silicon Compounds*. The section numbers in the appendix are preceded by an asterisk; some section numbers are omitted.

The numbers of equations and references run continuously in the original chapter and the appendix.

hydrofuran solvent. The polymerization, which was first order in monomer, exhibited a variable external order in catalyst ranging from 4 at catalyst concentrations of  $10^{-2}$  to  $10^{-1}$  molar to 3 at  $10^{-3}$  to  $10^{-2}$  molar. The authors conclude that polymerization occurs from reactive, deaggregated ion pairs which are in equilibrium with non-reactive ion-pair aggregates and the variable order in catalyst then reflects the average degree of aggregation of the lithium silanolate ion pairs. The presence of aggregates was confirmed by viscosity measurements on the living and deactivated polymer. Multifunctional chlorosilanes were used to kill the living polymer and specific viscosities ( $n_{sp}$ ) of the living (I) and deactivated (II) polymers were compared. Living polymer with an average degree of aggregation of 4 gave  $n_{sp(I)}/n_{sp(II)}$  of 0.98 when the living polymer was terminated with a tetrafunctional chlorosilane and 0.32 when terminated with the monofunctional trimethylchlorosilane. The induction period observed at low initiator concentrations was ascribed to the slow establishment of the lithium silanolate aggregation equilibrium. Suzuki<sup>265</sup> studied the polymerization of hexamethylcyclotrisiloxane using lithium silanolate catalyst in toluene solution with dimethyl sulphoxide as activator. The polymerization was first order in monomer and second order in dimethyl sulphoxide indicating that 2 molecules of dimethyl sulphoxide solvate one lithium silanolate ion pair. Suzuki confirms that redistribution reactions occur at the terminal silanolate/siloxane bonds and concludes that these redistribution reactions give rise to polydispersity in the polymer which is particularly evident when low molecular weight polymers are being sought. Veith and Cohen<sup>266</sup> used lithium silanolate catalyst with dimethyl sulphoxide as activator to polymerize tris(trifluoropropylmethyl)cyclotrisiloxane. They developed a kinetic model for the system which assumes that polymerization proceeds from solvent-separated ion pairs derived by interaction of the activator with the lithium silanolate ion-pair aggregates. The polymerization was first order in monomer and the authors derive the following expression for the measured, apparent first-order rate constant  $k$ :

$$k = k_1 [\text{SiO}^-]_s = \{k_1 K A^n / 2\} \{1 + (4I/K A^n)^{1/2} - 1\}$$

where  $k_1$  is the absolute propagation rate constant,  $[\text{SiO}^-]_s$  is the equilibrium concentration of solvent-separated ion pairs,  $A$  the concentration of activator,  $I$  the concentration of lithium silanolate initiator and  $n$  the number of activator molecules associated with each solvent-separated ion pair. Quantity  $K$ , the equilibrium constant for the formation of solvent-separated ion pairs from contact ion pairs, is given by:

$$K = [\text{SiO}^-]_s^2 / \{([I] - [\text{SiO}^-]_s) A^n\}$$

### \*B. Cationic Polymerization of Cyclotrisiloxanes

Whilst it is well known that the common Lewis acids such as  $\text{SbCl}_5$ ,<sup>3</sup>  $\text{FeCl}_3$ ,<sup>48</sup> and  $\text{SnCl}_4$ <sup>61</sup> do not polymerize cyclic siloxanes in the absence of proton releasing co-catalysts such as  $\text{H}_2\text{O}$ , recent work<sup>267,268</sup> with the new, more powerful Lewis acids such as  $\text{Hg}(\text{ClO}_4)_2$  and  $\text{SbCl}_5/\text{RC}(\text{O})\text{Cl}$  has re-examined the question of whether or not polymerization can be initiated by direct addition of a Lewis acid to a cyclic siloxane.

Sigwalt, Nicol and Masure<sup>267</sup> have studied the polymerization of  $\text{D}_3$  catalysed by the complexes  $\text{SbCl}_5/\text{CH}_3\text{C}(\text{O})\text{Cl}$  and  $\text{SbCl}_5/1$ -naphthoyl chloride in methylene dichloride. In the absence of the acid chloride and in the presence of 2,6-di-*t*-butyl-4-methylpyridine (DBMP) as proton scavenger,  $\text{SbCl}_5$  does not polymerize  $\text{D}_3$  to high polymer. In the presence of the acid chloride and DBMP,  $\text{SbCl}_5$  is an active catalyst for the polymerization. The major products are high polymer (50%),  $\text{D}_6$  (25%) and  $\text{D}_{3n}$  oligomers (12%). The molecular weight of the high polymer increases linearly with conversion, indicating a constant number of living polymers throughout the polymeriza-

tion. The nature of the active centres involved in the formation of the high polymer and in the formation of the  $D_6$  and  $D_{3n}$  is not clear, nor is the interrelationship between the two processes clearly understood. Jordan, Lestel, Boileau, Cheradame and Gandini<sup>268</sup> have investigated the catalytic activity of ethylboranesquitriflate (EBST) for the polymerization of  $D_3$ . They find that, under the most stringent conditions of purity and dryness and in the presence of DBMP proton scavenger, EBST in catalytic quantities does not polymerize  $D_3$ . However, when EBST concentrations are increased tenfold, high polymer is formed though the molecular weights obtained suggest a low efficiency for initiation. The authors conclude that  $D_3$  does polymerize by direct addition of the Lewis acid to the monomer and suggest that initiation involves self-ionization of the EBST followed by addition of the resulting cation to the  $D_3$ , to give an ionic or a polarized centre from which polymerization proceeds. Pierre and Limosin<sup>269</sup> describe the electroinitiated polymerization of  $D_3$  by anodic dissolution using aluminium or mercury anodes and tetrabutylammonium perchlorate in methylene dichloride as the supporting electrolyte. The electrophilic initiator is generated electrochemically and is thought to be  $M^+(\text{ClO}_4)_{n-1}$ .

#### \*IV. COPOLYMERIZATION OF CYCLOSILOXANES AND THE CHARACTERIZATION OF SILOXANE COPOLYMERS

##### \*A. Characterization of Siloxane Copolymers

Specialized instrumentation and/or specifically adapted classical techniques are now being extensively used for the characterization and structural determination of silicon-based materials. The field has been reviewed and has been published in book form<sup>270</sup>.

Cyclic vinylmethylsiloxanes have been prepared by equilibrium polymerization and sharp fractions separated by size exclusion chromatography (SEC). Their viscosity, density, refractive index and glass transition temperatures have been measured and compared with their PDMS analogues<sup>271</sup>. New copolymers made by the copolymerization of *cis* and *trans* decaorganocyclohexasiloxanes and of intermediate tacticity between *trans* and *cis* tactic and atactic were prepared and characterized by elemental analysis, IR, <sup>29</sup>Si NMR and SEC. The influence of chain tacticity on the formation of the mesophase and on the crystalline state was determined<sup>272</sup>.

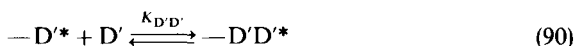
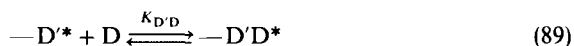
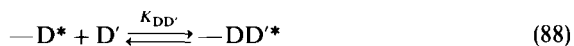
In the chromatographic field advances have been made in the detection of siloxane polymers by the use of on-line FT-IR and UV-visible spectrophotometry. The coupling of spectroscopy with chromatography allows the determination of copolymer composition as a function of molecular weight. SiH and SiOH and SiC<sub>6</sub>H<sub>5</sub> have been monitored by IR and UV spectroscopy respectively<sup>273</sup>. The kinetics of the hydrolysis reactions of tetramethoxysilane have been followed by <sup>1</sup>H NMR spectroscopy<sup>274</sup>. Hydrolysis proceeds stepwise and at different rates for acid and base catalysis. The rate-limiting step in the acid-catalysed system is the condensation reaction, whilst in the base-catalysed system the hydrolysis process itself is rate determining. The authors develop a model for the system that predicts the distribution of product species during the initial hydrolysis process. The hydrolysis and condensation kinetics of sol/gel species has been studied by <sup>29</sup>Si NMR and the results compared with a theoretical model<sup>275</sup>. The polycondensation of methyltrimethoxysilane<sup>276</sup> and of mixtures of trimethylethoxysilane and tetraethoxysilanes<sup>277</sup> has been studied in organic/water mixed solvent systems using <sup>29</sup>Si NMR. The kinetics of the hydrolysis and self-condensation reactions were described by a set of reactions and both the molecular weight distribution as a function of the extent of reaction and the gel point were deduced from the model. NMR spin-lattice relaxation times of PDMS at low temperatures together with measurements of their

mechanical, structural and dielectric properties have enabled the various second-order transitions to be characterized and measured<sup>278</sup>. The  $\gamma$  transition at  $-235^\circ\text{C}$  arises from methyl group rotation, the  $\beta$  transition at  $-220^\circ\text{C}$  is due to silicon oxygen bond rotation and that at  $-121^\circ\text{C}$  from methyl silicon methyl rotation about the chain axis. The  $\alpha$  transitions arise from segmental motion, that at  $-120^\circ\text{C}$  being associated with the linear chain and at  $-88^\circ\text{C}$  with crosslinks.

### \*B. Linear Siloxane Copolymers

Analytical techniques are increasingly being applied not only to characterize the copolymer but also to elucidate the mechanism of polymer reactions.

The determination of the sequence distribution of copolymers by analysis of their  $^{29}\text{Si}$  NMR spectra has been applied to trimethylsilyl end blocked poly(dimethyl-co-diphenylsiloxane) (PMPS) prepared by ring-opening polymerization and step-growth polymerization<sup>279</sup>. The glass transition temperature of the copolymer increases linearly with the increase in mole fraction of the diphenyl siloxane units. Ziemelis and Saam<sup>280</sup> have carried out a detailed and rigorous analysis of the microstructure of trimethylsilyl terminated poly(dimethyl-co-methylvinylsiloxane). Specific model compounds have been synthesized in order to assign the  $^{29}\text{Si}$  chemical shifts of the various pentads in cyclic and linear siloxane chains. The random sequencing observed in the copolymer chains could be seen in the vicinity of the chain ends as well as in the cyclosiloxanes. This study has led to a new model for describing cyclosiloxane copolymerization at thermodynamic equilibrium.



This model is similar to the model of Mayo and Lewis<sup>124</sup> with the competing rate constants now replaced by equilibrium constants and with the comonomer concentrations representing the total concentration of units for each comonomer regardless of the location of the unit in rings or chains. Reactions 87 through 90 and reactions involving the redistribution of siloxane units between rings and chains and between chains provide the pathways for the distribution of the various comonomer units throughout the system.

### \*V. DEGRADATION OF POLYSILOXANES

The thermal degradation of various trimethylsilyl terminated polysiloxanes has been studied by pyrolysis gas chromatography using a fused silica capillary column directly coupled to a mass spectrometer<sup>281</sup> (PGC-MS). In the pyrogram of PDMS, cyclic oligomers up to 24 units are observed along with small amounts of methane. The yield of each cyclic oligomer decreases as the molecular weight of the polymer increases with the single exception of the cyclic hexamer, which is always preferentially formed. Polymethylphenylsiloxane degrades to cyclic oligomers of up to 6 units and methane, benzene, toluene and biphenyl. Some bicyclic siloxane compounds are also formed. For polydiphenylsiloxanes the ring size of the cyclics in the degradation products decreases to 3 and 4 units and benzene is found in the degradation products. Poly(dimethyl-co-

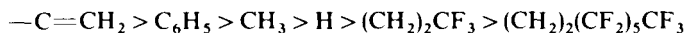
diphenylsiloxane) and poly(methylphenyl-co-diphenylsiloxane) give complex degradation products. It is noteworthy that the analysis of the pyrogram for poly(dimethyl-co-methylphenylsiloxane) provides useful information about the molecular composition of the copolymer as well as its sequence distribution. Cyanoethyl substituted polysiloxanes yield methane, acrylonitrile and cyclic oligomers of up to 5 comonomer units. Trimethylsilyl terminated oligomers, which were already present in the starting polymer, were also observed. Finally, the pyrogram of poly(methyltrifluoropropylsiloxane) reveals the presence of various stereoisomers of the cyclic tri-, tetra- and penta-siloxanes in the degradation products. The PGC-MS technique is a powerful tool for the elucidation of the chemical structures and thermal degradation of polymers.

On-line thermal desorption gas chromatography/Fourier transform IR spectroscopy has been applied to evaluate the outgassing phenomena of polymers<sup>282</sup>. The evaporation of low molecular weight products and possibly of degradation products may occur and give rise to a deterioration in the properties of the material. In addition the volatile products may be related to environmental, toxicological and aesthetic aspects associated with the use of the polymers and, not least, to the mechanism of degradation. A combined simulation and characterization technique has been developed with the capability of on-line temperature-controlled outgassing of polymers and the separation of the gaseous components and their subsequent detection and identification. The thermal desorption GC/FTIR configuration is described in the reference. The detection limits are in the  $\mu\text{g}\cdot\text{g}^{-1}$  range for 100 mg samples. The degree of post-cure of rubbers can be determined by this technique. High-resolution <sup>29</sup>Si and <sup>13</sup>C cross polarization/magic angle spinning (CP/MAS) NMR spectroscopies have been applied to polysulphophenylsiloxane (I) and polysulphopropylsiloxane (II) in order to examine their thermal and hydrothermal stability<sup>283</sup>. These polymers are used as acid catalysts in industrial processes. In the absence of steam both siloxanes are more stable than Amberlyst-15 (III) in the order I > II > III. In the presence of steam the stability of the siloxanes is reversed and the order of stability is now II > I = III.

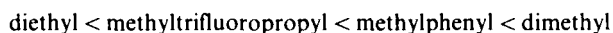
The thermal stability and degradation behaviour of a series of nine different, but exactly alternating silphenylenesiloxane copolymers which contain methyl, vinyl, hydrido, 3,3,3-trifluoropropyl and tridecafluoro-1,1,2,2-tetrahydrooctyl side-groups or their combinations were investigated by dynamic and isothermal gravimetric analysis in air and nitrogen<sup>284</sup>. A strong stabilizing effect of the vinyl side-groups on the degradation behaviour of these polymers was observed. The authors find that for polymer IV



the resistance to purely thermal degradation is a function of the side-groups R and R' and that the stability decreases in the following order:

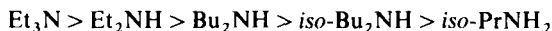


The effect of the nature of the organic group attached to silicon on the thermal degradation of polyorganosiloxanes has also been studied by Metkin and coworkers<sup>285</sup>. They find that the thermal stability depends on the steric effect of the organic substituents on silicon and that the stability increases in the order:



A study of the amine-catalysed decomposition of polysiloxane model compounds, e.g.  $\text{Me}_3\text{SiOSiMe}_3$ ,  $\text{Me}_3\text{SiOSi}(\text{Me})_2\text{OSiMe}_3$  and  $(\text{Me}_3\text{SiO})_4\text{Si}$ , which simulate the chains and nodes in crosslinked polysiloxane structures, showed that degradation is more pronounced in the case of the tetrafunctional siloxane<sup>286</sup>. Attempts to decompose linear PDMS<sup>287</sup> confirmed this finding. With diethylamine the polysiloxane degrades very slowly, typically

over 40 days. However, in the presence of KOH and diethylamine degradation was measurable after 2–3 hours. Degradation of siloxane networks showed that the cleavage of network bonds in the presence of amines occurred at the crosslink nodes as well as in the chains between the nodes<sup>288</sup> and the activity of the amines was:



The addition of basic compounds, such as KOH or NaOEt, increased the reactivity but not the selectivity of the amines in the cleavage of the siloxanes.

A new ionization technique in mass spectrometry, called  $\text{K}^+$  ionization of desorbed species ( $\text{K}^+$ IDS), has been applied to polycyanoethylmethylsiloxane<sup>289</sup>. Ions representative of the sample are formed when volatile compounds placed on a potassium thermionic emitter are rapidly heated. Potassium ion adducts of intact molecules and thermal degradation products are observed and analysed. The technique offers the advantage of both pyrolytic methods and desorption/ionization techniques. Interpretation of the mass spectra is discussed in terms of known thermal degradation pathways.

Another report has appeared on the use of a pulsed  $\text{CO}_2$  transversely excited, atmospheric pressure (TEA) laser which confirms that the degradation of PDMS in the gas phase proceeds via  $\text{Si}-\text{C}$  bond cleavage and not the  $\text{Si}-\text{O}$  bond rearrangement<sup>290</sup>.

## \*VI. ORGANOFUNCTIONAL SILOXANES

A survey of the most recent publications covering the synthesis and uses of new organofunctional siloxanes reveals that interest in these materials continues at a high level<sup>291,292</sup> and that applications envisaged for them are growing ever more diverse as the materials themselves become more readily available.

### \*C. Synthesis of Organofunctional Siloxanes

The most convenient route to organofunctional siloxanes continues to be the hydrosilylation of SiH containing siloxane copolymers (either main chain or terminal SiH). Alternatives to the hydrosilylation reaction are of major commercial interest, because of the problems associated with catalyst poisoning by many organic functional groups and the requirement for unusual unsaturated substrates which may be expensive and not readily available. Several other approaches have been studied; for example  $\alpha,\omega$ -chlorofunctional siloxanes can be reduced to silicon hydride terminated polymers by metallic hydrides such as LiH, NaH, KH,  $\text{CaH}_2$  or  $\text{MgH}_2$ <sup>293</sup>. The reaction is conducted in an inert solvent such as THF and the metal hydride may be stirred continuously and subjected to ultrasonic irradiation to ensure exposure of a fresh surface for reaction. This represents one alternative route to  $\alpha,\omega$ -hydridofunctional siloxanes (I) using more readily available chlorosilane precursors, but the organofunctional products must still be made by hydrosilylation of I. The use of phase transfer catalysts to convert chloropropyl silanes and siloxanes into more valuable functional materials which are not easily accessible by other routes has been extensively explored<sup>294,295</sup>. Typically this is done in a two-phase (polar/non-polar) system by nucleophilic displacement of the halogen atom in the presence of quaternary ammonium or phosphonium salts. Products made by this route include silicone glycols, sulphides, acetates and nitrophenols. Novel polysiloxanes containing different functionalities at either end or optionally on one end and having a narrow molecular weight distribution can be prepared by the non-equilibrium, ring-opening polymerization of hexamethylcyclotrisiloxane using a lithium vinylsilylanolate initiator and subsequent treatment of the living chain ends with an appropriate chain terminating agent<sup>265,296–299</sup>. Monovinyl/monomethacrylate end blocked siloxane macromonomers prepared in this way are useful for the preparation

of siloxane acrylate graft copolymers. These can then be further crosslinked through the vinyl group via the hydrosilylation reaction with hydridosiloxanes or through photochemical addition of thioalkyl siloxanes. One of the more unusual methods of functionalizing a siloxane polymer is by plasma polymerization of allyl alcohol or allyl amine over a silicone elastomeric substrate<sup>300</sup>. Analysis by FTIR/ATR (ATR = attenuated total reflectance) or derivatization combined with ESCA proves the presence of hydroxyl and amine groups at the siloxane surface.

#### \*E. Applications of Organofunctional Siloxanes

There are many new fields of application for organofunctional siloxane materials. Electronics applications are numerous and include the use of the acrylic siloxane macromonomers in photoresists in which very fine patterns can be obtained by a photodelineation process<sup>297</sup>. Radiation cure chemistry is also used in the fabrication of optical waveguide coatings into which organofunctional siloxanes have been incorporated<sup>301</sup>. Liquid crystal polymers (LCPs) containing various mesogens (i.e. materials capable of generating mesophases) grafted onto a polysiloxane backbone are a growing area of interest. New polysiloxane LCPs display liquid crystallinity at relatively low or ambient temperatures<sup>302</sup> and ferroelectric LCPs capable of controlled orientation in thin films have recently been synthesized<sup>303</sup>. Measurements of ferroelectric polarization in thin films of mixtures of a polysiloxane LCP and a low molecular weight host showed that polarization was linearly dependent on concentration. The synthesis, solid state NMR characterization and electrical properties of siloxane-based polymer electrolytes prepared by the reaction of hydrido siloxane, polyethyleneglycol monomethyl ether and polyethylene glycol has recently been reported<sup>304,305</sup>. The polymer forms complexes with  $\text{LiSO}_3\text{CF}_3$  and  $\text{NaSO}_3\text{CF}_3$  and exhibits good ionic conductivities.

Complex organofunctional siloxane molecules are used in applications where subsequent recovery of the reactive species is a requirement for purity or cost reasons. The synthesis, characterization and catalytic properties of poly[methyl(1-oxypyridin-3-yl)siloxane] have been investigated<sup>306,307</sup> and the polymers were found to be effective catalysts for tranacylation reactions of carboxylic and phosphoric acid derivatives. For bio-separations the use of crown ether functionalized siloxanes as selective liquid extractants for protonated secondary and tertiary amine salts of pharmacological interest has been demonstrated<sup>308,309</sup> and in the field of synthetic membranes organosiloxanes containing both ester and hydride functionalities have been the subject of a detailed NMR study<sup>310</sup>.

Novel betaine and sulphobetaine functional siloxane surfactants are obtained from the reaction of chloroacetic acid sodium salt or alkylsulfones with tertiary amine functional siloxanes. These compounds are highly efficient aqueous surfactants which lower the surface tension of water to 21 dyne  $\text{cm}^{-1}$  at low concentrations<sup>311,312</sup>. Specific low molecular weight silicone glycol copolymers are also highly surface active wetting agents and can be used as adjuvants to increase the activity and rainfastness of a variety of industrial herbicides<sup>313,314</sup>.

Applications for organofunctional siloxanes in the cosmetic and textile industries continue to increase. Hair and skin care products such as shampoos and mousses often contain silicone fluids to give a soft and smooth feel and silicone resins for improved substantivity and durability. New hair shampoo formulations with longer lasting conditioning effects are obtained if simple siloxanes are replaced by functional materials such as silicone glycol graft copolymers or amine functional siloxanes<sup>315</sup>. Improved depth and colour retention can also be achieved in hair dyeing by pretreating the hair with organofunctional siloxane formulations containing amino, amido or quaternary ammonium groups<sup>316</sup>. Quaternary ammonium functional polysiloxanes are also useful



for the treatment of polyester-cotton fabrics where they are used as conditioners to impart softness but retain good rewettability<sup>317</sup>. Amino silicones have been further modified by treatment with lactones to give hydroxyl amido functional polymers that are effective fabric treatments in production or laundering cycles<sup>318</sup>. These materials provide a finish which not only gives good handle and softness, but also avoids undesirable yellowing associated with unmodified treatments. New organosiloxane polymers are also reported for use in sunscreen preparations where up to 20 mol% of the siloxane units are grafted to a UV absorber, such as an alkyl cinnamate. These materials are stable to hydrolysis and can be obtained in a highly purified form<sup>319</sup>.

Silicone-modified organic polymers and coatings have been known for many years but more recently attention has focussed on the use of organofunctional siloxanes to chemically link the siloxane into the organic matrix. There is much activity in this area of technology and the several hundreds of publications and patents in this field have been the subject of a number of reviews<sup>302,320-322</sup>. One new area of interest is in antifouling coatings<sup>323,324</sup>. Here, many types of resin binders have been modified with organofunctional siloxanes in an attempt to make coatings having controlled ablation rates or reduced interfacial tension or to provide some biocidal activity, all with the objective of preventing organisms adhering to the surface. The driving force in this case is the environmental concern over the current tin and copper based self-polishing coatings.

#### **\*VII. THE SURFACE ACTIVITY OF LINEAR SILOXANE POLYMERS AND COPOLYMERS**

Recent publications attest to a resurgence of interest in siloxane copolymers, most of them directed to the synthesis of siloxane/organic block copolymers and evaluation of their bulk properties. There have been a number of significant papers concerned with the surface properties of siloxane block copolymers and a comprehensive review<sup>292</sup> of the synthesis and properties of siloxane block copolymers.

Wanigatunga and Wagener<sup>325</sup> have synthesized a wide range of PDMS/polypivalo-lactone (PV) graft copolymers and investigated their surface morphology by measuring contact angles under water using air bubbles. They conclude that copolymers containing less than 70% PV all show a surface richer in PDMS. Arnold, Summers and McGrath<sup>326</sup> have synthesized segmented PDMS/polyimide (PI) block copolymers and used X-ray photoelectron spectroscopy to estimate the wt% of PDMS at the surface of the copolymer. They find that the surface structure is predominately PDMS even when the bulk composition was rich in PI. Smith, York, Dwight and McGrath<sup>327</sup> have synthesized PDMS/polymethylmethacrylate (PMMA) and PDMS/polystyrene (PS) graft copolymers using the macromonomer technique<sup>328</sup>. Measurement of the contact angle of water on PMMA/PDMS copolymers indicates a change in surface composition depending on the actual composition of the graft copolymer and on the molecular weight of the PDMS macromonomer. Copolymers containing higher molecular weight macromonomers have higher contact angles due to the presence of excess PDMS at the interface. ESCA results on PS/PDMS graft copolymers confirm this finding. Chujo, Samukawa and Yamashita<sup>329</sup> have cast films of PMMA homopolymer containing small amounts of PMMA/PDMS graft copolymer from solution on glass plates. They find that at the PMMA/air interface as little as 0.01 wt% of the graft makes the PMMA surface hydrophobic whilst higher levels (1 wt%) are required to obtain the same effect at the PMMA/glass interface. McGrath and his coworkers<sup>330</sup> have undertaken a comprehensive study of the surface and bulk morphology of PDMS/polysulphone (PSO) block copolymers and their blends with PSO homopolymer. They used angle-dependent X-ray photoelectron spectroscopy to determine the distribution of the PDMS component of the block copolymer in the surface layers of both the neat copolymer and in the blends. In the neat copolymer the

surface is essentially a siloxane monolayer with the subsurface consisting of siloxane-rich layers of decreasing siloxane content. Similar studies of blends of the copolymer with PSO homopolymer show that surface enrichment with siloxane varies with the percentage of the copolymer in the blend. Above 10 wt% copolymer the surface region is relatively homogeneous and enriched in siloxane by a factor of 1.8 over that for the composition in the bulk. At lower copolymer concentrations there is still a significant surface excess of siloxane, though there is now a pronounced concentration gradient in the subsurface layers. The bulk morphology is also dependent on copolymer concentration in the blend. At 0.05 wt% siloxane the blend is homogeneous by transmission electron microscopy. At 4.5 wt% siloxane the block copolymer forms domains in a homopolymer matrix. The domains have the inherent microstructure of the neat copolymer. Between 15 and 30 wt% copolymer phase inversion occurs and the PSO homopolymer forms macrodomains in the copolymer continuous phase. Each PSO macrodomain contains small amounts of the block copolymer which, in turn, comprises microdomains of the PSO and PDMS components of the copolymer. Homopolymers with a molecular weight less than that of the chemically identical component of the block copolymer mix completely with the block copolymer in the melt. However, homopolymers whose molecular weight is greater than that of the chemically identical component of the block copolymer exhibit complex phase diagrams when mixed with the block copolymer. Wang and Krause<sup>3,31</sup> have studied the latter system using mixtures of a low molecular weight PDMS/PS block copolymer with PS homopolymer of molecular weight 1–2 orders of magnitude greater than the PS segment in the block copolymer. Mixtures containing < 30 wt% PS consist of two phases: a pure block copolymer microphase which is in equilibrium with a mesophase in which appreciable amounts of PS are mixed into the PS phase of the copolymer. Mixtures containing from 60 to 90 wt% of PS homopolymer exist as one phase whilst mixtures containing more than 90% PS homopolymer exist as two phases, namely the mesophase and pure PS homopolymer.

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# Organosilicon derivatives of phosphorus, arsenic, antimony and bismuth

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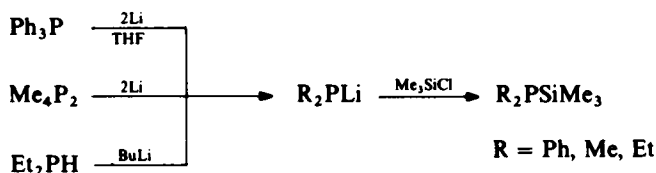
## I. INTRODUCTION

The first organosilicon compound containing a silicon-phosphorus bond,  $\text{Me}_3\text{SiPPh}_2$ , was reported in 1959, and to date is the only such compound reported in *Inorganic Syntheses*<sup>1</sup>. Most of the chemistry of organosilicon derivatives of the heavier pnictogens (Gk. *pniktos*, meaning strangled, stifled) concentrates on phosphorus. Silicon-arsenic chemistry resembles that of silicon-phosphorus compounds as far as it has been studied, but the chemistry of the silicon derivatives of the two heaviest elements of the group is too limited as yet for comparison to be drawn, though some significant differences are emerging.

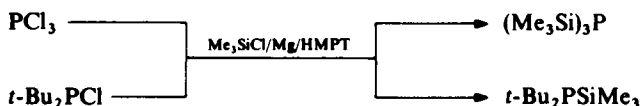
Organosilicon-pnictide chemistry was reviewed several times between 1961 and 1970<sup>2</sup>, then updated with *Comprehensive Organic Chemistry* and *Comprehensive Organometallic Chemistry* in 1979 and 1982<sup>3</sup>. Subsequently, extensive work in the field of phospho-alkene and phospho-alkynes, and silyl-substituted polyphosphines and silapolyphosphines, both linear and cyclic, has spawned reviews from three of the main research groups<sup>4</sup>.

## II. SILYL-SUBSTITUTED MONOPHOSPHINES

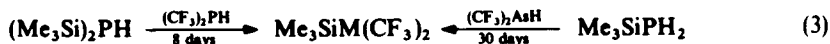
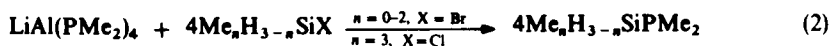
Silyl phosphines are normally made from an alkali metal phosphide and chlorosilane (Scheme 1)<sup>1, 2, 5</sup>, but can be synthesized by directly coupling the phosphorus halide and chlorosilane using magnesium (Scheme 2)<sup>6</sup>. Those containing a Si-H bond result in good yield from phosphidoaluminates, since metal exchange at the silicon-hydrogen bond does not take place with aluminium (equations 1 and 2)<sup>7</sup>. Trifluoromethylphosphino- and arsino-silanes are formed through phosphine elimination from phosphinosilanes using  $(\text{CF}_3)_2\text{MH}$  ( $\text{M} = \text{P}, \text{As}$ ) (equation 3)<sup>8</sup>.



SCHEME 1

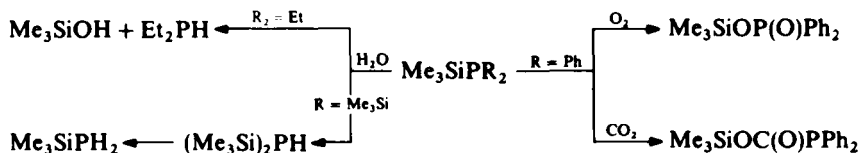


SCHEME 2

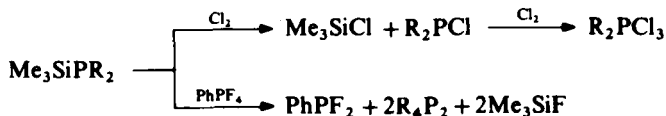


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Silicon-phosphorus compounds are highly reactive. They are readily oxidized, hydrolyzed and insert carbon dioxide, so should be handled in an inert atmosphere (Scheme 3)<sup>3</sup>. Halogens cleave the Si-P bond, with subsequent oxidation to the organophosphorus(V) halide, though  $\text{PhPF}_4$  is reduced to  $\text{PhPF}_2$  (Scheme 4)<sup>9</sup>. Complexes form with diborane (6) and boron halides, these decomposing on heating to give phosphinoboranes which cyclize through association (Scheme 5)<sup>3b</sup>.



SCHEME 3

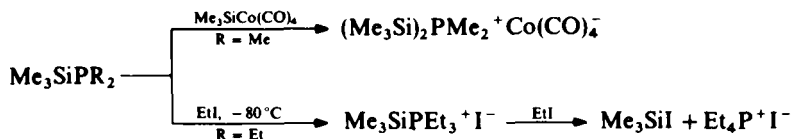


SCHEME 4

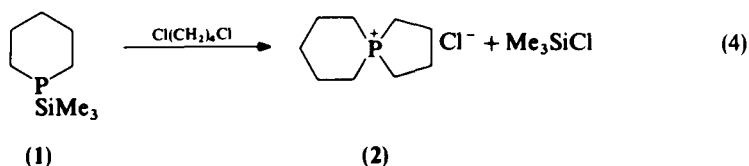


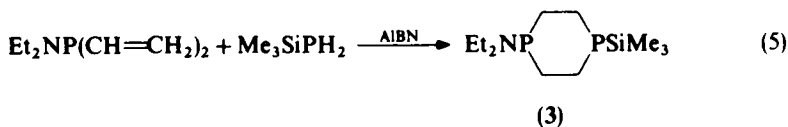
SCHEME 5

Silyl-substituted phosphonium salts can only be stabilized by non-halogen substituted counter ions, e.g.  $\text{Co}(\text{CO})_4^-$  (Scheme 6). Thus iodoethane gives the phosphonium salt from  $\text{Me}_3\text{SiPEt}_2$ , while condensing 1,4-dichlorobutane with the phosphacyclohexane **1** gives the spirophosphonium salt **2** (equation 4)<sup>10</sup>. The addition of  $\text{Me}_3\text{SiPH}_2$  to vinyl phosphines has been used as a synthetic route to substituted phosphacycloalkanes, notably **3** (equation 5)<sup>11</sup>.

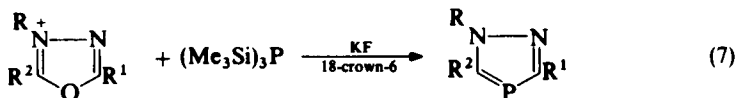
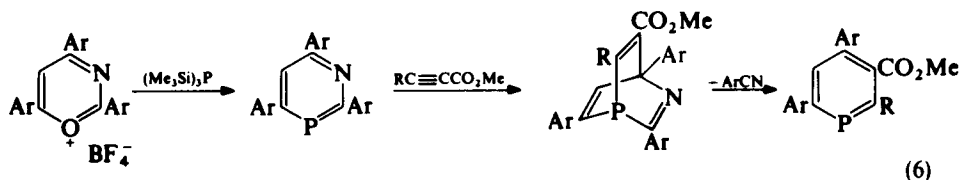


SCHEME 6



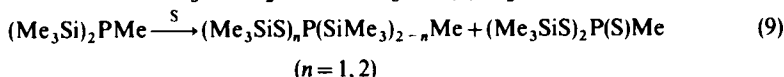


Tris(trimethylsilyl)phosphine ( $\text{Me}_3\text{Si}$ )<sub>3</sub>P readily reacts with pyrylium salts, giving substituted phosphabenzene<sup>12</sup>, and the reaction can be conveniently extended to include the preparation from 3-azapyrylium tetrafluoroborate of 1,3-azaphosphorines which, with acetylene carboxylates, gives the phosphabenzene with nitrile elimination (equation 6)<sup>13</sup>. Both 1,3,4-oxadiazolium and oxazolium salts react similarly to form the five-membered azaphospholes (equation 7)<sup>14</sup>.

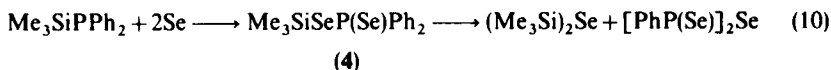


The heavier chalcogens (Gk. *khalkos*, copper or brass) sulphur, selenium and tellurium all react with silicon-phosphorus compounds, but oxidation lessens with increasing atomic weight of the chalcogen.

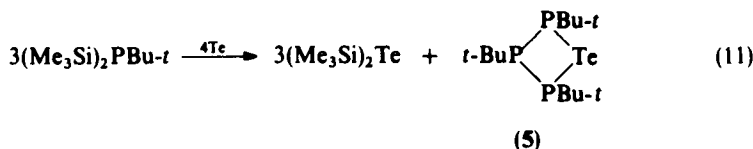
Mono-, di- and trisilylphosphines are all readily oxidized to the silylated thiophosphinate, phosphonate or phosphate  $\text{R}_n\text{P}(\text{S})(\text{SiMe}_3)_{3-n}$  ( $n = 2, 1, 0$ ), though for  $\text{R} = \text{Me}$ , some sulphur-substituted trivalent phosphorus intermediates have been characterized (equations 8 and 9)<sup>15</sup>.



With selenium, however, the selenophosphinate **4** first formed further decomposes to the bisilyl selenide and the selenophosphinic anhydride (equation 10)<sup>15a</sup>.

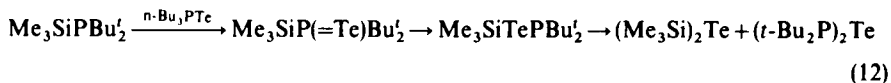


The reaction of  $(\text{Me}_3\text{Si})_2\text{PBu-}t$  with tellurium gives the bisilyl telluride and no phosphorus(V) derivatives, but only the heterocycle **5** (equation 11). Indeed  $\text{Me}_3\text{SiPBu}_2^t$

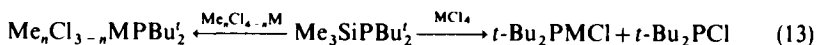


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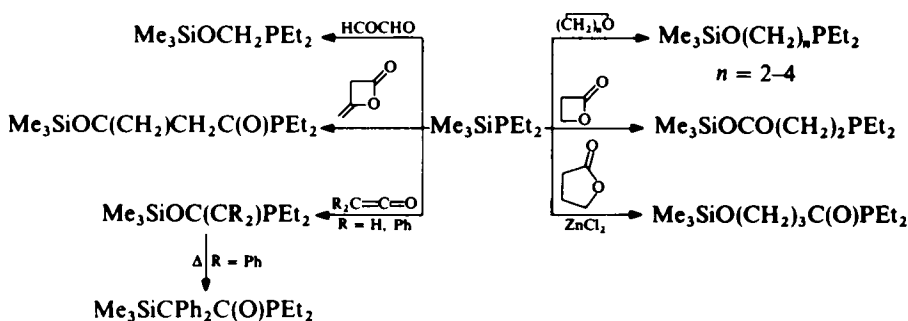
abstracts tellurium from tri-*n*-butylphosphine telluride to give  $\text{Me}_3\text{SiP}(\text{Te})\text{Bu}_2^t$ , which rearranges to  $\text{Me}_3\text{SiTePBu}_2^t$ , then decomposes to the bissilyl and bisphosphino telluride (equation 12)<sup>16</sup>.



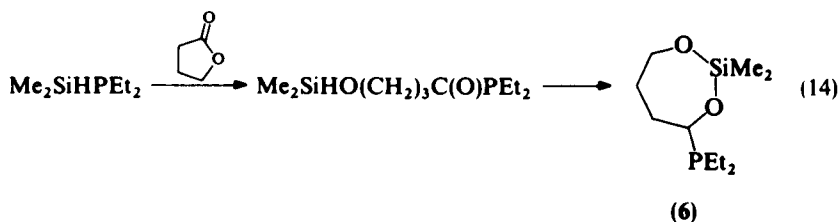
Di-*t*-butylphosphinotrimethylsilane is oxidized by hexachloroethane to the diphosphine<sup>17</sup>, while the tetrachlorides  $\text{MCl}_4$  ( $\text{M}=\text{Ge}, \text{Sn}$ ) are reduced to the phosphinometalloid(II) chloride<sup>18</sup>. With  $\text{Me}_n\text{Cl}_{4-n}\text{M}$ , however, substitution occurs with no oxidation, giving  $\text{Me}_n\text{Cl}_{3-n}\text{MPBu}_2^t$  (equation 13)<sup>19</sup>.



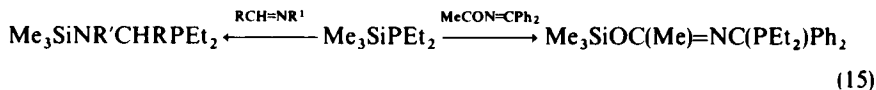
Diethylphosphinotrimethylsilane readily cleaves the carbon–oxygen bond of cyclic ethers and adds to ketene to give the adduct with a silicon–oxygen bond<sup>20</sup>. With lactones, however, ring size determines which C–O bond is broken (Scheme 7). With  $\text{Me}_2\text{HSiPEt}_2$ ,



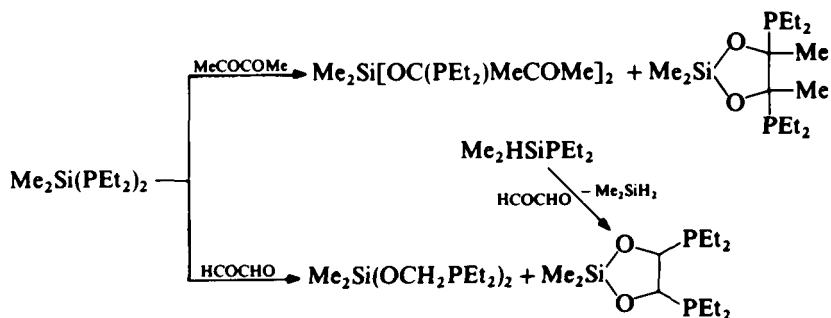
SCHEME 7



similar addition occurs with subsequent cycloaddition to give the 4-phosphino-2-sila-1,4-dioxacycloheptane **6** (equation 14)<sup>21</sup>. With glyoxal and biacetyl, bis(diethylphosphino)dimethylsilane reacts to give both linear and cyclic products through decarbonylation and dimethylsilane elimination (Scheme 8)<sup>22</sup>. Aldimines, diimines and ketimines behave similarly, but *N*-acylimines undergo 1,4-addition (equation 15)<sup>23</sup>.

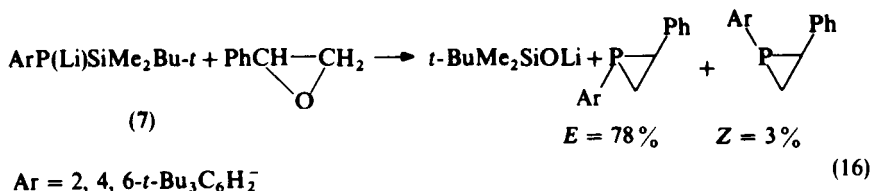




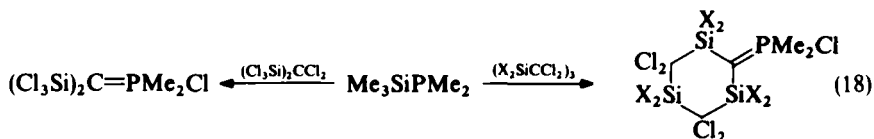
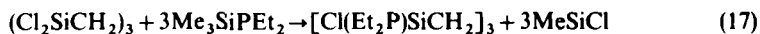


SCHEME 8

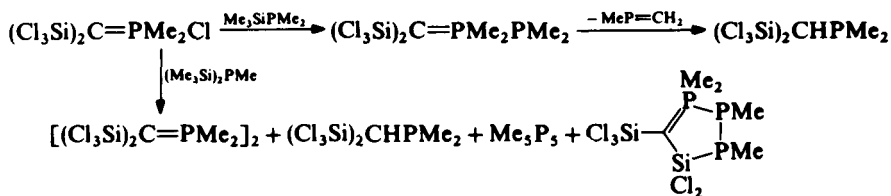
The reaction of the lithium phosphide **7** with styrene oxide eliminates siloxide to give an isomeric mixture of phosphiranes dominated by the *E*-isomer (equation 16)<sup>24</sup>.



While carbosilanes chlorinated at silicon readily exchange with phosphinotrimethylsilanes, (e.g. equation 17), fully chlorinated carbosilanes are substituted at carbon, giving ylid derivatives (equation 18)<sup>25</sup>. These ylids react with more phosphinosilane to give



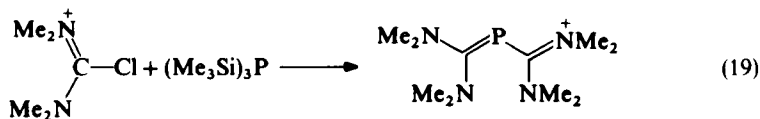
substitution at phosphorus, followed by proton abstraction by the ylidic carbon made more basic by silicon. With  $(\text{Me}_3\text{Si})_2\text{PMe}$ , the same phosphinomethane results together with a complex mixture of other products resulting from coupling and cyclization (Scheme 9)<sup>26</sup>.



SCHEME 9

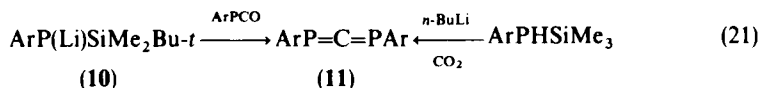
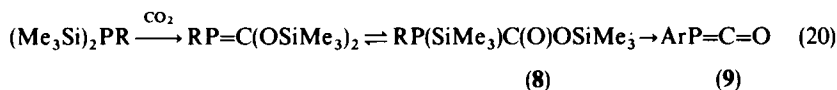
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With tetramethylchloroformamidinium chloride, the reaction with tris(trimethylsilyl)phosphine  $(\text{Me}_3\text{Si})_3\text{P}$  provides an elegant route to the air-stable 2-phosphaallyl cation (equation 19)<sup>27</sup>.

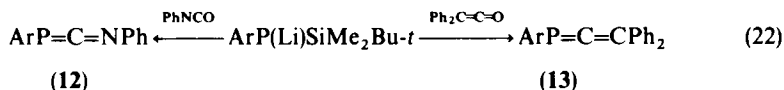


### III. PHOSPHORUS-SUBSTITUTED HETEROCUMULENES

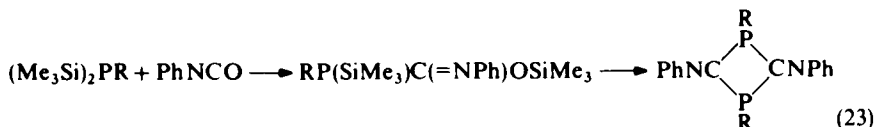
The reactions of silylphosphines with electron-rich compounds are complex, involving insertion into the Si-P bond as the first step. With carbon dioxide, bis(silyl)phosphines give an equilibrium (equation 20) dominated by the phosphacarbamic acid ester **8** which loses disiloxane if  $\text{R} = 2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2$  (henceforth represented as Ar) to give the phosphaketene **9**. This in turn reacts with the silylphosphide **10** to form the 1,3-phosphaallene **11**, an analogue of carbodiimides, and also results directly from  $\text{ArPHSiMe}_3$ ,  $n\text{-BuLi}$  and  $\text{CO}_2$  (equation 21)<sup>28</sup>.



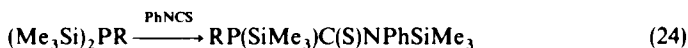
A similar siloxide elimination also occurs for both phenyl isocyanate and diphenylketene giving the heterocumulenes **12** and **13**, which are both stable to heat, water and air, and do not dimerize if  $\text{R} = \text{Ar}$  (equation 22)<sup>29</sup>.

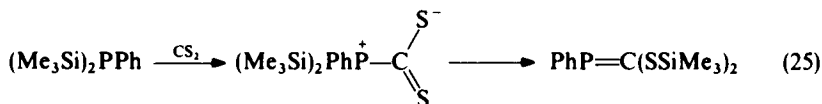


Phenyl isocyanate inserts the Si-P bond of bis-silylphosphines to give the adduct which eliminates siloxane to yield the dimer with a four-membered  $\text{C}_2\text{P}_2$  ring (equation 23).

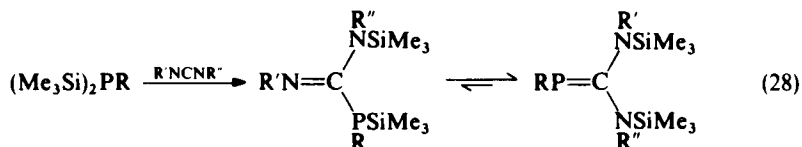
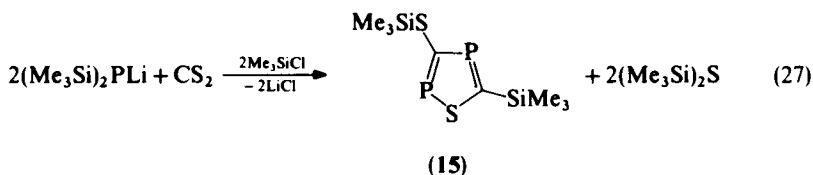
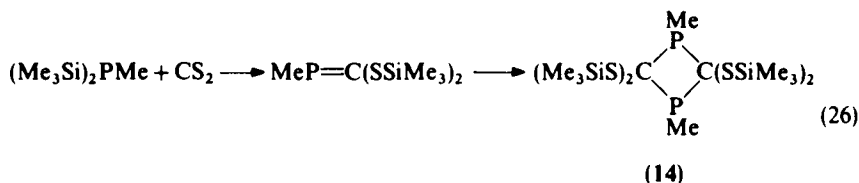


Diphenyl ketene behaves similarly<sup>30</sup>. With phenyl isothiocyanate, however, no silthiane is eliminated and the adduct equilibrium is dominated by the phosphathiourea isomer (equation 24)<sup>31</sup>. With carbon disulphide, a red zwitterion intermediate forms at first, then decomposes to the dithiomethylene derivative rather than, as with carbon dioxide, the phosphacarbamic ester (equation 25)<sup>32</sup>. A similar reaction occurs with  $(\text{Me}_3\text{Si})_2\text{PMe}$ . but

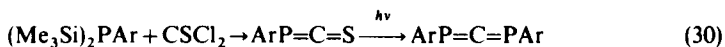
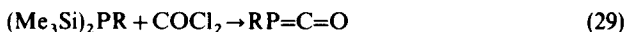




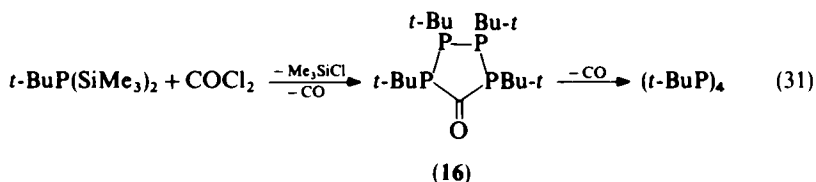
the relatively unhindered dithiomethylene derivative then dimerizes to the four-membered ring **14** (equation 26). With the phosphide, a novel cyclization/condensation in the presence of  $\text{Me}_3\text{SiCl}$  yields the stable 1,2,4-thiadiphosphole **15** (2,4-diphosphathiophene) (equation 27)<sup>33</sup>. Carbodiimides interact similarly, giving phosphaguanidine derivatives (equation 28)<sup>34</sup>.

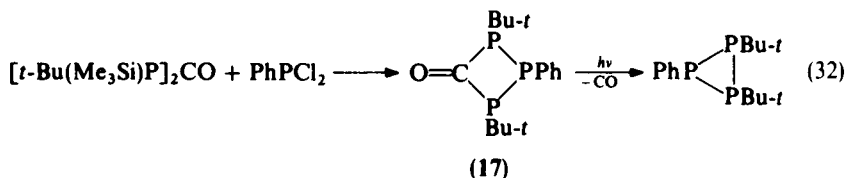


Phosphaketenes result from bis-silylphosphines and phosgene, with the 2,4,6-tri-*t*-butylphenyl (Ar) derivative being stable at room temperature (equation 29), as is its phosphathiaketene, though this eliminates carbon disulphide on irradiation to give the diphosphocarbodiimide analogue (equation 30)<sup>35</sup>. While phosgene and  $(\text{Me}_3\text{Si})_2\text{PBu-}t$



give the phosphaketene, it is only stable below  $-60^\circ\text{C}$ , the main product being the tetraphosphacyclopentanone **16** which loses carbon monoxide to give the cyclotetraphosphine  $(t\text{-BuP})_4$  (equation 31). Condensing the diphosphaurea  $[t\text{-Bu}(\text{Me}_3\text{Si})\text{P}]_2\text{CO}$  with  $\text{PhPCl}_2$  gives the analogous triphosphacyclobutanone **17**, which likewise decarbonylates to the cyclotriphosphine (equation 32)<sup>36</sup>.

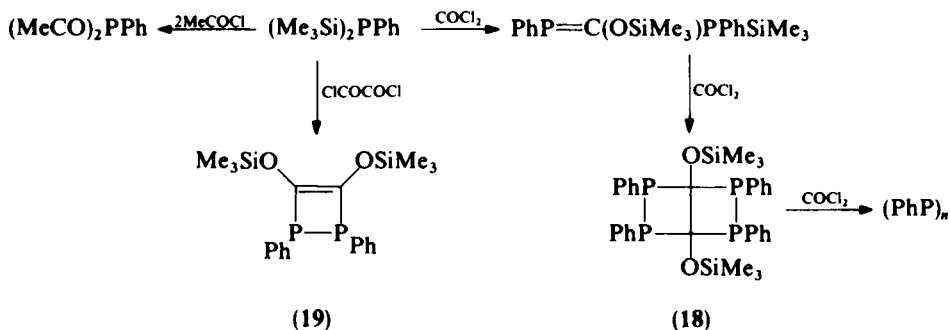
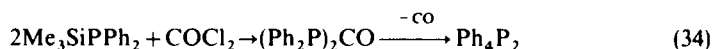
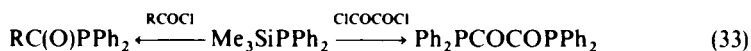




#### IV. REACTIONS OF ACYL AND AROYL CHLORIDES WITH THE SILICON-PHOSPHORUS BOND<sup>4a</sup>

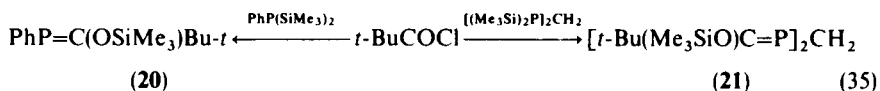
Examples of this type of reaction are very numerous and illustrate further the manner in which phosphorus tends to mimic carbon in the types of products it forms.

Acyl phosphines are readily formed from phosphinosilanes but, with phosgene and oxalyl chloride, decarbonylation and rearrangement results with formation of intermediate methylenephosphanes which cyclize giving **18** and **19** (equations 33 and 34 and Scheme 10)<sup>37</sup>. With the more hindered pivaloyl chloride, the methylenephosphane

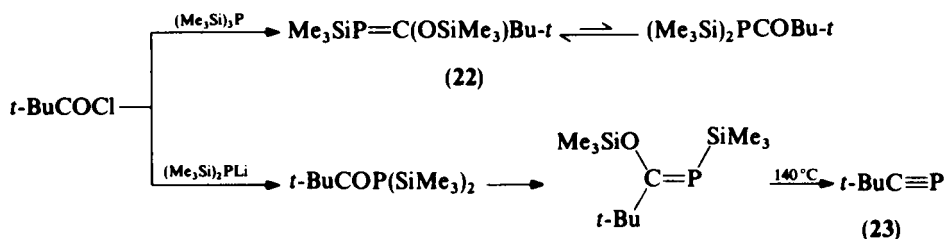


SCHEME 10

results as the final product for bis-silylphosphines. Thus  $(\text{Me}_3\text{Si})_2\text{PPh}$  gives **20** and  $[(\text{Me}_3\text{Si})_2\text{P}]_2\text{CH}_2$  gives **21**, through silyl migration to oxygen, the structure of **21** showing the  $\text{P}=\text{C}$  bond to be 169 pm, some 16 pm shorter than the  $\text{P}-\text{C}$  single bonds (equation 35)<sup>38</sup>. The 1:1 reaction of  $(\text{Me}_3\text{Si})_3\text{P}$  with pivaloyl chloride gives an equilibrium

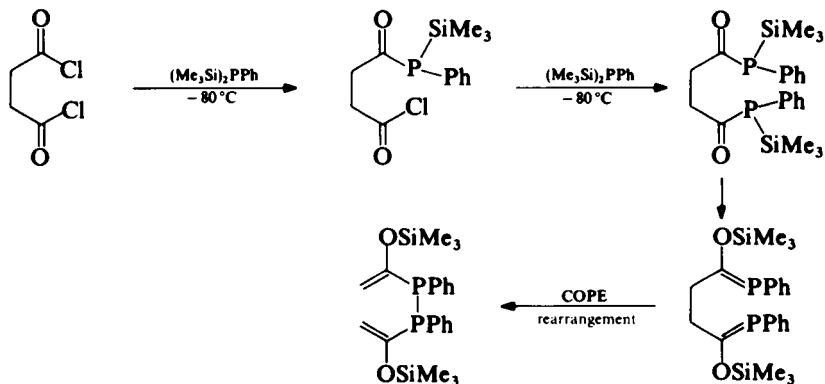


dominated by the siloxy isomer **22** which, as the (*Z*) isomer, loses siloxane at 140 °C to give the phosphyne **23** (Scheme 11). No phosphyne was detected when the *E*-isomer was heated<sup>39</sup>. Adamantyl and 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub> phosphynes result similarly<sup>40</sup>. With saturated diacid chlorides such as succinyl or *trans*-cyclohexane dicarboxylic acid chloride,

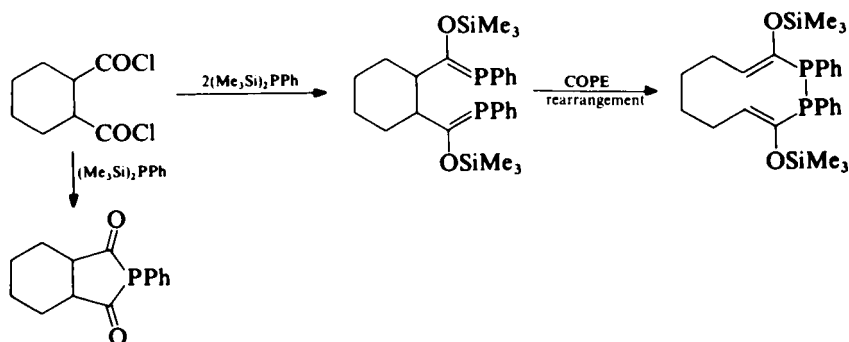


SCHEME 11

substitution occurs followed by silyl migration and a Cope rearrangement (Schemes 12 and 13)<sup>41</sup>. Similar [2 + 2] and [4 + 2] Diels–Alder cycloadditions occur for the products of



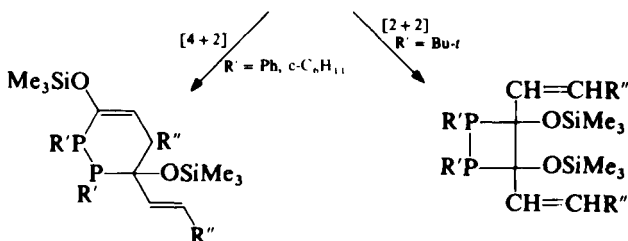
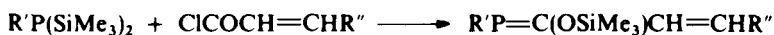
SCHEME 12



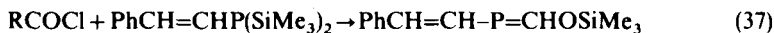
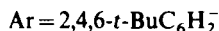
SCHEME 13

the  $\alpha,\beta$ -unsaturated acid chlorides and bis-silylphosphines (Scheme 14). However if Ar = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, then the 1-substituted phosphabuta-1,3-diene results (equation 36), and is stable as is the 2-isomer formed from the styryl phosphine **24** (equation 37)<sup>42</sup>.

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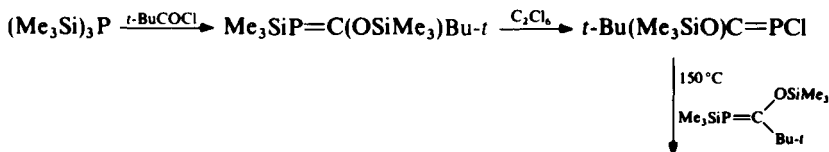


SCHEME 14



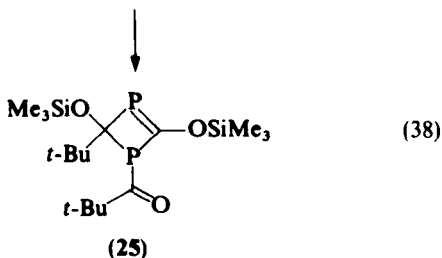
(24)

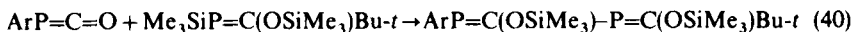
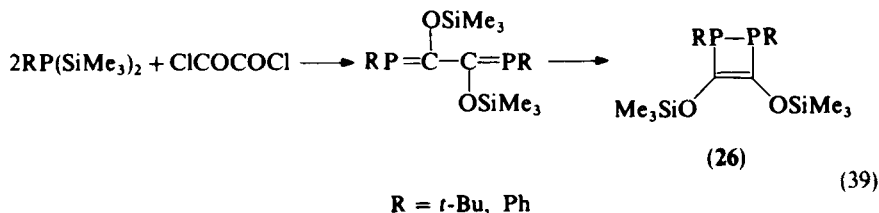
By appropriate functionalization and rearrangement, the 2,3-diphosphabuta-1,3-dienes can be made from either  $(Me_3Si)_3P$  or  $(Me_3Si)_4P_2$  and pivaloyl chloride (Scheme 15), and have a short P-P bond (217.1 pm), supporting  $\pi$ -delocalization<sup>43</sup>. The 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>



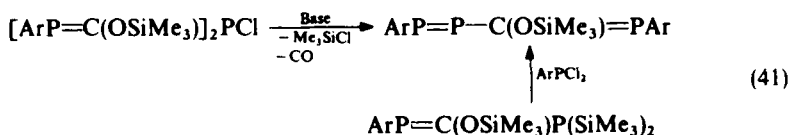
SCHEME 15

derivative results similarly, together with  $ArC\equiv P^{44}$ . The 1,3- and 1,4-isomers are unstable, the former cyclizing into the 1,3-diphosphacyclobutene **25** (equation 38) and the latter into the 1,2-isomer **26** (equation 39)<sup>43</sup>. With  $Ar = 2,4,6-t-Bu_3C_6H_2$ , the 1,3-diphosphabuta-1,3-diene can be isolated from the phosphaketene (equation 40), and this group provides the stabilization for a 1,2,4-triphosphabuta-1,3-diene, prepared from

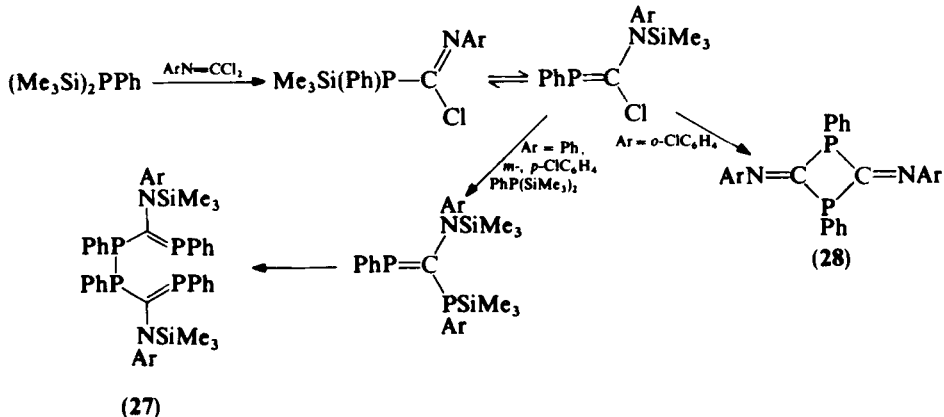




either  $[\text{ArP}=\text{C}(\text{OSiMe}_3)]_2\text{P}Cl$  with base, or from  $\text{ArP}=\text{C}(\text{OSiMe}_3)\text{P}(\text{SiMe}_3)_2$  and  $\text{ArP}Cl_2$  (equation 41). The bond lengths in the diene residue support  $\pi$ -bonding in the terminal bonds<sup>45</sup>.



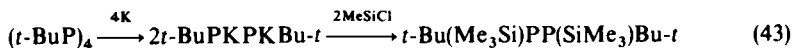
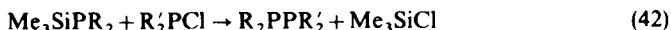
In a similar manner, condensing aryl isocyanide dichloride with  $(\text{Me}_3\text{Si})_2\text{PPh}$  gives products dependent upon the hindrance of the aryl group. With  $\text{PhN}=\text{CCl}_2$ , the 1,3,4,6-tetraphospha-1,5-diene **27** results, while with  $o\text{-ClC}_6\text{H}_4\text{N}=\text{CCl}_2$ , the 1,3-diphosphetane **28** is formed (Scheme 16)<sup>46, 41a</sup>.



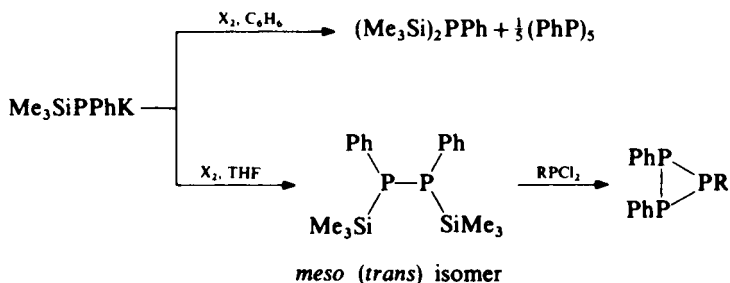
SCHEME 16

### V. LINEAR POLYPHOSPHINES<sup>4b</sup>

Silyl-substituted diphosphines are useful synthetic intermediates in the preparation of longer-chain linear and cyclopolyphosphines. They result through routes involving condensation and coupling (Scheme 17, equations 42 and 43)<sup>47</sup>.

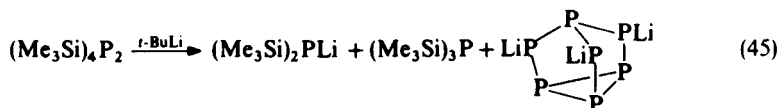
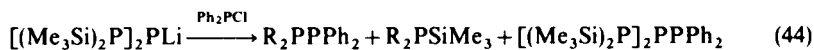


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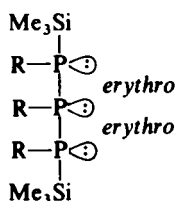


Scheme 17

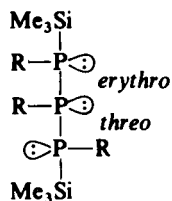
The chemistry of silylpolyposphines is complicated however by not just oxygen and water sensitivity, but also by their tendency to couple and exchange if chloro substituted, and to extensively rearrange in the presence of strong base such as BuLi. Thus coupling  $[(\text{Me}_3\text{Si})_2\text{P}]_2\text{PLi}$  with  $\text{Ph}_2\text{PCl}$  gives a series of mono and diphosphines as well as the expected tetraphosphine **29** (equation 44)<sup>48</sup>, while both  $(\text{Me}_3\text{Si})_4\text{P}_2$  and  $(\text{Me}_3\text{Si})_5\text{P}_3$  with *t*-BuLi give monophosphine derivatives, together with the nortricyclene cage phosphide  $\text{Li}_3\text{P}_7$  (equation 45)<sup>49</sup>.



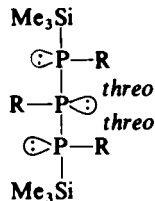
While the triphosphine  $\text{Me}_3\text{Si}(\text{PR})_3\text{SiMe}_3$  ( $\text{R} = \text{Ph}$ ) exists in solution as an 8:3:1 mixture of isomers **30**, **31** and **32**, respectively, the derivative ( $\text{R} = \text{Bu-}t$ ) only occurs as the *threo-erythro* isomer **31** with a  $^{31}\text{P}$  NMR spectrum showing an ABC pattern. Hydrolysis gives a 2:1 mixture of *threo-threo* and *threo-erythro* isomers of  $\text{H}(\text{PBu-}t)_3\text{H}$ <sup>50</sup>.



(30)

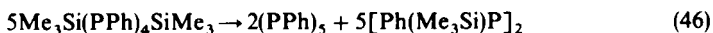


(31)



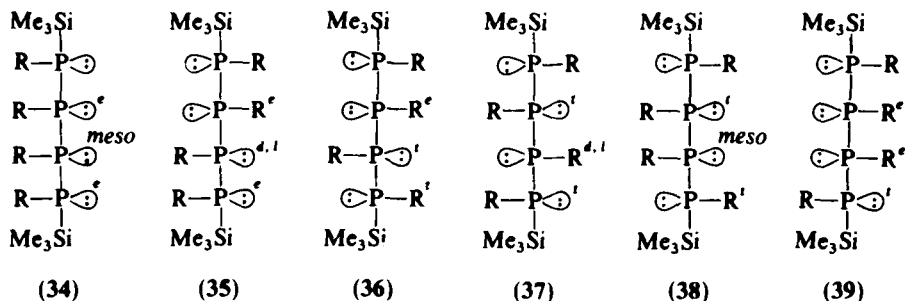
(32)

The tetraphosphine  $\text{Me}_3\text{Si}(\text{PPh})_4\text{SiMe}_3$  (**33**) results from  $\text{K}_2(\text{PPh})_4$  and rearranges on heating to cyclopentaphosphine and the diphosphine  $[\text{Ph}(\text{Me}_3\text{Si})\text{P}]_2$  (equation 46). In solution, however, it is stable but present as a mixture of four of the six possible isomers in the ratio of 11:7:9:3 for **34**, **35**, **36** and **37**, respectively<sup>51</sup>.



(33)





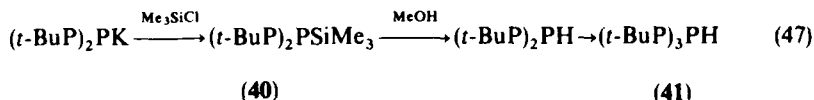
*e* = erythro, *t* = threo

The analogous *t*-butyl tetraphosphine  $\text{Me}_3\text{Si}(\text{PBu-}t)_4\text{SiMe}_3$  results from  $(t\text{-BuP})_4$  and potassium, followed by silylation. It is stable to disproportionation below  $-30^\circ\text{C}$ , occurring solely as the *erythro-(d,l)-erythro* isomer **35** with large coupling constants  $^3J(\text{PP})$  due to the *trans* arrangement of neighbouring *t*-butyl groups<sup>52</sup>. The crystal structure shows the Si-P bonds to be 228.5 pm and the middle P-P bond of 221.4 pm to be longer than the two other P-P bonds<sup>53</sup>. Hydrolysis gives a 10:5:1 mixture of isomers equivalent to **37**, **36** and **35** of  $\text{H}(\text{PBu-}t)_4\text{H}$ <sup>54</sup>.

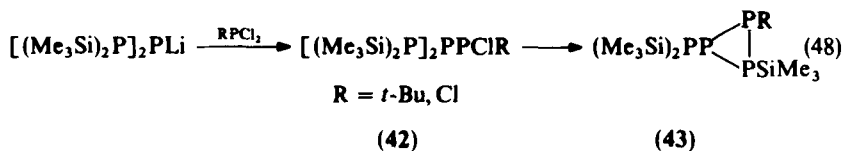
## VI. CYCLOPOLYPHOSPHINES<sup>4c</sup>

### A. Cyclotriphosphines

Reacting  $(t\text{-BuP})_{3,4}$  with potassium gives  $(t\text{-BuP})_2\text{PK}$ , which gives the silyl cyclotriphosphine **40** on silylation. Methanol yields the unstable cyclotriphosphine, which disproportionates to the cyclotetraphosphine **41** (equation 47)<sup>55</sup>.



Cyclotriphosphines **43** ( $\text{R} = t\text{-Bu, Cl}$ ) result from the condensation of  $[(\text{Me}_3\text{Si})_2\text{P}]_2\text{PLi}$  with  $t\text{-BuPCl}_2$  or  $\text{PCl}_3$ . Initially the intermediate tetraphosphine **42** is produced which gives the cyclotriphosphine on elimination of  $\text{Me}_3\text{SiCl}$  (equation 48)<sup>48a</sup>.

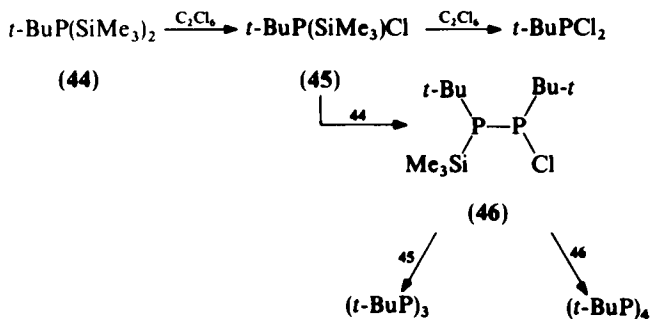


### B. Cyclotetraphosphines

The five cyclotetraphosphines  $t\text{-Bu}_{4-n}(\text{Me}_3\text{Si})_n\text{P}_4$  ( $n=0-4$ ) have all been isolated as yellow crystalline solids. The first of the series, though not a Si-P compound, is included for completeness and was the first to be isolated. It results from the Wurtz-type reaction of sodium with  $t\text{-BuPCl}_2$  in dioxan in 63% yield<sup>56</sup>. It is also formed from the partial chlorination of  $t\text{-BuP}(\text{SiMe}_3)_2$  (**44**) by hexachloroethane to give the first characterisable

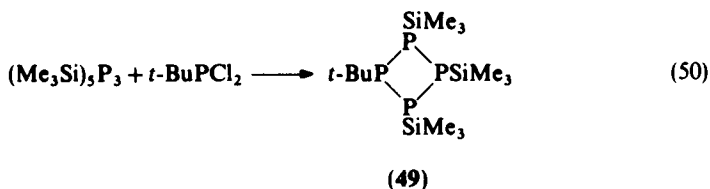
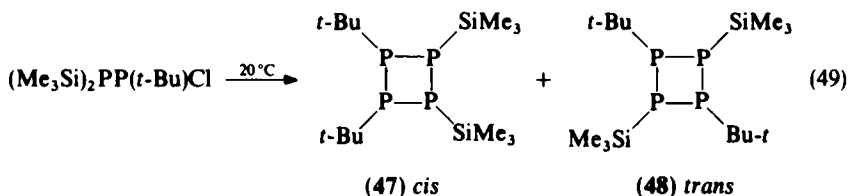
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P-chloro silylphosphine **45**, which condenses with **44** to form the diphosphine **46**. This reacts with **45** or itself to form the cyclotri or tetraphosphine (Scheme 18)<sup>57</sup>. Excess



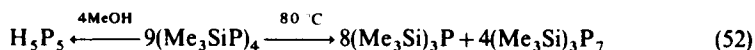
SCHEME 18

*t*-butyllithium attacks white phosphorus to give *t*-Bu<sub>3</sub>P<sub>4</sub>Li and *t*-Bu<sub>2</sub>P<sub>3</sub>Li as the main products. Silylation gives the monosilylcyclotri and tetraphosphines<sup>58</sup>. This cyclotetraphosphine is also among the products of the reaction of (Me<sub>3</sub>Si)<sub>2</sub>PLi·2THF, PCl<sub>3</sub> and *t*-BuLi (ratio 1:1:2) at -78 °C in pentane. The diphosphine (Me<sub>3</sub>Si)<sub>2</sub>PP(Bu-*t*)Cl, which results from (Me<sub>3</sub>Si)<sub>2</sub>PLi and *t*-BuPCl<sub>2</sub>, condenses at 20 °C to give a mixture of 1,2- and 1,3-disilylcyclotetraphosphine isomers, **47** and **48** (equation 49)<sup>49b</sup>. The former (**47**) also results from the condensation of the triphosphine (Me<sub>3</sub>Si)<sub>2</sub>PP(SiMe<sub>3</sub>)P(*t*-Bu)SiMe<sub>3</sub> with *t*-BuPCl<sub>2</sub><sup>59</sup>, a method equally useful for the preparation of trisilylcyclotetraphosphine **49**, using the pentasilyltriphosphine (equation 50)<sup>60</sup>.



The tetrasilylcyclotetraphosphine results from the coupling of trimethylsilylphosphine using di-*t*-butylmercury, and proceeds via the diphosphine (equation 51). It decomposes at 80 °C to give the trisilylphosphine and (Me<sub>3</sub>Si)<sub>3</sub>P<sub>7</sub>, and is desilylated by methanol with ring expansion to cyclopentaphosphine H<sub>3</sub>P<sub>5</sub> (equation 52)<sup>61</sup>.

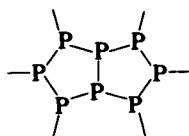




The reaction of these cyclotetraphosphines  $t\text{-Bu}_{4-n}(\text{Me}_3\text{Si})_n\text{P}_4$  with  $n\text{-BuLi}$  gives Si-P cleavage for  $n=1$  or 2 (*trans*) **48** and maintains the cyclic  $\text{P}_4$  ring. With  $n=2$  [*cis*] **47**, 3 and 4, however, the P-P bond is cleaved, then  $\text{Me}_3\text{Si}/\text{Li}$  exchange gives linear tetraphosphides and consequently a wide range of linear and cyclic products including  $\text{Li}_3\text{P}_7$ <sup>58, 62</sup>.

### C. Cyclopentaphosphines

Though there has been little systematic study as yet of silyl-substituted cyclopentaphosphines, they do result among the many silylated products of the reaction of  $t\text{-BuLi}$  with white phosphorus.  $\text{P}_3$  and  $\text{P}_4$  rings are found, together with  $(\text{Me}_3\text{Si})_3\text{P}$  and  $t\text{-BuP}(\text{SiMe}_3)_2$  if equimolar quantities of  $t\text{-BuLi}$  and white phosphorus are used in DME or THF. The cyclopentaphosphine ring is present in  $(\text{Me}_3\text{Si})_3\text{P}_7$  and in the isomeric mixtures of  $t\text{-Bu}_3(\text{Me}_3\text{Si})_2\text{P}_5$  and the bicyclo derivatives  $t\text{-Bu}_n(\text{Me}_3\text{Si})_{6-n}\text{P}_8$  ( $n=1-5$ ) **(50)**, formed with excess  $t\text{-BuLi}$  in hexane/THF as solvent<sup>63</sup>.



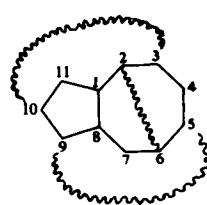
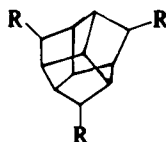
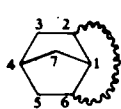
(50)

### D. Phosphorus-rich Silyl Cage Phosphines

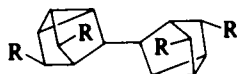
Silylation of the Na/K alloy-white phosphorus with  $\text{Me}_3\text{SiCl}$  gives the two cage compounds 3,5,7-tris(trimethylsilyl)tricyclo[2.2.1.0<sup>2,6</sup>]heptaphosphane  $(\text{Me}_3\text{Si})_3\text{P}_7$ , **51**, and  $(\text{Me}_3\text{Si})_4\text{P}_{14}$ , **52** (two molecules of **51** coupled through phosphorus)<sup>64</sup>. Using pure  $\text{M}_3\text{P}_{11}$  ( $\text{M}=\text{Na}, \text{Cs}$ ) with  $\text{Me}_3\text{SiCl}$  gives the silyl derivative 4,7,11-tris(trimethylsilyl)pentacyclo[6.3.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecaphosphane, **53**, that is much less stable to oxygen and water than **51** which, unlike **53**, possesses three-membered as well as five-membered rings<sup>65</sup>.



(51)



(53)

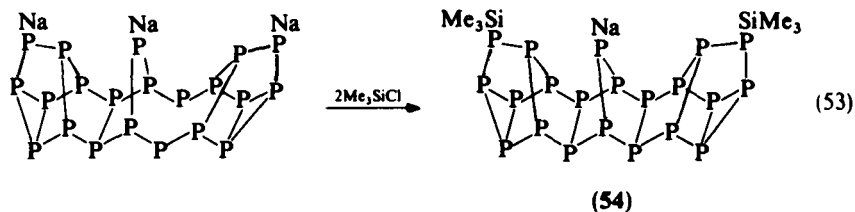


(52)

## 5. Organosilicon derivatives of phosphorus, arsenic, antimony and bismuth 167

**51** can be readily desilylated with methanol to give  $P_7H_3$ , the proton NMR spectrum of which indicates a mixture of conformational isomers<sup>66</sup>. **51** reacts with  $Me_3MCl$  ( $M=Sn, Pb$ ) to give the stannyl and plumbyl derivatives, and with  $Ph_3M'Cl$  ( $M'=Si, Ge, Sn$ ) likewise. The equilibrium with  $Ph_3SiCl$  is driven by the lower solubility of the phenyl compound, and these products occur as racemates with the  $P_7$  cage slightly twisted about the three-fold axis<sup>67</sup>.

The stability of the heptaphosphanortricyclene cage is emphasized by its presence as the terminal group in trisodium hencosaphosphide  $Na_3P_{21}$ , which is preferentially silylated terminally rather than at the middle phosphide atom to give **54** (equation 53)<sup>68</sup>.

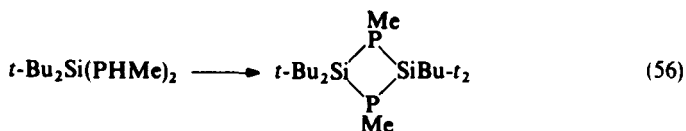
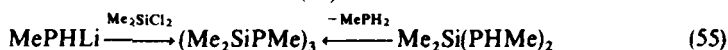
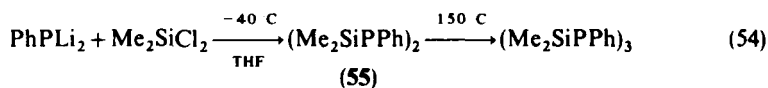


While heavily silylated cyclotetraphosphines have the tendency on lithiation with  $BuLi$  to give  $P_7$  residues among the products, lithiation of  $(Me_3Si)_3P_7$  using  $t-BuLi$  gives monophosphine derivatives as well as  $Li_3P_7$  and the cyclotetraphosphine  $t-Bu_3(Me_3Si)P_4$ <sup>49a</sup>.

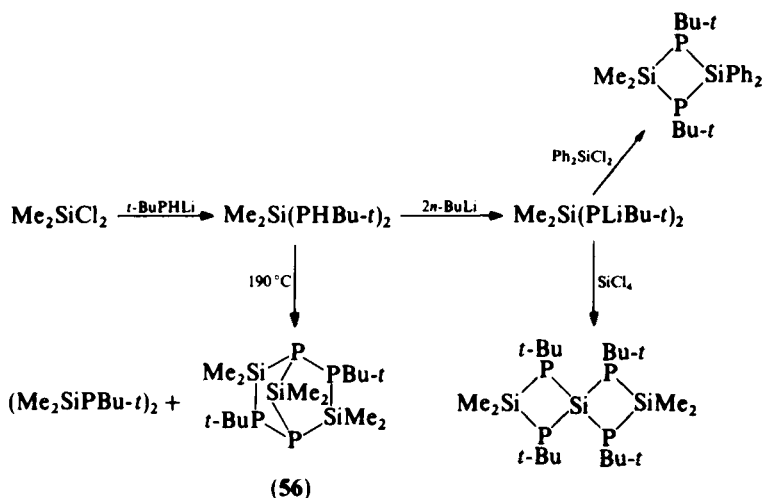
The chemistry of linear and cyclic polyphosphines illustrates a very labile system, with nucleophilic attack cleaving  $Si-P$  and/or  $P-P$  bonds, exchange, coupling, rearrangement and ring conformational changes all contributing factors to the ultimate range of products<sup>4c</sup>.

## VII. CYCLOSILAPHOSPHANES<sup>3b, 4c</sup>

The cyclodisilaphosphane **55** results when  $PhPLi_2$  and  $Me_2SiCl_2$  react at  $-40^\circ C$ , but at higher temperatures the cyclic trimer forms and both are in equilibrium in solution (equation 54)<sup>69</sup>. In the absence of bulky substituents, the cyclic trimer forms (equation 55), but with  $t$ -butyl substituting either silicon or phosphorus, the four-membered ring results through phosphine elimination (equation 56). The tetraphosphatrisilanorbornane **56** is also formed in this pyrolysis through condensation involving  $P-P$  bond formation (Scheme 19)<sup>70</sup>. This behaviour contrasts with that of cyclosilthianes where, with small groups, the cyclic dimer is the more stable (see the chapter on  $Si-S$  compounds).

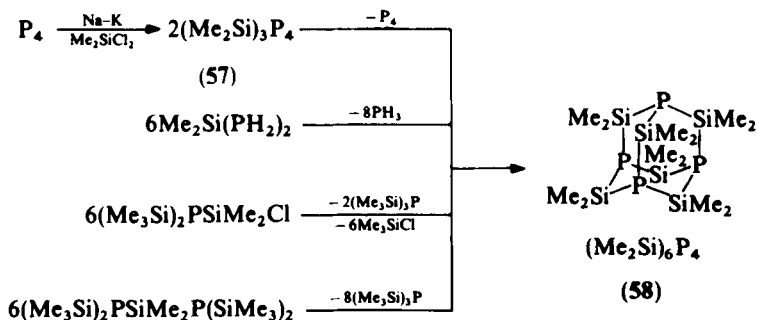


Treating a white phosphorus/ $Na-K$  alloy with  $Me_2SiCl_2$  gives the cage 3,3,5,5,7,7-hexamethyl-3,5,7-trisilatetraphosphanortricyclene **57** which, like many linear phosphine-dimethylsilanes not organosubstituted at phosphorus, will condense to give the adamant-



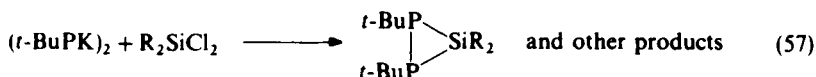
SCHEME 19

tane-like cage  $(\text{Me}_2\text{Si})_6\text{P}_4$  (**58**), illustrating the lability of the unhindered Si-P system (Scheme 20) (see equation 91 for analogous Si-As behaviour)<sup>71</sup>.



SCHEME 20

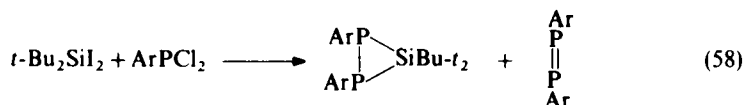
The first stable three-membered  $\text{P}_2\text{Si}$  heterocycles were prepared by the [2+1]-cyclocondensation of  $\text{R}_2\text{SiCl}_2$  ( $\text{R} = \text{Me}, \text{Ph}$ ) with  $(t\text{-BuPK})_2$ . In addition, the monophosphine  $t\text{-BuP}(\text{SiPh}_2\text{Cl})_2$  and the diphosphine  $\text{H}(t\text{-Bu})\text{PP}(t\text{-Bu})\text{SiR}_2\text{Cl}$  was also formed, along with the rings  $(t\text{-BuP})_4$ ,  $(t\text{-BuP})_3\text{SiR}_2$ ,  $(t\text{-BuP})_3(\text{SiMe}_2)_2$  (1,3-isomer) and  $(t\text{-BuP})_4(\text{SiMe}_2)_2$  (1,4-isomer) (equation 57). The structure of  $(t\text{-BuP})_2\text{SiPh}_2$  shows the triangle to be equilateral with the *t*-butyl groups *trans*, with Si-P bond lengths 222.5 pm<sup>72</sup>.



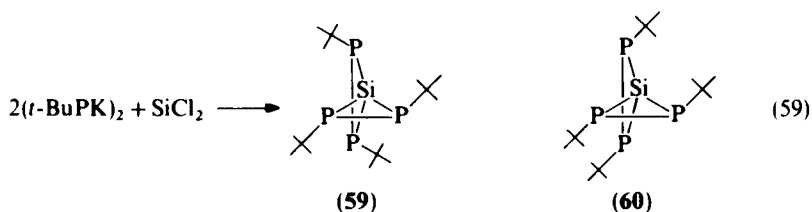
Mixing  $t\text{-Bu}_2\text{SiI}_2$  with lithium naphthalenide, then adding 2,4,6-tri-*t*-butylphenylphosphorus dichloride ( $\text{ArPCL}_2$ ), gives the diphosphene along with the air-stable, more

5. Organosilicon derivatives of phosphorus, arsenic, antimony and bismuth 169

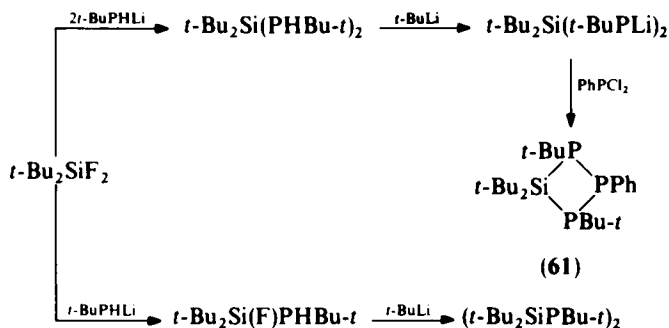
hindered  $P_2Si$  ring with slightly longer Si-P (224.3 pm) and P-P (223.4 pm) bonds (equation 58)<sup>73</sup>.



The NMR spectrum of the spiro derivative 1,2,4,5-tetra-*t*-butyl-1,2,4,5-tetraphospha-3-silaspiro[2.2]pentane, which results from  $(t\text{-BuPK})_2$  and  $\text{SiCl}_4$  shows a mixture of the two isomers **59** and **60** in the ratio 7:3 (the  $^{29}\text{Si}$  NMR spectrum shows two quintets, which differ in the arrangement of the two pairs of *trans*-orientated *t*-butyl groups (equation 59). The less stable **60** rearranges to **59** on warming<sup>74</sup>.

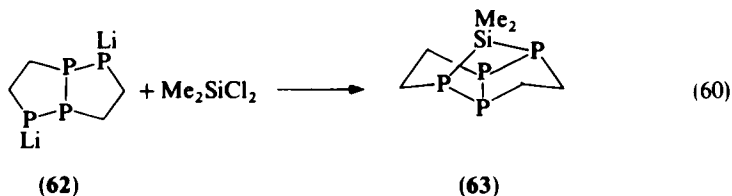


Condensing  $t\text{-BuPHLi}$  with  $t\text{-Bu}_2\text{SiF}_2$  gives the mono and bisphosphinosilanes, the former yielding the cyclodisilaphosphane with  $t\text{-BuLi}$ , and the latter the bisphosphidosilane which, with  $\text{PhPCl}_2$ , gives the trisphosphasilacyclobutane **61** (Scheme 21)<sup>75</sup>.

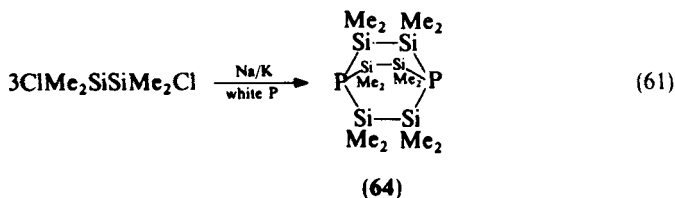


SCHEME 21

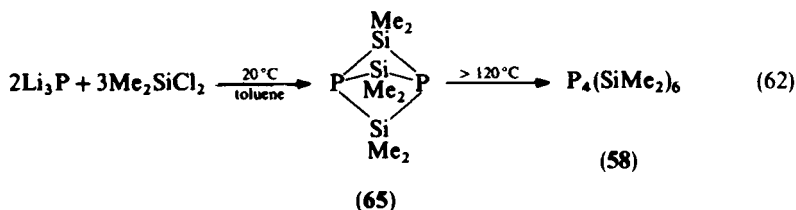
Coupling the dilithio derivative of 1,2,5,6-tetraphosfabicyclo[3.3.0]octane **62** with  $\text{Me}_2\text{SiCl}_2$  gives 9,9-dimethyl-1,2,5,6-tetraphospha-9-silatricyclo[3.3.1.0<sup>2,6</sup>]nonane **63** containing the  $\text{SiP}_4$  five-membered ring (equation 60)<sup>76</sup>.



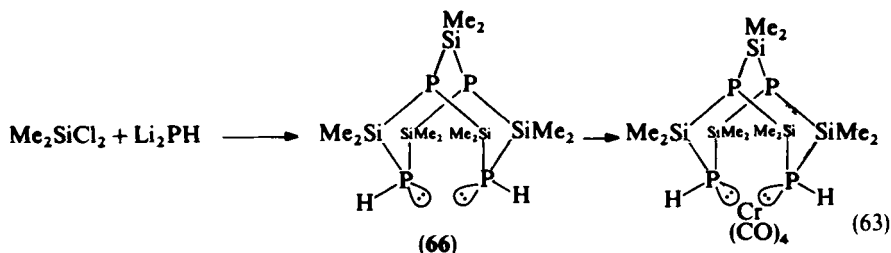
The phosphide formed from Na/K alloy and white phosphorus condenses with  $(\text{ClMe}_2\text{Si})_2$  to give the barrel-like cage compound **64** which is highly thermally stable, melting above  $300^\circ\text{C}$  (equation 61)<sup>77</sup>. This contrasts with the condensation with



$\text{Me}_2\text{SiCl}_2$  which gives the cage compound **65** which, on heating above  $120^\circ\text{C}$ , dimerizes to the more stable adamantane cage of **58** (equation 62)<sup>78</sup>.

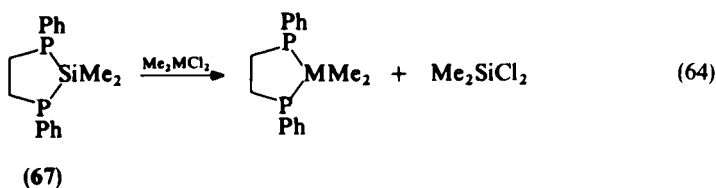


An extensive range of silyl phosphines results from the condensation of  $\text{R}_2\text{SiCl}_2$  ( $\text{R} = \text{Me}, \text{Et}, t\text{-Bu}$ ) with the phosphides  $\text{LiPH}_2$  and  $\text{Li}_2\text{PH}$ . Many form part of the adamantane cage structure of **58**. These include the remarkable **66** which acts as a bidentate ligand to the  $\text{Cr}(\text{CO})_4$  residue, this completing the cage (equation 63)<sup>79</sup>.



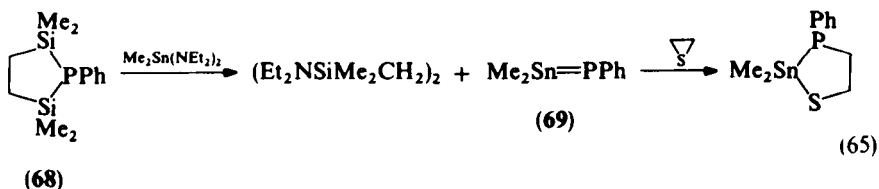
The crystal structures of **56**, **58**<sup>80</sup> and **66**<sup>79b</sup>, the nortricyclenes **51** and **57**<sup>81</sup>, of the five-membered 1,2-diphosphatrisilacyclopentane  $(\text{PhP})_2(\text{SiMe}_2)_3$  and the six-membered tetraphospha-1,4-disilacyclohexane  $[\text{Me}_2\text{SiP}(\text{Bu}-t)\text{P}(\text{Bu}-t)]_2$  (boat conformation with *trans* *t*-butyl groups)<sup>82</sup> show Si-P bond lengths to be in the range 224–229 pm.

The 1,3-diphospha-2-silacyclopentane **67** is a useful intermediate for the synthesis of both the germa- and stanna-substituted rings (equation 64)<sup>83</sup>, using  $\text{Me}_2\text{MCl}_2$



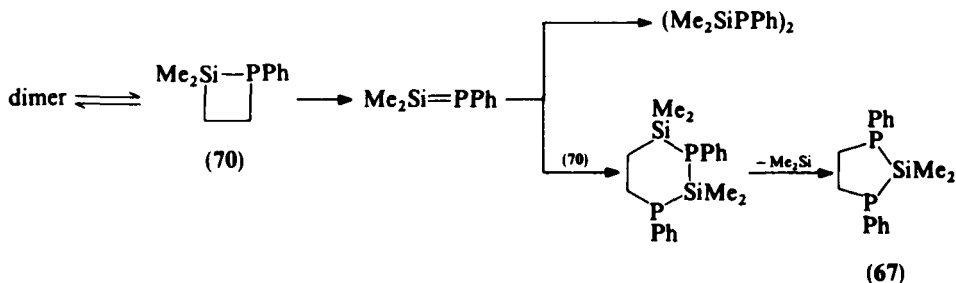
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(M = Ge, Sn), and illustrating the tendency of the heavier metalloids to prefer the softer phosphorus. 2-Phospha-1,3-disilacyclopentane **68** proves a useful intermediate in the synthesis of the stannaphosphene **69** using  $\text{Me}_2\text{Sn}(\text{NEt}_2)_2$ . It can be trapped through thiirane insertion (equation 65) or it may trimerize<sup>84</sup>.

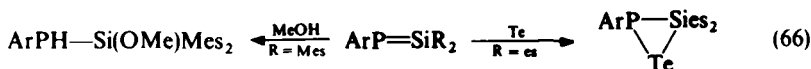


**VIII. THE SILICON-PHOSPHORUS DOUBLE BOND, SILICON-PHOSPHORUS(V) COMPOUNDS AND SILYL-PHOSPHORUS RADICALS**

The thermal decomposition of 2-silaphosphetane (**70**) is thought to give the intermediate  $\text{Me}_2\text{Si}=\text{PPh}$ , since its cyclic dimer and **67** are found among its products (Scheme 22)<sup>85</sup>. Bulky groups assist in the stabilization of the Si-P double bond, enabling its characterization in solution. Thus 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>PH<sub>2</sub> condenses with  $\text{Me}_2\text{SiCl}_2$  to give the phosphasilene (silaphosphene). A series of these compounds prepared in solution show <sup>31</sup>P and <sup>29</sup>Si NMR spectra with strong deshielding of silicon (148–176 ppm) and large Si and P coupling constants (around 150 Hz). They react with methanol and tellurium to give adducts (equation 66)<sup>86</sup>.

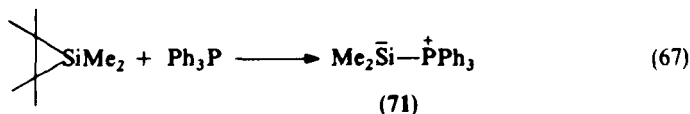


SCHEME 22



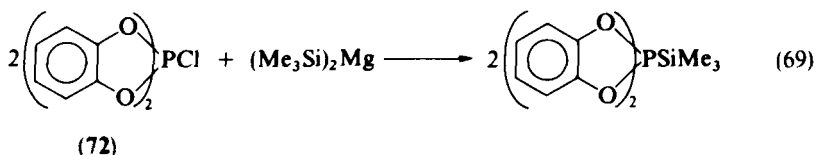
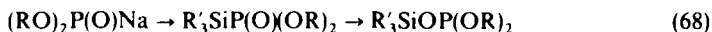
Ar = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, Mes = mesityl, es = 2,4,6-Et<sub>3</sub>C<sub>6</sub>H<sub>2</sub>

The silene-phosphorane (**71**) may well be formed as an intermediate from the reaction of hexamethylsilacyclopropane with triphenylphosphine (equation 67)<sup>87</sup>. Compounds once thought to contain the silicon-phosphorus(V) bond result from the Michaelis

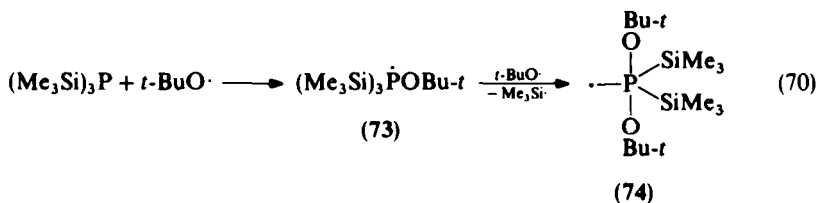




coupling reaction, but are now considered to rearrange to the phosphite (equation 68)<sup>2d</sup>. However, silylating bis(catechyl)chlorophosphorane **72** with  $(\text{Me}_3\text{Si})_2\text{Mg}$  does give the first  $\lambda^5\text{P-Si}$  bonded phosphorane as a crystalline solid (equation 69)<sup>88</sup>.



Tris(trimethylsilyl)phosphine reacts with the *t*-butoxy radical to give the adduct **73**, which undergoes Si-P cleavage to give, notably, the trigonal bipyramidal species with the *t*-butoxy groups axial **74** (equation 70). The phosphacyclopolsilanes  $(\text{Me}_2\text{Si})_n\text{PMe}$  ( $n=5, 6$ ) also give radicals with *t*-BuO $\cdot$ , these having much smaller coupling constants than either **73** or **74**<sup>89</sup>.

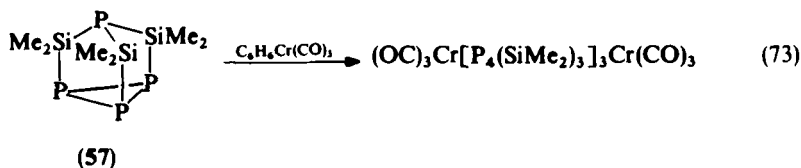
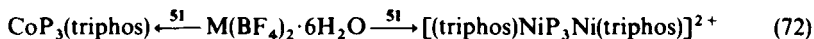


## IX. TRANSITION METAL DERIVATIVES

Prior to 1970, few complexes of silylphosphines had been prepared<sup>2d</sup>. However, the ensuing decade saw the isolation of many low-oxidation-state transition metal complexes in which, for example,  $(\text{Me}_3\text{Si})_n\text{P}(\text{Bu-t})_{3-n}$  functions as a monodentate ligand,  $(\text{PhPSiMe}_2\text{SiMe}_2)_2$  bidentate and  $(\text{PhPSiPh}_2)_3$  tridentate to a single metal, while  $\text{MeSi}(\text{PBu}_2)_3$  acts as a tridentate ligand to an  $\text{M}_3$  triangle of  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{M}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$  (equation 71)<sup>3b, 90</sup>.

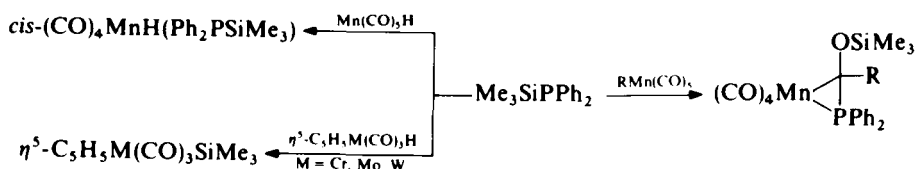


The cage phosphines tris(trimethylsilyl)heptaphosphanortricyclene  $(\text{Me}_3\text{Si})_3\text{P}_7$  (**51**) and hexamethyltrisilatetraphosphanortricyclene  $(\text{Me}_2\text{Si})_3\text{P}_4$  (**57**) readily react with transition metal residues, the former giving metal- $\text{P}_3$  complexes with  $\text{M}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Co}, \text{Ni}$ ) in the presence of triphos,  $(\text{Ph}_2\text{P})_3\text{CCH}_3$  (equation 72), while the latter acts as a bidentate ligand bridging two  $\text{Cr}(\text{CO})_3$  residues thrice on reaction with benzene chromium tricarbonyl (equation 73)<sup>91</sup>.



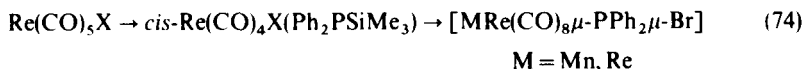
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$\text{Me}_3\text{SiPPh}_2$  assists in the insertion of CO into the Mn-R bond or  $\text{RMn}(\text{CO})_5$  (R = alkyl or aryl) followed by silyl migration to oxygen. With  $\text{Mn}(\text{CO})_5\text{H}$ , however, only *cis*-substitution by the phosphine occurs, while with the cyclopentadienyl metal tricarbonyl hydrides, silylation occurs at the metal (Scheme 23)<sup>92</sup>.

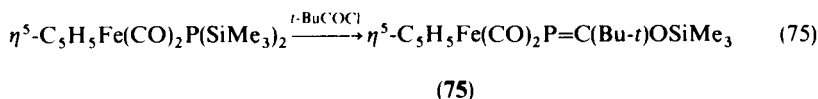


SCHEME 23

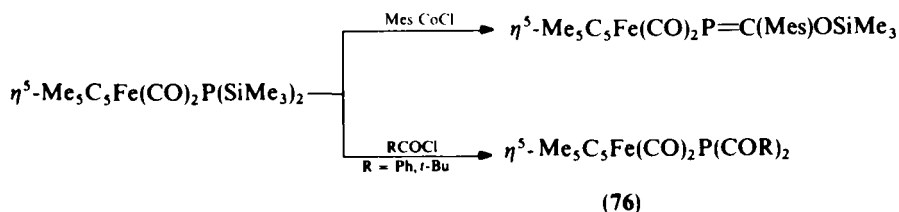
With rhenium carbonyl halides, however, the phosphine gives monosubstitution, with excess carbonyl bromide then eliminating halosilane to give the mixed bridged complex (equation 74)<sup>93</sup>.



The silylphosphide  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{P}(\text{SiMe}_3)_2$  results from the carbonyl halide and  $(\text{Me}_3\text{Si})_2\text{PLi}$ . It readily reacts with both  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}_2(\text{CO})_9$  to give phosphide-bridged derivatives, and with pivaloyl chloride forms the phosphaaalkenyl derivative **75**, with a P=C bond (170.1 pm) in the range found for phosphaaalkenes (equation 75)<sup>94</sup>. With

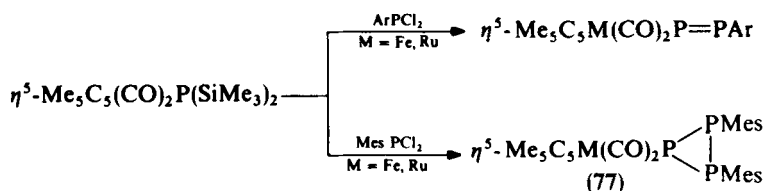


$\eta^5\text{-Me}_5\text{C}_5\text{Fe}(\text{CO})_2\text{P}(\text{SiMe}_3)_2$ , a similar product results using mesitoyl chloride, but both benzoyl and pivaloyl chlorides displace both silyl groups to give the bis-acyl (-aroyl) derivatives **76** (Scheme 24)<sup>95</sup>, a reaction also observed for ruthenium and osmium<sup>96</sup>. With



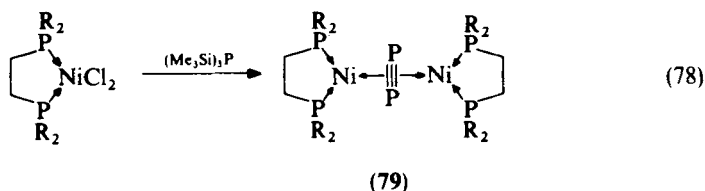
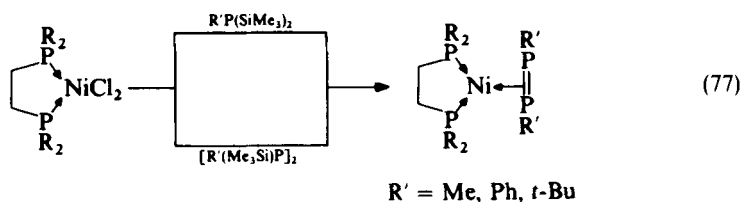
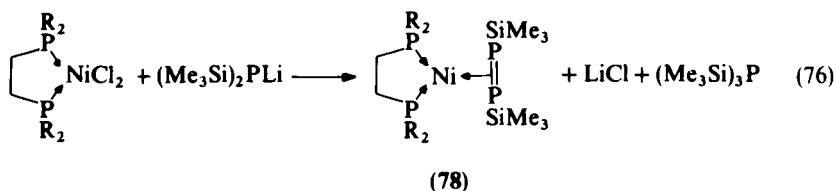
SCHEME 24

$\eta^5\text{-Me}_5\text{C}_5\text{M}(\text{CO})_2\text{P}(\text{SiMe}_3)_2$  (M = Fe, Ru) and 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>(ArPCL<sub>2</sub>), the first  $\sigma$ -bonded phosphanyl complexes are formed through loss of chlorosilane<sup>97</sup>. The manganese diphosphenyl complex  $\eta^5\text{-Me}_5\text{C}_5(\text{CO})(\text{NO})\text{MnP}=\text{PC}_6\text{H}_2(\text{Bu}-t)_3\text{-2,4,6}$  results similarly. The less hindered  $\text{mesPCL}_2$  gives the cyclotriphosphido derivative **77**, along with the cyclotetraphosphanes  $[\eta^5\text{-Me}_5\text{C}_5(\text{CO})_2\text{M}]_2\text{P}_4\text{Mes}_2$  as a mixture of isomers (Scheme 25)<sup>98</sup>.



SCHEME 25

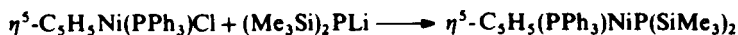
The  $\sigma$ -bonded diphosphene complex **78** results from the reaction of  $(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)\text{NiCl}_2$  and  $(\text{Me}_3\text{Si})_2\text{PLi}$  through oxidative coupling and loss of  $(\text{Me}_3\text{Si})_3\text{P}$  (equation 76). Consequently the method can be expanded to include silyl phosphines  $\text{R}'\text{P}(\text{SiMe}_3)_2$  and diphosphines  $[\text{R}'(\text{Me}_3\text{Si})\text{P}]_2$  (equation 77), while with  $(\text{Me}_3\text{Si})_3\text{P}$  alone the diphosphine derivative **79** results (equation 78)<sup>99</sup>.  $\eta^5\text{-C}_5\text{H}_5\text{Ni}(\text{PPh}_3)\text{P}(\text{SiMe}_3)_2$  (**81**) represents the first terminal phosphide nickel complex to



be made. It results from **80** and with  $\text{Ni}(\text{CO})_4$  and methanol yields the bridged phosphide **82**, which can also be generated from **80** and  $\text{Me}_3\text{SiPH}_2$  (Scheme 26). Such derivatives **84** also result from the bisphosphide **83** along with the diphosphene complex **85**, which has a P-P bond shorter than single bond length (214.9 pm) (equation 79)<sup>100</sup>.

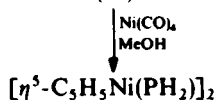
Condensing [2,3-bis(diphenylphosphino)*N*-methylmaleimide] nickel dichloride **86** with  $\text{PhE}(\text{SiMe}_3)_2$  ( $\text{E} = \text{P, As}$ ) gives the complexed diphosphene or diarsine **87** through oxidative coupling and silyl migration. Both P-P and As-As bonds are shorter than expected for single bonds (equation 80)<sup>101</sup>.

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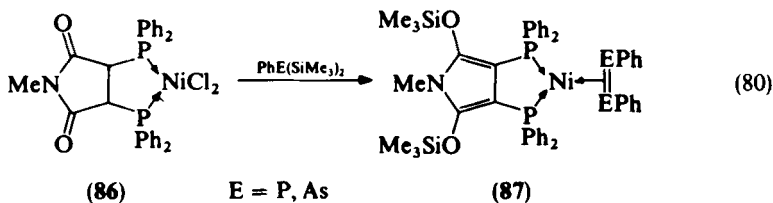
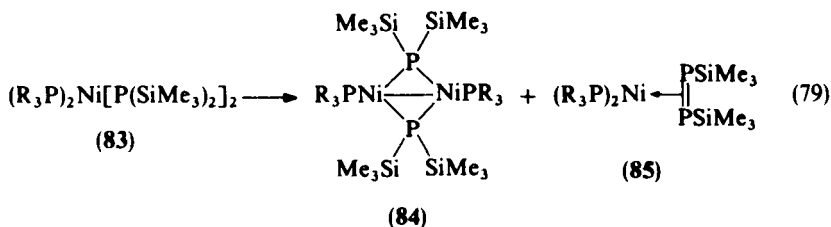
(80)

(81)

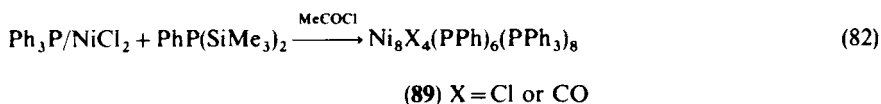
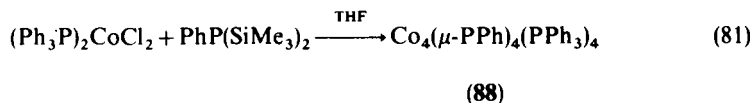


(82)

SCHEME 26



However, reacting  $(\text{Ph}_3\text{P})_2\text{CoCl}_2$  with  $(\text{Me}_3\text{Si})_2\text{PPh}$  gives the  $\text{Co}_4$  complex **88** with a tetrahedron of cobalt atoms, which can be oxidized in acetyl chloride to its monocation (equation 81). Adding  $(\text{Me}_3\text{Si})_2\text{PPh}$  to a solution of  $\text{NiCl}_2$  and  $\text{Ph}_3\text{P}$ , followed by addition of acetyl chloride gives remarkably, a mixture of the two complexes **89** ( $\text{X} = \text{Cl}$  or  $\text{CO}$ ), both of which possess a cube of nickel atoms (equation 82)<sup>102</sup>. An extensive range of sulphides and selenides result similarly (see the chapter on Si/S compounds).

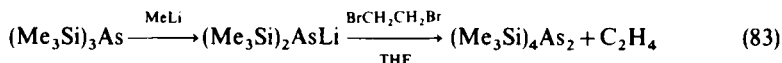


X. SILYL ARSINES

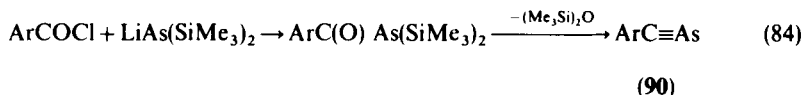
Silyl arsines are normally made from alkali metal arsenides and the chlorosilane. However the first ones to be prepared,  $(\text{Ph}_3\text{Si})_2\text{AsMe}$ ,  $\text{Ph}_3\text{SiAsMe}_2$  and  $\text{Ph}_3\text{SiAsEt}_2$ , were obtained from the coupling of triphenylsilyl lithium and the bromoarsine<sup>103</sup>. They are

readily oxidized and hydrolyzed, substitute  $\text{BF}_3$  to give the bis(arsino)fluoroborane and are oxidized to the diarsine by  $\text{PF}_5$ . Carbon disulphide, fluoro-substituted propan-2-one and dimethyl acetylene dicarboxylate all give adducts with arsinosilanes, while bis and tris(arsino)silanes form 1:1 adducts with metal carbonyl residues<sup>2d</sup>. With gallium trichloride, the arsinosilanes  $\text{R}_2\text{AsSiMe}_3$  ( $\text{R} = \text{Me}_3\text{SiCH}_2$ , mesityl) mono and disubstitute to give the associated arsinochlorogallane as a dimer or trimer, while trisubstitution yields  $(\text{R}_2\text{As})_3\text{Ga}$  ( $\text{R} = \text{mesityl}$ ), which is monomeric<sup>104</sup>.

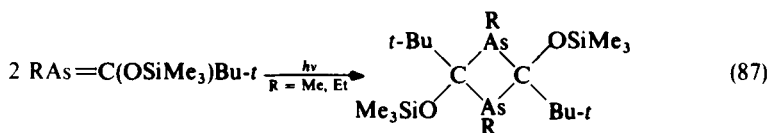
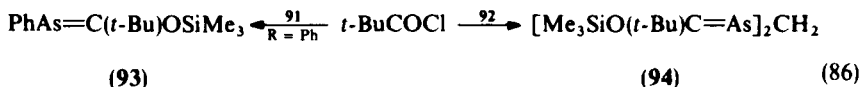
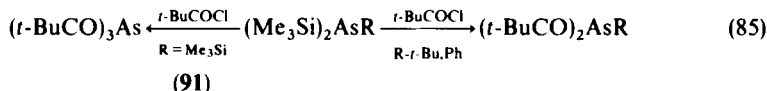
Tris(trimethylsilyl)arsine  $(\text{Me}_3\text{Si})_3\text{As}$  is formed in good yield from  $\text{Na}_3\text{As}$  in DME, or by reductively coupling arsenic trichloride using magnesium in HMPT. It reacts with  $\text{Me}_3\text{MCl}$  ( $\text{M} = \text{Ge}, \text{Sn}$ ) to give the trisgermyl or stannyl arsine which, like the silylarsine, readily forms 1:1 complexes with metal hexacarbonyls<sup>105</sup>. Methyl lithium cleaves the Si-As bond of  $(\text{Me}_3\text{Si})_3\text{As}$  to give the bis-silyl arsenide which crystallizes from DME as a 1:1 coordinated dimer, and has Si-As bonds of 230.7 pm. It is oxidized in THF by 1,2-dibromoethane to the pale yellow tetrasilyldiarsine with longer Si-As bonds (236 pm), and an As-As distance of 245.8 pm, much shorter than the intermolecular As---As distance of 662 pm (equation 83)<sup>106</sup>. This contrasts sharply with the analogous antimony and bismuth compounds.



The first arsaethyne results from the reaction of  $(\text{Me}_3\text{Si})_2\text{AsLi}$  with 2,4,6-*t*-Bu) $_3\text{C}_6\text{H}_2\text{COCl}$  ( $\text{ArCOCl}$ ). The intermediate aroyl derivative decomposes through loss of siloxane to give the arsaethyne **90** as a pale yellow crystalline solid (equation 84)<sup>107</sup>.



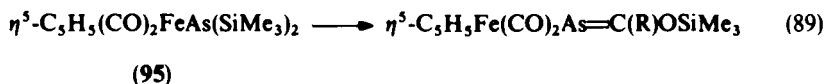
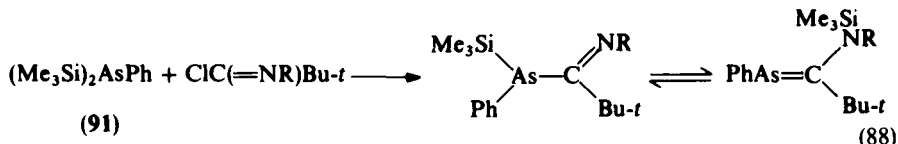
The reaction of excess pivaloyl chloride in polar solvents with the silyl arsines  $(\text{Me}_3\text{Si})_2\text{AsR}$  ( $\text{R} = \text{Ph}, t\text{-Bu}, \text{Me}_3\text{Si}$ ) (**91**) provides a route to bis- and trisacyl arsines (equation 85). However, the reaction of a deficiency of pivaloyl chloride in cyclopentane with **91** ( $\text{R} = \text{Ph}, t\text{-Bu}$ ) or the bis(arsino)methane  $[(\text{Me}_3\text{Si})_2\text{As}]_2\text{CH}_2$  (**92**) gives the substituted arsaethenes **93** and **94** through silyl migration (equation 86)<sup>108</sup>. With less



hindered substituents on arsenic, dimerization occurs on irradiation to give the 1,3-diarsetane (equation 87). *t*-Butyl substituted imidoyl chlorides react with **91** ( $\text{R} = \text{Ph}$ ) in a similar manner, the iminosilylarsines rearranging to an equilibrium mixture

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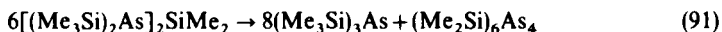
with the *N*-silylated arsaethene (equation 88). From the silylarsenido-iron complex **95**, the  $\sigma$ -bonded arsaethene derivative results which shows an As-C bond length of 182.1 pm, distinctly shorter than that in arsabenzenes or the As-C single bond (196 pm) (equation 89)<sup>109</sup>.



Unlike cyclic silicon-phosphorus compounds, which occur as dimers and/or trimers, the cyclic silicon-arsenic ring of  $(\text{Me}_2\text{SiAsMe})_4$  is eight-membered. It results from  $\text{MeAsHLi}$  and  $\text{Me}_2\text{SiCl}_2$  along with polymer, and occurs in solution as a mixture of conformers (equation 90)<sup>110</sup>.

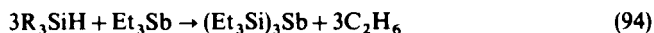
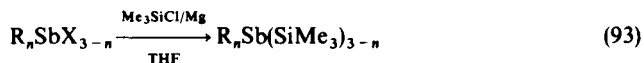
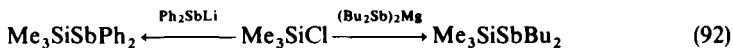


The cage compounds  $(\text{Me}_3\text{Si})_3\text{As}_7$  (made from  $\text{Rb}_3\text{As}_7$ ) and  $(\text{Me}_2\text{Si})_6\text{As}_4$  show As-Si bonds of 239.7<sup>65</sup> and 235.1 pm, respectively, the latter compound resulting from the decomposition of  $[(\text{Me}_3\text{Si})_2\text{As}]_2\text{SiMe}_2$  on heating<sup>105a</sup>. It possesses the adamantane-like structure with chair six-membered rings (equation 91)<sup>111</sup>. Similar lability is a feature of the chemistry of Si-P compounds (Scheme 20).



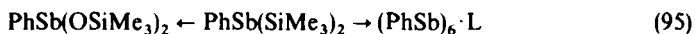
## XI. SILYL STIBINES AND SILYL BISMUTHINES<sup>2d</sup>

Silyl stibines are conveniently made from the metal stibide and chlorosilane, and by reductively coupling organohalostibines with chlorosilanes using magnesium (equations 92 and 93)<sup>112</sup>. Trisilylstibines can also be made from triethylstibine and a triorganosilane (equation 94)<sup>113</sup>. While oxygen and moisture sensitive, these stibines are generally very stable thermally, though  $(\text{Me}_3\text{Si})_3\text{Sb}$  decomposes above 50 °C.

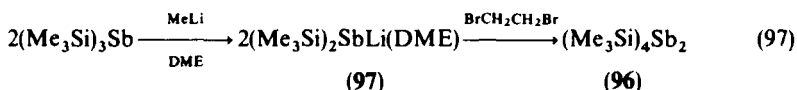
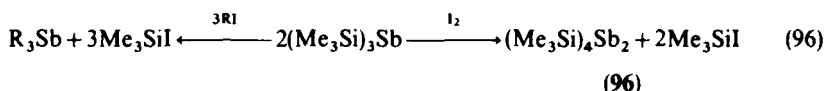


Slowly oxidizing  $(\text{Me}_3\text{Si})_2\text{SbPh}$  in dioxan gives the cyclohexastibine  $(\text{PhSb})_6$ , a rather surprising reaction, since metalloid-metalloid bonds are usually formed on reduction and not oxidation. Excess oxygen yields antimony(III) derivatives, whether mono, di or trisilylated, but no antimony(V) derivatives were characterized (equation 95)<sup>114</sup>. The trisilylstibine  $(\text{Me}_3\text{Si})_3\text{Sb}$  readily coordinates to metal carbonyl residues<sup>115</sup>, and is oxidized by iodine or *t*-butyl iodide to the tetrasilyldistibine **96**, though excess iodide gives the trialkyl stibine and stibonium salt and excess iodine, antimony metal (equation 96)<sup>116</sup>. The tetrasilyldistibine **96** also results when  $(\text{Me}_3\text{Si})_2\text{SbLi}$  (**97**) is oxidized by 1,2-

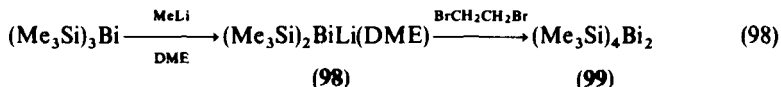
dibromoethane (equation 97). Unlike its arsenic analogue, which is dimeric in solid and in solution, the antimonide (stibide) **97** possesses an infinite chain structure of antimony atoms bridged by coordinated lithium atoms, with the Si-Sb bond 253.2 pm<sup>117</sup>. While the distibine **96** is yellow in solution or when molten, like the arsenic analogue, it is a deep-red solid with Si-Sb distances of 259.4 pm. The Sb-Sb bonds are 286.7 pm long and, more significantly, show a short intermolecular interaction distance of 399 pm, much shorter than that in the diarsine<sup>118</sup>.



L = dioxan, C<sub>6</sub>H<sub>6</sub>, PhMe



Trisilylbismuthines are the only Si-Bi compounds to have been prepared to date, and result both from the coupling of Na/K/Bi with chlorosilanes<sup>119</sup>, and from Et<sub>3</sub>Bi and Et<sub>3</sub>SiH<sup>113</sup>. Like Si-Sb compounds, they react with Me<sub>3</sub>SnCl to give the stannyl bismuthine, and are cleaved by MeLi at the Si-Bi bond. The bismuthide **98** so formed, like the antimonide, can be oxidized by 1,2-dibromoethane to give the thermochromic lustrous green dibismuthine **99** (equation 98)<sup>119</sup>.



The bismuthide **98** has a chain structure like the antimonide, with alternating bismuth and coordinated lithium atoms. The Si-Bi bond length of 263.3 pm is shorter than that in the dibismuthine **99** (Si-Bi 268 pm), where the centrosymmetric molecules, with Bi-Bi bonds of 303.5 pm, fit into a zig-zag chain with intermolecular Bi-Bi interactions of 380.4 pm<sup>120</sup>. The thermochromism has been explained for 2,2',5,5'-tetramethylbistibole [transition from Sb-Sb σ-band (HOMO) to the diene π\* (LUMO)] and the tetrakis(methylene)bistibolane and bibismolane<sup>121</sup>. The Raman spectrum of (Me<sub>3</sub>Si)<sub>4</sub>Sb<sub>2</sub> gives a strong band at 47 cm<sup>-1</sup> assigned to the longitudinal acoustic mode of the infinite antimony chain. This band is absent in the liquid, while no band equivalent to this for the diarsine is present, even as a solid<sup>122</sup>.

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## CHAPTER 6

# Appendix to 'Organosilicon derivatives of phosphorus, arsenic, antimony and bismuth'<sup>†</sup>

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### \*I. INTRODUCTION

This appendix follows exactly the layout of the main chapter and, where appropriate, refers to data included in it. The only recent review includes the use of the silyl phosphine  $(\text{Me}_3\text{Si})_2\text{PPh}$  and the silyl arsine  $(\text{Me}_3\text{Si})_2\text{AsPh}$  in the synthesis of transition metal-phosphorus and transition metal-arsenic clusters<sup>1,2,3</sup>.

<sup>†</sup>The material in this Appendix is divided in the same manner as in the original chapter (reprinted as Chapter 5 in the present volume). Section numbers in the Appendix are preceded by an asterisk. The numbers of structures, schemes, equations and references run continuously in Chapter 5 and this Appendix.

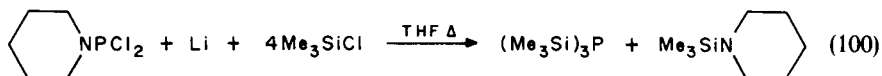
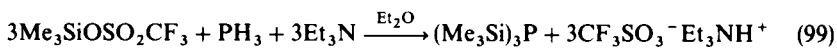
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The Silicon-Heteroatom Bond

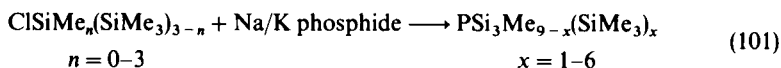
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## \*II. SILYL-SUBSTITUTED MONOPHOSPHINES

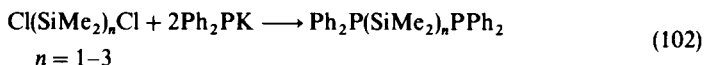
Tris(trimethylsilyl)phosphine ( $\text{Me}_3\text{Si}$ )<sub>3</sub>P forms in high yield when  $\text{PH}_3$  is silylated using trimethylsilyl triflate and  $\text{Et}_3\text{N}$  in  $\text{Et}_2\text{O}$ . The silylphosphines ( $\text{Me}_3\text{Si}$ )<sub>2</sub>PR and  $\text{Me}_3\text{SiPHR}$  ( $\text{R} = \text{Ph}, t\text{-Bu}$ ) result similarly (equation 99)<sup>124</sup>. ( $\text{Me}_3\text{Si}$ )<sub>3</sub>P also results from the reductive silylation of piperidinodichlorophosphine (equation 100)<sup>125</sup>.



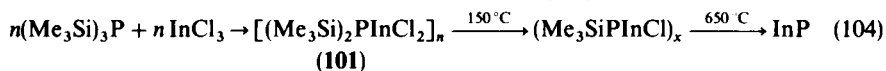
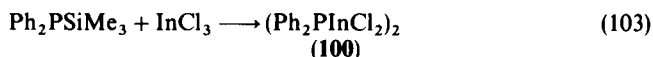
Na/K phosphide gives a mixture of polysilyl trisilylphosphines with polysilyl chloro(methyl)silanes or mixtures of methylchlorosilanes (equation 101). They can be readily separated to give  $\text{PSi}_3\text{Me}_{9-x}(\text{SiMe}_3)_x$  ( $x = 1-6$ ), and their <sup>31</sup>P and <sup>29</sup>Si NMR spectra and vibrational spectra were compared<sup>126</sup>.



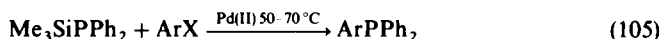
A series of diphenylphosphinopolysilanes has been prepared from  $\text{Ph}_2\text{PK}$  and the chlorosilanes  $\text{Cl}(\text{SiMe}_2)_n\text{Cl}$  ( $n = 1, 2, 3$ ) and  $\text{MeSi}(\text{SiMe}_2\text{Cl})_3$  (equation 102). All show Si—P stretching frequencies in the range 525–612  $\text{cm}^{-1}$ , and <sup>31</sup>P NMR absorptions at about –52 to –57 ppm<sup>127</sup>.



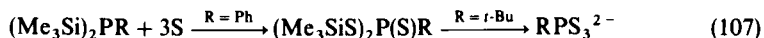
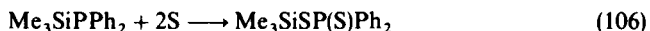
Condensing dimethylindium chloride with diphenylphosphinotrimethylsilane gives the dimeric indium phosphide **100** in good yield (equation 103). This route can also be used to prepare indium phosphide, which is used as a semi-conductor. It results from the room-temperature addition of ( $\text{Me}_3\text{Si}$ )<sub>3</sub>P to  $\text{InCl}_3$ . The orange polymeric monosubstitution product **101** so formed decomposes at 150 °C to give the dark brown disubstituted derivative which, at 650 °C, forms black indium phosphide (equation 104)<sup>128</sup>.

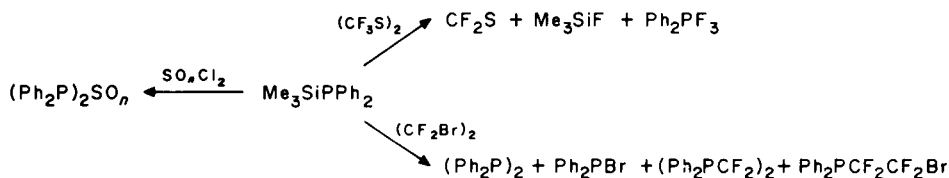


Pd(II) salts catalyse the cleavage of diphenylphosphinotrimethylsilane by aryl iodides and bromides, to give the aryldiphenyl phosphine. Yields are excellent and appear to be independent of the electronic properties of other ring substituents (equation 105)<sup>129</sup>.



Silylphosphines react with elemental sulphur to give the thiophosphinate and phosphonate P(V) oxidation products, the latter also resulting from  $t\text{-BuPS}_3^{2-}$  with  $\text{Me}_3\text{SiCl}$  (equations 106 and 107). Sulphur halides cleave the Si—P bond as do organic halides (Scheme 27)<sup>130</sup>.

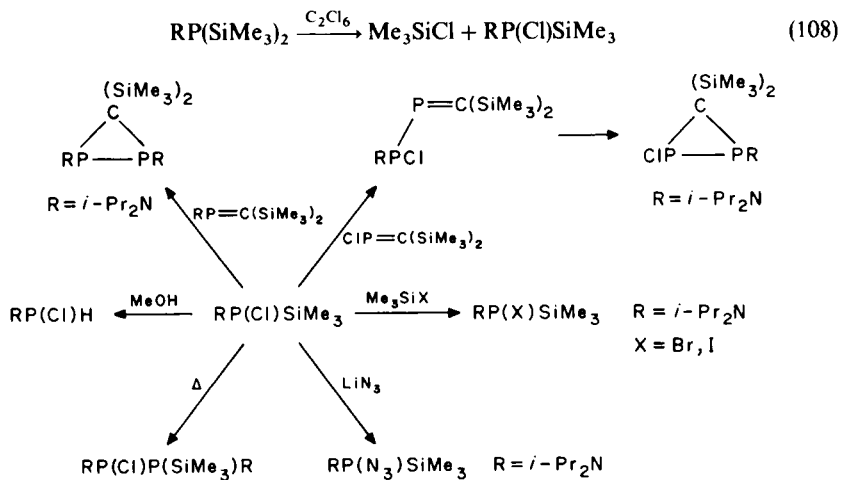




SCHEME 27

The hindered phosphine 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>P(SiMe<sub>3</sub>)<sub>2</sub>, 'Supermesityl P(SiMe<sub>3</sub>)<sub>2</sub>' = Sms P(SiMe<sub>3</sub>)<sub>2</sub>, m.p. 76–78 °C, has a structure showing flattening at phosphorus, while the two Si—P bonds (223.8 pm and 225.5 pm) are not shortened and the two CPSi angles differ considerably (102° and 127°). Steric constraints appear to be the main cause of these distortions<sup>131</sup>.

Bis(trimethylsilyl)phosphines react with hexachloroethane to give the chloro(trimethylsilyl)phosphines (equation 108). These normally decompose to cyclophosphanes well below room temperature, but hindered substituents such as Cp\*(Me<sub>5</sub>C<sub>5</sub>) and (Me<sub>3</sub>Si)<sub>2</sub>CH give distillable products. All can be desilylated with MeOH without substitution at chlorine, give 1-chlorodiphosphiranes with chloromethylenephosphane through the diphosphapropene intermediate and with phosphalkenes yield a wide range of diphosphiranes (Scheme 28)<sup>132</sup>.

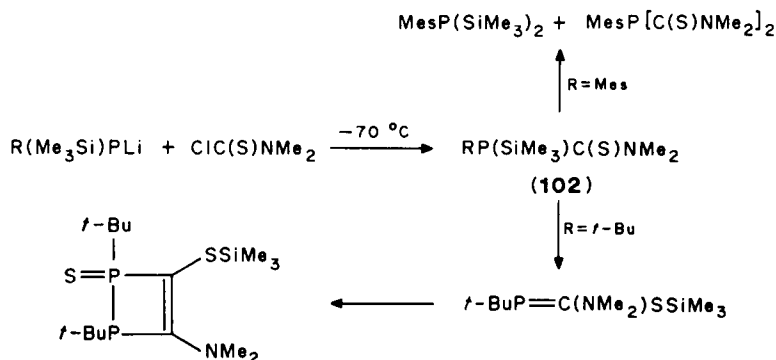


SCHEME 28

Treating  $\text{RSiCl}_3$  ( $\text{R} = \text{Me, Et, } i\text{-Pr, Ph}$ ) with  $\text{LiAl}(\text{PH}_2)_4$  in the ratio 4:3 gives the tris(phosphino)silanes as thermally stable liquids (equation 109)<sup>133</sup>.

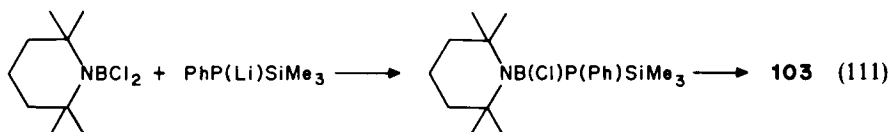
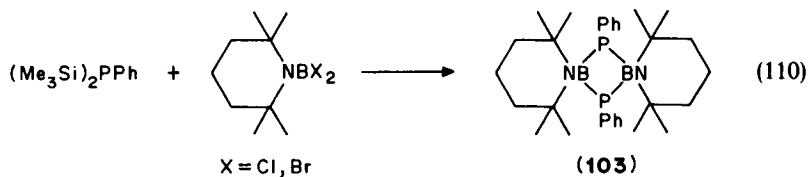


Condensing  $\text{R}(\text{Me}_3\text{Si})\text{PLi}$  with *N,N*-dimethylthiocarbamoyl chloride at  $-78$  °C gives **102** which disproportionates if  $\text{R} = \text{mesityl (Mes)}$  but rearranges through silyl migration if  $\text{R} = t\text{-Bu}$ , then dimerises head to head with aminosilane loss and sulphur migration to give the diphosphacyclobutene almost quantitatively (Scheme 29)<sup>134</sup>.

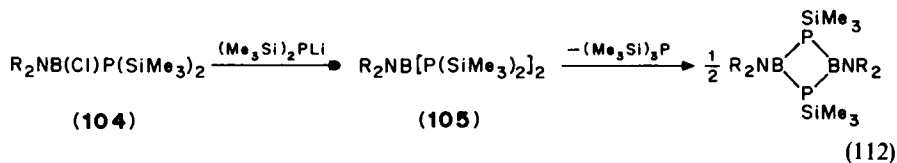


SCHEME 29

Condensing bissilylphosphines with the piperidinodihaloborane gives the four-membered boron-phosphorus ring **103** (equation 110), which also can be prepared from the lithium silylphosphide through first LiX then  $\text{Me}_3\text{SiCl}$  elimination (equation 111)<sup>135</sup>.



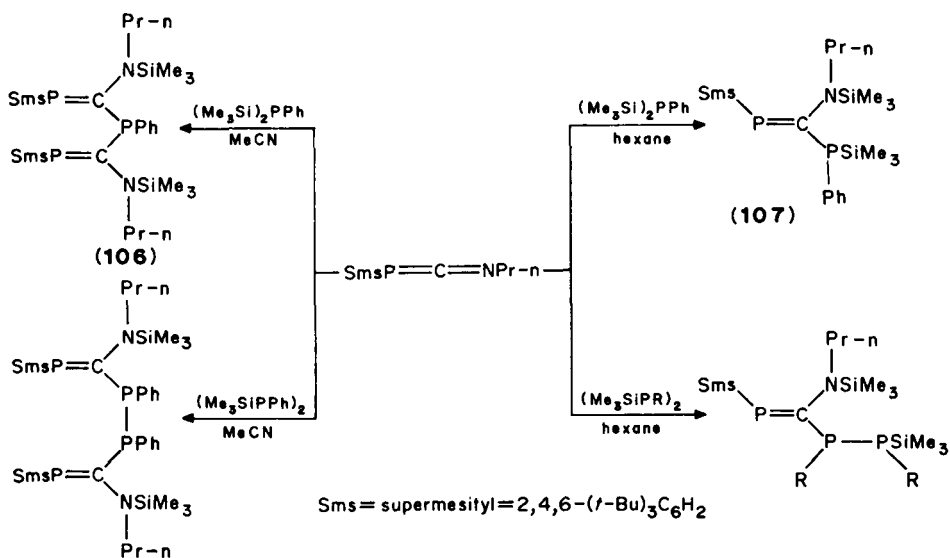
This B—P ring system also results from the disproportionation of the aminobis(phosphino)borane **105**, prepared from the chloroborane **104** as indicated (equation 112), while **104** with  $i\text{-Pr}_2\text{NBCl}_2$  in the ratio 2:1 give  $\text{P}_2(\text{BNPr-}i_2)_3$  with a trigonal bipyramidal  $\text{P}_2\text{B}_3$  structure (equation 113)<sup>136</sup>.



R =  $i\text{-Pr}$

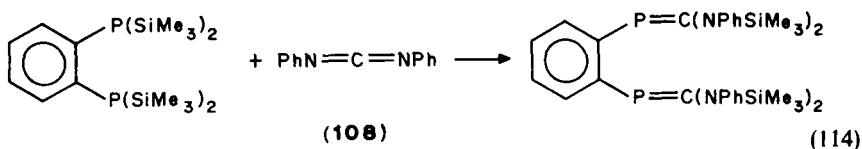
## \*III. PHOSPHORUS-SUBSTITUTED HETEROCUMULENES

The bis(silyl)phosphine  $(\text{Me}_3\text{Si})_2\text{PPh}$  adds to the mono-P-substituted carbodiimide  $\text{SmsP}=\text{C}=\text{NPr-n}$  to give the 1,3,5-triphospha-1,4-pentadiene **106**. In non-polar solvents with mono-, di- and trisilylphosphines, 2-amino-1,3-diphosphapropenes **107** result. With diphosphanes, the 1,3,4-triphospha-1-butenes result if the solvent is non-polar, but in acetonitrile the less hindered phenyl-substituted diphosphane produces a new 1,3,5,6-tetraphospha-1,5-hexadiene with no tendency to undergo a Cope rearrangement [unlike the less hindered system described in the main chapter (Scheme 13)] (Scheme 30)<sup>137</sup>.



SCHEME 30

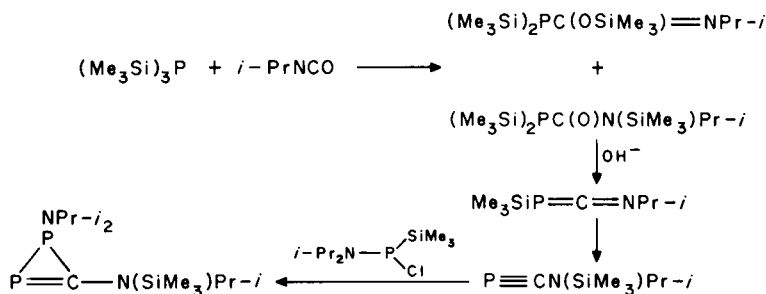
The silylated bis-*o*-phenylenediphosphine with carbodiimide **108** gives the phosphaguanidino derivative through a double silyl migration from P to N (equation 114)<sup>138</sup>.



Tris(trimethylsilyl)phosphine adds to *i*-PrNCO and, through rearrangements and silyl migrations, the monophosphorus-substituted carbodiimide results and then rearranges to the phosphalkyne, which can be distilled, b.p. 40°C/1.5 mm<sup>139</sup>. This amino-substituted phosphalkyne adds the fragments *i*-Pr<sub>2</sub>N—P, generated from the chloro(silyl)phosphane, to give the 1*H*-diphosphirene with a structure suggesting a 4-electron 3-centre bond through P—C—N (Scheme 31)<sup>140</sup>.

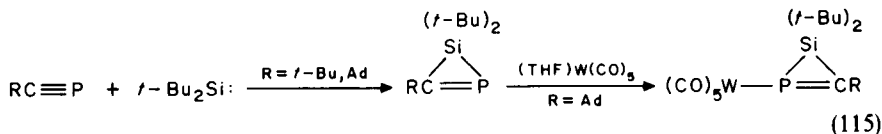
Phosphaalkynes also add silylenes, giving phosphasilirenes which remain monomeric and complex with metal carbonyl residues. The analogous azasiliranes dimerise due



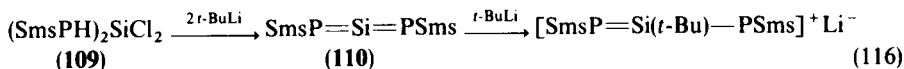


SCHEME 31

to excessive ring strain. This is not as great in the P-substituted silirene system (equation 115)<sup>141</sup>.



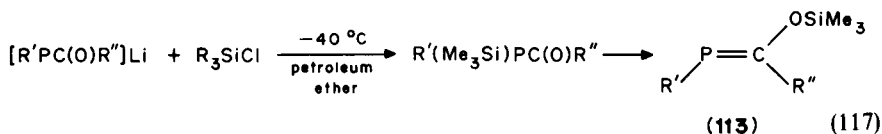
Attempts to prepare the silicon-phosphorus analogue of carbodiimides have been partially successful. The elimination of two moles of HCl from the bis(phosphino)dichlorosilane **109** using *t*-BuLi leads to the isolation of the adduct of *t*-BuLi with **110**. The 1,3-diphospha-2-silaallyl anion so formed has been characterized by <sup>31</sup>P and <sup>29</sup>Si NMR spectroscopy (equation 116)<sup>142</sup> (see also Scheme 53<sup>174</sup>).

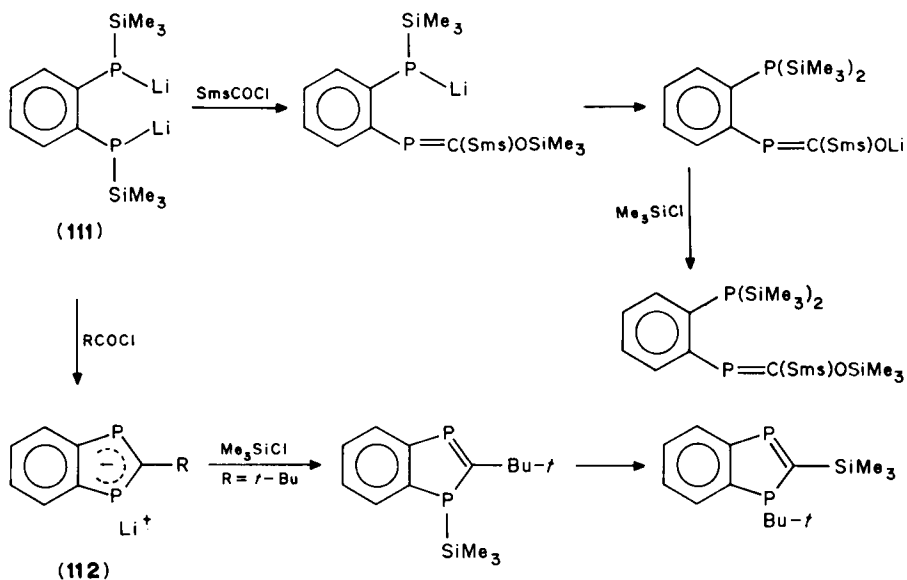


#### IV. REACTIONS OF ACYL AND AROYL CHLORIDES WITH THE SILICON-PHOSPHORUS BOND

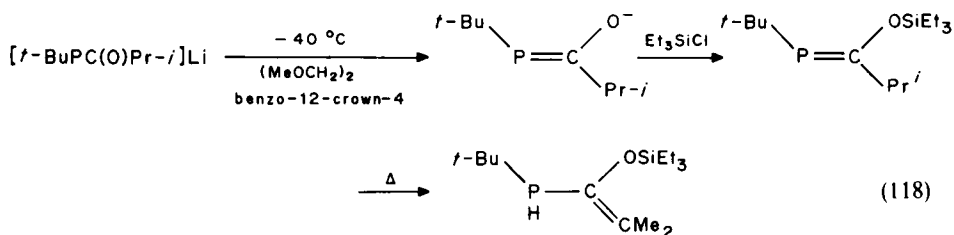
Condensing acyl chlorides with the *o*-bisphosphidobenzene **111** gives the 1,3-dibenzophosphole anions **112**, which react with Me<sub>3</sub>SiCl to substitute at phosphorus initially, rearrangement yielding the 1-Bu-*t*, 2-trimethylsilyl isomer, while **112** gives an η<sup>5</sup>-complex with Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub> and an η<sup>1</sup>-complex with (THF)W(CO)<sub>5</sub>. SmsCOCl gives the expected phospho-alkene (Scheme 32)<sup>143</sup>.

The kinetically controlled interaction of (R'PCOR'')Li with R<sub>3</sub>SiCl (R=Me,Et) in non-solvating media gives P-silylated acylphosphines which rearrange to O-substituted *E* isomers **113** (equation 117). The O-substituted *Z* isomers result directly in solvating media, due to delithiation of the O<sup>-</sup> in solvating media, thereby giving the more stable *trans* anion. Phospho-alkenes can be vacuum distilled, but isomerize to the vinyl phosphine if R''=*i*-Pr, in contrast to the situation with nitrogen, where azomethines are more thermodynamically stable than enamines (equation 118)<sup>144</sup>.

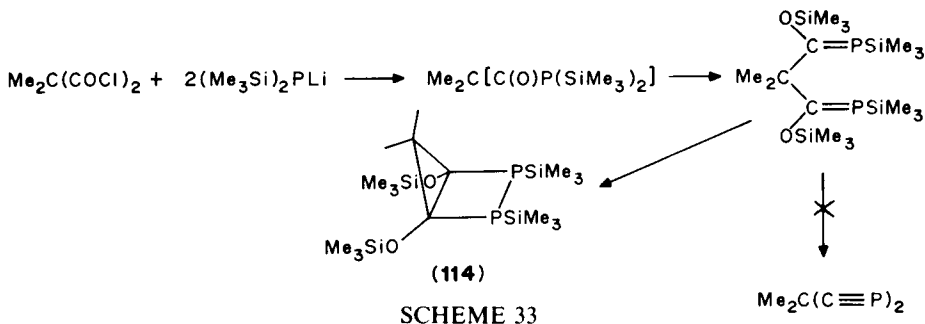




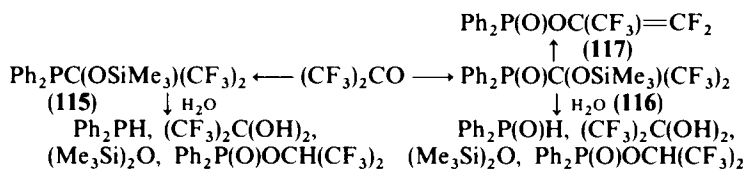
SCHEME 32



Dimethylmalonyl dichloride and the silylphosphide  $(\text{Me}_3\text{Si})_2\text{PLi}$  condense and rearrange to give the 1,5-diphosphapenta-1,4-diene which, instead of losing siloxane to give the 1,5-diphosphadiyne, undergoes an intra-molecular [2 + 2] rearrangement to give the diphosphabicyclo[2.1.0]pentane **114** (Scheme 33)<sup>145</sup>.

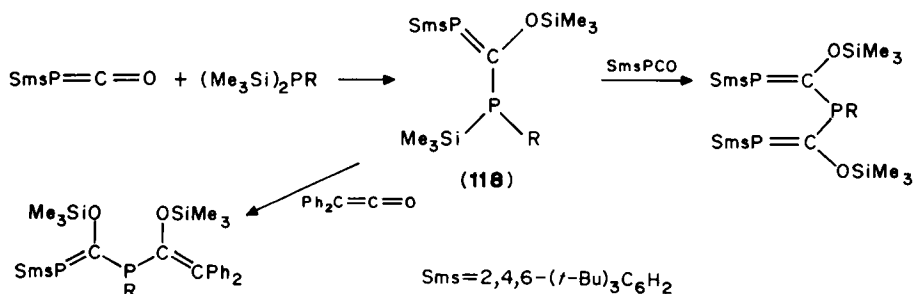


$\text{Ph}_2\text{PSiMe}_3$  and  $\text{Ph}_2\text{P(O)SiMe}_3$  add, across the  $>\text{C}=\text{O}$  bond of trifluoromethyl ketones  $\text{CF}_3\text{C(O)R}$ . The adducts **115** and **116** hydrolyse if  $\text{R} = \text{CF}_3$  to give analogous products (Scheme 34). Heating **116** eliminates  $\text{Me}_3\text{SiF}$  to give the fluoroalkene **117**<sup>146</sup>.

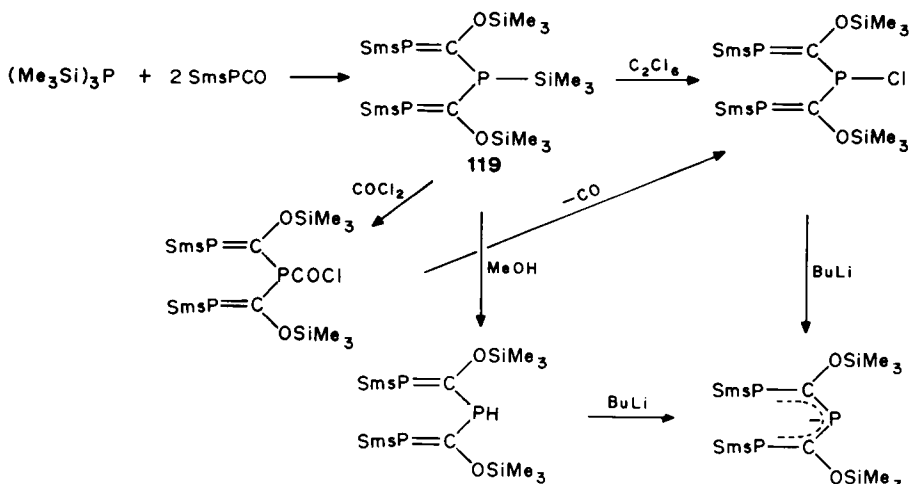


SCHEME 34

$(\text{Me}_3\text{Si})_2\text{PR}$  condenses with two moles of the phosphaketene  $\text{SmsP}=\text{C}=\text{O}$ , with addition across two  $>\text{C}=\text{O}$  bonds, to give the 1,3,5-triphospha-1,4-pentadiene through the intermediacy of P-silylated 1,3-diphosphapropenes. The 1:1 intermediate 1,3-diphosphapropenes **118** with diphenyl ketene give 1,3-diphosphapenta-1,4-diene (Scheme 35).  $(\text{Me}_3\text{Si})_3\text{P}$  similarly adds 2 moles of the phosphaketene, the adduct **119** undergoing a series of exchanges at the middle phosphorus atom (Scheme 36)<sup>147</sup>.

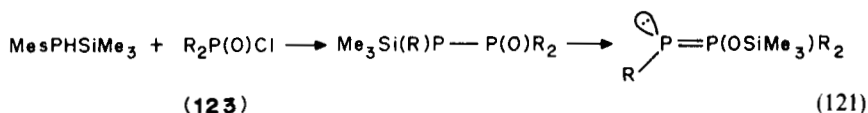
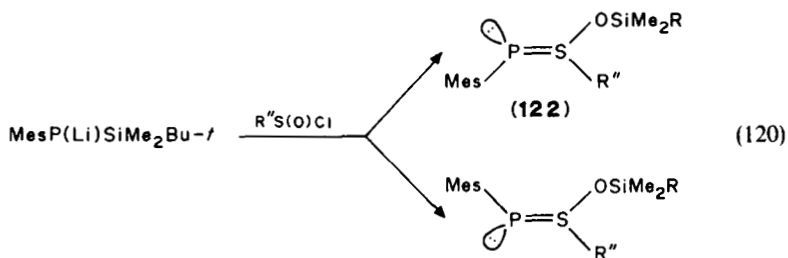
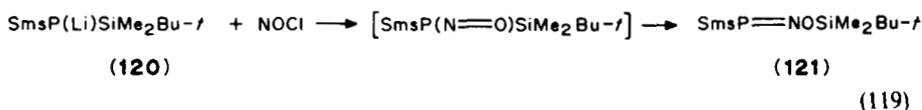


SCHEME 35

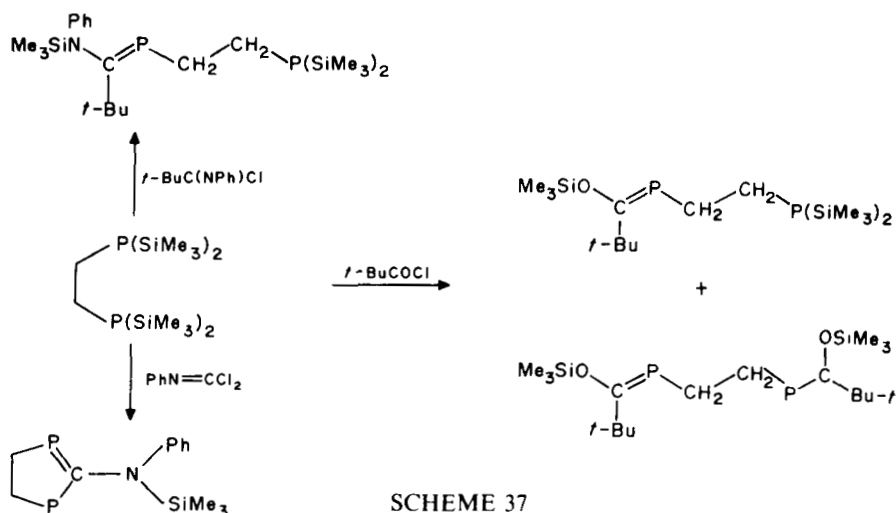


SCHEME 36

The highly hindered aryl phosphide **120** reacts with nitrosyl chloride to give the thermally stable iminophosphine **121** through silyl migration from phosphorus to oxygen (equation 119). The less hindered mesityl phosphide reacts with a range of inorganic acid chlorides of phosphorus and sulphur to give again the silyl migrated isomer, present in the case of the sulphuranylidene phosphanes **122** as a mixture of *E* and *Z* isomers (equation 120). With the phosphinyl chloride **123**, silyl migration leads to the phosphorinylidene phosphane with a double bond between P(III) and P(V) (equation 121)<sup>148</sup>.



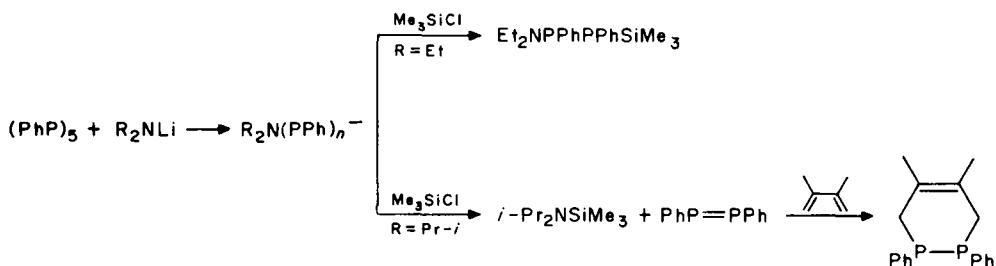
A similar range of products result from the reaction of the tetrasilyl-substituted bis-phosphinoethane with *t*-BuCOCl, *t*-BuC(=NPh)Cl and PhN=CCl<sub>2</sub> (Scheme 37)<sup>149</sup>.



## \*V. LINEAR POLYPHOSPHINES

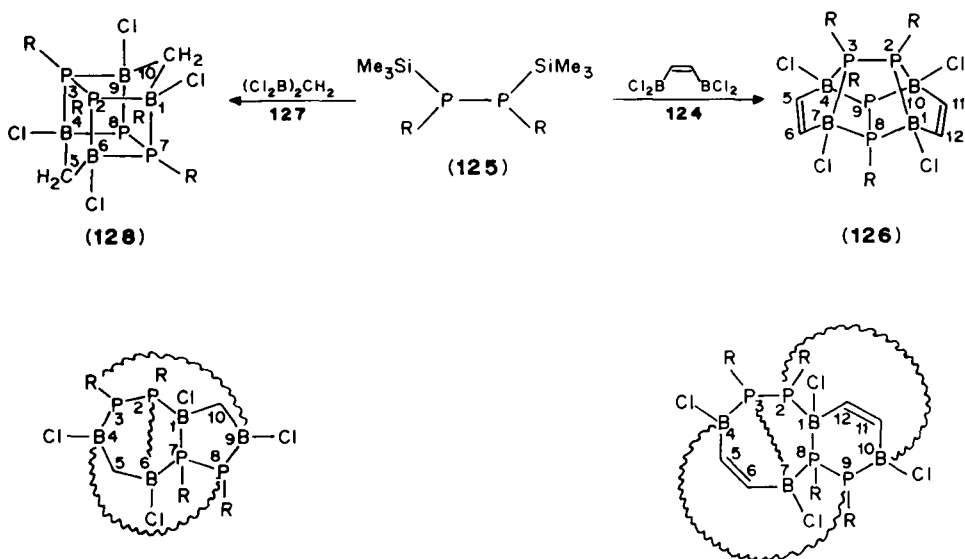
## A. Diphosphines

Pentaphenylcyclopentaphosphine is ring-opened by lithium amides in THF to give an equilibrium mixture of aminopolyphosphines  $R_2N(PPh)_n^-$  dominated by those for which  $n = 2$  and 3. With  $R = Et$ , silylating gives the silyl-substituted aminodiphosphine in 70% yield, but with  $R = i\text{-Pr}$ , deamination occurs to give the diphosphene which adds to dienes (Scheme 38)<sup>150</sup>.



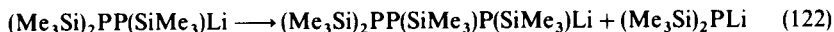
SCHEME 38

Condensing the *cis*-1,2-diborylalkene **124** with the 1,2-disilyldiphosphine **125** in equimolar ratio gives the boron–phosphorus cage derivative 2,3,8,9-*t*-Bu<sub>4</sub>-1,4,7,10-Cl<sub>4</sub>-2,3,8,9-tetraphosphonia-1,4,7,10-tetraboratapentacyclo[6.4.0.0<sup>2,10</sup>.0<sup>3,7</sup>.0<sup>4,9</sup>]dodeca-5,11-diene **126**, while the diborylmethane **127** gives 2,3,7,8-*t*-Bu<sub>4</sub>-1,4,6,9-Cl<sub>4</sub>-2,3,7,8-tetraphosphonia-1,4,6,9-tetraboratapentacyclo[5.3.0<sup>2,6</sup>.0<sup>3,9</sup>.0<sup>4,8</sup>]decane **128** which, like **126**, contains condensed five-membered heterocyclic rings (Scheme 39)<sup>151</sup>.

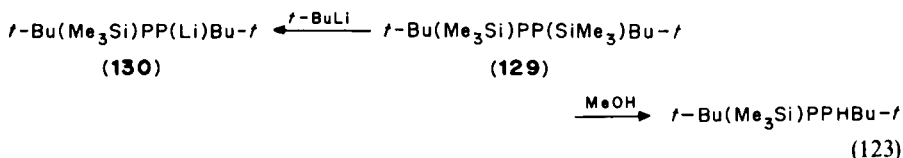


SCHEME 39

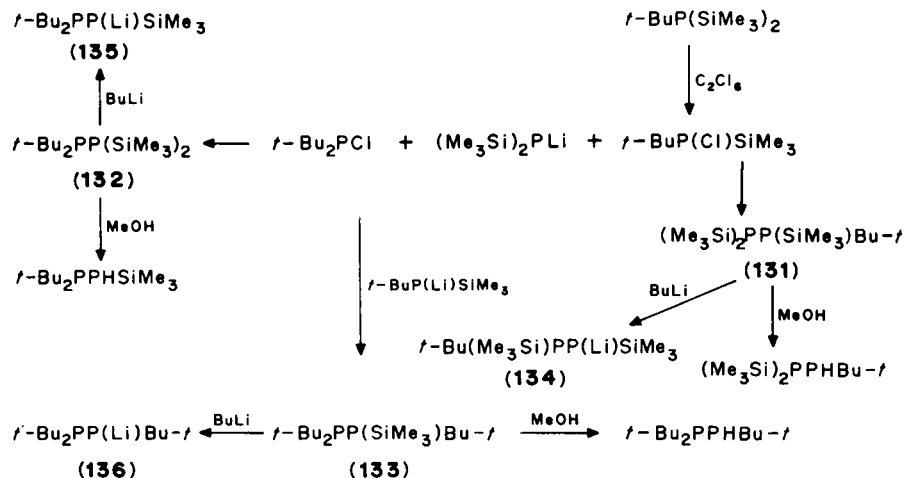
Monodesilylation of the tetrasilyldiphosphine  $(\text{Me}_3\text{Si})_4\text{P}_2$  at  $-20^\circ\text{C}$  gives  $\text{Li}(\text{Me}_3\text{Si})\text{PP}(\text{SiMe}_3)_2$ , which decomposed further to give both mono- and triphosphides. The ultimate decomposition product is  $\text{Li}_3\text{P}_7$  (equation 122)<sup>152</sup>.



The only mixed trimethylsilyl-*t*-butyldiphosphine prepared prior to this appendix was *t*-Bu( $\text{Me}_3\text{Si}$ )PP( $\text{SiMe}_3$ )Bu-*t* (**129**) (Chapter 5, equation 43), which can be desilylated with methanol, and lithiated with *t*-BuLi to give **130** (equation 123). The other mixed



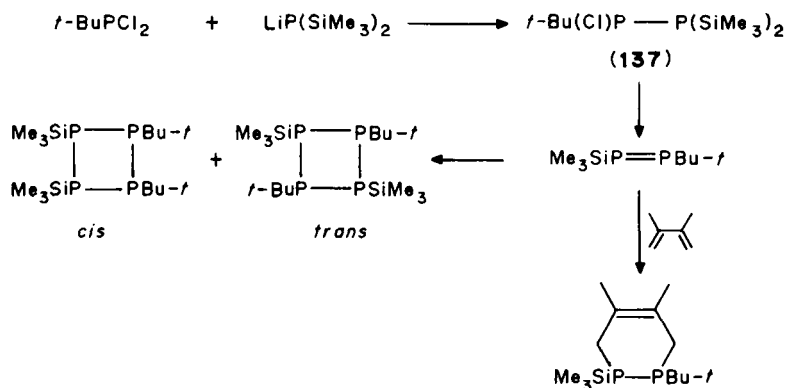
diphosphines result by the appropriate condensation reactions of chlorophosphines with lithium phosphides, to give the trisilyl-*t*-butyl diphosphine **131**, the unsymmetrical disilyldi-*t*-butyl diphosphine **132** and silyltri-*t*-butyl diphosphine **133**. Desilylation with methanol occurs at the lesser silylated site of **131**, while lithiation of the silyldiphosphines with BuLi cleaves at the more silylated phosphorus atom. *t*-Bu<sub>3</sub>P<sub>2</sub>Li also results from the P—H precursor. A *t*-butyl group is needed to stabilize these diphosphides, and lithiation of the P—H bond formed by methanolysis readily occurs with BuLi to give the phosphides **134–136** (Scheme 40)<sup>153</sup>.



SCHEME 40

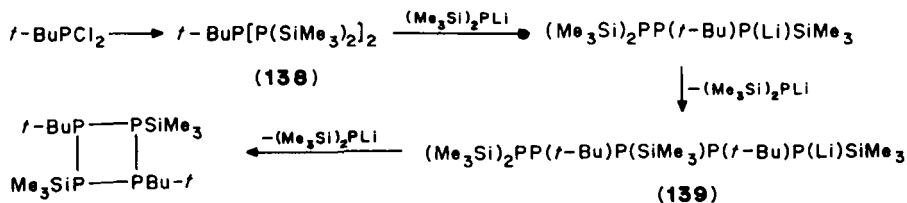
The 1:1 reaction of *t*-BuPCl<sub>2</sub> with LiP( $\text{SiMe}_3$ )<sub>2</sub>·2THF at  $-60^\circ\text{C}$  gives the chlorodiphosphine **137**, which decomposes on warming to room temperature through  $\text{Me}_3\text{SiCl}$  elimination to form the silyl-*t*-butyl diphosphene. This adds to 2,3-dimethylbuta-1,3-diene or dimerises to give a mixture of the *cis*- and *trans*-cyclotetraphosphines (Scheme 41).

Substitution of the second chlorine atom of *t*-BuPCl<sub>2</sub> by LiP( $\text{SiMe}_3$ )<sub>2</sub> is much slower, so in forming the triphosphine  $[(\text{Me}_3\text{Si})_2\text{P}]_2\text{PBU}-t$  (**138**), cleavage of one Si—P bond



SCHEME 41

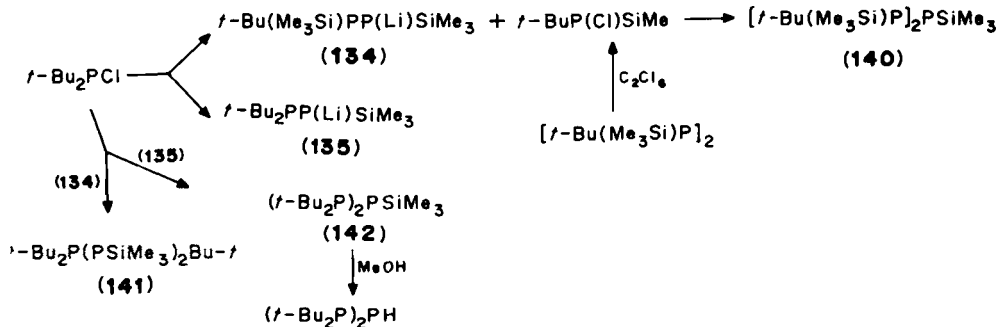
of this occurs to give a lithium derivative, which condenses to the pentaphosphide **139** through attack at the  $(\text{Me}_3\text{Si})_2\text{P}$  group. This pentaphosphide then cyclizes through elimination of  $(\text{Me}_3\text{Si})_2\text{PLi}$  to give the *trans*-cyclotetraphosphine exclusively (Scheme 42). Such a mechanism is also suggested for the decomposition of other silyl substituted triphosphides<sup>154</sup>.



SCHEME 42

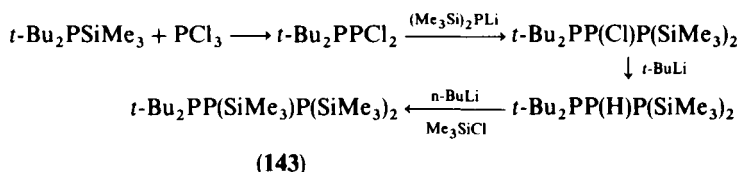
### B. Triphosphines and Tetraphosphines

The lithiated diphosphides **134** and **135** resulting from the reactions in Scheme 40 readily condense with the chlorophosphines  $\text{Me}_3\text{SiP}(\text{Bu-}t)\text{Cl}$  (generated from  $[t\text{-Bu}(\text{Me}_3\text{Si})\text{P}]_2$  by oxidizing with  $\text{C}_2\text{Cl}_6$ ) and  $t\text{-Bu}_2\text{PCl}$  to give the triphosphines  $[t\text{-Bu}(\text{Me}_3\text{Si})\text{P}]_2\text{PSiMe}_3$  (**140**),  $t\text{-Bu}(\text{Me}_3\text{Si})\text{PP}(\text{SiMe}_3)\text{PBu-}t_2$  (**141**) and  $(t\text{-Bu}_2\text{P})_2\text{PSiMe}_3$  (**142**). Methanolysis of **142** gives the solid P—H derivative (Scheme 43).



SCHEME 43

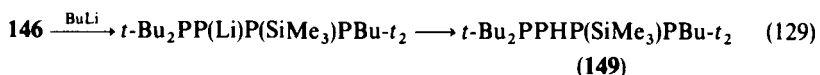
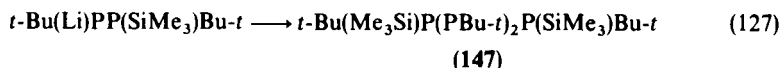
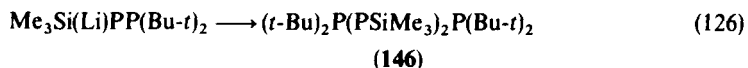
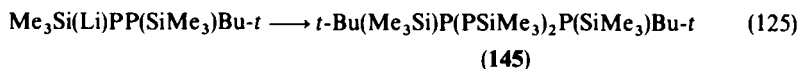
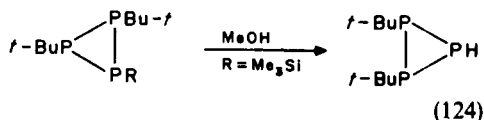
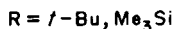
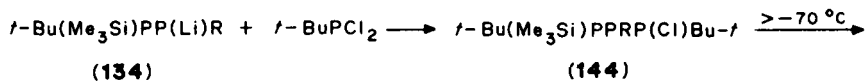
However, preparation of the triphosphine  $t\text{-Bu}_2\text{PP}(\text{SiMe}_3)\text{P}(\text{SiMe}_3)_2$  (**143**) requires a more extensive synthetic route involving low-temperature substitution of  $t\text{-Bu}_2\text{PPCl}_2$  followed by protonation using  $t\text{-BuLi}$ , then lithiation using  $n\text{-BuLi}$ , followed by silylation (Scheme 44).



SCHEME 44

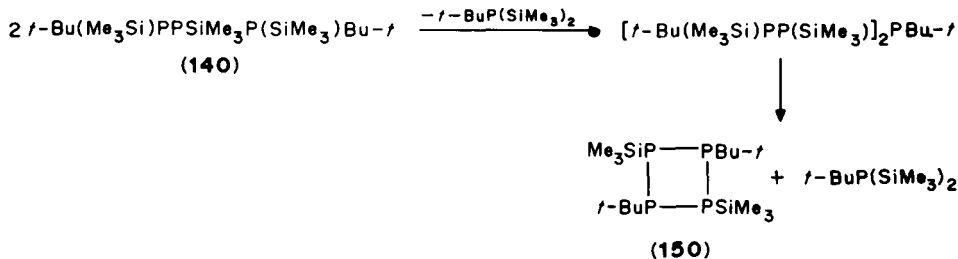
The 2-lithio derivative of **143** results using  $\text{BuLi}$  in ether, and decomposes readily giving the diphosphide  $t\text{-Bu}_2\text{PP}(\text{SiMe}_3)\text{Li}$ . This contrasts to the less silylated 2-lithio triphosphides  $t\text{-Bu}_2\text{PPLiP}(t\text{-Bu})\text{SiMe}_3$  and  $(t\text{-Bu}_2\text{P})_2\text{PLi}$ , which are stable in ether solution.

The chlorotriphosphine **144** ( $\text{R}=\text{Me}_3\text{Si}$ ), prepared from **134** with  $t\text{-BuPCl}_2$ , decomposes on warming above  $-70^\circ\text{C}$  to give the cyclotriphosphine, which can be desilylated with  $\text{MeOH}$ . A similar condensation with  $\text{Li}(t\text{-Bu})\text{PP}(t\text{-Bu})\text{SiMe}_3$  gives the tri- $t$ -butylcyclotriphosphine (equation 124). The four tetraphosphanes **145** to **148** result on oxidatively coupling the appropriate diphosphide using 1,2-dibromoethane (equations 125-128). The 2-lithio derivative of **145** is unstable, but that of **146** with  $\text{MeOH}$  gives the crystalline phosphine **149** (equation 129).



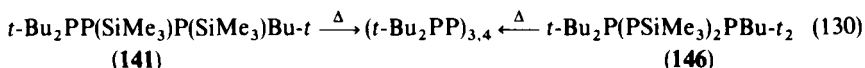
The silyl triphosphines and silyl tetraphosphines show variable thermal stability. Thus the triphosphine **140** with no  $t\text{-Bu}_2\text{P}$  groups gives the *trans*-cyclotetraphosphine **150**



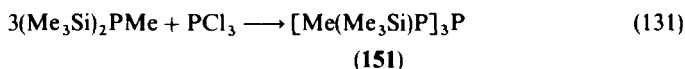


SCHEME 45

and  $\textit{t}\text{-BuP}(\text{SiMe}_3)_2$  via a linear pentaphosphine intermediate (Scheme 45). The triphosphines and tetraphosphines containing a  $\textit{t}\text{-Bu}_2\text{P}$  group all decompose to the cyclotri- and cyclotetra-phosphanes ( $\textit{t}\text{-Bu}_2\text{PP}$ )<sub>3,4</sub>, through generation of what is thought to be the phosphorus analogue of a nitrene, the phosphinidene  $\textit{t}\text{-Bu}_2\text{P}-\overset{\ominus}{\text{P}}$  (equation 130). The exception is **147**, which is stable at 100 °C in toluene for 3 days<sup>155</sup>. Condensing the

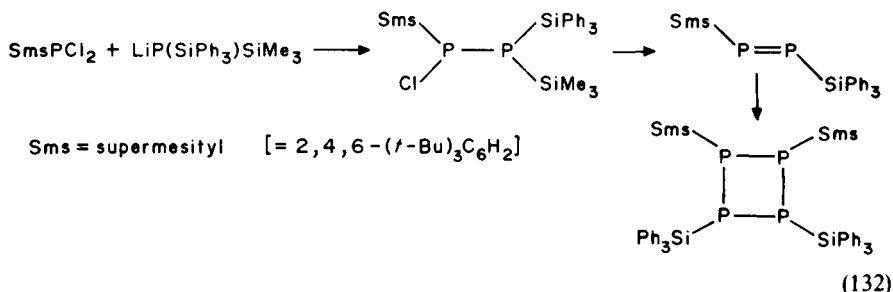


disilylphosphine  $(\text{Me}_3\text{Si})_2\text{PMe}$  with  $\text{PCl}_3$  in pentane in the ratio 3:1 gives rapid monosubstitution at  $-78^\circ\text{C}$ , further substitution occurring on slowly warming to room temperature. The product **151** is a colourless crystalline solid, m.p.  $65^\circ\text{C}$ , and possesses  $C_3$  symmetry, with Si—P (225.2 pm) and P—P (220.1 pm) bonds of normal length (equation 131)<sup>156</sup>.



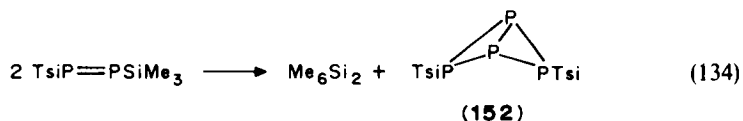
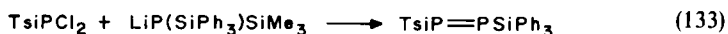
### \*VI. CYCLOPOLYPHOSPHINES

The tendency for diphosphenes to oligomerise to cyclopolyposphines depends on the size of the substituents at phosphorus. 1-[2,4,6-tri(*t*-butyl)phenyl]-2-(triphenylsilyl)diphosphene results from  $\text{SmsPCl}_2$  and  $\text{LiP}(\text{SiPh}_3)\text{SiMe}_3$  through LiCl and  $\text{Me}_3\text{SiCl}$  elimination. It slowly dimerises through head-to-head coupling (equation 132).

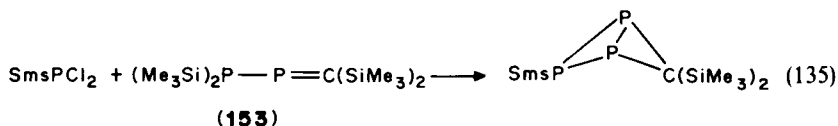


With the tris(trimethylsilyl)methyl (Tsi) group, however, the diphosphene is stable if triphenylsilyl is the other substituent, and has a P=P bond of 200.5 pm and Si—P

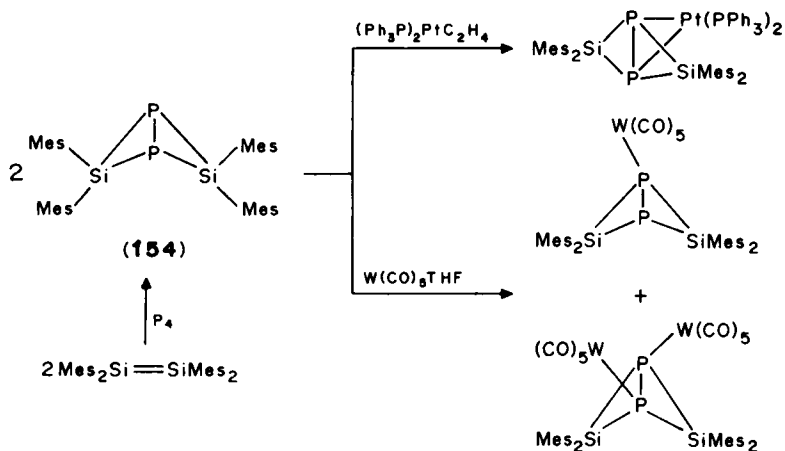
bond of 226.9 pm (equation 133). With trimethylsilyl as the other substituent, however, disproportionation occurs to give hexamethyldisilane and the tetraphosphabicyclo[1.1.0]butane **152** (equation 134). Dimerisation appears to be restricted by the steric demands of the very bulky Tsi group, which appear even greater than those of the Sms group in this situation<sup>157</sup>.



The 1,2,4-isomer was the first triphosphabuta-1,3-diene to be prepared (Chapter 5, equation 41) but attempts to prepare the 1,2,3-isomer by condensing the tetrasilyl-2,3-diphosphaprop-1-ene **153** with  $\text{SmsPCl}_2$  gives the triphosphabicyclo[1.1.0]butane with a butterfly-like structure in which the spinal P—P bond of 213.6 pm is the shortest of the three in the molecule (equation 135)<sup>158</sup>.



Tetramesityldisilene and white phosphorus give a similar bicyclobutane (**154**) in which the two phosphorus atoms provide the spine and coordinate to tungsten and platinum (Scheme 46)<sup>159</sup>.

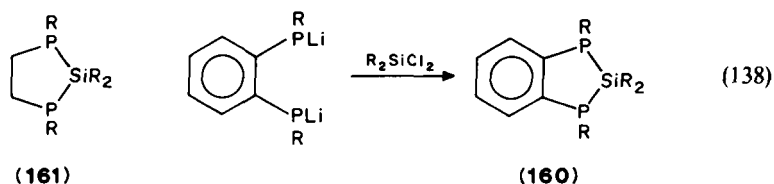


SCHEME 46

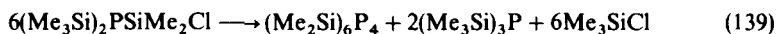


## \*VII. CYCLOSILAPHOSPHANES

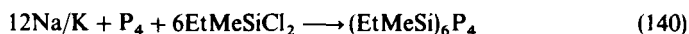
2-Sila-1,3-benzodiphospholenes result from bis-substituted 1,2-diphosphinobenzene and  $R_2SiCl_2$  (equation 138). Barriers to inversion at phosphorus are lower than those at phosphorus in 1,3-diphospholanes, where the *cis/trans* conversion energy  $\Delta G_{T_c}^\ddagger$  is  $73.9 \text{ kJ mol}^{-1}$  for the benzophospholene **160** and  $75.6 \text{ kJ mol}^{-1}$  for the diphospholane **161**<sup>162</sup>.



Heating  $(Me_3Si)_2PSiMe_2Cl$  to  $300^\circ\text{C}$  gives the  $Si_6P_4$  adamantane cage (equation 139) (Chapter 5, Scheme 20). Other chlorosilyl bis(trimethylsilyl)phosphines decompose similarly, with  $(Me_3Si)_2PSiEt_2Cl$  giving a range of cage products  $(Et_2Si)_x(Me_2Si)_{6-x}P_4$  ( $x = 2$  to  $6$ ) with isomers resulting for  $x = 2$  to  $4$ , along with  $(Me_3Si)_n(SiEt_2Me)_{3-n}$  ( $n = 1-3$ ) and the chlorosilanes  $Me_3SiCl$  and  $MeEt_2SiCl$  through Me/Et exchange.  $(Me_3Si)_2PSiMeEtCl$  gives a similar range of products with chiral isomers for  $(EtMeSi)_x(Me_2Si)_{6-x}P_4$  ( $x = 0-6$ ) for  $x = 2$  to  $6$ .



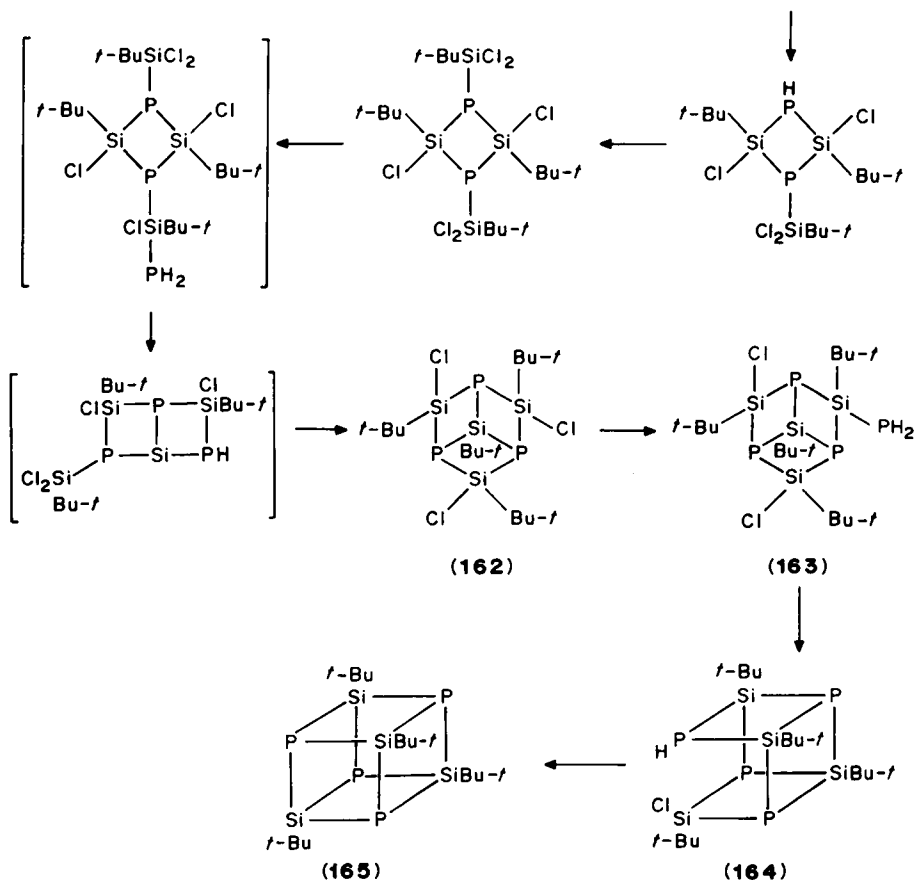
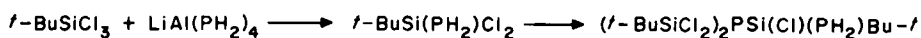
This cage also results through reductively silylating white phosphorus using a Na/K alloy with dichlorosilanes (equation 140). Many examples can be prepared this way, but remarkably no reaction is observed with  $t\text{-Bu}_2SiCl_2$  and  $Ph_2SiCl_2$ <sup>163</sup>.



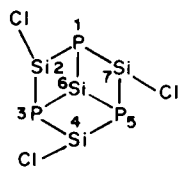
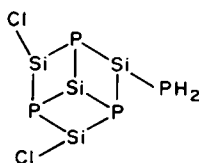
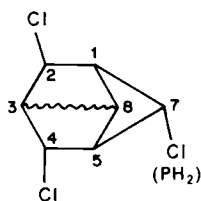
While the trisphosinosilanes  $RSi(PH_2)_3$  result from  $RSiCl_3$  ( $R = \text{Me, Et, } i\text{-Pr, Ph}$ ) and  $LiAl(PH_2)_4$  in the ratio 4:3 (equation 109),  $t\text{-BuSiCl}_3$  gives a series of cyclic condensation products which lead ultimately to the tetraphosphatetrasilacubane **165** in dimethoxyethane at  $-40^\circ\text{C}$  (Scheme 48). It is thermally stable, m.p.  $323-4^\circ\text{C}$  and has a highly distorted cube structure with Si---Si distances less than P---P. The accuracy of the structure determination indicates two different molecules in the unit cell, of symmetry  $S_4$  and  $T$ , in the ratio 6:2 with very slightly different Si—P bond lengths of 228.1 and 227.8 pm, respectively, though the PSiP and SiPSi angles are each the same for the two molecules and  $101.61^\circ$  and  $77.03^\circ$ , respectively<sup>164</sup>. The formation of **165**, a pentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octane, is thought to result through the condensation pathway indicated since most intermediates could be detected (Scheme 48). Thus **162** results as a crystalline solid, m.p.  $229-231^\circ\text{C}$ , and has a norcubane structure with the three inner Si—P bonds some 4.5 pm longer than the six outer Si—P bonds (225.4–226.1 pm) (equation 141)<sup>165</sup>.

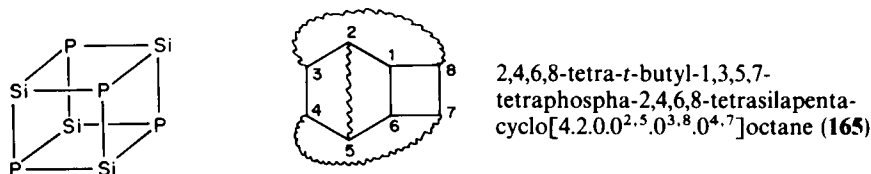
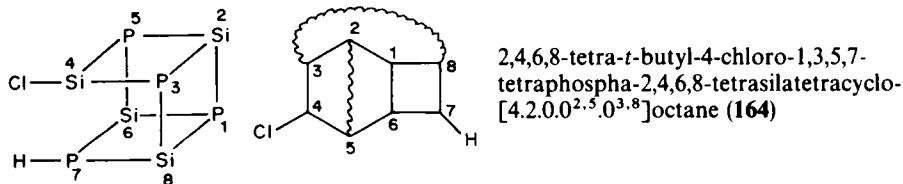
The remarkable thermal stability of **165** compares with that of tetra-*t*-butyltetraphosphacubane (*t*-BuCP)<sub>4</sub>, m.p.  $241^\circ\text{C}$ , and contrasts with that of the tin-phosphorus cube  $(PhSnP)_4$ , which decomposes without melting at about  $160^\circ\text{C}$ , and even at room temperature in an inert atmosphere decomposes to a polymer within two days<sup>166</sup>.

1,2,5-Phosphasilaboroles **167** result by the condensing of the alkene **166** with  $PhPLi_2$  (see Chapter 8, equation 91). Unlike the sulphur analogue, **167** dimerises to give a four-membered (P—B)<sub>2</sub> ring, and forms complexes with  $\gamma$ -picoline and trimethylphosphine. With methylene triphenylphosphorane, the adduct loses  $Ph_3P$  on heating

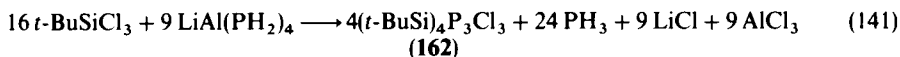


SCHEME 48

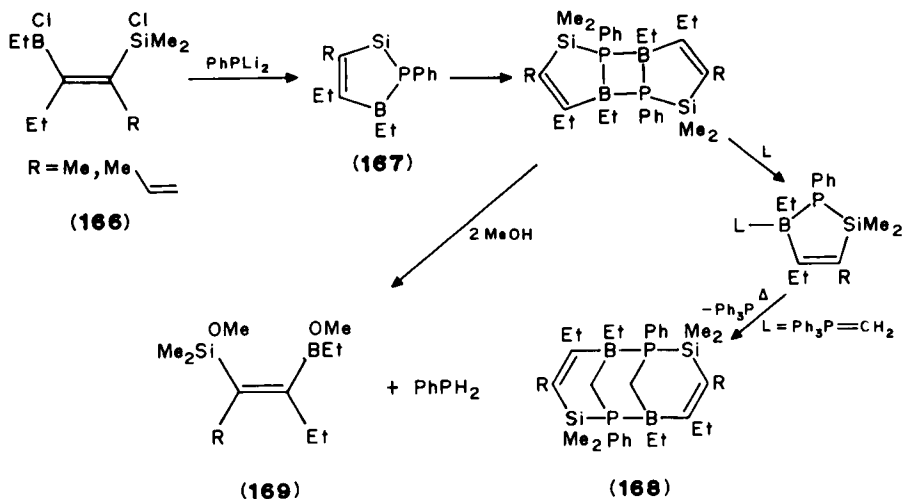
2,4,6,7-tetra-*t*-butyl-2,4,7-trichloro-1,3,5-triphospha-2,4,6,7-tetrasilatricyclo[3.1.1.0<sup>3,6</sup>]heptane (162)2,4,6,8-tetra-*t*-butyl-2,4-dichloro-7-phosphino-1,3,5-triphospha-2,4,6,7-tetrasilatricyclo[3.1.1.0<sup>3,6</sup>]heptane (163)



*t*-Bu groups omitted for clarity



under vacuum to give the bicyclic derivatives **168** through methylene insertion into the B—P bond. Amine oxides induce PhP/O exchange, (Et<sub>3</sub>Al)<sub>2</sub> exchanges at boron and MeOH opens the ring to give the alkene **169** and phenylphosphine (Scheme 49)<sup>167</sup>.

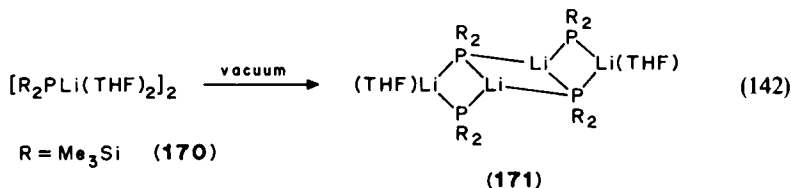


SCHEME 49

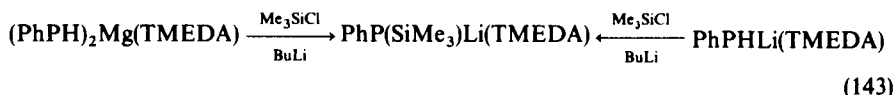
### \*VIII. SILYLPHOSPHIDES AND THE SILICON-PHOSPHORUS DOUBLE BOND

The two dimeric ether complexes [(Me<sub>3</sub>Si)<sub>2</sub>PLi(THF)<sub>2</sub>]<sub>2</sub> (**170**) and [(Me<sub>3</sub>Si)<sub>2</sub>PLiDMF]<sub>2</sub>, prepared from (Me<sub>3</sub>Si)<sub>3</sub>P and RLi, possess regular rhombus-like four-membered Li<sub>2</sub>P<sub>2</sub>

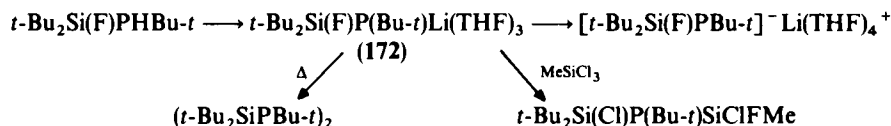
rings with P—Li bonds of 262 and 256 pm, respectively, and Si—P bond lengths of about 220 pm. **170** slowly loses THF under vacuum to give the ladderane complex **171**, which possesses 3-coordinate Li atoms with Li—P bonds in the range of 244–264 pm (equation 142)<sup>168</sup>.



The phosphide complexes PhPHLi(TMEDA) and (PhPH)<sub>2</sub>Mg(TMEDA) on silylation/lithiation yield [PhP(SiMe<sub>3</sub>)Li(TMEDA)]<sub>2</sub>, which is dimeric just above 0 °C, but dissociates on warming, according to NMR spectroscopic evidence (equation 143)<sup>169</sup>.



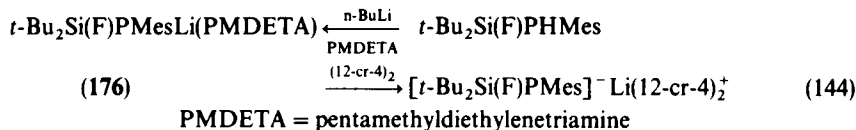
The phosphide **172** occurs as an ion contact pair with a Si—P bond length of 220.0 pm and Li—P distance of 254.7 pm. It dissociates in excess THF into separate ions and decomposes on heating to give the four-membered (Si—P)<sub>2</sub> ring. It also forms a range of bis(silyl)phosphines with a range of both fluoro- and chlorosilanes, the reactions with MeSiCl<sub>3</sub> and SiCl<sub>4</sub> also resulting in Cl/F exchange (Scheme 50)<sup>170</sup>.

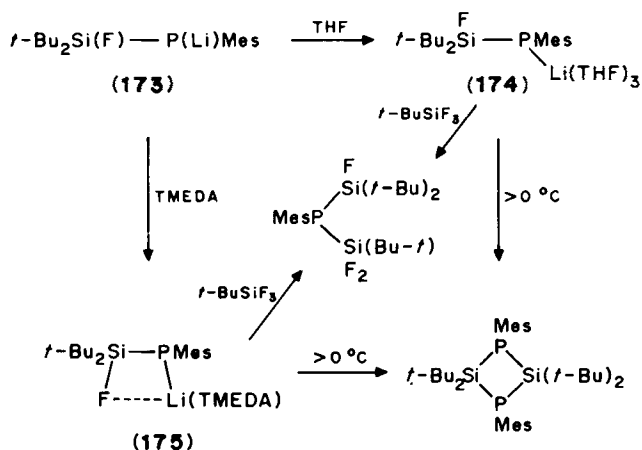


SCHEME 50

The fluorosilylphosphide **173** results from the condensation of *t*-Bu<sub>2</sub>SiF<sub>2</sub> with MesP(Li)H followed by *n*-BuLi. The THF complex **174**, with Si—P 216.1 pm, has Li 4-coordinate and shows no Li—F interaction, whereas the diamine complex **175** has a strong Li—F interaction (167.9 pm) and Si—P bond of 218.7 pm (Scheme 51). Both complexes decompose above 0 °C with LiF elimination to give the cyclic silaphosphane, which has two distinct molecules in the unit cell. The Si—P bond lengths in one differ from 223.4 pm to 230.8 pm, and in the other from 223.7 pm to 231.1 pm, showing that the steric limit for dimerisation of silaphosphenes has been reached since equal bond lengths cannot be accommodated comfortably. Both **174** and **175** react with *t*-BuSiF<sub>3</sub> to give the bis(silyl)phosphine<sup>171</sup>.

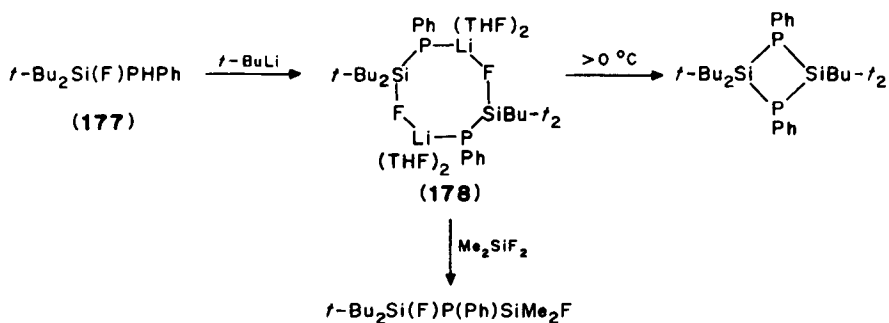
The analogous *N,N',N''*-pentamethyldiethylenetriamine (PMDETA) derivative **176** also appears to be an ion contact pair, with a Li—P bond of 255.0 pm and an Si—P bond of 216.9 pm. However, in the presence of 12-crown-4 the free ions result, though the Si—P bond length is almost the same as in **176** (equation 144)<sup>172</sup>.



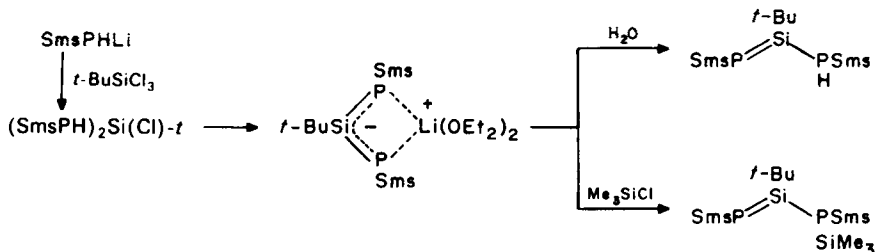


SCHEME 51

Lithiating the fluorosilylphosphine **177** in THF gives the complex **178** as a dimeric eight-membered ring with short Si—P bonds of 217.1 pm and a large Si—P coupling constant, suggesting multiple bond character. The Li—F bond length is 190.4 pm and LiF elimination readily occurs to give the four-membered (Si—P)<sub>2</sub> ring, while Me<sub>2</sub>SiF<sub>2</sub> forms the bis(fluorosilyl)phosphane (Scheme 52)<sup>173</sup>.



SCHEME 52

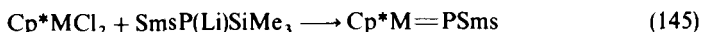


SCHEME 53



Condensing *t*-BuSiCl<sub>3</sub> with SmsPHLi in diethyl ether gives the 1,3,2-diphosphasilaallyl anion in which the Si—P bonds are 211 pm, some 13 pm shorter than single. Hydrolysis and silylation give the appropriate phosphinosilaphosphene (Scheme 53)<sup>174</sup> (see equation 116<sup>142</sup>).

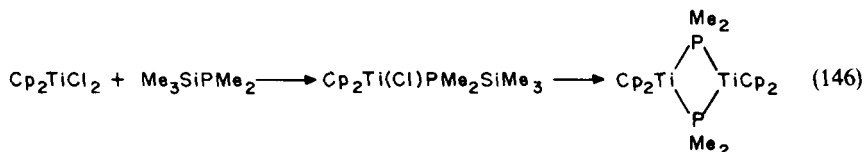
Condensing Cp\*MCl<sub>2</sub> (M = P, As) with SmsP(Li)SiMe<sub>3</sub> gives the diphosphene and arsaphosphene (equation 145) as orange crystalline solids, m.p. 110 and 115°C, respectively<sup>175</sup>.



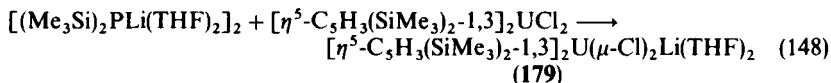
### \*IX. TRANSITION METAL DERIVATIVES

A wide range of silylphosphido derivatives of titanium, zirconium and hafnium have been prepared and their reactions investigated.

Titanocene dichloride gives a paramagnetic complex with *P,P*-dimethylphosphinotrimethylsilane through chloride displacement, and has an Si—P bond length of 228.3 pm and a long Ti—P bond. Subsequent reaction with sodium amalgam gives the Ti(III) phosphide bridged derivative with Ti—Ti distance of 391.8 pm, too long for electron pairing in the paramagnetic complex (equation 146)<sup>176</sup>.



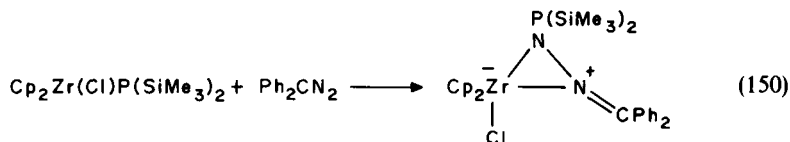
[(Me<sub>3</sub>Si)<sub>2</sub>PLi(THF)<sub>2</sub>]<sub>2</sub> will also reduce Cp<sub>2</sub>TiCl<sub>2</sub> and CpTiCl<sub>3</sub> to give Ti(III)THF complexes (equation 147). [η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>-1,3]<sub>2</sub>UCl<sub>2</sub> gives the mixed metal complex **179** incorporating Li, again with no phosphide substitution at the high oxidation state metal (equation 148)<sup>177</sup>.



Zirconocene and hafnocene dichlorides can be mono- and disubstituted by (Me<sub>3</sub>Si)<sub>2</sub>PLi. Cp<sub>2</sub>Hf[P(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> shows different bonding in the two phosphido ligands with one pyramidal to Zr and the other trigonal planar with the shorter bond, supporting π-bonding between phosphorus and zirconium (equation 149)<sup>178</sup>.

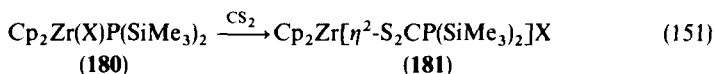


The monosubstituted zirconium derivative adds to diphenyldiazomethane through addition of the Zr—P bond across the N—N multiple bond (equation 150)<sup>179</sup>.

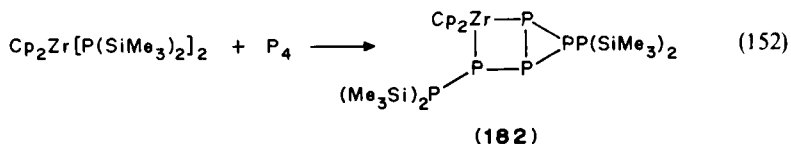


The methyl derivatives Cp<sub>2</sub>M(Me)P(SiMe<sub>3</sub>)<sub>2</sub> can be prepared similarly from Cp<sub>2</sub>M(Me)Cl (M = Zr, Hf), that of Zr and the chloro analogue **180** readily inserting CS<sub>2</sub>

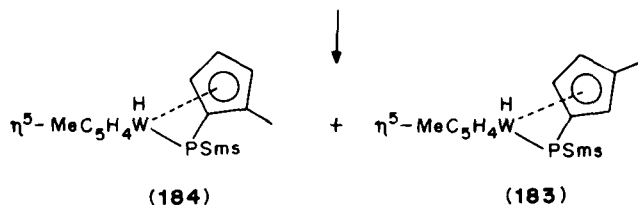
into the Zr—P bond to give the phosphinodithioformate **181** (equation 151)<sup>180</sup>.



White phosphorus reacts with the bisphosphido derivative of zirconocene to give the bicyclo[2.1.0]pentane complex **182** in which both Zr—P bonds are inserted (equation 152)<sup>181</sup>.

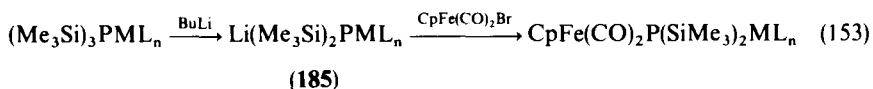


The more hindered phosphide SmsP(Li)SiMe<sub>3</sub> also monosubstitutes zirconocene dichloride, the product possessing an Si—P bond length of 226.8 pm, but with the methylcyclopentadienyltungsten derivative ( $\eta^5\text{-MeC}_5\text{H}_4$ )<sub>2</sub>WCl<sub>2</sub>, chloride substitution, chlorosilane elimination and C—H insertion all occur to give an isomeric mixture of the tungsten hydride complexes **183** and **184** (Scheme 54)<sup>182</sup>.



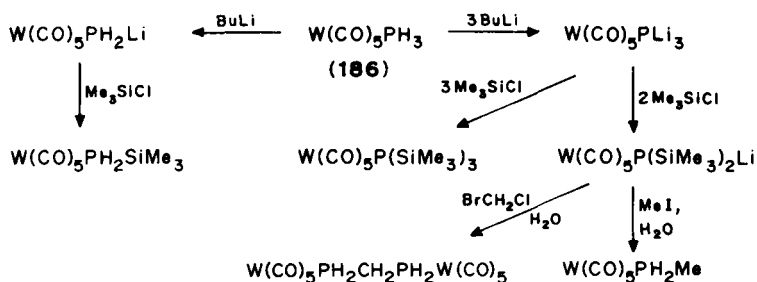
SCHEME 54

The iron phosphide complex CpFe(CO)<sub>2</sub>P(SiMe<sub>3</sub>)<sub>2</sub> itself functions as a ligand, displacing CO but not NO from Co(CO)<sub>3</sub>NO, Fe(CO)<sub>2</sub>(NO)<sub>2</sub> and Mn(CO)(NO)<sub>3</sub>, and THF from M(CO)<sub>5</sub>THF (M = Cr, Mo, W) and the two cyclopentadienyl complexes CpMn(CO)<sub>2</sub>THF and MeC<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>2</sub>THF. Other examples of these bimetallic complexes result from the lithium-substituted complex **185** (prepared from the trisilylphosphine derivative and butyl-lithium) by coupling with CpFe(CO)<sub>2</sub>Br (equation 153)<sup>183</sup>.



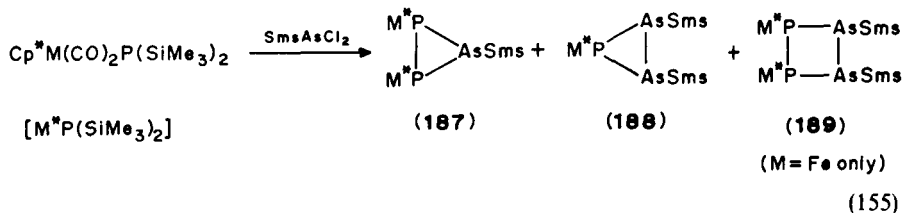
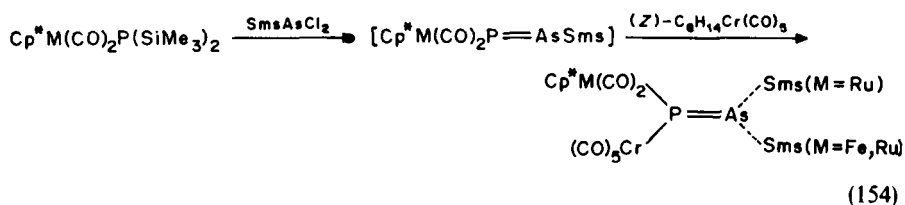
The phosphine complex **186** can be mono-, di- and trilitiated, silylphosphine complexes resulting with Me<sub>3</sub>SiCl, while partial silylation followed by methylation and hydrolysis of the Si—P bond leads to the methylphosphine complex (Scheme 55)<sup>184</sup>.

The more hindered Cp\*M(CO)<sub>2</sub>P(SiMe<sub>3</sub>)<sub>2</sub> (M = Fe, Ru) condenses with SmsAsCl<sub>2</sub> to give the unstable arsaphosphenyl derivatives which can be trapped as the Cr(CO)<sub>5</sub> adducts. With M = Ru, a mixture of geometric isomers results (equation 154). In addition, the

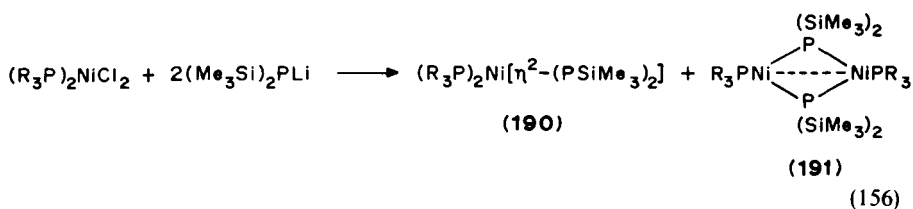


SCHEME 55

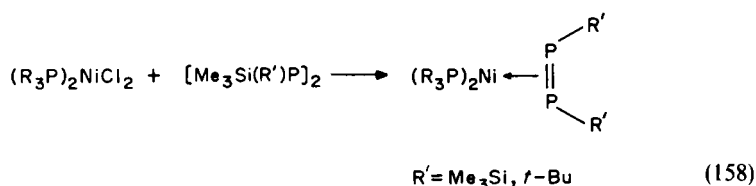
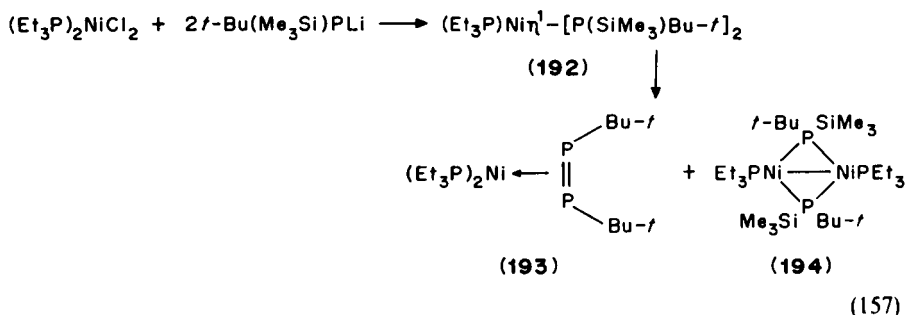
diphosphaarsirane **187**, diarsaphosphirane **188** and 1,2-diphospha-3,4-diarsetane **189** ( $M = \text{Fe}$  only) complexes are also formed (equation 155)<sup>185</sup>.



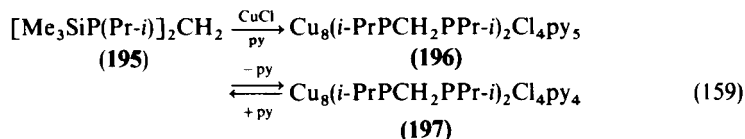
The phosphine nickel(II) complexes  $(\text{R}_3\text{P})_2\text{NiCl}_2$  condense with  $(\text{Me}_3\text{Si})_2\text{PLi}$  in the ratio 1:2 to give both diphosphene and bridged phosphino complexes **190** and **191** through  $(\text{R}_3\text{P})_2\text{Ni(Cl)P(SiMe}_3)_2$  and  $\text{R}_3\text{PNi}[\eta^1\text{-P}_2(\text{SiMe}_3)_4]$  as intermediates (equation 156).



With  $t\text{-Bu}(\text{Me}_3\text{Si})\text{PLi}$ ,  $(\text{Et}_3\text{P})_2\text{NiCl}_2$  gives the first Ni(0) diphosphine complex **192**, isolable at low temperature, which decomposes to  $(\text{Et}_3\text{P})_2\text{Ni}[\eta^2\text{-(PBu-}t\text{)}_2]$  (**193**) and  $\{(\text{Et}_3\text{P})\text{Ni}[t\text{-BuPSiMe}_3]\}_2$  (**194**) (equation 157). **194** and its P-phenyl analogue also result from  $\text{R}'\text{P(SiMe}_3)_2$  ( $\text{R}' = t\text{-Bu, Ph}$ ), but the best yields of the diphosphene complexes occur from the  $[2 + 1]$  cycloaddition of  $(\text{R}_3\text{P})_2\text{NiCl}_2$  with  $(\text{Me}_3\text{Si})_2\text{P}_2$  or  $t\text{-BuPSiMe}_3$  (equation 158)<sup>186</sup>.



Adding the phosphine **195** to cuprous chloride and pyridine in acetonitrile gives the cluster complexes **196** and **197** (equation 159)<sup>187</sup>.

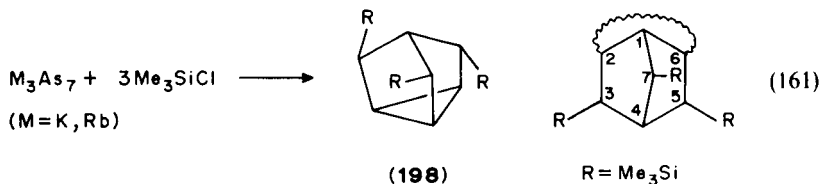


### \*X. SILYL ARSINES

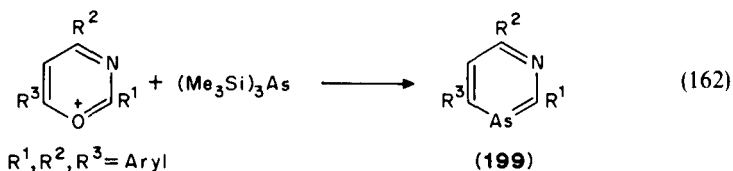
The silylarsines  $\text{Ph}(\text{Me})\text{AsSiMe}_3$  and  $\text{PhAs}(\text{SiMe}_3)_2$  can be prepared in good yield from the parent arsine and trimethylsilyl triflate (equation 160)<sup>124</sup>. The trisilyltricyclo[2.2.1.0<sup>2,6</sup>]-



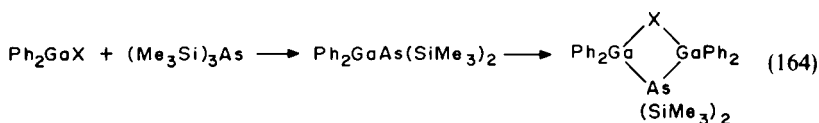
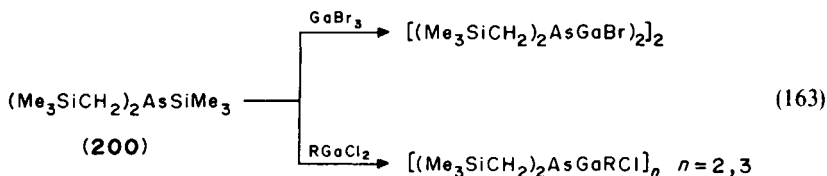
heptaarsane **198** results from the potassium or rubidium heptaarsenide and  $\text{Me}_3\text{SiCl}$  (equation 161). The structure shows  $C_3$  symmetry with Si—As bond lengths 239.7 pm and the crystal containing pairs of enantiomers. The basal As—As distances (244.3 pm) are longer than basal-equatorial (242.7 pm), which are longer than equatorial-apical (240.7 pm)<sup>188</sup>.



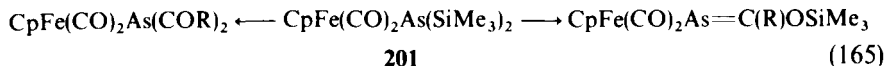
Just as phosphabenzene derivatives result from pyrylium and azapyrylium salts with  $(\text{Me}_2\text{Si})_3\text{P}$  (Chapter 5, equation 6), so the heterocycle 3-arsapyridine **199** results from the 3-azaonium salt and the trisilylarsine (equation 162)<sup>189</sup>.



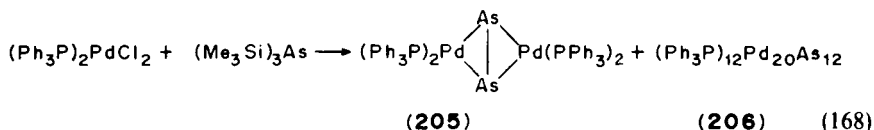
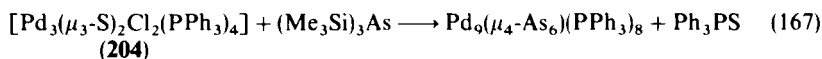
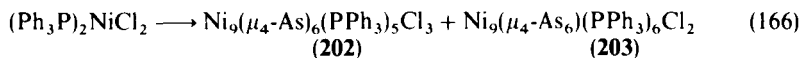
The silylarsine **200** is cleaved by GaBr<sub>3</sub> and organogallium dichlorides RGaCl<sub>2</sub> (R = Me, Ph). The products are associated (equation 163). With tris(trimethylsilyl)arsine, diphenylgallium chloride and bromide give Ph<sub>2</sub>(GaAs(SiMe<sub>3</sub>)<sub>2</sub>), which forms adducts with the original Ph<sub>2</sub>GaX, the products containing both halide and arsenide bridges (equation 164)<sup>190</sup>.



The silyl arsenide of Fe(I) (**201**) reacts with acyl chlorides to give the arsaalkene derivatives through silyl migration from As to O (see Section \*IV). With excess halide, disubstitution occurs with the formation of the bis(acyl) product (equation 165)<sup>191</sup>. (Me<sub>3</sub>Si)<sub>2</sub>AsPh reacts



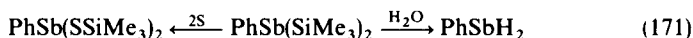
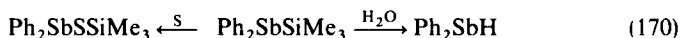
with Ni(II) phosphine complexes with cleavage of As—Ph as well as As—Si bonds to give the Ni<sub>9</sub> clusters **202** and **203**, which contain arsenic face-capping a cube of Ni atoms body-centered with Ni (equation 166). A similar palladium cluster results from the disulphide **204** and (Me<sub>3</sub>Si)<sub>3</sub>As (equation 167), while with (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>, the butterfly complex **205** with a μ<sub>2</sub>,η<sup>2</sup>-As<sub>2</sub> bridge, together with the cluster **206** containing a Pd<sub>8</sub> cube with each edge bridge by 12 Pd atoms (equation 168)<sup>192</sup>.



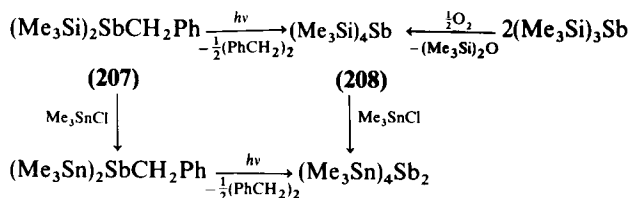
A comparison of the He(I) photoelectron spectra of  $\text{Ph}_2\text{ESiMe}_3$  ( $\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}$ ) show destabilization of the lone pair of electrons compared with  $\text{Ph}_2\text{EH}$  for  $\text{E} = \text{P}, \text{As}$  and  $\text{Sb}$ . The stabilization for  $\text{E} = \text{N}$  is thought to result through less planarity at nitrogen in the silyl compound<sup>193</sup>. The syntheses of silyl-rich trisilyl arsenides, antimonides and bismuthides result from the sodium/potassium pnictide and  $\text{ClSiMe}_n(\text{SiMe}_3)_{3-n}$  ( $n = 1, 2$ ), and the vibrational spectra for all are compared together with that of  $(\text{Me}_3\text{Si})_3\text{B}$ . The frequencies of the symmetric and asymmetric  $\text{ESi}_3$  vibrations decrease with increasing mass of  $\text{E}$  and increasing silyl substitution at silicon<sup>194</sup>.

### \*XI. SILYL STIBINES AND SILYL BISMUTHINES

Reductively coupling  $\text{Me}_3\text{SiCl}$  with the chlorostibines  $\text{Ph}_2\text{SbCl}$  and  $\text{PhSbCl}_2$  using  $\text{Mg}$  gives the silylstibines (equation 169), which insert sulphur without oxidation, in contrast to silylphosphines and silylarsines, and hydrolyse to the stibines (equations 170 and 171)<sup>195</sup>.

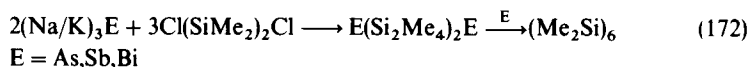


The stibide  $(\text{Me}_3\text{Si})_2\text{SbLi} \cdot 2\text{THF}$  condenses with benzyl chloride to give the bis(silyl)benzylstibine **207** in very good yield. This readily photolyses to the tetrasilyldistibine **208**, which shows shortening of the  $\text{Sb}-\text{Sb}$  contacts by 10 pm on cooling from  $20^\circ\text{C}$  to  $-120^\circ\text{C}$ , and also results from the oxidation of  $(\text{Me}_3\text{Si})_3\text{Sb}$  in air. Both **207** and **208** can be readily stannylated using  $\text{Me}_3\text{SnCl}$  (Scheme 55)<sup>196</sup>.



SCHEME 56

1,2-Dichlorotetramethyldisilane with  $\text{Na}/\text{K}$  arsenide, antimonide and bismuthide all give the bicyclo[2.2.2]octanes in low yield. Their vibrational spectra have been compared. Catalytic amounts of the elemental pnictogen cause decomposition to the cyclohexasilane (equation 172)<sup>197</sup>.



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# Chemistry of compounds with silicon–sulphur, silicon– selenium and silicon–tellurium bonds

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The chemistry of organosilicon–sulphur compounds has been reviewed periodically since 1960<sup>1</sup>. *Comprehensive Organometallic Chemistry* (published 1982) provides the most extensive up-to-date summary of the field of organosilicon chemistry, including sections on sulphur, selenium and tellurium compounds and their use in organic synthesis, which is also mentioned in *Comprehensive Organic Chemistry* (published 1979)<sup>2</sup>.

Organosilicon–sulphur compounds will be considered under six headings defined by structure type. Organothiosilanes  $R_nSi(SR')_{4-n}$ , linear and cyclic silthianes with the SiSSi

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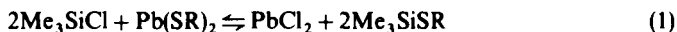
The Silicon–Heteroatom Bond

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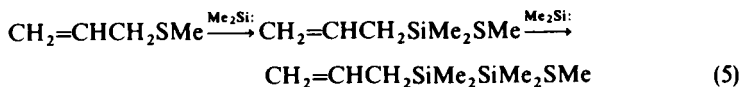
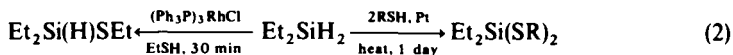
linkage provide the most extensively studied. Silane thiols and bis-silyl polysulphides appear to be less stable than their carbon or oxygen counterparts, while the silicon-sulphur double bond is briefly mentioned in the section following miscellaneous cyclic silicon-sulphur compounds. Selenium and tellurium derivatives have been less extensively studied, little work being reported before 1978. *Inorganic Syntheses* (McGraw-Hill) includes the preparation of  $(\text{Me}_3\text{Si})_2\text{S}$  and  $(\text{Me}_2\text{Si})_3\text{S}$  (Vol. XV),  $(\text{Me}_n\text{SiH}_{3-n})_2\text{S}$  ( $n = 1, 2, 3$ ) (Vol. XIX) and  $(\text{Me}_3\text{Si})_2\text{X}$  ( $\text{X} = \text{Se}, \text{Te}$ ) (Vol. XX).

### I. THIOSILANES

These compounds are best prepared from the chlorosilane and sodium thiolate, or thiol and a tertiary amine. Well-dried yellow lead dithiolates  $\text{Pb}(\text{SR})_2$  proved to be convenient synthetic intermediates<sup>3</sup> but the product has to be washed from the resulting white lead chloride as the reaction reverses on heating (equation 1).

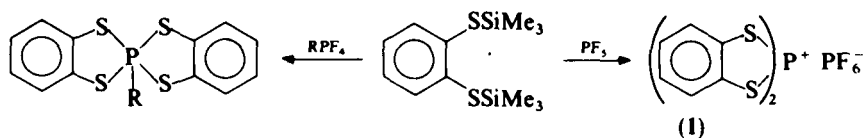


The thiolysis of silanes in the presence of transition metal catalysts provides a convenient route to thiosilanes (equation 2), and silanes also cleave disulphides on heating (equation 3)<sup>4</sup>. Sodium will cleave disulphides, trimethylchlorosilane giving the thiosilane, but surprisingly, with dimethyl disulphide, hexamethyldisilthiane is produced exclusively, through C-S cleavage, and with dibenzyl disulphide the thiosilane and silthiane are formed in similar proportions (equation 4). Dimethylsilylene  $\text{Me}_2\text{Si:}$  inserts into the allyl C-S bond of allyl methyl sulphide with no addition to the double bond, then further inserts into the Si-S bond so formed (equation 5)<sup>5</sup>. Similarity between the bond energies of the Si-S and Si-N bonds ( $300\text{--}330 \text{ kJ mol}^{-1}$ ) makes thiolysis of aminosilanes and disilazanes a convenient small-scale route to thiosilanes, particularly if the generated amine is the most volatile component, or imidazole is used as catalyst (equation 6)<sup>6</sup>.



Thiosilanes are vile-smelling, readily distillable liquids though some phenyl derivatives are crystalline solids. They are thermally stable but  $\text{Et}_3\text{SiSEt}$  will undergo C-S bond cleavage at  $350^\circ\text{C}$  to give diethyl sulphide and the disilthiane. They are not oxygen sensitive but the Si-S bond is readily cleaved by many protic reagents, notably those containing the O-H group, in part because the Si-O bond is stronger than the Si-S one<sup>1a</sup>. They react with a wide range of main group covalent halides, giving both full and partial thiolysis<sup>1c</sup>.

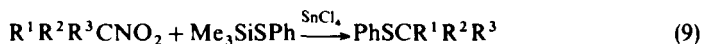
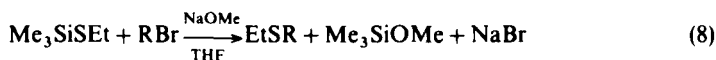
While phosphorus trichloride and excess thiosilane give the trithiophosphite  $(RS)_3P$ , phosphorus pentafluoride with an aryl bis(thiosilane) yields the ionic salt **1**<sup>7</sup>. Similarly the



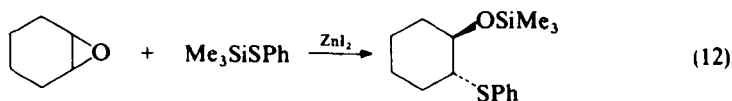
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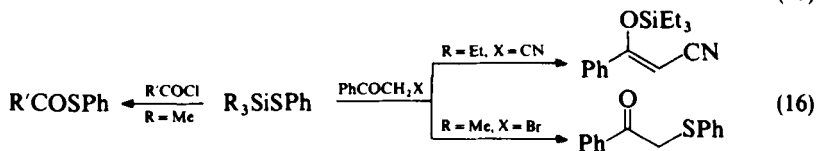
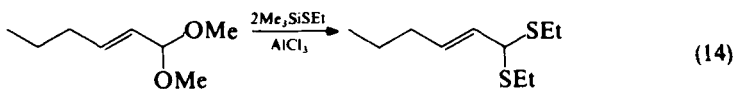
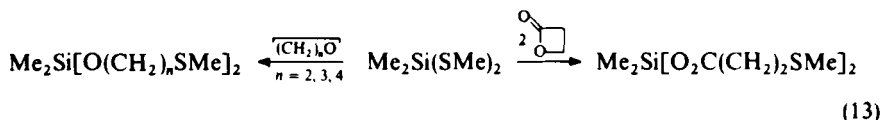
trifluorides of arsenic, antimony, and bismuth all yield trithiolates with *t*-butylthio-trimethylsilane, and stannic chloride  $(t\text{-BuS})_4\text{Sn}$ . However, organoarsenic(V) and organoantimony(V) chlorides all oxidise the thiosilane to the disulphide, as does sulphur(IV)<sup>8</sup>. More recently, an extensive range of gallium-sulphur and tin(II)-sulphur compounds has been similarly made<sup>9</sup>.

Thiosilanes are convenient intermediates for the synthesis of organic mono-, di- and trisulphides. The former can either be made by heating the thiosilane with alkyl bromide or iodide for long periods under reflux, or by adding NaOMe in THF at room temperature (equation 8). Secondary and tertiary alkyl and benzyl phenyl sulphides result in good yield from nitro derivatives in the presence of  $\text{SnCl}_4$  (equation 9)<sup>10</sup>. Symmetrical disulphides are formed on oxidizing thiosilanes with bromine or iodine, while phenylthio-trimethylsilane reduces sulphoxides and sulphimides in the presence of  $\text{Bu}_4\text{N}^+\text{Br}^-$ <sup>11</sup>. Asymmetric disulphides can be synthesized using an organosulphenyl chloride prepared *in situ* (equation 10), while trisulphides, both linear and cyclic, are formed using sulphur dichloride (equation 11)<sup>12</sup>.

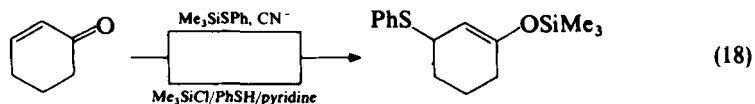
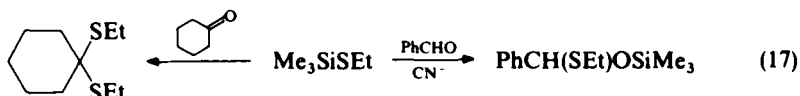


Cyclic ethers, notably epoxides (equation 12), and lactones are readily ring opened by thiosilanes through C-O bond cleavage to give the siloxy derivative (equation 13)<sup>13</sup>. Thiosilanes, both linear and cyclic, substitute ketals (equation 14) and insert fluoro-ketones and chloral across the Si-S bond (equation 15)<sup>14</sup>. With readily enolizable ketones, the enol ether results,  $\alpha$ -bromoacetophenone is substituted, and acyl chlorides give thiocarboxylates (equation 16)<sup>15</sup>.

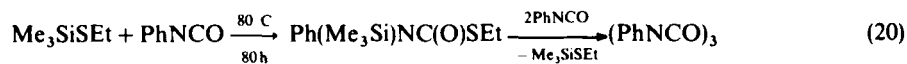
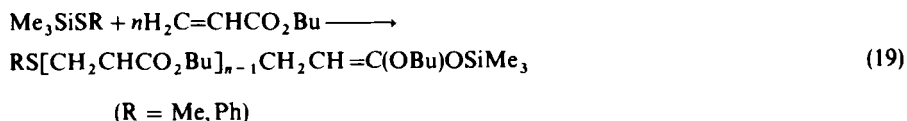




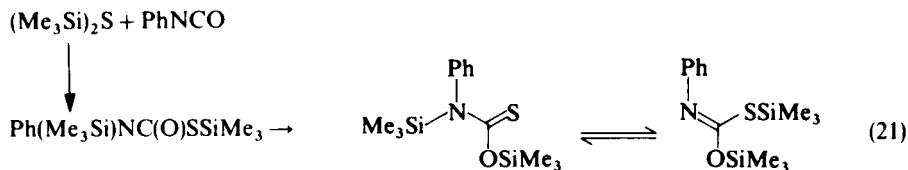
Aldehydes and ketones give *O*-silyl hemithioacetals and dithioketals respectively (equation 17) through 1,2-addition, but with  $\alpha,\beta$ -unsaturated carbonyl compounds 1,4-addition occurs exclusively.  $\text{Me}_3\text{SiCl}/\text{PhSH}/\text{pyridine}$  induce similar substitution (equation 18). Hemithioacetals can be readily reduced, providing a route for the conversion of aldehydes to asymmetric sulphides<sup>16</sup>.



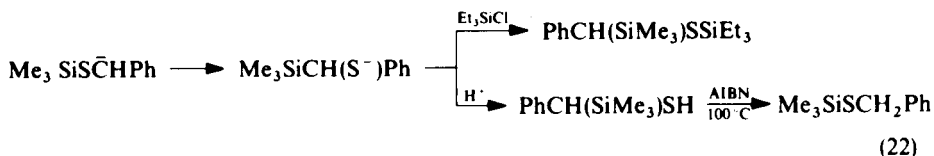
Thiosilanes act as initiators through 1,4-addition for group transfer polymerization of acrylic acid esters (equation 19), and catalyse the cyclotrimerization of phenyl isocyanate through addition across the C=N bond (equation 20) to give first the thiocarbamate and thence the isocyanurate<sup>17</sup>.



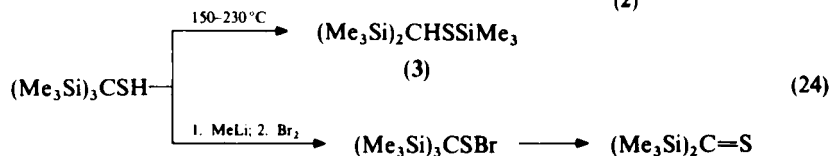
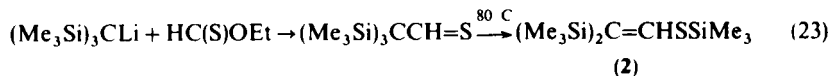
Hexamethyldisilthiane ( $\text{Me}_3\text{Si})_2\text{S}$  gives a similar adduct through addition across the C=N bond followed by silyl migration to oxygen. This is found to be in equilibrium with its *S*-silyl isomer, again reflecting similarity in the Si-N and Si-S bond enthalpies (equation 21).



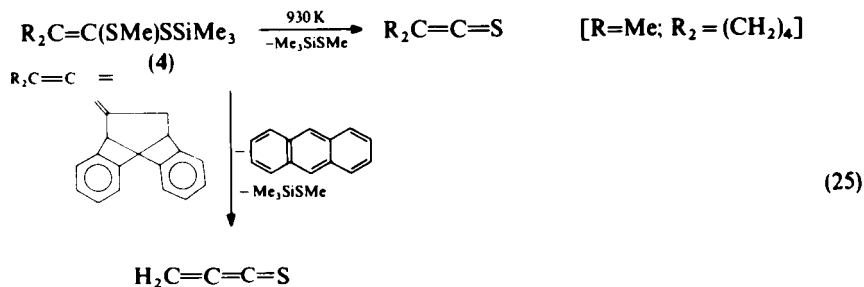
Deprotonation of benzylthiotrimethylsilane using *t*-BuLi induces a Wittig-type rearrangement to the more stable sulphide anion (equation 22). The carbanion generated from methylthiotrimethylsilane behaves similarly, and derivatives can be readily obtained. Thus the protic derivative readily reverts to the thermodynamically more stable thiosilane on heating or under free radical conditions (e.g., with azo isobutyronitrile (AIBN)), but in the presence of base remains as the more stable sulphide anion rather than as a carbanion<sup>18</sup>.



The first isolable thioaldehyde  $(\text{Me}_3\text{Si})_3\text{CCH}=\text{S}$ , stabilized by the bulky tris(trimethylsilyl)methyl group, has been prepared from  $(\text{Me}_3\text{Si})_3\text{CLi}$  and *O*-ethyl thioformate in 16% yield. It is a pink, air stable, crystalline solid, and undergoes a Brook-type rearrangement at 80 °C to give the vinylthiosilane **2** (equation 23). Rearrangement is also observed on pyrolysing tris(trimethylsilyl)methane thiol  $(\text{Me}_3\text{Si})_3\text{CSH}$ , the product being the bis(silyl)methylthiosilane **3**, while  $(\text{Me}_3\text{Si})_3\text{CSBr}$ , formed from  $(\text{Me}_3\text{Si})_3\text{CSH}$  with  $\text{MeLi}$  and then  $\text{Br}_2$ , decomposes to the thioketone  $(\text{Me}_3\text{Si})_2\text{C}=\text{S}$  (equation 24). Flash



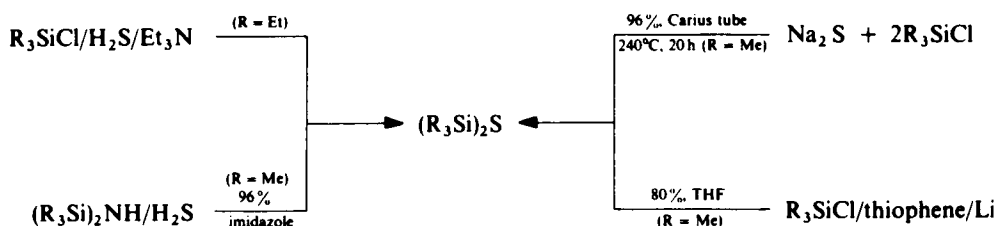
vacuum thermolysis of silylated ketene dithioacetals **4** provides a convenient synthetic route to thioketenes and, in the case of the bridged anthracene derivative, propadienethione (equation 25)<sup>19</sup>.



Thiosilanes will substitute metal carbonyls. With  $[(t\text{-Bu})_3\text{As}(\text{CO})\text{RhCl}]_2$ ,  $\text{Me}_3\text{SiSR}$  [ $\text{R} = t\text{-Bu}$  or  $-(\text{CH}_2)_n\text{Si}(\text{OMe})_3$  ( $n = 2, 3$ )] gives the mixed chloro-alkylthio bridged compound, the trialkoxysilyl group providing the surface-active group for bonding to silica. Irradiating  $\text{Ph}_3\text{SiSPh}$  (having a Si-S bond length of 215.6 pm), prepared from  $\text{DABCO} \cdot \text{HSPH}$  (DABCO is 1,4-diazabicyclo[2.2.2]octane) and  $\text{Ph}_3\text{SiCl}$ , with  $\text{W}(\text{CO})_6$  induces Si-S bond scission to form the diamagnetic metal-metal bonded complex  $\text{W}_2(\text{CO})_8(\mu\text{-SPh})_2$ <sup>20</sup>.

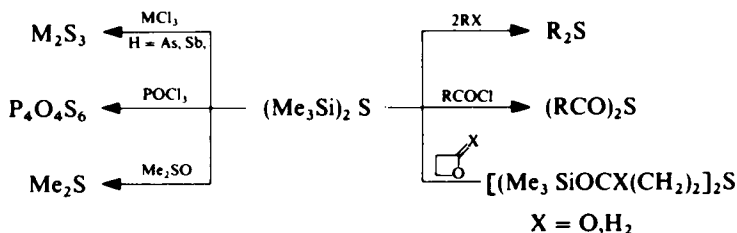
## II. LINEAR SILTHIANES

Eaborn prepared the first organosilicon-sulphur compounds  $(\text{R}_3\text{Si})_2\text{S}$  ( $\text{R} = \text{Me}, \text{Et}$ ) in 1950<sup>21</sup>. They were made from  $\text{R}_3\text{SiI}$  and  $\text{Ag}_2\text{S}$ , and despite the good yields, the inherent expense of silver sulphide and the inconvenience of preparing the very moisture-sensitive iodosilane has led to the method being superseded by ones involving commercially available chlorosilanes and hexamethyldisilazane where, as with alkylthiosilanes, imidazole proves to be a good catalyst (Scheme 1)<sup>21</sup>.



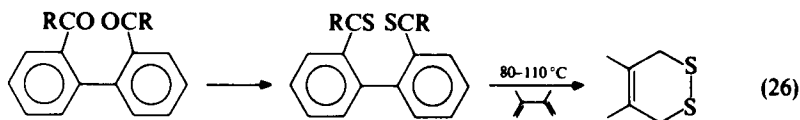
SCHEME 1

Hexamethyldisilthiane has a vile smell and is readily hydrolysed; once mixed with water it reacts with alcohols and acids to give alkoxy- and acylsilanes, and with amines the volatility of  $\text{H}_2\text{S}$  drives the equilibrium to favour the aminosilane. Silthianes, unlike dialkyl sulphides, do not form stable complexes with borane, but will, like thiosilanes, undergo exchange reactions with a variety of main group covalent halides including boron, giving a wide range of sulphides<sup>22</sup>. They will also reduce the oxides  $\text{Ph}_2\text{MO}$  ( $\text{M} = \text{Se}, \text{Te}$ ) and dimethyl sulphoxide, precipitating sulphur<sup>23</sup>. Both alkyl and acyl halides give the appropriate dialkyl sulphide or thioanhydride<sup>10, 24</sup> while oxirane and  $\beta$ -propiolactone give  $\gamma$ -siloxy and  $\beta$ -carboxy sulphides (Scheme 2)<sup>13</sup>.

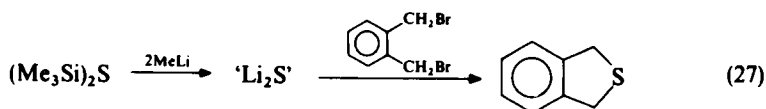


SCHEME 2

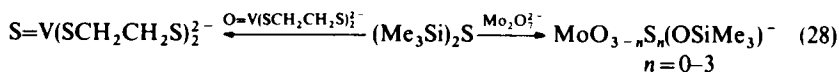
2,2'-Bis(acyl)biphenyl can be converted with  $(\text{Me}_3\text{Si})_2\text{S}$  and  $\text{BCl}_3$  to the bis thioketone. This on heating with 2,3-dimethylbuta-1,3-diene gives the dithiacyclohexane, providing a useful low-temperature generation of disulphur  $\text{S}_2$  (equation 26)<sup>25</sup>.



At room temperature in THF, hexamethyldisilthiane and methyl lithium give a soluble form of lithium sulphide which proves more reactive than the insoluble form which slowly precipitates on ageing. Thus 1,3-dihydroisothianaphthene results from the dibromide in 95% yield if prepared promptly, but in only 40% yield after 24 h ageing (equation 27)<sup>26</sup>.

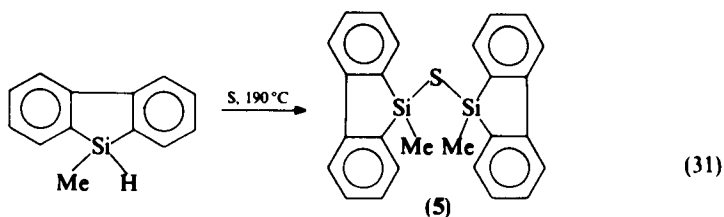
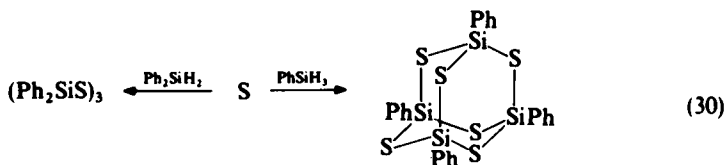
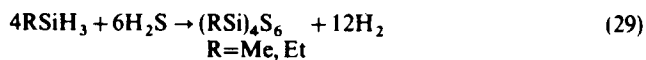


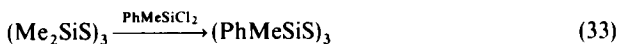
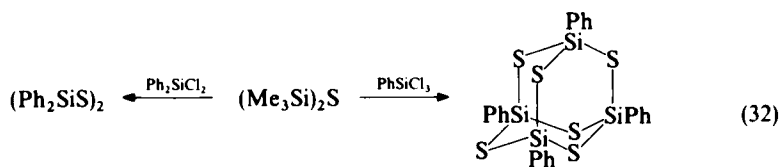
Low oxidation state transition-metal sulphide clusters of unpredictable composition can also be made from hexamethyldisilthiane.  $(\text{Ph}_3\text{P})_2\text{CoCl}_2(\text{L}_2\text{CoCl}_2)$  gives  $\text{Co}_6\text{S}_n\text{L}_6^+$  and  $\text{Co}_7\text{S}_6\text{L}_5\text{Cl}_2$ , while  $\text{L}_2\text{NiCl}_2$  forms the  $\text{Ni}_8$  clusters  $\text{Ni}_8\text{S}_6\text{L}_6\text{Cl}_2$  and  $\text{Ni}_8\text{S}_5\text{L}_7$ . ( $\text{L} = \text{Ph}_3\text{P}$ ). In parallel with the conversion of ketones to thioketones, hexamethyldisilthiane will convert the vanadyl dithiolate  $\text{O}=\text{V}(\text{SCH}_2\text{CH}_2\text{S})_2^-$  into the thiovanadyl derivative, and molybdates into thiomolybdates (equation 28)<sup>27</sup>.



### III. CYCLIC AND CAGE SILTHIANES

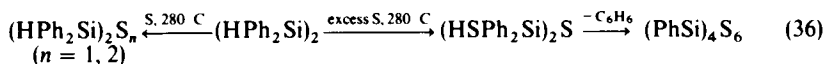
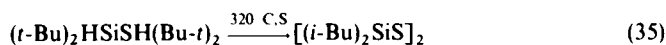
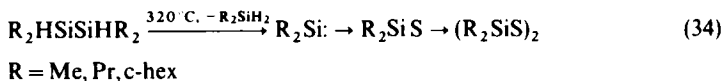
In addition to the methods available for preparing linear silthianes, cyclic and cage silthianes can also be made by heating organosilanes with hydrogen sulphide (equation 29)<sup>28</sup> or sulphur (equation 30). The linear disilthiane **5** results from the dibenzosilole and sulphur at 190 °C (equation 31)<sup>29</sup>. Cyclic and cage silthianes also result from the *trans*-silylation of  $(\text{Me}_3\text{Si})_2\text{S}$  or  $(\text{Me}_2\text{SiS})_3$  using chlorosilanes and pyridine (equations 32 and 33)<sup>30</sup>.



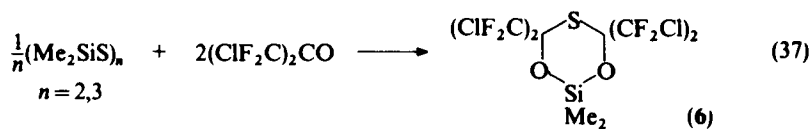


In sharp contrast to the siloxanes, no cyclosilthiane rings have been isolated with more than six members, though larger mixed siloxthianes are known. The cyclotrisilthiane is normally isolated in a room-temperature preparation if the substituent is alkyl, but the ring contracts to the cyclodisilthiane on heating. With phenyl derivatives, the cyclotrisilthiane appears to be the more stable. Few cyclodisiloxanes have been prepared to date, the mesityl (Mes) derivative resulting from the exposure of the disilene  $\text{Mes}_2\text{Si}=\text{SiMes}_2$  to air<sup>31</sup>. This behaviour of cyclosilthianes sharply contrasts with that of four-membered silicon-phosphorus rings which expand on heating.

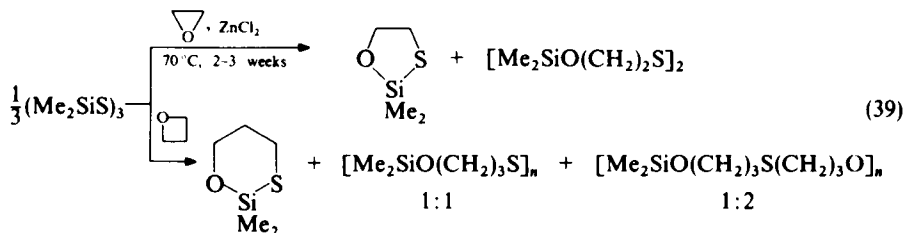
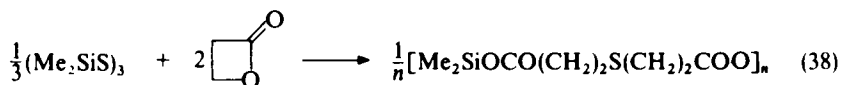
Heating alkyldisilanes with sulphur therefore leads to the cyclodisilthiane. The mechanism is thought to involve the generation of silylene  $\text{R}_2\text{Si}$ : which picks up sulphur to give the monomeric silathione. This then dimerizes (equation 34). No silathione has been isolated—even the bulky *t*-butyl compound appears to isomerize to the less hindered *i*-butyl derivative before dimerizing rather than remain monomeric (equation 35)<sup>32</sup>. By way of contrast, the pyrolysis of *sym*-tetraphenyldisilane with sulphur gives products indicative of first insertion of the Si-Si bond followed by that of Si-H. Thus sulphur first yields the disilthiane and disildithiane, then excess sulphur gives the silthiane dithiol  $(\text{HSPH}_2\text{Si})_2\text{S}$  which intramolecularly condenses through benzene elimination to the cage compound  $(\text{PhSi})_4\text{S}_6$  (equation 36)<sup>33</sup>.



Cyclosilthianes undergo many reactions similar to those of linear silthianes, notably with protic reagents and main-group covalent halides. They also insert fluoroacetones into each Si-S bond on heating to give the cyclic thioether **6** (equation 37), while in contrast,  $\beta$ -propiolactone immediately gives the polymer exothermically (equation 38). With trimethylene oxide, monomeric and polymeric products are formed by insertion into only one Si-S bond per Si, while oxirane gives monomer and polymer through insertion of one or both Si-S bonds (equation 39)<sup>13</sup>.





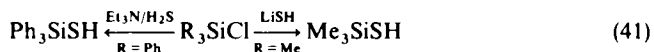
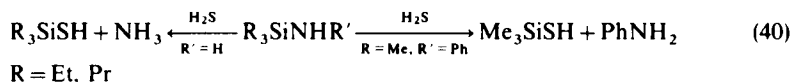


While  $(\text{Me}_2\text{SiS})_2$  has a planar structure with Si-S bond lengths of 215.2 pm<sup>34</sup>, spectroscopic evidence indicates that the cyclotrisilthiane is probably puckered, in contrast to the cyclotrisiloxanes. The cyclotrisilthiane resulting from  $\text{PhMeSiCl}_2$ ,  $\text{H}_2\text{S}$  and pyridine, however, occurs as a mixture of isomers in solution but crystallizes solely as the *trans*-isomer with a twisted-boat conformation with two methyl groups axial and Si-S bond length of 214.3 pm. In solution, however, it is thought to rapidly convert between one boat and two chair conformers. Distilling the trimer gives an equimolar mixture of the *cis*- and *trans*-cyclodisilthianes. Methyleneethyl and methylvinyl cyclotrisilthianes behave similarly, giving a mixture of isomers in solution, but heating  $[\text{Me}(\text{CH}_2=\text{CH})\text{SiS}]_3$  is also thought to cause polymerization as well as ring contraction<sup>35</sup>.

Despite the greater thermal stability of the four-membered alkyl substituted cyclodisilthianes, the cage compounds  $(\text{RSi})_4\text{S}_6$  are thought to possess the adamantane-like structure. The methyl derivative has such a structure (Si-S bond lengths 212.9 pm), like the germanium and tin derivatives<sup>36</sup>.

#### IV. SILANE THIOLS AND POLYSULPHIDES

Silane thiols are the first product of the thiolysis of an aminosilane (equation 40) or chlorosilane in the presence of a tertiary amine. They also result from chlorosilane and  $\text{LiSH}$  (equation 41)<sup>37</sup>.



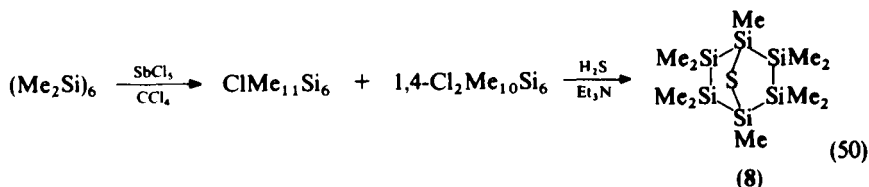
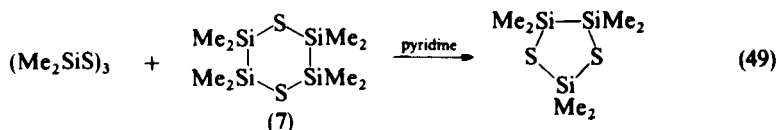
Silane thiols can also be prepared by heating the silane and sulphur. While  $\text{Me}_3\text{SiSH}$  slowly disproportionates to the silthiane on heating, arylsilane thiols are thermally much more stable. The diphenyl *n*-propyl derivative  $\text{Ph}_2\text{PrSiSH}$  can be distilled at 209.5 °C/25 mm (equation 42)<sup>33, 38</sup>.  $\text{Ph}_2\text{SiSH}$  is a stronger acid than thiopenol and, like



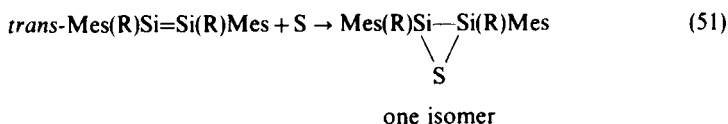
alkylsilane thiols, can be readily metallated, thence substituting  $\text{VOCl}_3$ . It also forms sharp melting salts with amines, without inducing disproportionation to the disilthiane



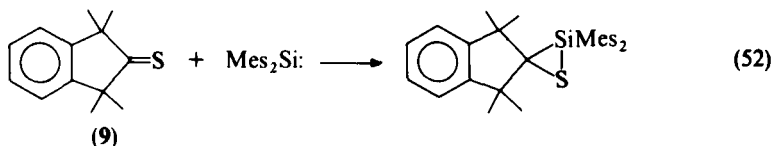
$[(Et_2Si)_2S]_2$  and the silathione  $Et_2Si=S$  (equation 48)<sup>43</sup>. Similar behaviour has been observed for  $R = Me$ ,  $(Me_2Si)_4$  giving monosubstitution at  $50^\circ C$ , while the cyclosilthiane  $(Me_2SiS)_3$  and the *sym*-dithiatetrasilacyclohexane (7) gives the 5-membered derivative (equation 49)<sup>44</sup>. The bicyclic 7-thiahexasilanorbornane (8) results through 1,4-chlorination of  $(Me_2Si)_6$  using  $SbCl_5$  followed by thiolysis with  $H_2S$  (equation 50)<sup>45</sup>.



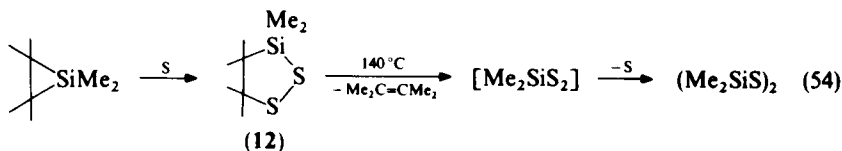
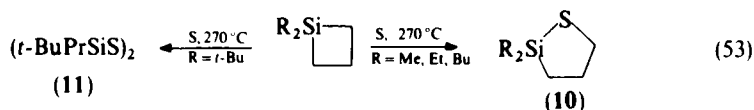
The disilenes  $[Mes(R)Si]_2$  ( $R = Mes$  or  $t-Bu$ ) will both add sulphur stereospecifically in solution to give colourless crystalline adducts. The structure of the tetramesityl derivative shows the product to have a three-membered isosceles ring which shows no tendency to dimerise to the 1,4-dithia six-membered one reported for less hindered substituents (equation 51)<sup>46</sup>. A double-bond addition is also reported for silylenes to thioketones.



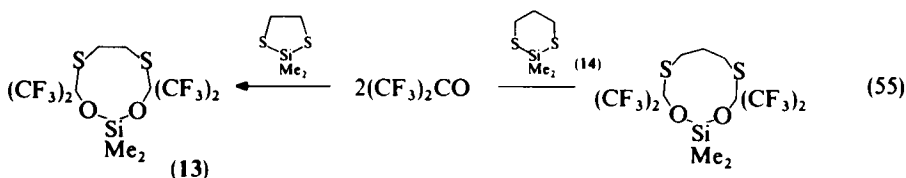
Surprisingly, the three-membered ring so formed is again isosceles despite three different ring atoms, and the silathiacyclopropanes so formed from the tetramethyl-2-indanethione **9** or adamantanethione are both crystalline solids stable to oxygen, water and heat. Unlike the  $Si_2S$  ring above, the  $SiSC$  ring shows Si-S bonds to be shorter than usual (209.3 pm) (equation 52)<sup>47</sup>. Sulphur readily inserts into the Si-C bond of strained rings on



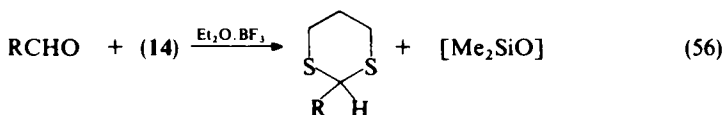
heating, 1,1-dialkyl-1-silacyclobutane giving the silathiacyclopentane **10**, but if substituted by  $t$ -butyl, then the cyclodisilthiane **11** results through loss of isobutene (equation 53)<sup>32</sup>. With hexamethylsilirane, again a five-membered ring results through insertion of two sulphur atoms, but this reaction occurs at room temperature. The product **12** is a yellow solid, which shows the large fragment ion of  $Me_2SiS_2$  in the mass spectrum. Heating **12** gives tetramethylcyclodisilthiane and sulphur as the main sulphur products (equation 54)<sup>48</sup>.



2-Sila-1,3-dithiacyclopentane readily inserts strained ethers and lactones, as well as chlorofluoroketones, to give 1:2 polymers. With  $(\text{CF}_3)_2\text{CO}$ , however, the cyclic monomer **13** has been reported, though slight changes in reaction conditions give only polymer. In contrast, the six-membered dithiasilacyclohexane **14** only yields the monomer (equation 55)<sup>13</sup>.



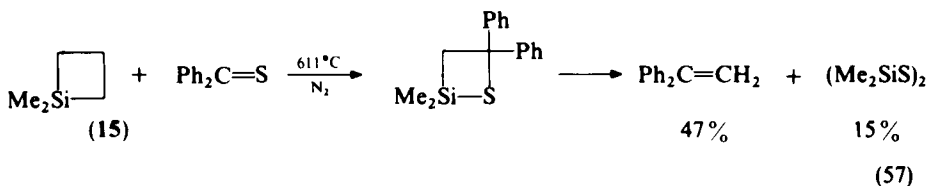
Aldehydes and acetals are rapidly converted to dithianes with **14** in the presence of stoichiometric amounts of  $\text{Et}_2\text{O} \cdot \text{BF}_3$ , and the reaction is completely selective in the presence of ketones (equation 56)<sup>49</sup>.



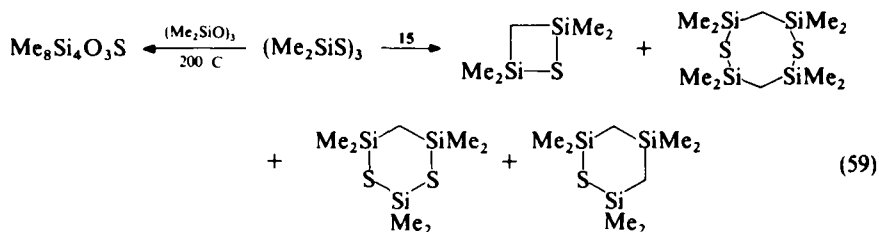
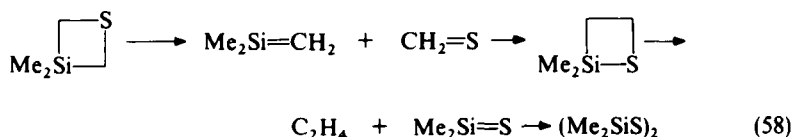
## VI. THE SILICON-SULPHUR DOUBLE BOND

The ring contraction of cyclotrisilthianes and the rearrangements of the ring compounds mentioned in the last section support the intermediacy of monomeric silathiones  $\text{R}_2\text{Si}=\text{S}$ , though none have been isolated to date. Cyclotetrasiloxanes also ring contract on heating, through silanone elimination<sup>50</sup>.

The first conclusive evidence for the intermediacy of silathiones came in 1975 from the pyrolysis of 1,1-dimethyl-1-silacyclobutane **15** with thiobenzophenone, giving a Wittig-type reaction, and forming olefin and cyclodisilthiane (equation 57)<sup>51</sup>. 2,2-dimethyl-2-

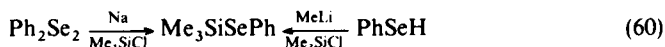


silathietane is also thought to result as an intermediate in the pyrolysis of 3,3-dimethyl-3-silathietane, since trapping in argon yields  $\text{Me}_2\text{Si}=\text{CH}_2$  and  $\text{CH}_2=\text{S}$  as well as  $(\text{Me}_2\text{SiS})_2$  (equation 58). Heating  $(\text{Me}_2\text{SiS})_3$  with **15**, gives a series of silicon substituted four-, six- and eight-membered rings, while with  $(\text{Me}_2\text{SiO})_3$  the eight-membered mixed siloxthiane is formed (equation 59). Calculations give a Si-S bond length for  $\text{Me}_2\text{Si}=\text{S}$  of 199.3 pm<sup>52</sup>.

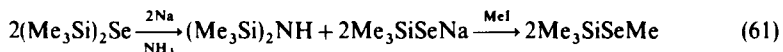


## VII. SILYL DERIVATIVES OF SELENIUM

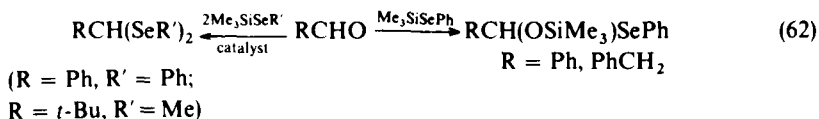
Many of the synthetic methods used for silicon-sulphur compounds are equally applicable to selenosilanes, though yields are rarely as good<sup>53</sup>. Phenylselenol gives good yields but its air sensitivity makes the reductive silylation of diphenyl diselenide a more attractive method (equation 60)<sup>54</sup>. Yields of selenosilanes prepared from an alkyl or aryl



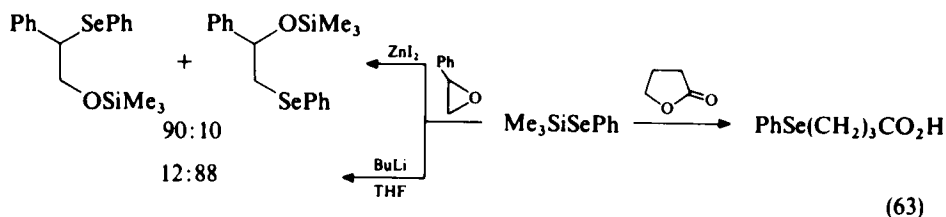
bromo-Grignard reagent, elemental selenium, and then  $\text{Me}_3\text{SiCl}$  are generally around 30%, while the phenyl derivative prepared in this way also gives the bis-silyl selenide  $(\text{Me}_3\text{Si})_2\text{Se}$ <sup>55</sup>. A better method of preparing methylselenotrimethylsilane involves metalation of  $(\text{Me}_3\text{Si})_2\text{Se}$  (prepared in good yield from  $\text{Na}_2\text{Se}$ ), with sodium in liquid ammonia, followed by methylation (equation 61)<sup>56</sup>.



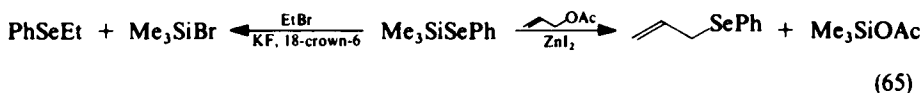
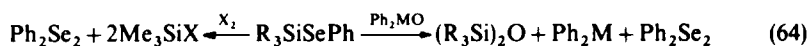
Both methyl and phenylselenosilanes react readily with carbonyl compounds in the presence of a catalyst. Aldehydes give *O*-silyl hemiselenoacetals and diselenoketals through 1,2-addition (equation 62). By way of a contrast,  $\alpha,\beta$ -enones add 1,4- and saturated ketones do so slowly, though with  $\text{AlCl}_3$  the bis-selenoacetal results<sup>57</sup>.



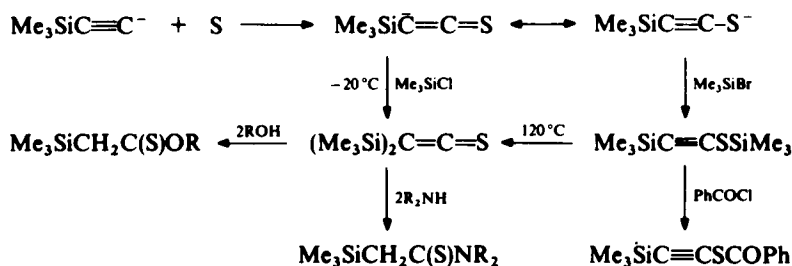
As with thiosilanes, so the selenosilanes open oxygen substituted rings, but better yields result if selenium is rendered hard through using 18-crown-6 and K.F. Acid catalysis also influences the regioselectivity of the reactions (equation 63)<sup>58</sup>.



Phenylselenosilanes reduce the oxides  $\text{Ph}_2\text{MO}$  ( $\text{M} = \text{S}, \text{Se}, \text{Te}$ ) and other functionally substituted sulphoxides to the divalent derivatives and are oxidised by halogens (equation 64). They substitute the trichlorides  $\text{MCl}_3$  ( $\text{M} = \text{B}, \text{P}, \text{As}$ ), readily substitute allyl acetate in the presence of  $\text{ZnI}_2$  and bromoethane with 18-crown-6 and  $\text{KF}$  (equation 65)<sup>58,59</sup>.



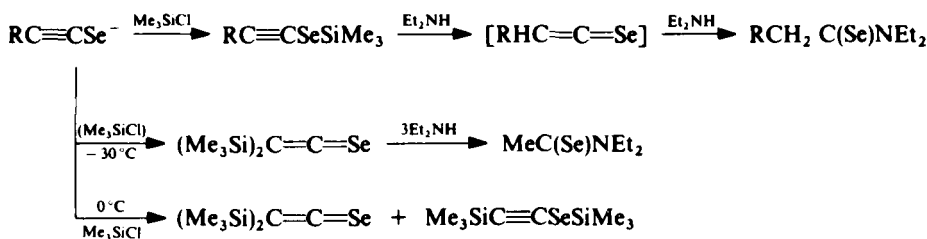
The anion formed from  $\text{Me}_3\text{SiC}\equiv\text{ClI}$  and sulphur gives the bis-silylthio ketene with  $\text{Me}_3\text{SiCl}$ , which is thermally stable and reacts with 2 moles of alcohol or amine to give the thioester or thioamide. With  $\text{Me}_3\text{SiBr}$  however, the anion behaves as the thioynol to form the isomeric silylated alkyne thiol which gives the *S*-ethynyl thioester with  $\text{PhCOCl}$  and isomerizes to the thio ketene at  $120^\circ\text{C}$  (Scheme 4)<sup>60</sup>.



SCHEME 4

With selenium, silylated alkyne selenols can be readily prepared if  $\text{R}$  is alkyl. They are more stable than the isomeric selenoketene but react with amines through such an intermediate. If  $\text{R}$  is  $\text{Me}_3\text{Si}$  however, then the bis-silylselenoketene results as the sole product at  $-30^\circ\text{C}$ , but as an isomeric mixture with the thermally unstable alkyne selenol at higher temperatures (Scheme 5)<sup>61</sup>.

Bis(trimethylsilyl)selenide, like the silthiane<sup>27</sup>, reacts readily with divalent cobalt complexes ( $\text{Ph}_3\text{P}$ )<sub>2</sub>CoCl<sub>2</sub> ( $\text{L}_2\text{CoCl}_2$ ) and  $\text{Ph}_3\text{PCoCl}_3^-$  ( $\text{LCoCl}_3^-$ ) to give a wide range of polynuclear cage compounds of formal oxidation state two or more. With the former, the three clusters  $\text{Co}_4\text{Se}_4\text{L}_4$ ,  $\text{Co}_6\text{Se}_8\text{L}_6$  and  $\text{Co}_9\text{Se}_{11}\text{L}_6$  result, while  $\text{LCoCl}_3^-$  gives, in addition to these neutral complexes,  $\text{Co}_6\text{Se}_8\text{L}_6^+$  and  $\text{Co}_8\text{Se}_8\text{L}_6^{n+}$  ( $n=0, 1$ )<sup>62</sup>. The analogous nickel complexes (with  $\text{Ph}_3\text{P}=\text{L}$ ) also form an extensive range of clusters with

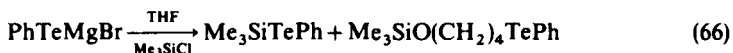


SCHEME 5

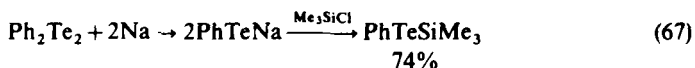
( $\text{Me}_3\text{Si}$ )<sub>2</sub>Se, using acetonitrile as solvent. They have a tendency to contain less selenium atoms than metal, and to be larger in size.  $\text{Ni}_6\text{Se}_5\text{L}_6$ ,  $\text{Ni}_{12}\text{Se}_{11}\text{L}_8\text{Cl}^{2+}$ ,  $\text{Ni}_{15}\text{Se}_{15}\text{L}_6$ , along with  $\text{Ni}_{12}\text{Se}_{12}(\text{PEt}_3)_6$  result from  $(\text{Et}_3\text{P})_2\text{NiCl}_2$  in toluene, while  $\text{L}_2\text{NiCl}_2$  and ( $\text{Me}_3\text{Si}$ )<sub>2</sub>Se in toluene gives  $\text{Ni}_{34}\text{Se}_{22}\text{L}_{10}$ <sup>63</sup>. With  $\text{CpFe}(\text{CO})_2\text{Br}$ , the ionic complex  $\{[\text{CpFe}(\text{CO})_2]_3\text{Se}^+\}_2(\text{Fe}_4\text{Se}_4\text{Br}_4)^{2-}$  results<sup>64</sup>.

### VIII. SILYL DERIVATIVES OF TELLURIUM

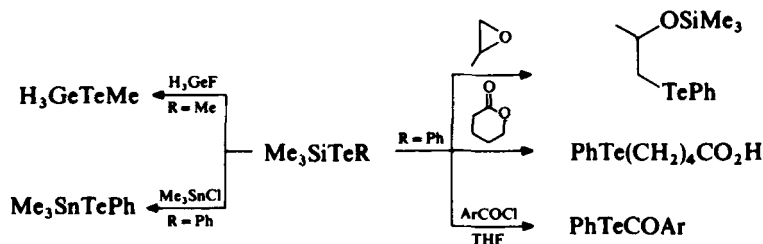
*p*-Tolytellurotrimethylsilanes result in low yield if prepared from a bromo-Grignard tellurium system while with bromobenzene, only the bis-silyl telluride forms<sup>55</sup>. Using THF as solvent gives  $\text{PhTeSiMe}_3$  in 40% yield, but ( $\text{Me}_3\text{Si}$ )<sub>2</sub>Te (10%) and the silyl ether  $\text{Me}_3\text{SiO}(\text{CH}_2)_4\text{TePh}$  (45%) are also formed, the latter through cleavage of THF (equation 66)<sup>65</sup>.



Better yields result from the addition of Te to RLi (R = Me, Ph) in THF, followed by addition of the chlorosilane, and while small quantities of ( $\text{Me}_3\text{Si}$ )<sub>2</sub>Te are observed, there is no evidence of the THF cleavage product. Cleavage of  $\text{Ph}_2\text{Te}_2$  by Na in THF, followed by silylation, also gives a good yield of the tellurosilane (equation 67)<sup>66</sup>.



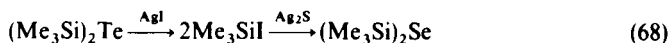
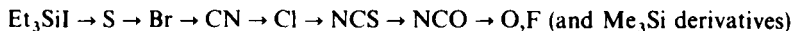
The absence of THF cleavage may well be a result of the absence of an iodide catalyst. Organic iodides can be used to prepare the Grignard reagent, often initiated by a crystal of iodine. Many ethers, strained and unstrained, esters and lactones are readily cleaved by  $\text{PhTeSiMe}_3$  in the presence of catalytic amounts of  $\text{ZnI}_2$ . The reactions are more facile



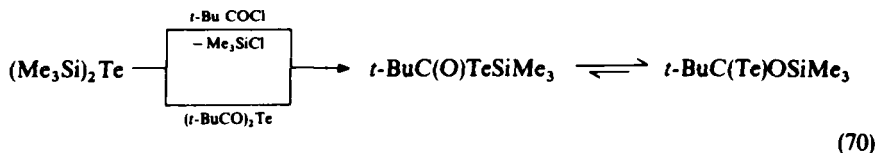
SCHEME 6

than with the other chalcogenosilanes. Aroyl chlorides readily cleave  $\text{PhTeSiMe}_3$  in THF to give the tellurol esters in good yield. In addition they react with germyl fluoride and trimethyltin chloride, the reactions befitting the formation of soft-soft and hard-hard products (Scheme 6)<sup>66</sup>.

$(\text{Me}_3\text{Si})_2\text{M}$  ( $\text{M} = \text{Se}, \text{Te}$ ) can be readily made by silylation of the lithium chalcogenide. The telluride can be converted to the selenide using first  $\text{AgI}$  then  $\text{Ag}_2\text{Se}$ , providing an extension to the Conversion Series established by Eaborn for silver salts (equation 68)<sup>21a, 65, 67</sup>.



$(\text{Me}_3\text{Si})_2\text{M}$  ( $\text{M} = \text{Se}, \text{Te}$ ) both react with germyl fluoride to give  $(\text{H}_3\text{Ge})_2\text{M}$  while, for  $\text{M} = \text{Te}$ , acyl chlorides give the diacyl telluride if in excess. However, addition of  $(\text{Me}_3\text{Si})_2\text{Te}$  to  $(\text{MeCO})_2\text{Te}$  immediately precipitates  $\text{Te}$  through the intermediacy of  $\text{MeC(Te)OSiMe}_3$  and gives a mixture of isomeric silyl enols (equation 69). With pivaloyl chloride, however, hindrance impedes precipitation of  $\text{Te}$  and an isomeric mixture of carbonyl and tellurocarbonyl derivatives results in the ratio 1:2 through 1,3-silyl shifts (equation 70)<sup>68</sup>.



Both sulphur and selenium react with  $\text{Et}_3\text{SiH}$  to give only  $\text{Si-H}$  insertion, the thiol and selenol cleaving  $\text{Et}_3\text{Al}$ . With tellurium however, the disiltellurane results. This gives the silyltellurol with  $\text{CF}_3\text{CO}_2\text{H}$ .  $\text{Et}_3\text{SiMH}$  ( $\text{M} = \text{S}, \text{Se}, \text{Te}$ ) all react 1:1 with  $\text{Et}_3\text{Al}$ , the product then disproportionating to give  $(\text{Et}_3\text{Si})_2\text{M}$  and  $(\text{EtAlM})_x$  (equation 71). With tribenzylsilane, selenium gives the cyclic dimer  $[(\text{PhCH}_2)_2\text{SiSe}]_2$  illustrating, as with sulphur, the greater stability of the four-membered ring. With the methyl derivatives, an equilibrium between four- and six-membered rings is observed at room temperature<sup>69, 56</sup>.



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# Appendix to 'Chemistry of compounds with silicon–sulphur, silicon–selenium and silicon–tellurium bonds'<sup>†</sup>

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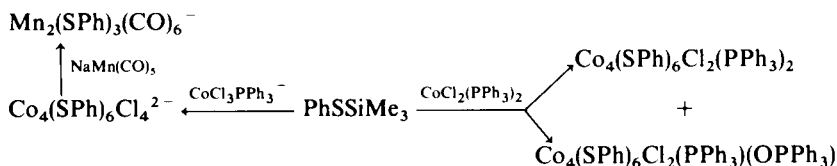
This appendix covers the years 1987 to early 1990. Two reviews cover the chemistry of silyl-substituted organosulphur compounds in organic synthesis, including the 1,2-anionic rearrangement of thiosilanes, and the use of  $(\text{Me}_3\text{Si})_2\text{E}$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ) in preparing new transition metal chalcogen clusters<sup>70</sup>.

## \*I. THIOSILANES

Thiosilanes  $\text{Me}_3\text{SiSR}$  form adducts with aluminium halides  $\text{AlX}_3$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), which are stable at room temperature, but decompose on warming to give the organothioaluminium dihalides<sup>71</sup>. Phenylthiotrimethylsilane gives the tetranuclear cluster complexes

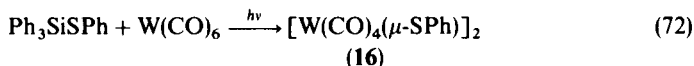
<sup>†</sup>The material in this appendix is divided in the same manner as in the body of the original Chapter 23 in *The Chemistry of Organic Silicon Compounds*. The section numbers in the appendix are preceded by an asterisk. The numbers of structures, equations, schemes and references run continuously in the original chapter and the appendix.

$\text{Co}_4(\text{SPh})_6\text{Cl}_4^{2-}$  or  $\text{Co}_4(\text{SPh})_6\text{Cl}_2(\text{PPh}_3)_2$  from  $\text{CoCl}_3(\text{PPh}_3)^-$  or  $\text{CoCl}_2(\text{PPh}_3)_2$ , the former giving  $\text{Mn}_2(\text{SPh})_3(\text{CO})_6^-$  with  $\text{NaMn}(\text{CO})_5$  (Scheme 7)<sup>72</sup>.

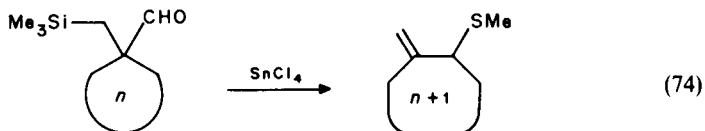
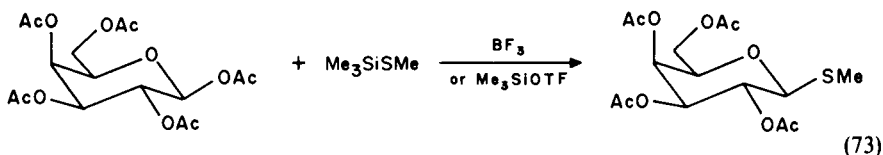


SCHEME 7

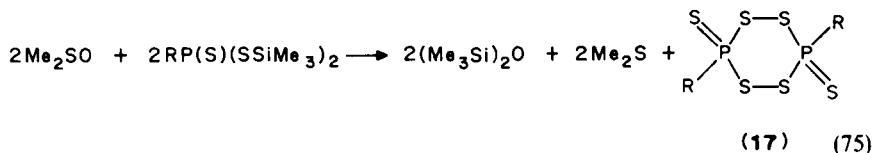
Phenylthiotriphenylsilane, which can be conveniently prepared from DABCO·HSPH and  $\text{Ph}_3\text{SiCl}$ , has a Si—S bond length of 215.6 pm, and substitutes tungsten hexacarbonyl on photolysis to give the binuclear phenylthio bridged complex **16**. This has a short W—W bond and is thought to be diamagnetic (equation 72)<sup>73</sup>.



Methylthiotrimethylsilane converts *per-O*-acetyl glycopyranosides in the presence of  $\text{BF}_3$  or trimethylsilyl trifluoromethanesulphonate to the 1,2-*trans*-1-methyl thioglycosides stereoselectively (equation 73, for example), and 1-(trimethylsilylmethyl)cycloalkancarboxaldehydes to 2-methylenecycloalkyl sulphides, in the presence of  $\text{SnCl}_4$  (equation 74)<sup>74</sup>. The smells of carbinols and silanols, thiocarbinols (thiols) and silane thiols are compared and discussed in the light of the Amoore theory which relates size and structure to odour<sup>75</sup>.



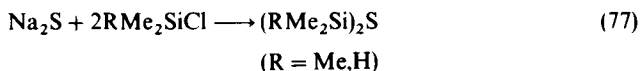
The silyl trithiophosphonates  $\text{RP}(\text{S})(\text{SSiMe}_3)_2$  ( $\text{R} = \text{Me}, t\text{-Bu}$ ) can be oxidized by dimethyl sulphoxide to the six-membered phosphorus-sulphur heterocycle **17** (equation 75), which occurs as four structural isomers in solution if  $\text{R} = \text{Me}$ , 2 chair and 2 twist-boat, with Me preferring the axial position. With  $\text{R} = t\text{-Bu}$ , only the twist-boat isomer with *trans*  $t\text{-Bu}$  groups is observed. The trithiophosphonates also condense with the polysulphur dichlorides  $\text{S}_n\text{Cl}_2$  ( $n = 3, 4, 5$ ) to give the P(V) substituted polysulphur rings (equation 76)<sup>76</sup>.



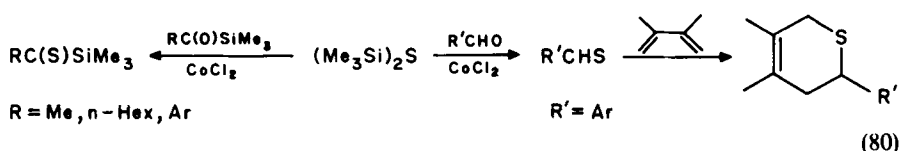
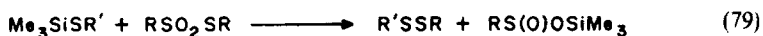
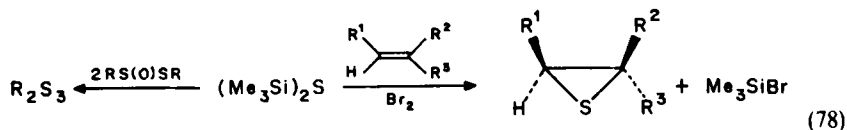


## \*II. LINEAR SILTHIANES

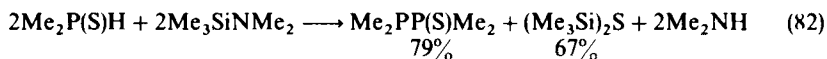
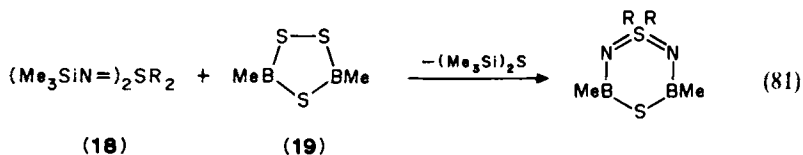
Hexamethyldisilthiane ( $\text{Me}_3\text{Si}$ )<sub>2</sub>S results in excellent yield from sodium sulphide if this is prepared from its elements using 10% naphthalene in THF. *Sym*-tetramethyldisilthiane can be prepared similarly (equation 77)<sup>77</sup>.



Thiiranes form in 30% yield from alkenes with ( $\text{Me}_3\text{Si}$ )<sub>2</sub>S and bromine at  $-78^\circ\text{C}$ . The reaction is thought to involve  $\text{Me}_3\text{SiSBr}$  as intermediate, which then adds to the alkene, eliminating  $\text{Me}_3\text{SiBr}$  (equation 78). With thiosulphinates and thiosulphonates, hexamethyldisilthiane gives symmetrical trisulphides, while thiosilanes form unsymmetrical disulphides (equation 79)<sup>78</sup>. In the presence of  $\text{CoCl}_2$ , hexamethyldisilthiane converts acyl silanes and aldehydes to their thio analogues; the thioaldehydes then add to 2,3-dimethylbuta-1,3-diene (equation 80)<sup>79</sup>.

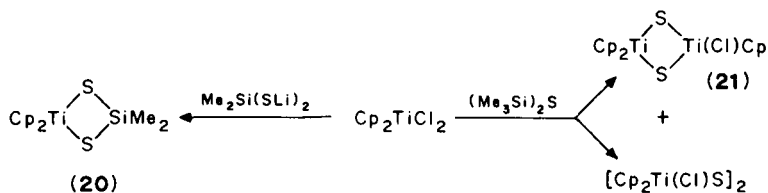


Hexamethyldisilthiane is eliminated in the reaction of the silylated sulphur(VI) diimide **18** with the boron-sulphur heterocycle **19** (equation 81). Attempts to make the silyl ester of dimethylthiophosphorous acid  $\text{Me}_3\text{SiSPMe}_2$  from  $\text{Me}_2\text{P(S)H}$  and  $\text{Me}_3\text{SiNMe}_3$  result in silthiane elimination and formation of the diphosphine monosulphide in very good yield (equation 82)<sup>80</sup>.



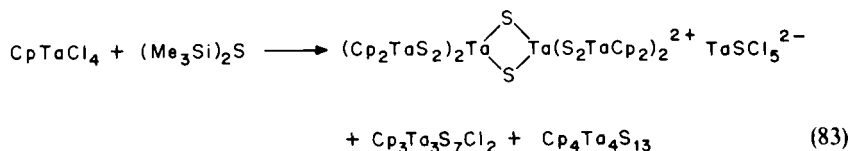
Titanocene dichloride couples with  $\text{Me}_2\text{Si(SLi)}_2$  to give the four-membered heterocycle (**20**)<sup>81</sup>, which converts  $\text{WOS}_3^{2-}$  and  $\text{WO}_4^{2-}$  into  $\text{WS}_4^{2-}$  without the tendency to reduce,

inherent in using  $(\text{Me}_3\text{Si})_2\text{S}$  (see Chapter 6, Section IX).  $(\text{Me}_3\text{Si})_2\text{S}$  and titanocene dichloride give two dimetallo products through partial chlorine substitution and bridging, either with two separate sulphur atoms forming the four-membered ring **21**, or as an  $\mu_2\text{-}\eta^1\text{-S}_2$  unit giving a Ti-S-S-Ti chain (Scheme 8)<sup>82</sup>.

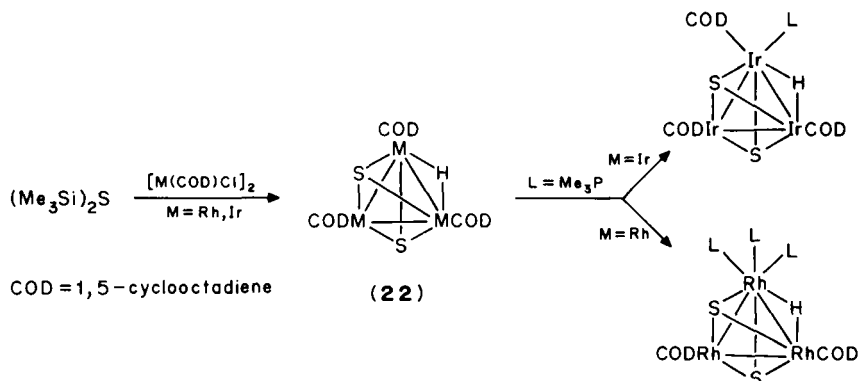


SCHEME 8

Titanium tetrachloride gives  $\text{TiSCl}_2$  with  $(\text{Me}_3\text{Si})_2\text{S}$ , hydrolysis or oxidation giving the two clusters  $\text{Ti}_3\text{O}(\text{S}_2)_3\text{Cl}_4$  and  $\text{Ti}_4\text{O}(\text{S}_2)_4\text{Cl}_6$ , while chloride gives  $\text{TiSCl}_4^{2-}$ , which oxidizes to  $\text{Ti}_3\text{O}(\text{S}_2)_3\text{Cl}_5^{2-}$  with oxygen centred between the three metal atoms<sup>83</sup>. Niobium and tantalum, molybdenum and tungsten polychlorides also give thiochlorides using  $(\text{Me}_3\text{Si})_2\text{S}$ <sup>84</sup>, while  $\text{CpTaCl}_4$  forms a variety of sulphur bridged metal clusters containing mono-, bi-, tri- and tetra-dentate sulphide and bi- and tri-dentate disulphide bridges (equation 83)<sup>85</sup>.



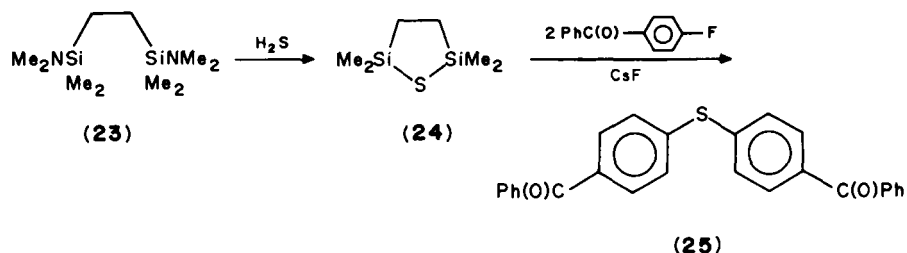
Low oxidation state rhodium and iridium complexes behave similarly, the chlorides  $[\text{M}(\text{COD})\text{Cl}]_2$  with  $(\text{Me}_3\text{Si})_2\text{S}$  giving the 48-electron bridged hydride complexes (**22**), which in the presence of  $\text{Me}_3\text{P}$  yield the 50-electron complexes  $\text{Rh}_3(\text{H})(\mu_3\text{-S})_2(\text{COD})_2(\text{PMe}_3)_3$  and  $\text{Ir}_3(\text{H})(\mu_3\text{-S})_2(\text{COD})_3\text{PMe}_3$  (Scheme 9)<sup>86</sup>.



SCHEME 9

## \*III. CYCLIC SILTHIANES

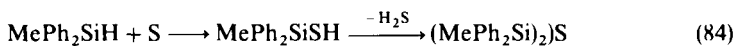
Condensing the 2,5-bis(amino)-2,5-disilohexane derivative (23) with  $H_2S$  gives the 1,3-disila-2-thiacyclopentane (24), which acts as a useful sulphur transfer agent, condensing 2 moles of 4-fluorobenzophenone in the presence of CsF, to give the bisaryl sulphide (25) (Scheme 10)<sup>87</sup>.



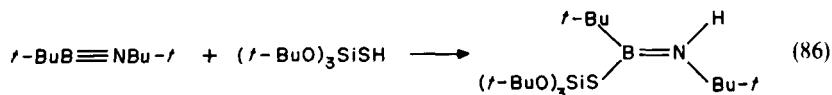
SCHEME 10

## \*IV. SILANE THIOLS AND POLYSULPHIDES

Sulphur reacts with methyl-diphenylsilane to give the silane thiol. This, on heating to  $200^\circ C$ , forms the disilthiane, m.p.  $109-111^\circ C$ , with SiSSi angle of  $108.7^\circ$  and Si-S bonds of 214.0 and 215.4 pm (equation 84). Heating the disilanes  $R_3SiR'_2SiH$  ( $R = R' = Ph$  or  $Me$ ;  $R = Ph$ ,  $R' = Me$ ) with  $(p-FC_6H_4)_2S_2$  gives the disilanyl aryl sulphides and thiol, whereas with sulphur, the silane thiol  $R_3SiSH$  and the diorganosilathione result, the latter dimerising to the cyclic disilthiane  $(R'_2SiS)_2$  (equation 85)<sup>88</sup>.



The kinetics of the alcoholysis of the Si-S bond in  $t-Bu_n(i-PrO)_{3-n}SiSH$  in the presence of imidazole indicates nucleophilic attack at silicon as the rate-determining step, with reactivity decreasing in the order  $n = 1 > 2 > 0 > 3$ <sup>89</sup>. With carboxylic acids,  $(RO)_3SiSH$  gives the acyloxysilanes almost quantitatively, while the silane thiols  $R_3SiSH$  ( $R = Ph, RO$ ) condense with glycols to give the silyl ether<sup>90</sup>.  $(t-BuO)_3SiSH$  also adds to the triple bond of  $t-BuB \equiv NBu-t$ , to give the (Z)-conformer with B-N and Si-S bond lengths of 137 and 211 pm, respectively (equation 86)<sup>91</sup>.

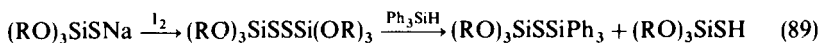
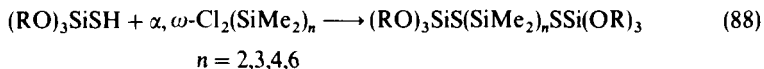


A series of polysilanes terminally substituted by  $(RO)_3SiS$  results from  $(RO)_3SiSH \cdot NEt_3$  and the appropriate chloropolysilanes (equations 87 and 88), their NMR and charge-transfer spectra supporting conjugation between the  $\sigma-Si-S$  and  $\sigma-Si-Si$  bonds<sup>92</sup>. Similarly, bis-silyl polysulphides result from  $(RO)_3SiSNa$  with iodine or  $S_2Cl_2$ , the disulphide, which has Si-S bonds of 213.2 pm, forming the silthiane and silane thiol on heating with  $Ph_3SiH$  at  $180^\circ C$  (equation 89)<sup>93</sup>.

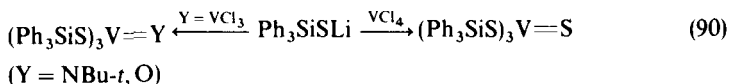


$$n = 2, 4$$



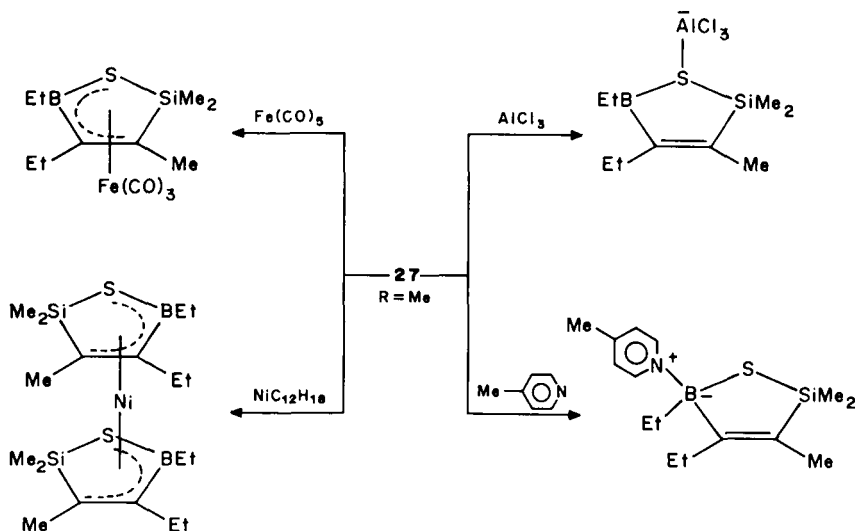
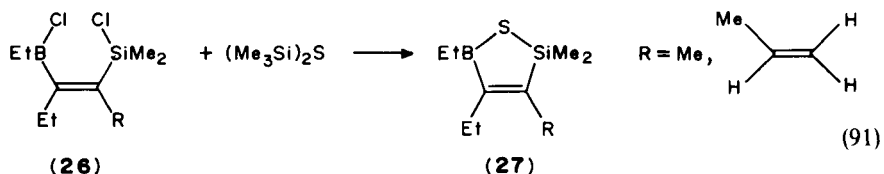


The thiovanadates  $(\text{Ph}_3\text{SiS})_3\text{V}=\text{X}$  ( $\text{X} = t\text{-BuN, O, S}$ ) are formed from  $\text{Ph}_3\text{SiSLi}$  with  $t\text{-BuN}=\text{VCl}_3$ ,  $\text{VOCl}_3$  and  $\text{VCl}_4$ , the last through disproportionation. The imide shows Si—S bond lengths between 213.6 and 215.4 pm, while the  $^{51}\text{V}$  NMR spectra show downfield (increasing positive) shifts on increasing sulphur substitution, relative to  $\text{VOCl}_3$  as standard (equation 90)<sup>94</sup>.



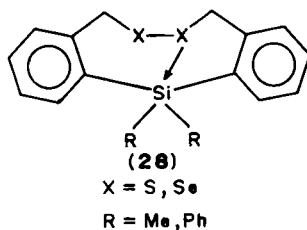
#### \*V. MISCELLANEOUS RINGS CONTAINING THE SI—S BOND

The 2,5-dihydro-1,2,5-thiasilaborole (**27**) is formed from the alkene (**26**), appropriately chlorinated, and  $(\text{Me}_3\text{Si})_2\text{S}$  (equation 91). It gives 1:1 adducts with amines, amine oxides and phosphines, and acts as a 4 $\pi$ -electron donor to metal carbonyl residues, and to nickel through the intermediacy of the cyclododecatriene complex (Scheme 11)<sup>95</sup>.



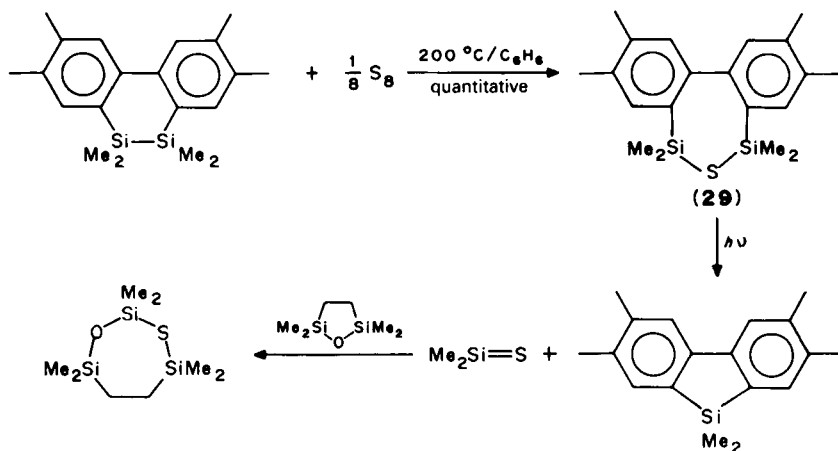
SCHEME 11

The structures of a series of 8,13-dihydro-5*H*-dibenzol[*d,g*][1,2,6]dithiasiloinines (**28**) with Me or Ph substituents at Si show transannular S → Si interactions with transannular distances of about 3.4 Å, some 0.5 Å shorter than the van der Waals interaction distance. The bond energy is estimated to be less than 3 kcal mol<sup>-1</sup>. A shortening of 0.4 Å is also observed for the selenium derivative with Ph substitution at Si, but no shortening is found for Me substituents at Si<sup>96</sup>.

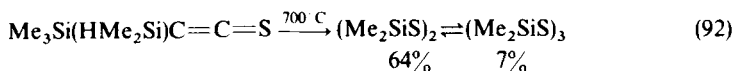


### \*VI. THE SILICON-SULPHUR DOUBLE BOND

Dimethylsilathione Me<sub>2</sub>Si=S results on irradiating the bridged biphenyl derivative **29**, and is trapped as the insertion adduct of 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane in 36% yield (Scheme 12). It can also be extruded from silylthioketenes on thermolysis to give the cyclodi- and trisilthianes (equation 92), and is detected in the electron impact mass spectra of 2-thienylsilanes<sup>97</sup>.

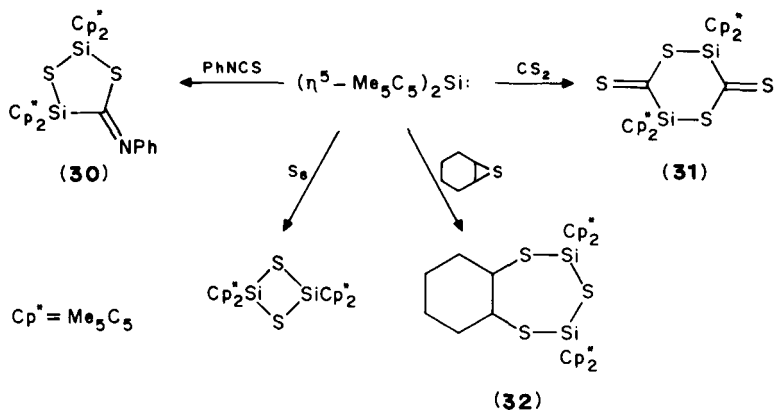


SCHEME 12



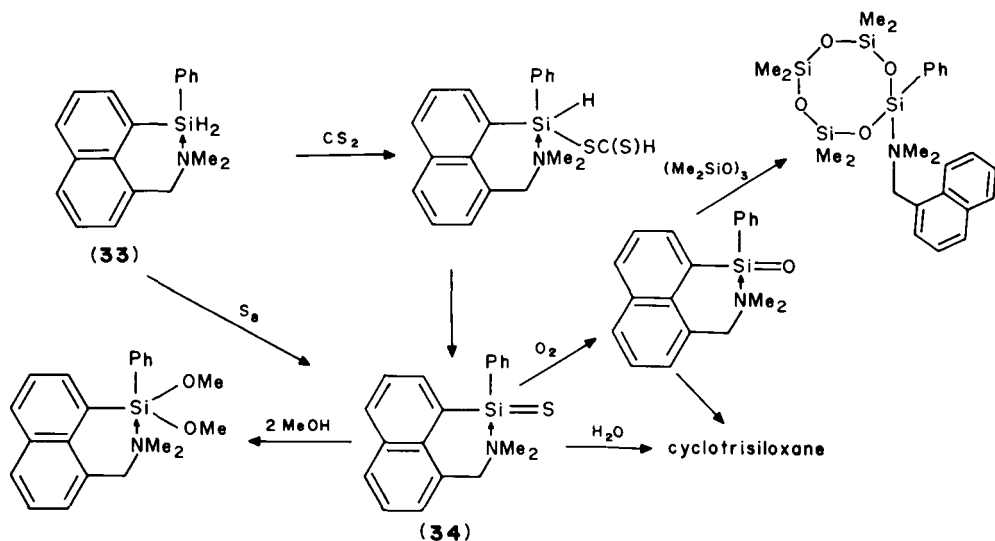
( $\eta^5\text{-Me}_5\text{C}_5$ )<sub>2</sub>Si: reacts with phenyl isothiocyanate to give the five-membered heterocycle **30** as the final product. This is thought to result from addition to the silylene and elimination of the isonitrile, the silathione so formed then adding to the isothiocyanate, this adduct inserting the original silylene. With CS<sub>2</sub>, the final product is the six-membered

dithione (31)<sup>98</sup>. However, sulphur gives the cyclodisilthiane directly, and cyclohexene sulphide the silathione insertion product (32) (Scheme 13)<sup>99</sup>. So far, the silathione ( $\eta^5\text{-Me}_5\text{C}_5$ )<sub>2</sub>Si=S has not been trapped.



SCHEME 13

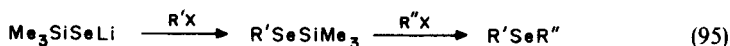
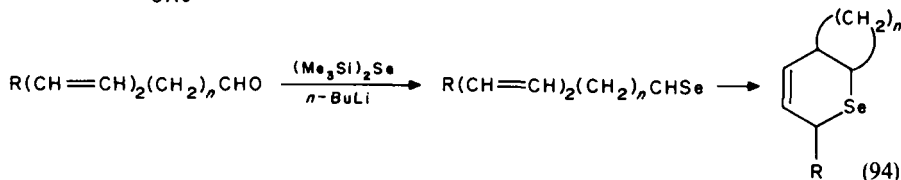
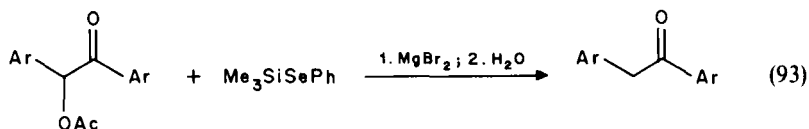
The five-coordinate silane (33) reacts with CS<sub>2</sub> to give the dithioformate through addition across the C=S double bond. This decomposes at room temperature to give the silathione (34) which is stable and has a Si—S bond length of 201.3 pm, some 7–8% shorter than the single bond length. It is also formed very easily from 33 and elemental sulphur at room temperature, in contrast to the normal rate of insertion of sulphur into Si—H bonds (equation 84). It reacts with MeOH to give the dimethoxy derivative, and with oxygen to form the silanone which inserts (Me<sub>2</sub>SiO)<sub>3</sub> and trimerises, this product also resulting on hydrolysis of 34 (Scheme 14)<sup>100</sup>.



SCHEME 14

## \*VII. SILYL DERIVATIVES OF SELENIUM

Aryl-substituted acyloin acetates can be readily deacyloxyated by phenylselenotrimethylsilane, hydrolysis giving the ketone (equation 93)<sup>101</sup>. Bis(trimethylsilyl)selenide with *n*-BuLi gives Me<sub>3</sub>SiSeLi, which converts dienals to bicyclic selenides (equation 94) and forms mixed selenides with alkyl bromides and acyl chlorides consecutively (equation 95)<sup>102</sup>.

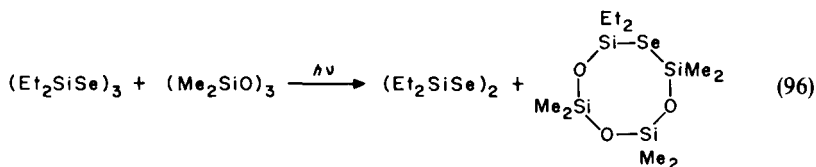


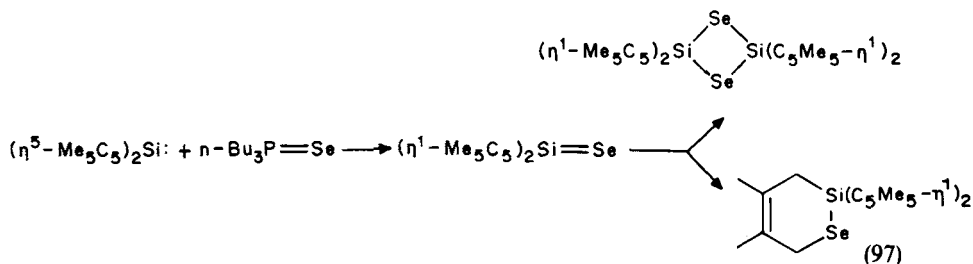
Bis(trimethylsilyl)selenide readily condenses with a variety of organometal halide derivatives to give the appropriate metal selenide clusters. Titanocene dichloride yields the bimetallic bridged complex Cp<sub>2</sub>Ti<sub>2</sub>Se<sub>2</sub>Cl, analogous to the sulphur derivative **21**, and CpTiCl<sub>3</sub> yields (CpTi)<sub>4</sub>Se<sub>7</sub>O with the oxygen within the Ti<sub>4</sub> tetrahedron<sup>82</sup>. CpNbCl<sub>4</sub> gives Cp<sub>3</sub>Nb<sub>3</sub>Se<sub>5</sub>Cl<sub>2</sub>, with the coordination environment of each of the chains of three niobium atoms different, one bridge provided by Se and Se<sub>2</sub> units, and the other by two separate Se atoms<sup>85</sup>.

Many nickel cluster complexes have been prepared from (Me<sub>3</sub>Si)<sub>2</sub>Se. Thus CpNi(PPh<sub>3</sub>)Cl gives Cp<sub>4</sub>Ni<sub>4</sub>Se<sub>2</sub> and Cp<sub>4</sub>Ni<sub>4</sub>Se<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, the former containing a Ni<sub>4</sub>Se<sub>2</sub> octahedron, and the latter an almost square Ni<sub>2</sub>Se<sub>2</sub> unit with each Se atom coordinated to a CpNi(PPh<sub>3</sub>) residue (see equation 101)<sup>103</sup>. MeC<sub>5</sub>H<sub>4</sub>Ni(CO)Br forms clusters with 4, 6 and 15 metal atoms, namely Ni<sub>4</sub>Se<sub>2</sub>(CO)Br(C<sub>5</sub>H<sub>4</sub>Me)<sub>3</sub>, Ni<sub>6</sub>Se<sub>4</sub>(C<sub>5</sub>H<sub>4</sub>Me)<sub>5</sub>, and both Ni<sub>15</sub>Se<sub>10</sub>(CO)<sub>3</sub>(C<sub>5</sub>H<sub>4</sub>Me)<sub>8</sub> and Ni<sub>15</sub>Se<sub>10</sub>(CO)Cl<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>Me)<sub>8</sub><sup>104</sup>.

(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>PdCl)<sub>2</sub> gives the hexametallic (η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>Pd)<sub>6</sub>Se<sub>3</sub> with a triangular prism of metal atoms, each rectangular face containing a selenium atom<sup>105</sup>.

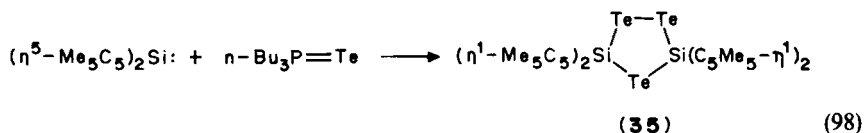
Photolysing the cyclotriselenide (Et<sub>2</sub>SiSe)<sub>3</sub> gives the cyclodiselenide and, in the presence of hexamethylcyclotrisiloxane, insertion of one Et<sub>2</sub>SiSe unit into the cyclodisiloxane ring occurs, supporting the intermediacy of the silaselenone (equation 96)<sup>106</sup>. Such an intermediate also results from the hindered silylene (η<sup>5</sup>-Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Si: and the phosphine selenide *n*-Bu<sub>3</sub>P=Se, the haptotropic rearrangement giving (η<sup>1</sup>-Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Si=Se which dimerises, and adds to conjugated dienes, unlike the silathione (equation 97)<sup>99</sup>. The reaction of **33** (Scheme 14) with elemental selenium gives the monomeric silaselenone<sup>100</sup>.



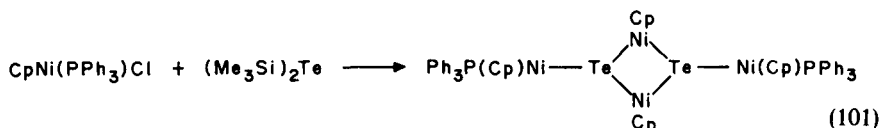
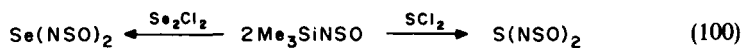
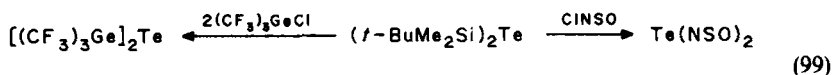


### \*VIII. SILYL DERIVATIVES OF TELLURIUM

The silylene  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Si:}$  and  $n\text{-Bu}_3\text{P=Te}$  give the first neutral Si—Te heterocycle (35) as a crystalline solid, m.p.  $335^\circ\text{C}$  (equation 98)<sup>99</sup>, and contrasts with the behaviour of the silaselenone which dimerises.



The bis(silyl)tellurides  $(\text{RMe}_2\text{Si})_2\text{Te}$  ( $\text{R} = \text{Me}, t\text{-Bu}$ ) are cleaved by  $(\text{CF}_3)_3\text{GeX}$  ( $\text{X} = \text{F}, \text{Cl}$ )<sup>107</sup>, while  $\text{ClNSO}$  oxidizes the telluride ( $\text{R} = t\text{-Bu}$ ) to tellurium(II) isothiazate (equation 99)<sup>108</sup>. By way of contrast, the selenium and sulphur analogues result from selenium monochloride  $\text{Se}_2\text{Cl}_2$  or sulphur dichloride  $\text{SCl}_2$ , and  $\text{Me}_3\text{SiNSO}$  (equation 100).<sup>109</sup>  $\text{CpNi}(\text{PPh}_3)\text{Cl}$  and  $(\text{Me}_3\text{Si})_2\text{Te}$  give the tetrametallic cluster  $\text{Cp}_4\text{Ni}_4\text{Te}_2(\text{PPh}_3)_2$  (equation 101), with a structure like the Se analogue<sup>103</sup>.



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# Transition-metal silyl derivatives

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The Silicon-Heteroatom Bond

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## I. INTRODUCTION

The study of transition-metal silyl derivatives ( $L_nM-SiR_3$ ) began in 1956 with Wilkinson's preparation of  $Cp(CO)_2FeSiMe_3$  ( $Cp = \eta^5-C_5H_5$ )<sup>1</sup>. Initial development of the area was slow, and it was not until 1965 that other derivatives [of the type  $(CO)_4CoSiR_3$ ] were described<sup>2,3</sup>. Interest in transition-metal-silicon bonded compounds then grew steadily, being stimulated by discovery of the transition-metal catalyzed hydrosilylation of olefins<sup>4</sup> and related studies on the mechanism of metal insertions into Si-H bonds (oxidative additions)<sup>5</sup>. Today, silyl derivatives of nearly all the transition elements are known. The large majority of these complexes are coordinatively saturated and contain carbon monoxide, phosphines, or cyclopentadienyl ancillary ligands. Most are diamagnetic and involve low-valent, electron-rich transition-metal centers, although the chemistry of electron-poor early transition-metal derivatives is being rapidly developed.

In many respects the structures and reactivities of transition-metal silyl compounds parallel those of the analogous alkyl derivatives but there are some important differences. For example, many metal-silicon bonded compounds, particularly those of the late transition metals, are quite inert toward insertion reactions. This low reactivity toward insertions is consistent with observations that metal-silicon bonds are often shorter than expected for single covalent bonds, and presumably strengthened by  $\pi$ -bonding between the transition metal and silicon. On the other hand, silanes (and silyl ligands) exhibit a greater tendency to participate in addition/elimination reactions than analogous alkanes (and alkyl ligands).

Transition-metal silyl compounds are important synthetic intermediates in laboratory and industrial applications. Recent investigations indicate that a number of useful transformations involving metal-silicon bonds are possible, but in many respects this area is at an early stage of development. Certainly there is still much to learn from research with metal-silicon bonds, and interest in both stoichiometric and catalytic transformations involving transition-metal silyl derivatives continues. This chapter is not intended to provide comprehensive coverage of the area, but to give a general overview with an emphasis on newer developments. Other relevant reviews are available<sup>6-14</sup>.

## II. THE FORMATION OF COMPOUNDS CONTAINING TRANSITION-METAL-SILICON BONDS

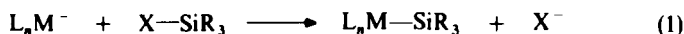
A wide range of synthetic methods for forming metal-silicon bonds has been described, and there even appear to be more methods available for preparing transition-metal silyl



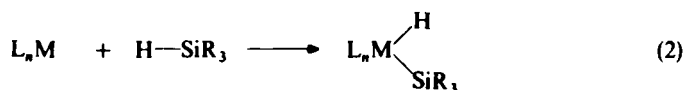
than transition-metal alkyl derivatives. Methods based on both electrophilic and nucleophilic silicon reagents have been widely used. The synthetic route of choice depends somewhat on the type of transition-metal silyl complex desired. Various preparative methods are described below, with late and early transition elements being treated separately. The distinction between these two classes of metals can be somewhat vague, but is nonetheless convenient for discussion of metal-silicon bond properties. A late transition metal is usually regarded as one occurring to the right of group 6 in the periodic table, with early transition metals belonging to groups 3, 4, or 5. The terms 'late' and 'early' are therefore often used to reflect electron density at the metal center in a transition-metal complex. The group 6 metals (Cr, Mo, W) are borderline, since both electron-poor (high oxidation state) and electron-rich (low oxidation state) complexes are common. Here, the term 'early transition-metal silyl complex' is used for silyl derivatives that have few nonbonding electrons (usually zero) at the metal center ( $d^n$  configurations with  $n < 3$ ). Late transition-metal complexes are more electron-rich, with more than three metal-based electrons. Earlier reviews<sup>6-14</sup> should be consulted for more exhaustive coverage of synthetic reactions.

### A. Late Transition-metal Derivatives

Studies of transition-metal silyl chemistry have focused mainly on the later members of the transition series. To some degree this reflects the availability of convenient preparative routes based on oxidative additions to low-valent, electron-rich complexes (e.g. equations 1 and 2).

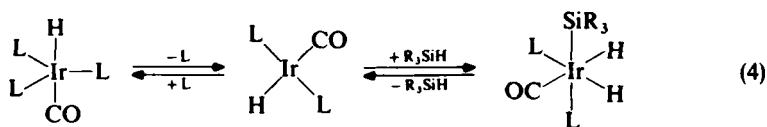
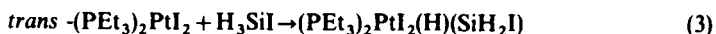


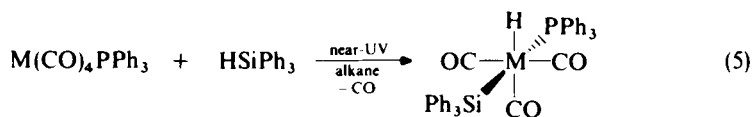
X = halide



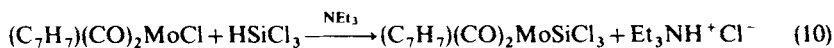
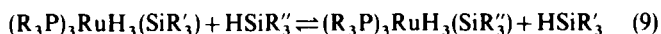
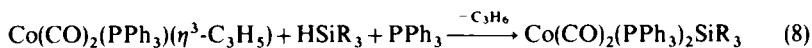
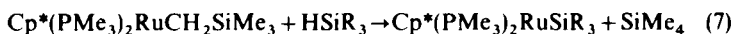
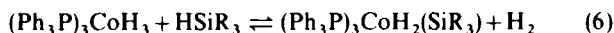
#### 1. Methods involving oxidative addition of Si-H bonds

Silicon-hydrogen bonds readily add to basic, low-valent transition-metal complexes that possess vacant coordination sites (e.g. equation 3)<sup>15</sup>. Note that the Si-H bond of  $H_3SiI$  adds to platinum in preference to the Si-I bond. In general Si-H bonds are more reactive toward oxidative addition reactions than other Si-X bonds. Also, addition of silanes  $HSiX_3$  is more favored as the X substituents become more electronegative and less sterically demanding. The vacant coordination site may be generated in solution via dissociation of a ligand (equations 4<sup>16</sup> and 5<sup>17</sup>,  $L = PPh_3$ ).



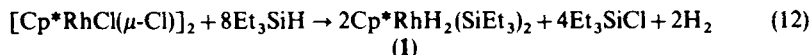


Many reactions are known for which addition of silane is accompanied by the elimination of a small molecule ( $\text{H}_2$ , hydrocarbon, a different silane, hydrogen halide). Examples of such reactions are shown in equations 6–10 ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ )<sup>18–22</sup>. Generally these reactions can be viewed as proceeding through successive oxidative addition and reductive elimination steps (or vice versa).

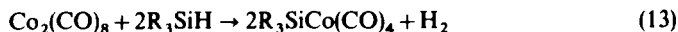


Low-temperature spectroscopic studies on the light-induced reaction in equation 11 have allowed detection of two intermediates, the 16-electron complex  $\text{R}_3\text{SiCo}(\text{CO})_3$  and the bis(silyl) complex  $(\text{R}_3\text{Si})(\text{R}'_3\text{Si})\text{CoH}(\text{CO})_3$ <sup>23</sup>. Recently, an investigation of the oxidative addition of silanes to photochemically generated 16-electron species such as  $(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_2$ ,  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2$  ( $\text{M} = \text{Mn, Re}$ ) and  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$  has been reported. The reactivity of these dicarbonyl intermediates toward neat  $\text{HSiEt}_3$  at 100 K revealed the following trends:  $\text{Cr} > \text{Mn} > \text{Fe} > \text{Re}$  and  $\text{C}_5\text{Me}_5 > \text{C}_5\text{H}_5$ <sup>24</sup>.

In many respects, Si–H oxidative additions resemble H–H oxidative additions<sup>25</sup>. For example, addition of silane may result in an unusually high oxidation state for the metal, as in the formation of  $(\text{Ph}_3\text{P})_3\text{RuH}_3(\text{SiR}_3)$  species from  $(\text{Ph}_3\text{P})_4\text{RuH}_2$  and  $\text{HSiR}_3$ <sup>21,26</sup>, and in the preparation of the rhodium(V) silyl I (equation 12)<sup>27</sup>. Studies on the analogous reaction involving iridium demonstrated the intermediacy of  $[\text{Cp}^*\text{IrHCl}]_2$  and  $\text{Cp}^*\text{IrH}_2\text{Cl}(\text{SiEt}_3)$ <sup>28</sup>.



Silicon–hydrogen bonds also add to dinuclear complexes in reactions that are formally one-electron oxidative additions, or simply metal–metal bond cleavage reactions. The reaction of dicobalt octacarbonyl with an excess of silane leads to silylcobalt carbonyls (equation 13)<sup>2,3</sup>. Similar reactions involving Mn–Mn<sup>29</sup>, Re–Re<sup>30</sup>, Fe–Fe<sup>31</sup>, Ru–Ru<sup>32</sup>,

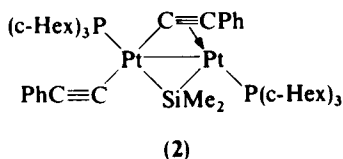


Rh–Rh<sup>33</sup> and Ir–Ir<sup>33</sup> bonds are known. Reaction of optically active (1-Naph)PhMeSiH with  $\text{Co}_2(\text{CO})_8$  yields the optically active cobalt silyl derivative with retention (> 85%) of configuration about silicon<sup>34</sup>. A recent investigation of the mechanism of the reaction in

equation 13 has shown that, contrary to earlier proposals,  $\text{HCo}(\text{CO})_4$  is not an intermediate. The authors suggest that  $\text{HSiEt}_3$  is instead activated by radical cobalt species,  $\text{Co}(\text{CO})_4$  and/or  $\text{Co}(\text{CO})_3$ , formed from  $\text{Co}_2(\text{CO})_8$ <sup>35</sup>.

## 2. Methods involving oxidative addition of other Si-X bonds

There are only a few reports of the preparation of transition-metal silyl compounds based on Si-C or Si-Si bond oxidative addition. The alkynyl silane  $\text{Me}_2\text{Si}(\text{C}\equiv\text{CPh})_2$  adds to  $(\text{c-Hex}_3\text{P})_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$  with cleavage of two Si-C bonds and loss of ligated ethylene to produce the  $\text{SiMe}_2$ -bridged platinum dimer **2**<sup>36</sup>. Many examples involve cleavage of a

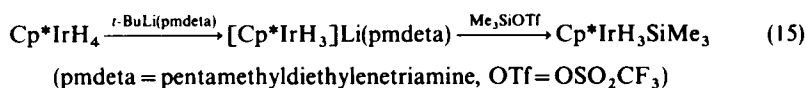
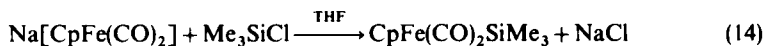


bond in a strained heterocycle, although  $\text{Si}_2\text{Cl}_6$  adds to a number of low-valent complexes<sup>37</sup>. Reactions of  $\text{Fe}_2(\text{CO})_9$  with substituted silacyclobutanes show that insertion of  $\text{Fe}(\text{CO})_4$  proceeds with both regio- and stereospecificity<sup>38</sup>. Although reactions of this type seem to have limited synthetic utility, they appear to play an important role in certain transition-metal catalyzed reactions, such as redistribution of silanes<sup>39</sup>.

Oxidative addition of silicon-halogen bonds has rarely been observed or implied. The iridium methyl derivative *trans*- $\text{MeIr}(\text{CO})[\text{P}(p\text{-Tol})_3]_2$ , however, has recently been reported to react with  $\text{Me}_3\text{SiI}$  to give the addition product  $\text{Me}_3\text{SiIrI}_2(\text{CO})[\text{P}(p\text{-Tol})_3]_2$ , along with  $\text{Me}_4\text{Si}$  and some *trans*- $\text{IrI}(\text{CO})[\text{P}(p\text{-Tol})_3]_2$ . No reaction with  $\text{Me}_3\text{SiCl}$  was observed<sup>40</sup>.

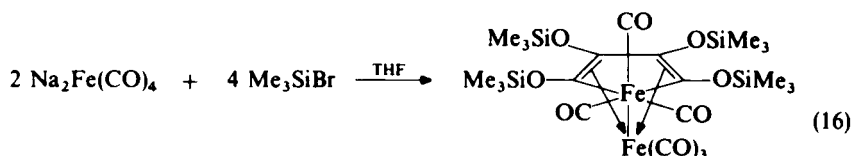
## 3. Methods employing transition-metal anions

This method was used by Wilkinson to obtain the first compound with a transition-metal-silicon bond (equation 14)<sup>1</sup>, and has now been extended to many other systems<sup>6-14</sup>. Formally, this reaction is also an oxidative addition,  $\text{Fe}(0) \rightarrow \text{Fe}(\text{II})$ . To a large degree, application of this method has been restricted to first-row transition-metal carbonyl anions, however, this is probably due simply to the limited availability of other types of transition-metal anions. Recently Bergman and coworkers reported silylation of an iridium hydrido anion (equation 15)<sup>41</sup>. Generally these reactions are sensitive to electronic and steric properties of the halosilane; hydridohalosilanes therefore react more readily than organohalosilanes. In addition, triflate and iodide appear to be better leaving groups than chloride.



The nature of the solvent is another critical factor that can influence the course of this type of silylation reaction. In particular tetrahydrofuran, a convenient solvent for the preparation of many transition-metal anions, can cause problems in two ways. First, it

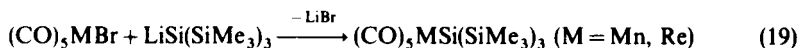
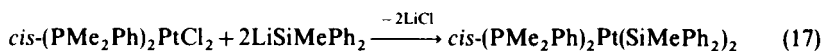
provides a polar medium that appears to promote nucleophilic attack by a carbonyl oxygen of a transition-metal anion onto the silicon halide. This results in formation of silicon-oxygen bonded species, usually disiloxanes  $(R_3Si)_2O$ <sup>42</sup>. A well-characterized metal-containing product from such a reaction is shown in equation 16. In this case



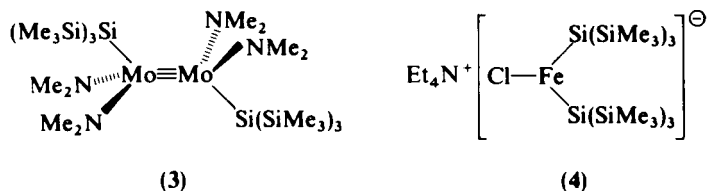
silylation results in carbonyl coupling at the iron center to produce a siloxy-substituted metallacyclopentadiene fragment<sup>43</sup>. A second problem that may arise from use of cyclic ethers as solvents is facile ring-opening of the ether by a metal-silicon bond<sup>44</sup>. It is therefore desirable to avoid THF as a solvent; diethyl ether or, if possible, a saturated hydrocarbon is preferred<sup>45</sup>.

#### 4. Methods employing main-group metal silyl compounds

Use of main-group metal silyls to prepare transition-metal silyls appears to be a generally applicable method that is primarily limited by the availability of suitable starting materials, since these 'silyl anion reagents' are sometimes rather difficult to obtain. Typically an alkali-metal silyl is generated in solution and then treated with the appropriate transition-metal halide. Displacement of halide by the silyl anion, with salt elimination, then leads to product (equations 17-19)<sup>46-49</sup>. The lithium silyl in equation



19 can be isolated as the crystalline solvate  $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$ <sup>50</sup>, and appears to be useful for the preparation of a number of metal-silicon bonded compounds, including 3<sup>51</sup> and 4<sup>52</sup>. Compounds 3 and 4 are noteworthy in that they contain no  $\pi$ -accepting



ancillary ligands such as CO, cyclopentadienyl or phosphines. Furthermore 4 (Figure 1), and similar derivatives of chromium and manganese<sup>52</sup>, are unusual silyl complexes in possessing exceptionally low coordination numbers and large magnetic moments<sup>6-14</sup>.

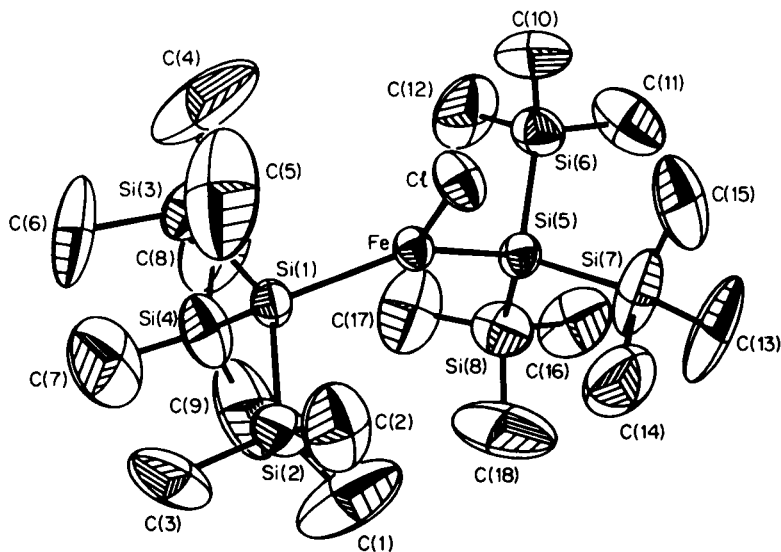
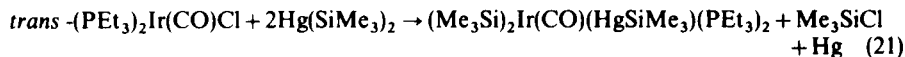
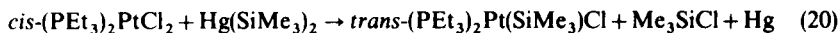
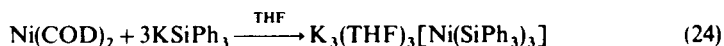
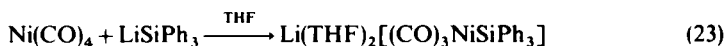


FIGURE 1. ORTEP view of the structure of the anion in 4

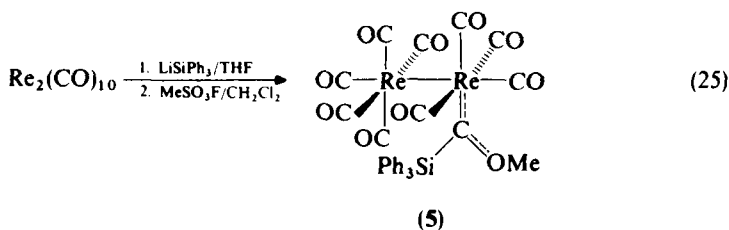
Mercury silylating agents have also been used with success (equation 20)<sup>53</sup>. In reactions of this kind the mercury reagent usually delivers only one  $-\text{SiMe}_3$  group, presumably owing to rapid decomposition of  $\text{Me}_3\text{SiHgCl}$  to  $\text{Me}_3\text{SiCl}$  and Hg metal<sup>54</sup>. These reagents may also participate in oxidative addition reactions to give silyl complexes (equations 21 and 22)<sup>55,56</sup>.



Two reports describe the use of alkali metal silyls to prepare anionic silyl complexes via displacement of neutral ligands (equations 23 and 24, COD = 1,5-cyclooctadiene)<sup>57,58</sup>.

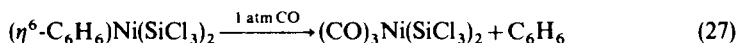
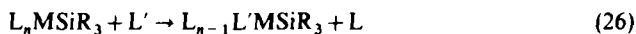


It was suggested that the  $-\text{SiPh}_3$  anion, being isoelectronic with  $\text{PPh}_3$ , can stabilize low-valent transition-metal centers<sup>57</sup>. This novel, potentially useful route to transition-metal silyls does not seem to have been explored much beyond these two investigations. A possible limitation to this method is the ability of silyl anions to attack coordinated carbon monoxide, giving silicon-carbon bonded products<sup>59,60</sup> (e.g. 5 in equation 25<sup>59</sup>).

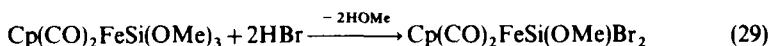
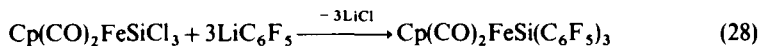


### 5. Miscellaneous methods

Many silyl complexes have been obtained by straightforward ligand exchange processes at the metal (equation 26)<sup>6-14</sup>; most of these involve substitution of carbonyl ligands. An example of a reaction in which an arene ligand is displaced by CO is shown in equation 27. By X-ray crystallography, the product carbonyl complex was shown to have a slightly distorted trigonal bipyramid structure with the CO ligands in the equatorial plane and the two trichlorosilyl ligands in the axial positions<sup>61</sup>. A related process involves displacement of dihydrogen by a neutral donor ligand, as in photolysis of the *cis*-dihydrido-iridium(III) complex  $\overline{\text{Ir}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)(\text{PPh}_3)(\text{CO})\text{H}_2}$  in the presence of CO to give the novel iridium(I) silyl  $\overline{\text{Ir}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)(\text{PPh}_3)(\text{CO})_2}$ <sup>62</sup>.

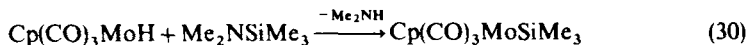


In addition, it is possible to modify the silyl ligand via substitutions at silicon. This can be done with nucleophilic displacements at silicon (e.g. equation 28)<sup>63</sup>, or by using electrophilic reagents (e.g. equation 29)<sup>64</sup>.

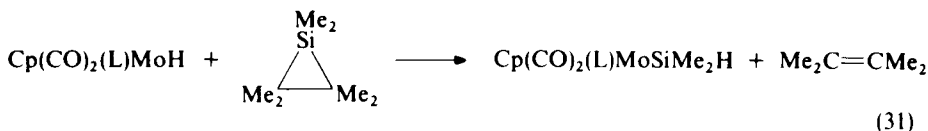


Modification of a metal-bound silyl group is the basis for a new synthesis of silanes  $\text{Ph}_2\text{SiHX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$  and  $\text{I}$ ) from  $\text{Ph}_2\text{SiH}_2$ . The synthesis consists of an oxidative addition of  $\text{Ph}_2\text{SiH}_2$  to  $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_3$  to form  $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{H})(\text{SiHPh}_2)$ , which is then halogenated with  $[\text{Ph}_3\text{C}]\text{BF}_4$ ,  $\text{CCl}_4/\text{PCl}_5$ ,  $\text{Br}_2$ , or  $\text{I}_2$  to form  $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{H})(\text{SiXPh}_2)$ . The  $\text{Ph}_2\text{SiHX}$  products are then formed by treatment of the latter manganese compound with carbon monoxide at high pressure<sup>65</sup>.

Acidic transition-metal hydrides have been used to prepare metal-silicon bonded compounds by an interesting condensation reaction that proceeds with amine elimination (equation 30)<sup>66</sup>. An attempt to carry out a similar reaction between  $\text{Ph}_3\text{SiH}$  and the zirconium amide  $\text{Cp}_2\text{Zr}(\text{NMe}_2)_2$  failed<sup>67</sup>.



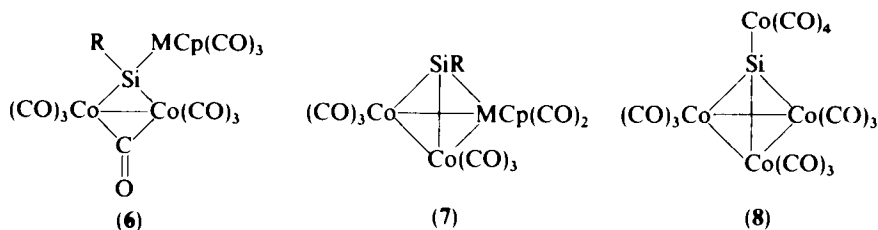
A new method for preparing dimethylsilyl derivatives, based on silylene transfer from hexamethylsilacyclopropane to a transition-metal hydride, has been reported (equation



31, L = CO, PMe<sub>3</sub>). This process was shown to proceed by a radical chain mechanism in which the three-membered ring was opened by Cp(CO)<sub>2</sub>(L)Mo· to give the Cp(CO)<sub>2</sub>(L)MoSiMe<sub>2</sub>CMe<sub>2</sub>CMe<sub>2</sub>· radical, which eliminates alkene to yield a transient silyl radical, Cp(CO)<sub>2</sub>(L)MoSiMe<sub>2</sub>·. In the product-forming step, this radical abstracts hydrogen from Cp(CO)<sub>2</sub>(L)MoH to give Cp(CO)<sub>2</sub>(L)MoSiMe<sub>2</sub>H<sup>68</sup>.

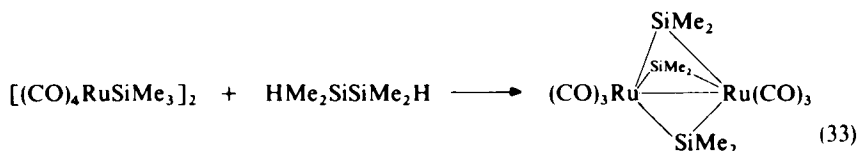
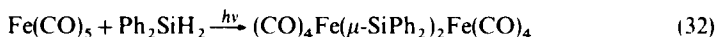
### B. Transition-metal Silicon Clusters

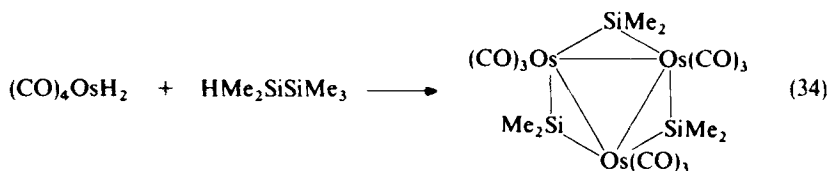
A number of transition-metal cluster compounds containing silicon ligands are now known. These are principally obtained by condensing late transition-metal carbonyl fragments about a silicon center via the methods described above. For example, the Si-H bonded compounds Cp(CO)<sub>2</sub>(PMe<sub>3</sub>)MSiH<sub>2</sub>R (M = Mo, W; R = Me, Ph) react with Co<sub>2</sub>(CO)<sub>8</sub> to produce the mixed-metal clusters **6**. Thermolysis of **6** results in decarbonylation to the silyne-bridged species **7**<sup>69</sup>. The silicide cluster **8** is produced by the



interaction of SiI<sub>4</sub> with NaCo(CO)<sub>4</sub><sup>70</sup>. In contrast, reaction of SiCl<sub>4</sub> with NaCo(CO)<sub>4</sub> in ether gave Cl<sub>3</sub>SiOC[Co<sub>3</sub>(CO)<sub>9</sub>], which did not react further with NaCo(CO)<sub>4</sub><sup>71</sup>. More recently, reaction of (μ<sub>4</sub>-Si)[Co<sub>2</sub>(CO)<sub>7</sub>]<sub>2</sub> with [NEt<sub>4</sub>][Co(CO)<sub>4</sub>] has led to isolation of the paramagnetic cluster anion [μ<sub>8</sub>-SiCo<sub>9</sub>(CO)<sub>21</sub>]<sup>2-</sup>. An X-ray crystal structure determination revealed a silicon atom encapsulated by a capped square anti-prismatic array of cobalt atoms<sup>72</sup>. The hindered clusters ISi[M(CO)<sub>5</sub>]<sub>3</sub> and Si[M(CO)<sub>5</sub>]<sub>4</sub> (M = Mn, Re) have been obtained by prolonged reaction of SiI<sub>4</sub> with NaM(CO)<sub>5</sub><sup>73</sup>.

Another class of cluster-forming reactions generate bridging silylene ligands via extrusion of the silylene unit from a silane R<sub>2</sub>SiH<sub>2</sub> or a disilane HSiR<sub>2</sub>SiR'<sub>3</sub>. Most of these reactions have utilized group 8 metal carbonyl complexes as starting materials. Examples of such reactions are shown in equations 32–34<sup>74, 75</sup>. Although little is known





about the mechanisms involved in such processes, it seems likely that oxidative cleavages of Si–H and Si–Si bonds are involved, and that migrations of silyl groups from silicon to a transition metal are relatively facile. Furthermore, these reactions represent simple means for introducing silylene units into the coordination sphere of a metal.

So far few reports have dealt with the reaction chemistry of transition-metal silicon clusters, but the diversity of structural types and the interesting ways in which silicon-based ligands can become incorporated into clusters suggest that new and useful types of transformations should be possible.

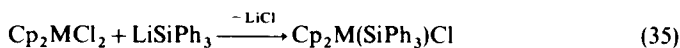
### C. Early Transition-metal Derivatives

Early transition-metal silyl compounds have received much less attention, largely due to the fact that general, straightforward synthetic routes have not been available. Syntheses based on oxidative additions are less applicable, given the more electropositive character of the early metals. Particularly for  $d^0$  silyl complexes, most syntheses are based on nucleophilic displacement of halide by a silyl anion reagent, usually an alkali metal derivative.

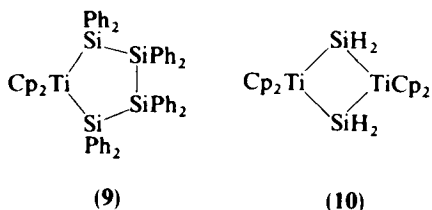
#### 1. Methods employing main-group metal silyl compounds

An early report of  $\text{Ti}(\text{SiPh}_3)_4$ <sup>76</sup>, prepared from  $\text{TiCl}_4$  and  $\text{KSiPh}_3$ , has since been refuted and the compound reformulated as the siloxide  $\text{Ti}(\text{OSiPh}_3)_4$ <sup>67</sup>. Further studies have shown that early metal–silicon bonds are quite reactive toward oxygen<sup>77</sup>, underscoring the importance of excluding air in preparations in early metal silyls.

The first well-characterized zirconium and hafnium silyls were obtained by the reaction in equation 35 ( $M = \text{Zr}, \text{Hf}$ )<sup>67</sup>. A similar procedure was used to prepare the



metallacycle **9** from  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Li}(\text{SiPh}_2)_4\text{Li}$ <sup>78</sup>. An attempt to prepare  $\text{Cp}_2\text{Ti}(\text{SiH}_3)_2$  by reaction of  $\text{Cp}_2\text{TiCl}_2$  with  $\text{KSiH}_3$  led instead to the dimeric silyl derivative **10**, characterized by X-ray diffraction<sup>79</sup>.



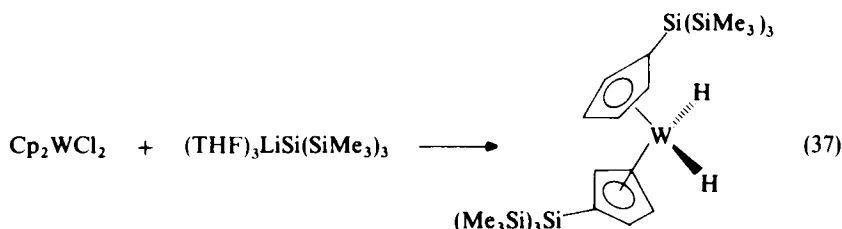
The aluminum reagent  $\text{Al}(\text{SiMe}_3)_3 \cdot \text{OEt}_2$ <sup>80</sup> has been used to prepare crystalline trimethylsilyl derivatives of titanium<sup>81</sup>, zirconium<sup>77</sup> and hafnium<sup>77</sup> (equation 36). The



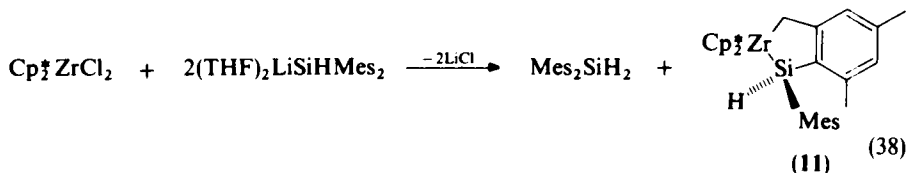


same aluminum reagent was used in the preparation of the dark green, reactive tantalum(V) complex  $\text{Cp}^*\text{Ta}(\text{SiMe}_3)\text{Cl}_3$ <sup>82</sup>. In these examples  $\text{Al}(\text{SiMe}_3)_3 \cdot \text{OEt}_2$  delivers only one silyl group, even when in excess.

Tris(trimethylsilyl)silyl derivatives analogous to the products in equation 35,  $\text{Cp}_2\text{M}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  ( $\text{M} = \text{Zr}, \text{Hf}$ ), are obtained by reaction of the metallocene dichlorides with  $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$ <sup>83</sup>. In contrast, reaction of  $\text{Cp}_2\text{WCl}_2$  with  $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$  does not give a tungsten silyl compound, but instead the hydride complex shown in equation 37 was obtained<sup>84</sup>.

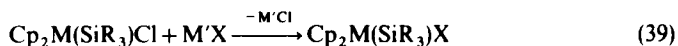


The lithium silyl compound  $(\text{THF})_2\text{LiSiHMe}_2$  ( $\text{Mes} = \text{mesityl}$ ) reacts with zirconium alkyls of the type  $\text{Cp}'_2\text{Zr}(\text{Me})\text{X}$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ ,  $\text{X} = \text{Cl}$ ;  $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ ,  $\text{X} = \text{Br}$ ) to provide good yields of the mixed alkyl silyl complexes  $\text{Cp}'_2\text{Zr}(\text{SiHMe}_2)\text{Me}$ . It has proven difficult to prepare silyl complexes from  $(\text{THF})_2\text{LiSiHMe}_2$  and metal halide starting materials that contain more than one halide ligand, such as  $\text{Cp}^*\text{MCl}_3$ ,  $\text{MCl}_4$  ( $\text{M} = \text{Zr}, \text{Hf}$ ),  $\text{TaCl}_5$  and  $\text{FeCl}_2$ . In each case,  $\text{Mes}_2\text{SiH}_2$  was observed as the major silicon-containing product. A reason for this is suggested by the observed products of reaction between  $\text{Cp}^*_2\text{ZrCl}_2$  and two equivalents of the lithium silyl derivative (equation 38). It



was shown that the metallacycle **11** forms by rapid dehydrohalogenation of the initial product  $\text{Cp}^*_2\text{Zr}(\text{SiHMe}_2)\text{Cl}$  by  $(\text{THF})_2\text{LiSiHMe}_2$ . Presumably,  $\text{M-SiHMe}_2$  bonded species can be consumed by the unreacted lithium silyl compound as soon as they are formed<sup>85</sup>.

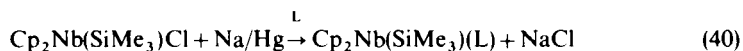
Halide ligands in early transition-metal silyl complexes are readily displaced with nucleophilic reagents (equation 39) to introduce a variety of functionalities *cis* to the silyl



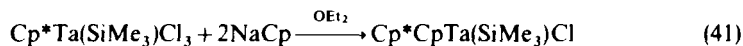
group. Such compounds have been prepared where  $\text{X} = \text{OCMe}_3$ ,  $\text{BH}_4$ ,  $-\text{SC}(=\text{S})\text{NEt}_2$ ,  $\text{Si}(\text{SiMe}_3)_3$  and  $\text{Me}$ <sup>77, 83</sup>. In addition, the alkyl silyl complex  $\text{Cp}^*\text{Ta}(\text{SiMe}_3)\text{Me}_3$  has been obtained by reaction of  $\text{Cp}^*\text{Ta}(\text{SiMe}_3)\text{Cl}_3$  with  $\text{MeMgBr}$ <sup>82</sup>.

The mercury silyl compound  $\text{Hg}(\text{SiMe}_3)_2$  has been used in the silylation of niobocene dichloride to produce purple, paramagnetic ( $d^1$ )  $\text{Cp}_2\text{Nb}(\text{SiMe}_3)\text{Cl}$ . This material is

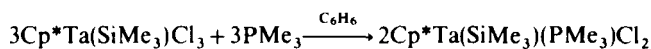
readily reduced in the presence of suitable donor ligands to give crystalline niobium(III) silyl complexes (equation 40; L = CO, PMe<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>)<sup>86</sup>. Tantalum(IV) (d<sup>1</sup>) silyl derivatives



**12** and **13** were prepared from Cp\*Ta(SiMe<sub>3</sub>)Cl<sub>3</sub> via the reactions shown in equations 41 and 42. Paramagnetic **12** is further reduced to the tantalum(III) silyl complex Cp\*CpTa(SiMe<sub>3</sub>)(PMe<sub>3</sub>) by reaction with Na/Hg in the presence of PMe<sub>3</sub><sup>82</sup>.



(12)



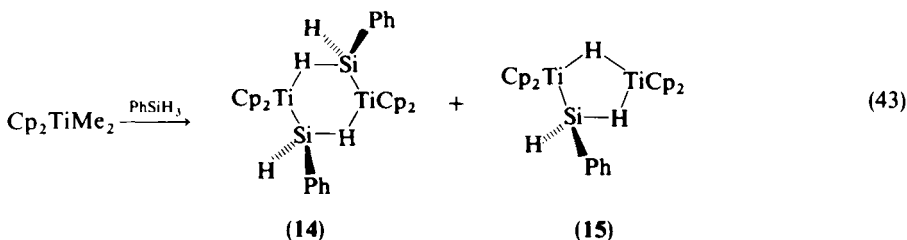
(13)



## 2. Methods involving cleavage of Si-H bonds

A different method for obtaining early metal silyl complexes was reported by Curtis and coworkers. Interaction of the trihydrides Cp<sub>2</sub>MH<sub>3</sub> (M = Nb, Ta) with HSiMe<sub>2</sub>Ph at elevated temperatures affords Cp<sub>2</sub>M(SiMe<sub>2</sub>Ph)H<sub>2</sub> in high yield. These reactions presumably proceed by reductive elimination of H<sub>2</sub>, followed by oxidative addition of silane to Cp<sub>2</sub>MH. No Nb-Si bonded products were obtained from a similar reaction between Cp<sub>2</sub>NbH<sub>3</sub> and HSiEt<sub>3</sub><sup>87</sup>.

Harrod and colleagues<sup>88</sup> have recently described an intriguing new entry into early metal silyl chemistry, a rather complex reaction resulting from addition of a primary silane to an alkyl complex (equation 43). X-ray crystal structures of both **14** and **15** were



determined; compound **14** is a dimer of Cp<sub>2</sub>TiSiH<sub>2</sub>Ph possessing a *cis* arrangement of the phenyl groups and Ti-H-Si bridges. The hydride-bridged compound **15** is a decomposition product of **14**<sup>88</sup>. An analogous reaction between Cp<sub>2</sub>ZrMe<sub>2</sub> and PhSiH<sub>3</sub> gave the bridging hydride dimer Cp<sub>2</sub>Zr(SiH<sub>2</sub>Ph)(μ-H)<sub>2</sub>ZrCp<sub>2</sub>(SiMeHPh)<sup>89</sup>.

## 3. Related f-element derivatives

The electropositive lanthanide and actinide elements are expected to form silyl complexes with properties similar to those of the early transition metals. Recently the first

examples of compounds possessing lanthanide-silicon bonds were described. These were prepared by interaction of two equivalents of  $\text{LiSiMe}_3$  with  $\text{Cp}_2\text{Ln}(\mu\text{-Cl})_2\text{Na}(\text{DMF})$  ( $\text{Ln} = \text{Sm, Lu}$ ) in pentane. The products of these reactions are the anionic bis(silyl) complexes  $[\text{Li}(\text{DME})_3]^+ [\text{Cp}_2\text{Ln}(\text{SiMe}_3)_2]^-$ . The crystal structure of the samarium silyl complex consists of discrete cations and anions<sup>90</sup>.

No actinide silyl complexes have been reported.

### III. TRANSITION-METAL SILYLENE COMPLEXES

Although carbenes<sup>91</sup>, germylenes<sup>92</sup>, stannylenes<sup>92</sup> and plumblyenes<sup>92</sup> are well established as ligands for transition metals, little is known about the coordination chemistry of silylenes ( $\text{:SiR}_2$ ). There are numerous examples of compounds with silylene units bridging two metal atoms, but evidence for terminal silylene complexes ( $\text{L}_n\text{M}=\text{SiR}_2$ ) is scarce. Nevertheless, they are postulated intermediates in a number of transition-metal mediated transformations. There have been numerous attempts to prepare and isolate them, and recent discoveries of compounds containing double bonds between silicon and main group elements<sup>93</sup> lend further support to the notion that stable silylene complexes are synthetically accessible.

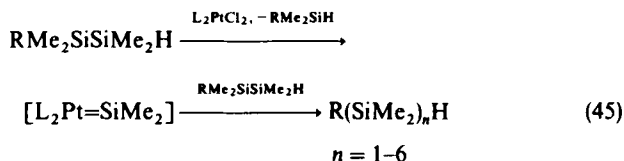
#### A. Indirect Evidence for Coordinated Silylenes

Coordinated silylene ligands have been invoked or suggested as intermediates in a number of chemical processes, including Rochow's Direct Process<sup>94</sup>, catalytic redistribution of silanes<sup>39</sup> and various silylene-transfer reactions<sup>95-99</sup>. Evidence for such species is primarily circumstantial, and  $\text{M}=\text{Si}$  double bonds have never been detected in these systems. Presently there is no conclusive evidence for the involvement of silylene coordination compounds in any transition-metal-mediated silylene-transfer reactions. Some reactions that may involve silylene ligands are discussed below.

Transition-metal-catalyzed redistribution reactions (equation 44) are synthetically useful but not well understood mechanistically<sup>39</sup>. For some of these reactions, intermediate metal-bound silylenes have been proposed. For example, disilanes  $\text{RMe}_2\text{SiSiMe}_2\text{H}$

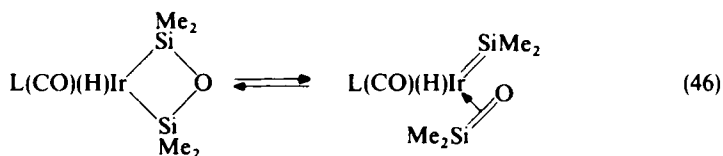


( $\text{R} = \text{Me, H}$ ) are catalytically oligomerized by  $(\text{R}'_3\text{P})_2\text{PtCl}_2$  complexes according to equation 45. Generation of an intermediate  $\text{Pt}=\text{SiMe}_2$  silylene as well as product



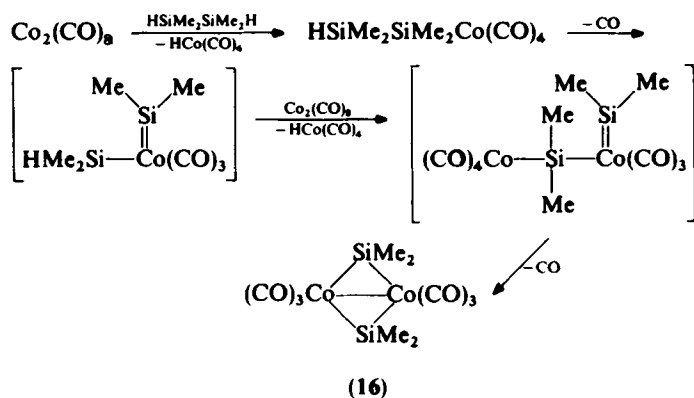
formation are suggested to proceed through migrations of hydride and silyl groups between platinum and an adjacent silicon atom<sup>95,100</sup>. A related mechanism was proposed to account for the formation of polysilanes in the  $(\text{Ph}_3\text{P})_3\text{RhCl}$ -catalyzed redistribution of  $\text{Ph}_2\text{SiH}_2$ <sup>101</sup>.

Studies by Curtis' group have offered evidence for the participation of silylene and silanone ( $\text{R}_2\text{Si}=\text{O}$ ) ligands in other catalyzed redistributions. These reactions effect the disproportionation of  $\text{HMe}_2\text{SiOSiMe}_2\text{H}$  into  $\text{Me}_2\text{SiH}_2$  and linear polysiloxanes, poss-



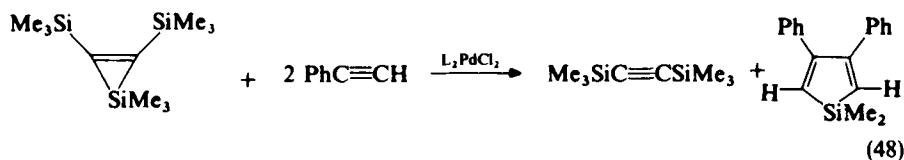
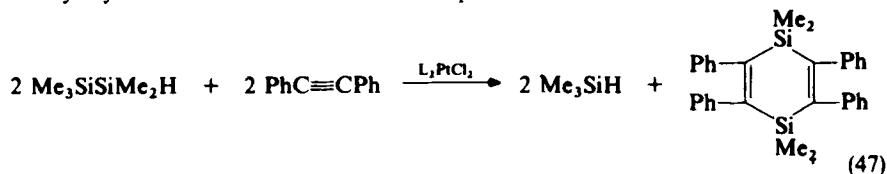
ibly via the Si–O bond cleavage process depicted in equation 46<sup>39, 102–104</sup>. Curtis has pointed out that in many cases, silylene complexes do not need to be invoked to explain redistribution products, since simple oxidative addition/reductive elimination cycles can account for the observed results<sup>39</sup>.

Reactions in which transition-metal complexes extrude silylene ligands from silanes have already been mentioned (equations 32–34). Although the mechanisms of these reactions remain ill-defined, it seems possible that terminal silylene complexes may be involved as intermediates. Such a proposal has been made regarding the formation of the silylene-bridged dicobalt species **16** from  $\text{Co}_2(\text{CO})_8$  and tetramethyldisilane (Scheme 1)<sup>105</sup>.

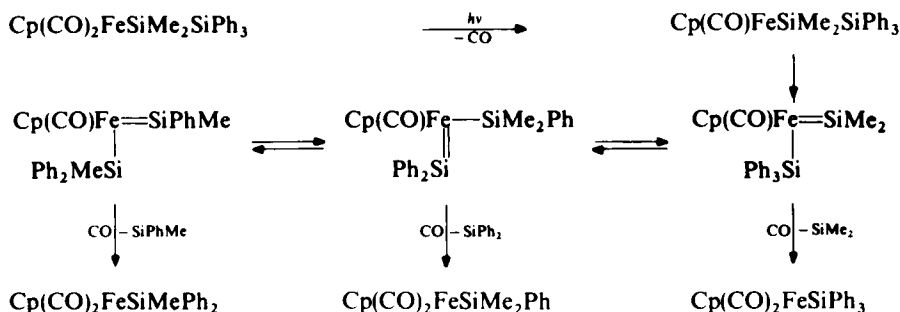


SCHEME 1

Additional support for the existence of silylene species comes from trapping experiments with alkynes<sup>95–99</sup>. From the platinum system in equation 45, dimethylsilylene was trapped by diphenylacetylene (equation 47)<sup>95</sup>. Similarly,  $(\text{PPh}_3)_2\text{PdCl}_2$  catalyzes the dimethylsilylene-transfer reaction shown in equation 48<sup>98</sup>.



The photochemical degradation of polysilyl derivatives of iron leads to mixtures of monosilyl complexes. A possible mechanism involving iron silylene complexes and 1,3 migrations of groups between ligated silicon atoms was proposed (Scheme 2)<sup>106</sup>.

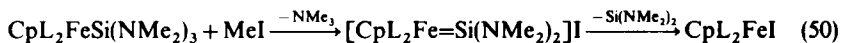
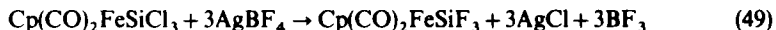


SCHEME 2

### B. Attempted Preparations

Terminal transition-metal silylene complexes have proven to be elusive synthetic targets, but it seems likely that future investigations will uncover viable routes to stable  $\text{M}=\text{Si}$  double-bonded species. Such compounds are of interest as model systems for investigating the reactivity discussed in the previous section, and for providing new synthetic intermediates for silylene transfer reactions. Recent *ab initio* SCF MO calculations predict that  $(\text{CO})_5\text{Cr}=\text{SiH}(\text{OH})$  should be a relatively stable molecule, but that it may be difficult to isolate due to its susceptibility to nucleophilic attack at the silicon atom. The  $\text{Cr}=\text{Si}$  bond dissociation energy was calculated to be  $29.6 \text{ kcal mol}^{-1}$ , compared to the analogous  $\text{Cr}=\text{C}$  bond dissociation energy of  $44.4 \text{ kcal mol}^{-1}$ <sup>107</sup>.

It is curious that straightforward synthetic routes are known for compounds containing  $\text{M}=\text{C}$ ,  $\text{M}=\text{Ge}$ ,  $\text{M}=\text{Sn}$  and  $\text{M}=\text{Pb}$  double bonds but not for ones with  $\text{M}=\text{Si}$  double bonds<sup>91,92</sup>. It appears that many of these synthetic routes are simply not applicable to analogous silicon systems. For example, many carbene complexes are prepared from metal acyls  $[\text{L}_n\text{MC}(=\text{O})\text{R}]$ <sup>91</sup>, but the analogous silicon compounds  $[\text{L}_n\text{MSi}(=\text{O})\text{R}]$  are unknown. Carbene complexes are also commonly prepared by abstraction of an alkyl group functionality with an external electrophilic reagent. Analogous attempts to prepare silylene complexes by similar routes have failed due to secondary reactions of the metal-bound silicon with the abstracting reagent<sup>108-110</sup>. For example, halide ion abstraction with  $\text{AgBF}_4$ ,  $\text{AgPF}_6$  or  $\text{AgSbF}_6$  led to fluorination of the silyl ligand (e.g. equation 49)<sup>108</sup>. Similar results were obtained in attempts to use  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  as an abstraction reagent<sup>9</sup>. The iron silyl compound **17** reacts with  $\text{MeI}$  via cleavage of the  $\text{Fe}-\text{Si}$  bond, and intermediate silylene complex **18** was proposed to explain the observed products (equation 50,  $\text{L}=\text{PMe}_3$ )<sup>109</sup>. Abstraction of chloride from  $[\text{NEt}_4][(\text{CO})_4\text{FeSiCl}_3]$  with  $\text{AlCl}_3$  leads to the trimeric complex  $[(\text{CO})_4\text{FeSiCl}_2]_3$ , possibly by way of a monomeric silylene species. The latter compound, characterized by mass spectroscopy, probably contains bridging silylene ligands<sup>111</sup>.

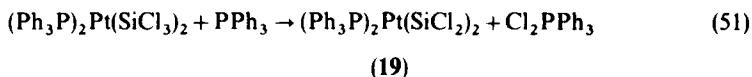


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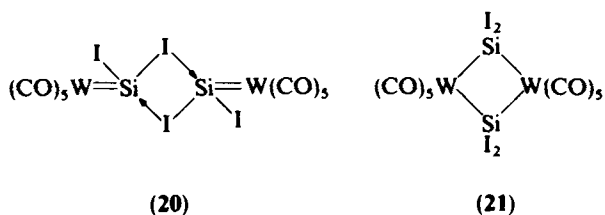
(18)

Many  $L_nM=ER_2$  compounds ( $E=Ge, Sn$  or  $Pb$ ) are prepared by direct combination of a transition-metal complex with a stable divalent  $ER_2$  derivative<sup>92</sup>. Silylenes ( $SiR_2$ ), however, are not stable even under mild reaction conditions and their generation requires high temperatures or irradiation<sup>112</sup>. Other  $L_nM=ER_2$  compounds have been prepared by salt elimination between a dianion complex and a main group-element dihalide  $R_2EX_2$ . As discussed in Section II.A.3, such reactions involving halosilanes often result in attack of a carbonyl ligand oxygen onto silicon.

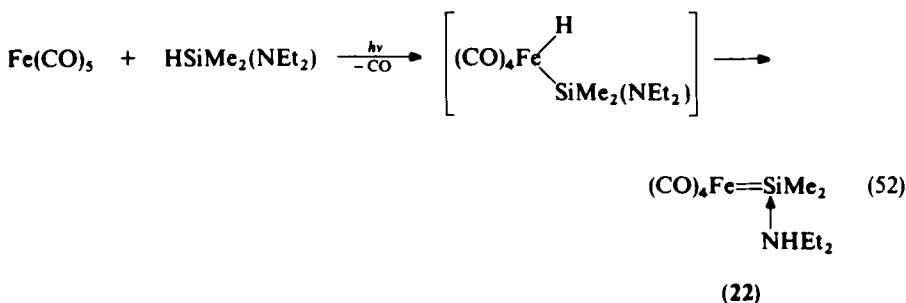
Some reports of silylene complexes have appeared, but many of these involve incomplete characterization or have subsequently been disproved. One problem is that the presence of a  $M=Si$  double bond is difficult to establish unequivocally with spectroscopy. The product in equation 51 was formulated as the monomeric bis(silylene) complex



19<sup>113</sup>, but was later shown to be a product of hydrolysis, the cyclic platinadisiloxane  $(Ph_3P)_2Pt\overline{SiCl_2OSiCl_2}$ <sup>114</sup>. The dimeric tungsten silylene complex **20** was reported to result from irradiation of  $W(CO)_6$  and  $Si_2I_6$ <sup>115</sup>. However, the alternative structure **21**, with bridging silylene ligands, seems more likely<sup>10</sup>.

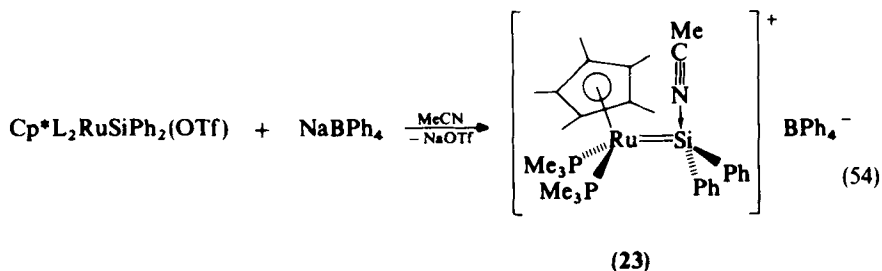
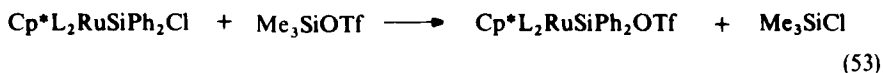


A base-stabilized dimethylsilylene iron complex (**22**) is reported as the product of a photoinduced oxidative addition of an aminosilane to iron pentacarbonyl (equation 52).



The analogous silylene  $(CO)_4Fe\overline{SiCINPhCH_2CH_2NHP}$  was prepared similarly. These compounds are unstable above  $-20^\circ C$ , but were characterized by IR, mass spectroscopy, elemental analysis and molecular weight determinations<sup>116</sup>.

Recently use of the less reactive, non-coordinating anion tetraphenylborate has allowed isolation of an acetonitrile-complexed ruthenium silylene by the sequence of reactions shown in equations 53 and 54 ( $L=PMe_3$ ). The  $\nu(CN)$  stretching frequency for **23**,  $2290\text{ cm}^{-1}$ , is only  $30\text{ cm}^{-1}$  greater than that of free acetonitrile, indicating some



donation of electron density from acetonitrile to the silylene silicon [cf.  $\text{F}_3\text{BNCCH}_3$  for which  $\nu(\text{CN}) = 2359 \text{ cm}^{-1}$ ]<sup>117</sup>. An X-ray crystal structure of the dichloromethane solvate  $\mathbf{23} \cdot \text{CH}_2\text{Cl}_2$  (Figure 2) revealed a short Ru–Si bond length, 2.328 (2) Å. This is the shortest Ru–Si distance known, and is 0.06 Å shorter than the Ru–Si distance in  $\text{Cp}^*\text{L}_2\text{RuSiPh}_2\text{H}$ , 2.387 (1) Å. The Si–N distance of 1.932 (8) Å, which is significantly longer than typical Si–N single bonds to tetrahedral silicon, and distances and angles within the coordinated acetonitrile are consistent with a dative interaction between nitrogen and silicon. The silicon atom in  $\mathbf{23} \cdot \text{CH}_2\text{Cl}_2$  lies 0.34 Å above the plane defined

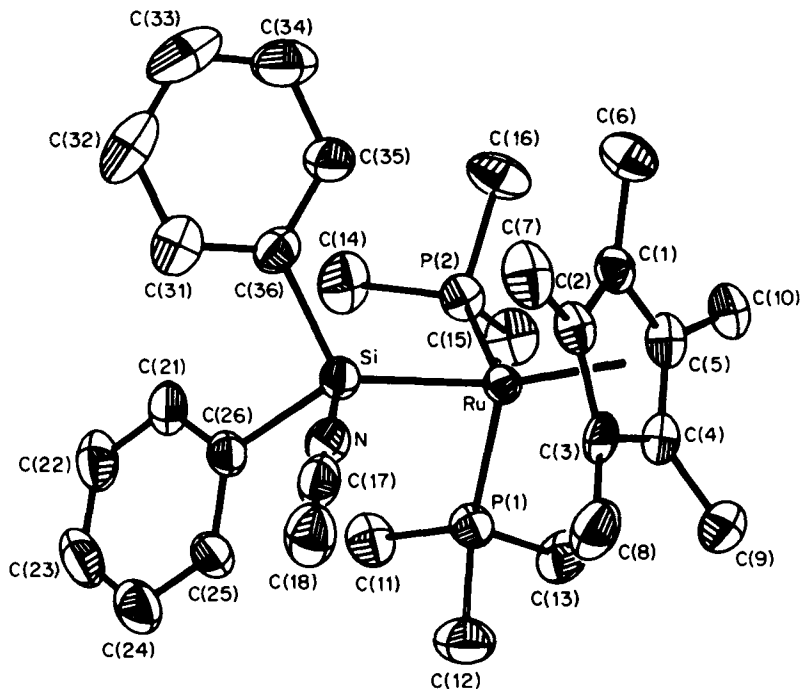
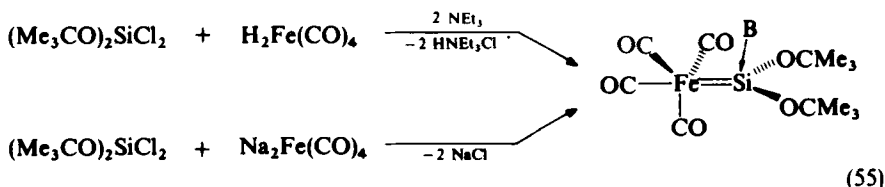


FIGURE 2. ORTEP view of the cation in  $\mathbf{23} \cdot \text{CH}_2\text{Cl}_2$

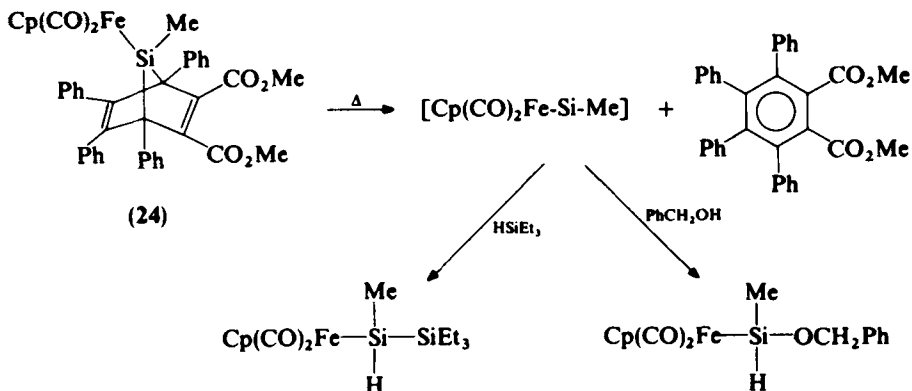
by Ru and the two ipso phenyl carbons. The corresponding value for  $\text{Cp}^*\text{L}_2\text{RuSiPh}_2\text{H}$  is  $0.51 \text{ \AA}^{19}$ .

In addition, it has been observed that base-stabilized silylene complexes of iron may be prepared via two routes (equation 55,  $\text{B} = \text{THF}$  or  $\text{HMPA}$ ). An X-ray structure of



$(\text{CO})_4\text{Fe}=\text{Si}(\text{OCMe}_3)_2(\text{HMPA})$  revealed a trigonal-bipyramid coordination geometry for the iron atom, and a  $\text{Fe}-\text{Si}$  bond distance of  $2.289(2) \text{ \AA}$ . The  $\text{Si}-\text{O}(\text{HMPA})$  distance of  $1.730(3) \text{ \AA}$  is significantly longer than the other  $\text{Si}-\text{O}$  distances [ $1.610(3)$  and  $1.636(4) \text{ \AA}$ ] in the molecule. Rotation about the  $\text{Fe}-\text{Si}$  bond is unrestricted down to  $-30^\circ\text{C}^{118}$ .

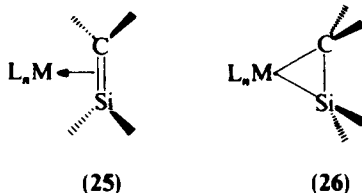
Somewhat related to transition-metal silylene complexes are transition-metal-substituted silylenes ( $\text{L}_n\text{M}-\ddot{\text{Si}}-\text{R}$ ). One report of such a species has appeared. Thermolysis of the 7-silanorbornadienyl iron derivative **24** in the presence of silylene trapping reagents provides evidence for the silylene  $\text{Cp}(\text{CO})_2\text{Fe}-\text{Si}-\text{Me}$  (Scheme 3)<sup>119</sup>.



SCHEME 3

#### IV. TRANSITION-METAL SILENE COMPLEXES

Given the ability of transition-metal complexes to stabilize species via coordination, it is reasonable to expect that given the proper choice of transition metal fragment  $\text{L}_n\text{M}$ , silene complexes can be isolated and studied. As with analogous alkene coordination





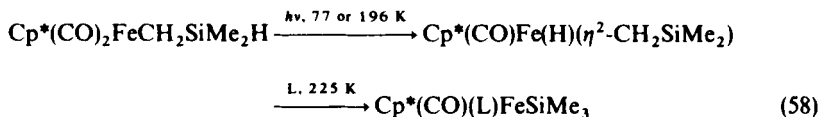
complexes, there should be two contributing resonance forms for such a complex (**25** and **26**). Resonance hybrid **26** is expected to be more important, given the marked preference of silicon for tetravalent structures.

Silene complexes are possible intermediates resulting from  $\beta$ -transfer during rearrangements that interconvert M–C and M–Si bonds<sup>120–123</sup> (e.g. equations 56<sup>120</sup> and 57<sup>121</sup>).



Such intermediates have been spectroscopically observed in related photochemical conversions of  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3\text{WCH}_2\text{SiMe}_2\text{H}$  (R=H, Me) to  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3\text{WSiMe}_3$ . The intermediate silene complexes  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{W}(\text{H})(\eta^2\text{-CH}_2\text{SiMe}_2)$  were observed in hydrocarbon matrices at 77 K by infrared spectroscopy, and in solution at 200 K by NMR. The NMR data are most consistent with a metallasilacyclopropane structure (resonance form **26**)<sup>124</sup>.

More recently, the near-UV photolysis of  $\text{Cp}^*(\text{CO})_2\text{FeCH}_2\text{SiMe}_2\text{H}$  in the presence of ligand L (CO or  $\text{PPh}_3$ ) was shown to proceed via  $\beta$ -H transfer to  $\text{Cp}^*(\text{CO})(\text{L})\text{FeSiMe}_3$  (equation 58). The intermediate silene complex  $\text{Cp}^*(\text{CO})\text{Fe}(\text{H})(\eta^2\text{-CH}_2\text{SiMe}_2)$ , characterized by low-temperature infrared, UV-vis and NMR studies, was stable to 225 K.



Although  $\beta$ -H transfer is the major photoprocess observed, direct rearrangement of the  $\text{FeCH}_2\text{SiMe}_2\text{H}$  derivative to the  $\text{FeSiMe}_3$  compound, possibly via radical species, accounts for 20% of reaction<sup>125</sup>.

Related silapropadiene nickel complexes have been proposed for nickel-catalyzed reactions of silacyclopropenes (see Section VI.E.4 and Scheme 15).

## V. STRUCTURE AND BONDING

Transition-metal silicon compounds exhibit a range of interesting structural features that have been characterized by various physical methods. Most of these studies have been concerned simply with the identification of new compounds, while some attention has been directed toward developing a detailed description of metal–silicon bonding. The principal techniques that have been applied are discussed below, particularly with regard to investigations of the characteristics of silyl groups as ligands.

### A. Structural Information

Structures of transition-metal silicon compounds have been determined principally by X-ray crystallography, and to a lesser extent by electron and neutron diffraction.

#### 1. Metal–silicon bond distances

Structural data for late or low-valent transition-metal silyl derivatives show that metal–silicon distances are commonly shorter than expected for single covalent bonds. These observations have often been attributed to  $d_\pi$ – $d_\pi$   $\pi$ -bonding involving donation of

d-electron density from the transition metal to empty silicon d orbitals of appropriate symmetry. Although empty d orbitals on silicon have often been invoked to explain silyl substituent effects, it appears that at least in some cases, the acceptor orbital on silicon is best described as a  $\sigma^*$  orbital<sup>126, 127</sup>. One theoretical study based on extended Huckel

TABLE 1. Selected M-Si distances in late transition-metal silyl complexes

Compound	M-Si Obsvd. (Å)	M-Si Calcd (Å)	Reference
1. Cp(CO) <sub>2</sub> MnH(SiPh <sub>3</sub> )	2.424 (2)		129
2. Cp(CO) <sub>2</sub> MnH(SiPhCl <sub>2</sub> )	2.310 (2)		129
3. (CO) <sub>5</sub> MnSiF <sub>3</sub>	2.360 (7)		130
4. (CO) <sub>5</sub> MnSiH <sub>3</sub>	2.407 (5)		131
5. (CO) <sub>5</sub> MnSiMe <sub>3</sub>	2.497 (5)	2.63	132, 133
6. <i>trans</i> -(CO) <sub>4</sub> (PPh <sub>3</sub> )MnSiMe <sub>3</sub>	2.453 (4)	2.55	134
7. (CO) <sub>5</sub> MnSi(SiMe <sub>3</sub> ) <sub>3</sub>	2.564 (6)	2.56	135
8. (CO) <sub>5</sub> ReSiH <sub>3</sub>	2.56 (1)		136
9. (CO) <sub>5</sub> ReSiMe <sub>3</sub>	2.600 (1)		49
10. (CO) <sub>2</sub> ReSi(SiMe <sub>3</sub> ) <sub>3</sub>	2.665 (9)		49
11. ( $\mu$ -SiPh <sub>2</sub> )Re <sub>2</sub> H <sub>2</sub> (CO) <sub>8</sub>	2.544 (9)	2.68	137
12. Cp(CO) <sub>2</sub> ReH(SiPh <sub>3</sub> )	2.49 (1)		138
13. Cp(CO)FeH(SiCl <sub>3</sub> ) <sub>2</sub>	2.252 (3)	2.51	133
14. NEt <sub>4</sub> [(CO) <sub>4</sub> FeSiCl <sub>3</sub> ]	2.224		139
15. <i>trans</i> -(CO) <sub>4</sub> Fe(SiCl <sub>3</sub> ) <sub>2</sub>	2.326 (2)		140
16. <i>cis</i> -(CO) <sub>4</sub> Fe(SiMe <sub>3</sub> ) <sub>2</sub>	2.456 (2)		140
17. Cp(PMe <sub>2</sub> Ph) <sub>2</sub> FeSiMe <sub>2</sub> Ph	2.339 (2)		140
18. Cp(CO) <sub>2</sub> FeSiCl <sub>3</sub>	2.216 (1)		141
19. Cp(CO) <sub>2</sub> FeSiFPh <sub>2</sub>	2.278 (1)		141
20. NEt <sub>4</sub> {Fe[Si(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> Cl} (4)	2.488 (6)		52
21. ( $\eta^5$ -C <sub>8</sub> H <sub>9</sub> SiMe <sub>3</sub> )(CO) <sub>2</sub> RuSiMe <sub>3</sub>	2.414 (2)	2.59	142
22. [(CO) <sub>3</sub> Ru(SiMe <sub>3</sub> )( $\mu$ -SiMe <sub>2</sub> ) <sub>2</sub> ]	2.391 (7), 2.491 (8), 2.507 (8)	2.44	143
23. ( $\eta^6$ -1,4- <sup>1</sup> Bu <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )(CO)Ru(SiCl <sub>3</sub> ) <sub>2</sub>	2.338 (1), 2.340 (1)		144
24. Cp*(PMe <sub>3</sub> ) <sub>2</sub> RuSiHPh <sub>2</sub> *	2.387 (1)		19
25. Os <sub>3</sub> ( $\mu$ -H) <sub>3</sub> (CO) <sub>9</sub> (SiMeCl <sub>2</sub> )	2.420 (5), 2.400 (6)		145
26. <i>trans</i> -Os(PPh <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SiMe <sub>2</sub> ) <sub>2</sub> (CO) <sub>2</sub>	2.472 (4), 2.471 (4), 2.479 (4), 2.485 (4)		146
27. (CO) <sub>4</sub> CoSiF <sub>3</sub>	2.226 (5)	2.51	133, 147
28. (CO) <sub>4</sub> CoSiCl <sub>3</sub>	2.254 (3)	2.51	148
29. (CO) <sub>4</sub> CoSiH <sub>3</sub>	2.381 (4)	2.51	149
30. RhHCl(SiCl <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	2.203 (4)	2.48	133, 150
31. Cp*Rh(SiEt <sub>3</sub> ) <sub>2</sub> H <sub>2</sub> * (1)	2.379 (2)		27
32. (PPh <sub>3</sub> ) <sub>2</sub> (CO)HrSiMe <sub>2</sub> OSiMe <sub>2</sub>	2.399 (2), 2.416 (2)		151
33. (PPh <sub>3</sub> )(CO) <sub>2</sub> IrSiMe <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub>	2.454 (6)		152
34. Cp*Ir(SiEt <sub>3</sub> ) <sub>2</sub> H <sub>2</sub> *	2.390 (1)		153
35. (CO) <sub>3</sub> Ni(SiCl <sub>3</sub> ) <sub>2</sub>	2.283 (3), 2.289 (3)		154
36. ( $\eta^6$ -C <sub>6</sub> H <sub>3</sub> Me <sub>3</sub> )Ni(SiCl <sub>3</sub> ) <sub>2</sub>	2.194 (2)		154
37. <i>trans</i> -(PMe <sub>2</sub> Ph) <sub>2</sub> Pt(SiMePh <sub>2</sub> )Cl	2.29	2.46	155
38. <i>trans</i> -(Pc-Hex <sub>3</sub> ) <sub>2</sub> Pt(SiH <sub>3</sub> )H	2.382 (3)		156

\* Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>.

MO calculations for  $(\text{CO})_4\text{CoSiX}_3$  ( $X = \text{F}, \text{Cl}$ ) supports the presence of small but significant Co–Si  $\pi$ -bonding involving Si d orbitals<sup>128</sup>.

Table 1 lists selected metal–silicon distances in late transition-metal complexes with some calculated covalent bond lengths. There is some difficulty in estimating covalent single-bond distances, given the sensitivity of covalent radii to substituent effects, and to coordination number and oxidation state of the metal. However, the differences between observed and predicted values are in many cases too large to be accounted for by errors in the calculated bond distances. Therefore some bond shortening is clearly present, and it is appealing to attribute this to a  $\pi$  component in the M–Si bond. This shortening is greatest with electronegative substituents in the silyl ligand (see Table 1), but the observed bond shortening does not appear to be just a function of such electronegativity effects (i.e., contraction of silicon d orbitals by electron-withdrawing groups, increasing their involvement in  $\pi$ -bonding)<sup>133</sup>. Consistent with the presence of some  $\pi$ -bonding, the Rh–Si distance for  $\text{RhHCl}(\text{SiCl}_3)(\text{PPh}_3)_2$ , 2.203 (4) Å, in which  $\text{SiCl}_3$  is not *trans* to a  $\pi$ -accepting ligand, is one of the shortest M–Si distances known<sup>133, 150</sup>. Also, comparison of the structures of  $(\text{CO})_5\text{MnSiMe}_3$  and *trans*- $(\text{CO})_4(\text{PPh}_3)\text{MnSiMe}_3$  shows that the shorter Mn–Si distance is found *trans* to the weakest  $\pi$ -accepting ligand, where competition for d  $\pi$ -electrons is minimized<sup>134</sup>. The shortest Fe–Si distance is found in the anionic Fe(0) ( $d^8$ ) complex  $[(\text{CO})_4\text{FeSiCl}_3]^-$ , for which a high degree of  $\pi$ -backbonding might be expected<sup>139</sup>.

Further support for the presence of  $\pi$ -bonding in the above compounds comes from structural studies with  $d^0$  silyl complexes, which should not exhibit  $d_{\pi}-d_{\pi}$  backbonding since d orbitals on the transition metal are unoccupied. As can be seen from Table 2, M–Si distances in  $d^0$  complexes are close to, or even greater than, the predicted values. Note that the reported Zr–Si distances (2.81 Å) are remarkably greater than the M–Si distances found in other second transition series silyl complexes, such as the  $d^6$   $\text{RhHCl}(\text{SiCl}_3)(\text{PPh}_3)_2$  [2.203 (4) Å]<sup>150</sup> and the  $d^4$   $\text{Cp}^*\text{Rh}(\text{SiEt}_3)_2\text{H}_2$  [2.379 (2) Å]<sup>27</sup>.

The silylene-bridged complex  $\text{Cp}_2\text{Ti}(\mu\text{-SiH}_2)_2\text{TiCp}_2$  is anomalous in possessing an inexplicably short Ti–Si bond length<sup>79</sup>. The reported distance, 2.159 (13) Å, is much

TABLE 2. M–Si bond distances in early transition-metal silyl complexes

Compound	$d^n$ config	M–Si Obsvd. (Å)	M–Si Calcd (Å)	Reference
1. $\text{Cp}_2\text{Ti}(\mu\text{-SiH}_2)_2\text{TiCp}_2$ (10)	$d^0$	2.159 (13)		79
2. $\text{CpTi}(\text{SiMe}_3)\text{Cl}$	$d^0$	2.67 (1)		81
3. $\text{Cp}_2\text{Ti}(\mu\text{-SiPhH}_2)_2\text{TiCp}_2$ (14)	$d^1$	2.604 (2), 2.583 (2)		88
4. $\text{Cp}_2\text{Ti}(\mu\text{-SiPhH}_2)(\mu\text{-H})\text{TiCp}_2$ (15)	$d^1$	2.61 (2)		88
5. $\text{Cp}_2\text{Zr}(\text{SiPh}_3)\text{Cl}$	$d^0$	2.813 (2)	2.63	8, 157
6. $\text{Cp}_2\text{Zr}(\text{SiMe}_3)(\text{S}_2\text{CNEt}_2)$	$d^0$	2.815 (1)	2.63	77
7. $\text{Cp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}_2^a$ (42)	$d^0$	2.748 (4)		158
8. $\text{Cp}_2\text{Nb}(\text{SiMe}_3)(\eta^2\text{-C}_2\text{H}_4)$	$d^2$	2.669 (1)	2.67	86
9. $\text{Cp}_2\text{Ta}(\text{SiMe}_2\text{Ph})\text{H}_2$	$d^0$	2.651 (4)	2.61	87
10. $\text{Cp}^*\text{Ta}(\text{SiMe}_3)\text{Cl}_3^a$	$d^0$	2.669 (4)	2.47	82
11. $\text{Cp}^*\text{Ta}(\text{SiMe}_3)(\text{PMe}_3)\text{Cl}_2^a$ (13)	$d^1$	2.642 (1)	2.53	82
12. $\text{Mo}_2[\text{Si}(\text{SiMe}_3)_3]_2(\text{NMe}_2)_4$ (3)	$d^3$	2.670 (2)	2.585	51
13. $(\text{PMe}_3)_3\text{W}(\text{SiMe}_3)\text{H}_2\text{I}$	$d^2$	2.388 (6)		159
14. $[\text{Li}(\text{DME})_3]^+ [\text{Cp}_2\text{Sm}(\text{SiMe}_3)_2]^-$	$d^{0f2}$	2.880 (2)		90

<sup>a</sup>  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$

shorter than other Ti-Si distances, and is even shorter than analogous Ti-C(sp<sup>3</sup>) distances reported for Cp<sub>2</sub>TiCH<sub>2</sub>CRRCH<sub>2</sub> complexes<sup>160</sup>. The W-Si bond in (PMe<sub>3</sub>)<sub>3</sub>W(SiMe<sub>3</sub>)H<sub>2</sub>I also appears to be unusually short [2.388 (6) Å] and, curiously, is significantly shorter than the W-P bonds in the molecule (av 2.50 Å)<sup>159</sup>.

The Ta-Si distance observed for Cp<sub>2</sub>Ta(SiMe<sub>3</sub>,Ph)H<sub>2</sub> is close to what is predicted based on covalent radii, implying that M(d<sup>0</sup>)-Si bonds are not inherently elongated and weak, as was suggested by structures for the zirconium silyl derivatives<sup>87</sup>. The Nb-Si bond in the d<sup>2</sup> complex Cp<sub>2</sub>Nb(SiMe<sub>3</sub>)(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>) is also what is expected for a single covalent bond<sup>86</sup>. However, Cp\*Ta(SiMe<sub>3</sub>)Cl<sub>3</sub> (d<sup>0</sup>)<sup>82</sup>, Cp\*Ta(SiMe<sub>3</sub>)(PMe<sub>3</sub>)Cl<sub>2</sub> (d<sup>1</sup>)<sup>82</sup> and Mo<sub>2</sub>[Si(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> (d<sup>3</sup>)<sup>51</sup> exhibit M-Si bond lengths that are greater than those predicted from covalent radii. The latter two tantalum compounds (Figures 3 and 4) offer the opportunity to examine the effect of electron density at the metal on the M-Si bond length, since these structures are closely related, with similar four-legged piano-stool geometries. The Ta-Si distance in the Ta(IV) complex is shorter than that in the Ta(V) case, despite the fact that the covalent radius of the Ta(IV) center should be greater. This reduction in bond length of about 0.03 Å per d electron may reflect some degree of π-bonding between Si and Ta in Cp\*Ta(SiMe<sub>3</sub>)(PMe<sub>3</sub>)Cl<sub>2</sub>. Similar effects have been observed for metal-phosphine bonding, where a reduction in M-P bond lengths of 0.02-0.05 Å per d electron are observed<sup>161</sup>.

Despite the evidence just presented, the case for π-bonding in transition-metal silyl complexes is still open to criticism. An alternative explanation for short M-Si distances based only on σ-effects is possible, as has been discussed for analogous stannyl derivatives<sup>162</sup>. It is argued that the electropositive transition-metal substituents in L<sub>n</sub>MSiR<sub>3</sub> compounds direct a high degree of s-character in the silicon contribution to the M-Si bond, thus shortening the bond. Concomitantly, more p-character is directed

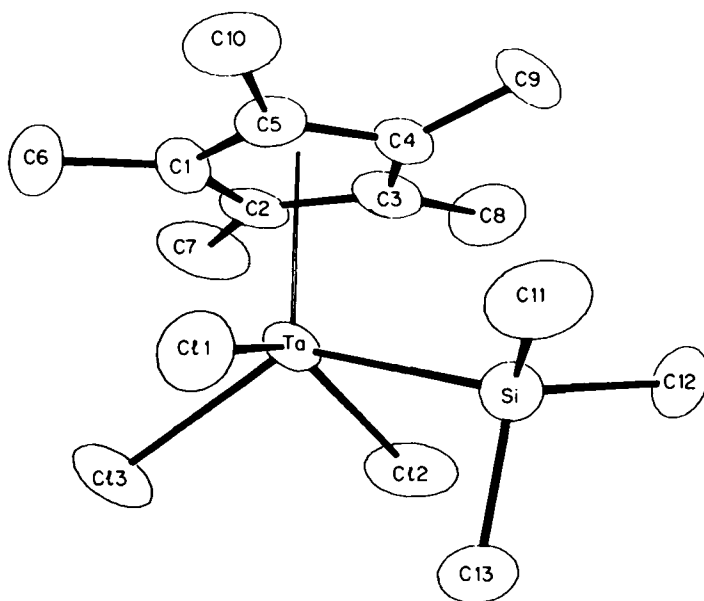
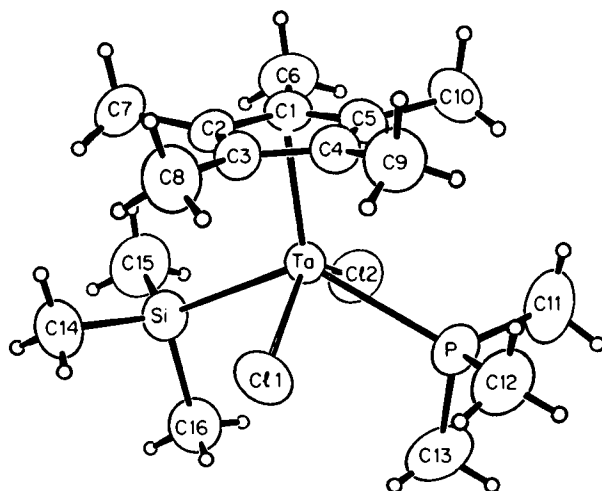


FIGURE 3. ORTEP view of Cp\*Ta(SiMe<sub>3</sub>)Cl<sub>3</sub>

FIGURE 4. ORTEP view of  $\text{Cp}^*\text{Ta}(\text{SiMe}_3)(\text{PMe}_3)\text{Cl}_2$ 

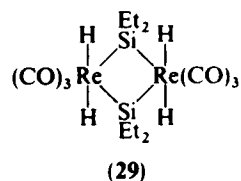
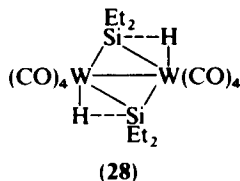
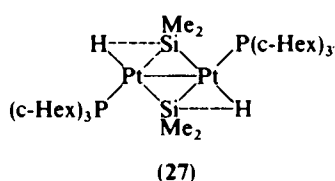
toward the Si–R bonds. This rationale therefore explains the relatively long Si–R bond lengths, the somewhat acute R–Si–R angles, and the large M–Si–R angles that are commonly observed.

## 2. Other structural features

The Pt–Cl bond length of 2.45 (1) Å for *trans*-( $\text{PMe}_2\text{Ph}$ )<sub>2</sub>Pt(SiMePh<sub>2</sub>)Cl is quite long, providing evidence for the high *trans*-influence of the silyl ligand<sup>155</sup>. Rather long Os–P distances in  $\overline{\text{Os}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)_2(\text{CO})_2}$  also provide evidence for the exceptional *trans*-influencing property of silyl ligands<sup>146</sup>. Silyl ligands are also known to have a high kinetic *trans*-effect, showing the tendency to labilize ligands in the *trans* coordination site<sup>163</sup>.

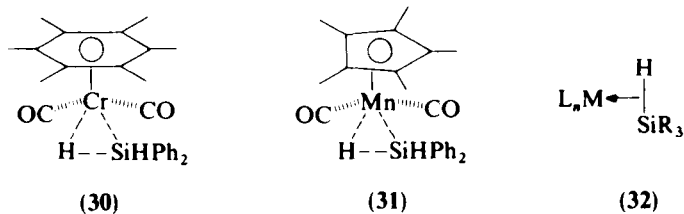
The coordination geometries of octahedral and trigonal bipyramidal carbonyl complexes  $[(\text{CO})_5\text{MSiR}_3]$  and  $(\text{CO})_4\text{MSiR}_3$  are distorted such that the equatorial carbonyl ligands are bent slightly toward the silyl group. This has been observed in other carbonyl complexes and has been attributed to  $\pi$ -bonding effects<sup>7,8,10,14</sup>. This distortion is, of course, less pronounced in complexes with bulky silyl groups [e.g.  $(\text{CO})_5\text{MSi}(\text{SiMe}_3)_3$ , M = Mn, Re]<sup>49,135</sup>.

A number of transition-metal silyl compounds possessing M  $\cdots$  H  $\cdots$  Si bridges have been structurally characterized. For example, bridging hydrogens have been identified in the dinuclear compounds **27**<sup>164</sup> and **28**<sup>165</sup>. In **27**, the Si–H distances are 1.72 Å<sup>164</sup>.



Compound **29**, which closely resembles **28**, does not have Si  $\cdots$  H interactions, presumably because the structure is less sterically congested<sup>166</sup>. Most M  $\cdots$  H  $\cdots$  Si bridges appear to involve a direct M-Si bond, but this does not seem to be the case for the titanium dinuclear silyl compounds **14** and **15** mentioned earlier<sup>88</sup>.

Other examples of M  $\cdots$  H  $\cdots$  Si bridges are found in mononuclear silyl complexes, e.g.  $(\eta^6\text{-C}_6\text{Me}_6)(\text{CO})_2\text{Cr}(\text{H})\text{SiHPh}_2$  (**30**)<sup>167</sup> and  $\text{Cp}^*(\text{CO})_2\text{Mn}(\text{H})\text{SiHPh}_2$  (**31**)<sup>168</sup>. In such



complexes, the Si-H(bridge) distances are 0.15–0.20 Å longer than typical Si-H distances in tetrahedral silanes. The  $\text{HSiR}_3$  coordination may be described by three-center two-electron bonding with the silane acting as a two-electron ligand, donating an Si-H bonding electron pair to the metal (**32**). These structures are therefore likely representations for the three-center transition state that may be involved in the oxidative addition of silanes to transition metals. Substitutions at both the metal and silicon affect the M-H and Si-H distances, but mainly influence the M-Si bond (Table 3). The M-Si distances seem to correlate well with the degree of three-center bonding, with longer M-Si distances being found in compounds with the shortest Si-H bonds. Generally, steric congestion in the coordination sphere of the metal decreases the Si-H distance, and favors reductive elimination of the silane. Thus, the Si-H distance in **30** is shorter than the corresponding distance in the isoelectronic **31** due to the greater steric bulk of  $\text{C}_6\text{Me}_6$  relative to  $\text{C}_5\text{Me}_5$ <sup>167</sup>. As expected, electron-donating ligands favor the oxidative addition product, and opening of the Si-H bond<sup>167,168</sup>. The degree of three-center bonding may be judged from  $^2J_{\text{SiMH}}$  coupling constants (*vide infra*), and is also reflected in the activation enthalpies for reductive elimination of  $\text{HSiR}_3$  from  $\text{Cp}(\text{CO})(\text{L})\text{Mn}(\text{H})\text{SiR}_3$  complexes<sup>168,172</sup>.

TABLE 3. Structural data for mononuclear complexes with coordinated Si-H bonds

Compound	M-Si, Å	M-H, Å	Si-H, Å	Reference
1. $(\eta^6\text{-C}_6\text{Me}_6)(\text{CO})_2\text{Cr}(\text{H})\text{SiHPh}_2$ ( <b>30</b> )	2.456 (1)	1.61 (4)	1.61 (4)	167
2. $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Mn}(\text{H})\text{SiHPh}_2$ ( <b>31</b> )	2.395 (1)	1.52 (3)	1.77 (3)	168
3. $(\eta^3\text{-C}_3\text{H}_4\text{Me})(\text{CO})(\text{PMe}_3)\text{Mn}(\text{H})\text{SiHPh}_2$	2.327 (1)	1.49 (4)	1.78 (4)	168
4. $(\eta^3\text{-C}_3\text{H}_4\text{Me})(\text{CO})_2\text{Mn}(\text{H})\text{SiFPh}_2$	2.352 (4)	1.569 (4)	1.802 (5)	168, 169
5. $(\eta^3\text{-C}_3\text{H}_4\text{Me})(\text{CO})_2\text{Mn}(\text{H})\text{SiCl}_3$	2.254 (1)	1.47 (3)	1.79 (4)	170
6. $(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mn}(\text{H})\text{SiPh}_3$	2.424 (2)	1.55 (4)	1.76 (4)	171

## B. Information from NMR Studies

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy have been used extensively to assign structures and study fluxional processes in transition-metal silyl complexes. For example, cobalt silyls  $(\text{CO})_4\text{CoSiR}_3$  ( $\text{R} = \text{Ph}, \text{F}, \text{Cl}$ ) are fluxional in solution as determined by variable-

temperature  $^{13}\text{C}$  NMR spectra. The free-energy barriers to intramolecular rearrangement (involving exchange of axial and equatorial carbonyl ligands) seem to be determined mainly by the steric requirements of the silyl group $^{173}$ . Variable-temperature  $^1\text{H}$  NMR spectra reveal that the mixed alkyl/silyl  $\text{Cp}^*\text{Ta}(\text{SiMe}_3)\text{Me}_3$  is stereochemically nonrigid, with one methyl resonance being observed at room temperature. The  $\Delta G^\ddagger$  for the methyl exchange process was found to be  $12.5 \pm 0.5 \text{ kcal mol}^{-1}$  $^{82}$ .

Solution NMR studies have also provided information regarding molecular isomerizations. The carbonyl species  $(\text{CO})_4\text{M}(\text{SiR}_3)_2$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) undergo *cis-trans* isomerizations in solution. The free energies of activation for this process are greatest for the heavier metals ( $\text{Fe} < \text{Ru} < \text{Os}$ ), and with silyl groups the barriers increase in the order  $\text{Me}_3\text{Si} < \text{Me}_2\text{ClSi} < \text{MeCl}_2\text{Si} < \text{Cl}_3\text{Si}^{174}$ .

$^{29}\text{Si}$  NMR spectroscopy is potentially a useful technique for characterizing silicon compounds, given the sensitivity of chemical shifts to changes in the coordination environment of silicon, and the wide range of  $^{29}\text{Si}$  chemical shifts (ca. 550 ppm at present). Unfortunately, there are as yet no accurate methods for predicting the magnitudes of these shifts $^{175}$ . Good techniques are now available for overcoming the low NMR sensitivity of  $^{29}\text{Si}$ , such as selective population transfer (SPT) $^{176}$  and insensitive nuclei enhanced by polarization transfer (INEPT) $^{177}$ . A few reports specifically address  $^{29}\text{Si}$  NMR spectroscopy of transition-metal silyls $^{178-180}$ .

In general, substitution of a transition-metal group into a silane results in a marked shift of the  $^{29}\text{Si}$  resonance to low field. In fact one of the largest downfield  $^{29}\text{Si}$  NMR shifts has been observed for the iron silyl derivative  $\text{Fe}_2(\text{CO})_8(\mu_2\text{-SiMe}_2)$  [ $\delta(^{29}\text{Si}) = 173 \text{ ppm}$ ] $^{181}$ . The tantalum silyl compound  $\text{Cp}^*\text{Ta}(\text{SiMe}_3)\text{Cl}_3$  also exhibits a remarkable downfield shift for an  $-\text{SiMe}_3$  derivative [ $\delta(^{29}\text{Si}) = 122.9 \text{ ppm}$ ] $^{182}$ . Typical  $^{29}\text{Si}$  NMR shift values for transition-metal silyl compounds are in the range  $-30$  to  $+70 \text{ ppm}$  (Table 4). In general, for a homologous series of complexes, there is an upfield shift of the  $\delta(^{29}\text{Si})$  as a transition-metal group is descended $^{178}$ . The opposite trend seems to predominate, however, for  $d^0$  complexes and for the main-group silyls  $\text{M}[\text{Si}(\text{SiMe}_3)_3]_2$  ( $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$ ) $^{183}$ .

From  $|^2J_{\text{SiCH}}|$  coupling constants in  $(\text{CO})_4\text{M}(\text{SiMe}_n\text{Cl}_{3-n})_2$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) complexes it appears that there is considerable s character in the  $\text{M}-\text{Si}$  bonds $^{178}$ . This is consistent with Bent's rule $^{186}$ , which states that s character should concentrate in orbitals directed toward electropositive substituents. Also,  $|^1J_{\text{SiH}}|$  coupling constants in  $\text{L}_n\text{MSiHRR}'$  derivatives are smaller than typical values for silane derivatives $^{175}$ , suggesting that there is considerable p character in the  $\text{Si}-\text{H}$  bonds. This has been discussed at length for complexes of the type  $(\text{L}_n\text{M})_2\text{SiH}_2$  $^9$ . The lower  $|^1J_{\text{SiH}}|$  value for  $\text{Cp}_2^*\text{Zr}(\text{SiHMe}_2)\text{Cl}$  (148 Hz) compared to *trans*- $\text{PtCl}(\text{SiH}_2\text{Cl})(\text{PEt}_3)_2$  (204 Hz) is consistent with the more electropositive character of zirconium (Table 4).

A correlation has also been made between  $|^2J_{\text{SiMH}}|$  coupling constants and the degree of three-center  $\text{M} \cdots \text{H} \cdots \text{Si}$  bonding, with high values of  $|^2J_{\text{SiMH}}|$  being observed for complexes with a strong  $\text{Si}-\text{H}$  interaction $^{168,184}$ . For complexes with significant  $\text{Si} \cdots \text{H}$  interactions, these coupling constants may be as high as 70 Hz. The  $|^2J_{\text{SiMH}}|$  value of only 8 Hz for  $\text{Cp}^*\text{RhH}_2(\text{SiEt}_3)_2$  is consistent with the X-ray crystal structure which demonstrates the absence of a significant  $\text{Si} \cdots \text{H}$  interaction $^{27}$ .

### C. Information from Infrared and Raman Studies

Vibrational spectroscopy has been widely applied to the characterization of transition-metal silyl complexes. In many cases  $\nu(\text{MSi})$  stretching frequencies have been assigned; these usually fall in the  $250\text{--}350 \text{ cm}^{-1}$  range $^{6-10,14}$ . Assignment of these values can be difficult, since coupling between  $\nu(\text{MSi})$ ,  $\nu(\text{CO})$  and  $\nu(\text{SiX})$  stretching modes is possible $^{10,14}$ .

TABLE 4. Selected  $^{29}\text{Si}$  NMR data for transition-metal silyl complexes

Compound	$^{29}\text{Si}$ NMR shift, $\delta$	Assignments	Reference
1. $\text{Zn}[\text{Si}(\text{SiMe}_3)_3]_2$	-123.9	$\text{Si}(\text{SiMe}_3)_3$	183
	-7.18	$\text{Si}(\text{SiMe}_3)_3$	
2. $\text{Cd}[\text{Si}(\text{SiMe}_3)_3]_2$	-109.2	$\text{Si}(\text{SiMe}_3)_3$	183
	-6.28	$\text{Si}(\text{SiMe}_3)_3$	
3. $\text{Hg}[\text{Si}(\text{SiMe}_3)_3]_2$	-54.5	$\text{Si}(\text{SiMe}_3)_3$	183
	-2.84	$\text{Si}(\text{SiMe}_3)_3$	
4. $\text{Zn}[\text{Si}(\text{SiMe}_3)_3]_2(\text{bipy})$	-150.8	$\text{Si}(\text{SiMe}_3)_3$	183
	-6.60	$\text{Si}(\text{SiMe}_3)_3$	
5. $\text{Cp}_2\text{Ti}(\text{SiMe}_3)\text{Cl}$	42.93		182
6. $\text{Cp}_2\text{Ti}(\mu\text{-H})(\mu\text{-SiHPh})\text{TiCp}_2$ ( <b>15</b> )	87.2	( $^1J_{\text{SiH}} = 148.58 \text{ Hz}$ ; $^2J_{\text{SiH}} = 14 \text{ Hz}$ )	88
7. $\text{Cp}_2\text{Zn}(\text{SiMe}_3)\text{Cl}$	24.48		182
8. $\text{Cp}_2\text{Hf}(\text{SiMe}_3)\text{Cl}$	41.20		182
9. $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$	-87.30		182
	-6.30	$\text{Si}(\text{SiMe}_3)_3$	
10. $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$	-77.87		182
	-4.85	$\text{Si}(\text{SiMe}_3)_3$	
11. $\text{Cp}^*\text{Cl}_2\text{ZrSi}(\text{SiMe}_3)_3$ ( <b>40</b> )	-55.65		182
	-6.26	$\text{Si}(\text{SiMe}_3)_3$	
12. $\text{Cp}^*\text{Cl}_2\text{HfSi}(\text{SiMe}_3)_3$ ( <b>42</b> )	-49.77		182
	-3.69	$\text{Si}(\text{SiMe}_3)_3$	
13. $\text{Cp}_2^*\text{Zr}[\text{SiHMe}_2]\text{Cl}$	-20.29	( $^1J_{\text{SiH}} = 148 \text{ Hz}$ )	182
14. $\text{Cp}_2\text{Zr}(\text{SiH}_2\text{Ph})(\mu\text{-H})_2\text{ZrCp}_2(\text{SiMeHPh})$	-7.86	$\text{SiH}_2\text{Ph}$ ( $^1J_{\text{SiH}} = 147 \text{ Hz}$ )	89
	15.81	$\text{SiMeHPh}$ ( $^1J_{\text{SiH}} = 168 \text{ Hz}$ )	





For silyl derivatives of the type  $\text{SiH}_n[\text{ML}_m]_{4-n}$  ( $n=2,3$ ), low  $\nu_{\text{as}}(\text{SiH})$  stretching frequencies are in accord with Bent's rule<sup>186</sup>, implying that the  $\text{ML}_m$  groups have low effective electronegativities<sup>9</sup>. Such vibrational data can be correlated by simple additivity relationships that consider the inductive power of the silicon substituents<sup>7</sup>.

A number of studies have addressed the role of  $d_{\pi}-d_{\pi}$  interactions in M-Si bonds. Analyses of CO stretching force constants in carbonyl/silyl complexes have been offered as evidence for M-Si  $\pi$ -bonding, but these interpretations are controversial<sup>8,10,14</sup>. A study of  $\text{CpFe}(\text{CO})_2\text{X}$  (X = alkyl and silyl) compounds by Mössbauer and infrared spectroscopy revealed greater s-electron density at the iron nucleus for the silyl derivatives, suggesting that silyl groups are superior  $\sigma$ -donors. Although  $\sigma$ -effects appear to be most important in explaining the data, trends in the  $\nu(\text{CO})$  stretching frequencies of  $\text{Cp}(\text{CO})_2\text{FeSiMe}_{3-n}\text{Ph}_n$  compounds are consistent with significant  $\pi$ -bonding<sup>187</sup>.

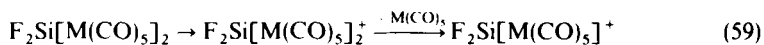
The *trans* influence of silyl ligands has been evaluated from  $\nu(\text{MCl})$  stretching frequencies. Generally very low  $\nu(\text{MCl})$  values are observed, consistent with silyl ligands having a high *trans* influence. The lowest  $\nu(\text{MCl})$  values are observed for silyl groups with electron-releasing substituents<sup>188</sup>.

#### D. Information from Mass Spectrometric Studies

Mass spectroscopy also appears to be a valuable technique for the characterization of silyl complexes, particularly in cases where the nuclearity (or degree of association) of the compound is in question. For carbonyl complexes common fragmentation patterns consist of loss of CO, loss of silicon substituent, or, less frequently, rupture of the M-Si bond.

Appearance potentials have been measured to provide estimates of  $D(\text{M-Si})$  dissociation energies. Studies with  $(\text{CO})_4\text{CoSiR}_3$  compounds have led to estimates of rather high  $D(\text{M-Si})$  values, which were offered as evidence for  $d_{\pi}-d_{\pi}$  bonding<sup>189</sup>. The  $D(\text{M-Si})$  for  $(\text{CO})_5\text{MSiMe}_3$  is  $255 \text{ kJ mol}^{-1}$  for  $\text{M}=\text{Mn}$  and  $300 \text{ kJ mol}^{-1}$  for  $\text{M}=\text{Re}$ <sup>190,191</sup>. Appearance potentials show that the Fe-Si bond in phosphine-substituted  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeSiMe}_3$  [ $D(\text{Fe-Si})=215 \text{ kJ mol}^{-1}$ ] is stronger than that of  $\text{Cp}(\text{CO})_2\text{FeSiMe}_3$  [ $D(\text{Fe-Si})=190 \text{ kJ mol}^{-1}$ ]<sup>192</sup>.

Mass spectra of the fluorosilyl complexes  $\text{F}_2\text{Si}[\text{M}(\text{CO})_5]_2$  ( $\text{M}=\text{Mn}, \text{Re}$ ) show the fragmentation process shown in equation 59. The silicenium ions  $\text{F}_2\text{Si}[\text{M}(\text{CO})_5]^+$  were formed in high abundance, but attempts to prepare such derivatives failed<sup>9</sup>. The mass spectrum of  $[(\text{CO})_4\text{FeSiCl}_2]_3$ , prepared from  $[\text{Et}_4\text{N}][(\text{CO})_4\text{FeSiCl}_3]$  and  $\text{AlCl}_3$ , exhibits peaks for the trimer and also provides evidence for the monomeric silylene species  $(\text{CO})_4\text{FeSiCl}_2^+$  in the gas phase<sup>111</sup>.



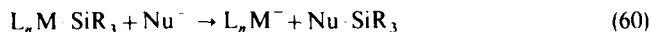
### VI. REACTIONS INVOLVING M-SI BONDS

Aspects of the reaction chemistry of transition-metal silyl derivatives have been extensively reviewed<sup>6-14</sup>. This section will focus primarily on reactivity in which M-Si bonds actively participate. Note that reactions involving oxidative additions and reductive eliminations of Si-X bonds with transition-metal centers are also considered separately in Sections II, III, IV and V.

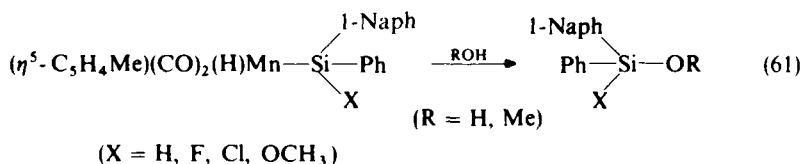
#### A. Cleavage of M-Si Bonds by Nucleophiles

Many late or low-valent transition-metal silyl complexes  $\text{L}_n\text{M-SiR}_3$  are susceptible to nucleophilic attack at silicon. The ease of such reactions is influenced heavily by the

properties of the  $L_nM^-$  anion as a leaving group (equation 60). Thus some M-Si bonds are sensitive to hydrolysis or alcoholysis with Si-O bonded products resulting, possibly



via initial attack at the metal-bound silicon. Solvolysis of  $(CO)_5MnSiMe_3$  in methanol to  $(CO)_5MnH$  and  $Me_3SiOMe$  has been reported as a convenient preparation of the manganese hydride compound.<sup>193</sup> Treatment of manganese silyl complexes with water or methanol displaces the silyl ligand with inversion of stereochemistry at silicon (equation 61)<sup>11, 194, 195</sup>. The Co-Si bond of optically active  $(S)(+)-(CO)_4CoSi-$



$(1\text{-Naph})(\text{Ph})(\text{Me})$  is also cleaved by  $H_2O$  with inversion, giving  $(R)(-)-\text{HOSi}(1\text{-Naph})(\text{Ph})(\text{Me})$ <sup>196</sup>. In contrast, the Fe-Si bond in  $(R)(+)-\text{Cp}(\text{CO})_2\text{-FeSi}(1\text{-Naph})(\text{Ph})(\text{Me})$  is cleaved by  $H_2O$  with retention of configuration at silicon<sup>197</sup>. These differences in reactivity between the manganese, cobalt and iron silyl derivatives were explained as being due to the poorer properties of  $\text{Cp}(\text{CO})(\text{L})\text{Fe}^-$  as a leaving group<sup>197</sup>. Note that some silyl complexes, particularly those of the more electropositive early transition metals, react with  $H_2O$  or alcohols to afford  $\text{H-SiR}_3$  products (*vide infra*). Addition of dimethylamine to  $\text{Cp}(\text{CO})_3\text{MoSiH}_3$  gives an isolable 1:1 adduct that on further heating to 70°C decomposes to  $\text{H}_3\text{SiNMe}_2$  and  $\text{Cp}(\text{CO})_3\text{MoH}$ <sup>198</sup>.

Anionic nucleophiles ( $\text{LiAlH}_4$ ,  $\text{RLi}$ ,  $\text{RMgX}$ ,  $\text{R}_3\text{SiLi}$ , etc.) cleave M-Si bonds, but these reagents may also attack other ligands<sup>11, 194-197</sup>. In some optically active silyl complexes,  $\text{LiAlH}_4$  can displace the silyl group as the silane  $\text{HSiR}_3$  by direct attack at silicon. The platinum silyl complexes *cis*- $(S)(-)-[(1\text{-Naph})\text{PhMeSi}]\text{PtH}(\text{PPh}_3)_2$  and *trans*- $(S)(+)-[(1\text{-Naph})\text{PhMeSi}]\text{PtCl}(\text{PPhMe}_2)_2$  react with  $\text{LiAlH}_4$  in ether to give the corresponding silanes with a high degree of retention of configuration at silicon<sup>199</sup>. These observations, and the poor leaving-group character of the platinum centers suggest that these reactions may occur via initial attack at platinum to form a hydride ligand, followed by reductive elimination of the silane. Retention of configuration is predominantly observed in the displacement of the silyl ligand from iron compounds of the type  $(R)(+)-\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{Si}(1\text{-Naph})\text{PhMe}]$ <sup>197</sup>. A general trend has been recognized in the nucleophilic cleavages of 6-coordinate silyl complexes of Mn, Re and W. These reactions proceed with relatively low retention of configuration (stereoselectivity 55-70%) under a variety of reaction conditions for a range of complexes with different ligands<sup>200</sup>.

In contrast, inversion of configuration is observed for  $\text{LiAlH}_4$ -cleavage of the Mn-Si bonds of manganese silyl complexes  $(\eta^5-C_5H_4Me)Mn(\text{CO})_2(\text{H})(\text{SiR}_3)$ . The rather unique behavior of these complexes may be accounted for by their Si-H interactions<sup>11, 195</sup>. The cobalt complex  $(S)(+)-(CO)_4\text{Co}[\text{Si}(1\text{-Naph})\text{PhMe}]$  also reacts with  $\text{LiAlH}_4$  with inversion at silicon with high stereoselectivity. Replacement of a carbonyl ligand in the latter complex with more electron-donating phosphines results in a poorer leaving group,  $(\text{L})(\text{CO})_3\text{Co}^-$ , and less stereoselectivity in the cleavage process. Where  $\text{L} = \text{P}(\text{c-Hex})_3$ , 58% retention was observed<sup>195, 196</sup>.

Addition of Grignard reagents to  $(\text{CO})_4\text{CoSiPh}_3$  leads to *in situ* formation of the silyl Grignard reagent ' $\text{BrMgSiPh}_3$ '. Similarly, methyl lithium cleaves Co-Si bonds to give silyl lithium compounds. These reactions are thought to occur by attack of the carbanion

onto a carbonyl ligand, with displacement of the silyl group as a silyl anion<sup>196</sup>. In contrast, PhLi reacts with  $(S)(+)-(CO)_4Co[Si(1-Naph)PhMe]$  to give the benzoylsilane  $PhCOSi(1-Naph)PhMe$ , probably via the intermediate  $(PhCO)(CO)_3Co[Si(1-Naph)PhMe]^-Li^+$ <sup>201</sup>.

Many transition-metal silyl derivatives form 1:1 or 1:2 adducts with Lewis bases (primarily amines and phosphines) in which silicon appears to have increased its coordination number<sup>7-10,14</sup>. M-SiH<sub>3</sub> derivatives are particularly reactive in this regard. For example, pyridine interacts with  $(CO)_5MnSiH_3$  to produce the ionic  $[SiH_3 \cdot 2pyr][Mn(CO)_5]$ <sup>9,10</sup>. In general, spectroscopic data are consistent with considerable weakening of the M-Si bond upon adduct formation. Phosphines  $[PMe_3, PMe_2(SiMe_3)$  and  $PMe(SiMe_3)_2]$  react with the cobalt silyl  $Me_3SiCo(CO)_4$  with cleavage of the Co-Si bond, forming silylphosphonium salts  $[PMe_{4-n}(SiMe_3)_n]^+[Co(CO)_4]^-$ . The crystal structure of  $[PMe_2(SiMe_3)_2]^+[Co(CO)_4]^-$  was determined<sup>202</sup>.

Incoming nucleophiles may also cause cleavage of the M-Si bond by inducing a reductive elimination reaction. Thus, MeLi and phosphines displace silanes HSiR<sub>3</sub> from  $Cp(CO)_2Mn(H)(SiR_3)$  compounds<sup>11,195</sup>.

## B. Cleavage of M-Si Bonds by Electrophiles

Normally, protic reagents (HX) cleave M-Si bonds to give Si-X and M-H bonded compounds. However, in a few instances, particularly with early transition-metal silyl complexes, Si-H and M-X bonded products are observed<sup>7-10,14</sup>. Reactions of the latter type are consistent with a bond polarity of  $M(\delta+)-Si(\delta-)$ . The zirconium silyl derivative  $Cp_2Zr(SiPh_3)Cl$  reacts with HCl to give  $Cp_2ZrCl_2$  and  $HSiPh_3$ <sup>67</sup>. The trimethylsilyl analogue reacts with water in a similar fashion (equation 62)<sup>77</sup>.

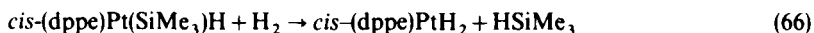
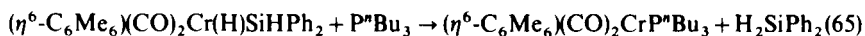


In optically active  $Cp(CO)(L)FeSiR_3$  complexes, cleavage reactions with chlorine or bromine are rather complex, and can lead to both retention and inversion (generally low stereoselectivity is observed), depending on the nature of the ligands L and the reaction conditions<sup>197</sup>. For  $(S)(+)-(CO)_4Co[Si(1-Naph)PhMe]$ , Cl<sub>2</sub> or Br<sub>2</sub> cleavage occurs predominantly with retention of configuration at silicon<sup>196</sup>. Similar reactions of the platinum complex *trans*-(S)(+)-[(1-Naph)PhMeSi]PtCl(PPhMe<sub>2</sub>)<sub>2</sub> with I<sub>2</sub> or Br<sub>2</sub> lead in each case to nearly complete racemization with formation of the silyl chloride ( $\pm$ )-(1-Naph)PhMeSiCl<sup>199</sup>. For these halogen reactions both an electron transfer and an oxidative addition mechanism are possible<sup>11,195</sup>. It has been argued that these reactions proceed via an initial electrophilic attack of 'X<sup>+</sup>' onto the silyl complex<sup>195</sup>. The relative rates of reaction of  $(CO)_5Mn(MMe_3)$  (M = Si, Ge, Sn, Pb) compounds with I<sub>2</sub> are Si:Ge:Sn:Pb = 1:21:10<sup>3</sup>:3 × 10<sup>4</sup>, and seem to depend on the electron-releasing power of the MMe<sub>3</sub> group<sup>203</sup>.

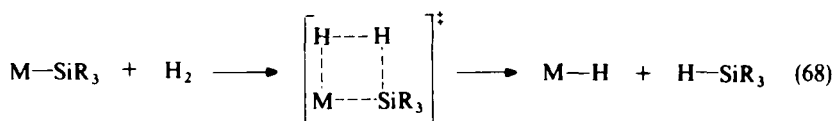
## C. Cleavage of M-Si Bonds by Other Reagents

As mentioned earlier, reductive elimination reactions are commonly observed processes that involve M-Si bond cleavage. Usually the transition-metal reductive elimination product is trapped by an added reagent such as a silane (equation 63)<sup>204</sup>, a germane (equation 64)<sup>205</sup>, a phosphine (equation 65)<sup>167</sup> or hydrogen (equation 66, dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sup>206</sup>. The latter reaction with hydrogen probably proceeds via initial oxidative addition of H<sub>2</sub> to form a Pt(IV) intermediate. In the case of chiral complex *cis*-(S)(-)-[(1-Naph)PhMeSi]PtH(PPh<sub>3</sub>)<sub>2</sub>, elimination of the silane upon addi-

tion of phenylacetylene occurs with 92.5% retention of configuration. The platinum-containing product was  $\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CH})^{199}$ .



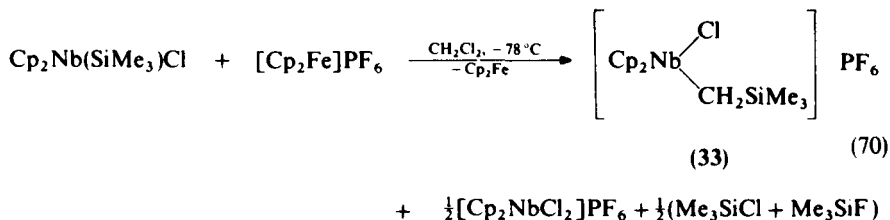
Hydrogen also cleaves M–Si bonds in  $d^0$  complexes.  $\text{Cp}_2\text{Zr}(\text{SiMe}_3)\text{Cl}$  reacts rapidly under 100 psi of  $\cdot$ hydrogen (equation 67), and the bis(silyl) compound  $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3](\text{SiMe}_3)$  undergoes a similar reaction to yield  $[\text{Cp}_2\text{ZrH}_2]_n$  and the silanes  $\text{HSiMe}_3$  and  $\text{HSi}(\text{SiMe}_3)_3$ .<sup>83</sup> In these reactions, an oxidative addition mechanism is unlikely since the  $d^0$  metal center is oxidatively inert. A four-center transition state (equation 68) is probably involved<sup>207</sup>.



An unusual reaction type discovered for early transition metal–silyl species involves reductive elimination of a silyl group with chlorine. These reactions have been observed in  $\text{Ti}^{83}$ ,  $\text{Nb}^{86}$  and  $\text{Ta}^{82}$  complexes, and are induced by oxidation or an incoming ligand. They are clean, convenient methods for generation of low-valent complexes such as  $\text{Cp}_2\text{Ti}(\text{CO})_2$  and  $\text{Cp}^*\text{TaCl}_2(\text{alkyne})$  (equation 69), or reactive intermediates such as  $\text{Cp}^*\text{TaCl}_2(\text{PMe}_3)$  and  $[\text{Cp}_2\text{Nb}]^+$ .

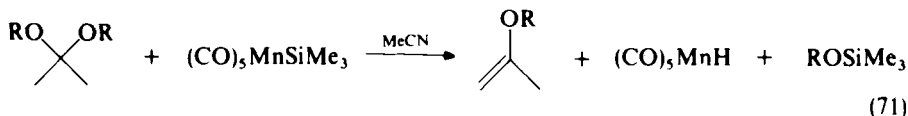


Attempts to chemically oxidize  $\text{Cp}_2\text{Nb}(\text{SiMe}_3)\text{Cl}$  to a niobium(V) silyl complex led only to uncharacterized mixtures of paramagnetic solids, unless the reaction was carried out in dichloromethane. Oxidation of  $\text{Cp}_2\text{Nb}(\text{SiMe}_3)\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$  (with  $\text{AgPF}_6$  or  $[\text{Cp}_2\text{Fe}]PF_6$ ) yields two niobium-containing products (equation 70). Compound **33** was

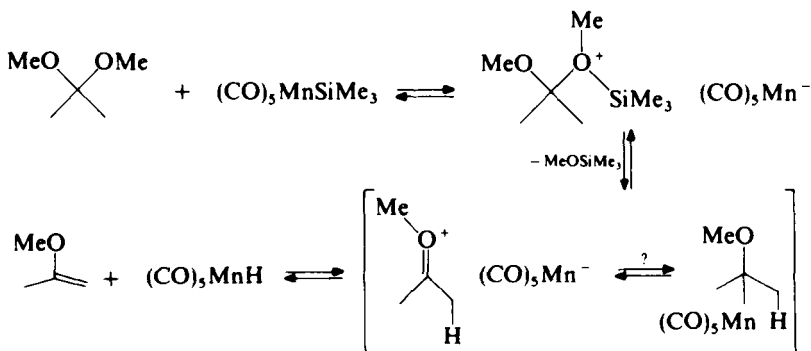


characterized by X-ray crystallography. The source of the methylene unit in **33** is the dichloromethane solvent, as determined by deuterium-labeling. Mechanistic studies suggest that this reaction involves oxidative addition of  $\text{CH}_2\text{Cl}_2$  to  $[\text{Cp}_2\text{Nb}]PF_6$ , which is produced by an oxidatively-induced elimination of  $\text{Me}_3\text{SiCl}$  from  $\text{Cp}_2\text{Nb}(\text{SiMe}_3)\text{Cl}$ .<sup>86</sup>

The cleavage of M–Si bonds by ether solvents has already been noted (Section II.A.3). Cleavages of the Mn–Si bond in  $(\text{CO})_5\text{MnSiMe}_3$  by acetals and ketals have also been observed. Methyl ketals react to provide good yields of methyl enol ethers (equation 71).



The proposed mechanism involves initial transfer of the silyl group from manganese to the ketal (Scheme 4). This view is supported by the fact that the reaction is slowed considerably in less polar solvents<sup>208</sup>.



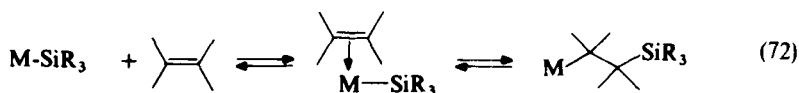
SCHEME 4

## D. Insertion Reactions

Although there are numerous reactions in which transition metal–silane systems catalytically reduce unsaturated molecules (Section VI.E), the degree to which insertions into M–Si bonds contribute to this reactivity is unclear, since few insertions involving M–Si bonds have been directly observed. This low reactivity toward insertions is consistent with observations that transition metal–silicon bonds are usually shorter than expected, presumably strengthened by  $\pi$ -bonding between the transition metal and silicon (Section V). Clearly, much work is needed to determine conditions that make insertion reactions favorable.

### 1. Insertion of alkenes

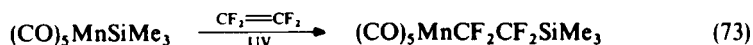
There is mounting evidence that insertion of an alkene into a transition metal–silicon bond (equation 72) may be an important step in hydrosilylation catalysis<sup>209</sup>. Such an



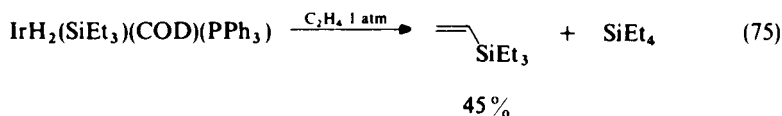
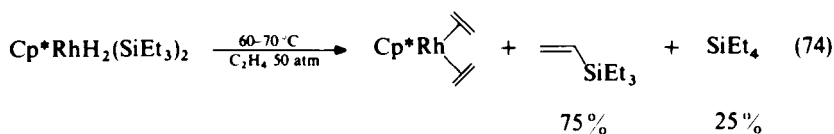
insertion step can explain the formation of vinylsilanes as by-products in the hydrosilylation of alkenes, since vinylsilanes can result from  $\beta$ -H elimination in the insertion

product (see Section VI.E.1). Discovery and study of observable alkene insertions into M–Si bonds (or migrations of silyl groups to coordinated alkene) are therefore of interest. Additionally, such reactions could be useful synthetic methods for introducing silyl groups into organic molecules.

A few examples of insertion of activated alkenes into M–Si bonds are known. For example, tetrafluoroethylene inserts into a Mn–Si bond under the influence of UV radiation (equation 73)<sup>210</sup>.

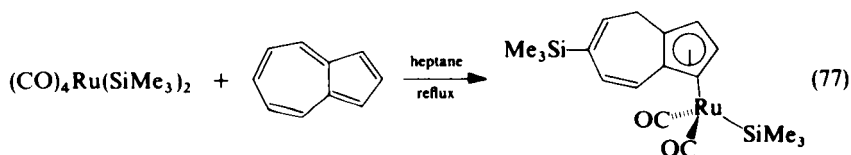
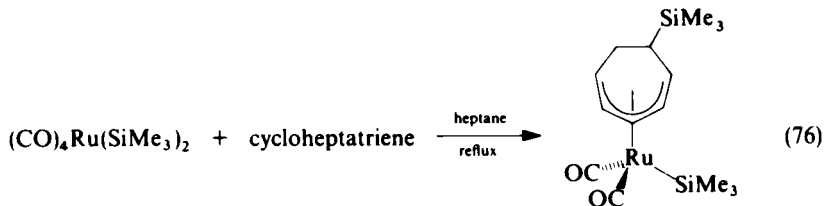


Stoichiometric reactions of silyl complexes with ethylene are reported to give vinylsilanes in addition to the normal hydrosilylation product (equations 74<sup>211</sup> and 75<sup>212</sup>, COD

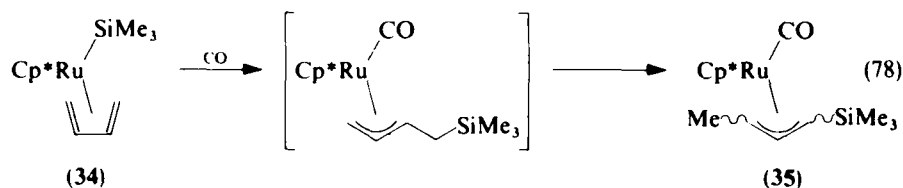


= 1,5-cyclooctadiene). These results suggest that insertion of ethylene into the M–Si bonds has occurred, followed by  $\beta$ -H elimination to give the vinylsilane. The iridium complex in equation 75 is a rare example of an isolated [M](alkene)(SiR<sub>3</sub>)H complex. Such complexes are postulated intermediates in hydrosilylation catalysis (see Section VI.E.1)<sup>8, 209, 213</sup>. Irradiation of a solution of Cp\*RhH<sub>2</sub>(SiEt<sub>3</sub>)<sub>2</sub> in the presence of ethylene produced Cp\*Rh(C<sub>2</sub>H<sub>4</sub>)(SiEt<sub>3</sub>)H, characterized in solution<sup>211</sup>. Similarly, photolysis of CpRh(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> in the presence of HSiR<sub>3</sub> (R = Me, Et) produced CpRh(C<sub>2</sub>H<sub>4</sub>)(SiR<sub>3</sub>)H complexes, also characterized in solution<sup>214</sup>.

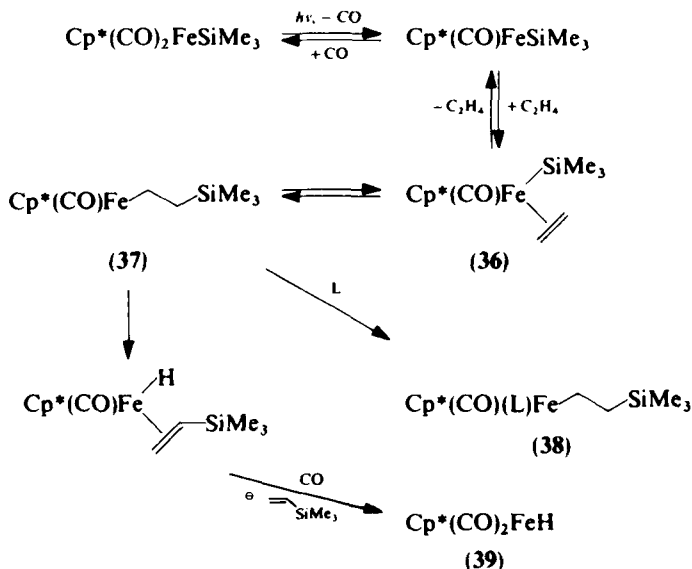
In a series of papers<sup>215–220</sup>, Stone and coworkers show that upon reaction of ruthenium carbonyl silyl complexes such as (CO)<sub>4</sub>Ru(SiMe<sub>3</sub>)<sub>2</sub> and [(CO)<sub>4</sub>RuSiMe<sub>3</sub>]<sub>2</sub> with cyclic polyolefins, silyl groups migrate from ruthenium to the ring. Examples are shown in equations 76<sup>216</sup> and 77<sup>217</sup>.



A related process has been observed by Fagan. Treatment of the ruthenium silyl **34** with carbon monoxide results in a ligand-induced migration of the silyl group to coordinated butadiene. The migration product undergoes an interesting rearrangement to the allyl complex **35** (equation 78)<sup>221</sup>.



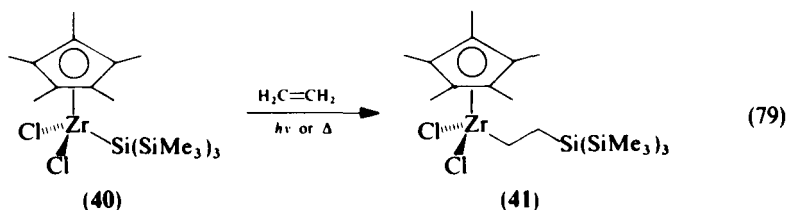
Randolph and Wrighton have recently shown that photolysis of  $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_3$  in  $\text{C}_2\text{H}_4$ -saturated alkane solution results in formation of the ethylene complex  $\text{Cp}^*(\text{CO})(\text{C}_2\text{H}_4)\text{FeSiMe}_3$  (**36**, Scheme 5). Compound **36** undergoes insertion of ethylene into the Fe-Si bond to give the 16-electron intermediate **37**, which can be trapped by added ligand ( $\text{L} = \text{CO}, \text{PPh}_3$ ) to afford isolable  $\beta$ -silylalkyl complexes **38**. Intermediate **37** also undergoes rapid  $\beta$ -H elimination leading eventually to the hydride **39**. The insertion step appears to be reversible, since photolysis of  $\text{Cp}^*(\text{CO})_2\text{FeCH}_2\text{CH}_2\text{SiMe}_3$  generates **36**. Photolysis of  $\text{Cp}^*(\text{CO})_2\text{FeCH}_2\text{CH}_2\text{SiMe}_3$  at room temperature results in both  $\beta$ -H (65%) and  $\beta$ -SiMe<sub>3</sub> (15%) transfer<sup>209</sup>.



SCHEME 5

Although some early transition metal-silyl compounds are inert toward alkenes<sup>83</sup>, the sterically congested mixed-ring complex  $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  reacts with ethylene under the influence of ordinary room light to afford the insertion product  $\text{CpCp}^*\text{Zr}[\text{CH}_2\text{CH}_2\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ . This reaction does not proceed at a measurable rate in the dark. Zirconium silyl compound **40**, however, inserts ethylene in the dark ( $t_{1/2}$



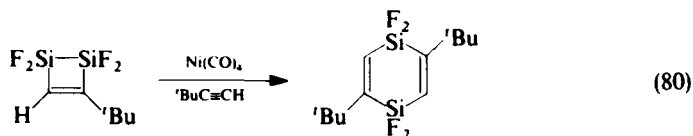


= 30 min) according to equation 79. This 'silylzirconation' reaction is much faster in the presence of ambient room light, being complete within ca. 5 min at room temperature. The analogous hafnium reactions with  $\text{Cp}^*\text{Cl}_2\text{HfSi}(\text{SiMe}_3)_3$  (**42**) are somewhat slower, as expected. The latter two insertion processes therefore appear to follow both thermal and photochemical pathways, and the M–Si bonds in **40** and **42** are efficiently activated photochemically. Compounds **40** and **42** display moderately strong UV absorptions tailing well into the visible region, which disappear on insertion of ethylene to form the  $\beta$ -silyl alkyl derivatives<sup>222</sup>.

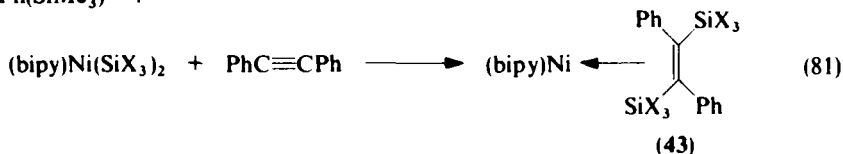
The scandium silyl  $\text{Cp}_2\text{Sc}[\text{Si}(\text{SiMe}_3)_3](\text{THF})$  reacts with ethylene (50 psi) in benzene to produce high-molecular-weight polyethylene, apparently because in this case the initially formed  $\beta$ -silyl alkyl complex is also reactive toward ethylene insertion<sup>223</sup>.

## 2. Insertion of alkynes

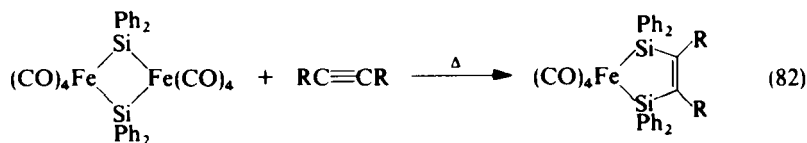
A number of transition-metal-mediated reactions involving addition of an alkyne to an organosilicon compound may involve an alkyne insertion step (Section III.A and Section VI.E.4). One example, for which alternative mechanisms are possible, is shown in equation 80<sup>224</sup>. Nickel silyl derivatives  $(\text{bipy})\text{Ni}(\text{SiX}_3)_2$  ( $\text{SiX}_3 = \text{SiCl}_3, \text{SiMeCl}_2$ ) react with



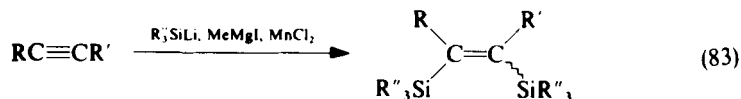
diphenyl acetylene to form a 'double-insertion' product, the *trans* alkene complex **43** (equation 81). Alkylation of **43** with  $\text{MeMgCl}$  gave the free alkene *trans*- $\text{Ph}(\text{SiMe}_3)\text{C}=\text{CPh}(\text{SiMe}_3)$ <sup>225</sup>.



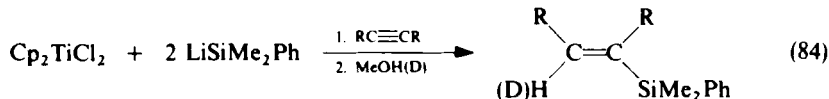
A diiron complex with bridging silylene ligands reacts with alkynes to give disilaferracyclopentenes (equation 82,  $\text{R} = \text{Ph}, \text{Et}, \text{Me}$ ). The  $\text{R} = \text{Et}$  derivative was characterized by an X-ray diffraction study.<sup>226</sup>



A useful synthetic method for the disilylation of alkynes makes use of an ill-defined manganese silyl reagent generated in situ (equation 83,  $R'_3 = \text{Me}_3$  or  $\text{Me}_2\text{Ph}$ ). It was



suggested that the active manganese species is  $(\text{R}''_3\text{Si})_3\text{MnMgMe}$ . The role of the Grignard reagent is unclear, but its presence is essential for the formation of disilylated products. Without  $\text{MeMgI}$ , only monosilylated products were obtained after aqueous workup<sup>227</sup>. Another transition-metal silylating agent is based on titanium. A red-brown solution, believed to contain the Ti(III) derivative  $\text{Cp}_2\text{TiSiMe}_2\text{Ph}$ , is obtained by reaction of  $\text{Cp}_2\text{TiCl}_2$  with 2 equivalents of  $\text{LiSiMe}_2\text{Ph}$ , or from  $\text{Cp}_2\text{TiCl}$  and 1 equivalent of  $\text{LiSiMe}_2\text{Ph}$ . Addition of alkyne, followed by quenching with alcohol, gives monosilylated products (equation 84). A mechanism involving insertion of alkyne into a Ti(III)–Si

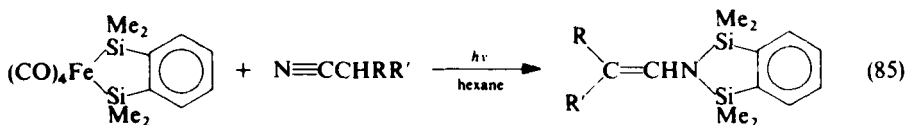


bond was proposed. The titanium silyl adds to alkynes in a stereoselectively *cis* fashion. This 'silyltitanation' reaction was also extended to 1,3-dienes<sup>228</sup>.

The complex **40** polymerizes acetylene<sup>222</sup>.

### 3. Insertion of nitriles

Chelated bis(silyl)iron complexes react photochemically with nitriles, providing routes to *N,N*-bis(silyl) enamines<sup>229, 230</sup>. A variety of aliphatic and benzylic nitriles may be employed (equation 85). The proposed mechanism (Scheme 6) involves addition of an

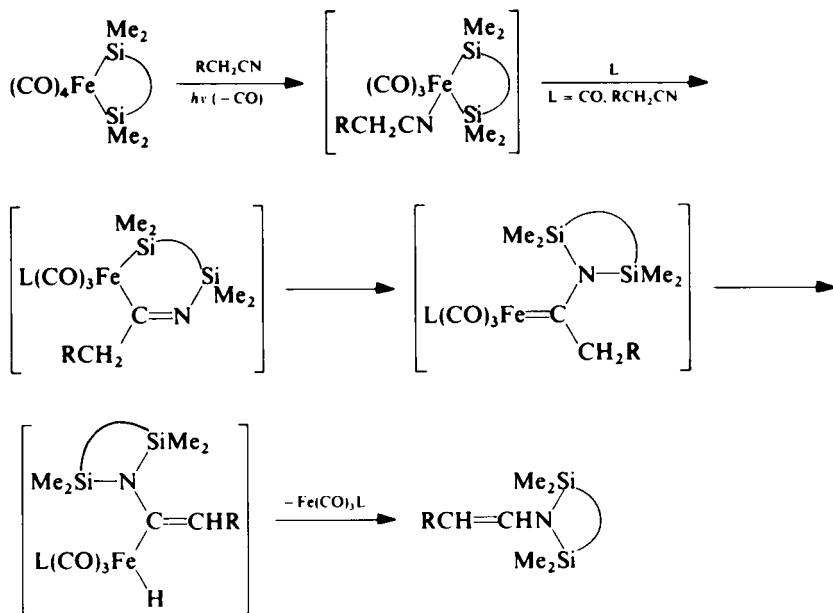


Fe–Si bond to the CN bond of the nitrile, followed by a second silicon migration to nitrogen. Migration of the hydrogen atom is then apparently mediated by the metal center<sup>230</sup>.

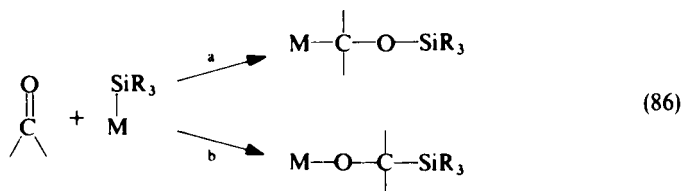
### 4. Insertion of organic carbonyl compounds

Given the oxophilicity of silicon, it is not too surprising that organic carbonyl groups are more reactive toward transition metal–silicon bonds than other, less polar multiple bonds. A number of transition-metal complexes catalyze the hydrosilylation of carbonyl functionalities, in some cases with a high degree of regio- or enantioselectivity<sup>231–237</sup>. In these reactions, it is postulated that a silyl group is transferred to the carbonyl oxygen by an insertion step that forms an  $\alpha$ -siloxyalkyl complex (equation 86, path a). This process involves electrophilic transfer of silicon from a transition metal to a carbonyl group.

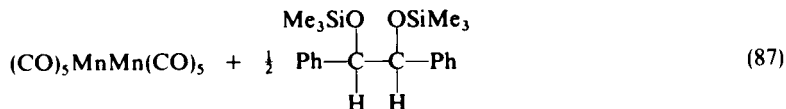
Stoichiometric insertion reactions of this kind have been studied in detail by Gladysz and coworkers<sup>238</sup>. At 5 °C, benzaldehyde reacts slowly with  $(\text{CO})_5\text{MnSiMe}_3$  to give the



SCHEME 6

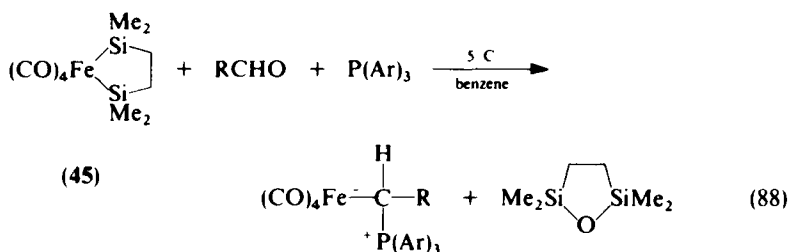


insertion product **44** in high yield (equation 87). **44** is somewhat thermally sensitive, and undergoes homolysis at slightly elevated temperatures. Based on solvent and substituent effects, it was proposed that the initial and rate-determining step in this reaction is nucleophilic attack of the benzaldehyde oxygen onto the silicon of  $(\text{CO})_5\text{MnSiMe}_3$  to

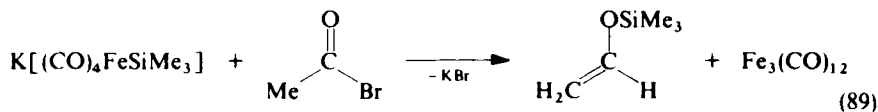


give the ion pair  $[\text{CHPh}(\text{OSiMe}_3)]^+ [\text{Mn}(\text{CO})_5]^-$ . Collapse of this intermediate to the observed product **44** completes the insertion process. Aliphatic aldehydes and ketones react with  $(\text{CO})_5\text{MnSiMe}_3$  to give silyl enol ethers and the hydride  $(\text{CO})_5\text{MnH}$ . These species presumably result from  $\beta$ -H elimination in the initially formed alkyl  $(\text{CO})_5\text{MnCRR}'(\text{OSiMe}_3)^{239}$ . If  $(\text{CO})_5\text{MnSiMe}_3$  is treated with aromatic or aliphatic aldehydes (RCHO) under 150–350 psi of CO, acyl compounds  $(\text{CO})_5\text{MnCOCHR}(\text{OSiMe}_3)$  are obtained in good yields (R = Me, Pr,  $\text{CH}_2\text{CH}_2\text{Ph}$ , c-Hex, Ph)<sup>240</sup>.

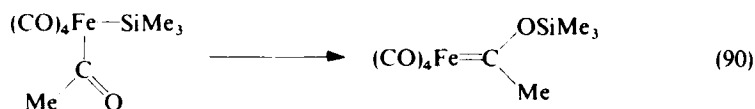
Although benzaldehyde is unreactive toward  $(\text{CO})_5\text{ReSiMe}_3$  or  $\text{Cp}(\text{CO})_2\text{FeSiMe}_3$  (18 h at 55°C)<sup>238</sup>, it reacts with *cis*- $(\text{CO})_4\text{Fe}(\text{SiMe}_3)_2$  rapidly at 5°C to give the iron alkyl complex *cis*- $(\text{CO})_4\text{Fe}[\text{CHPh}(\text{OSiMe}_3)]\text{SiMe}_3$ , which readily homolyzes at ambient temperatures to pinacol ether dimers  $[(\text{Me}_3\text{SiO})\text{PhHCCHPh}(\text{OSiMe}_3)]$ , erythro and threo] and the dinuclear iron silyl derivative *trans*- $[\text{Fe}(\text{CO})_4\text{SiMe}_3]_2$ <sup>241</sup>. If a mechanism involving displacement of the silyl group from the metal is assumed, the differences in reactivities toward benzaldehyde may be explained by the leaving group abilities of the  $L_n\text{M}^-$  species [i.e.  $(\text{CO})_4\text{FeSiMe}_3^- > (\text{CO})_5\text{Re}^-, \text{Cp}(\text{CO})_2\text{Fe}^-$ ]<sup>238</sup>. Reaction of the chelated bis(silyl) iron complex **45** with aldehydes results in deoxygenation and formation of iron carbene species that can be trapped by added phosphine (equation 88)<sup>242</sup>.



In related studies carried out by Gladysz and coworkers, the anionic silyl complex  $[(\text{CO})_4\text{FeSiMe}_3]^-$  was found to react relatively cleanly with acyl halides, producing silyl enol ethers. The reaction with acetyl bromide gives a 70% yield of acetaldehyde trimethylsilyl enol ether (equation 89). An observed intermediate in this reaction was the

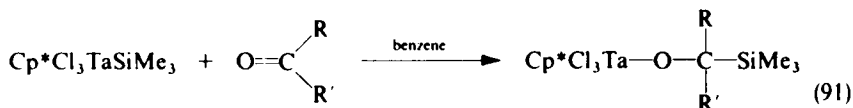


siloxycarbene species  $(\text{CO})_4\text{Fe}=\text{C}(\text{Me})\text{OSiMe}_3$ , which appears to undergo a 1,2-hydrogen shift to the silyl enol ether complex  $(\text{CO})_4\text{Fe}[\eta^2\text{-CH}_2=\text{CH}(\text{OSiMe}_3)]$ . Apparently, the siloxycarbene derivative is formed by a 1,3-silatropic shift in the initially formed silyl/acyl complex (equation 90)<sup>243</sup>.

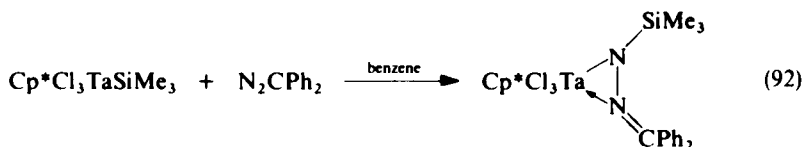


In the reactions that are known to follow path a (equation 86), the transition metal is electron-rich or low-valent. A recent report describes the reverse addition of a M–Si bond to a carbonyl group by an early transition-metal silyl (path b, equation 86). The  $d^0$  silyl

complex  $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$  reacts with aldehydes and ketones to give  $\alpha$ -silylalkoxides, and the first examples of nucleophilic transfer of a silyl group from a transition metal to a carbonyl functionality (equation 91). The reactions obey clean second-order kinetics,

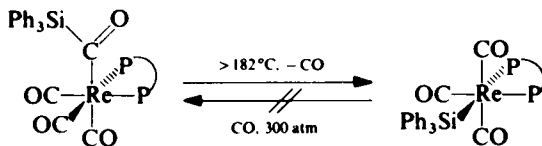
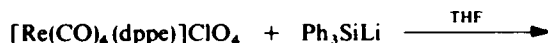


with the rates being highly dependent on the nature of the carbonyl substituents<sup>244</sup>. These results reveal the potential for using transition metal-silyl complexes to achieve chemoselective nucleophilic transfer of silyl groups to unsaturated substrates. Diphenyldiazomethane also inserts into the Ta-Si bond of  $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$  (equation 92)<sup>244</sup>.



### 5. Insertion of carbon monoxide and isocyanides

Insertion of carbon monoxide into transition metal-silicon bonds has long been considered unfavorable, since attempts to carbonylate a number of metal silyl derivatives failed<sup>6, 7, 10, 14, 245</sup>. In contrast, insertion of CO into transition metal-carbon bonds is a well-known reaction in organometallic chemistry<sup>246</sup>. Support for the view that migration of a silyl ligand to coordinated CO is thermodynamically unfavored came from the synthesis and study of the first silaacyl complex *fac*- $\text{Re}(\text{CO})_3(\text{dppe})(\text{COSiPh}_3)$  (Scheme 7,  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ). This compound decarbonylates irreversibly above 182 °C, and could not be obtained by subjecting the decarbonylation product, *mer*- $\text{Re}(\text{CO})_3(\text{dppe})(\text{SiPh}_3)$ , to CO pressures of 300 atm<sup>60</sup>.



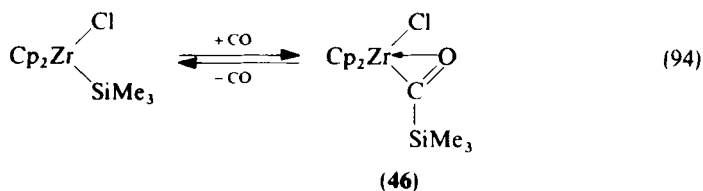
SCHEME 7

There are a few reports of silyl-carbonyl complexes that decompose by processes that may involve a migratory insertion. These reactions lead to siloxide derivatives by ill-defined processes that involve inter- or intramolecular silyl migration<sup>6, 7, 10, 14</sup>, and most commonly result in cleavage of the carbon monoxide C-O bond (e.g. equation 93)<sup>247</sup>.



A perhaps related deoxygenation of CO has been carried out in the Ni-catalyzed synthesis of siloxanes from CO and hexamethyldisilane<sup>248</sup>. These results point toward a migration of silicon to the oxygen atom of a coordinated CO ligand.

The first observation of CO insertion into a transition metal–silicon bond was made recently<sup>83, 249</sup>. Zirconium silyl  $\text{Cp}_2\text{Zr}(\text{SiMe}_3)\text{Cl}$  reacts rapidly with carbon monoxide with precipitation of a bright pink complex that has been identified as the silyacyl compound **46** (equation 94). An X-ray crystal structure of **46** confirmed the formation of a



Si–C rather than a Si–O bond (Figure 5), and revealed the presence of the  $\eta^2\text{-COSiMe}_3$  ligand. Factors that undoubtedly promote CO insertion in this case are the increase in electron count at zirconium and the formation of a strong Zr–O bond. Additionally, the  $d^0$  complex  $\text{Cp}_2\text{Zr}(\text{SiMe}_3)\text{Cl}$  does not have electrons available for a  $\pi$ -interaction that could strengthen the M–Si bond. The insertion reaction is reversible; mild heating of **46** results in slow decarbonylation. Spectroscopic data for **46** are similar to those reported for *fac*- $\text{Re}(\text{CO})_3(\text{dppe})(\text{COSiPh}_3)$ <sup>60</sup>. The chemical shift of the carbonyl carbon in **46** is at low field (391.6 ppm) and is characteristic for early transition metal  $\eta^2\text{-COSiR}_3$  derivatives<sup>83</sup>. The titanium silyl derivative  $\text{Cp}_2\text{Ti}(\text{SiMe}_3)\text{Cl}$  does not give an insertion product upon reaction with CO, but cleanly affords  $\text{Cp}_2\text{Ti}(\text{CO})_2$  and  $\text{Me}_3\text{SiCl}$ , apparently via a ligand-induced reductive elimination<sup>83</sup>.

Other early transition metal–silyl complexes undergo CO insertion reactions, but subtle factors appear to influence greatly the reactivity of these M–Si bonds. The bis(silyl)

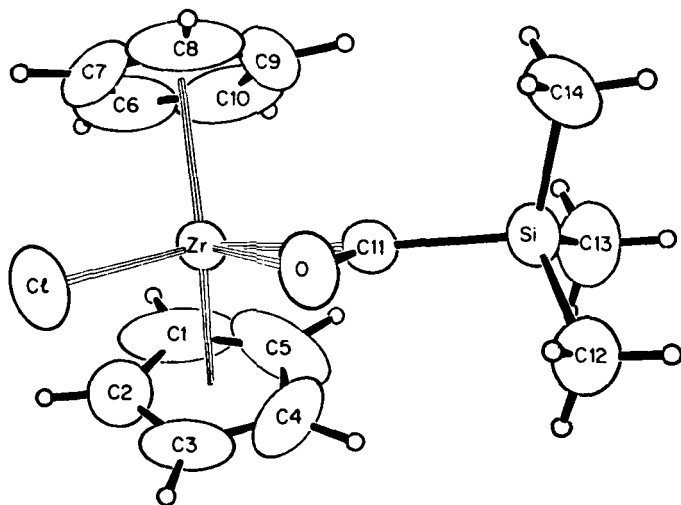
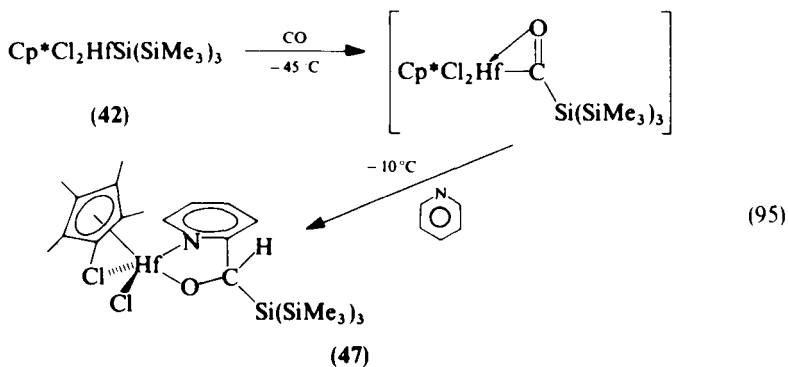


FIGURE 5. ORTEP view of **46**

species  $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3](\text{SiMe}_3)$  undergoes CO insertion exclusively into the Zr–SiMe<sub>3</sub> bond<sup>83</sup>. Whereas  $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  does not react appreciably with CO, the more sterically congested complex  $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  readily yields the silaacyl species  $\text{CpCp}^*\text{Zr}[\eta^2\text{-COSi}(\text{SiMe}_3)_3]\text{Cl}$ <sup>250</sup>. The compounds  $\text{Cp}^*\text{Cl}_2\text{MSi}(\text{SiMe}_3)_3$  (M = Zr, Hf) react with CO to afford thermally sensitive silaacyl derivatives  $\text{Cp}^*\text{Cl}_2\text{M}[\eta^2\text{-COSi}(\text{SiMe}_3)_3]$  that were characterized at low temperature in solution. The hafnium derivative was trapped with pyridine to give a product in which the silaacyl carbon had inserted into an ortho C–H bond of pyridine (equation 95). Diastereomer **47**, formed in a



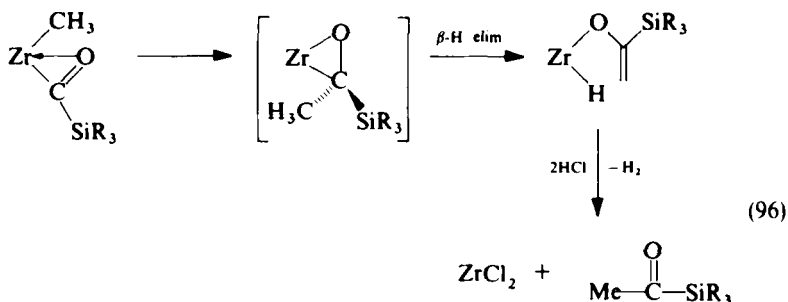
highly diastereoselective process, was characterized by a single crystal X-ray diffraction study. The crystal structure shows **47** to be the diastereomer with the Cp\* ligand and the –Si(SiMe<sub>3</sub>)<sub>3</sub> group on opposite sides of the HfOC<sub>2</sub>N chelate ring. Reaction of  $\text{Cp}^*\text{Cl}_2\text{Hf}(\text{C}, \text{N}-\eta^2\text{-NC}_5\text{H}_4)$  with the formylsilane  $(\text{Me}_3\text{Si})_3\text{SiCHO}$  (*vide infra*) affords both **47** and its diastereomer<sup>251</sup>.

Early transition metal–silyl complexes are also reactive toward isocyanides. For example, insertion of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC into the Zr–Si bonds of  $\text{Cp}_2\text{Zr}(\text{SiMe}_3)\text{Cl}$  and  $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  occurs readily to give the  $\eta^2$ -iminosilaacyl compounds  $\text{Cp}_2\text{Zr}[\eta^2\text{-C}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{SiMe}_3]\text{Cl}$  and  $\text{Cp}_2\text{Zr}[\eta^2\text{-C}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ , respectively<sup>83</sup>.

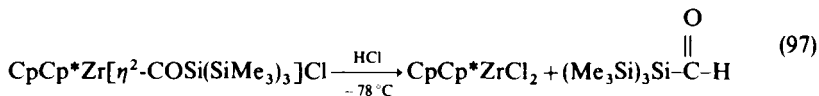
Mixed alkyl silyl complexes of the type  $\text{Cp}_2\text{Zr}(\text{SiR}_3)\text{R}'$  are readily prepared via chloride displacement reactions by addition of an alkylating agent ( $\text{R}'\text{MgX}$  or  $\text{R}'\text{Li}$ ) to the chloro derivatives  $\text{Cp}_2\text{Zr}(\text{SiR}_3)\text{Cl}$ <sup>83, 85, 252, 253</sup>. These species allow chemical reactivity studies that compare M–Si bonds to the better understood M–C bonds. Intramolecular competition experiments with  $\text{Cp}_2\text{Zr}(\text{SiR}_3)\text{R}'$  compounds have shown that M–C bonds are preferentially cleaved by acids, suggesting greater bond polarity between the metal and carbon. Less polar reagents (e.g. H<sub>2</sub> and CO) can react preferentially with either Zr–C or Zr–Si bonds, depending on subtle steric and electronic factors in the alkyl silyl complex. Oxidizing agents ( $\text{Ag}^+$ ,  $\text{Cp}_2\text{Fe}^+$ ) preferentially cleave Zr–Si bonds, indicating that these may be weaker than comparable Zr–C bonds. Overall, these results suggest that Zr–Si and Zr–C bonds in these systems are more similar in reactivity than might have been predicted initially<sup>85, 252, 253</sup>.

In most mixed alkyl silyl zirconium derivatives, CO insertion occurs preferentially into the Zr–C bond<sup>83, 85, 252, 253</sup>. However, in sterically congested complexes, insertion occurs into the Zr–Si bond to give silaacyl alkyl compounds such as  $\text{Cp}_2^*\text{Zr}[\eta^2\text{-COSiHMe}_2]\text{Me}$  (**48**)<sup>85</sup> and  $\text{CpCp}^*\text{Zr}[\eta^2\text{-COSi}(\text{SiMe}_3)_3]\text{Me}$  (**49**)<sup>250, 253</sup>. Complexes **48** and **49** readily and cleanly isomerize to the hydrido, silyl-substituted enolates

$\text{Cp}^*_2\text{Zr}[\text{OC}(=\text{CH}_2)\text{SiHMe}_2]\text{H}^{85}$  and  $\text{CpCp}^*\text{Zr}[\text{OC}(=\text{CH}_2)\text{Si}(\text{SiMe}_3)_3]\text{H}^{253}$ , respectively. These reactions are believed to involve carbon-carbon coupling to give intermediate acylsilane  $(\text{R}_3\text{SiCOMe})^{254}$  complexes that undergo  $\beta$ -H elimination to yield the enolates. Treatment of the enolate complexes with 2 equivalents of HCl gives high yields of acylsilanes (equation 96)<sup>85, 253</sup>. These reactions therefore represent a new, Zr-mediated acylsilane synthesis from silyllithium compounds, CO and Grignard reagents.



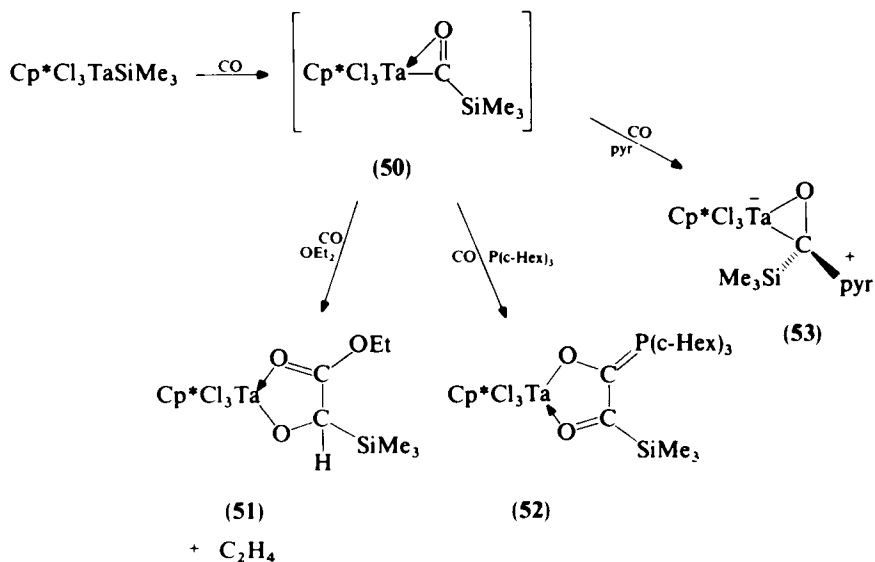
Another application of zirconium  $\eta^2$ -silaacyl complexes is in the first synthesis of formylsilanes ( $\text{R}_3\text{SiCHO}$ ). Attempts to prepare formylsilanes, dating back to 1947, led to the opinion that these species were unstable under a variety of conditions<sup>254, 255</sup>. Acidification of **46** by 1 equivalent of HCl at low temperature generates  $\text{Me}_3\text{SiCHO}$ , which is unstable above  $-25^\circ\text{C}^{83}$ . The analogous reaction with  $\text{CpCp}^*\text{Zr}[\eta^2\text{-COSi}(\text{SiMe}_3)_3]\text{Cl}$  provides the first stable, isolable formylsilane ( $\text{Me}_3\text{Si})_3\text{SiCHO}$  (equation 97)<sup>256</sup>.



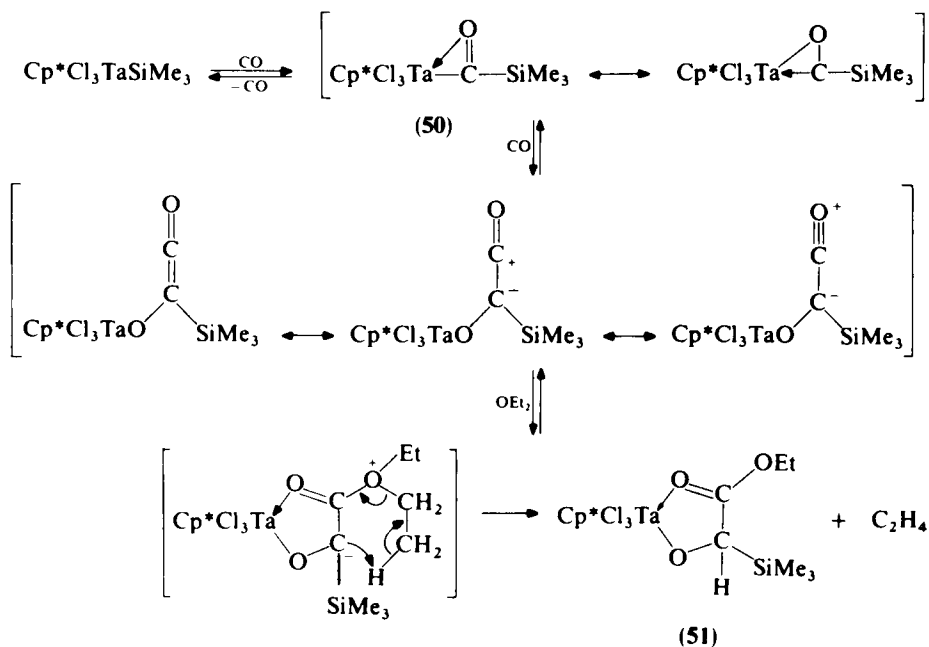
Reaction of  $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$  with 1 equivalent of CO followed by cooling to  $-45^\circ\text{C}$  allows isolation of the thermally sensitive silaacyl derivative  $\text{Cp}^*\text{Cl}_3\text{Ta}(\eta^2\text{-COSiMe}_3)$  (**50**), which readily reacts with more CO under a variety of conditions to provide products resulting from carbon-carbon coupling<sup>256, 257</sup>. An intermediate in these processes appears to be the highly reactive ketene  $\text{Cp}^*\text{Cl}_3\text{Ta}[\text{O}(\text{Me}_3\text{Si})\text{C}=\text{C}=\text{O}]$ . Carbonylation of  $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$  in the presence of ethers containing  $\beta$ -hydrogens leads to remarkably facile cleavage of the ether (Scheme 8). In diethyl ether, the alkoxy ester **51** and ethylene are formed; a proposed mechanism is shown in Scheme 9<sup>256</sup>. The intermediate ketene can also be trapped by sterically hindered Lewis bases such as  $\text{P}(\text{c-Hex})_3$ . The ylid derivative **52** was crystallographically characterized<sup>257</sup>.

The reactive silaacyl species **50** is therefore an exceptionally electrophilic carbonyl compound that undergoes a number of unusual reactions. If the carbonylation of  $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$  is carried out in the presence of relatively small Lewis bases, **50** is trapped to form stable adducts in which the Lewis donor is bound to the carbonyl carbon (e.g. compound **53** in Scheme 8). An X-ray crystal structure of **53** has been determined (Figure 6)<sup>258</sup>. Analogous tetrahedral adducts with phosphorous donors,  $\text{Cp}^*\text{Cl}_3\text{Ta}[\eta^2\text{-OC}(\text{SiMe}_3)(\text{L})]$  [ $\text{L} = \text{PMe}_3, \text{PEt}_3$  and  $\text{P}(\text{OMe})_3$ ], have been obtained<sup>258</sup>. The trimethyl phosphite complex  $\text{Cp}^*\text{Cl}_3\text{Ta}[\eta^2\text{-OC}(\text{SiMe}_3)\text{P}(\text{OMe})_3]$  undergoes a spontaneous Arbuzov-like dealkylation to MeCl and the  $\eta^4$ -phosphonatosilaacyl(2-) complex  $\text{Cp}^*\text{Cl}_2\text{Ta}[\eta^4\text{-OC}(\text{SiMe}_3)\text{P}(\text{OMe})_2\text{O}]^{259}$ . Studies of the acyl compound  $\text{Cp}^*\text{Cl}_3\text{Ta}$





SCHEME 8



SCHEME 9

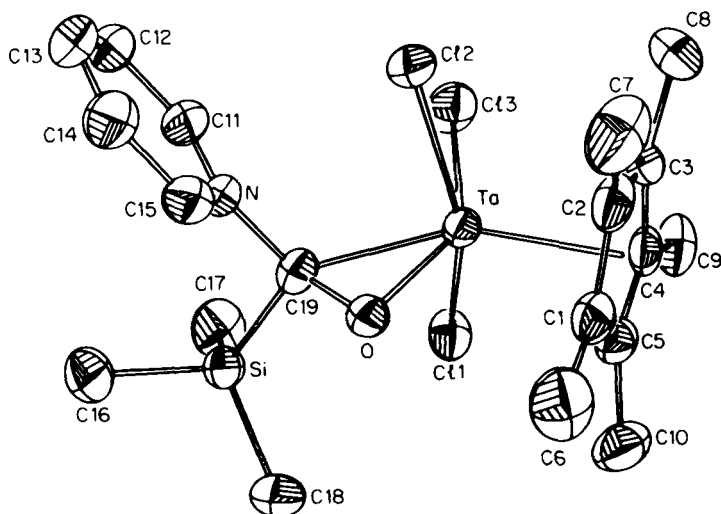
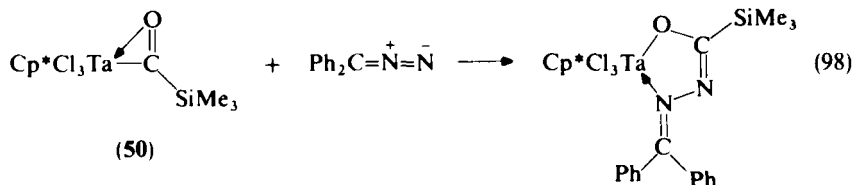


FIGURE 6. ORTEP view of 53

( $\eta^2$ -COCH<sub>2</sub>CMe<sub>3</sub>) indicate that the observed reactivity of **50** requires the presence of the silyl group<sup>257</sup>.

The CO-insertion product **50** reacts rapidly with diphenyldiazomethane to provide a product in which the Ta-C bond has been cleaved (equation 98)<sup>260</sup>.

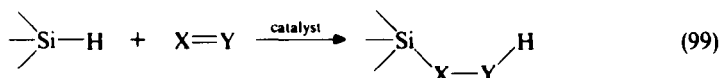


## E. Catalytic Reactions

Numerous transition-metal-catalyzed reactions of organosilanes are known, and some, like hydrosilylation, are industrially important. Typically these reactions involve metal-mediated Si-X bond-breaking and bond-forming processes. In this field mechanistic information is scarce, in part because relatively little is known about factors that govern the reactivity of transition metal-silyl complexes. Some of the basic types of catalytic reactions which seem to involve M-Si bonds are surveyed below.

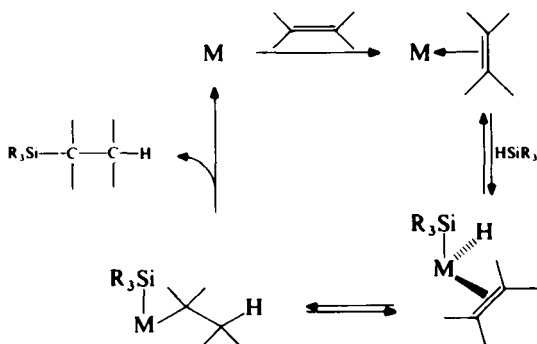
### 1. Hydrosilylation

Catalytic hydrosilylation involves addition of a Si-H bond to an unsaturated substrate (equation 99). Alkene hydrosilylation is a useful Si-C bond-forming reaction that has been extensively reviewed<sup>8, 195, 213, 261-263</sup>. It may be used to introduce functional groups



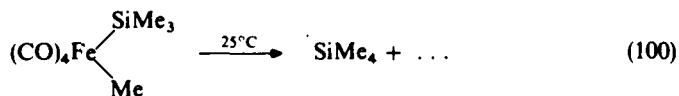
into silanes to make silicone/organic copolymers, or to cross-link siloxane polymers<sup>264</sup>. These reactions are catalyzed heterogeneously or homogeneously by transition metals. Various soluble, late transition-metal complexes catalyze hydrosilylation, but the most commonly used catalyst is chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , Speier's catalyst).

The mechanism of catalytic hydrosilylation is not well understood. Study of these reactions is hampered by their complexity; induction periods are often involved, reaction conditions such as the nature of the catalyst and reacting groups are critical factors, and side-reactions, such as alkene rearrangements, are common. A widely accepted mechanism for homogeneous catalysis by platinum complexes is based on the work of Chalk and Harrod (Scheme 10)<sup>5, 8, 262</sup>. With Speier's catalyst, it appears that initially, and probably during the induction period, silane reduces the platinum to a Pt(0) or Pt(II) complex that is the active catalytic species<sup>265</sup>.

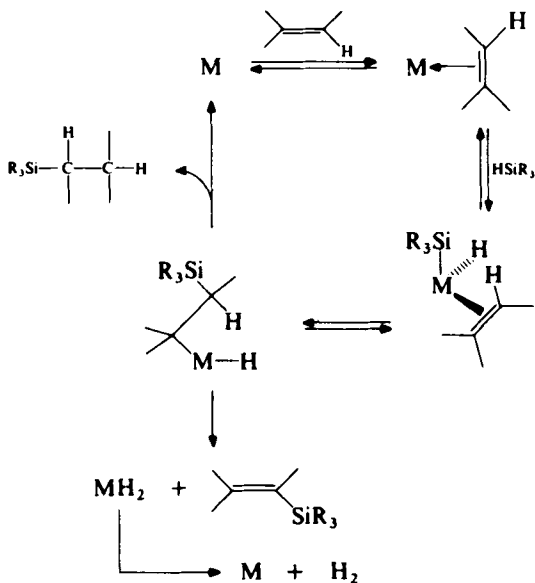


SCHEME 10

All of the steps in this mechanism have precedent in stoichiometric reaction chemistry. It is assumed that alkene adds before silane, but these steps may be reversed in some cases. The reversibility of two steps in the mechanism accounts for both the observed isotopic exchange between the alkene and silane, and the accompanying isomerization of alkenes. The fact that hydrosilylation occurs with retention of configuration at silicon<sup>266</sup> is consistent with this mechanism, since oxidative addition of silane to a metal center is known to proceed in a *cis* manner and with retention<sup>199, 267</sup>. The product-releasing step (elimination from an alkyl/silyl complex) has recently been observed in the thermal decomposition of an iron alkyl/silyl derivative (equation 100)<sup>268</sup>. Hydrosilylation as catalyzed by  $\text{Co}_2(\text{CO})_8$  appears to proceed by a somewhat different pathway<sup>8, 35, 262</sup>.



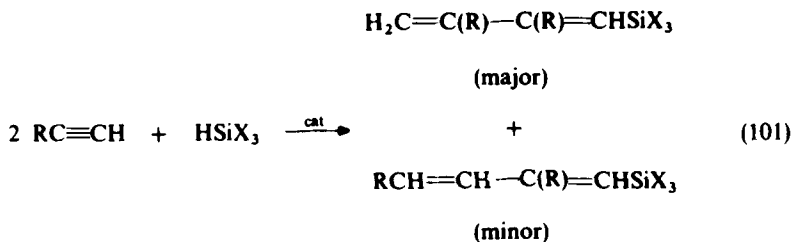
Studies cited earlier (Section VI.D.1)<sup>209, 211, 212</sup> and the observation of vinylsilane products under conditions of some catalyzed hydrosilylation reactions<sup>262, 269, 270</sup> have implicated another possible mechanism involving alkene insertion into a M-Si bond. This possibility is shown in Scheme 11. Insertion into the M-Si bond would produce a



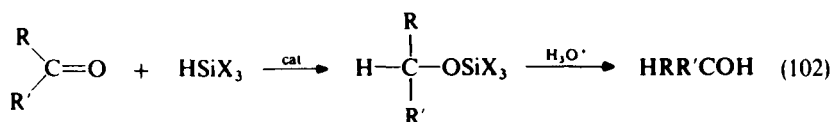
SCHEME 11

$\beta$ -silyl alkyl intermediate that can undergo  $\beta$ -hydrogen elimination to give the observed vinylsilane products. Hydrogen elimination from the metal would then complete the dehydrogenative process.

Hydrosilations of dienes and alkynes have been studied, and in both cases single and double silylations are possible. For 1,3-dienes, both 1,2 and 1,4 addition products can be observed<sup>8, 195, 213, 271, 272</sup>. A Ziegler-type catalyst composed of nickel(II) pentadienoate and triethylaluminum is active in hydrosilylation of terminal alkynes, but this reaction is accompanied by oxidative dimerization of the alkyne (equation 101). The major product in most cases was the head-to-head dimer<sup>273</sup>.



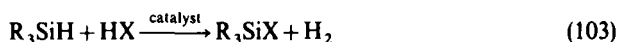
Given the high strength of Si-O bonds, it is not too surprising that hydrosilylation of aldehydes and ketones to silyl ethers is a facile process (equation 102). Since the resulting silyl ethers are readily hydrolyzed to the corresponding alcohols, these reactions offer alternatives to catalytic hydrogenation. A mechanism involving silyl group migration from the transition metal to the carbonyl oxygen of a coordinated ketone or aldehyde seems likely. With prochiral carbonyl compounds and a chiral metal catalyst, some



enantioselectivity can be achieved. Other reviews should be consulted for more details<sup>195, 231-237, 263, 272, 274</sup>.

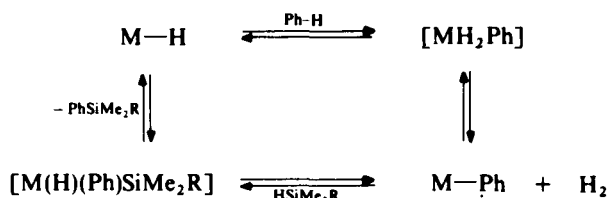
## 2. Dehydrogenative coupling reactions involving hydrosilanes

Dehydrogenative couplings that form new Si-X bonds from silanes  $\text{R}_3\text{SiH}$  and protic molecules (equation 103) are accelerated by various heterogeneous and homogeneous transition-metal catalysts. For alcoholysis of silanes in the presence of  $(\text{Ph}_3\text{P})_3\text{RhCl}$  as catalyst, a mechanism involving nucleophilic attack of the alcohol onto a metal-bound silyl group has been proposed<sup>195, 275</sup>.



(X = OH, OR, NRR', O<sub>2</sub>CR, SR, Cl, etc.)

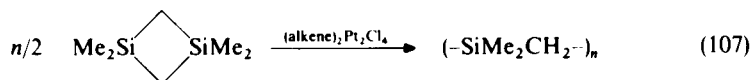
Silane couplings with less polar X-H bonds are perhaps more interesting, since such reactions could provide useful methods for making Si-C and Si-Si bonds. For forming Si-C bonds by dehydrogenative coupling, activation of the C-H bond of a hydrocarbon by the metal complex is required. One report describing such a process has appeared. When pentamethyldisiloxane,  $\text{Me}_3\text{SiOSiMe}_2\text{H}$ , was stirred in benzene with 2 mol% of Vaska's complex,  $(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl}$ , at 60 °C, the phenylsiloxane  $\text{PhMe}_2\text{SiOSiMe}_3$  (2%) was detected in addition to the redistribution products  $\text{Me}_3\text{SiOSi(H)MeOSiMe}_3$  (75%),  $\text{Me}_3\text{SiOSiMe}_2\text{OSiMe}_3$  (5%) and  $\text{Me}_3\text{Si(OSiMe}_2)_2\text{OSiMe}_3$  (4%). This Si-C bond-forming reaction may be generalized according to equation 104. A possible catalytic cycle was suggested (Scheme 12)<sup>276</sup>. Clearly, progress in this area will be greatly influenced by the development of homogeneous C-H activation systems.



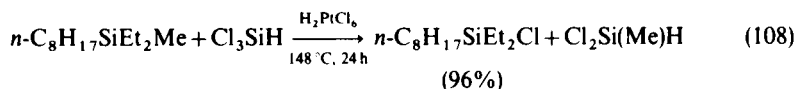
SCHEME 12

Interest in the synthesis of Si-Si bonds has increased rapidly with the realization that polysilane polymers,  $-(\text{SiRR}')_n-$ , have useful properties and applications. Polysilanes have been used as precursors to ceramic materials<sup>277-282</sup>, as dopable semiconductors<sup>283</sup>, as photoinitiators in olefin polymerization<sup>284</sup>, as photoresists<sup>285-287</sup> and as photoconductors<sup>288</sup>. A transition-metal-based coordination polymerization route could perhaps offer a useful alternative to the only general synthetic method currently available for the synthesis of polysilanes. This is the Wurtz-type coupling of dihalosilanes in the

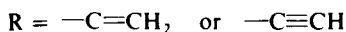
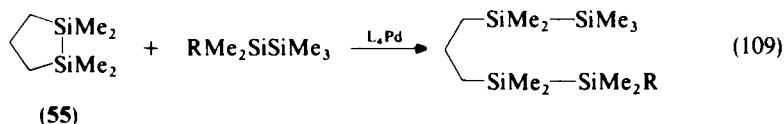




In addition to C/C exchanges, catalytic C/H, H/D, C/Cl, H/Cl, C/O, Si/C and Si/Si exchanges are known. These reactions have been used to make new monosilane derivatives, Si-Si bonded compounds and siloxane polymers<sup>39</sup>. An example of a selective Me/Cl exchange reaction is shown in equation 108<sup>300</sup>.



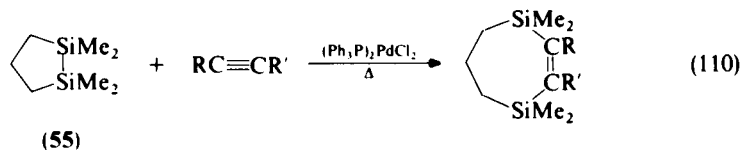
Sakurai and coworkers have reported the interesting Si-Si bond-forming reaction in equation 109<sup>301</sup>. A mechanism for the reaction with the vinyldisilane was proposed to involve an  $\eta^3$ -silaallyl ( $\text{Me}_2\text{SiCHCH}_2$ ) complex<sup>302, 303</sup>.



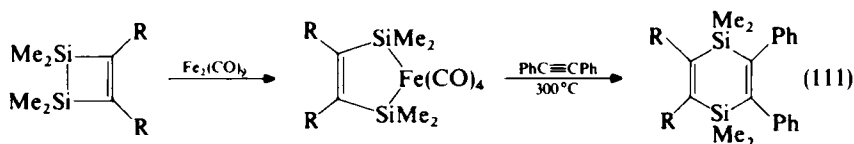
Again, very little is known concerning the mechanisms of these transformations. It seems, however, that oxidative addition–reductive elimination cycles involving Si–X bonds probably play a strong role. In some cases, silylene complexes may be involved (see Section III.A)<sup>39</sup>.

#### 4. Other Si–C bond-forming reactions

In reactions that are formally analogous to hydrosilylation, transition-metal complexes catalyze the insertion of unsaturated hydrocarbons into other Si–X (X = C, Si, Sn, etc.) bonds. Palladium catalysts seem to work best in many of these reactions. The work of Kumada and coworkers has already been referred to in connection with metal-catalyzed silylene transfer to alkynes (see equation 47)<sup>95–97</sup>. Sakurai's group has shown that the cyclic disilane **55** will add to alkynes in the presence of a palladium catalyst (equation 110, see also equation 80). The unstrained disilane  $\text{Me}_3\text{SiSiMe}_3$  undergoes a similar reaction

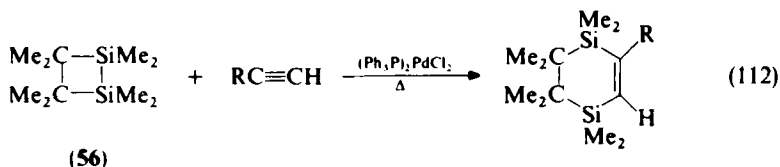


with  $\text{MeO}_2\text{C}\equiv\text{CO}_2\text{Me}$ , though the addition product is formed more slowly and in only 3.4% yield<sup>304</sup>. These processes probably involve activation of the disilane by oxidative addition of the Si–Si bond to the transition metal, as indicated by the observed conversions shown in equation 111<sup>305</sup>. Simple palladium complexes also catalyze the insertion of 1,3-dienes into Si–Si bonds. In many cases insertion of two diene units

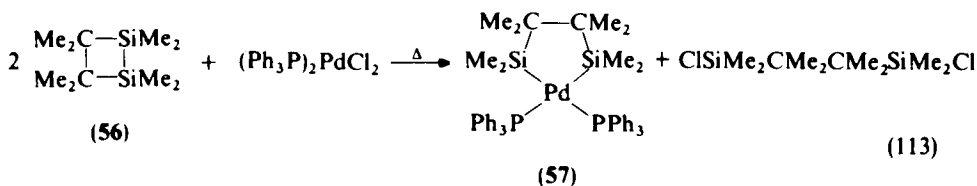


occurs<sup>96, 305-307</sup>. The regioselective 1,2-addition of disilanes to allene and 1,3-butadiene was found to be catalyzed by  $\text{Pd}(\text{PPh}_3)_4$ <sup>308</sup>.

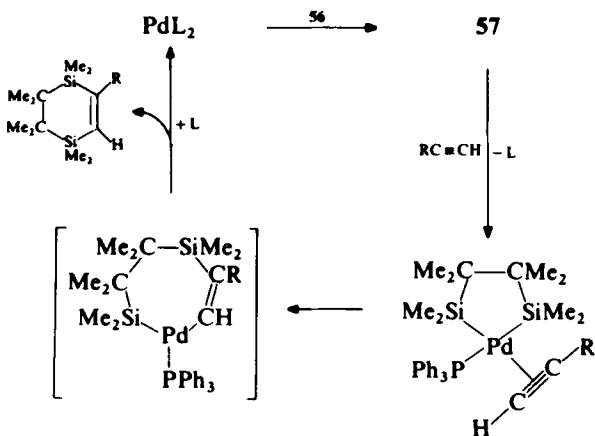
Octamethyl-1,2-disilacyclobutane (**56**) reacts with terminal alkynes in refluxing benzene in the presence of  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  as catalyst (equation 112) to give high yields of 1,4-disilacyclohexene products. Activated internal alkynes react analogously. 1,3-Butadiene



and isoprene undergo a palladium-catalyzed reaction with **56** that gives products of double insertion into the Si-Si bond. Allene reacts under similar conditions to give a 1,2-insertion product. It was shown that  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  reacts stoichiometrically with **56** according to equation 113. This suggests that initially **56** reduces  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  to



$\text{Pd}(\text{PPh}_3)_2$ , which then inserts into the Si-Si bond of a second equivalent of **56**. It was also found that the metallacycle **57** reacts rapidly with phenylacetylene in refluxing

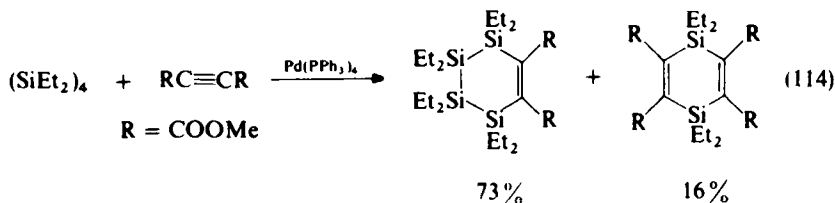


SCHEME 13



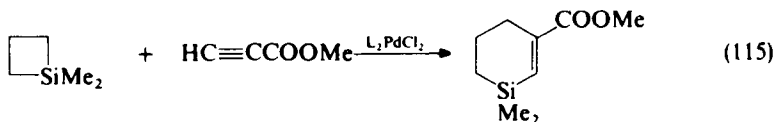
benzene to give the expected 1,4-disilacyclohexene derivative (equation 112). This result suggests the mechanism shown in Scheme 13 for the catalysis of equation 112<sup>309</sup>.

The strained cyclo-tetrasilane  $(\text{Et}_2\text{Si})_4$  also undergoes palladium-catalyzed addition to alkynes. With dimethyl acetylenedicarboxylate, the products shown in equation 114 were

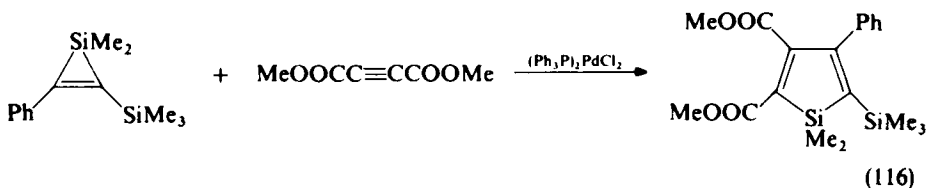


observed. A mechanism analogous to that shown in Scheme 13 was proposed. The  $(\text{PPh}_3)_2\text{PdCl}_2$ -catalyzed reaction of  $(\text{SiEt}_2)_4$  with isoprene gave both single and double insertion products<sup>310</sup>.

Insertions into the Si-C bonds of strained rings are also known<sup>39,98</sup>. One example is shown in equation 115<sup>311</sup>. Similar Pd-catalyzed insertion reactions are found for



silacyclopropenes<sup>98, 312-321</sup> (for an example, see equation 48). In addition to the silylene-transfer process of equation 48, single insertion of an alkyne into the silacyclopropene ring is observed under certain conditions (equation 116)<sup>314</sup>. For reactions of this type,

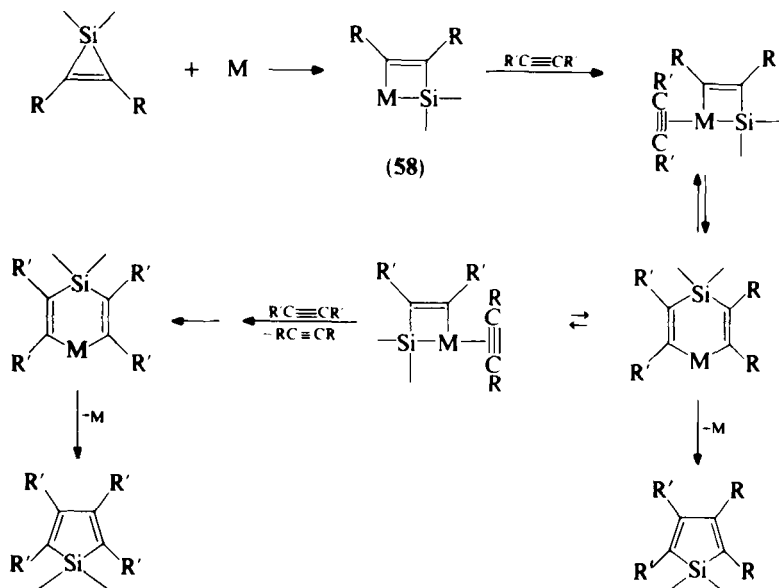


silametallacyclobutene derivatives (**58**) have been proposed. The mechanism in Scheme 14 can account for the processes represented in equations 48 and 116<sup>98</sup>.

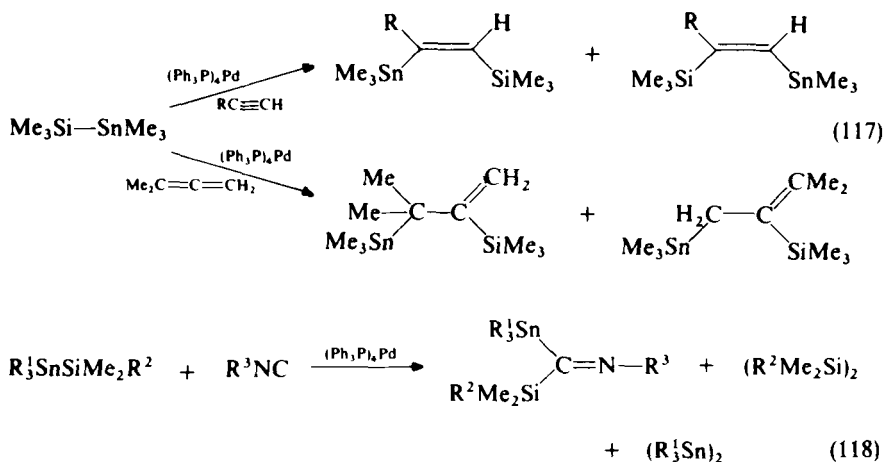
Ishikawa and coworkers have postulated that nickelsilacyclobutenes are in equilibrium with silapropadiene nickel complexes (**59**), and that this rearrangement explains the observed products of nickel-catalyzed reactions with alkynes, such as those shown in Scheme 15<sup>318-321</sup>. More recently, the nickelsilacyclobutene **62** has been observed by NMR<sup>321</sup>.

$\text{PdCl}_2/\text{pyridine}$  acts as a catalyst for the *cis* addition of  $\text{Me}_3\text{SiCN}$  to terminal arylacetylenes giving  $\beta$ -cyano- $\beta$ -arylalkenylsilanes,  $(\text{Ar})(\text{NC})\text{C}=\text{CH}(\text{SiMe}_3)$ <sup>322</sup>.

Catalytic additions of Si-Sn bonds to unsaturated substrates have been reported (equations 117<sup>323</sup> and 118<sup>324</sup>). The addition of  $\text{Me}_3\text{SiSnMe}_3$  to terminal alkynes tends to be quite regio- and stereospecific for formation of the isomer with *trans* R and  $\text{SiMe}_3$  groups (equation 117). Under similar catalytic conditions,  $\text{Me}_3\text{SiSnMe}_3$  adds to isocyanides to give organosilyl(*N*-substituted imino)stannanes in moderate to good yield (equation 118). This reaction, which also produces Si-Si and Sn-Sn bonded dispropo-



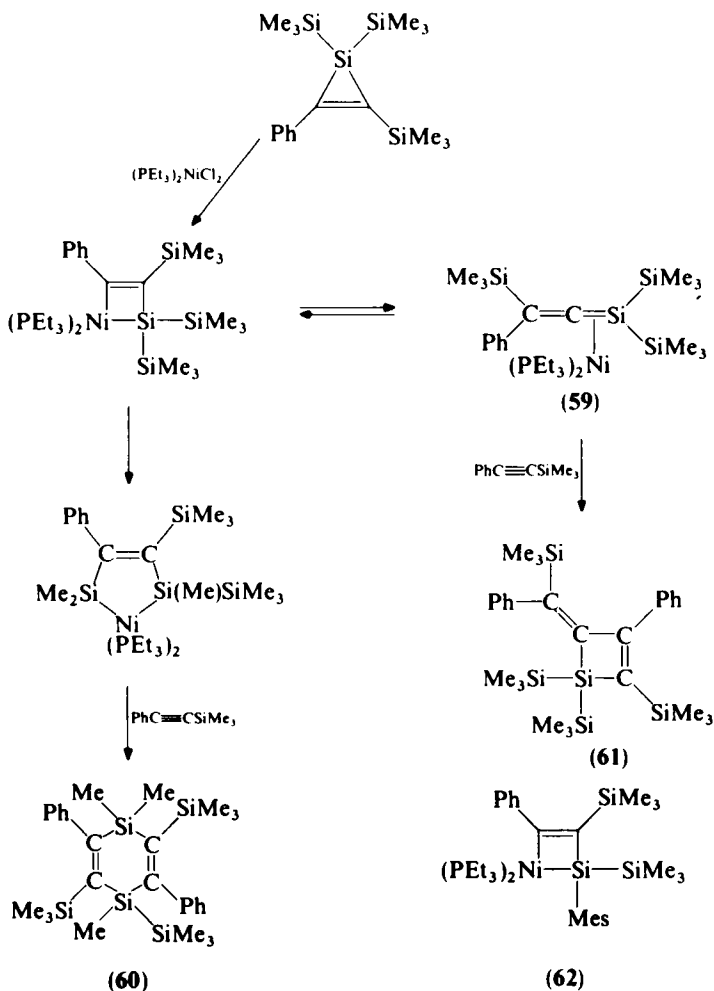
SCHEME 14



rtionation products, may involve insertion of the isocyanide into a Pd-Si or a Pd-Sn bond<sup>324</sup>.

Acylsilanes are prepared from acid chlorides and  $\text{Me}_3\text{SiSiMe}_3$  via the palladium-catalyzed reaction shown in equation 119<sup>325, 326</sup>. Alkyl and aryl halides  $\text{RX}$  undergo analogous reactions with disilanes to give Si-R bonded derivatives<sup>326-329</sup>.

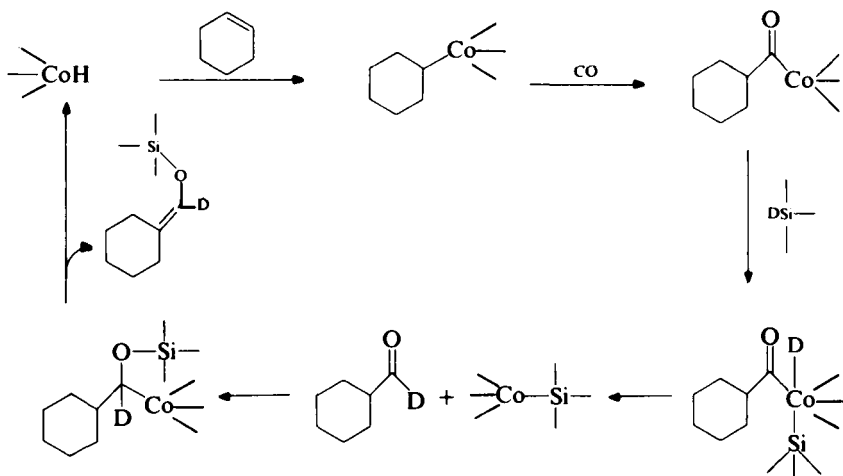
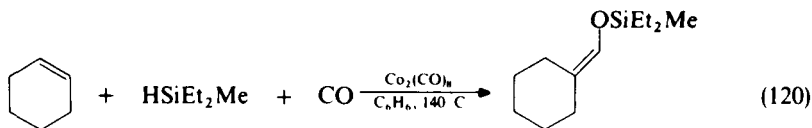




SCHEME 15

### 5. Catalytic reactions with hydrosilanes and carbon monoxide

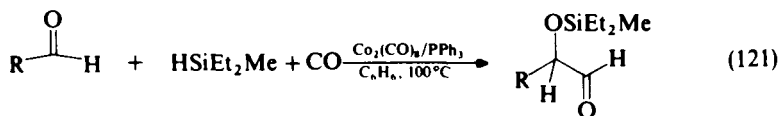
Murai and Sonoda have reported a number of cobalt-catalyzed reactions that results in addition of a silane and carbon monoxide to the substrate<sup>330-338</sup>. With alkene substrates, the catalysis leads to a silyl enol ether (equation 120)<sup>330</sup>. The reaction is therefore somewhat analogous to catalytic hydroformylation, which involves addition of hydrogen and carbon monoxide to an alkene to produce an aldehyde<sup>25</sup>. With the aid of deuterium-labeling studies, the mechanism in Scheme 16 was proposed. The catalyst is believed to be a cobalt hydride, obtained from  $\text{Co}_2(\text{CO})_8$  and the silane by the metal-metal bond cleavage process shown in equation 13. The proposed intermediate cyclohexanecarboxaldehyde was isolated from the reaction mixture by adding *tert*-butyl acetate to intercept the cobalt silyl intermediate<sup>330</sup>.



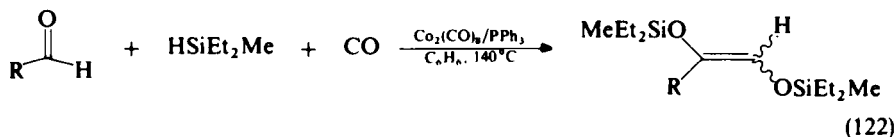
SCHEME 16

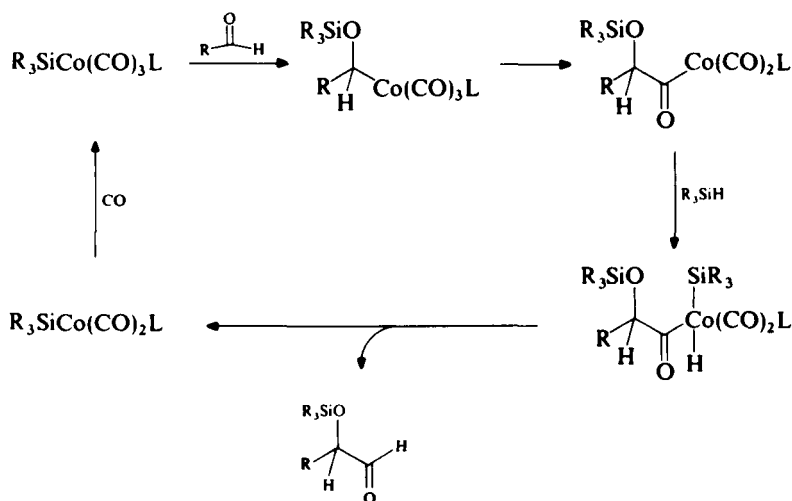
The ruthenium cluster anions  $[\text{HRu}_3(\text{CO})_{11}]^-$  and  $[\text{HRu}_3(\text{CO})_{10}(\text{SiEt}_3)_2]^-$  catalyze a similar reaction, converting ethylene, carbon monoxide and  $\text{HSiEt}_3$  to a mixture of unsaturated silyl ethers. It was found that in the reaction system,  $[\text{HRu}_3(\text{CO})_{11}]^-$  and  $[\text{HRu}_3(\text{CO})_{10}(\text{SiEt}_3)_2]^-$  are interconverted<sup>339</sup>.

The addition of triphenylphosphine to the cobalt catalyst allows the conversion of aldehydes to  $\alpha$ -siloxyaldehydes (equation 121). The  $\text{PPh}_3$  co-catalyst was used to



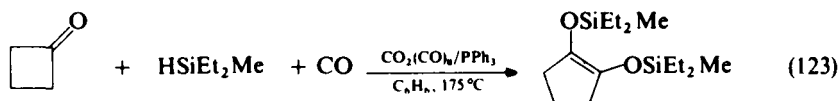
suppress hydrosilylation of the aldehyde to  $\text{RCH}_2\text{OSiEt}_2\text{Me}$ . It is believed that the active catalyst in this reaction is a cobalt silyl  $\text{MeEt}_2\text{SiCo}(\text{CO})_3\text{L}$  ( $\text{L} = \text{CO}$  or  $\text{PPh}_3$ ), and that activation of the aldehyde occurs by insertion into the Co-Si bond (Scheme 17)<sup>330, 331</sup>. This reaction requires an excess of the starting aldehyde over the silane to avoid secondary reactions of the  $\alpha$ -siloxyaldehydes. If an excess of the silane is used, the product is a 1,2-bis(siloxy)alkene (equation 122). The product could arise from  $\beta$ -hydrogen



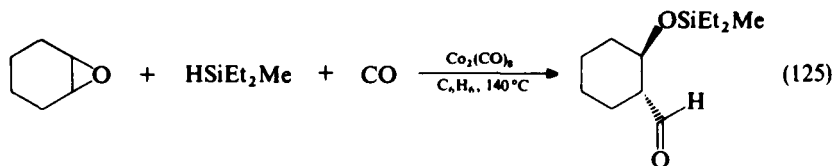
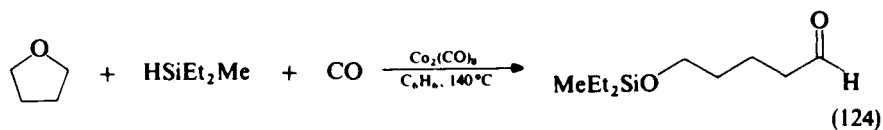


SCHEME 17

elimination from a  $\text{CoCH}(\text{OSiR}_3)\text{CRH}(\text{OSiR}_3)$  species formed by addition of a Co-Si bond to an  $\alpha$ -siloxyaldehyde<sup>330, 331</sup>. A similar reaction takes place with cyclobutanones, which undergo ring expansion to disiloxycyclopentene derivatives in high yield (equation 123)<sup>332</sup>.



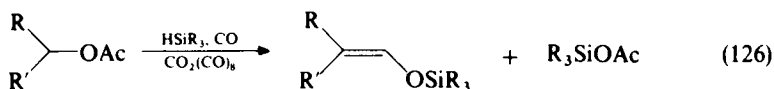
Cyclic ethers are ring-opened to give a variety of siloxy-substituted aldehydes (equations 124 and 125). Three-, four- or five-membered cyclic ethers, and an excess of the ether



are required. A likely mechanism involves ring-opening of the ether by a cobalt silyl species to give the alkyls  $\text{Co}(\text{CH}_2)_n\text{OSiEt}_2\text{Me}$ . The aldehyde products in these reactions can undergo further reactions in the presence of excess silane to 1,2-tris(siloxy)alkene derivatives<sup>330, 333</sup>. With slight modifications of reaction conditions, tetrahydrofuran can

also be converted to 1,5-disiloxypentane or to 1,5-disiloxo-1-pentene<sup>334</sup>. The  $\text{Co}_2(\text{CO})_8$ -catalyzed reaction of oxetanes with  $\text{HSiR}_3$  and CO can lead to 1,4-disiloxobutanes, 1-siloxopropanes and silyl enol ethers, depending on reaction conditions<sup>335,340</sup>. Oxiranes are converted with high regio- and stereoselectivities to 1,3-disiloxo ether derivatives<sup>336</sup>.

Finally, this cobalt catalyst system has been shown to be useful for the preparation of silyl enol ethers from alkyl acetates (equation 126)<sup>337,338</sup>.



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# Appendix to 'Transition-metal silyl derivatives'<sup>†</sup>

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<sup>†</sup>The material in this Appendix is divided in the same manner as in the original Chapter 24 in the volume *The Chemistry of Organic Silicon Compounds*. Corresponding section numbers in The Appendix are preceded by an asterisk. Note that some section numbers are omitted while some new ones (not preceded by an asterisk) have been added. Structures, equations, tables, schemes and references run continuously in the original chapter and this in Appendix.

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## ABBREVIATIONS

cod	cyclooctadiene
coe	cyclooctene
cot	cyclooctatetraene
Cp	$\eta^5\text{-C}_5\text{H}_5$
Cp*	$\eta^5\text{-C}_5\text{Me}_5$
dcpe	(c-Hex) <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> P(c-Hex) <sub>2</sub> (1,2-bis(dicyclohexylphosphino)ethane)
dpam	Ph <sub>2</sub> AsCH <sub>2</sub> AsPh <sub>2</sub>
dppe	bis(1,2-diphenylphosphino)ethane
dppm	bis(1,1-diphenylphosphino)methane
OTf	triflate
PPN <sup>+</sup>	Ph <sub>3</sub> P=N <sup>+</sup> =PPh <sub>3</sub>
TPP	tetraphenylporphyrin
tripsi	Si(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub>

## \*I. INTRODUCTION

Research with transition-metal silyl derivatives has yielded many fundamental advances over the past few years. The increasing pace of developments in this field, on all fronts, indicates that there is much interest in the stoichiometric and catalytic chemistry of metal-silicon bonds. This appendix serves to update information on some of the newer developments, covering literature up to approximately the middle of 1990. Aspects of this literature have also been reviewed by Schubert<sup>341</sup>.

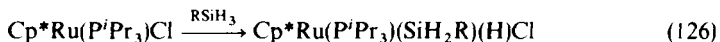
## \*II. THE FORMATION OF COMPOUNDS CONTAINING TRANSITION-METAL-SILICON BONDS

### \*A. Late Transition-metal Derivatives

An understanding of how late transition-metal-silicon bonds can form is relevant to synthetic, mechanistic and catalytic investigations.

#### \*1. Methods involving oxidative addition of Si—H bonds

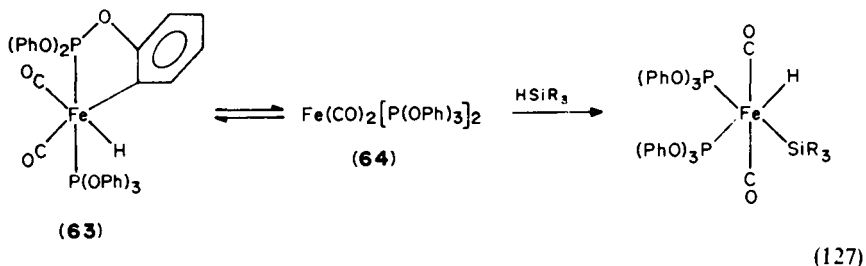
The 16-electron ruthenium complex ( $\eta^5\text{-C}_5\text{Me}_5$ )Ru(P<sup>i</sup>Pr<sub>3</sub>)Cl oxidatively adds primary silanes to produce ruthenium(IV) silyl derivatives (equation 126, R = Ph, *p*-Tol, Cp\* =  $\eta^5\text{-C}_5\text{Me}_5$ ). In each case the silyl group adopts a position *trans* to the phosphine



ligand. The silane HSiMe<sub>2</sub>Cl also adds in this manner, but bulkier silanes such as HSiPh<sub>2</sub>Cl do not<sup>342</sup>.

Photochemical dissociation of carbon monoxide from [(CO)<sub>4</sub>Fe]<sub>2</sub>(dppe) allows oxidative addition of hydrosilanes to produce the complexes [*mer*-(CO)<sub>3</sub>Fe(H)SiR<sub>3</sub>]<sub>2</sub>(dppe) (SiR<sub>3</sub> = SiCl<sub>3</sub>, SiMeCl<sub>2</sub>, SiMe<sub>2</sub>Cl). Further photolysis of the latter species in the presence of silanes leads to elimination of hydrogen and formation of the bis(silyl)iron complexes [*mer*-(CO)<sub>3</sub>Fe(SiR<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(dppe) (SiR<sub>3</sub> = SiCl<sub>3</sub>, SiMeCl<sub>2</sub>). Related transformations starting from (dppe)Fe(CO)<sub>3</sub> allow preparations of (CO)<sub>2</sub>(dppe)Fe(H)SiR<sub>3</sub> [SiR<sub>3</sub> = SiCl<sub>3</sub>, SiMeCl<sub>2</sub>, SiMe<sub>2</sub>Cl, SiMe<sub>3</sub>, Si(OEt)<sub>3</sub>, SiMe<sub>2</sub>H, SiMe<sub>2</sub>Ph] and *cis*-(CO)<sub>2</sub>(dppe)Fe(SiR<sub>3</sub>)<sub>2</sub> (SiR<sub>3</sub> = SiCl<sub>3</sub>, SiMeCl<sub>2</sub>)<sup>343</sup>. The fluxional trihydrido silyl complexes (CO)(dppe)FeH<sub>3</sub>(SiR<sub>3</sub>) [SiR<sub>3</sub> = Si(OEt)<sub>3</sub>, Si(OMe)<sub>3</sub>, SiMe<sub>3</sub>, SiMe<sub>2</sub>Ph, SiPh<sub>3</sub>] were prepared by the photochemical reaction of HSiR<sub>3</sub> with (CO)<sub>2</sub>(dppe)Fe(H)SiR<sub>3</sub> or (CO)<sub>2</sub>(dppe)FeH<sub>2</sub><sup>344</sup>.

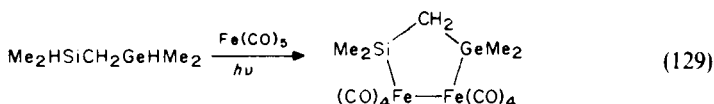
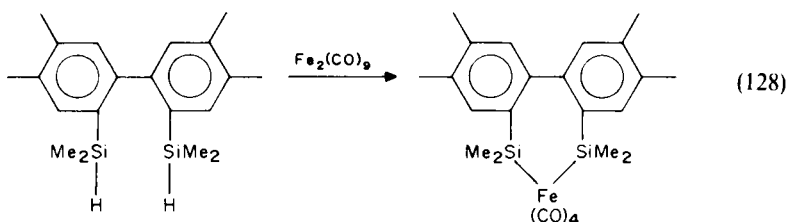
Irradiation of phosphite derivatives Fe(CO)<sub>4</sub>[P(OR)<sub>3</sub>] (R = Ph, Et) with silanes HSiR'<sub>3</sub> [SiR'<sub>3</sub> = SiMePh<sub>2</sub>, Si(OEt)<sub>3</sub>, SiPh<sub>3</sub>] provides *mer*-[P(OR)<sub>3</sub>]<sub>2</sub>(CO)<sub>3</sub>FeH(SiR'<sub>3</sub>) complexes. Photolysis of Fe(CO)<sub>3</sub>[P(OEt)<sub>3</sub>]<sub>2</sub> in the presence of HSiMeCl<sub>2</sub> also leads to replacement of a carbon monoxide to give *cis*-[P(OEt)<sub>3</sub>]<sub>2</sub>(CO)<sub>2</sub>FeH(SiMeCl<sub>2</sub>), but the corresponding reaction with HSiPh<sub>3</sub> leads to products of both CO and phosphite-substitution. A cleaner route to bis(phosphite)iron complexes containing silyl ligands is via thermal generation of the 16-electron intermediate **64**, which is in equilibrium with the orthometallated species **63**. Reaction of this equilibrium mixture with hydrosilanes produces the silyl complexes shown in equation 127 [SiR<sub>3</sub> = SiMeCl<sub>2</sub>, Si(OEt)<sub>3</sub>, SiPh<sub>3</sub>, SiMePh<sub>2</sub>, SiMe<sub>2</sub>Ph, SiMe<sub>3</sub>]. With HSiCl<sub>3</sub>, the silane somehow acts as a source of chloride, and [P(OPh)<sub>3</sub>]<sub>2</sub>(CO)<sub>2</sub>FeHCl is obtained as the major product. Deprotonation of the above [P(OR)<sub>3</sub>]<sub>2</sub>(CO)<sub>2</sub>FeH(SiR'<sub>3</sub>) complexes with KH gives the anionic silyls K{[P(OR)<sub>3</sub>]<sub>2</sub>(CO)<sub>2</sub>FeSiR'<sub>3</sub>}<sup>345</sup>.



Cyclic species containing Fe—Si bonds have been obtained from reagents with Si—H



bonds (equations 128<sup>346</sup> and 129<sup>347</sup>).

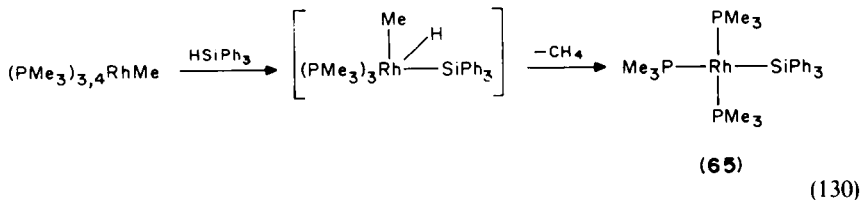


Kinetic studies on the addition of  $\text{HSiEt}_3$  to  $(\eta^5\text{-C}_5\text{R}_5)\text{Mn}(\text{CO})_2$  ( $\text{R} = \text{Cl, H, Me}$ ), generated by photolytic dissociation of CO from  $(\eta^5\text{-C}_5\text{R}_5)\text{Mn}(\text{CO})_3$ , demonstrate that for each process  $\Delta H^\ddagger$  is about the same, and that differences in reaction rate may be attributed to  $\Delta S^\ddagger$ . For  $\text{R} = \text{Cl}$  the reaction rate constant is  $10^7$  times smaller than the reaction rate constant for  $\text{R} = \text{Me}$ . The large and negative  $\Delta S^\ddagger$  for the  $(\eta^5\text{-C}_5\text{Cl}_5)\text{Mn}(\text{CO})_2$  reaction is attributed to the electron-poor metal center, which gives rise to a late transition state characterized by a relatively strong interaction between metal center and silane<sup>348</sup>.

2-Dimethylsilylpyridine,  $2\text{-(Me}_2\text{HSi)NC}_5\text{H}_4$ , can potentially provide metal-silicon bonds as part of a chelate ring. This silane reacts with  $\text{Re}_2(\text{CO})_{10}$  to give such a complex,  $(\text{CO})_4\text{ReSiMe}_2(\text{NC}_5\text{H}_4)$ , but the reaction with Vaska's complex apparently gives  $(\text{PPh}_3)_2(\text{CO})(\text{Cl})\text{IrH}(\text{SiMe}_2\text{NC}_5\text{H}_4)$ , without an  $\text{Ir-N}$  bond<sup>349</sup>.

Another functionalized silane,  $\text{HSi}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$  (Htripsi), reacts with  $[(\text{cod})\text{RhCl}]_2$  to afford the six-coordinate rhodium(III) silyl  $\text{Rh}(\text{tripsi})\text{HCl}$ , which reduces under CO to form  $(\text{tripsi})\text{Rh}(\text{CO})$ , with a trigonal bipyramid structure featuring silicon *trans* to the carbonyl ligand. This complex, and the related  $(\text{tripsi})\text{Rh}(\text{PPh}_3)$ , are of interest as rare examples of rhodium(I) silyl complexes<sup>350</sup>.

A second rhodium(I) silyl complex (**65**) is obtained via the methane-elimination reaction of equation 130. Carbon monoxide displaces one of the  $\text{PMe}_3$  ligands in **65** to produce  $(\text{PMe}_3)_2(\text{CO})_2\text{RhSiPh}_3$ , and hydrogen adds to give  $(\text{PMe}_3)_3\text{RhH}_2(\text{SiPh}_3)$ . The latter product is also formed upon oxidative addition of  $\text{HSiPh}_3$  to  $\text{RhH}(\text{PMe}_3)_4$ <sup>351</sup>.



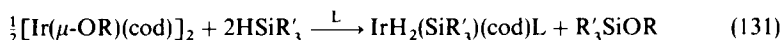
The rhodium(V) silyl complex  $\text{Cp}^*\text{RhH}_2(\text{SiMe}_3)_2$  can be obtained by reaction of either  $[\text{Cp}^*\text{RhCl}_2]_2$  or  $\text{Cp}^*\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$  with  $\text{HSiMe}_3$ . Also,  $\text{Cp}^*\text{Rh}(\text{CO})(\text{H})\text{SiMe}_3$  is formed by addition of  $\text{HSiMe}_3$  to  $\text{Cp}^*\text{Rh}(\text{CO})_2$ <sup>352</sup>.

Several reports have appeared regarding the reactions between silylalkyne derivatives containing  $\text{Si-H}$  bonds (e.g.  $\text{Me}_2\text{HSiC}\equiv\text{CSiHMe}_2$ ) and  $\text{Co}_2(\text{CO})_8$ . A number of interesting multinuclear species have been obtained, some with  $\text{Co-Si}$  bonds. The reactions occur via initial formation of  $\text{Co}_2(\text{CO})_6(\text{alkyne})$  complexes<sup>353-357</sup>.

Transition-metal alkyl derivatives react with hydrosilanes to give silyl complexes, presumably by way of distinct Si—H oxidative addition and C—H reductive elimination steps. Thus, reaction of *cis*-(PMePh<sub>2</sub>)<sub>2</sub>PdMe<sub>2</sub> with H<sub>2</sub>SiMePh or H<sub>2</sub>SiPh<sub>2</sub> gives the corresponding *cis*-(PMePh<sub>2</sub>)<sub>2</sub>Pd(SiHR<sub>2</sub>)<sub>2</sub> complexes, which are unstable and decompose by elimination of R<sub>2</sub>HSiSiHR<sub>2</sub>. The bis(chelate) silyl Pd(SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>, obtained from *cis*-(PMePh<sub>2</sub>)<sub>2</sub>PdMe<sub>2</sub> and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiHMe<sub>2</sub>, is much more stable. Chlorinated silanes (HSiCl<sub>3</sub> and HSiMeCl<sub>2</sub>) react with *cis*-(PMePh<sub>2</sub>)<sub>2</sub>PdMe<sub>2</sub> to give (PMePh<sub>2</sub>)<sub>2</sub>PdCl<sub>2</sub> and methylated silanes rather than isolable palladium silyl complexes. However, *trans*-(PMePh<sub>2</sub>)<sub>2</sub>Pd(SiCl<sub>3</sub>)<sub>2</sub> was obtained by the novel reaction of (PMePh<sub>2</sub>)<sub>2</sub>PdCl<sub>2</sub> with HSiCl<sub>3</sub> and KH<sup>358</sup>. Synthetic procedures based on elimination of a hydrocarbon have also been described for cobalt<sup>359</sup> and ruthenium<sup>360</sup> silyl complexes.

Addition of HSiPh<sub>3</sub> to (PMe<sub>3</sub>)<sub>2</sub>PtH<sub>2</sub> results in evolution of hydrogen and formation of *cis*-(PMe<sub>3</sub>)<sub>2</sub>PtH(SiPh<sub>3</sub>). This reaction appears to proceed through the six-coordinate platinum(IV) intermediate (PMe<sub>3</sub>)<sub>2</sub>PtH<sub>3</sub>(SiPh<sub>3</sub>), since addition of HEPH<sub>3</sub> (E = Ge, Sn) to (PMe<sub>3</sub>)<sub>2</sub>PtH<sub>2</sub> yields *cis,trans,cis*-PtH<sub>2</sub>(EPH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> complexes as isolated products<sup>361</sup>.

Alkoxide ligands may serve as leaving groups in the synthesis of iridium(III) silyls [equation 131, L = PPh<sub>3</sub>, AsPh<sub>3</sub>, P(c-Hex)<sub>3</sub>; SiR'<sub>3</sub> = SiEt<sub>3</sub>, SiMe<sub>2</sub>Ph; R = Me, Et].



These processes are believed to proceed via oxidative addition of HSiR'<sub>3</sub> to Ir(OR)(cod)L, followed by reductive elimination of R'<sub>3</sub>SiOR and subsequent oxidative addition of the second equivalent of HSiR'<sub>3</sub> to IrH(cod)L. Silyl group exchange occurs between the IrH<sub>2</sub>(SiR'<sub>3</sub>)(cod)L complexes and HSiR'<sub>3</sub><sup>362,363</sup>.

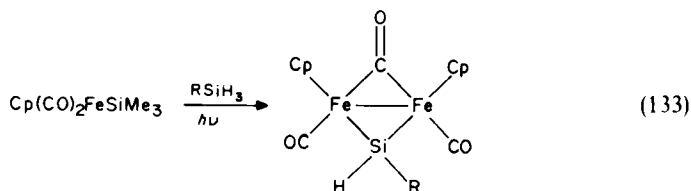
Atwood and coworkers<sup>364</sup> have noted that reactions of silanes with the alkoxyiridium complexes *trans*-ROIr(CO)L<sub>2</sub> [R = Me, Ph; L = P(*p*-Tol)<sub>3</sub>] occur readily at room temperature [equation 132; SiR'<sub>3</sub> = SiMe<sub>2</sub>Ph, SiPh<sub>3</sub>, Si(OMe)<sub>3</sub>], unlike analogous reactions with *trans*-IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> which require more forcing conditions. In the



reaction of HSiPh<sub>3</sub> with *trans*-MeOIr(CO)[P(*p*-Tol)<sub>3</sub>]<sub>2</sub>, the intermediate IrH(SiPh<sub>3</sub>)(OMe)[P(*p*-Tol)<sub>3</sub>]<sub>2</sub> was observed by low-temperature <sup>1</sup>H NMR spectroscopy. Kinetic studies established a second-order rate law, and as expected silanes with electronegative substituents reacted faster.

New types of bimetallic complexes have been obtained via the synthesis of cyclopentadienyldimethylsilane complexes (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>H)Mn(CO)<sub>3</sub>, (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>H)CpFe and (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>H)<sub>2</sub>Ru. The Si—H functionality of these complexes adds to Co<sub>2</sub>(CO)<sub>8</sub> or IrH(CO)(PPh<sub>3</sub>)<sub>3</sub> to afford (CO)<sub>3</sub>Mn(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>—ML<sub>n</sub>), CpFe(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>—ML<sub>n</sub>) [ML<sub>n</sub> = Co(CO)<sub>4</sub>, IrH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] and Ru[η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>—Co(CO)<sub>4</sub>]<sub>2</sub>. In a similar way (CO)<sub>3</sub>Cr(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>SiMe<sub>2</sub>—ML<sub>n</sub>) complexes were obtained<sup>365</sup>.

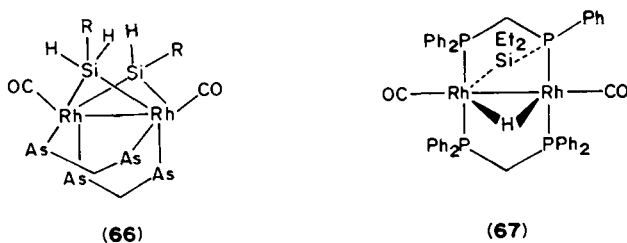
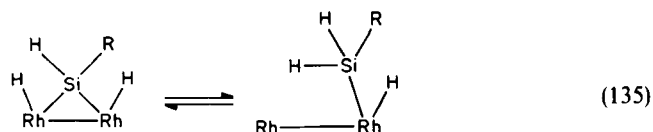
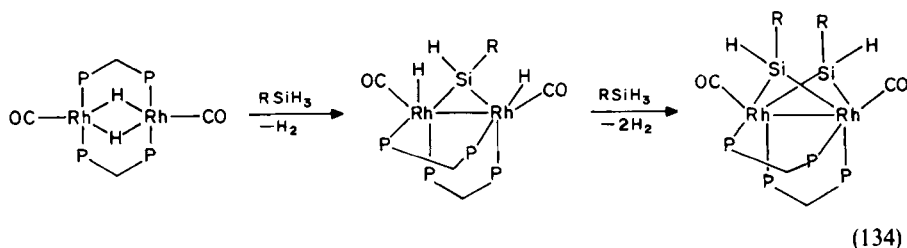
Activation of more than one Si—H bond in a hydrosilane can lead to silylene-bridged



dinuclear complexes. A recent example of this is found in the photolysis of a mixture of  $\text{CpFe}(\text{CO})_2\text{SiMe}_3$  and  $\text{RSiH}_3$  ( $\text{R} = \text{'Bu}, \text{CMe}_2\text{CMe}_2\text{H}$ ), which produces the *cis* isomers shown in equation 133. Mononuclear  $\text{Cp}(\text{CO})_2\text{FeSiH}_2\text{R}$  species are presumed intermediates. The observed preference for the *cis* geometry is attributed to the steric influence of the bulky R groups<sup>366</sup>. Replacement of hydrogen on the  $\mu$ -silylene silicon atoms by halogen or methyl groups leads to stabilization of the *trans* isomers<sup>367</sup>.

Heterobimetallic  $\mu$ -silylene complexes were obtained by reactions of  $(\text{CO})_5\text{MnSiR}_2\text{H}$  ( $\text{R} = \text{Me}, \text{Ph}, \text{Cl}$ ) with  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  or  $\text{Pt}(\text{PPh}_3)_4$ . The products,  $(\text{CO})_4\text{Mn}(\mu\text{-SiR}_2)(\mu\text{-H})\text{Pt}(\text{PPh}_3)_2$ , undergo ligand substitution reactions at platinum. The complex  $(\text{CO})_4\text{Mn}(\mu\text{-SiPh}_2)(\mu\text{-H})\text{Pt}(\text{PPh}_3)_2$  reacts with methanol via the presumed formation of  $\text{Ph}_2\text{Si}(\text{OMe})_2$  to give  $(\text{CO})_4\text{Mn}(\mu\text{-PPh}_2)(\mu\text{-H})\text{PtPh}(\text{PPh}_3)$ <sup>368</sup>.

Oxidative additions of primary silanes  $\text{RSiH}_3$  ( $\text{R} = \text{Ph}, \text{Et}, \text{n-Hex}$ ) to  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$  ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) have been investigated (equation 134)<sup>369,370</sup>. The intermediates  $\text{Rh}_2(\mu\text{-SiHR})\text{H}_2(\text{CO})_2(\text{dppm})_2$  are fluxional, exhibiting exchange of hydrogen atoms between rhodium and silicon. This exchange is proposed to occur via the steps in equation 135. Analogous reactions of the arsine complex  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dpam})_2$  ( $\text{dpam} = \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ ) give  $\text{Rh}_2(\mu\text{-SiHR})_2(\text{CO})_2(\text{dpam})_2$  via the intermediates  $\text{Rh}_2(\mu\text{-SiHR})(\text{SiH}_2\text{R})\text{H}_3(\text{CO})_2(\text{dpam})_2$ . A second product in the reaction of  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dpam})_2$  with  $\text{EtSiH}_3$  is proposed to have the unusual structure **66**. Additions of  $\text{RSiH}_3$  to  $\text{Rh}_2(\text{CO})_3(\text{dppm})_2$  produce  $\text{Rh}_2(\mu\text{-SiHR})(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2$  via reductive elimination of  $\text{H}_2$ . Secondary silanes  $\text{RR}'\text{SiH}_2$  react with  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$  to give  $\text{Rh}_2(\mu\text{-SiRR}')\text{H}_2(\text{CO})_2(\text{dppm})_2$ , and eventually products with structure **67**. The latter product arises from an interesting process involving P—Ph bond cleavage and P—Si bond formation<sup>370</sup>. Related transformations have been reported for iridium 'A-frame' complexes. Addition of secondary silanes  $\text{R}_2\text{SiH}_2$  to  $\text{Ir}_2(\text{CO})_3(\text{dppm})_2$  forms isolable  $\text{Ir}_2(\mu\text{-SiR}_2)\text{H}_2(\text{CO})_2(\text{dppm})_2$  ( $\text{R} = \text{Me}, \text{Et}, \text{Ph}$ ) complexes, and the analogous reaction with  $\text{PhSiH}_3$  yields  $\text{Ir}_2(\mu\text{-SiHPh})\text{H}_2(\text{CO})_2(\text{dppm})_2$ <sup>371</sup>.

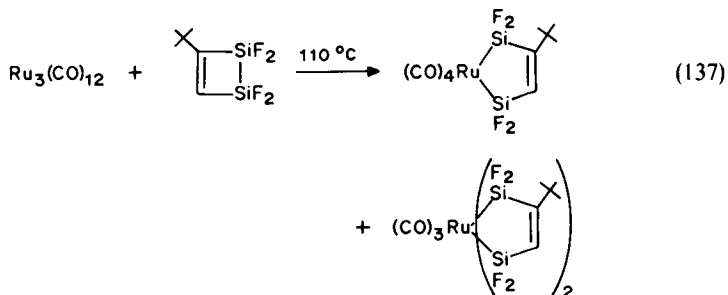
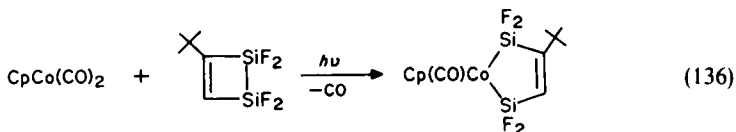


## \*2. Methods involving oxidative addition of other Si—X bonds

The complex  $\text{Rh}[\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3]\text{CO}$  was isolated from the reaction mixture obtained from the hydroformylation of 1-butene by rhodium in the presence of  $\text{MeSi}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ . This rhodium(I) silyl complex is therefore formed via a  $\text{CH}_3-\text{Si}$  bond cleavage<sup>372</sup>.

Addition of  $\text{Me}_4\text{Si}$  to  $(\text{tBu}_2\text{PCH}_2\text{P}^t\text{Bu}_2)\text{Pt}$ , generated *in situ* by reductive elimination of  $\text{Me}_4\text{C}$  from  $(\text{tBu}_2\text{PCH}_2\text{P}^t\text{Bu}_2)\text{Pt}(\text{H})\text{CH}_2\text{CMe}_3$ , affords the silyl methyl  $(\text{tBu}_2\text{PCH}_2\text{P}^t\text{Bu}_2)\text{Pt}(\text{SiMe}_3)\text{Me}$ . Apparently, this reaction involves initial oxidative addition of a C—H bond of  $\text{Me}_4\text{Si}$  to platinum, rather than direct insertion of Pt into the Si—C bond<sup>373</sup>.

Liu and coworkers have exploited the metal activation of an Si—Si bond to develop the cycloaddition chemistry of 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene with conjugated dienes (see Section \*VI.E.4)<sup>374-382</sup>. In some of the systems studied, products resulting from oxidative addition of the Si—Si bond to the metal center have been isolated. Examples are shown in equations 136<sup>379</sup> and 137<sup>381</sup>.



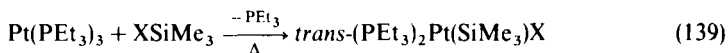
Recently, significant results regarding the oxidative addition of halosilanes to transition-metal compounds have been obtained. Whereas trimethylsilyl chloride does not react with  $\text{MeIr}(\text{CO})[\text{P}(p\text{-Tol})_3]_2$ <sup>40</sup>, it does react with analogous iridium alkoxides to produce alkoxy-silanes [equation 138, R = Me, Ph; L =  $\text{P}(p\text{-Tol})_3$ ]. Since in other



oxidative additions, methyliridium derivatives are more reactive than analogous iridium alkoxides, it appears that in the above reactions with  $\text{Me}_3\text{SiCl}$ , oxidative addition may not be involved. An alternative mechanism involving nucleophilic attack of the alkoxide ligand onto  $\text{Me}_3\text{SiCl}$  has been suggested<sup>364</sup>.

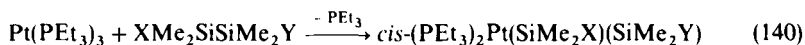
Related halogen-exchange processes have been reported for  $\text{MCl}(\text{CO})\text{L}_2$  complexes (M = Rh, Ir; L = tertiary phosphine), which react with silyl halides  $\text{Me}_3\text{SiX}$  (X = Br, I) to give  $\text{MX}(\text{CO})\text{L}_2$  and  $\text{Me}_3\text{SiCl}$ . Similarly,  $\text{RhCl}(\text{PPh}_3)_3$  undergoes halogen exchange with  $\text{Me}_3\text{SiX}$ . Reactivity trends observed for these processes suggest that oxidative additions of the usual type may not be involved. The rhodium hydride  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  reacts with  $\text{MeSiCl}_3$  via hydrogen-chlorine exchange, giving  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ <sup>383</sup>.

Well-defined oxidative additions of trimethylsilyl halides to platinum(0) have been reported by Tanaka and coworkers (equation 139, X = Br, I). Trimethylsilyl chloride did



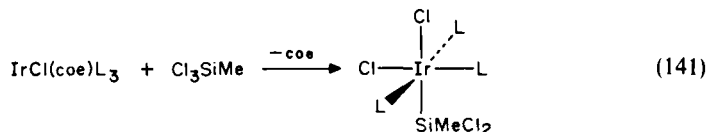
not react, presumably because of the higher Cl—SiMe<sub>3</sub> bond strength (98 kcal mol<sup>-1</sup> vs 76 and 57 kcal mol<sup>-1</sup> for Br—SiMe<sub>3</sub> and I—SiMe<sub>3</sub>, respectively). Also, PtL<sub>4</sub> (L = PPh<sub>3</sub>, PMe<sub>2</sub>Ph) and Pt(dppe)<sub>2</sub> do not react with BrSiMe<sub>3</sub> up to 120 °C, but BrSiMe<sub>2</sub>Ph does react with Pt(PEt<sub>3</sub>)<sub>3</sub><sup>384</sup>. It had previously been reported that Pd(PPh<sub>3</sub>)<sub>4</sub> reacts with XSiMe<sub>3</sub> (X = Cl, Br) to afford Me<sub>3</sub>SiSiMe<sub>3</sub><sup>385,386</sup>.

Reactions of halosilanes with Pt(PEt<sub>3</sub>)<sub>3</sub> provide comparisons of the tendencies of Si—Si and Si—X (X = halide) bonds to undergo oxidative addition. In most cases insertion of platinum(0) into the Si—Si bond occurs (equation 140), with the following



relative rates: FMe<sub>2</sub>SiSiMe<sub>2</sub>F > ClMe<sub>2</sub>SiSiMe<sub>2</sub>Cl > ClMe<sub>2</sub>SiSiMe<sub>3</sub>, BrMe<sub>2</sub>SiSiMe<sub>3</sub> » PhMe<sub>2</sub>SiSiMe<sub>2</sub>Ph, Me<sub>3</sub>SiSiMe<sub>3</sub> (no reaction). In contrast, IMe<sub>2</sub>SiSiMe<sub>3</sub> undergoes selective oxidative addition via addition of the Si—I bond, providing *trans*-(PEt<sub>3</sub>)<sub>2</sub>Pt(SiMe<sub>2</sub>SiMe<sub>3</sub>)I<sup>387</sup>.

A facile Si—Cl bond oxidative addition has been described as the room temperature reaction of equation 141 (coe = cyclooctene; L = PMe<sub>3</sub>)<sup>388</sup>. Further examples of silicon-halogen bond oxidative addition to iridium(I) have been communicated. The species <sup>1</sup>IrH(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>, generated *in situ* via reaction of IrH<sub>5</sub>(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> with two equivalents of neohexene, adds Cl<sub>3</sub>SiMe, ISiMe<sub>3</sub> and Cl<sub>2</sub>SiMe<sub>2</sub>. In some reactions of this type, hydride species IrH<sub>2</sub>X(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> (X = Cl, Br) are observed as byproducts (see Section IV.A.1)<sup>389</sup>.

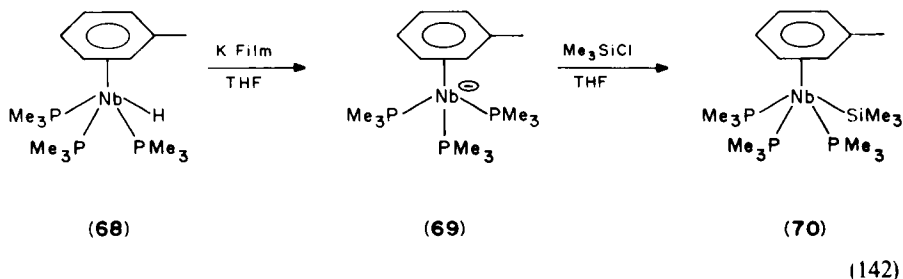


Addition of ISiMe<sub>3</sub> to [(CO)<sub>2</sub>L<sub>2</sub>Fe]<sub>2</sub>(μ-N<sub>2</sub>) [L = P(O<sup>i</sup>Pr)<sub>3</sub>] appears to produce *cis,trans,cis*-Fe(CO)<sub>2</sub>L<sub>2</sub>(SiMe<sub>3</sub>)I, which reacts with the methanol solvent to give Me<sub>3</sub>SiOMe and *cis,trans,cis*-Fe(CO)<sub>2</sub>L<sub>2</sub>(H)I<sup>390</sup>. Both Si—H and Si—Cl oxidative additions are thought to occur upon reaction of trichlorosilane with (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub><sup>391</sup>.

### \*3. Methods employing transition-metal anions

The syntheses of [PPN][[(CO)<sub>5</sub>MSiR<sub>3</sub>] (M = Cr, W; R = Me, Et) were accomplished via treatment of the dianions Na<sub>2</sub>M(CO)<sub>5</sub> with the appropriate silyl chlorides R<sub>3</sub>SiCl<sup>392</sup>. Other examples of the use of anionic carbonyl complexes are found in the syntheses of *cyclo*-Si<sub>6</sub>Me<sub>11</sub>[FeCp(CO)<sub>2</sub>], *cyclo*-Si<sub>6</sub>Me<sub>10-1,4</sub>[FeCp(CO)<sub>2</sub>]<sub>2</sub> and *cyclo*-Si<sub>6</sub>Me<sub>11</sub>[MoCp(CO)<sub>3</sub>]<sup>393</sup>, and in the formation of (η<sup>2-4</sup>PrN=CH—CH=N<sup>i</sup>Pr)-(CO)<sub>2</sub>Ru(SiMe<sub>3</sub>)I upon addition of a mixture of Me<sub>3</sub>SiOTf and I<sup>-</sup> to [(η<sup>2-4</sup>PrN=CH—CH=N<sup>i</sup>Pr)(CO)<sub>2</sub>RuI]<sup>-394</sup>. Silyl derivatives (CO)<sub>3</sub>Re—Si<sub>n</sub>R<sub>m</sub> and Cp(CO)<sub>2</sub>Ru—Si<sub>n</sub>R<sub>m</sub> [Si<sub>n</sub>R<sub>m</sub> = SiMe<sub>3</sub>, Si<sub>2</sub>Me<sub>5</sub>, Si<sub>3</sub>Me<sub>7</sub>, SiMe(SiMe<sub>3</sub>)<sub>2</sub>] were prepared by reactions of the appropriate carbonylated anions and silyl chlorides<sup>395</sup>. Reaction of Li[Cp(NO)(PPh<sub>3</sub>)Re] with Me<sub>3</sub>SiOTf, Me<sub>2</sub>SiHCl, Me<sub>2</sub>(CH<sub>2</sub>=CH)SiOTf or ClMe<sub>2</sub>SiSiMe<sub>2</sub>Cl gives Cp(NO)(PPh<sub>3</sub>)ReSiMe<sub>2</sub>X complexes (X = Me, H, CH=CH<sub>2</sub> and SiMe<sub>2</sub>Cl, respectively)<sup>396</sup>.

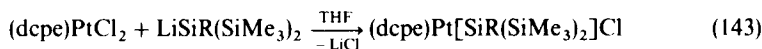
Reduction of the hydride **68** with potassium apparently produces the anion **69**, which upon treatment with  $\text{Me}_3\text{SiCl}$  gives the novel niobium(I) silyl complex **70** as an orange oil in 33% yield (equation 142)<sup>397</sup>.



Anionic silyl complexes  $[\text{L}_n\text{MSiR}_3]^-$  are convenient precursors to families of neutral silyl complexes via reactions with electrophiles. For example,  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnSiR}_3]^-$  ( $\text{SiR}_3 = \text{SiMePh}_2, \text{SiPh}_3$ ) react with the appropriate metal halides to afford the bimetallic complexes  $(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}(\text{SiR}_3)(\text{ML}_n)$ , where  $\text{ML}_n = \text{SnMe}_3, \text{PbMe}_3, \text{AuPPh}_3, \text{HgPh}$  and  $\text{Fe}(\text{CO})_2\text{Cp}$ . In the presence of  $\text{H}_2\text{O}$ ,  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnSiR}_3]^-$  anions behave as synthetic equivalents for  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnH}]^-$ <sup>398,399</sup>. Similarly, reactions of  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnSiMePh}_2]^-$  and  $[(\text{CO})_3(\text{PPh}_3)\text{FeSiR}_3]^-$  ( $\text{SiR}_3 = \text{SiMePh}_2, \text{SiPh}_3$ ) with  $\text{MX}_2$  ( $\text{MX}_2 = \text{ZnCl}_2, \text{CdCl}_2, \text{HgBr}_2$ ) give  $(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}(\text{SiMePh}_2)\text{MX}$  and  $(\text{CO})_3(\text{PPh}_3)\text{Fe}(\text{SiR}_3)(\text{MX})$ , respectively. Reactions of the latter compounds with a second equivalent of an anionic silyl complex allowed isolation of  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}(\text{SiMePh}_2)]_2\text{M}$  ( $\text{M} = \text{Cd}, \text{Hg}$ ),  $[(\text{CO})_3(\text{PPh}_3)\text{Fe}(\text{SiR}_3)]_2\text{Hg}$  and  $(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2(\text{Ph}_2\text{MeSi})\text{Mn}-\text{Hg}-\text{Fe}(\text{CO})_3(\text{PPh}_3)(\text{SiR}_3)$ <sup>400</sup>. This approach has also been used in the preparations of  $(\text{CO})_2[\text{P}(\text{OR})_3]_2\text{Fe}[\text{Si}(\text{OEt})_3]\text{ML}_n$  ( $\text{ML}_n = \text{SnMe}_3, \text{SnMe}_2\text{Cl}, \text{AuPPh}_3$ )<sup>345</sup> and *mer*- $(\text{CO})_3(\text{PR}'_3)\text{Fe}(\text{SiR}_3)\text{ML}_n$  ( $\text{ML}_n = \text{SiHMe}_2, \text{SnMe}_3, \text{AgPPh}_3, \text{AuPPh}_3, \text{HgPh}, \text{HgBr}, \text{Me}$ )<sup>401</sup>.

#### \*4. Methods employing main-group metal silyl compounds

Silyl lithium reagents have been used to obtain platinum silyl complexes in good yields [equation 143;  $\text{dcpe} = (\text{c-Hex})_2\text{PCH}_2\text{CH}_2\text{P}(\text{c-Hex})_2$ ]. Only one of the chloride ligands

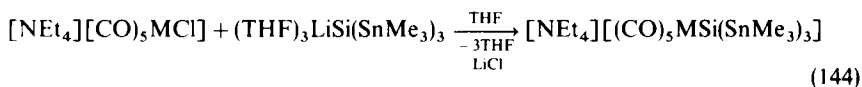


(71)  $\text{R} = \text{SiMe}_3$

(72)  $\text{R} = \text{Ph}$

could be displaced with these silyl anions<sup>402</sup>.

The synthesis of  $(\text{THF})_3\text{LiSi}(\text{SnMe}_3)_3$ , isolated as light-yellow crystals from pentane, allows preparations of group 6 anionic silyl complexes (equation 144). The tris(trimethyl-



$[\text{NEt}_4][\text{73}]$ ,  $\text{M} = \text{Cr}$

$[\text{NEt}_4][\text{74}]$ ,  $\text{M} = \text{Mo}$

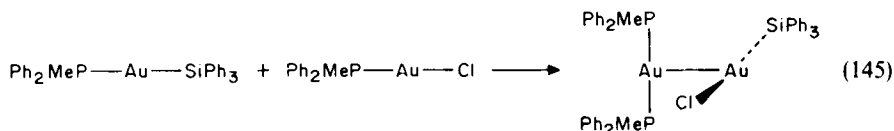
$[\text{NEt}_4][\text{75}]$ ,  $\text{M} = \text{W}$

stannyl)silyl lithium reagent was prepared by the reaction of  $\text{Si}(\text{SnMe}_3)_4$  with methyl lithium<sup>403</sup>.

The first silyliron porphyrin complexes have been reported. Trimethylsilyl lithium in HMPA was added to a toluene solution of (TPP)FeCl (TPP = tetraphenylporphyrin) to generate the relatively unstable, paramagnetic iron(III) silyl (TPP)FeSiMe<sub>3</sub>. Addition of LiSiMe<sub>3</sub> to (TPP)Fe gives the diamagnetic iron(II) silyl [(TPP)FeSiMe<sub>3</sub>]<sup>-</sup>, which is oxidized by iodine to the silyliron(III) derivative. These new silyl complexes were characterized in solution by <sup>1</sup>H NMR<sup>404</sup>.

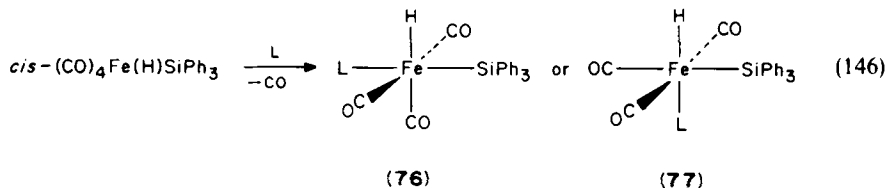
A novel silylating reagent, Cd(SiF<sub>3</sub>)<sub>2</sub>·glyme, is available via the reaction of ·SiF<sub>3</sub> radicals with cadmium vapor. Reaction of this cadmium silyl compound with the dibromides (PMe<sub>3</sub>)<sub>2</sub>MBr<sub>2</sub> (M = Ni, Pd, Pt) affords the complexes Ni(SiF<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>, Pd(SiF<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> and Pt(SiF<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub><sup>405</sup>. The nickel and palladium silyl derivatives had previously been obtained by reaction of ·SiF<sub>3</sub> radicals (generated in a radio-frequency glow discharge of Si<sub>2</sub>F<sub>6</sub>) with the corresponding metal atoms. The complex Ni(SiF<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> adopts a trigonal bipyramidal structure with SiF<sub>3</sub> groups in the axial positions<sup>406</sup>.

The solution structures of silylcuprates derived from addition of LiSiMe<sub>2</sub>Ph to CuBr·SMe<sub>2</sub> and CuCN have been probed by NMR spectroscopy<sup>407,408</sup>. Addition of LiSiPh<sub>3</sub> to CuCl in the presence of PMe<sub>3</sub> gives (PMe<sub>3</sub>)<sub>3</sub>CuSiPh<sub>3</sub><sup>409</sup>. The relatively unstable silver silyls Ph<sub>3</sub>PAgSiR<sub>3</sub>, (Ph<sub>2</sub>MeP)<sub>2</sub>AgSiR<sub>3</sub> [SiR<sub>3</sub> = SiPh<sub>2</sub>(*p*-Tol), Si(SiMe<sub>3</sub>)<sub>3</sub>] and (Ph<sub>2</sub>MeP)<sub>3</sub>AgSiPh<sub>2</sub>(*p*-Tol) were obtained by related methods<sup>410</sup>, as were gold silyls of the types (Ph<sub>2</sub>RP)AuSiR'<sub>3</sub> and (PhNC)AuSiR'<sub>3</sub> [R = Me, *p*-Tol; SiR'<sub>3</sub> = SiPh(*p*-Tol)<sub>2</sub>, SiPh<sub>2</sub>(*p*-Tol), SiPh<sub>3</sub>, Si(SiMe<sub>3</sub>)<sub>3</sub>, SiMePh<sub>2</sub>]<sup>411</sup>. A dinuclear gold silyl complex is obtained by the reaction in equation 145<sup>412</sup>.



#### \*5. Miscellaneous methods

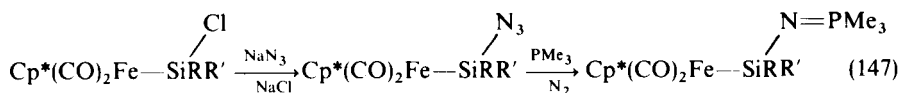
Investigations into ligand substitution in *cis*-(CO)<sub>4</sub>Fe(H)SiPh<sub>3</sub> show that with incoming ligands of low nucleophilicity (CO, SbPh<sub>3</sub>, AsPh<sub>3</sub>), reductive elimination of silane is observed. More nucleophilic reactants [L = PPh<sub>3</sub>, P(OPh)<sub>3</sub>] replace a carbon monoxide ligand to give **76** or **77**, depending on the reaction solvent (equation 146). More basic phosphines [PEt<sub>3</sub>, P(*c*-Hex)<sub>3</sub>] deprotonate *cis*-(CO)<sub>4</sub>Fe(H)SiPh<sub>3</sub> to form [(CO)<sub>4</sub>FeSiPh<sub>3</sub>]<sup>-</sup>. The (CO)<sub>3</sub>LFe(H)SiPh<sub>3</sub> compounds react with L via displacement of silane to afford Fe(CO)<sub>3</sub>L<sub>2</sub> complexes. The isomers with structure **77** are significantly more reactive in this regard, probably because of the steric effect of the *cis* ligand L. The reaction of *cis*-(CO)<sub>4</sub>Fe(H)SiPh<sub>3</sub> with isoprene gives the dimer [(CO)<sub>4</sub>FeSiPh<sub>3</sub>]<sub>2</sub><sup>413</sup>.



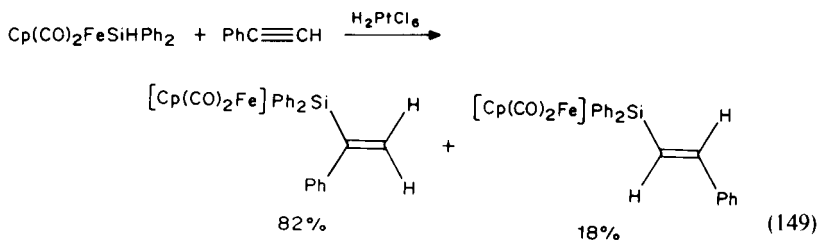
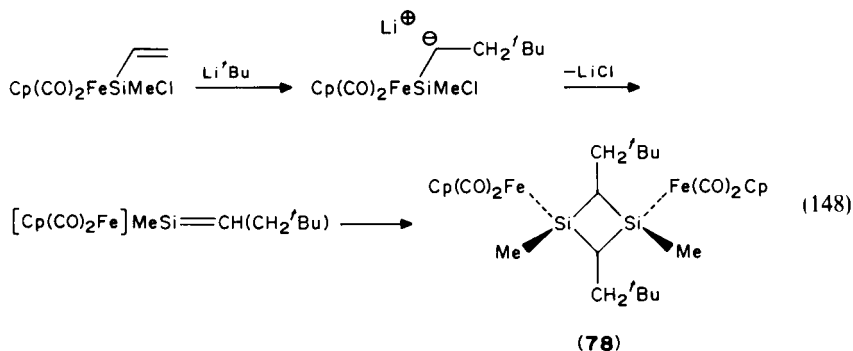
Ligand substitution reactions of ( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Me)Ni(SiCl<sub>3</sub>)<sub>2</sub> lead to displacement of the arene ligand. Addition of small donors [L = PMe<sub>3</sub>, P(OMe)<sub>3</sub>, P(OEt)<sub>3</sub>, PF<sub>3</sub>, pyr] to

$(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Ni}(\text{SiCl}_3)_2$  provides trigonal bipyramidal  $\text{L}_3\text{Ni}(\text{SiCl}_3)_2$  complexes with axial silyl ligands. More sterically demanding nucleophiles ( $\text{L} = \text{PEt}_3$ , lutidine, collidine) lead to square planar  $\text{L}_2\text{Ni}(\text{SiCl}_3)_2$  complexes<sup>414</sup>. Displacement of the arene ligand with halide anions gives dimeric  $[(\text{Cl}_3\text{Si})_2\text{Ni}(\mu\text{-X})_2\text{Ni}(\text{SiCl}_3)_2]^{2-}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) species<sup>415</sup>.

The modification of metal-bound silyl groups continues to provide important ways to introduce functionality into a transition-metal silyl complex. For example, chloride/triflate exchanges have been used to provide  $\text{Cp}^*(\text{PMe}_3)_2\text{RuSiR}_2\text{OTf}$  derivatives, which are precursors to silylene complexes<sup>360,416</sup>. The sequence of reactions in equation 147



provides novel examples of azidosilyl and (iminophosphorane)silyl ligands<sup>417</sup>. Vinylsilyl derivatives of iron have been used to generate a metal-substituted silene (equation 148), which dimerizes to the 1,3-disilacyclobutane derivative **78**<sup>418</sup>. The hydrosilylation of phenylacetylene with  $\text{Cp}(\text{CO})_2\text{FeSiHPh}_2$  and related derivatives provides unusual routes to vinylsilyl complexes (equation 149)<sup>419</sup>.



### \*B. Transition-metal Silicon Clusters

Reaction of  $\text{SiH}_4$  with  $\text{Fe}_2(\text{CO})_9$  gave  $\text{Si}[\text{Fe}_2(\text{CO})_8]_2$ , which possesses two mutually perpendicular  $\text{SiFe}_2$  triangles linked by a common *spiro*-silicon atom<sup>420</sup>. The cluster  $[\mu_3\text{-SiFe}(\text{CO})_2\text{Cp}]_2\text{Fe}_3(\text{CO})_9$ , prepared in good yield by reaction of  $\text{Fe}(\text{CO})_5$  and  $[\text{CpFe}(\text{CO})_2]_2$  with  $\text{SiH}_4$  at  $150^\circ\text{C}$ , has a  $\text{Si}_2\text{Fe}_3$  core<sup>421</sup>. The interaction of  $\text{Si}_2\text{H}_6$  with  $\text{Co}_2(\text{CO})_8$  produces  $\text{Si}_2\text{Co}_6(\text{CO})_{10}$ , shown by X-ray crystallography to adopt a pseudo-octahedral *trans*- $\text{Si}_2\text{Co}_4$  core with each silicon bonded to terminal  $\text{Co}(\text{CO})_4$



groups<sup>422</sup>. Addition of  $\text{HSiR}_3$  ( $\text{R} = \text{Me, Ph}$ ) to  $\text{Os}_4(\text{CO})_{14}$  readily affords  $\text{Os}_4(\mu\text{-H})(\text{CO})_{14}(\text{SiR}_3)$  complexes in good yield<sup>423</sup>.

Upon photolysis or thermolysis, small amounts of polynuclear metal clusters ( $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{Co}_2(\text{CO})_8$ ,  $\text{Co}_4(\text{CO})_{12}$  and  $\text{Rh}_6(\text{CO})_{16}$ ) serve to crosslink SiH containing organosilicon polymers, probably by formation of metal-silicon bonds. This crosslinking results in higher ceramic yields of metal-containing silicon carbide when the polymers are pyrolyzed<sup>424</sup>.

### \*C. Early Transition-metal Derivatives

Many of the recent advances in transition-metal silicon chemistry have been produced by investigations with the early transition metals. The increased attention that this area receives is reflected in the development of new preparative methods.

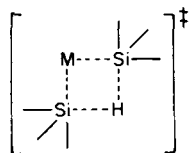
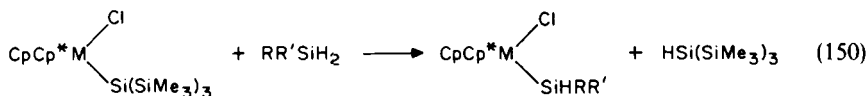
#### \*1. Methods employing main-group metal silyl compounds

The synthesis and chemistry of  $\text{Cp}'_2\text{Zr}(\text{SiHMe}_2)\text{Me}$  ( $\text{Cp}' = \text{Cp, Cp}^*$ ) complexes have been published<sup>425</sup>. The  $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$  reagent has proven to be particularly useful in preparing early metal silyls, as exemplified by reports describing its use in the synthesis of  $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ <sup>426</sup>,  $\text{Cp}^*\text{Cl}_2\text{MSi}(\text{SiMe}_3)_3$  ( $\text{M} = \text{Zr, Hf}$ )<sup>427</sup> and  $(\text{Me}_3\text{CO})_3\text{MSi}(\text{SiMe}_3)_3$  ( $\text{M} = \text{Zr, Hf}$ )<sup>428</sup>. The first group 3 transition-metal silyl derivative,  $\text{Cp}_2\text{Sc}[\text{Si}(\text{SiMe}_3)_3](\text{THF})$ , has been obtained by reaction of  $[\text{Cp}_2\text{ScCl}]_2$  with  $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$ <sup>429</sup>.

In contrast to the reaction shown in equation 37, treatment of  $\text{Cp}_2\text{W}(\text{H})\text{Cl}$  with  $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$  yields a tungsten silyl,  $\text{Cp}_2\text{W}(\text{H})\text{Si}(\text{SiMe}_3)_3$ , as product. This compound reacts with methyl iodide to afford isolable  $[\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{SiMe}_3)_3]\text{CpW}(\text{H})\text{I}$ , which reacts with  $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$  to form  $[\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{SiMe}_3)_3]_2\text{WH}_2$ . These conversions, and the fact that  $\text{Cp}_2\text{W}(\text{H})\text{Si}(\text{SiMe}_3)_3$  is not deprotonated by  $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$ , imply that in the reaction of  $\text{Cp}_2\text{WCl}_2$  with  $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$  (equation 37), the intermediate  $\text{Cp}_2\text{W}(\text{Cl})\text{Si}(\text{SiMe}_3)_3$  rearranges to  $[\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{SiMe}_3)_3]\text{CpW}(\text{H})\text{Cl}$ , which reacts further with the lithium silyl reagent to give  $[\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{SiMe}_3)_3]\text{CpW}(\text{H})\text{Si}(\text{SiMe}_3)_3$ , which then rearranges to the final product<sup>430</sup>.

#### \*2. Methods involving cleavage of Si—H bonds

A general route to  $d^0$  metal silyl complexes with  $\alpha$  Si—H bonds is provided by  $\sigma$ -bond metathesis reactions of primary and secondary silanes with  $\text{M—Si}(\text{SiMe}_3)_3$  derivatives (equation 150,  $\text{M} = \text{Zr, Hf}$ ;  $\text{R, R}' = \text{hydrogen or organic derivatives}$ ). A variety of new hafnium silyl complexes were prepared by this method. The zirconium products are less

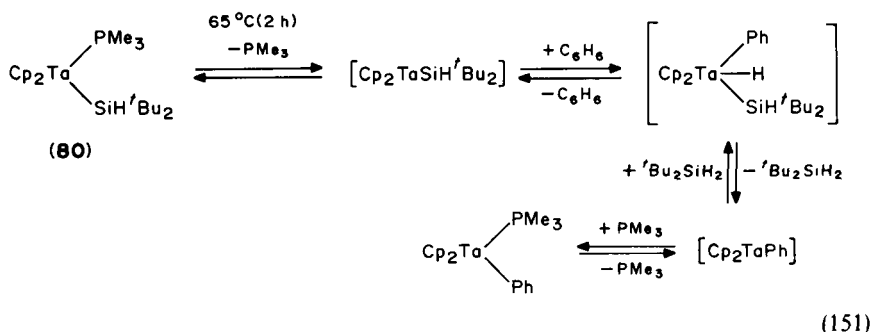


(79)

stable. For example,  $\text{CpCp}^*\text{Zr}(\text{SiH}_2\text{Ph})\text{Cl}$  is observed to form cleanly, but it decomposes at room temperature to  $\text{CpCp}^*\text{ZrHCl}$  and a mixture of polysilanes  $(-\text{SiHPh}-)_n$ . Such thermal processes probably proceed via four-center transition states (structure **79**). These  $\sigma$ -bond metathesis reactions are accelerated by room light<sup>431</sup>.

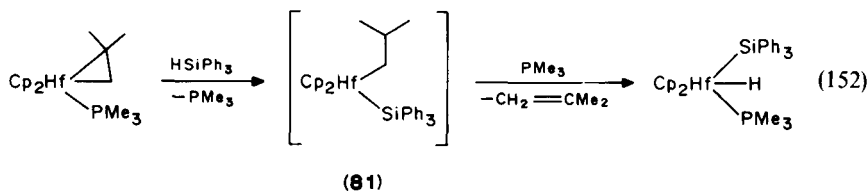
The 16-electron tantalum methyl derivative  $\text{Cp}_2^*\text{TaCH}_3$ , which is in equilibrium with  $\text{Cp}_2^*\text{Ta}(\text{=CH}_2)(\text{H})$ , is trapped by silane to give  $\text{Cp}_2^*\text{Ta}(\text{CH}_3)(\text{SiH}_3)\text{H}$ , with the  $\text{SiH}_3$  group in the central equatorial position<sup>432</sup>.

The tantalum complex  $\text{Cp}_2\text{TaMe}(\text{PMe}_3)$  reacts with neat  $^t\text{Bu}_2\text{SiH}_2$  to give  $\text{Cp}_2\text{Ta}[\text{SiH}^t\text{Bu}_2](\text{PMe}_3)$  (**80**), probably via oxidative addition of  $^t\text{Bu}_2\text{SiH}_2$  to  $\text{Cp}_2\text{TaMe}$ , followed by reductive elimination of methane and return of the phosphine ligand. The  $\text{PMe}_3$  ligand in **80** is apparently labile, so that upon exposure of this complex to benzene, the  $\text{C}-\text{H}$  activation process of equation 151 ensues. Thus, the reaction of benzene with  $\text{Cp}_2\text{TaMe}(\text{PMe}_3)$  [to give  $\text{Cp}_2\text{TaPh}(\text{PMe}_3)$  and methane] is catalyzed by  $^t\text{Bu}_2\text{SiH}_2$ . Interestingly, these results indicate that 16-electron  $\text{Cp}_2\text{Ta}(\text{silyl})$  complexes are more reactive toward benzene than are  $\text{Cp}_2\text{TaR}$  ( $\text{R} = \text{alkyl}, \text{aryl}$ ) derivatives<sup>433</sup>.

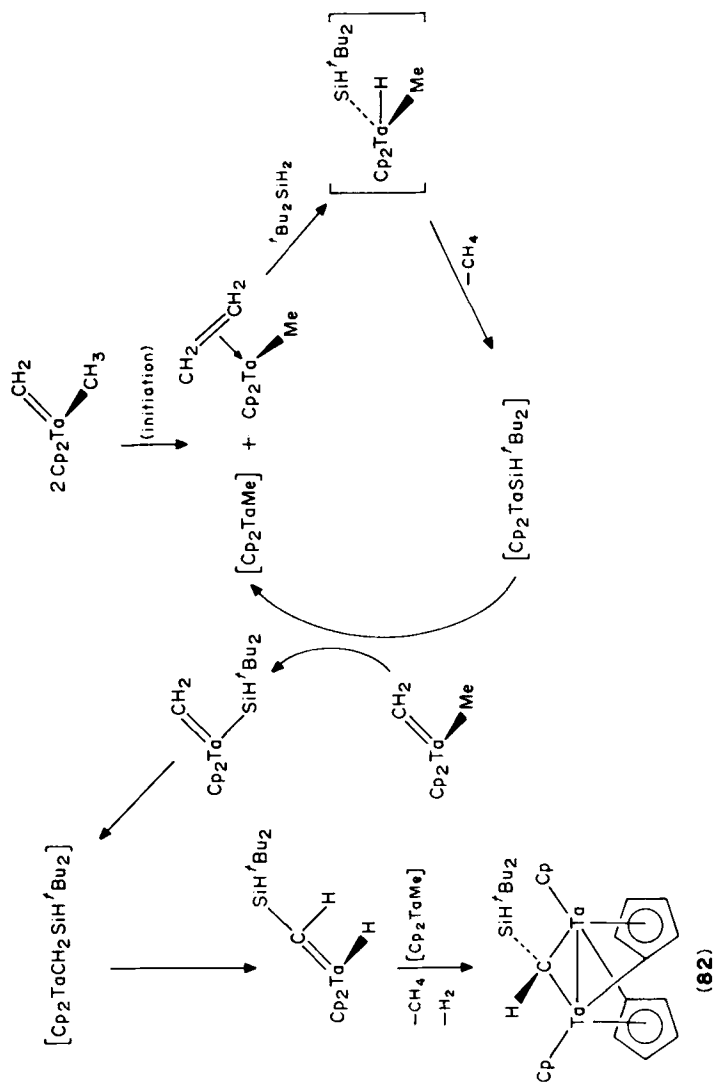


Titanium(III) silyls  $\text{Cp}_2\text{Ti}(\text{SiH}_2\text{Ph})(\text{PEt}_3)$  and  $\text{Cp}_2\text{Ti}(\text{SiHRPh})(\text{PMe}_3)$  ( $\text{R} = \text{H}, \text{Me}$ ) have been prepared by reaction of  $\text{Cp}_2\text{TiMe}_2$  with the appropriate silane in the presence of the phosphine, or by cleavage of  $[\text{Cp}_2\text{Ti}(\text{SiHRR}') ]_2$  dimers by phosphine<sup>434</sup>.

Addition of  $\text{HSiPh}_3$  to  $\text{Cp}_2\text{M}(\text{alkene})(\text{PMe}_3)$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) provides novel examples of  $d^0$  metal silyl hydride complexes,  $\text{Cp}_2\text{M}(\text{H})(\text{SiPh}_3)(\text{PMe}_3)$ . In the hafnium reaction, the intermediate **81** was observed (equation 152). An X-ray crystal structure of the zirconium derivative showed that the silyl and phosphine ligands occupied outer positions in the  $\text{Cp}_2\text{Zr}$  wedge, with the hydride ligand in between. The compound  $\text{Cp}_2\text{Zr}(\text{H})(\text{SiPh}_3)(\text{PMe}_3)$  reacts with  $^t\text{BuNC}$ ,  $^i\text{BuCN}$  and acetone via insertion into the  $\text{Zr}-\text{H}$  bond, and undergoes  $\sigma$ -bond metathesis with  $\text{Ph}_2\text{SiH}_2$  to produce  $\text{HSiPh}_3$  and two isomers of  $\text{Cp}_2\text{Zr}(\text{H})(\text{SiHPh}_2)(\text{PMe}_3)$ <sup>435</sup>.



A rather unique approach to the synthesis of  $d^2$  tantalum silyl derivatives has been described. These reactions are based on the silylene transfer agent hexamethylsilacyclopropane (see also equation 31), which reacts with  $\text{Cp}_2\text{TaH}(\text{L})$  ( $\text{L} = \text{PMe}_3, \text{CO}$ ) to afford



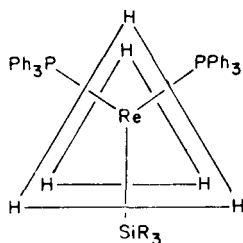
SCHEME 18

$\text{Cp}_2\text{TaSiHMe}_2(\text{L})$  silyls. Also,  $\text{Cp}_2\text{TaH}_3$  is converted by hexamethylsilacyclopropane to a mixture of  $\text{Cp}_2\text{Ta}(\text{H})_2\text{SiHMe}_2$  isomers. These reactions work much better in the presence of added  $\text{PMe}_3$ , a fact that can be rationalized by the intermediacy of  $\text{Me}_2\text{Si} \leftarrow \text{PMe}_3$  as a silylene transfer agent<sup>436</sup>.

A study of the reactions of  $\text{Cp}_2\text{Ta}(\text{=CH}_2)\text{Me}$  with silanes has produced new tantalum silyl complexes and examples of alkylidene-transfer processes. Reactions of  $\text{Me}_3\text{SiH}$  or  $\text{Me}_2\text{SiH}_2$  with  $\text{Cp}_2\text{Ta}(\text{=CH}_2)\text{Me}$  afford equimolar mixtures of  $\text{Cp}_2\text{Ta}(\text{CH}_2=\text{CH}_2)\text{Me}$  and  $\text{Cp}_2\text{Ta}(\text{SiR}_3)_2\text{H}$ . These reactions occur via initial, rate-limiting disproportionation of  $\text{Cp}_2\text{Ta}(\text{=CH}_2)\text{Me}$  to  $\text{Cp}_2\text{Ta}(\text{CH}_2=\text{CH}_2)\text{Me}$  and  $\text{Cp}_2\text{TaMe}$ . The latter 16-electron species is highly reactive and combines rapidly with silane via reductive elimination of methane to give  $\text{Cp}_2\text{TaSiR}_3$ , which oxidatively adds a second equivalent of silane in forming the  $\text{Cp}_2\text{Ta}(\text{SiR}_3)_2\text{H}$  product. Surprisingly, the reaction of  $\text{Cp}_2\text{Ta}(\text{=CH}_2)\text{Me}$  with  $\text{tBu}_2\text{SiH}_2$  is faster than the corresponding reactions with smaller silanes, and takes a different course, producing  $\text{Cp}_2\text{Ta}(\text{=CHSiH}^t\text{Bu}_2)(\text{H})$  and the bridging alkylidene complex  $[\text{CpTa}(\mu_2\text{-}\eta^1:\eta^5\text{-C}_5\text{H}_4)]_2(\mu\text{-CHSiH}^t\text{Bu}_2)$  (**82**). In benzene solvent the latter reaction also produces some  $\text{Cp}_2\text{Ta}(\text{=CH}_2)\text{Ph}$ .

The reaction of  $\text{tBu}_2\text{SiH}_2$  can be explained by the chain mechanism of Scheme 18 involving alkylidene transfer between tantalum centers, and  $\text{Cp}_2\text{TaMe}$  as the key chain-carrying species. The  $\text{Cp}_2\text{Ta}(\text{=CH}_2)\text{Ph}$  product may be explained by reaction of benzene with  $\text{Cp}_2\text{TaSiH}^t\text{Bu}_2$  to give  $\text{Cp}_2\text{TaPh}$  and  $\text{tBu}_2\text{SiH}_2$ , followed by methylidene transfer from  $\text{Cp}_2\text{Ta}(\text{=CH}_2)\text{Me}$  to  $\text{Cp}_2\text{TaPh}$ . The silyl methylidene complex  $\text{Cp}_2\text{Ta}(\text{=CH}_2)\text{SiH}^t\text{Bu}_2$ , generated independently via photolysis of  $\text{Cp}_2\text{Ta}(\text{PMe}_3)\text{SiH}^t\text{Bu}_2$  in the presence of  $\text{CH}_2=\text{PMe}_3$ , was observed to rapidly combine with  $\text{PMe}_3$  to form  $\text{Cp}_2\text{Ta}(\text{PMe}_3)\text{CH}_2\text{SiH}^t\text{Bu}_2$ . The order of migratory aptitudes in the  $\text{Cp}_2\text{Ta}(\text{=CHR})\text{X}$  system is  $\text{X} = \text{H} > \text{SiH}^t\text{Bu}_2 \gg \text{Ph} > \text{Me}$ <sup>437</sup>.

Crabtree and coworkers have reported the high-valent rhenium silyl complexes  $\text{ReH}_6(\text{SiR}_3)(\text{PPh}_3)_2$  ( $\text{SiR}_3 = \text{SiPh}_3, \text{SiEt}_3, \text{SiHtEt}_2$ ), obtained by reaction of  $\text{HSiR}_3$  with  $\text{ReH}_7(\text{PPh}_3)_2$ . These compounds appear to have a tricapped trigonal prism structure with the P and Si atoms occupying the capping sites (**83**). (Note that **83** is drawn according to the customary presentation of such complexes in the inorganic chemical literature. The lines connecting the H atoms do not represent bonds, but are meant to outline a trigonal prism.) The reaction of  $\text{ReD}_7(\text{PPh}_3)_2$  with  $\text{Et}_2\text{SiH}_2$  gave  $\text{ReHD}_5(\text{SiHtEt}_2)(\text{PPh}_3)_2$  as the only product, indicating a mechanism involving reductive elimination of  $\text{D}_2$  to form the intermediate  $\text{ReD}_5(\text{PPh}_3)_2$ , which then oxidatively adds silane<sup>438</sup>.



(83)

### \*3. Related f-element derivatives

The syntheses of  $[\text{Li}(\text{DME})_x][\text{Cp}_2\text{Ln}(\text{SiMe}_3)_2]$  ( $\text{Ln} = \text{Sm}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Lu}$ ) derivatives from  $\text{Cp}_2\text{Ln}(\mu\text{-Cl})_2\text{Na}(\text{DME})_x$  and  $\text{LiSiMe}_3$  have been described in detail<sup>439-441</sup>.

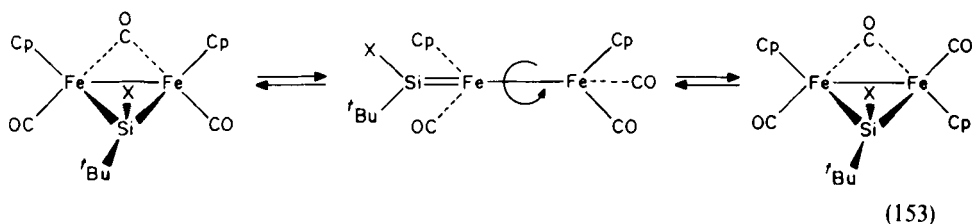
The first actinide silyl complex,  $\text{Cp}_3\text{USiPh}_3$ , has been synthesized from  $\text{Cp}_3\text{UCl}$  and  $\text{LiSiPh}_3$  at low temperature. It was noted that only  $\text{LiSiPh}_3$  prepared from lithium and  $\text{SiPh}_4$  gave satisfactory results. Also, if the synthesis of  $\text{Cp}_3\text{USiPh}_3$  is attempted in tetrahydrofuran, the main product is  $\text{Cp}_3\text{UOSiPh}_3$ . This uranium silyl derivative reacts with  $\text{HSnPh}_3$  to give  $\text{HSiPh}_3$  and  $\text{Cp}_3\text{USnPh}_3$ , and with  $\text{CN-2,6-Me}_2\text{C}_6\text{H}_3$  via insertion into the U—Si bond<sup>442</sup>.

### \*III. TRANSITION-METAL SILYLENE COMPLEXES

Reactions of transition-metal ions with silanes in the gas phase produce silylenes  $\text{MSiH}_2^+$  ( $\text{M} = \text{Co}, \text{Ni}$ ) with strong metal–silicon interactions. Methylsilanes ( $\text{MeSiH}_3$ ,  $\text{Me}_2\text{SiH}_2$ ) also react with  $\text{M}^+$  ions to produce metal silylenes. Transition-metal–silylene bond energies were estimated; for example  $D^0(\text{M}^+ - \text{SiH}_2) = 67 \pm 6 \text{ kcal mol}^{-1}$  ( $\text{M} = \text{Co}, \text{Ni}$ )<sup>443</sup>.

#### \*A. Indirect Evidence for Coordinated Silylenes

Tobita and coworkers have proposed that the *cis*–*trans* isomerization process for  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SiX}^t\text{Bu})$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{Me}$ ) complexes occurs by the mechanism of equation 153 involving an intermediate with a terminal silylene ligand<sup>367</sup>.

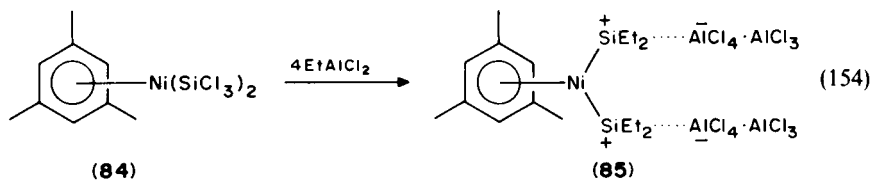


Unlike  $\text{Cp}(\text{CO})_2\text{FeSiMe}_2\text{SiPh}_3$ , the polysilane derivatives  $(\text{CO})_5\text{Re}-\text{Si}_n\text{R}_m$  and  $\text{Cp}(\text{CO})_2\text{Ru}-\text{Si}_n\text{R}_m$  [ $\text{Si}_n\text{R}_m = \text{Si}_2\text{Me}_5, \text{Si}_3\text{Me}_7, \text{SiMe}(\text{SiMe}_3)_2$ ] do not deoligomerize upon photolysis (see Scheme 2)<sup>395</sup>. Further evidence for the mechanism of Scheme 2 has been obtained by comparing the product distributions for the photochemical deoligomerizations of a series of  $\text{Cp}(\text{CO})_2\text{FeSi}_2\text{Ph}_{3-n}\text{Me}_{2+n}$  complexes. These comparisons provide good evidence for the intermediacy of equilibrating silyl(silylene) complexes<sup>444</sup>. Interestingly, photolyses of  $\text{Cp}(\text{CO})_2\text{Fe}(\text{SiMe}_2)_n\text{SiMe}_3$  ( $n = 3, 5$ ) and  $\text{Cp}(\text{CO})_2\text{FeSiMe}(\text{SiMe}_2)_4\text{SiMe}_2$  result in skeletal rearrangements of the silyl ligands rather than silylene extrusion. The products of these photochemical conversions are  $\text{Cp}(\text{CO})_2\text{FeSi}(\text{SiMe}_3)_3$ ,  $\text{Cp}(\text{CO})_2\text{FeSi}(\text{SiMe}_3)_2\text{SiMe}_2\text{SiMe}_2\text{SiMe}_3$  and  $\text{Cp}(\text{CO})_2\text{FeSi}(\text{SiMe}_3)(\text{SiMe}_2)_3\text{SiMe}_2$ , respectively. The results can be explained by a mechanism analogous to that in Scheme 2 involving 1,3-silicon and 1,3-methyl shifts in silyl(silylene) intermediates. However, in these reactions the silylene ligands do not dissociate from the metal center<sup>445</sup>.

Tobita, Ueno and Ogino<sup>446</sup> have studied similar photochemical reactions of disilanyl-iron(II) complexes, and have obtained additional mechanistic information. Photolysis of  $(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})_2\text{FeSiMe}_2\text{SiMe}_3$  ( $\text{R} = \text{H}, \text{Me}$ ) results in silylene extrusion to afford  $(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})_2\text{FeSiMe}_3$ , along with  $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Fe}$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_2]_2$  as by-products. Additionally, after 69% photochemical conversion of  $\text{Cp}(\text{CO})_2\text{FeSiMe}_2\text{SiMeEt}_2$ ,  $\text{Cp}(\text{CO})_2\text{FeSiMeEt}_2$  (26%),  $\text{Cp}(\text{CO})_2\text{FeSiMe}_2\text{Et}$  (33%),  $\text{Cp}(\text{CO})_2\text{FeSiMe}_3$  (4%) and  $\text{Cp}_2\text{Fe}$  (7%) were obtained. The efficient silylene traps 2,3-dimethyl-1,3-butadiene, diethylmethylsilane and hexamethylcyclotrisiloxane failed to intercept dimethylsilylene during this reaction. A crossover experiment involving photolysis of a 1:1 mixture of  $(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{FeSiMe}_2\text{SiMe}_3$  and  $\text{Cp}(\text{CO})_2\text{FeSiMe}_2\text{SiMeEt}_2$  established that the observed alkyl

migrations are *intramolecular*. For these reactions the authors favor the Pannell mechanism (Scheme 2), but details concerning the loss of silylene groups are quite clouded since free silylenes are not involved<sup>446</sup>. The above results by Pannell and Ogino are consistent with rapid 1,3-alkyl migrations between silicons in the silyl(silylene) intermediates. This has been established convincingly by photolysis of  $\text{Cp}(\text{CO})_2\text{FeSi}_2\text{Me}_{5-m}(\text{CD}_3)_m$  ( $m = 1, 2$ ) complexes, and examination of the product distributions which are consistent with rapidly equilibrating silyl(silylene)iron intermediates<sup>447</sup>.

Klabunde and coworkers found that  $(\eta^6\text{-arene})\text{NiR}_2$  ( $\text{R} = \text{SiF}_3, \text{SiCl}_3, \text{C}_6\text{H}_5$ ; arene = benzene, toluene, mesitylene) complexes are highly active catalysts for the dimerization of ethylene and propylene, especially in the presence of  $\text{EtAlCl}_2$  as cocatalyst.  $(\eta^6\text{-Mesitylene})\text{Ni}(\text{SiCl}_3)_2$  reacts with four equivalents of  $\text{EtAlCl}_2$  to form an adduct **85**, which is assigned the structure shown in equation 154. Whereas **84** has a  $^{29}\text{Si}$  NMR shift of 16.2 ppm, **85** exhibits a  $^{29}\text{Si}$  NMR shift of 111.0 ppm. Adduct **85** was isolated as a yellow-orange liquid of limited thermal stability. It is proposed that species like **85** are more reactive toward the coordination and insertion of alkenes, which should promote formation of a catalytically active nickel hydride species via  $\beta$ -elimination<sup>448</sup>.



The possible role of silylene complexes as intermediates in metal-catalyzed silane redistribution reactions<sup>449</sup> and in metal-catalyzed dehydrogenative silane coupling reactions<sup>450</sup> is still a topic of active discussion.

Compounds **71** and **72** (see equation 143) undergo remarkable thermolyses in refluxing toluene and benzene, respectively, to the rearranged products  $(\text{dcpe})\text{Pt}[\text{SiClR}(\text{SiMe}_3)]\text{SiMe}_3$  ( $\text{R} = \text{SiMe}_3, \text{Ph}$ ). These reactions appear to involve 1,2-migrations between the metal and silicon, and may therefore be related mechanistically to the  $\alpha$ -silyl migrations that are sometimes proposed to explain metal-catalyzed redistribution at silicon (see Section VI.E.3. of chapter 9)<sup>402</sup>.

### \*B. Attempted Preparations

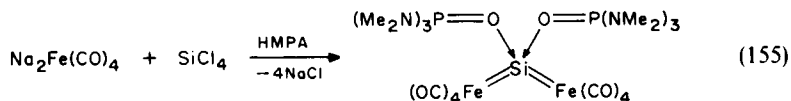
A number of recent reports describe the synthesis and characterization of silylene complexes which are stabilized by donation of electron density to the silylene silicon from free Lewis bases, or by intramolecular adduct formation via groups covalently attached to either the transition metal or the silicon. These compounds do not contain tri-coordinate silicon, and are therefore not strictly analogous to the familiar carbene complexes ( $\text{L}_n\text{M}=\text{CR}_2$ ). Base-free silylene complexes,  $\text{L}_n\text{M}=\text{SiR}_2$ , possess an unsaturated silicon center and are considered more relevant as intermediates that could be important in metal-mediated transformations.

Attempts have been made to develop a route to  $(\text{CO})_5\text{W}=\text{Si}(\text{SnMe}_3)_2$  via cleavage of a Si—Sn bond in  $[(\text{CO})_5\text{WSi}(\text{SnMe}_3)_3]^-$ . However, for a variety of reagents, W—Si bond cleavage is preferred over Si—Sn bond cleavage<sup>403</sup>.

#### 1. Base adducts of silylene complexes

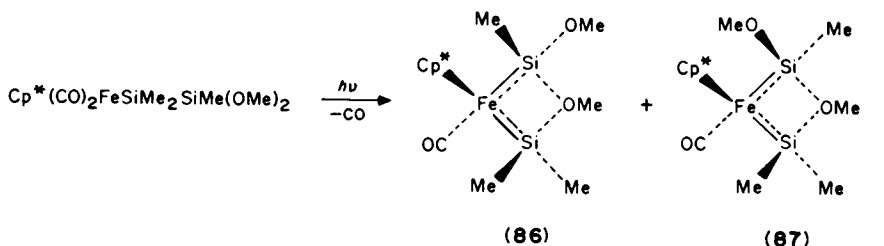
Zybill and Müller have published a detailed description of the synthesis and characterization of  $(\text{CO})_4\text{Fe}=\text{Si}(\text{OCMe}_3)_2(\text{B})$  ( $\text{B} = \text{THF}, \text{HMPA}$ ) complexes (see equation 55). In

addition,  $(\text{CO})_5\text{Cr}=\text{Si}(\text{OCMe}_3)_2(\text{HMPA})$  has been described. The chromium compound has a Cr—Si distance of 2.431(1) Å, Si—OCMe<sub>3</sub> distances of 1.639(2) and 1.644(2) Å and a Si—O(HMPA) distance of 1.736(2) Å<sup>451</sup>. A donor-stabilized, formally silicon(0) complex has been obtained similarly (equation 155). The silicon has a dramatically distorted tetrahedral coordination geometry, with an Fe—Si—Fe angle of 122.6(1)° and an O—Si—O angle of 92.1(1)°. The Fe—Si bonds of 2.339(1) and 2.341(1) Å are somewhat longer than the corresponding Fe—Si bond in  $(\text{CO})_4\text{Fe}=\text{Si}(\text{OCMe}_3)_2(\text{HMPA})$  [2.289(2) Å]<sup>452</sup>.



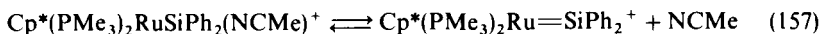
Reaction of  $\text{Na}_2\text{Fe}(\text{CO})_4$  with  $\text{Me}_2\text{SiCl}_2$  in HMPA provides  $(\text{CO})_4\text{Fe}=\text{SiMe}_2(\text{HMPA})$ , in 40% yield after workup. For the two independent molecules in the unit cell, the Fe—Si bond lengths are 2.279(2) and 2.292(2) Å, and the Si—O(HMPA) distances are 1.731(4) and 1.736(4) Å. Overall, there is surprising similarity to the structure of  $(\text{CO})_4\text{Fe}=\text{Si}(\text{OCMe}_3)_2(\text{HMPA})$ . Interestingly,  $(\text{CO})_4\text{Fe}=\text{SiMe}_2(\text{HMPA})$  thermally decomposes to  $\text{Fe}_3(\text{CO})_{12}$  and  $(\text{SiMe}_2)_n$  ( $M_n = 550 \pm 10$ )<sup>453</sup>.

Photolysis of  $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{SiMe}(\text{OMe})_2$  results in a 2:1 mixture of two geometrical isomers (**86** and **87** in equation 156), which resolve upon crystallization to the single isomer **86**. When **86** is redissolved in benzene-*d*<sub>6</sub>, it repartitions into the original mixture of **86** and **87**. The Fe—Si bond lengths in **86** are 2.207(3) and 2.222(3) Å, and the Si—O distances to the three-coordinate oxygen atom are 1.793(9) and 1.799(8) Å. The latter values reflect partial dative bond character. Also, the silicon atoms of the  $\text{FeSiMe}_2$  and  $\text{FeSiMe}(\text{OMe})$  groups lie 0.32 and 0.30 Å, respectively, above the planes defined by the silicon substituents. The  $\text{Si}_2(\mu\text{-OMe})$  group is approximately planar. These results lend significant support to Pannell's proposed mechanism for the photochemical reactions of disilanyliron complexes<sup>106</sup>. It is envisioned that **86** and **87** form by photochemical dissociation of CO from the starting material, followed by a 1,2-shift of the —SiMe(OMe)<sub>2</sub> group to give the silyl(silylene)iron complex  $\text{Cp}^*(\text{CO})\text{Fe}(\text{=SiMe}_2)[\text{SiMe}(\text{OMe})_2]$  as a final intermediate. Cyclization of the latter species is apparently reversible, since **86** and **87** readily interconvert at room temperature. Photolysis of  $\text{Cp}(\text{CO})_2\text{FeSiMe}_2\text{SiMe}(\text{O}^i\text{Bu})_2$  produces exclusively one isomer of  $\text{Cp}(\text{CO})_2\text{FeSiMe}(\text{O}^i\text{Bu})(\mu\text{-O}^i\text{Bu})\text{SiMe}_2$ , which has the Cp and O<sup>i</sup>Bu substituents of the  $\text{FeSi}_2\text{O}$  ring in a *trans* arrangement. The silylene derivatives  $\text{Cp}^*(\text{CO})\text{FeSiMe}_2(\mu\text{-OMe})\text{SiMe}_2$ ,  $\text{Cp}^*(\text{CO})\text{FeSiMe}_2(\mu\text{-O}^i\text{Bu})\text{SiMe}_2$ ,  $\text{Cp}(\text{CO})\text{FeSiMe}_2(\mu\text{-O}^i\text{Bu})\text{SiMe}_2$  and  $\text{Cp}(\text{CO})\text{FeSiMe}_2(\mu\text{-OMe})\text{SiMe}_2$  were also prepared. The latter complex was obtained by photolysis of  $\text{Cp}(\text{CO})_2\text{FeSi}(\text{OMe})\text{MeSiMe}_3$ , and therefore results from migration of a methyl group from one silicon to another<sup>454,455</sup>.



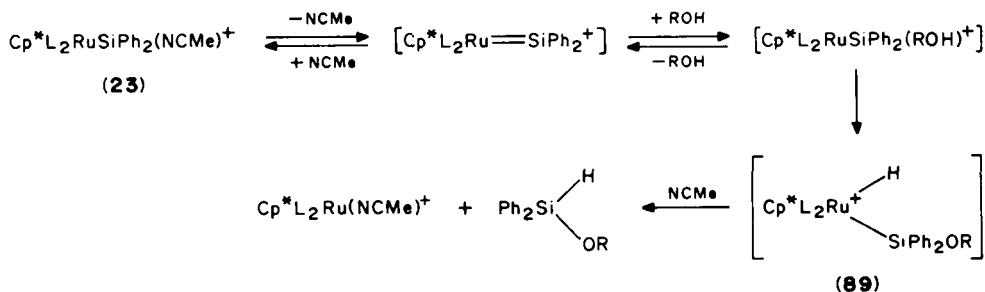
The formation of  $[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{SiPh}_2(\text{NCMe})]^+\text{BPh}_4^-$  (**23**) from  $\text{Cp}^*(\text{PMe}_3)_2\text{RuSiPh}_2(\text{OTf})$  (**88**) (equation 54) has been described in a recent full paper<sup>360</sup>. Infrared spectroscopy and X-ray crystallography confirm the presence of a covalent Si—O bond in **88**. However, the Si—O distance of 1.853(5) Å reflects a relatively weak bond, and the downfield <sup>29</sup>Si NMR shift for **88** ( $\delta$  112.39) suggests considerable silylene character. Conductivity measurements, and infrared and NMR spectroscopy demonstrate that in acetonitrile solution, **88** is converted quantitatively to the ionic silylene adduct  $[\text{Cp}^*(\text{PMe}_3)_2\text{RuSiPh}_2(\text{NCMe})](\text{OTf})$ . Addition of  $\text{NaBPh}_4$  to this solution allows isolation of crystalline  $\mathbf{23} \cdot \text{CH}_2\text{Cl}_2$ , which decomposes slowly in dichloromethane to  $[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}(\text{NCMe})]\text{BPh}_4$ .

X-ray structural studies and infrared spectroscopy indicate that the acetonitrile in **23** is weakly bonded as a Lewis base. This bound acetonitrile is quite labile and exchanges rapidly with free acetonitrile in solution. The kinetics of this exchange in dichloromethane-*d*<sub>2</sub> was examined by line-shape analysis of <sup>1</sup>H NMR spectra over the temperature range -75°C to +15°C. The activation parameters,  $\Delta H^\ddagger = 14.5 \pm 0.3 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 14 \pm 2 \text{ eu}$ , and the fact that the exchange rate is independent of acetonitrile concentration, indicate a dissociative mechanism for the exchange (equation 157).



Therefore, there is kinetic evidence for existence of the base-free silylene complex  $\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{SiPh}_2^+$  in solution. Overall, the spectroscopic, structural and chemical studies of **23**, **88** and related derivatives indicate that the electron-rich  $\text{Cp}^*(\text{PMe}_3)_2\text{Ru}$  fragment is effective in stabilizing the diphenylsilylene ligand<sup>360</sup>.

The first reactions of silylene complexes with small molecules have been described. Silylene derivative **23** reacts with alcohols ROH (R = Me, Et, <sup>t</sup>Bu) to produce  $[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}(\text{NCMe})]^+\text{BPh}_4^-$  and the corresponding alkoxy silanes  $\text{HSiPh}_2\text{OR}$ . Experimental observations are consistent with the mechanism of Scheme 19 (L =  $\text{PMe}_3$ ). The reactions are inhibited by excess acetonitrile, indicating that the initial step is dissociation of acetonitrile to form the base-free silylene complex. The intermediate **89** was observed for the ethanol reaction by low-temperature <sup>1</sup>H NMR spectroscopy. Enolizable ketones RCOMe (R = Me, Ph) react with **23** to give  $[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}(\text{NCMe})]^+\text{BPh}_4^-$  and the silyl enol ethers  $\text{HSiPh}_2(\text{OCR}=\text{CH}_2)$ . Acetic acid reacts similarly to afford  $\text{HSiPh}_2(\text{OOCMe})$ <sup>456</sup>.



SCHEME 19

The rhenium silyls  $\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{SiMe}_2\text{X})$  (X = Cl, Br, I) are prepared from the corresponding Re—SiHMe<sub>2</sub> derivative by reactions with  $\text{CHCl}_3$ ,  $\text{CBr}_4$  and  $\text{CHI}_3$ , respectively. Addition of  $\text{Me}_3\text{SiOTf}$  to  $\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{SiMe}_2\text{Cl})$  gives  $\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{SiMe}_2\text{OTf})$ , which contains a covalently bound triflate group. Pyridine displaces the triflate group to form  $[\text{CpRe}(\text{NO})(\text{PPh}_3)\text{SiMe}_2(\text{pyr})]^+\text{OTf}^-$ . The diastereotopic



methyl groups of  $\text{CpRe(NO)}(\text{PPh}_3)\text{SiMe}_2\text{Cl}$  are equilibrated in solution upon addition of  $\text{AlCl}_3$ , which suggests an equilibrium involving the base-free silylene complex  $[\text{CpRe(NO)}(\text{PPh}_3)(=\text{SiMe}_2)]^+ \text{X}^-$ <sup>457</sup>.

Coordination of decamethylsilicocene to gold(I) occurs upon reaction of  $\text{Cp}^*\text{Si}$  with  $(\text{CO})\text{AuCl}$ . The product,  $\text{ClAuSi}(\eta^1\text{-Cp}^*)(\eta^5\text{-Cp}^*)$ , was isolated as a very dark red powder. It reacts with pyridine and  $\text{tBuNC}$  to form adducts of the type  $\text{ClAuSi}(\eta^1\text{-Cp}^*)_2(\text{B})$  ( $\text{B} = \text{pyr}, \text{tBuNC}$ )<sup>458</sup>. Although  $\text{ClAuSi}(\eta^1\text{-Cp}^*)(\eta^5\text{-Cp}^*)$  might be considered to be a unique type of silylene complex (and in a sense 'base-free'), it does not have a strong analogy to carbene complexes since the silicon atom is bonded to seven other atoms. Although it contains no Lewis base that could dissociate as a free molecule, the silicon possesses a high degree of 'internal' base-stabilization via  $\eta^5$ -coordination of a  $\text{Cp}^*$  group. The  $(\eta^1\text{-Cp}^*)(\eta^5\text{-Cp}^*)\text{Si}$  unit, with 10 valence electrons at silicon, is therefore more electron-rich than the base-stabilized silylene ligands discussed previously.

For comparison the physical properties of known silylene complexes, and related derivatives, are collected in Table 5. Note that for the most part, the base-stabilized

TABLE 5. <sup>29</sup>Si NMR and structural parameters for metal silylene derivatives

Compound	<sup>29</sup> Si NMR shift (ppm)	Si...X (donor) distance (Å) <sup>a</sup>	Reference
$(\text{CO})_4\text{FeSi}(\text{O}^t\text{Bu})_2(\text{HMPA})$	7.1	1.730(3)	451
$(\text{CO})_4\text{FeSi}(\text{O}^t\text{Bu})_2(\text{THF})$	-9.4		451
$(\text{CO})_4\text{FeSi}(\text{HMPA})_2\text{Fe}(\text{CO})_4$		1.745(2), 1.748(3)	452
$(\text{CO})_4\text{FeSiMe}_2(\text{HMPA})$	92.4	1.731(4), 1.736(4)	453
$(\text{CO})_5\text{CrSi}(\text{O}^t\text{Bu})_2(\text{HMPA})$	12.7	1.736(2)	451
$\text{Cp}^*(\text{CO})\text{FeSiMe}_2(\mu\text{-OMe})\text{SiMe}(\text{OMe})$ <b>86, 87</b>	93.9, 98.9, 121.1, 127.4 <sup>b</sup>	1.793(9), 1.799(8)	455
$\text{Cp}^*(\text{CO})\text{FeSiMe}_2(\mu\text{-OMe})\text{SiMe}_2$	125.2		455
$\text{Cp}^*(\text{CO})\text{FeSiMe}_2(\mu\text{-O}^t\text{Bu})\text{SiMe}_2$	126.2		455
$\text{Cp}(\text{CO})\text{FeSiMe}_2(\mu\text{-O}^t\text{Bu})\text{SiMe}_2$	122.3		455
$\text{Cp}(\text{CO})\text{FeSiMe}_2(\mu\text{-O}^t\text{Bu})\text{SiMe}(\text{O}^t\text{Bu})$	121.6, 89.6		455
$\text{Cp}(\text{CO})\text{FeSiMe}_2(\mu\text{-OMe})\text{SiMe}_2$	123.7		455
$\text{Cp}^*(\text{PMe}_3)_2\text{RuSiPh}_2\text{OTf}$ ( <b>88</b> )	112.39 ( $J_{\text{PSi}} = 33 \text{ Hz}$ )	1.853(5)	360
$\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{STol-}p)_2\text{OTf}$ ( <b>90</b> )	77.14 ( $J_{\text{PSi}} = 36 \text{ Hz}$ )	1.856(5)	416
$\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{SEt})_2\text{OTf}$ ( <b>91</b> )	86.05 ( $J_{\text{PSi}} = 37 \text{ Hz}$ ) <sup>c</sup>		416
$\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{STol-}p)(\text{OTf})_2$	37.10 ( $J_{\text{PSi}} = 39 \text{ Hz}$ )	1.780(7), 1.765(7)	416
$[\text{Cp}^*(\text{PMe}_3)_2\text{RuSiPh}_2(\text{NCMe})]\text{BPh}_4$ ( <b>23</b> )	95.75	1.932(8)	360
$\{\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{STol-}p)_2(\text{NCMe})\}\text{-BPh}_4$	58.30 ( $J_{\text{PSi}} = 39 \text{ Hz}$ )	1.872(8)	459
$\{\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{STol-}p)_2\}\text{BPh}_4$ ( <b>92</b> )	259.4 ( $J_{\text{PSi}} = 34 \text{ Hz}$ )		416
$[\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{SEt})_2]\text{BPh}_4$ ( <b>93</b> )	264.4 <sup>d</sup>		416
$\{\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}[\text{Si}(\text{CH}_2)_8\text{CH}_3]_2\}\text{BPh}_4$	276.1 ( $J_{\text{PSi}} = 34 \text{ Hz}$ )		459
$\{\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{SHex-}c)_2\}\text{BPh}_4$	268.7 ( $J_{\text{PSi}} = 35 \text{ Hz}$ )		459
$\{\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{STol-}p)(\text{phen})\}^{2+} \text{-}(\text{OTf})_2^-$	72.95 ( $J_{\text{PSi}} = 32 \text{ Hz}$ )	1.909(14), 1.951(14)	460
$\text{ClAuSi}(\eta^1\text{-Cp}^*)(\eta^5\text{-Cp}^*)$	82.8		458
$\text{ClAuSi}(\eta^1\text{-Cp}^*)_2(\text{CN}^t\text{Bu})$	71.2		458
$\text{ClAuSi}(\eta^1\text{-Cp}^*)_2(\text{pyr})$	54.3		458

<sup>a</sup>X = Lewis base or triflate.

<sup>b</sup>Two isomers present in solution.

<sup>c</sup>-80 °C.

<sup>d</sup>Broad resonance at -60 °C.

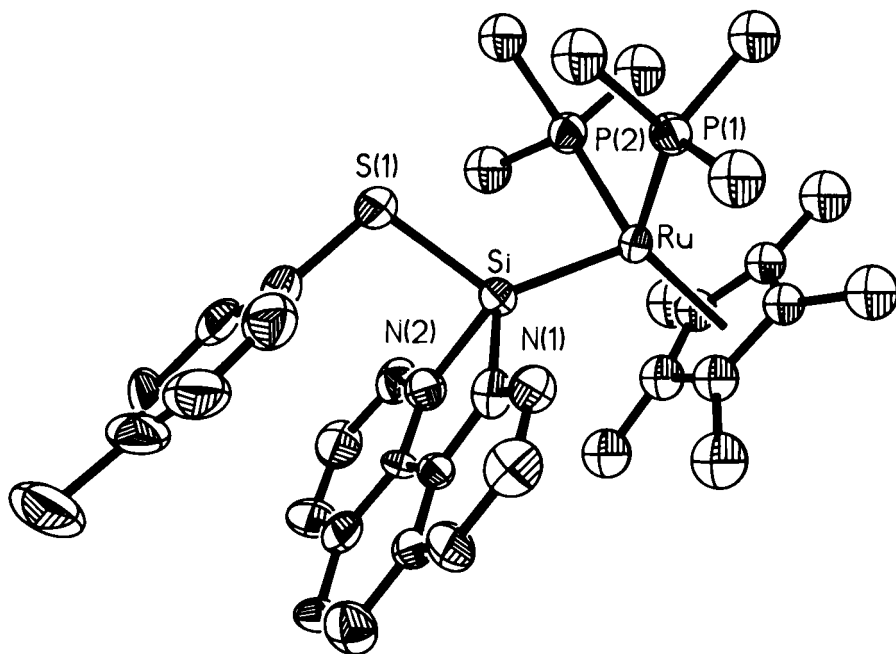


FIGURE 7. ORTEP view of the cation in  $\{\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{STol-}p)(\text{phen})\}^{2+}(\text{OTf})_2^-$

adducts and triflate derivatives exhibit downfield  $^{29}\text{Si}$  NMR shifts (*ca* 100 ppm) that are consistent with some silylene (or silylenium) character at silicon. The exceptions are  $(\text{CO})_4\text{FeSi}(\text{O}^t\text{Bu})_2(\text{B})$  ( $\text{B} = \text{HMPA}, \text{THF}$ ) and  $(\text{CO})_5\text{CrSi}(\text{O}^t\text{Bu})_2(\text{HMPA})$ , which exhibit shifts near 0 ppm. It may be that the alkoxy groups in these compounds are responsible for the relatively high-field  $^{29}\text{Si}$  NMR shifts.

Complexes that formally possess a base-stabilized silylyne ligand,  $[\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{STol-}p)(\text{L}_2)]^{2+}(\text{OTf})_2^-$  ( $\text{L}_2 = \text{bipyridine}, \text{phenanthroline}$ ) have been obtained by addition of the chelating Lewis base to  $\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{STol-}p)(\text{OTf})_2$ . A crystal structure of the violet phenanthroline adduct (Figure 7) revealed a 4-coordinate silicon center in an unusual coordination geometry. The Ru—Si bond length of 2.269(5) Å is quite short, and the long Si—N distances (1.909(14) and 1.951(14) Å) clearly correspond to dative interactions. The distortion from tetrahedral geometry at silicon is described by the N—Si—N angle of 81.5(6)° and the Ru—Si—S angle of 126.1(2)°<sup>460</sup>.

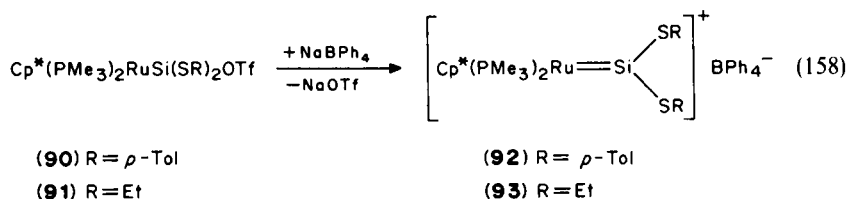
## 2. Base-free silylene complexes

The first base-free silylene complexes have recently been described<sup>416</sup>. Isolation of these compounds,  $[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{Si}(\text{SR})_2]\text{BPh}_4$  (**92**,  $\text{R} = p\text{-Tol}$ ; **93**,  $\text{R} = \text{Et}$ ), is apparently made possible by a stabilizing influence of the thiolate groups<sup>461</sup>.

The triflate derivatives  $\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{SR})_2\text{OTf}$  (**90**,  $\text{R} = p\text{-Tol}$ ; **91**,  $\text{R} = \text{Et}$ ) are obtained by exchange reactions of  $\text{Me}_3\text{SiOTf}$  with the corresponding ruthenium silyls  $\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{SR})_3$ . Compounds **90** and **91** possess covalent Si—O(triflate) bonds. As with **88**, the triflate groups of **90** and **91** are displaced in acetonitrile solution to produce  $[\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{SR})_2(\text{NCMe})]\text{OTf}$  complexes. Rapid exchange of the

inequivalent methylene protons of the —SEt groups of **91** in dichloromethane- $d_2$  can be attributed to a mechanism consisting of dissociation of triflate anion to form  $\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{Si}(\text{SEt})_2^+$ , and return of triflate to the opposite face of the silylene ligand.

Compounds **90** and **91** react with  $\text{NaBPh}_4$  in dichloromethane according to equation 158. Both **91** and **93** give rise to remarkably low-field  $^{29}\text{Si}$  NMR resonances. For **92**, a triplet ( $\delta$  259.4,  $J_{\text{PSi}} = 34$  Hz) at  $-80^\circ\text{C}$  was observed, and **93** has a broad peak in the  $^{29}\text{Si}$  NMR spectrum at  $\delta$  264.4 ( $-60^\circ\text{C}$ ). It is interesting to note, for comparison, that the  $^{13}\text{C}$  NMR shift for the carbene carbon in  $[\text{Cp}(\text{CO})_2\text{Ru}=\text{C}(\text{SMe})_2]\text{PF}_6$  is  $\delta$  285.3<sup>462</sup>. A dimeric structure for **92** is ruled out by solution molecular weight data, and the fact that the silicon nucleus is coupled to only two phosphorous nuclei. Silylene complex **92** combines rapidly with acetonitrile to give  $[\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{STol-}p)_2(\text{NCMe})]\text{BPh}_4$ . A pyridine adduct was obtained similarly<sup>416</sup>.



#### \*IV. TRANSITION-METAL SILENE, DISILENE AND SILANIMINE COMPLEXES

Major developments in this area include the first isolations of  $\eta^2$ -silene,  $\eta^2$ -disilene and  $\eta^2$ -silanimine complexes, and the identification of catalytic processes that probably involve  $\eta^2$ -silene complexes as key intermediates.

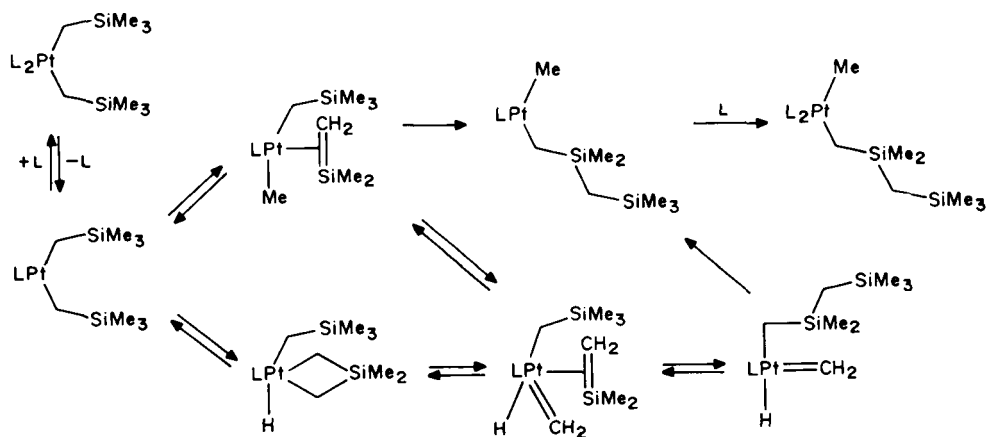
##### \*A. Silene Complexes

###### 1. Silene ligands as intermediates

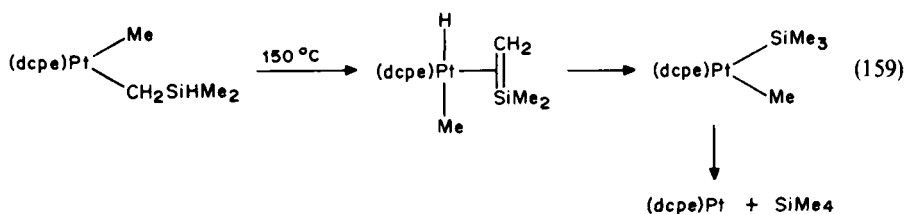
The reaction of  $\text{Me}_3\text{SiCl}$  with  $\text{IrCl}(\text{coe})(\text{PMe}_3)_3$  produces the iridium hydride  $\text{IrHCl}_2(\text{PMe}_3)_3$  and presumably  $\text{Me}_2\text{Si}=\text{CH}_2$  via  $\beta$ -hydrogen elimination from an intermediate  $\text{Ir}-\text{SiMe}_3$  species (cf. equation 141). Analogous  $\beta$ -hydrogen eliminations are also observed in reactions of  $\text{Me}_3\text{SiCl}$  with  $[\text{Ir}(\text{PMe}_3)_4]\text{PF}_6$  or  $\text{Ir}(\text{PEt}_3)_3\text{Cl}$ <sup>388</sup>. Tanaka and coworkers have made similar observations. The reaction of  $[\text{IrH}(\text{P}^i\text{Pr}_3)_2]$  with  $\text{Me}_3\text{SiCl}$  or  $\text{Me}_2\text{SiCl}_2$  gives  $\text{IrH}_2\text{Cl}(\text{P}^i\text{Pr}_3)_2$ , and  $\text{Me}_3\text{SiBr}$  interacts with  $[\text{IrH}(\text{P}^i\text{Pr}_3)_2]$  to afford  $\text{IrH}_2\text{Br}(\text{P}^i\text{Pr}_3)_2$  among other products. When  $\text{Ir}(\text{SiMe}_3)\text{HI}(\text{P}^i\text{Pr}_3)_2$  was heated at  $120^\circ\text{C}$ ,  $\text{IrH}_2\text{I}(\text{P}^i\text{Pr}_3)_2$  formed in 64% yield. These hydride-forming reactions were attributed to  $\beta$ -hydrogen eliminations from silyl iridium derivatives<sup>389</sup>.

The quantitative thermal rearrangements of  $\text{L}_2\text{Pt}(\text{CH}_2\text{SiMe}_3)_2$  ( $\text{L} = \text{PEt}_3, \text{PMePh}_2, \text{PPh}_3$ ) to  $\text{cis-L}_2\text{Pt}(\text{Me})\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_3$  complexes may involve platinum  $\eta^2$ -silene intermediates. Kinetic data and a labeling experiments  $\{\text{cis-(PMePh}_2)_2\text{Pt}[\text{CH}_2\text{Si}(\text{CD}_3)_3]_2 \rightarrow \text{cis-(PMePh}_2)_2\text{Pt}(\text{CD}_3)\text{CH}_2\text{Si}(\text{CD}_3)_2\text{CH}_2\text{Si}(\text{CD}_3)_3\}$  are consistent with the pathways of Scheme 20. It remains to be determined whether  $\beta$ -methyl or  $\gamma$ -hydrogen migration in the  $\text{LPt}(\text{CH}_2\text{SiMe}_3)_2$  intermediates is important for product formation<sup>463</sup>.

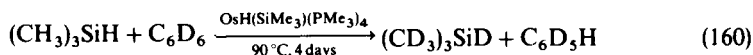
A related observation is found in the thermal decomposition of  $(\text{dcpe})\text{Pt}(\text{Me})\text{CH}_2\text{SiHMe}_2$  [ $\text{dcpe} = (\text{c-Hex})_2\text{PCH}_2\text{CH}_2\text{P}(\text{c-Hex})_2$ ] in benzene- $d_6$  to a mixture of  $\text{Pt}(\text{dcpe})_2$ ,  $(\text{dcpe})\text{Pt}(\text{D})\text{C}_6\text{D}_5$ , and  $\text{SiMe}_4$ . A reasonable mechanism that explains this result is shown in equation 159<sup>464</sup>.



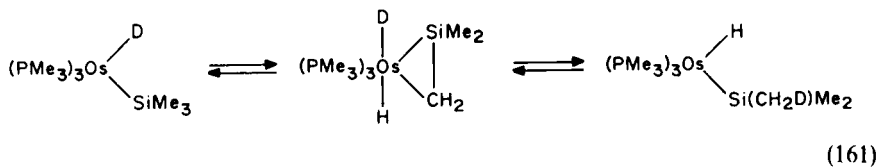
SCHEME 20



Selective H/D exchange between silanes and benzene- $d_6$  is catalyzed by osmium silyl derivatives that appear to undergo  $\beta$ -hydrogen elimination to transient  $\eta^2$ -silylene complexes (equation 160). Significantly,  $\text{Me}_2\text{EtSiH}$  is selectively deuterated to



$(\text{CD}_3)_2(\text{CH}_3\text{CD}_2)\text{SiD}$  under these conditions. This, and other mechanistic evidence argue for key steps involving deuterium incorporation into silane  $\alpha$ -CH positions via  $\beta$ -elimination cycles (equation 161)<sup>465</sup>.



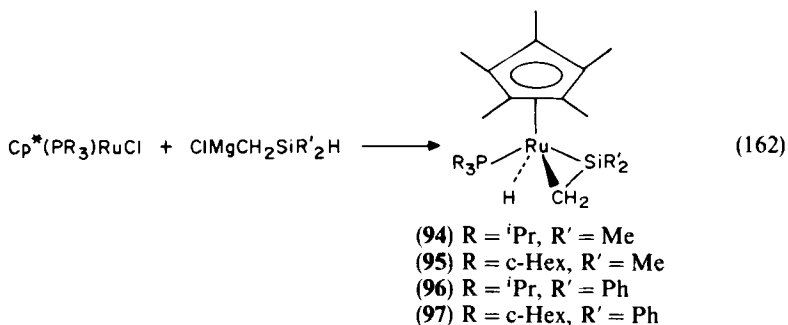
Under similar conditions ( $150^\circ\text{C}$ , cyclohexane solvent) the ruthenium silyl  $\text{RuH}_3(\text{SiMe}_3)(\text{PMe}_3)_3$  catalyzes the dehydrogenative coupling of  $\text{HSiMe}_3$  to oligomeric carbosilanes containing up to 8 silicon atoms. Products identified are  $\text{HSiMe}_2\text{CH}_2\text{SiMe}_3$ ,  $\text{HSiMe}(\text{CH}_2\text{SiMe}_3)_2$ ,  $\text{HSiMe}_2\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_3$ ,  $\text{Me}_3\text{SiCH}_2\text{SiHMeCH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_3$  and  $\text{HSi}(\text{CH}_2\text{SiMe}_3)_3$ . This process, which corresponds to hydrosilylation of

$\text{CH}_2=\text{SiMe}_2$ , probably involves conversion of  $\text{RuSiMe}_3$  to  $\text{Ru}(\text{H})(\eta^2\text{-CH}_2\text{SiMe}_2)$  derivatives, followed by insertion of the silene into a  $\text{Ru}-\text{SiMe}_3$  bond<sup>466</sup>.

The coupling of  $\text{CH}_2=\text{CHSiRR}'\text{SiMe}_3$  ( $\text{R}, \text{R}' = \text{Me}, \text{Ph}$ ;  $\text{R} = \text{Me}, \text{R}' = \text{Ph}$ ) to  $E\text{-Me}_3\text{SiCH}=\text{CHSiRR}'\text{CH}_2\text{CH}_2\text{SiRR}'\text{SiMe}_3$ , catalyzed by  $\text{Ni}(\text{PEt}_3)_4$ , is postulated to proceed via  $(\eta^2\text{-Me}_3\text{SiCH}_2\text{CH}=\text{SiRR}')\text{Ni}$  and  $(\eta^3\text{-Me}_3\text{SiCH}\cdots\text{CH}\cdots\text{SiRR}')\text{Ni}$  intermediates<sup>467</sup>. The thermolysis of **62** is proposed to involve initial rearrangement of **62** to  $[\eta^2\text{-Ph}(\text{Me}_3\text{Si})\text{C}=\text{C}=\text{Si}(\text{SiMe}_3)\text{Mes}]\text{Ni}(\text{PEt}_3)_2$ <sup>468</sup>.

## 2. Stable silene complexes

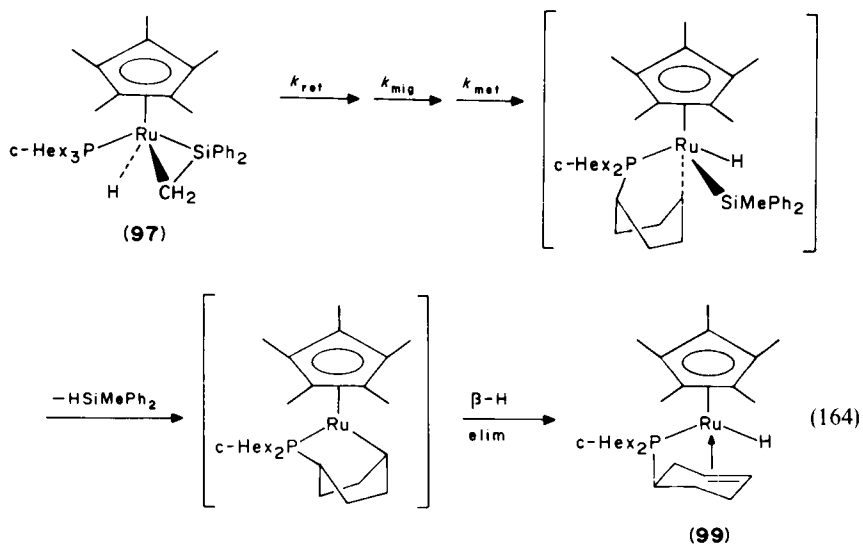
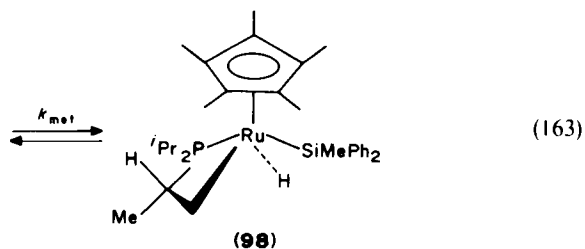
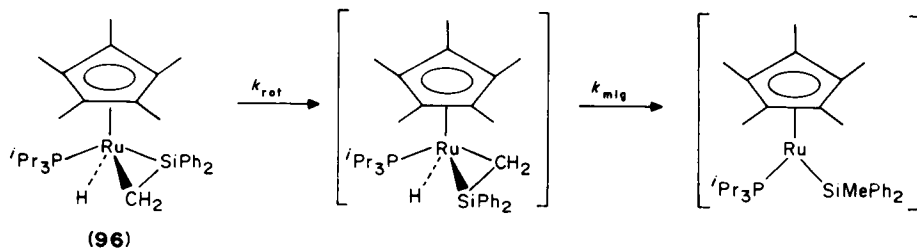
Stable, isolable  $\eta^2$ -silene complexes were recently obtained by the reactions shown in equation 162. This synthesis is based on  $\beta$ -hydrogen transfer from silicon in presumed 16-electron  $\text{Cp}^*(\text{PR}_3)\text{Ru}-\text{CH}_2\text{SiHR}'_2$  intermediates, and stabilization of the silene ligand by a sterically hindered, electron-rich metal center. The <sup>29</sup>Si NMR spectrum of **96** consists of a multiplet centered at  $\delta$  6.14 and, as expected, the <sup>13</sup>C NMR shift for the silene carbon of **96** ( $\delta$  -29.04) occurs upfield of shifts for analogous ruthenium ethylene complexes. The <sup>1</sup>J<sub>CH</sub> coupling constant observed for the  $\text{CH}_2=\text{Si}$  group of **96** (143 Hz) suggests significant  $\text{sp}^2$  character. The crystal structure of **96** consists of two independent molecules, for which the  $\text{Si}-\text{CH}_2$  bond distances are 1.78(2) and 1.79(2) Å. These distances are between values expected for  $\text{Si}-\text{C}$  single and  $\text{Si}=\text{C}$  double bonds. The  $\text{C}-\text{Si}-\text{C}$  angles sum to  $344^\circ$ , corresponding to a hybridization at silicon between  $\text{sp}^2$  ( $360^\circ$ ) and  $\text{sp}^3$  ( $329^\circ$ )<sup>469</sup>.



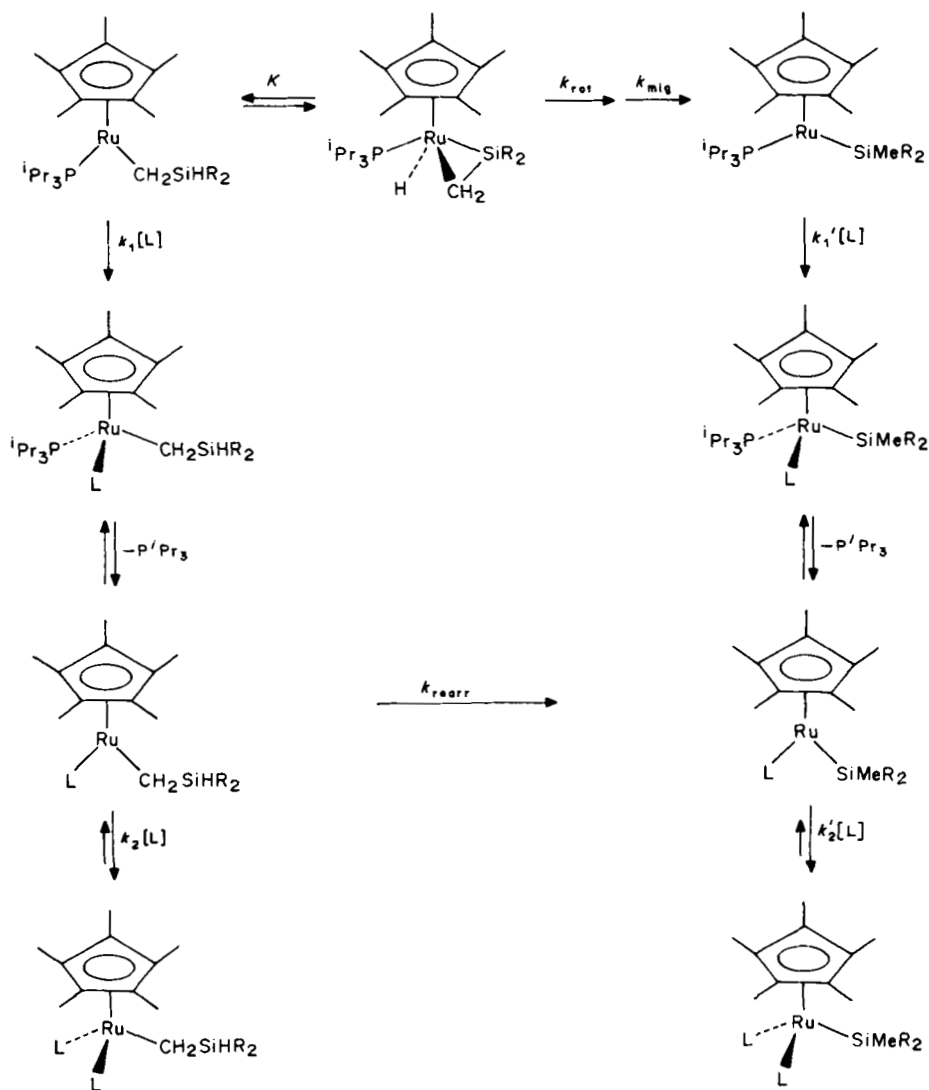
Whereas **94** and **95** thermally decompose in solution at room temperature over *ca* 1 hour, **96** and **97** are stable for months in the solid state and decompose cleanly in solution (over *ca* 24 h) according to equations 163 and 164.

Decomposition of **96** to **98** involves exclusive migration of hydride to the silene carbon atom, as determined by deuterium-labeling. For this first-order process,  $\Delta G^\ddagger = 23 \pm 3$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger = -17 \pm 3$  eu and  $k_{\text{H}}/k_{\text{D}} = 1.00$ . Overall, the mechanistic studies are consistent with irreversible, rate-determining rotation of the silene to place the silene carbon atom near the hydride ligand. This rotation rate is therefore a key factor in determining the stability of complexes of the type  $\text{Cp}^*(\text{PR}_3)\text{Ru}(\text{H})(\eta^2\text{-CH}_2\text{SiR}'_2)$ , with high barriers to rotation corresponding to more stable complexes. The observed ordering of stabilities for silene complexes with substituents  $\text{R}/\text{R}'$  is:  $\textit{c}\text{-Hex}/\text{Ph} > \textit{i}\text{Pr}/\text{Ph} > \textit{c}\text{-Hex}/\text{Me} > \textit{i}\text{Pr}/\text{Me} \gg \text{Me}/\text{Me}$ .

Reactions of **96** with small molecules provide evidence for migration of hydride to both ends of the silene ligand. Reaction of **96** with sterically unhindered phosphines  $\text{PMe}_2\text{R}$  ( $\text{R} = \text{Me}, \text{Ph}$ ) leads to hydride migration to the silene carbon atom and displacement of  $\text{P}^i\text{Pr}_3$  to afford  $\text{Cp}^*(\text{PMe}_2\text{R})_2\text{RuSiMePh}_2$  complexes. Kinetic and mechanistic



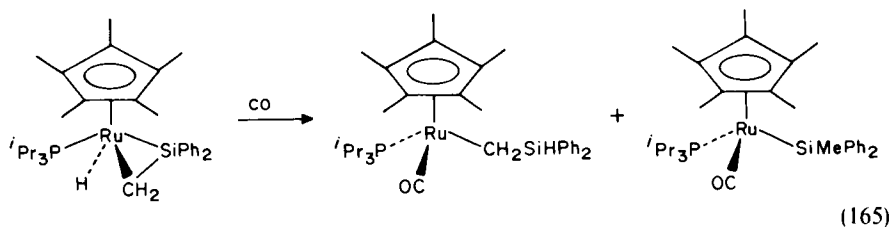
investigations indicate that these reactions proceed via competing first- and second-order pathways, with a rate law of the form:  $\text{rate} = k_{rot}[\mathbf{96}] + Kk_1[\mathbf{96}][\text{PMe}_2\text{R}]$ . This can be explained in terms of Scheme 21. The first-order term corresponds to migration of hydride to carbon as described above for the thermolysis. The pathway giving rise to second-order behavior is explained by a rapid pre-equilibrium involving migration of hydride to the silene silicon. Apparently, rearrangement of  $\text{Cp}^*(\text{PMe}_3)\text{RuCH}_2\text{SiPh}_2$  to  $\text{Cp}^*(\text{PMe}_3)\text{-RuSiMePh}_2$  is very rapid ( $k_{\text{rearr}} > k_2[\text{L}]$  in Scheme 21). Consistent with this, the reaction of **96** with neat  $\text{PMe}_3$  gives both  $\text{Cp}^*(\text{PMe}_3)_2\text{RuCH}_2\text{SiPh}_2$  and  $\text{Cp}^*(\text{PMe}_3)_2\text{RuSiMePh}_2$  in a 1:4 ratio.



SCHEME 21

Reactions of **96** with carbon monoxide (equation 165) can also be explained by competing hydrogen migration pathways, as represented by Scheme 21. Therefore as expected, the ratio of products in this reaction is dependent on the initial pressure of CO. Products of the reaction of **96** with hydrogen also reflect hydride migration to both ends of the silene ligand. Trapping of Cp\*(P<sup>i</sup>Pr<sub>3</sub>)RuCH<sub>2</sub>SiHPh<sub>2</sub> by hydrogen is followed by elimination of HSiMePh<sub>2</sub> and, via oxidative addition of H<sub>2</sub>, formation of the known trihydride Cp\*(P<sup>i</sup>Pr<sub>3</sub>)RuH<sub>3</sub><sup>470</sup>. The silyl Cp\*(P<sup>i</sup>Pr<sub>3</sub>)RuSiMePh<sub>2</sub> is also trapped by hydrogen to produce Cp\*(P<sup>i</sup>Pr<sub>3</sub>)Ru(H)<sub>2</sub>SiMePh<sub>2</sub>. In general, the reaction chemistry of

**96** appears to be dominated by hydrogen migrations that produce reactive 16-electron alkyl or silyl intermediates<sup>471</sup>.



An iridium silene complex without a hydride ligand has been prepared by the reaction in equation 166. Compound **100**, obtained as yellow crystals from pentane, was characterized by X-ray diffraction (Figure 8). Overall, the structural parameters are similar to those observed for **96**. For example, in **100** the Si—CH<sub>2</sub> bond length is 1.810(6) Å, and the C—Si—C angles sum to 341°. The nonplanarity of the diphenylsilylene ligand

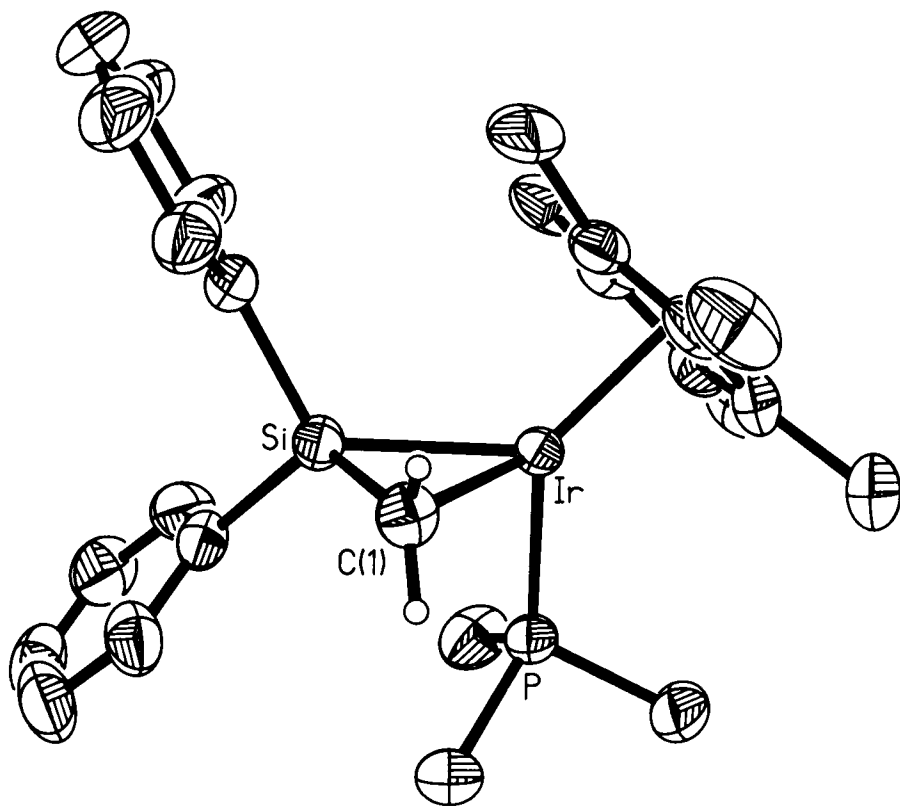
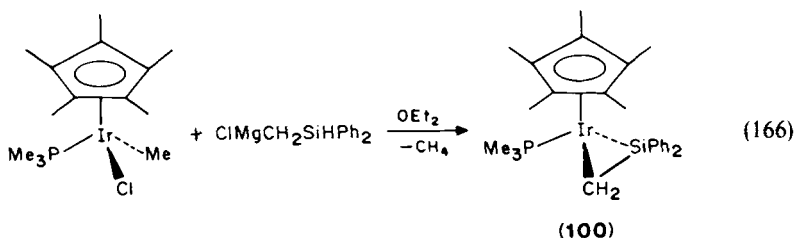


FIGURE 8. ORTEP view of **100**

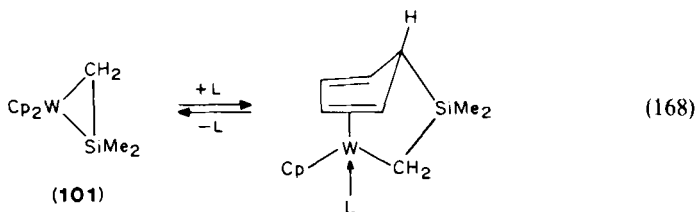
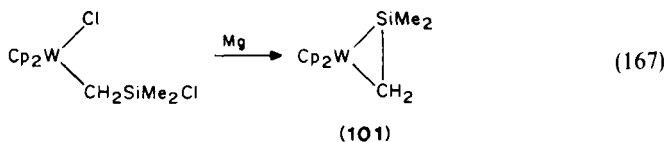


is described by angles between the Si—CH<sub>2</sub> bond and the CH<sub>2</sub> (17.3°) and Si[C(phenyl)]<sub>2</sub> (39.2°) planes. For comparison, the comparable angles in Cp\*(PPh<sub>3</sub>)Rh(η<sup>2</sup>-CH<sub>2</sub>=CH<sub>2</sub>)<sup>472</sup> that describe bending of the methylene groups away from rhodium are 19 and 29°. The similarity of <sup>1</sup>J<sub>CH</sub> coupling constants for the silene carbon of **100** (142.3 Hz) and for the ethylene carbons of Cp\*(PMe<sub>3</sub>)Ir(η<sup>2</sup>-CH<sub>2</sub>=CH<sub>2</sub>) (150.6 Hz)<sup>473</sup> suggests substantial sp<sup>2</sup> character at carbon.



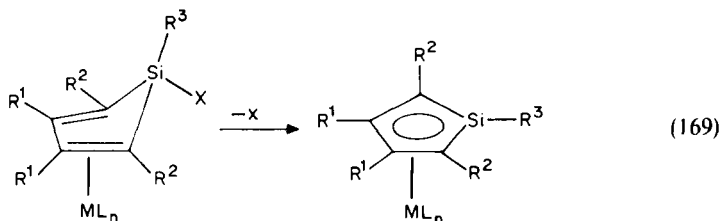
With no ligand that can readily migrate to the silene, compound **100** is quite robust, exhibiting no decomposition at 140 °C over several days. Complex **100** reacts cleanly with methanol via cleavage of the Ir—Si bond to produce Cp\*(PMe<sub>3</sub>)Ir(H)(CH<sub>2</sub>SiOMePh<sub>2</sub>), and with methyl iodide to afford Cp\*(PMe<sub>3</sub>)Ir(I)(CH<sub>2</sub>SiMePh<sub>2</sub>)<sup>474</sup>.

A tungsten silene complex has been prepared by the reductive dechlorination shown in equation 167. A relatively small <sup>1</sup>J<sub>183W 29Si</sub> coupling constant (57.1 Hz), and a <sup>1</sup>J<sub>CH</sub> coupling constant of 137 Hz for the methylene groups are observed. The latter coupling constant is smaller than the analogous value in Cp<sub>2</sub>Mo(η<sup>2</sup>-CH<sub>2</sub>=CH<sub>2</sub>) (<sup>1</sup>J<sub>CH</sub> = 153 Hz)<sup>475</sup>. The Si—C bond length in **101** is 1.800(8) Å. The W—C bond of **101** is cleaved by methanol to produce Cp<sub>2</sub>W(H)(CH<sub>2</sub>SiMe<sub>2</sub>OMe), and the nonpolar reagents H<sub>2</sub> and HSiMe<sub>3</sub> react with **101** to afford Cp<sub>2</sub>W(X)(SiMe<sub>3</sub>) (X = H and SiMe<sub>3</sub>, respectively). Since the donor ligands C<sub>2</sub>H<sub>4</sub> and PMe<sub>3</sub> add reversibly to **101** via migration of silicon to a Cp ring (equation 168, L = C<sub>2</sub>H<sub>4</sub>, PMe<sub>3</sub>), it is possible that H<sub>2</sub> and HSiMe<sub>3</sub> react with **101** via oxidative addition to a 16-electron CpW[(η<sup>4</sup>-C<sub>5</sub>H<sub>5</sub>)SiMe<sub>2</sub>CH<sub>2</sub>] intermediate<sup>476</sup>.



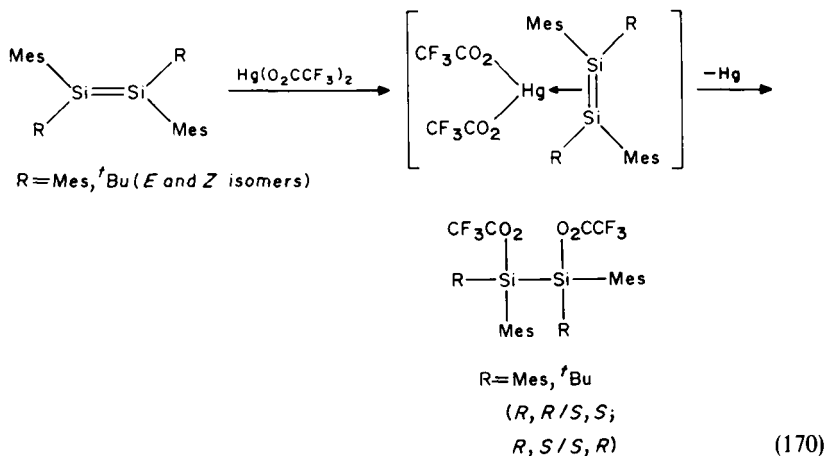
Various unsuccessful attempts have been made to prepare η<sup>5</sup>-silacyclopentadienyl complexes from η<sup>4</sup>-silole ligands (equation 169). Many η<sup>4</sup>-silole complexes have been prepared, and their reactivity at silicon has been examined in detail. In general, it has been found that siloles are very good η<sup>4</sup>-ligands, and that the *exo* group on silicon is highly reactive, with substitutions always occurring with retention of configuration. In

some cases M—Si  $\sigma$ -bonds have been introduced into a silole ring, but so far no M—Si bond-formations leading to an  $\eta^5$ -silacyclopentadienyl complex have been observed<sup>477,478</sup>. This area has been recently reviewed<sup>479</sup>.

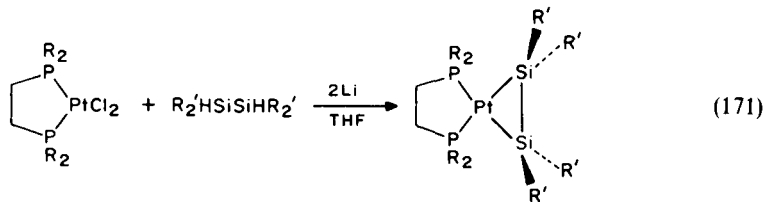


### B. Disilene Complexes

The first evidence for a disilene complex was obtained by low-temperature NMR spectroscopy, which suggested the intermediate shown in equation 170<sup>480</sup>.



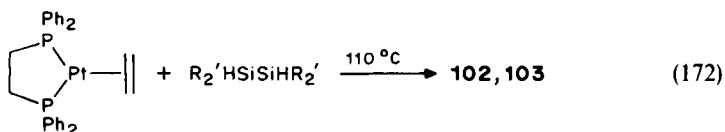
Stable  $\eta^2$ -disilene complexes of platinum were first reported in 1989. The syntheses of these compounds, based on dehydrogenation of a disilane, are described in equations 171 and 172. The disilene complexes  $(R_3P)_2Pt(\eta^2\text{-Mes}_2\text{Si}=\text{SiMes}_2)$  (**105**, R = Et; **106**,



(**102**) R = Ph, R' = <sup>i</sup>Pr

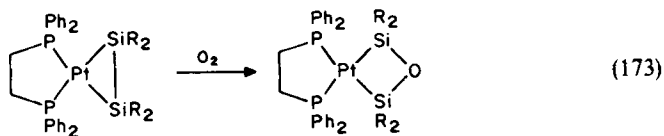
(**103**) R = Ph, R' = Me

(**104**) R = *c*-Hex, R' = Ph

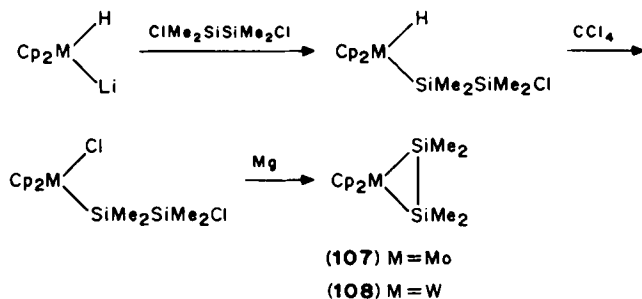


R = Ph) were obtained by photolysis of  $(\text{PR}_3)_2\text{Pt}(\text{C}_2\text{O}_4)$  in the presence of the free disilene. The characterization of **102–106** is based on mass spectral, infrared, NMR and combustion analysis data<sup>481,482</sup>.

Interestingly, these disilene species display rich reaction chemistry associated with the Si—Si bonds. For example, **102** reacts with hydrogen to produce the bis(silyl) complex  $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Pt}(\text{SiH}^i\text{Pr}_2)_2$ . Compounds **102** and **103** react with oxygen as shown in equation 173. Finally, **103** undergoes a curious reaction with ammonia to produce  $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{PtSiMe}_2(\text{NH})\text{SiMe}_2$ <sup>482</sup>.



Molybdenum and tungsten disilene complexes have been obtained by the reductive coupling method outlined in Scheme 22. The  $^1J_{183\text{W}-29\text{Si}}$  coupling constant for **108** (50.7 Hz) is small compared to those found in tungstocene silyl derivatives, indicating that the W—Si bonding involves a high degree of p character on the  $\text{Si}_2$  fragment. The molecular structure of **108** is shown in Figure 9. The W—Si bond length in **108** is 2.606(2) Å, and the Si—Si bond distance of 2.260(2) Å falls between expected values for single (2.35 Å) and double (2.14 Å) bonds. The  $\text{SiMe}_2$  planes are bent away from the metal center by  $30.2^\circ$ <sup>483</sup>.



SCHEME 22

Some quite intriguing platinum–silicon complexes that appear to have disilene character are obtained by the two methods of equation 174. A mixture of **109–111** is obtained, but **110** can be purified from this mixture by treatment with carbon dioxide, which apparently reacts selectively with **109** and **111** to give unidentified products. The crystal structures of these complexes reveal a significant Si—Si interaction. Thus, the Si—Si separations [2.575(15)–2.602(4) Å] are within the range of known Si—Si single bonds (2.33–2.70 Å), and the Si—Pt—Si angles [65.9(3)–66.5(1)°] are rather acute<sup>484</sup>. Analogous  $(\text{Et}_3\text{P})_2\text{Pt}[\mu\text{-SiX}(\text{c-Hex})][\mu\text{-SiY}(\text{c-Hex})]\text{Pt}(\text{PEt}_3)_2$  dimers with *trans* cyclohexyl groups have been obtained by similar means, and these also have short Si—Si contacts

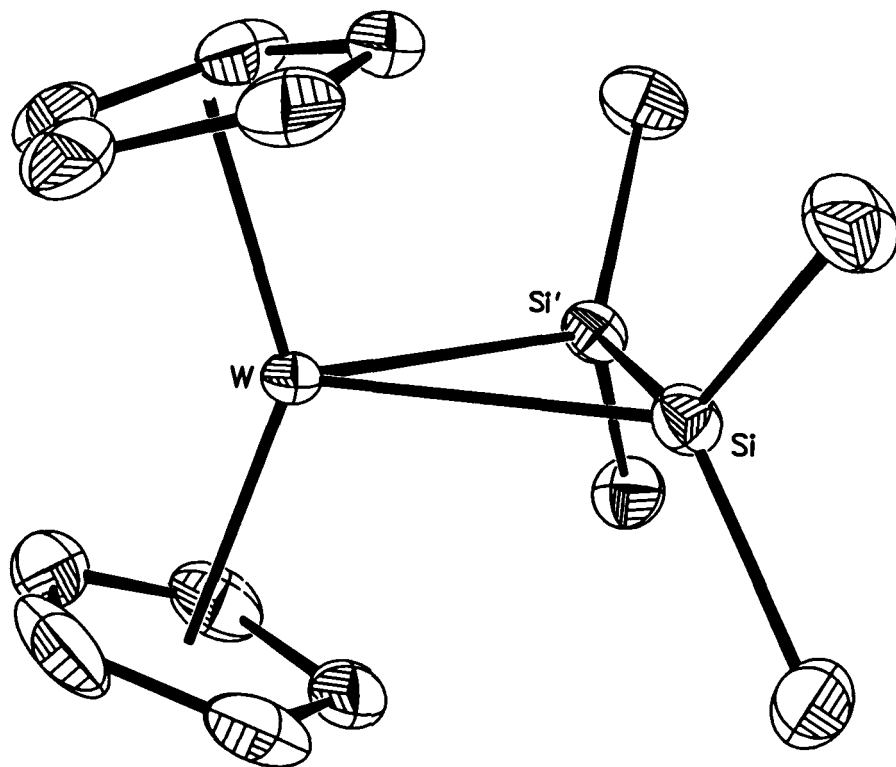
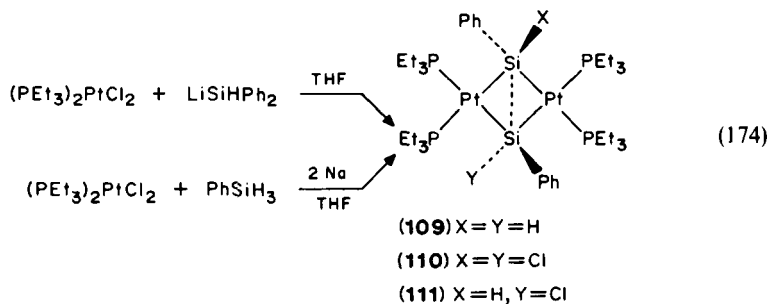


FIGURE 9. ORTEP view of 108

and planar  $\text{Pt}_2\text{Si}_2$  cores. However a *cis* isomer of  $(\text{Et}_3\text{P})_2\text{Pt}[\mu\text{-SiH}(\text{c-Hex})]_2\text{Pt}(\text{PEt}_3)_2$ , which cocrystallizes with the *trans* derivatives, has a bent  $\text{Pt}_2\text{Si}_2$  core<sup>485</sup>.



Molecular orbital calculations support the view that the above diplatinum compounds may be regarded as consisting of a disilene bonded to two  $\text{L}_2\text{Pt}(0)$  fragments. The bonding may be described as involving donation of both Si—Si  $\sigma$  and Si—Si  $\pi$  bonds to the platinum atoms. There is some  $\pi$  back-donation from Pt d orbitals to the

Si—Si  $\sigma^*$  and  $\pi^*$  levels. The Mulliken overlap population for the Si—Si bond of  $(\text{H}_3\text{P})_4\text{Pt}_2(\mu\text{-SiPhCl})_2$  is 0.27, and the Pt—Pt bond order is zero<sup>486</sup>.

### C. Silanimine Complexes

The  $\eta^2$ -silanimine complex  $\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_2\text{Si}=\text{N}^t\text{Bu})(\text{PMe}_3)$  has recently been prepared. The complex was obtained by addition of  $\text{LiCH}_2\text{SiMe}_3$  to  $\text{Cp}_2\text{Zr}(\text{I})(\text{N}^t\text{BuSiMe}_2\text{H})$  in the presence of  $\text{PMe}_3$ . Presumably the  $\eta^2$ -silanimine ligand results from elimination of  $\text{Me}_4\text{Si}$  from  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{SiMe}_3)(\text{N}^t\text{BuSiMe}_2\text{H})$ . The structure of  $\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_2\text{Si}=\text{N}^t\text{Bu})(\text{PMe}_3)$  (Figure 10) revealed short Zr—Si [2.654(1) Å] and long Si—N [1.687(3) Å]

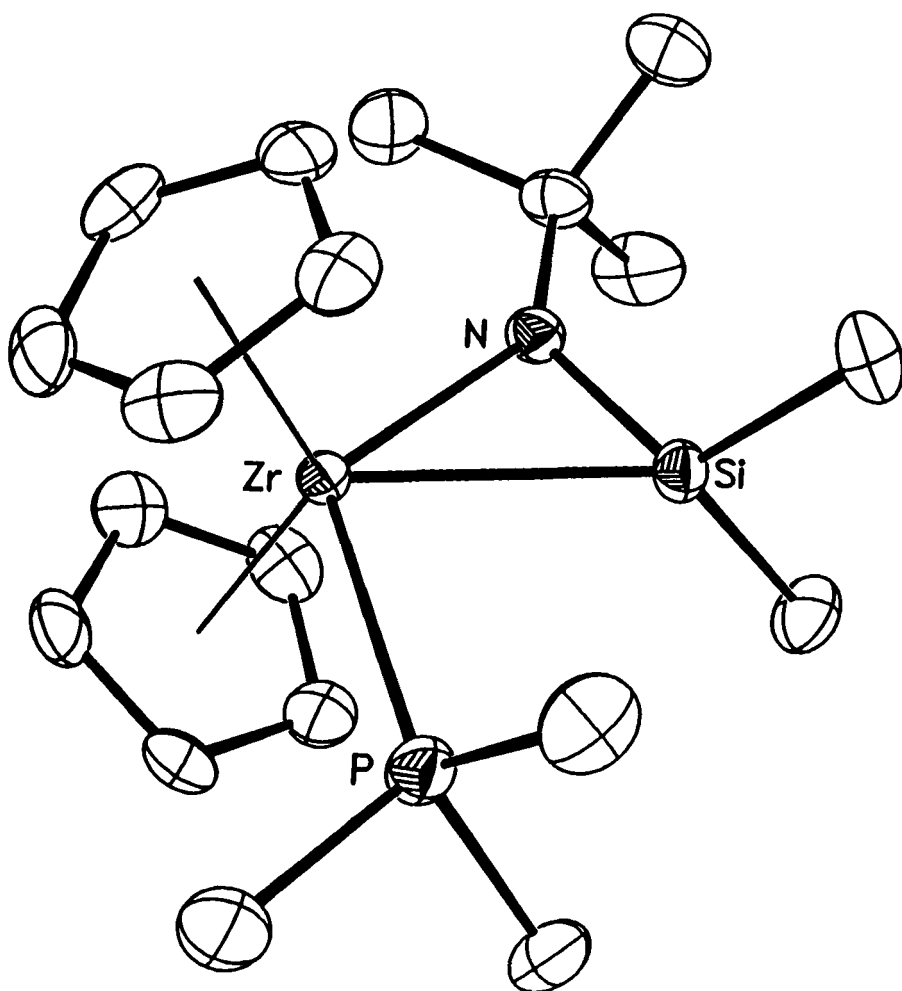
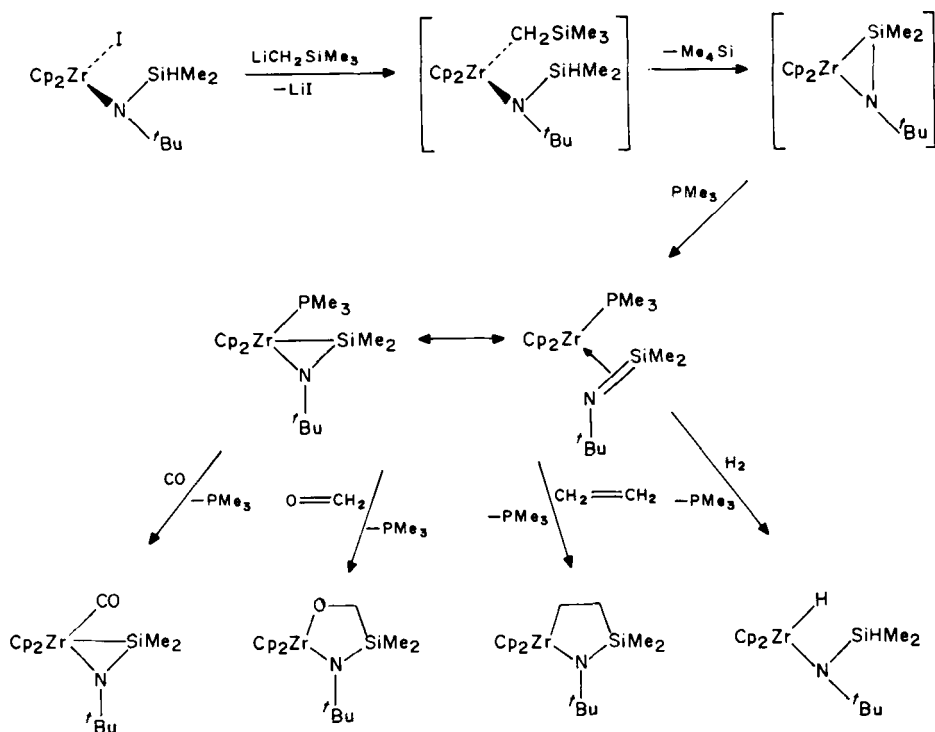


FIGURE 10. ORTEP view of  $\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_2\text{Si}=\text{N}^t\text{Bu})(\text{PMe}_3)$

distances, suggesting the importance of the metallacyclic, Zr(IV) resonance form. Some reactions of this complex are shown in Scheme 23<sup>487</sup>.



SCHEME 23

## \*V. STRUCTURE AND BONDING

### \*A. Structural Information

#### \*1. Metal-silicon bond distances

Much of the attention focused on structural aspects of metal silyl complexes concerns the possible role of d orbitals in  $\pi$ -bonding. For example, *ab initio* and extended Hückel calculations by Lin and Ortiz have addressed this question in search of an explanation for the observed bond shortening in going from  $d^0$   $\text{Cp}^*\text{Ta}(\text{SiMe}_3)\text{Cl}_2$  to  $d^1$   $\text{Cp}^*\text{Ta}(\text{SiMe}_3)(\text{PMe}_3)\text{Cl}_2$  (**13**) (see Table 2). They find no evidence for involvement of the d electron of  $\text{CpTa}(\text{SiH}_3)(\text{PH}_3)\text{Cl}_2$  in bonding with the silyl group. Calculations show that the  $d^0$  complex  $\text{CpTaCl}_3(\text{SiH}_3)$  has a longer Ta—Si bond than  $\text{CpTa}(\text{SiH}_3)(\text{PH}_3)\text{Cl}_2$ , in agreement with experiment. The 'short' bond in the latter complex apparently arises from population of a d-level that possesses Ta—Cl antibonding character. This leads to longer Ta—Cl separations, which allow the Ta—Si distance to decrease in the  $d^1$  complex<sup>488</sup>.

The nature of the Fe—Si bonds in  $\text{Cp}(\text{CO})_2\text{FeSiCl}_3$  and  $\text{Cp}(\text{CO})_2\text{FeSiMe}_3$  has been

probed by HeI and HeII photoelectron spectroscopy. The metal-based ionization energies for the  $\text{SiMe}_3$  complex are similar to those for the analogous  $\text{Cp}(\text{CO})_2\text{FeMe}$  and  $\text{Cp}(\text{CO})_2\text{FeH}$  complexes. The observed d-level splittings convincingly show that in  $\text{Cp}(\text{CO})_2\text{FeSiMe}_3$ , the  $\text{SiMe}_3$  ligand does not stabilize the bonding through  $\pi$  interactions with the metal. However, the  $\pi$ -accepting ability of the  $\text{SiCl}_3$  ligand (involving primarily the  $\text{Si}-\text{Cl}$   $\sigma^*$  orbitals) appears to be slightly better than that of the CN ligand, and about half that of a carbonyl ligand. The short  $\text{Fe}-\text{Si}$  bond in  $\text{Cp}(\text{CO})_2\text{FeSiCl}_3$  (2.21 Å) is due to a combination of  $\pi$ -backbonding and ionic bonding contributions<sup>489</sup>.

A theoretical study by Ziegler and coworkers has sought to compare metal-ligand bond strengths for early and late transition-metal systems. The  $\text{Ti}-\text{L}$  bonds in  $\text{Cl}_3\text{TiL}$  complexes were found to be relatively polar, and  $D(\text{Ti}-\text{L})$  bond strengths (in  $\text{kJ mol}^{-1}$ ) were calculated to be  $\text{OH}$  (453) >  $\text{OMe}$  (427) >  $\text{CN}$  (410) >  $\text{NH}_2$  (365) >  $\text{SH}$  (283) >  $\text{Me}$  (268) >  $\text{H}$  (251) >  $\text{SiH}_3$  (211) >  $\text{PH}_2$  (191). The corresponding bond energies in  $\text{Cl}_3\text{ZrL}$  complexes were 25–50  $\text{kJ mol}^{-1}$  higher, and those for the  $\text{Cl}_3\text{HfL}$  system were an additional 10–20  $\text{kJ mol}^{-1}$  higher. For  $\text{LCo}(\text{CO})_4$ , the  $\text{Co}-\text{L}$  bonds were found to be weaker and less polar than the analogous bonds in  $\text{Cl}_3\text{TiL}$ :  $\text{CN}$  (304) >  $\text{OH}$  (232) >  $\text{H}$  (230) >  $\text{SiH}_3$  (212) >  $\text{SH}$  (169) >  $\text{Me}$  (160) >  $\text{NH}_2$  (146) >  $\text{PH}_2$  (145). This is apparently due primarily to the greater electronegativity for cobalt. Interestingly, the  $\text{Ti}-\text{SiH}_3$  and  $\text{Co}-\text{SiH}_3$  bond energies are predicted to be quite comparable<sup>490</sup>.

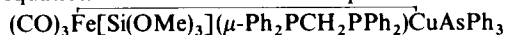
For  $\text{Cp}_2\text{Ti}(\text{H})\text{SiH}_3$ , the  $\text{Ti}-\text{H}$  and  $\text{Ti}-\text{SiH}_3$  bond disruption energies were calculated to be 245.6 and 113.4  $\text{kJ mol}^{-1}$ , respectively<sup>491</sup>.

Table 6 lists selected  $\text{M}-\text{Si}$  distances in late ( $d^n$ , where  $n > 3$ ) transition-metal silyl complexes. Based on the structure of  $[\text{Na}(18\text{-crown-6})][(\text{CO})_5\text{WCH}_3]$ , the  $\text{W}-\text{Si}$  bond in  $[\text{PPN}][(\text{CO})_5\text{WSiMe}_3]$  is about 0.1 Å shorter than would be expected from covalent radii<sup>392</sup>. The  $\text{Fe}-\text{Si}$  separation in  $(\text{dppe})(\text{CO})_2\text{FeH}(\text{SiMe}_3)$  is shorter than that found in *cis*-( $\text{CO})_4\text{Fe}(\text{SiMe}_3)_2$  [2.456(2) Å], probably because of the *trans* effect of the phosphine ligand in the former compound<sup>343</sup>. For  $\text{Cp}(\text{CO})_2\text{FeSiMe}_2\text{SiMe}_2\text{Fe}(\text{CO})_2\text{Cp}$ , the  $\text{Si}-\text{Si}$  distance [2.390(4) Å] is significantly longer than the  $\text{Si}-\text{Si}$  distance found in  $(\text{CO})_2(\text{Me})\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{SiMe}_2-\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{Me})(\text{CO})_2$  [2.341(3) Å], indicating that metal substitution in a disilane weakens the  $\text{Si}-\text{Si}$  bond<sup>497</sup>. Analysis of the bonding parameters in a series of  $(\eta^5\text{-indenyl})(\text{CO})(\text{L})\text{Fe}$ -silyl complexes (entries 16–21, Table 6) led to the conclusion that  $\pi$ -bonding effects between the  $\text{Fe}$  and  $\text{Si}$  atoms are minimal, and that the observed variations in  $\text{Fe}-\text{Si}$  distances can be attributed primarily to steric factors<sup>498</sup>.

Table 7 lists metal-silicon distances that have been determined for early transition-metal and f-metal silyl derivatives. The  $\text{Ti}-\text{Si}$  distances in  $\text{Cp}_2\text{Ti}(\text{SiH}_2\text{Ph})(\text{PEt}_3)$  and  $\text{Cp}_2\text{Ti}(\text{SiHPh}_2)(\text{PMe}_3)$  are similar to the  $\text{Ti}-\text{Si}$  distance observed for  $\text{Cp}_2\text{Ti}(\text{SiMe}_3)\text{Cl}$  [2.67(1) Å, see Table 2], which is consistent with the odd electron on the former two complexes residing in a nonbonding orbital<sup>443</sup>. The large difference between the  $\text{Hf}-\text{Si}$  distances in  $\text{CpCp}^*\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$  and  $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  apparently indicates that the influence of steric factors on  $d^0 \text{M}-\text{Si}$  bonds can be quite dramatic<sup>500</sup>. The  $\text{Re}-\text{Si}$  bond in  $d^0 \text{ReH}_6(\text{SiPh}_3)(\text{PPh}_3)_2$  is significantly shorter than would be predicted by the sum of covalent radii (2.65 Å)<sup>438</sup>.

## \*2. Other structural features

A heterobimetallic silyl complex possessing an  $\eta^2\text{-}\mu_2\text{-SiO}$  bridge has been prepared by the reaction of equation 175. The bimetallic compounds



and

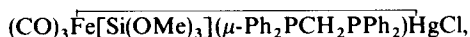


TABLE 6. Selected M—Si distances in late ( $d^n, n > 3$ ) transition-metal silyl complexes

Compound	$d^n$ config	M—Si (Å)	References
1. [PPN] <sup>+</sup> [(CO) <sub>5</sub> WSiMe <sub>3</sub> ] <sup>-</sup>	$d^6$	2.614(2)	392
2. [NEt <sub>4</sub> ] <sup>+</sup> [(CO) <sub>5</sub> WSi(SnMe <sub>3</sub> ) <sub>3</sub> ] <sup>-</sup> (75)	$d^6$	2.652(4)	403
3. ( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> Me)(CO)(Ph <sub>2</sub> P)Mn( $\eta^2$ -H—SiMe <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )	$d^6$	2.457(2)	492
4. (Me <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PMe <sub>2</sub> )Mn[Si(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>	$d^5$	2.643(4), 2.642(3)	493
5. (Ph <sub>2</sub> CO) <sub>2</sub> Mn[Si(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>	$d^5$	2.67(1), 2.64(1)	493
6. Cp(NO—BCl <sub>3</sub> )(PPh <sub>3</sub> )ReSiMe <sub>2</sub> Cl·CH <sub>2</sub> Cl <sub>2</sub>	$d^6$	2.476(3)	457
7. (dppe)(CO) <sub>2</sub> FeH(SiMe <sub>3</sub> )	$d^6$	2.360(2)	343
8. (dppe)(CO)FeH <sub>3</sub> [Si(OEt) <sub>3</sub> ]	$d^4$	2.258(4), 2.246(4), 2.246(4)	344
9. Cp <sub>2</sub> (CO) <sub>2</sub> Fe <sub>2</sub> ( $\mu$ -CO)( $\mu$ -SiH <sup>t</sup> Bu)	$d^6$	2.270(1), 2.272(1)	366
10. (CO) <sub>3</sub> Fe[Si(OMe) <sub>3</sub> ]( $\mu$ -Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> )CuAsPh <sub>3</sub>	$d^8$	2.282(3)	494
11. (CO) <sub>3</sub> Fe[Si(OMe) <sub>3</sub> ]( $\mu$ -Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> )PdCl	$d^8$	2.275(2)	495
12. <i>mer</i> -(CO) <sub>3</sub> (PPh <sub>3</sub> )Fe(SiMePh <sub>2</sub> )(AuPPh <sub>3</sub> )	$d^8$	2.357(3)	401
13. [PPN] <sup>+</sup> [(CO) <sub>3</sub> Fe(PPh <sub>3</sub> )(SiCl <sub>3</sub> )] <sup>-</sup>	$d^8$	2.197(3)	496
14. [PPN] <sup>+</sup> [(CO) <sub>3</sub> Fe[P(OPh) <sub>3</sub> ](SiCl <sub>3</sub> )] <sup>-</sup>	$d^8$	2.206(4)	496
15. Cp(CO) <sub>2</sub> FeSiMe <sub>2</sub> SiMe <sub>2</sub> Fe(CO) <sub>2</sub> Cp	$d^6$	2.375(2)	497
16. ( $\eta^5$ -indenyl)(CO) <sub>2</sub> FeSiMe <sub>3</sub>	$d^6$	2.325(3)	498
17. ( $\eta^5$ -indenyl)(CO)(PPh <sub>3</sub> )FeSiMe <sub>3</sub>	$d^6$	2.339(1), 2.341(1)	498
18. ( $\eta^5$ -indenyl)(CO) <sub>2</sub> FeSiMe <sub>2</sub> SiMe <sub>3</sub>	$d^6$	2.341(2)	498
19. ( $\eta^5$ -indenyl)(CO)(PPh <sub>3</sub> )FeSiMe <sub>2</sub> SiMe <sub>3</sub>	$d^6$	2.354(2)	498
20. ( $\eta^5$ -indenyl)(CO) <sub>2</sub> FeSiMe(SiMe <sub>3</sub> ) <sub>2</sub>	$d^6$	2.365(2)	498
21. ( $\eta^5$ -indenyl)(CO)(PPh <sub>3</sub> )FeSiMe(SiMe <sub>3</sub> ) <sub>2</sub>	$d^6$	2.378(1)	498
22. Cp*(PMe <sub>3</sub> ) <sub>2</sub> RuSi(STol- <i>p</i> ) <sub>3</sub>	$d^6$	2.350(1)	459
23. Cp*(PMe <sub>3</sub> ) <sub>2</sub> RuSi(SnMe <sub>3</sub> ) <sub>3</sub>	$d^6$	2.450(2)	493
24. Cp*(P <sup>t</sup> Pr <sub>3</sub> )RuH <sub>2</sub> [SiMes(H)Cl]	$d^4$	2.302(3)	429b
25. (PPh <sub>3</sub> ) <sub>2</sub> (CO) <sub>2</sub> CoSiMePh <sub>2</sub>	$d^8$	2.368(1)	359
26. Rh <sub>2</sub> ( $\mu$ -SiHPh) <sub>2</sub> (CO) <sub>2</sub> ( $\mu$ -Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub>	$d^{7,a}$	2.347(1), 2.354(2), 2.368(2), 2.335(1)	369
27. Rh <sub>2</sub> ( $\mu$ -SiHEt) <sub>2</sub> (CO) <sub>2</sub> ( $\mu$ -Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub>	$d^{7,a}$	2.363(2), 2.342(2)	370
28. Rh <sub>2</sub> ( $\mu$ -H)(CO) <sub>2</sub> ( $\mu$ -Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> )(Ph <sub>2</sub> PCH <sub>2</sub> PPh- SiEt <sub>2</sub> ) (67)	$d^8$	2.347(3)	370
29. [Si(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> ]RhCO <sup>b</sup>	$d^8$	2.379(5)	350
30. [Si(CH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> ]RhCO <sup>b</sup>	$d^8$	2.398(4)	372
31. (PMe <sub>3</sub> ) <sub>3</sub> RhSiPh <sub>3</sub> (65)	$d^8$	2.317(1)	351
32. (AsPh <sub>3</sub> )(cod)IrH <sub>2</sub> (SiEt <sub>3</sub> )	$d^6$	2.414(2)	362
33. [P( <i>p</i> -Tol) <sub>3</sub> ] <sub>2</sub> (CO)IrH <sub>2</sub> (SiMe <sub>2</sub> Ph)	$d^6$	2.414(2)	364
34. (P <sup>t</sup> Pr <sub>3</sub> ) <sub>2</sub> Ir(H)Cl(SiMeCl <sub>2</sub> )	$d^6$	2.235(5)	389
35. <i>mer</i> -(PMe <sub>3</sub> ) <sub>3</sub> IrCl <sub>2</sub> (SiMeCl <sub>2</sub> )	$d^6$	2.299(5)	388
36. Ir <sub>2</sub> ( $\mu$ -SiPh) <sub>2</sub> H <sub>2</sub> (CO) <sub>2</sub> ( $\mu$ -Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> ·2THF	$d^{7,a}$	2.371(4)	371
37. Ir <sub>2</sub> ( $\mu$ -SiPh) <sub>2</sub> H <sub>2</sub> (CO) <sub>2</sub> ( $\mu$ -Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> ·2THF	$d^{7,a}$	2.343(5), 2.349(5)	371
38. (PMe <sub>3</sub> ) <sub>3</sub> Ni(SiF <sub>3</sub> ) <sub>2</sub>	$d^8$	2.182(4)	406
39. [2,6- <sup>t</sup> Bu <sub>2</sub> NHC <sub>5</sub> H <sub>3</sub> ] <sub>2</sub> <sup>2+</sup> [Ni <sub>2</sub> (SiCl <sub>3</sub> ) <sub>4</sub> ( $\mu$ -Cl) <sub>2</sub> ] <sup>2-</sup>	$d^8$	2.161(3), 2.181(3)	415
40. (2,4,6-Me <sub>3</sub> NC <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> Ni(SiCl <sub>3</sub> ) <sub>2</sub>	$d^8$	2.195(1), 2.208(1)	414
41. <i>trans</i> -(PEt <sub>3</sub> ) <sub>2</sub> Pt(SiMe <sub>3</sub> )Br	$d^8$	2.330(17)	384
42. (dcpe)Pt[SiPh(SiMe <sub>3</sub> ) <sub>2</sub> ]Cl (72)	$d^8$	2.423(2)	402
43. (dppe)Pt(SiH <sup>t</sup> Pr <sub>2</sub> ) <sub>2</sub>	$d^8$	2.378(4), 2.355(3)	482
44. (dppe)PtSiMe <sub>2</sub> OSiMe <sub>2</sub>	$d^8$	2.374(2), 2.373(1)	482
45. <i>cis</i> -(PEt <sub>3</sub> ) <sub>2</sub> Pt(SiH <sub>2</sub> Ph) <sub>2</sub>	$d^8$	2.360(3)	493
46. (PMe <sub>3</sub> ) <sub>3</sub> CuSiPh <sub>3</sub>	$d^{10}$	2.340(2)	409
47. (PMePh <sub>2</sub> )AuSiPh <sub>3</sub>	$d^{10}$	2.354(4)	411
48. (PMePh <sub>2</sub> )AuSi(SiMe <sub>3</sub> ) <sub>3</sub>	$d^{10}$	2.356(2)	411
49. (PMePh <sub>2</sub> ) <sub>2</sub> AuAu(SiPh <sub>3</sub> )Cl	$d^{9,a}$	2.291(2)	412

<sup>a</sup>Assignment of a  $d^n$  configuration is somewhat arbitrary.

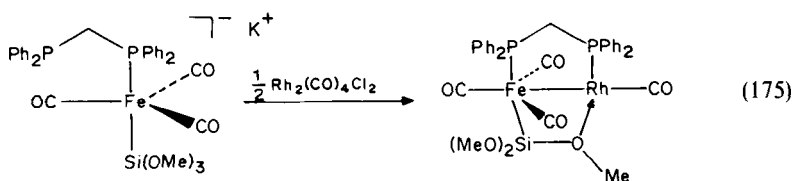
<sup>b</sup>These two structures were solved in different space groups.



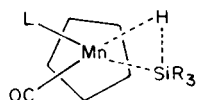
TABLE 7. Selected M—Si distances in early ( $d^n$ ,  $n \leq 3$ ) transition-metal and f-metal silyl complexes

Compound	$d^n$ config	M—Si (Å)	Reference
1. $\text{Cp}_2\text{Sc}[\text{Si}(\text{SiMe}_3)_3](\text{THF})$	$d^0$	2.863(1)	429b
2. $[\text{Li}(\text{DME})_3]^+[\text{Cp}_2\text{Lu}(\text{SiMe}_3)_2]^-$	$d^0f^{14}$	2.888(2)	440
3. $\text{Cp}_2\text{Ti}(\text{SiPh}_2)_2$	$d^0$	2.755(7), 2.765(8)	499
4. $\text{Cp}_2\text{Ti}(\text{SiH}_2\text{Ph})(\text{PEt}_3)$	$d^1$	2.634(5)	434
5. $\text{Cp}_2\text{Ti}(\text{SiHPh}_2)(\text{PMe}_3)$	$d^1$	2.652(1)	434
6. $(\text{Me}_3\text{CO})_3\text{ZrSi}(\text{SiMe}_3)_3$	$d^0$	2.753(4)	403
7. $\text{Cp}_2\text{Zr}[\text{Si}(\text{SnMe}_3)_3]\text{Cl}$	$d^0$	2.772(4)	493
8. $\text{Cp}_2\text{Zr}(\text{SiPh}_3)(\text{H})(\text{PMe}_3)$	$d^0$	2.721(2)	435
9. $\text{CpCp}^*\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$	$d^0$	2.729(3)	500
10. $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$	$d^0$	2.881(4), 2.887(4)	500
11. $\text{ReH}_6(\text{SiPh}_3)(\text{PPh}_3)_2$ ( <b>83</b> )	$d^0$	2.474(4)	438

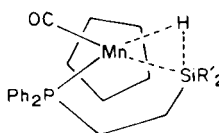
prepared in a similar manner, do not exhibit these  $\eta^2$ - $\mu_2$ - $\text{Si}(\text{OMe})_3$  ligands<sup>494</sup>, but related Fe—Pd and Fe—Pt complexes do<sup>495</sup>.



Complexes with  $\text{M} \cdots \text{H} \cdots \text{Si}$  bridges ( $\eta^2$ -silane ligands) have been reviewed recently<sup>501</sup>. In  $\eta^2$ -silane complexes of the type  $(\eta^2\text{-C}_5\text{H}_4\text{Me})(\text{L})(\text{CO})\text{Mn}(\eta^2\text{-HSiR}_3)$  [ $\text{L} = \text{PR}_3, \text{P}(\text{OR})_3$ ], the L and  $\text{SiR}_3$  groups are 'trans' in the pseudo four-legged piano stool structure (**112**). Use of the chelating ligands  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiR}'_2\text{H}$  ( $\text{R}' = \text{Me}, \text{Ph}$ ) results in a 'cis' arrangement (structure **113**). The properties of **113** ( $\text{R}' = \text{Me}, \text{Ph}$ ) closely resemble those observed for complexes with structure **112**<sup>492</sup>.



(112)



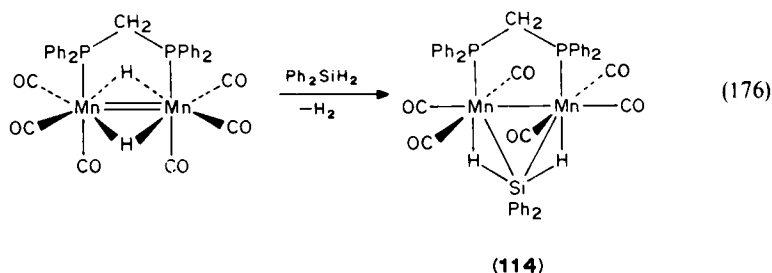
(113)

The bonding in complexes with  $\eta^2$ -silane ligands has been probed by extended Hückel calculations of  $\text{Cp}(\text{CO})_2\text{MnHSiH}_3$ , which gave the following overlap populations: Mn—H (0.44), Mn—Si (0.32), Si—H(bridge) (0.24), Si—H(terminal) (0.72 av). In this model the bonding is described adequately by donation of electron density in the Si—H  $\sigma$ -bond to the metal, with some delocalization of metal  $d_x$  electrons into the antibonding Si—H  $\sigma^*$  orbital. The metal in this case is best described as formally  $d^6$ <sup>502</sup>.

An interesting related study, based on the valence photoelectron spectrum of  $\text{Cp}(\text{CO})_2\text{MnHSiCl}_3$  and supporting Fenske–Hall calculations, provides good evidence for substantial electron flow from the metal to the Si—H  $\sigma^*$  orbital of  $\text{HSiCl}_3$ , resulting in distinct Mn—SiCl<sub>3</sub> and Mn—H bonds and a  $d^4$  Mn(III) center. The Fenske–Hall calculations also show that the metal orbitals used in forming the directed Mn—Si and

Mn—H bonds form an angle of 50–70°, which explains the observed geometry for  $(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnHSiCl}_3$ <sup>503</sup>. As expected, photoelectron experiments with  $(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{PMe}_3)\text{MnHSiCl}_3$  are also consistent with complete oxidative addition of the Si—H bond to the metal, and a d<sup>4</sup> Mn(III) center. However, for  $(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{PMe}_3)\text{MnHSiHPh}_2$ , the bonding is best described as involving coordination of a nearly intact Si—H bond to a formally d<sup>6</sup> Mn(I) center. It was determined that the extent of Si—H bond interaction with the metal is affected more by substitutions on silicon than by substitutions at manganese<sup>504</sup>. Studies with  $(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnHSiR}_3$  ( $\text{SiR}_3 = \text{SiHPh}_2, \text{SiPh}_3, \text{SiFPh}_2$ ) indicate that these complexes may also be described as possessing intact Si—H bonds coordinated to the metal<sup>505</sup>. Contrary to what might be predicted based on electronic factors, there is less donation from the metal center to the Si—H  $\sigma^*$  orbital in  $\text{Cp}^*(\text{CO})_2\text{MnHSiHPh}_2$  than for the analogous Cp and  $(\eta^5\text{-C}_5\text{H}_4\text{Me})$  derivatives. It therefore appears that for  $\text{Cp}^*(\text{CO})_2\text{MnHSiHPh}_2$ , the steric effect of the Cp\* ligand overrides electronic effects in determining the extent of Si—H bond addition<sup>506</sup>.

Reaction of  $\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)$  with diphenylsilane yields a product (114) that is proposed to have two Si—H—Mn interactions, based on spectroscopic data (equation 176)<sup>507</sup>.



Various substituted arenes have been used in the preparation of new  $(\eta^6\text{-arene})(\text{CO})_2\text{Cr}(\eta^2\text{-HSiHPh}_2)$  complexes<sup>508</sup>.

### \*B. Information from NMR Studies

Reporting <sup>29</sup>Si NMR data for transition-metal silyl derivatives is now almost routine. Few trends have yet emerged, and it is often difficult to interpret satisfactorily the meaning of chemical shift data. For example, it has been noted that <sup>29</sup>Si NMR shifts for  $\text{Cp}(\text{CO})_2\text{Fe—SiR}_3$  and  $\text{Cp}(\text{CO})_2\text{Ru—SiR}_3$  derivatives generally occur downfield of those for analogous Me—SiR<sub>3</sub> compounds, whereas for related  $(\text{CO})_5\text{Re—SiR}_3$  complexes the reverse is true<sup>395</sup>. However, <sup>29</sup>Si NMR spectroscopy can prove very useful in transition-metal—silicon chemistry, particularly in cases where coupling constants may be obtained, or where comparisons among closely related systems are possible.

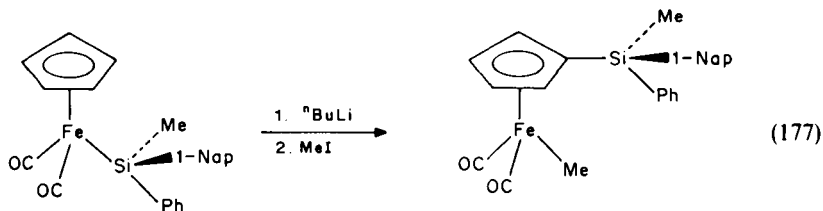
## \*VI. REACTIONS INVOLVING M—SI BONDS

### \*A. Cleavage of M—Si Bonds by Nucleophiles

The rhodium silyls  $\text{Cp}^*\text{RhH}_2(\text{SiR}_3)_2$  ( $\text{SiR}_3 = \text{SiMe}_3, \text{SiEt}_3, \text{SiMe}_2\text{Ph}$ ) are deprotonated by *n*-BuLi to the corresponding anionic complexes  $[\text{Cp}^*\text{RhH}(\text{SiR}_3)_2]^-$ . In contrast,  $\text{Cp}^*\text{RhH}_2(\text{SiEt}_3)_2$  reacts with  $\text{LiBEt}_3\text{H}$  via Rh—Si bond cleavage to give  $[\text{Cp}^*\text{RhH}_2(\text{SiEt}_3)]^-$ , which protonates to give  $\text{Cp}^*\text{RhH}_3(\text{SiEt}_3)$ . The reaction of

$\text{Cp}^*\text{RhH}_2(\text{SiMe}_3)_2$  with  $\text{LiBEt}_3\text{H}$  is more complex, and gives a mixture of  $[\text{Cp}^*\text{RhH}(\text{SiMe}_3)_2]^-$ ,  $[\text{Cp}^*\text{RhH}_3(\text{SiMe}_3)]^-$  and (curiously)  $[\text{Cp}^*\text{RhH}(\text{SiMe}_3)(\text{SiMe}_2\text{Et})]^-$ . It was also noted that  $[\text{Cp}^*\text{RhH}(\text{SiMe}_3)_2]^-$  reacts with  $\text{CO}_2$  to give  $\text{Cp}^*\text{Rh}(\text{CO})(\text{H})\text{SiMe}_3$  and (presumably)  $\text{Me}_3\text{SiO}^-$ <sup>352</sup>.

A well-known reaction of nucleophiles with cyclopentadienyl/silyl complexes involves deprotonation at the Cp ring and subsequent intramolecular migration of the silyl group to the ring. Berryhill and Corriu recently reported a case in which the silyl migration occurs with retention of configuration at silicon (equation 177)<sup>509</sup>. Deprotonation of *cis*- $\text{Cp}(\text{CO})_2\text{ReH}(\text{SiPh}_3)$  by  $\text{LiCH}_2\text{CMe}_3$  at  $-78^\circ\text{C}$  gives  $\text{Li}^+[(\eta^5\text{-C}_5\text{H}_4\text{SiPh}_3)(\text{CO})_2\text{ReH}]^-$ , which undergoes protonation at low temperature to give *cis*- $(\eta^5\text{-C}_5\text{H}_4\text{SiPh}_3)(\text{CO})_2\text{ReH}_2$ <sup>510</sup>. Silyl migrations to deprotonated Cp rings have also been observed for  $\text{Cp}(\text{CO})_2\text{RuSiMe}_3$ <sup>395</sup>,  $\text{Cp}(\text{CO})_2\text{FeSiHPh}_2$ <sup>419</sup> and  $\text{Cp}(\text{CO})_2\text{FeSiMe}_2\text{SiMe}_2\text{Fe}(\text{CO})_2\text{Cp}^*$ <sup>497</sup>. When  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{SiMe}_2\text{SiMe}_3$  is treated with *n*-BuLi and then MeI, rearrangement of the migrating group occurs to give  $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{SiMe}_3)(\text{CO})_2\text{FeMe}$ <sup>511</sup>. Reaction of  $\text{Cp}(\text{NO})(\text{PPh}_3)\text{ReSiMe}_3$  with *n*-BuLi/Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> gives  $(\eta^5\text{-C}_5\text{H}_4\text{Li})(\text{NO})(\text{PPh}_3)\text{ReSiMe}_3$ , which rapidly rearranges at  $-78^\circ\text{C}$  to  $\text{Li}^+[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{NO})(\text{PPh}_3)\text{Re}]^-$ . The anionic complex  $\text{Li}^+[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{SiMe}_2\text{Cl})(\text{NO})(\text{PPh}_3)\text{Re}]^-$ , prepared similarly, eliminates LiCl upon warming to give the disilametalacycle  $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)(\text{NO})(\text{PPh}_3)\text{ReSiMe}_2$ <sup>396</sup>. For  $\text{Cp}(\text{CO})(\text{NO})\text{ReMR}_3$  (M = Si, Ge, Sn) complexes, it was found that migration of SiMe<sub>3</sub>, but not GePh<sub>3</sub> or SnPh<sub>3</sub>, could be induced<sup>512</sup>.



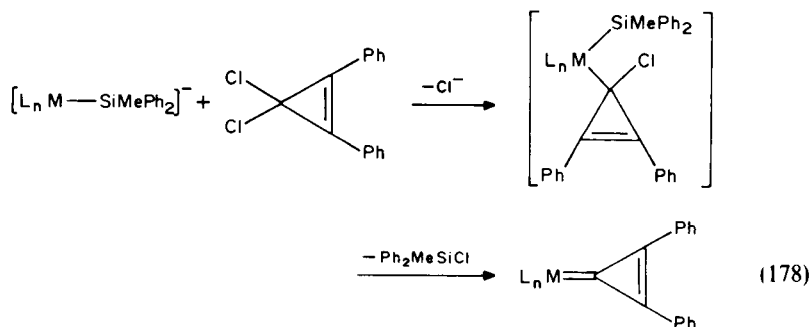
### \*B. Cleavage of M—Si Bonds by Electrophiles

The W—Si bond of  $[\text{NEt}_4][(\text{CO})_5\text{WSi}(\text{SnMe}_3)_3]$  is cleaved by  $\text{I}_2$  and  $\text{ICl}$  to yield  $[\text{NEt}_4][(\text{CO})_5\text{WI}]$  and  $\text{ISi}(\text{SnMe}_3)_3$  or  $\text{ClSi}(\text{SnMe}_3)_3$ , respectively. Two equivalents of HCl are required to effect complete conversion of  $[\text{NEt}_4][(\text{CO})_5\text{WSi}(\text{SnMe}_3)_3]$  to  $[\text{NEt}_4][(\text{CO})_5\text{WCl}]$  and  $\text{ClSi}(\text{SnMe}_3)_3$ . This reaction probably proceeds via initial W—Si bond cleavage to give  $\text{ClSi}(\text{SnMe}_3)_3$  and  $[\text{NEt}_4][(\text{CO})_5\text{WH}]$ , which reacts rapidly with HCl to give  $\text{H}_2$  and the observed tungsten product<sup>403</sup>.

Oxidative cleavage of the Zr—Si bond in  $\text{Cp}_2^*\text{Zr}(\text{SiHMe}_2)\text{Me}$  with  $\text{AgOTf}$  affords  $\text{Cp}_2^*\text{Zr}(\text{Me})\text{OTf}$ ,  $\text{Mes}_2\text{HSiSiHMe}_2$ ,  $\text{Mes}_2\text{SiH}(\text{OTf})$  and  $\text{Mes}_2\text{SiHMe}$ <sup>425</sup>.

### \*C. Cleavage of M—Si Bonds by Other Reagents

Schubert and coworkers have devised a novel approach to the synthesis of metal—element double bonds based on cleavage of the M—Si bond in anionic silyl complexes<sup>513–516</sup>. The utility of this method is demonstrated by the carbene complex synthesis of equation 178 [ $\text{L}_n = (\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}$ ,  $(\text{CO})_3(\text{PPh}_3)\text{Fe}$ ]<sup>513</sup>. Analogous 1,2-eliminations of  $\text{Ph}_2\text{MeSiX}$  have been used to obtain  $(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}(\text{EPh}_3)$  (E = As, Sb) complexes from  $\text{Ph}_3\text{AsCl}_2$  and  $\text{Ph}_3\text{SbBr}_2$ , respectively. The reaction of  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnSiMePh}_2]^-$  with  $\text{MesPCl}_2$  affords the dinuclear phosphinidene complex  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}]_2\text{PMes}$ <sup>514</sup>.



The most common M—Si bond cleavage process is reductive elimination of a silyl group with another ligand, often induced by attack of a reagent on the metal center. For example, hydrosilane (HSiR<sub>3</sub>) eliminations from L<sub>n</sub>M(H)(SiR<sub>3</sub>) complexes are frequently affected by incoming two-electron ligands<sup>360,413,517</sup>. Elimination of HSiMe<sub>3</sub> from (CO)<sub>3</sub>(PPh<sub>3</sub>)Fe(H)SiMe<sub>3</sub> or (CO)<sub>2</sub>(dppe)Fe(H)SiMe<sub>3</sub> occurs upon addition of HSnR<sub>3</sub> to afford *mer*-(CO)<sub>3</sub>(PPh<sub>3</sub>)Fe(H)SnR<sub>3</sub> and *cis, cis*-(CO)<sub>2</sub>(dppe)Fe(H)SnR<sub>3</sub> complexes, respectively. Addition of PPh<sub>3</sub> to *mer*-(CO)<sub>3</sub>(PPh<sub>3</sub>)Fe(SnMe<sub>3</sub>)SiMePh<sub>2</sub> induces elimination of the siloxy stannane Ph<sub>2</sub>MeSiOSnMe<sub>3</sub><sup>518</sup>.

A silicon-carbon bond-forming reductive elimination is observed upon addition of methyl iodide to (PMe<sub>3</sub>)<sub>3</sub>RhSiPh<sub>3</sub> (**65**) (see also equation 100). The presumed intermediate, (PMe<sub>3</sub>)<sub>3</sub>Rh(Me)(I)SiPh<sub>3</sub>, loses MeSiPh<sub>3</sub> to generate (PMe<sub>3</sub>)<sub>3</sub>RhI, which is trapped by a second equivalent of the MeI to give *mer*-(PMe<sub>3</sub>)<sub>3</sub>I<sub>2</sub>RhMe<sup>351</sup>. Rare examples of disilane reductive elimination have recently been described for bis(silyl) complexes of the types (PR'<sub>3</sub>)<sub>2</sub>Pd(SiR<sub>3</sub>)<sub>2</sub><sup>358</sup> and (PR'<sub>3</sub>)<sub>2</sub>Pt(SiR<sub>3</sub>)<sub>2</sub><sup>449</sup>. In the latter study, it was found that clean disilane formation was promoted by addition of free phosphine, apparently because the added phosphine can act to block competing redistribution processes<sup>449</sup>.

The cleavage of d<sup>0</sup> M—Si bonds via σ-bond metathesis reactions (see equations 68 and 150) can occur with a variety of substrates including H—H<sup>431</sup>, R<sub>3</sub>Si—H<sup>431</sup> and R<sub>3</sub>Sn—H<sup>519</sup>.

The silyliron porphyrin complex (TPP)FeSiMe<sub>3</sub> adds to propylene oxide or tetrahydrofuran to give ring-opened siloxyalkyliron(III) derivatives<sup>404</sup>. This ring-opening chemistry has been exploited with (CO)<sub>5</sub>MnSiR<sub>3</sub> derivatives to develop syntheses to β-hydroxycarbonyl, spiroketal lactone and cyclopentenone derivatives<sup>520</sup>.

#### \*D. Insertion Reactions

There has been steady progress in defining factors that influence the reactivity of M—Si bonds toward insertions of unsaturated substrates. This chemistry is far from being developed to its full potential, particularly with regard to catalytic applications.

##### \*1. Insertion of alkenes

The insertion reactions of ethylene with CpCp\*Zr[Si(SiMe<sub>3</sub>)<sub>3</sub>]Cl and Cp\*Cl<sub>2</sub>MSi(SiMe<sub>3</sub>)<sub>3</sub> (**40**, M = Zr; **42**, M = Hf) have been reported (see equation 79). The insertion product **41** was characterized by X-ray crystallography as the dimer [Cp\*Cl<sub>2</sub>ZrCH<sub>2</sub>CH<sub>2</sub>Si(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub><sup>521</sup>.

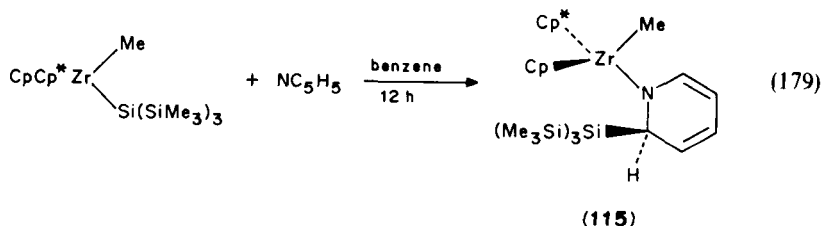
Seitz and Wrighton have observed the formation of (CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)CoSiEt<sub>3</sub> from ethylene and photochemically generated (CO)<sub>3</sub>CoSiEt<sub>3</sub> at 210 K in a methylocyclohexane matrix. Upon warming, reactions ensued to give Et<sub>3</sub>SiCH=CH<sub>2</sub> and (CO)<sub>4</sub>CoCOC<sub>2</sub>H<sub>5</sub>. These results are consistent with migratory insertion of ethylene into the Co—Si bond, followed

by  $\beta$ -hydrogen elimination of the vinylsilane, and trapping of  $(\text{CO})_3\text{CoH}$  by CO and ethylene to give  $(\text{CO})_4\text{CoCOC}_2\text{H}_5$ <sup>522</sup>. Analysis of the ionization energies for  $\text{Cp}(\text{CO})_2\text{FeR}$  ( $\text{R} = \text{H}, \text{Me}, \text{SiMe}_3$ ) complexes indicates that ethylene insertion is favored more for the  $\text{Fe}-\text{SiMe}_3$  bond than for the  $\text{Fe}-\text{H}$  bond<sup>489</sup>. The reaction of  $(\text{PMe}_3)_3\text{RhSiPh}_3$  with ethylene to produce  $\text{Ph}_3\text{SiCH}=\text{CH}_2$  probably proceeds via ethylene insertion into the  $\text{Rh}-\text{Si}$  bond<sup>351</sup>. Generally speaking, it appears that olefin insertions into  $\text{M}-\text{Si}$  bonds are more favorable than was previously anticipated.

### \*3. Insertion of nitriles and pyridine

The zirconium silyl complex  $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$  reacts with nitriles  $\text{RCN}$  ( $\text{R} = \text{Me}, \text{CH}=\text{CH}_2, \text{Ph}$ ) to form azomethine derivatives  $\text{CpCp}^*\text{Zr}[\text{N}=\text{C}(\text{R})\text{Si}(\text{SiMe}_3)_3]\text{Me}$ . Interestingly, analogous insertion reactions were not observed for the closely related complexes  $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$ ,  $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  and  $\text{CpCp}^*\text{ZrMe}_2$ , although  $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$  appeared to react very slowly with  $\text{MeCN}$  to give an insertion product<sup>523</sup>.

Pyridine reacts with  $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$  to give the unusual insertion product **115** (equation 179). The complex  $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$  does not add to pyridine<sup>523</sup>.



### \*5. Insertion of carbon monoxide and isocyanides

The reaction of  $\text{Cp}_2\text{Sc}[\text{Si}(\text{SiMe}_3)_3](\text{THF})$  with carbon monoxide gives rise to  $\text{CO}-\text{CO}$  coupling and ketene-derived products as was observed in the carbonylation of  $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$  (see Schemes 8 and 9). In methyltetrahydrofuran, the ketene adduct **116** (Scheme 24) is produced. Dissociation of the Lewis base quantitatively forms **117**, the dimer of the ketene complex  $\text{Cp}_2\text{ScOC}[\text{Si}(\text{SiMe}_3)_3]\text{CO}$ <sup>429a</sup>.

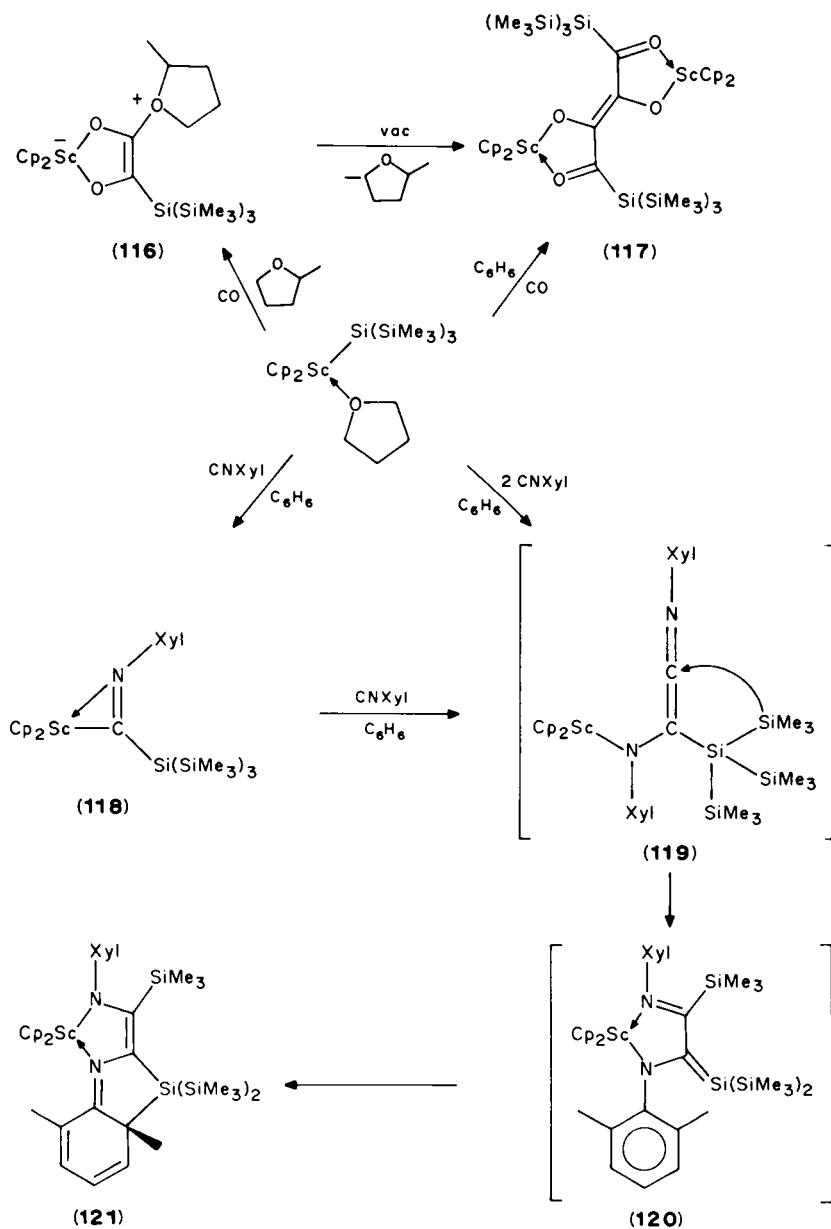
The scandium silyl complex reacts with  $\text{CNXyl}$  to afford an isolable monoinsertion product, the  $\eta^2$ -iminosilaacyl **118**. Coupling with a second equivalent of  $\text{CNXyl}$  occurs to give **121**, the structure of which was established by single-crystal X-ray diffractometry. Apparently,  $\text{CNXyl}$  adds to **118** to produce the intermediate ketenimine **119**, which undergoes migration of a trimethylsilyl group to the  $\alpha$ -carbon of the ketenimine ligand. The resulting structure, **120**, possesses a reactive  $\text{Si}=\text{C}$  double bond which adds to an adjacent xylyl ring<sup>429a</sup>.

### 6. Insertion of other unsaturated substrates

The silyl complex  $[\text{PPN}][(\text{CO})_5\text{WSiMe}_3]$  does not react with  $\text{CO}_2$ ,  $\text{CS}_2$  or benzaldehyde, but does insert  $\text{SO}_2$  to give a sulfinate-*S* complex<sup>392</sup>.

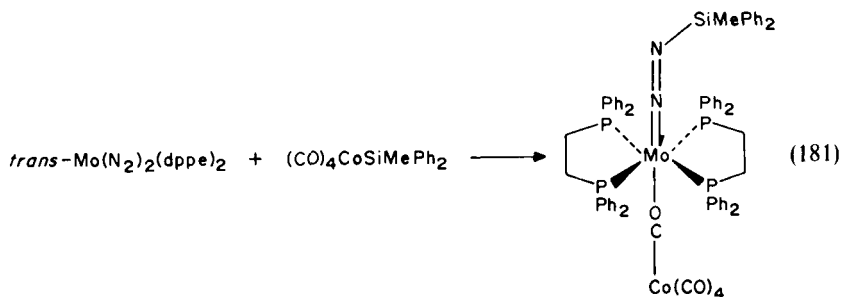
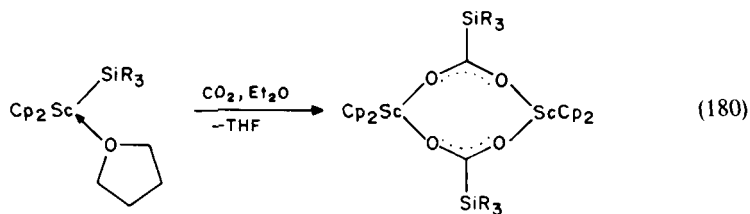
Examples of  $\text{CO}_2$  insertion into transition-metal-silicon bonds were recently reported for scandium silyls [equation 180,  $\text{SiR}_3 = \text{Si}(\text{SiMe}_3)_3, \text{Si}^i\text{BuPh}_2$ ]. The insertion products are dimeric silanecarboxylate complexes, as determined by X-ray crystallography<sup>524</sup>.

The reaction of equation 181 involves the intermolecular migration of a silyl group from one metal to the dinitrogen ligand of another. The structure of the resulting



SCHEME 24

silyldiazene complex, with a  $\mu$ -isocarbonyl ligand, was established by X-ray crystallography. This bimetallic system therefore gives rise to an unusual mode for  $\text{N}_2$  activation<sup>525</sup>.

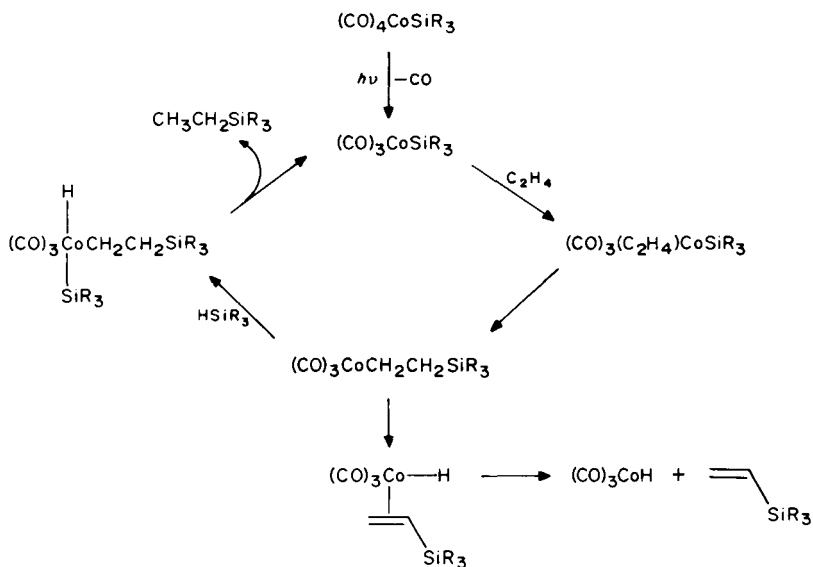


### \*E. Catalytic Reactions

#### \*1. Hydrosilylations

Recent reviews covering the hydrosilylation reaction have been published<sup>526,527</sup>.

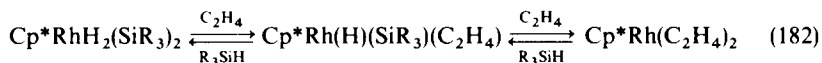
Evidence in support of a hydrosilylation mechanism (Scheme 25) involving migratory insertion of alkene into a M—Si bond (cf. Scheme 11) has been observed by matrix



SCHEME 25

isolation studies. The cobalt silyl  $(\text{CO})_4\text{CoSiEt}_3$ , an efficient hydrosilylation catalyst under irradiation, photochemically loses CO and binds ethylene to form  $(\text{CO})_3(\text{C}_2\text{H}_4)\text{-CoSiEt}_3$  in methylcyclohexane at 210 K. Upon warming, this species appears to react via  $(\text{CO})_3\text{CoCH}_2\text{CH}_2\text{SiEt}_3$  to give  $(\text{CO})_4\text{CoCOC}_2\text{H}_5$  and  $\text{Et}_3\text{SiCH}=\text{CH}_2$ . Insertion of ethylene into the Co—Si bond was rate-limiting. Finally, a precedent for the last two reactions in the catalytic cycle of Scheme 25 was observed in the reaction of  $(\text{CO})_4\text{CoMe}$  with  $\text{Me}_3\text{SiH}$ , which gave  $(\text{CO})_4\text{CoSiMe}_3$  and  $\text{CH}_4$  (not  $\text{SiMe}_4$ , as would be predicted by the Chalk–Harrod mechanism)<sup>522</sup>. Another conversion that appears to involve alkene insertion into a M—Si bond as a key step is the  $\text{Ru}_3(\text{CO})_{12}$ -catalyzed reaction of  $\text{Me}_3\text{SiCH}=\text{CH}_2$  with  $\text{Et}_3\text{SiH}$  to give both  $\text{Me}_3\text{SiCH}=\text{CHSiMe}_3$  and  $\text{Me}_3\text{SiCH}=\text{CHSiEt}_3$ <sup>528</sup>.

Probable intermediates in the conversion of ethylene and  $\text{Et}_3\text{SiH}$  to a 3:1 mixture of  $\text{Et}_3\text{SiCH}=\text{CH}_2$  and  $\text{Et}_4\text{Si}$ , catalyzed by  $\text{Cp}^*\text{RhH}_2(\text{SiEt}_3)_2$  or  $\text{Cp}^*\text{Rh}(\text{C}_2\text{H}_4)_2$ , have been isolated. These alkene–hydride–silyl species  $\text{Cp}^*\text{Rh}(\text{H})(\text{SiR}_3)(\text{C}_2\text{H}_4)$  are formed by the equilibria of equation 182. Only in the case of  $\text{Cp}^*\text{RhH}[\text{Si}(\text{OEt})_3](\text{C}_2\text{H}_4)$  was this type



of complex isolated free of other components in the equilibrium. Complex  $\text{Cp}^*\text{RhH}(\text{SiEt}_3)(\text{C}_2\text{H}_4)$  appeared to be a relatively stable catalytic intermediate<sup>529</sup>. In related studies, it was shown that  $\text{CpRh}(\text{C}_2\text{H}_4)_2$  reacted with  $\text{R}_3\text{SiH}$  ( $\text{R} = \text{Me}, \text{Et}$ ) upon photolysis to yield  $\text{CpRhH}(\text{SiR}_3)(\text{C}_2\text{H}_4)$ ,  $\text{CpRhH}_2(\text{SiR}_3)_2$ ,  $\text{C}_2\text{H}_6$  and  $\text{R}_4\text{Si}$ <sup>530</sup>.

Kinetic studies of hydrosilylation reactions catalyzed by  $\text{RhCl}(\text{cod})_2/\text{Ph}_2\text{PSiMe}_2\text{-OSiMe}_2\text{PPh}_2$  indicate that the mechanism involves initial replacement of phosphine by alkene, followed by oxidative addition of silane<sup>531</sup>.

The Ir(I) complex  $[\eta^2\text{-C}(\text{Ph}_2\text{PO})_3]\text{Ir}(\text{C}_2\text{H}_4)_2$  adds silanes to give, sequentially,  $[\eta^3\text{-C}(\text{Ph}_2\text{PO})_3]\text{IrH}(\text{SiR}_3)(\text{C}_2\text{H}_4)$  and then  $[\eta^3\text{-C}(\text{Ph}_2\text{PO})_3]\text{IrH}_2(\text{SiMePh}_2)_2$  ( $\text{SiR}_3 = \text{SiPh}_3, \text{SiMePh}_2$ ). All of these iridium complexes catalyze the *anti*-addition of silanes to alkynes, possibly by a mechanism involving insertion of alkyne into an Ir—Si bond<sup>532</sup>.

The complex *cis*- $\text{PtCl}_2(\text{CH}_2=\text{CHPh})_2$  is a catalyst precursor for the hydrosilylation of alkenes, alkynes and carbonyls, and for alcoholysis of hydrosilanes. The hydrosilylation of styrene appears to proceed via reduction of the platinum species to  $\text{Pt}(\text{CH}_2=\text{CHPh})_3$ , which is relatively stable<sup>533</sup>. Kinetic studies support a mechanism involving  $\text{Et}_3\text{SiH}$  addition to the latter complex to form  $(\text{PhCH}=\text{CH}_2)\text{Pt}(\text{H})(\text{SiEt}_3)$  or  $(\text{PhCH}=\text{CH}_2)\text{Pt}(\eta^2\text{-H}-\text{SiEt}_3)$ , which then undergoes hydrogen migration giving  $(\text{PhCH}=\text{CH}_2)_n\text{Pt}(\text{CH}_2\text{CH}_2\text{Ph})(\text{SiEt}_3)$ . Reductive elimination of  $\text{Et}_3\text{SiCH}_2\text{CH}_2\text{Ph}$  then regenerates an active  $\text{Pt}(0)$  complex<sup>534</sup>. An interesting proposal based on direct hydrogen migration from an  $\eta^2\text{-H}-\text{SiCl}_3$  ligand to coordinated vinylsilane has been put forth to explain the hydrosilylation of  $\text{Cl}_3\text{SiCH}=\text{CH}_2$  as catalyzed by palladium phosphine complexes<sup>391</sup>.

A key investigation into platinum-catalyzed hydrosilylations shows that the reactions involve reduction of platinum catalyst precursors [e.g.  $(\text{cod})\text{PtCl}_2$ ] to colloidal platinum by the hydrosilane. These platinum colloids are the active catalysts<sup>535-538</sup>. More recent observations with this heterogeneous system have resulted in the postulation of a very unusual hydrosilylation mechanism. It is proposed that adsorption of silane onto the platinum surface (which is activated by binding of  $\text{O}_2$  as a cocatalyst) occurs via  $\eta^2\text{-H}-\text{Si}$  coordination of the hydrosilane. The hydrosilylation product then arises from *direct nucleophilic attack* of alkene onto the coordinated H—Si bond. In support of this, it was noted that electron-rich alkenes and electron-poor silanes are the best substrates for the reaction<sup>538</sup>. Note, however, that these substituent effects are not necessarily inconsistent with a more traditional mechanism.

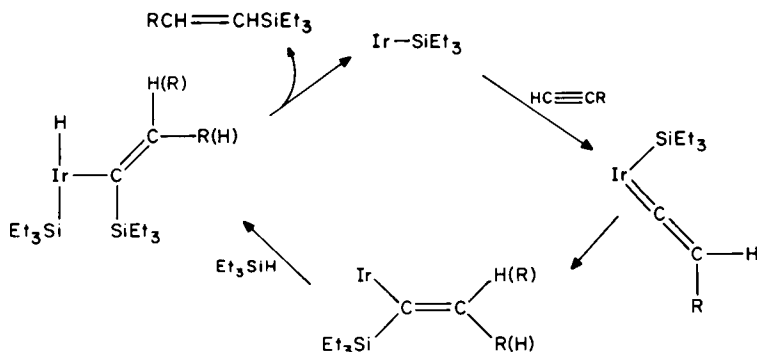
An interesting observation has been made for the  $(\text{Ph}_3\text{P})_3\text{RhCl}$ -catalyzed



hydrosilylation of ketones, alkenes and alkynes with  $\text{Me}_2\text{HSiCH}_2\text{CH}_2\text{SiHMe}_2$ . Only monohydrosilylation products  $\text{Me}_2\text{HSiCH}_2\text{CH}_2\text{SiXMe}_2$  (X = alkoxy, alkyl, vinyl) are formed. Also, the rates of these hydrosilylations are greatly increased over those for analogous reactions with monosilanes, suggesting the possibility that chelation of  $\text{Me}_2\text{HSiCH}_2\text{CH}_2\text{SiHMe}_2$  to the metal somehow enhances the catalysis<sup>539</sup>.

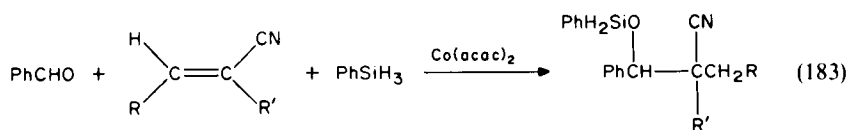
Clearly much research is needed to catalogue and define the regiochemistry of hydrosilylations as a function of metal, ligand set, substrate substituents and reaction conditions<sup>540,541</sup>. The platinum-catalyzed intramolecular hydrosilylation of  $\text{Me}_2\text{HSi}(\text{CH}_2)_n\text{SiMe}_2\text{C}\equiv\text{CR}$  (R = H, Ph;  $n = 2, 3$ ) gives predominantly exocyclic alkene products<sup>542</sup>. Hydrosilylation of 2-methyl-1-butene, 2-methyl-2-butene or 3-methyl-1-butene with  $\text{R}_3\text{SiH}$ , catalyzed by (cod)(cot)Ru, gave the same alkylsilane product, 3-methyl-1-trialkylsilyl-2-butene<sup>543</sup>. The search for useful asymmetric hydrosilylation reactions that produce high optical yields continues to be an active pursuit<sup>544-549</sup>.

It has been noted that hydrosilylations of alkynylsilanes can lead (in addition to the usual addition products) to new alkynylsilanes via transfer of silyl groups. For example, the platinum-catalyzed reaction of  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  with  $\text{C}_6\text{H}_{13}\text{Me}_2\text{SiH}$  gives  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_2\text{C}_6\text{H}_{13}$  and  $\text{C}_6\text{H}_{13}\text{Me}_2\text{SiC}\equiv\text{CSiMe}_2\text{C}_6\text{H}_{13}$  among other products<sup>550</sup>. The reaction of 1-hexyne with  $\text{Et}_3\text{SiH}$ , catalyzed by iridium complexes, gave *cis*- $\text{C}_4\text{H}_9\text{CH}=\text{CHSiEt}_3$ , *trans*- $\text{C}_4\text{H}_9\text{CH}=\text{CHSiEt}_3$ ,  $\text{C}_4\text{H}_9\text{C}\equiv\text{CSiEt}_3$  and  $\text{C}_4\text{H}_9\text{CH}=\text{CH}_2$ . The alkynylsilane may form by reductive elimination from an intermediate  $\text{IrH}(\text{SiEt}_3)(\text{C}\equiv\text{CC}_4\text{H}_9)$  complex. It was suggested that the vinylsilanes might arise from the reactions in Scheme 26<sup>551</sup>.



SCHEME 26

A new type of catalyst for the hydrosilylation of ketones is derived from the titanium compound  $\text{Cp}_2\text{TiPh}_2$ <sup>552</sup>. Also, bis(diketonato)cobalt(II) complexes have been used to catalyze the coupling reaction shown in equation 183<sup>553</sup>.



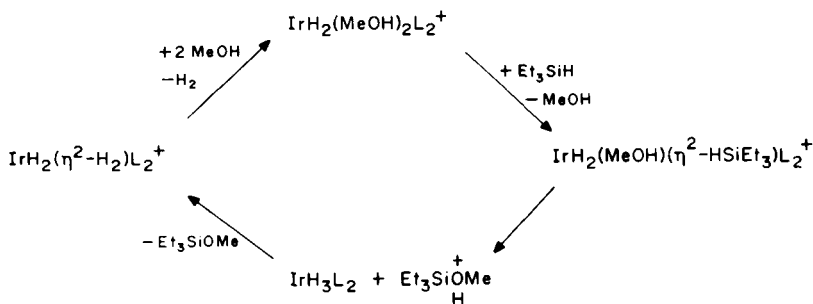
Hydrosilylation of iron acyl complexes by secondary silanes, using  $(\text{PPh}_3)_3\text{RhCl}$  as the catalyst, provides useful routes to  $\alpha$ -siloxy alkyl derivatives of the type  $\text{Cp}(\text{CO})_2\text{FeCHR}(\text{OSiHR}')_2$ <sup>554,555</sup>. Under similar conditions phenylsilane reduces  $\text{Cp}(\text{CO})_2\text{FeCOR}$  (R = Me, Ph) to the corresponding  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{R}$  (R = Me, Ph)

derivatives<sup>554</sup>. Analogous reactions have been observed for manganese and molybdenum complexes<sup>555</sup>. The uncatalyzed, thermal reaction of  $\text{Cp}(\text{CO})_2\text{FeR}$ ,  $\text{Cp}(\text{CO})_2\text{FeCOR}$  or  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCOR}$  with  $\text{HMMe}_3$  ( $\text{M} = \text{Si}, \text{Sn}$ ) gave  $\text{RCH}_2\text{OMMe}_3$  and  $\text{Cp}(\text{CO})\text{FeH}(\text{MMe}_3)_2$ <sup>556</sup>.

## \*2. Dehydrocoupling reactions involving hydrosilanes

Transition-metal catalyzed reactions of this type have been reviewed recently<sup>557</sup>.

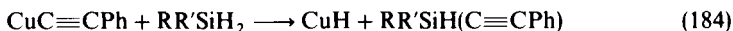
The alcoholysis of hydrosilanes (equation 103,  $\text{X} = \text{OR}$ ) is catalyzed by very active cationic iridium complexes of the type  $[\text{IrH}_2\text{S}_2\text{L}_2]^+$  ( $\text{S} = \text{THF}, \text{MeOH}, \text{H}_2\text{O}, \text{Me}_2\text{CO}$ ;  $\text{L} = \text{PPh}_3$ ). A mechanistic study provided the rate law:  $\text{rate} = k_{\text{obsd}} [\text{catalyst}][\text{Et}_3\text{SiH}]/[\text{MeOH}]$ , and indicated that  $\eta^2$ -silane complexes were important intermediates. The catalytic cycle in Scheme 27 was proposed. A key step is the elimination of  $\text{Et}_3\text{SiOHMe}^+$ , which is thought to involve intramolecular nucleophilic attack of methanol onto the  $\eta^2$ -H—SiEt<sub>3</sub> ligand. Support for this process comes from spectroscopic characterization of the bis( $\eta^2$ -silane) complex  $[\text{IrH}_2(\eta^2\text{-HSiEt}_3)_2(\text{PPh}_3)_2]\text{SbF}_6$ . The complex  $[\text{IrH}_2(\eta^4\text{-Et}_2\text{HSiSiHEt}_2)(\text{PPh}_3)_2]\text{SbF}_6$ , with a chelating silane ligand, was also prepared in solution<sup>558</sup>. Further evidence to suggest that transition-metal centers mediate dehydrocoupling reactions via  $\eta^2$ -silane complexes comes from a recent report that describes the use of  $(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_2\text{Cr}(\eta^2\text{-H—SiHPh}_2)$  as a catalyst for the dehydrocoupling of  $\text{Ph}_2\text{SiH}_2$  with water, amines and thiols<sup>559</sup>.



SCHEME 27

Dehydrocoupling reactions of Si—H with N—H groups has attracted attention as a route to polysilazanes. The best catalysts for reactions of this type appear to be simple palladium salts [e.g.  $\text{PdCl}_2$  and  $\text{Pd}(\text{OAc})_2$ ] and  $\text{Ru}_3(\text{CO})_{12}$ <sup>560-562</sup>.

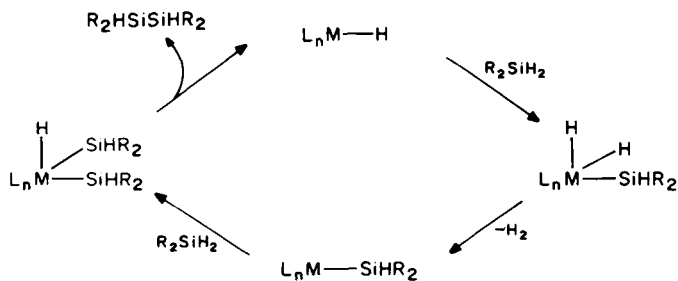
Examples of metal-catalyzed dehydrogenative condensations of hydrosilanes with hydrocarbons include the dehydrogenative hydrosilylations of alkenes and alkynes considered previously (Section VI.E.1). A  $\text{CuCl}/\text{amine}$  catalyst cross-couples primary or secondary silanes with ethynyl derivatives. For example, depending on reaction conditions,  $\text{PhSiH}_3$  and  $\text{PhC}\equiv\text{CH}$  can be dehydrogenatively coupled to give  $\text{PhSiH}_2(\text{CCPh})_2$ ,  $\text{PhSiH}(\text{CCPh})_2$  or  $\text{PhSi}(\text{CCPh})_3$ . High molecular weight polymers were obtained with 1,3-diethynylbenzene and  $\text{PhSiH}_3$  or  $\text{PhMeSiH}_2$ . The steps shown in equations 184 and 185 were suggested to account for the catalysis<sup>563</sup>.



Under irradiation,  $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$  catalyzes the condensation of benzene with  $\text{Et}_3\text{SiH}$  to produce  $\text{Et}_3\text{SiPh}$  (376% yield based on Rh) and hydrogen. A similar reaction

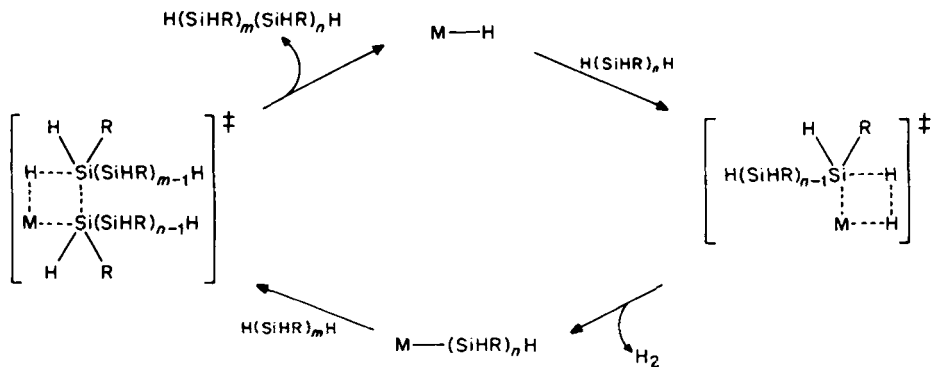
between benzene and  $\text{Me}_3\text{SiSiMe}_3$  gave  $\text{PhSiMe}_3$  (323% yield based on Rh). Mechanisms featuring oxidative addition/reductive elimination cycles were proposed<sup>564</sup>.

An overview of mechanistic considerations for transition-metal catalyzed dehydrogenative silane coupling reactions has recently appeared<sup>450</sup>. Although mechanisms based on silylene complexes seem plausible in some cases, little evidence exists to support their involvement in known reactions. In particular, a mechanism based on silylene intermediates seems highly unlikely for the dehydrogenative condensation of  $\text{PhMe}_2\text{SiH}$  to  $(\text{PhMe}_2\text{Si})_2$ , which is catalyzed by platinum complexes<sup>565</sup>. For late transition-metal catalysts, a more likely mechanism appears to be one based on oxidative addition/reductive elimination cycles such as the one shown in Scheme 28. Precedents for each step in this cycle exist in stoichiometric reactions<sup>450</sup>.



SCHEME 28

A mechanism based on addition/elimination cycles would seem to be less likely for reactions catalyzed by the early ( $d^0$ ) metal catalysts. For these metals, mechanisms involving silylene complexes have been considered<sup>566,567</sup>, but discounted based on the fact that the secondary germane  $\text{Ph}_2\text{GeH}_2$  is dehydrocoupled to oligogermanes by  $\text{Cp}_2\text{TiMe}_2$ <sup>568</sup>. Investigations with zirconium and hafnium catalysts suggest that a mechanism consisting of concerted,  $\sigma$ -bond metathesis steps (Scheme 29) operates for  $d^0$  metal catalysts. Considerable support for this mechanism has been accumulated, including kinetic data, observation of intermediates and confirmation of the step-growth nature of polymer formation. The real catalysts for these polymerizations therefore appear to be coordinatively unsaturated  $d^0$  metal hydride derivatives. Metallocene derivatives with Zr—Si or Hf—Si bonds provide active catalyst precursors for the



SCHEME 29

dehydrocoupling of primary silanes to polysilanes. Indications are that M—Si bonded species are converted more rapidly to the active catalysts than are analogous M—C bonded complexes<sup>450,569-572</sup>. It has also been determined that for the slower catalysts, the major chain propagation pathway involves reaction of the metal hydride with a monosilane (in Scheme 29,  $n = 1$ )<sup>570-572</sup>. The reversibility of the Si—Si bond-forming reactions are emphasized by the observation that linear polysilanes (with degree of polymerization *ca* 10) are converted to cyclic hexasilanes by the catalyst<sup>566</sup>.

The catalytic activity of a variety of early transition-metal and actinide metallocene derivatives in the dehydrocoupling of silanes was surveyed by Harrod and coworkers. It was found that Ti and Zr complexes offered the highest activity, and that vanadocene is an effective catalyst for the syntheses of  $\text{PhH}_2\text{SiSiH}_2\text{Ph}$  and  $\text{PhH}_2\text{SiSiHPhSiH}_2\text{Ph}$  from  $\text{PhSiH}_3$ <sup>573</sup>. Another interesting discovery is that  $\text{Cp}_2\text{TiMe}_2$  and  $\text{Cp}_2\text{ZrMe}_2$  catalytically dehydrocouple methylsilane to poly(methylsilane) containing up to several hundred silicon atoms<sup>574</sup>. Harrod's group has also presented evidence for the stereoregular polymerization of phenylsilane to cyclic oligosilanes  $(\text{PhSiH})_n$  ( $n = 6-9$ ) by bis(indenyl)dimethylzirconocene and [1,2-bis(indenyl)ethane]dimethylzirconocene<sup>575</sup>.

In their studies of the dehydrogenative polymerization of *n*-BuSiH<sub>3</sub> by  $\text{Cp}_2\text{ZrMe}_2$ , Hilty and coworkers determined that oligomers with 2–8 silicons were observed, and that a large percentage of the Si<sub>5</sub> through Si<sub>7</sub> oligomers were cyclic<sup>576</sup>.

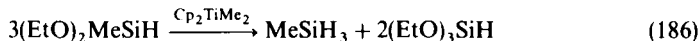
Corey recently found that  $(\text{PPh}_3)_3\text{RhCl}$  catalyzed dehydrocoupling of the secondary silane 9,10-dihydro-9-silaanthracene and related dibenzosilacycles to di- and trisilanes. The complexes  $\text{Cp}_2\text{MMe}_2$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) also produced short-chain oligomers with these silanes. The degree of polymerization was found to be a sensitive function of monomer, catalyst and reaction conditions. The rhodium catalyst promoted oxygenation of the product's Si—Si bonds in the presence of air<sup>577</sup>.

The titanium catalyst  $\text{Cp}_2\text{TiPh}_2$  has been used to obtain  $\text{H}(\text{PhSiH})_n\text{H}$  oligomers from  $\text{PhSiH}_3$  at 110°C. Under the same conditions,  $\text{Ph}_2\text{SiH}_2$  was converted to the corresponding disilane and a small amount of the redistribution product  $\text{Ph}_3\text{SiH}$ . Also,  $\text{PhMeSiH}_2$  gave disilane and trisilane<sup>578</sup>. Convenient, *in situ* generation of catalysts for silane coupling is accomplished by addition of 2 equivalents of *n*-BuLi to  $\text{Cp}_2\text{MCl}_2$  ( $\text{M} = \text{Ti}, \text{Zr}$  of Hf). Such catalysts react with  $\text{PhMeSiH}_2$  at elevated temperatures to produce the oligomers  $\text{H}(\text{PhMeSi})_n\text{H}$  (for  $\text{M} = \text{Zr}, n = 2-8$ ). The appearance of  $\text{PhMe}^*\text{BuSiH}$  early in the reaction is apparently related to formation of the active catalyst. A mechanism involving  $\text{Cp}_2\text{ZrH}(\text{SiHRR}')$  and 'zirconocene' intermediates, and concerted  $\sigma$ -bond metathesis steps was suggested for this oligomerization process<sup>579</sup>.

### \*3. Redistribution on silicon

Stoichiometric reactions that appear to be related to metal-catalyzed redistributions at silicon are the thermolyses of *cis*-( $\text{PR}_3$ )<sub>2</sub>Pt(SiMe<sub>2</sub>Ph)<sub>2</sub> complexes, which produce  $\text{PhMe}_2\text{SiSiMe}_2\text{Ph}$ ,  $\text{Ph}_2\text{SiMe}_2$ ,  $\text{PhSiMe}_3$  and a mixture of polysilanes. The monosilane redistribution products may arise via migration of a group from silicon to platinum. Addition of free phosphine suppressed formation of the redistribution products, possibly by blocking a coordination site required for the  $\alpha$ -migration. The reductive elimination of  $\text{PhMe}_2\text{SiSiMe}_2\text{Ph}$  obeys first-order kinetics, and is unaffected by added phosphine<sup>449</sup>.

Dimethyltitanocene catalyzes the redistribution of alkoxy- and siloxysilanes. The reaction in equation 186 converts  $\text{Cp}_2\text{TiMe}_2$  to  $[\text{Cp}_2\text{Ti}(\mu\text{-OEt})_2]$ , and *cis*- and



*trans*-isomers of  $\text{Cp}_2\text{Ti}(\mu\text{-SiH}_2\text{Me})_2\text{TiCp}_2$ . Low molecular weight siloxanes undergo redistributions to poly(dimethylsiloxane). For example,  $\text{Me}_2\text{HSiOSiHMe}_2$  is converted

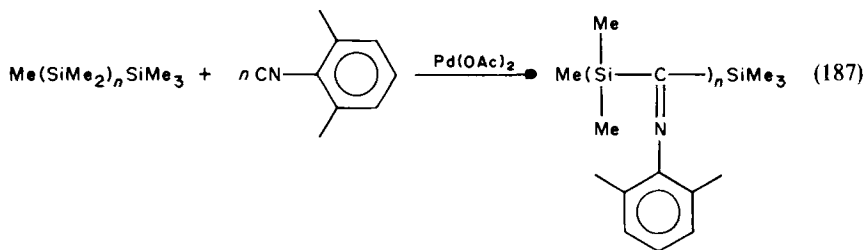
to cyclic  $(\text{Me}_2\text{SiO})_n$  and linear  $\text{H}(\text{Me}_2\text{SiO})_n\text{H}$  species. A mechanism involving bimetallic Ti(III) intermediates was proposed<sup>580</sup>. More recently, this chemistry has been extended to the redistribution of  $[\text{MeHSiO}]_n$  ( $n = 4, 5$ ) cyclomers or linear  $[\text{MeHSiO}]_n$  oligomers to  $\text{MeSiH}_3$  and copolymers of approximate composition  $[\text{MeHSiO}]_{0.3}[\text{MeSiO}_{1.5}]_{0.7}$ <sup>581</sup>.

Wu and Interrante have investigated the  $\text{H}_2\text{PtCl}_6$ -catalyzed ring-opening polymerization of  $(\text{MeClSiCH}_2)_2$  to  $(\text{MeClSiCH}_2)_n$ , which can be reduced to preceramic  $(\text{MeHSiCH}_2)_n$  polymers (compare equation 107)<sup>582</sup>.

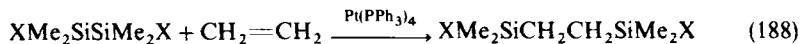
#### \*4. Other Si—C bond-forming reactions

Liu and coworkers have extensively investigated the transition-metal-mediated cycloaddition reactions of 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene with conjugated dienes under photochemical conditions. Depending on the nature of the transition metal, 1,4-, 1,2-, and 1,1-additions to the dienes are observed. The unusual 1,1-addition reactions occur via hydrogen or fluorine migrations<sup>374-382</sup>.

Palladium complexes catalyze the insertion of isonitriles into Si—Si bonds<sup>583,584</sup>. For example, the reaction in equation 187 ( $n = 2, 3, 5$ ) affords poly[sila(N-substituted)imines]<sup>584</sup>.



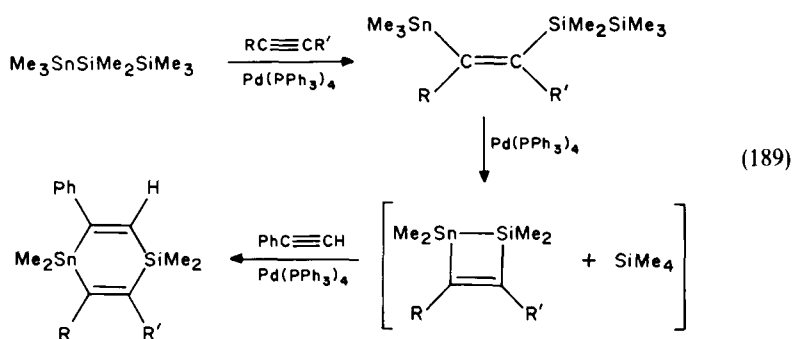
Tanaka's group has observed stoichiometric double silylations of  $\text{PhC}\equiv\text{CPh}$ ,  $\text{PhC}\equiv\text{CH}$ , isoprene and ethylene by *cis*-( $\text{PMePh}_2$ )<sub>2</sub> $\text{Pt}(\text{SiMe}_2\text{Ph})_2$ . These reactions result in *cis* addition of silyl groups to the alkynes, but for isoprene a mixture of *Z*- and *E*-1,4-bis(dimethylphenylsilyl)-2-methyl-2-butene (56/44) was obtained. Reaction of the platinum complex with styrene gave a 79% yield of the dehydrogenated product *E*- $\text{PhCH}=\text{CHSiMe}_2\text{Ph}$ <sup>585</sup>. The catalytic double silylation of ethylene is observed with platinum phosphine complexes (equation 188). Electronegative X groups were found to



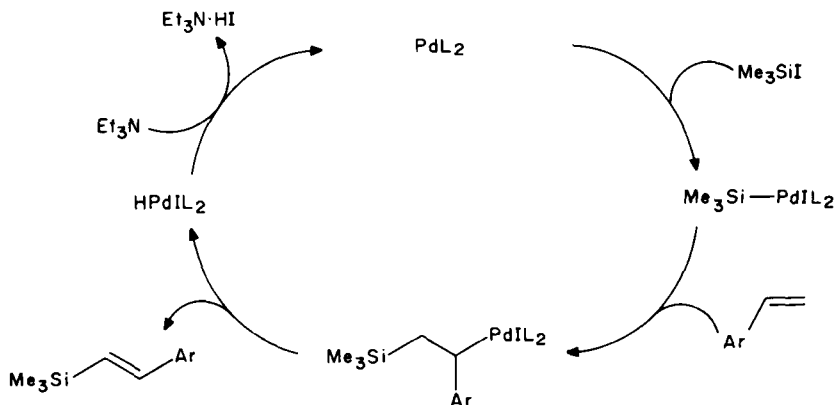
promote the reaction ( $\text{F} > \text{MeO} > \text{Cl} > \text{Me} > p\text{-CF}_3\text{C}_6\text{H}_4 > \text{C}_6\text{H}_5 > p\text{-CH}_3\text{C}_6\text{H}_4$ ), although steric factors also appear to be important since  $\text{PhMe}_2\text{SiSiMe}_2\text{Ph}$  reacted more sluggishly than  $\text{Me}_3\text{SiSiMe}_3$ . The activity of the platinum catalysts increases with more electron-donating and less sterically hindered phosphines [ $\text{Pt}(\text{PPh}_3)_4 < \text{Pt}(\text{PET}_3)_4 < \text{Pt}(\text{PMe}_2\text{Ph})_4 < \text{Pt}(\text{PMe}_3)_4$ ]. Interestingly palladium complexes, which are known to catalyze related double silylation reactions, are inactive for the reactions of equation 188. Use of norbornene as a substrate demonstrated that the addition occurs with *cis* stereochemistry. A mechanism involving migratory insertion of alkene into a Pt—Si bond was proposed<sup>586</sup>. Such a mechanism is consistent with the observation that for closely related reactions employing alkenes, disilanes and  $\text{Pt}(\text{PR}_3)_4$  catalysts, dehydrogenations to monosilylated products are obtained<sup>587</sup>. The new catalyst system  $\text{Pd}(\text{dibenzylideneacetone})_2/\text{P}(\text{OCH}_2)_3\text{CEt}$  efficiently catalyzes the insertion of  $\text{PhC}\equiv\text{CH}$  into the Si—Si bonds of  $\text{Me}_3\text{SiSiMe}_3$  and  $\text{Me}_3\text{SiSiMe}_2\text{SiMe}_3$ <sup>588</sup>.

Palladium complexes catalyze the 1,4-disilylation of  $\alpha,\beta$ -unsaturated ketones. With a chiral catalyst, this chemistry can be extended to the asymmetric synthesis of  $\beta$ -hydroxy ketones<sup>589</sup>.

The palladium-catalyzed reactions of disilanylstannanes with alkynes (equation 189) represent a two-step process that begins with *cis*-addition of the Si—Sn bond to the alkyne. With terminal alkynes, the stannyl group adds regioselectively to the internal carbon atom. The second step may proceed via a 1-sila-2-stannacyclobutene intermediate<sup>590</sup>. Insertions of alkynes, allenes and alkenes into the Si—C bonds of 1,1-dimesityl-2-*Z*-neopentylidene-silirane are catalyzed by palladium complexes<sup>591</sup>.

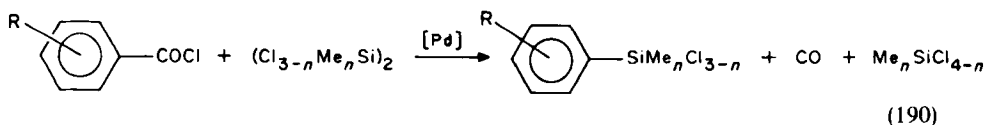


The demonstration of a Heck-type reaction for halosilanes has been communicated. These reactions involve styrene derivatives as substrates and are catalyzed by  $(\text{PEt}_3)_2\text{PdCl}_2$ . The mechanism of Scheme 30 was proposed to account for the observed chemistry<sup>592</sup>.



SCHEME 30

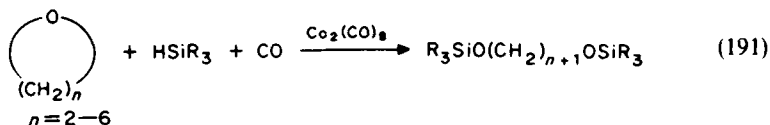
A new route to arylsilanes is based on the silylative decarbonylation of aromatic acid chlorides (equation 190). The presence of electron-withdrawing groups on the disilane favor formation of arylsilanes over aroylsilanes (cf. equation 119). The reaction tolerates a wide variety of substituents on the aromatic ring. With electron-withdrawing groups on the aromatic acid chloride, arylsilanes are also observed as products in significant quantities. Aliphatic acid chlorides are not useful in this synthesis<sup>593-595</sup>.



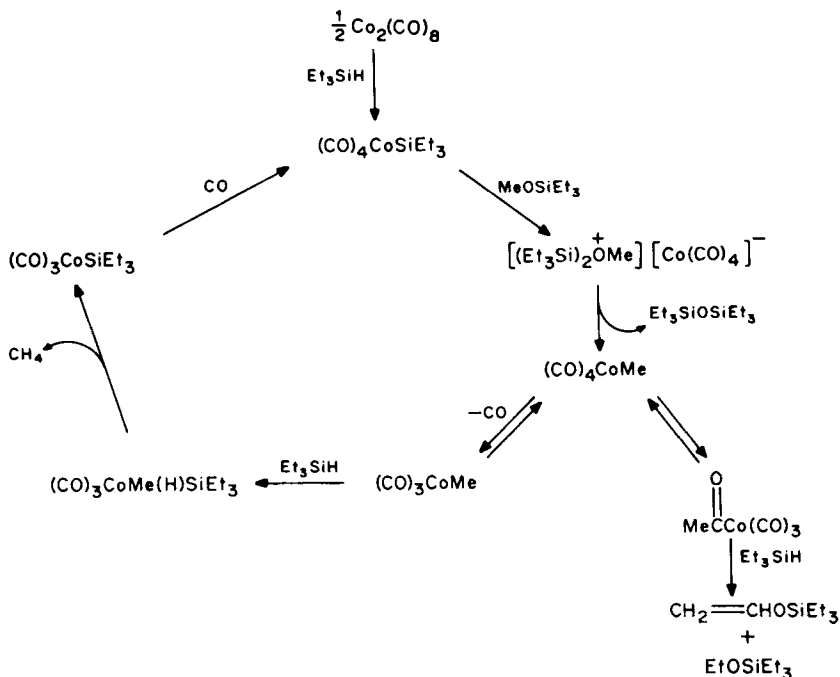
\*5. Catalytic reactions with hydrosilanes and carbon monoxide

Detailed kinetic and mechanistic studies have been reported for the rather complex reactions of  $\text{Me}_2\text{CHC(O)Co(CO)}_4$  with  $\text{Et}_3\text{SiH}$  under CO, and of  $\text{Me}_3\text{SiCo(CO)}_4$  with  $\text{Me}_2\text{CHCHO}$  under CO. Key intermediates in both reactions appear to be  $\alpha$ -siloxyalkyl complexes, which can produce silyl enol ethers via  $\beta$ -hydrogen elimination<sup>596</sup>.

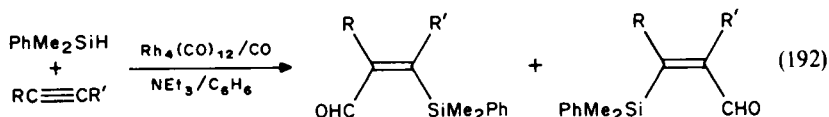
Catalytic reactions of the  $\text{R}_3\text{SiH/CO/Co}_2(\text{CO})_8$  system<sup>597</sup> have been extended to cyclic ether substrates, resulting in incorporation of carbon monoxide as part of a siloxymethyl group (equation 191). These reactions proceed under mild conditions, and electron-withdrawing groups in monosubstituted oxiranes result in highly regioselective ring openings at the primary carbon center<sup>598</sup>.



At  $180^\circ\text{C}$  under a CO pressure, dicobaltoctacarbonyl catalyzes the conversion of  $\text{MeOSiEt}_3$  and  $\text{Et}_3\text{SiH}$  to  $\text{CH}_4$  and  $\text{Et}_3\text{SiOSiEt}_3$ . The silyl ethers  $\text{CH}_2=\text{CHOSiEt}_3$  and  $\text{EtOSiEt}_3$  are produced as kinetic but minor products. The steps in Scheme 31 were suggested to account for the observed transformations<sup>599</sup>.



The silylformylation of alkynes is efficiently catalyzed by  $\text{Rh}_4(\text{CO})_{12}$  in the presence of triethylamine (equation 192). The terminal carbon of 1-alkynes is preferentially silylated<sup>600</sup>.



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# Organosilicon nitrogen compounds

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Organosilicon-nitrogen chemistry was first reviewed in 1960 as one chapter in Eaborn's excellent book on organosilicon chemistry<sup>1</sup>. This was followed a year later by a review of organosilicon-nitrogen chemistry alone, as a chapter in Ebsworth's monograph on volatile silicon compounds, and in the 1970s as part of the two series of *International Review of Science*<sup>2</sup>.

The use of organosilicon-nitrogen compounds as synthetic intermediates in organic synthesis is covered in both *Comprehensive Organic Chemistry* and *Comprehensive Organometallic Chemistry*<sup>3</sup>. More particularly, reviews cover silylation as a protective method in organic synthesis<sup>4</sup>, with specific reference to silyl pseudohalides<sup>5</sup>, notably silyl azides<sup>6</sup>, isocyanates and isothiocyanates<sup>7</sup>, together with mechanisms for the solvolysis of the silicon-nitrogen bond<sup>8</sup>.

*Comprehensive Organometallic Chemistry* also reviews all organosilicon-nitrogen chemistry<sup>9</sup>, while a series of articles covers the bis(silyl)amide group as a ligand in coordination chemistry<sup>10</sup>. Other reviews cover general silicon-nitrogen chemistry<sup>11</sup> and, more specifically, cleavage of the silicon-nitrogen bond by covalent halides<sup>12</sup>, the

cyclosilazanes<sup>13</sup>, 1,2-silyl migrations between nitrogen and nitrogen, carbon or oxygen<sup>14</sup>, the silicon–nitrogen double bond<sup>15</sup>, derivatives of diazenes and polyazenes<sup>16</sup> and heterocycles formed from bis(*t*-butylamino)dimethylsilane<sup>17</sup>.

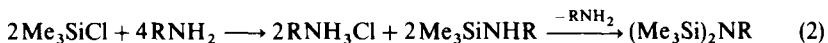
*Inorganic Syntheses* include the preparation of the aminosilanes  $\text{Me}_3\text{SiNHPh}$  and  $\text{Si}(\text{NHPh})_4$ , the linear disilazanes  $(\text{Me}_3\text{Si})_2\text{NH}$  and  $(\text{Me}_3\text{Si})_2\text{NMe}$ , the cyclosilazanes  $(\text{R}_2\text{SiNH})_{3,4}$  ( $\text{R} = \text{Me}, \text{Et}$ )<sup>18</sup>, the amides  $(\text{Me}_3\text{Si})_2\text{NM}$  ( $\text{M} = \text{Li}$  and  $\text{Na}$ ), the trisilylamine  $(\text{Me}_3\text{Si})_3\text{N}$ , the pseudohalides  $\text{Me}_n\text{Si}(\text{NCX})_{4-n}$  ( $\text{X} = \text{O}, \text{S}; n = 1-3$ )<sup>19</sup>, the amides  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{M}$  ( $\text{M} = \text{Sc}, \text{Ti}, \text{Cr}, \text{Fe}$ ) and dimethylaminotrimethylsilane  $\text{Me}_3\text{SiNMe}_2$ <sup>20</sup>.

### I. THE GENERAL SYNTHESIS OF AMINOSILANES, DISILAZANES AND TRISILYLAMINES<sup>2</sup>

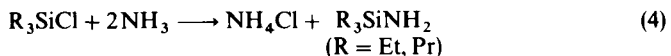
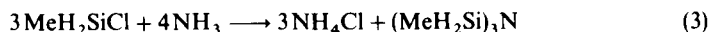
These three classes of silicon–nitrogen compounds result from the reaction of chlorosilanes with amines. The product formed depends not only on the number of substituents on nitrogen, but also on their bulkiness, and that of the substituents at silicon. Since secondary aminosilanes have a tendency to deaminate, particularly in the presence of an acid catalyst, several products often result on amination of chlorosilanes. The reaction is conveniently carried out in a non-protic solvent and is mildly exothermic, the hydrogen chloride generated being readily precipitated by excess amine. Secondary amines give the aminosilane, with more hindered amines requiring heating under pressure (equation 1).



With primary amines, the aminosilane is formed initially, but the size of substituents at nitrogen and silicon determines whether deamination subsequently occurs. Methylamine and trimethylchlorosilane will form the aminosilane, but prolonged heating under reflux in the presence of ammonium sulphate, or the precipitated amine hydrochloride as acid catalyst yields the disilazane in good yield (equation 2).



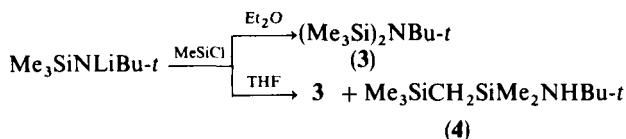
Chlorosilane and methylchlorosilane both give the trisilylamine with ammonia (equation 3), while the disilazane is the only silicon–nitrogen product formed from trimethylchlorosilane. Increasing the size of the silicon substituent impedes deamination, so both aminosilane and disilazane result, the latter increasingly on prolonged heating (equation 4).



By way of an aside, the longer M–N bonds found in the amino derivatives of the heavier group IV (14) elements encourage deamination by reducing steric effects, so primary amines only result for bulky organic groups. Chlorotrimethylgermane and ammonia give the digermazane and trigermylamine, with the isopropyl group necessary to stabilize the primary aminogermane. The aminotriphenylsilane and germane both lose ammonia on heating. With sodamide in liquid ammonia, triisopropyltin chloride gives both distannazane and tristannylamine, and the *t*-butyl group is necessary to stabilize the primary stannyl and plumbylamine<sup>21</sup>. Diaminosilanes  $\text{RR}'\text{Si}(\text{NH}_2)_2$  can only be isolated if at least one substituent is *t*-butyl, as is the case with silane diols<sup>1,2d</sup>.

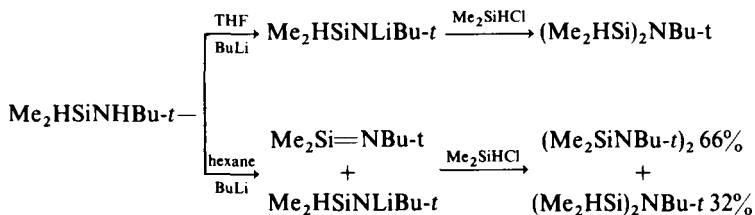






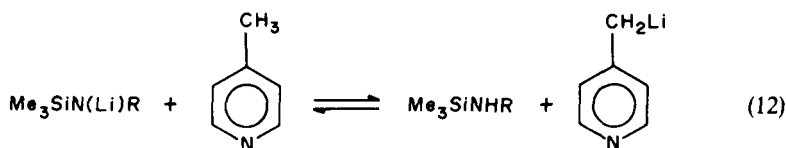
SCHEME 1

Lithiation of the silylamines  $\text{HMe}_2\text{SiNHR}$  ( $\text{R} = i\text{-Pr}, t\text{-Bu}, \text{HMe}_2\text{Si}$ ) in THF followed by methylation or silylation gives substitution solely at nitrogen. In hexane, however, this is the minor product, the cyclodisilazane dominating. Evidence supports the formation of a silimine intermediate through LiH elimination (see Section XII on fluorosilylamides for LiF elimination) rather than a two-step intermolecular coupling to give the cyclodisilazane product, since the intermediate aminodisilazane could not be prepared (Scheme 2)<sup>28</sup>.



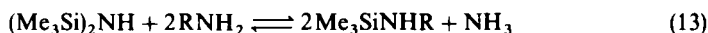
SCHEME 2

Silylamines generally have a  $\text{pK}$  range of 25–34, so their lithiated derivatives have been used to determine the  $\text{pK}$  values of picolines, benzylpyridines and fluorene using proton NMR spectroscopy. The aminosilanes  $\text{Me}_3\text{SiNHR}$  have  $\text{pK}$  values of 31.4 ( $\text{R} = \text{Pr-}i$ ), 33.6 ( $\text{R} = \text{Bu-}t$ ) and 25.8 ( $\text{R} = \text{Me}_3\text{Si}$ ) (equation 12)<sup>29</sup>.

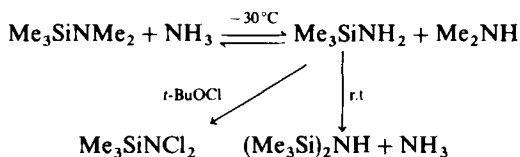


### 3. Transamination

Amino group exchange (transamination) readily results through heating the aminosilane with a primary or secondary amine with boiling point higher than that of the liberated amine. This is often ammonia, since hexamethyldisilazane  $(\text{Me}_3\text{Si})_2\text{NH}$  is commercially available, and its removal shifts the equilibrium to the right, though several days of refluxing are often required, particularly with hindered amines. Despite this inconvenience, this method avoids tedious separation of hygroscopic amine hydrohalide, or lithium salts, and is particularly useful for expensive amines (equation 13)<sup>30</sup>.

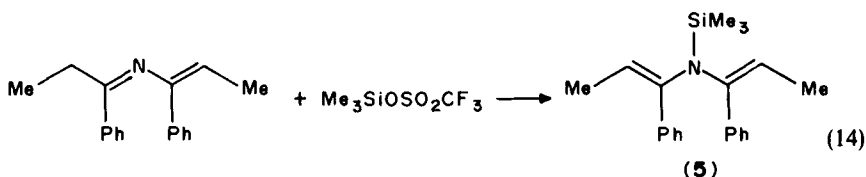


A noteworthy variation on this method involves the ammonolysis of dimethylaminotrimethylsilane at  $-30^\circ\text{C}$ . The aminotrimethylsilane so generated gives disilazane on warming, but can be *N*-dichlorinated using *t*-butyl hypochlorite, the chloramine being readily distillable (Scheme 3)<sup>31</sup>.



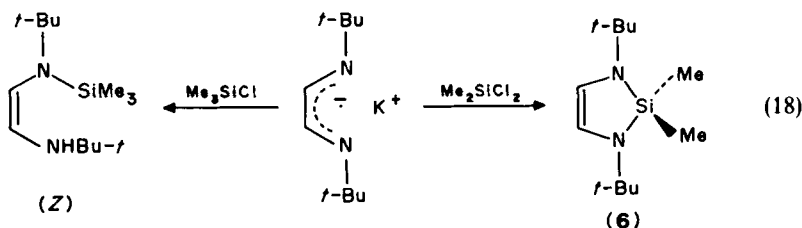
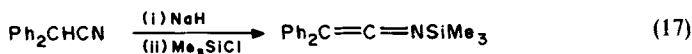
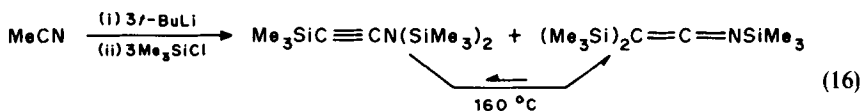
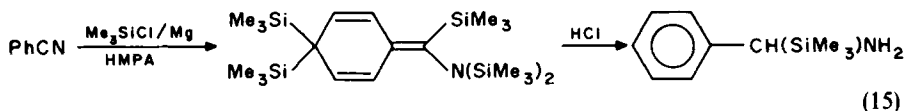
SCHEME 3

Though little is known of divinylamines, several *N*-silyl derivatives have been successfully prepared by silylating appropriately substituted 2-aza-1,3-dienes with trimethylsilyl trifluoromethanesulphonate. All are colourless, distillable liquids formed almost quantitatively as a single isomer (**5**) with silylation occurring exclusively at nitrogen (equation 14)<sup>32</sup>.

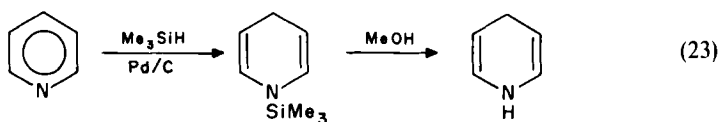


#### 4. Reductive silylation

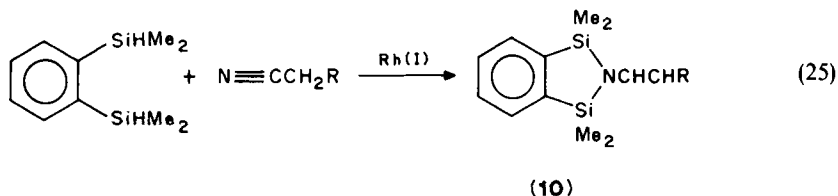
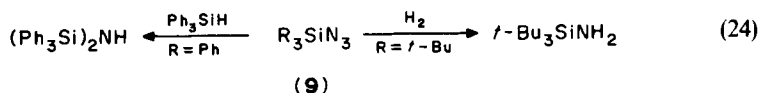
Silyl substituted enamines result from the reductive silylation of benzonitrile, though C-silylation dominates (equation 15)<sup>33</sup>. With acetonitrile, the isomeric enamine and ynamine result (equation 16)<sup>34</sup>, but diphenylacetone nitrile gives only the enamine (equation 17)<sup>35</sup>. With glyoxal diimines (RN=CH)<sub>2</sub>, however, potassium gives radical anions which, on silylation, form *Z*-mono and *E*-disilylated enediamines, together with diazacyclopentenes (**6**) with no C-silylation (equations 18 and 19)<sup>36</sup>.







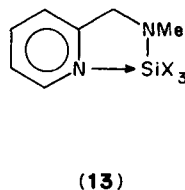
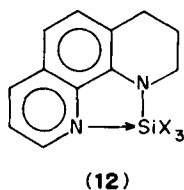
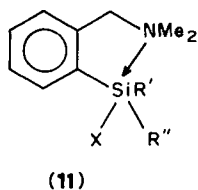
Azides **9** can also be reduced to the disilazane ( $R = \text{Ph}$ ) and aminosilane ( $R = \text{Bu-}t$ ) (equation 24)<sup>42</sup>, while the 1,2-bis(dimethylsilyl)benzene catalytically reduces nitriles to an enamine/amine mixture except for arylacetonitriles, when only the enamine **10** results (equation 25)<sup>43</sup>.



## B. Substitution at Silicon

Substitution at silicon can occur with inversion or retention of configuration, depending upon the leaving group. Amines attack chlorosilanes to give aminosilanes with inversion, and these hydrolyse with inversion, but are reduced by  $\text{LiAlH}_4$  with retention of configuration.

The predominant stereochemistry changes from inversion to retention with leaving groups in the order  $\text{Br} \sim \text{Cl} \gg \text{SR} \sim \text{F} \gg \text{OMe} > \text{H}$ . This order reflects that observed for the ease of formation of five-coordinate complexes of *o*-dimethylaminomethylarylsilanes *o*-( $\text{Me}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4\text{SiXR}'\text{R}''$  (**11**). Diastereotopy is observed for the two methyl groups in the  $^1\text{H NMR}$  spectrum, and the coalescence temperature is highest for  $\text{X} = \text{chlorine}$ , bromine and acetate substituents, lower for fluorine and ethylthio, and unobservable for alkoxy and hydrogen, even down to  $-100^\circ\text{C}$ , if  $\text{R}' = \text{Me}$ , and  $\text{R}'' = \text{H}$ . A similar  $^{19}\text{F NMR}$  spectroscopy study on **11** ( $\text{R}' = \text{Me}$ ,  $\text{R}'' = \text{F}$ ) shows that with  $\text{X}$  as substituted benzoate, the isomer with equatorial fluorine dominates, so  $\text{ArOCO} > \text{F}$  within the apicophilicity series  $\text{H, OR, NR}_2 < \text{F} < \text{Cl, OCOC}_6\text{H}_4\text{X}^{44}$ .



A study of the strength of chelation in 1-silyl-1,2,3,4-tetrahydro-1,10-phenanthroline (**12**) shows that the length of the coordinate silicon–nitrogen bond from the aromatic

TABLE 1. Silicon–nitrogen bond lengths in 1-silyl-1,2,3,4-tetrahydro-1,10-phenanthroline (12)

X <sub>3</sub>	F <sub>3</sub>	Cl <sub>3</sub>	Cl <sub>2</sub> Me	ClMe <sub>2</sub>	Me <sub>3</sub>
Si—N (pm)	172.2	173.7	173.8	177.0	174.6
Si---N (pm)	196.9	198.4	202.7	202.8	268.9
% Increase	13.7	14.2	16.6	14.6	54

nitrogen atom tends to increase relative to the other silicon–nitrogen bond as the electronegativity of the substituents on silicon decreases, though other factors certainly play a part (Table 1). The <sup>19</sup>F NMR spectrum of the fluorosilyl derivative shows a singlet at room temperature, indicating rapid interchange of the fluorine atoms between axial and equatorial positions in the trigonal bipyramidal structure. This probably results through cleavage of the coordinate Si---N bond rather than through the Berry pseudo-rotation proposed for the unconstrained five-coordinate system<sup>45</sup>. Similar behaviour is also observed for 2-(silylaminoethyl) pyridines (13) showing a 16.5% increase for the donor bond length<sup>46</sup>.

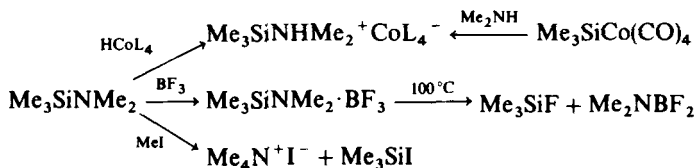
### C. Properties of Aminosilanes

The silicon–nitrogen bond dissociation energy of aminosilanes and disilazanes is some 320 kJ mol<sup>-1</sup>, about 100 kJ mol<sup>-1</sup> weaker than the silicon–oxygen bond, so reacts readily with water or alcohols, particularly if catalysed by acid. Base slows the reaction by preventing protonation of nitrogen, but encourages slow nucleophilic attack by hydroxide at silicon. The silicon–nitrogen bond is most stable in weakly alkaline media. Being immiscible with water, hexamethyldisilazane is stable to it, even at 100 °C, but hydrolyses immediately in aqueous methanol<sup>47</sup>. Both hexaphenyldisilazane and hexaphenylcyclo-trisilazane can be crystallized from ethanol and wet acetone, respectively<sup>1</sup>. Tertiary aminosilanes *t*-butyl-substituted at silicon are stable to hydrolysis and *t*-butyldimethyl-aminosilane *t*-BuMe<sub>2</sub>SiNH<sub>2</sub> to deamination up to its b.p. of 110 °C<sup>26</sup>.

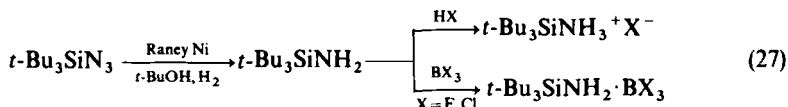
The aminosilanes R<sub>3</sub>SiNH<sub>2</sub> (R = Et, Pr) give silanethiol R<sub>3</sub>SiSH and disilthiane (R<sub>3</sub>Si)<sub>2</sub>S on reaction with hydrogen sulphide. With the silicon–nitrogen and silicon–sulphur bond energies being similar, thiosilanes and aminosilanes can be readily interconverted by removing an appropriate amine (or NH<sub>3</sub>) or thiol (or H<sub>2</sub>S) as the most volatile component<sup>48</sup>. The method is less suitable for the more acidic thiophenols, which tend to precipitate as amine thiolates R<sub>2</sub>NH<sub>2</sub><sup>+</sup>SPh<sup>-</sup> (equation 26).



Aminosilanes have been shown spectroscopically to be weaker bases than the isosteric organic amines<sup>49</sup> or analogous organogermanium and organotin amines<sup>50</sup>, and this is generally ascribed to stronger p<sub>π</sub>-d<sub>π</sub> bonding from nitrogen to silicon<sup>49</sup>. However, cleavage of the silicon–nitrogen bond is very rapid in most acids, and silylammonium salts with small substituents only result for non-nucleophilic anions such as Co(CO)<sub>4</sub><sup>-</sup> and Co(PF<sub>3</sub>)<sub>4</sub><sup>-51</sup>. Adducts with methyl iodide or boron trifluoride are thermally unstable, giving iodosilane and tetramethylammonium iodide, or fluorosilane and aminoborane (Scheme 5)<sup>52</sup>. With aminotri-*t*-butylsilane, however, both acids and boron trihalides will give thermally stable adducts (equation 27)<sup>42b</sup>. Polyxylylenylpiperazines result from disilylpiperazines and α,α'-dichloroxylenes through chlorosilane elimination<sup>53</sup>.

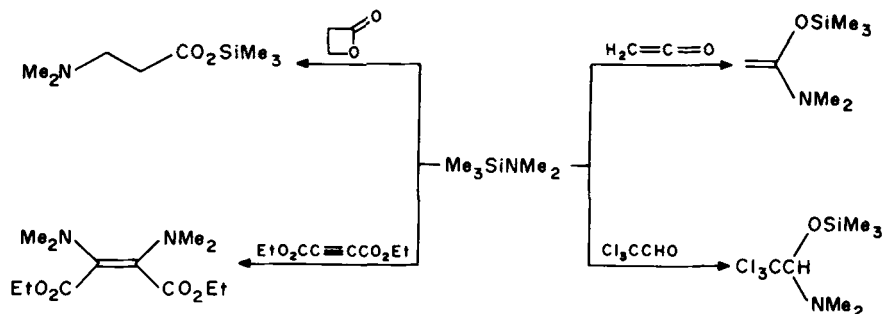


SCHEME 5



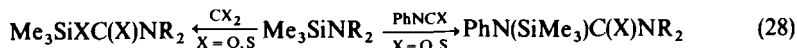
## 1. Addition to multiple bonds

Dimethylaminotrimethylsilane adds to carbonyl double bonds, chloral and ketene giving 1:1 adducts, that of the latter rearranging to the acetamide through O → C migration<sup>54</sup>. Lactones are ring opened and *cis*-adducts form from acetylene dicarboxylates (Scheme 6)<sup>55</sup>.



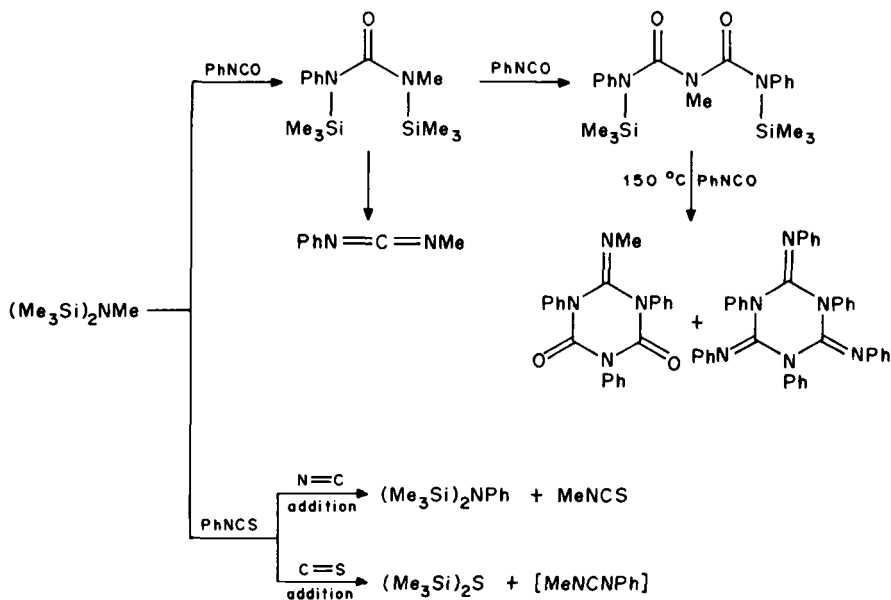
SCHEME 6

Electron-rich systems readily insert into the silicon–nitrogen bond of aminosilanes, (thio)carbmates and (thio)ureas resulting from aminosilanes and  $\text{CX}_2$  or  $\text{PhNCX}$  ( $\text{X} = \text{O}, \text{S}$ )<sup>56</sup> (equation 28), while tetrasulphur tetranitride is bisected to give the sulphur diimide **14** (equation 29)<sup>57</sup>. With disilazanes and isocyanates, both the 1:1 urea and 1:2 biuret adducts are formed<sup>58</sup>, while heating eliminates disiloxane to give the carbodiimide or triazine<sup>59</sup>. Phenyl isothiocyanate behaves similarly (Scheme 7)<sup>60</sup>.



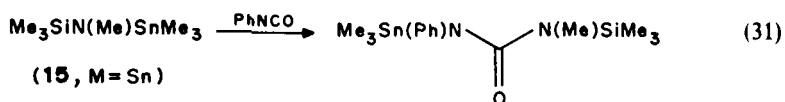
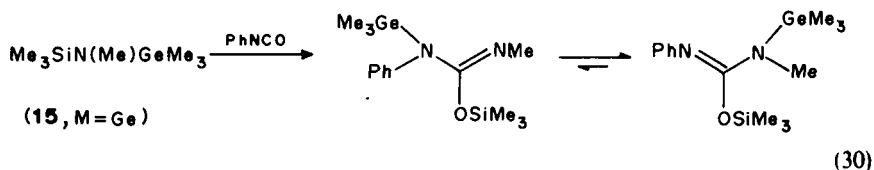
(14)

The mixed amines  $\text{Me}_3\text{SiN(Me)MMe}_3$  (**15**) ( $\text{M} = \text{Ge}, \text{Sn}$ ) add methyl isocyanate to give the *O*-silyl imidate through 1,3-silyl migration, as does **15** ( $\text{M} = \text{Ge}$ ) with phenyl isocyanate (equation 30). For **15** ( $\text{M} = \text{Sn}$ ), the urea alone results, the greater polarity of the tin–nitrogen bond leading to kinetic control of the products (equation 31). With



SCHEME 7

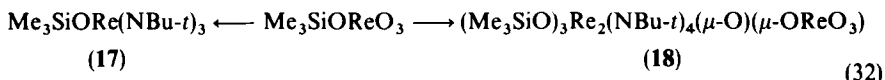
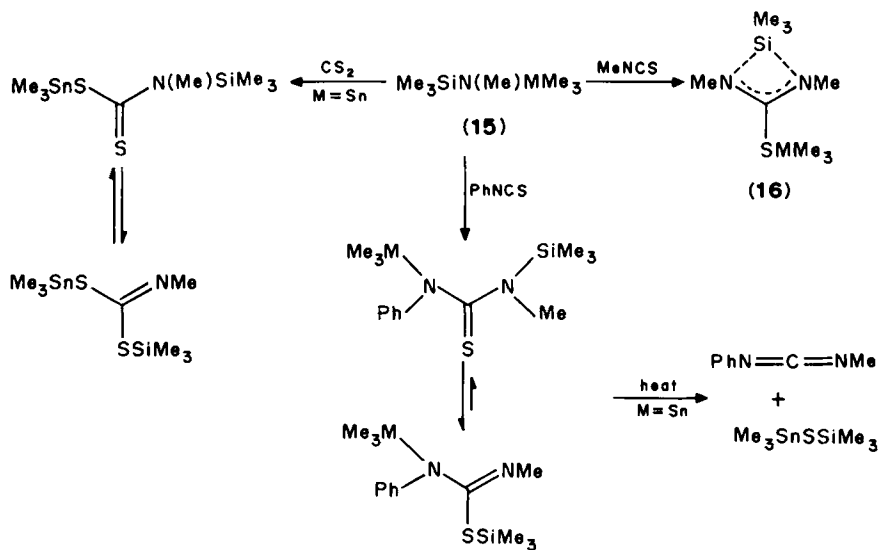
methyl isothiocyanate, **15** gives the five-coordinate adduct **16**, but with phenyl isothiocyanate and carbon disulphide, equilibrating mixtures form through 1,3-silyl migrations between nitrogen and sulphur (Scheme 8)<sup>61</sup>.



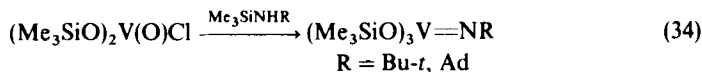
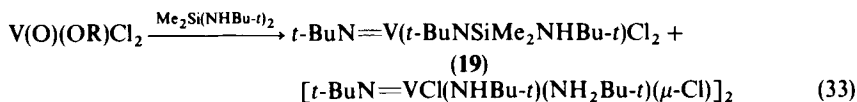
## 2. Transition metal derivatives

A range of high oxidation state early transition metal compounds react with silylamines and azides to give metal–nitrogen derivatives. Trimethylsilylperrhenate gives two products with *t*-butylaminotrimethylsilane. An excess yields the trisimide **17** while a deficiency gives the trimetallic complex **18** (equation 32).  $\text{MO}_2\text{Cl}_2$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) gives bis(siloxy)bisimides and  $\text{MoOCl}_4$  forms reduction products<sup>62</sup>.

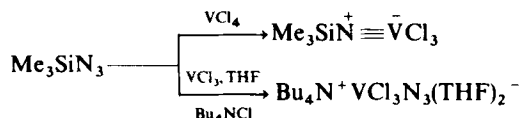




Vanadium(III), (IV) and (V) chlorides and oxychlorides all react with Si—N compounds, the latter to give derivatives with both vanadium–nitrogen single and double bonds, those of **19** being 163.5 pm (multiple bond with  $\angle\text{VNC } 161.5^\circ$ ), 184.3 pm (amide) and 238.6 pm (amino) in a distorted trigonal bipyramidal structure with equatorial chlorine atoms and amide group (equation 33)<sup>63</sup>. Attack at chlorine only occurs in the siloxy case, the adamantyl derivative showing a V—N bond length of 161.4 pm within an almost linear VNC skeleton (equation 34)<sup>62a</sup>.

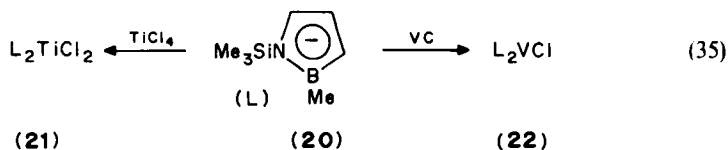


Trimethylsilyl azide oxidizes  $\text{VCl}_4$  to the trichloronitride, with long silicon–nitrogen bond (179.3 pm) and almost linear backbone with V—N 159.4 pm. With  $\text{VCl}_3(\text{THF})_3$ , the azide complex  $\text{VCl}_3\text{N}_3(\text{THF})_2^-$  results in the presence of  $\text{Bu}_4\text{NCl}$  (Scheme 9) (see Section XVII.A.3)<sup>63b</sup>.



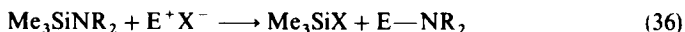
SCHEME 9

Cyclopentadienyltitanium trichloride is monosubstituted by secondary aminosilanes  $\text{Me}_3\text{SiNHR}$  ( $\text{R} = \text{Et}, i\text{-Pr}, t\text{-Bu}, \text{Ph}$ ) giving  $\text{CpTiCl}_2\text{NHR}$ , while the silyl substituted borazacyclopentadiene **20** forms sandwich complexes with  $\text{TiCl}_4$  and  $\text{VCl}_3$ , **21** and **22**. The ring conformations are set by weak  $\text{B}\cdots\text{Cl}$  interaction distances of 295–299 pm, while the  $\text{Si}-\text{N}$  bonds are close to single bond length in the titanium compound (179 pm), but shorter with the vanadium one (**22**) (176.8 pm) (equation 35)<sup>64</sup>.

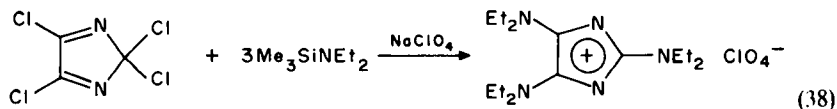
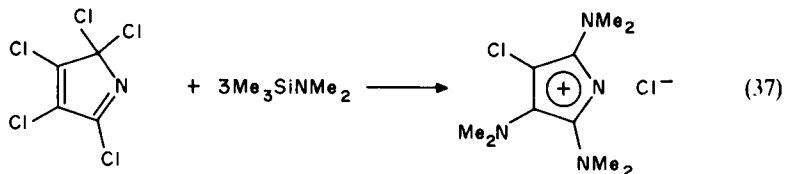


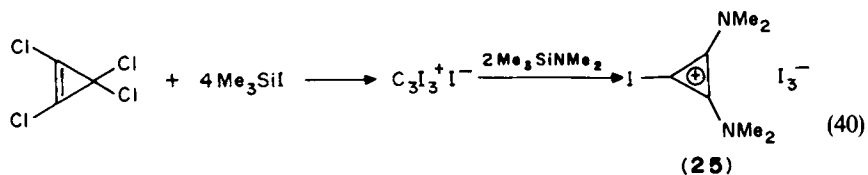
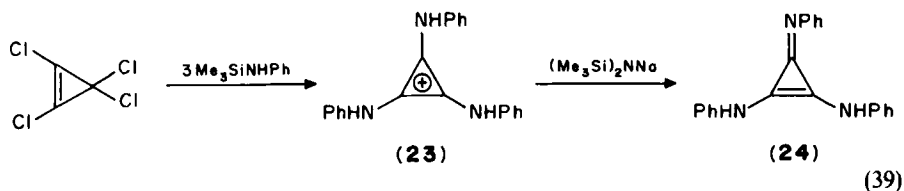
### 3. Use in organic synthesis<sup>3,4</sup>

Silicon–nitrogen compounds have become increasingly important as synthetic intermediates in organic synthesis. They are milder bases than organic amines, form only weak hydrogen bonds, are often more convenient to handle [e.g.  $\text{Me}_3\text{SiNMe}_2$  b.p. 86 °C and  $(\text{Me}_3\text{Si})_2\text{NMe}$  b.p. 146 °C] and do not precipitate ammonium salts with covalent halides if moisture is excluded. Indeed, the formation of strong  $\text{Si}-\text{F}$  and  $\text{Si}-\text{Cl}$  bonds, as well as  $\text{Si}-\text{O}$  bonds both encourages the reaction and assists in improving volatility. Thus, for instance, tryptophan is insoluble in organic solvents and has negligible vapour pressure, so it cannot be chromatographed, unlike its *N,N,O*-tris(trimethylsilyl) derivative which boils at 140 °C/0.2 mm and is soluble in organic solvents. Electrophiles, both organic and inorganic, cleave the silicon–nitrogen bond readily and cleanly (equation 36)<sup>4b</sup>.

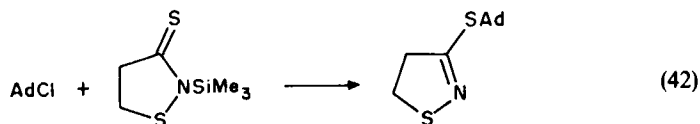
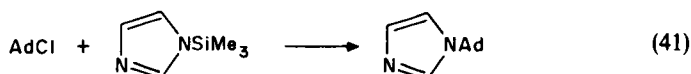


Aminosilanes react with both pentachloro-2*H*-pyrrole and tetrachloroimidazole to give the aza- and diaza-pentadienylum salts (equations 37 and 38)<sup>65</sup>. The first aza analogue of deltic acid results from the amination of tetrachlorocyclopropene with phenylaminotrimethylsilane giving **23**, followed by dehydrohalogenation with sodium bis(trimethylsilyl)amide. The <sup>13</sup>C NMR spectrum of **24** shows equivalent anilino groups and hence rapid proton exchange (equation 39)<sup>66</sup>. The ionic organic halide, cyclopropenium iodide  $\text{C}_3\text{I}_3^+ \text{I}^-$ , which results from tetrachlorocyclopropene and iodotrimethylsilane, yields the amino derivative **25** with dimethylaminotrimethylsilane (care! These iodides can detonate) (equation 40)<sup>67</sup>.

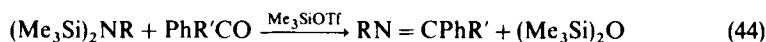
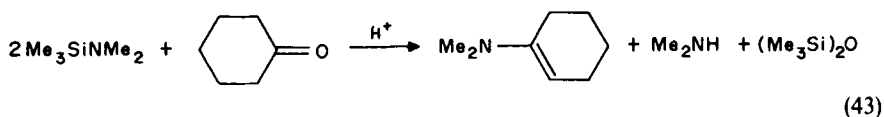




The activated silicon–nitrogen bonds of *N*-trimethylsilylimidazole or *N*-trimethylsilyl-*N*-methylacetamide react with bridgehead substituted adamantyl chloride in the presence of an acid catalyst to give the substituted nitrogen derivative, while with *N*-trimethylsilyl-2-mercaptothiazole, a 1,3-silyl migration occurs to give the thio derivative (equations 41 and 42)<sup>68</sup>.



Enamines result most conveniently from aminosilanes and a ketone with  $\beta$ -hydrogen under acid conditions (equation 43), while disilazanes and aldehydes or ketones in the presence of trimethylsilyl triflate yield the appropriate Schiff base (equation 44)<sup>69</sup>.



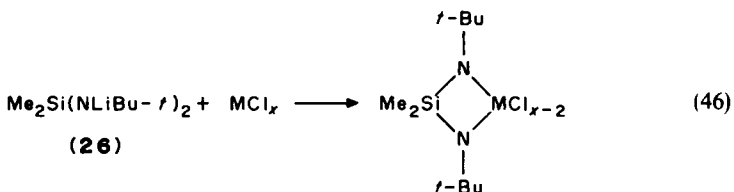
#### D. Structures of Aminosilanes

Calculations from the atomic radii of silicon and nitrogen and from their electro-negativity difference suggest that the silicon–nitrogen single bond should be 179–180 pm long<sup>70</sup>. That of dimethylaminotrimethylsilane  $\text{Me}_3\text{SiNMe}_2$  at 116 K shows the silicon–nitrogen bond to be 171.9 pm, and is slightly shorter in the vapour<sup>71</sup>. That for the aminosilanes  $\text{Me}_{3-n}\text{SiH}_n\text{NMe}_2$  ( $n = 1-3$ ) are 171.3–171.9 pm<sup>72</sup>. This shortening has been attributed to  $\pi$ -bonding between the nitrogen lone-pair electrons and either the vacant silicon d-orbitals, or the  $\sigma^*$ -orbital of the silicon–carbon bond. The former tends

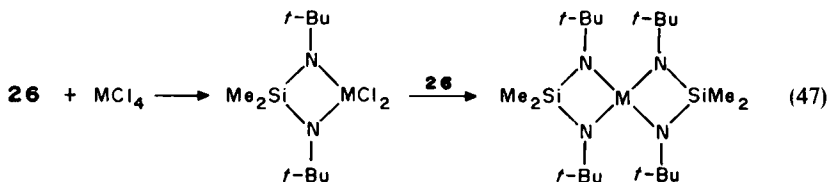
to be favoured<sup>73</sup> With the methylsulphonyl derivative  $\text{Me}_3\text{SiN}(\text{SO}_2\text{Me})_2$ , however, the silicon–nitrogen bond (185.1 pm) is much longer than expected for a single bond<sup>74</sup>.

### III. BISAMINOSILANES

Much of the chemistry of these compounds resembles that of monoaminosilanes. They can be prepared from the dihalosilane and primary or secondary amine in an appropriate ratio to precipitate all hydrogen halide (equation 45). The dilithio derivative **26** has been extensively used as an intermediate in the synthesis of hetero substituted cyclodisilazanes (equation 46), and is dimeric in the solid state with  $D_{2d}$  symmetry. The structure comprises a square antiprism of two  $\text{Li}_2\text{N}_2$  units connected through  $\text{Me}_2\text{Si}$  bridges and Si–N bonds of 173 pm<sup>75</sup>.



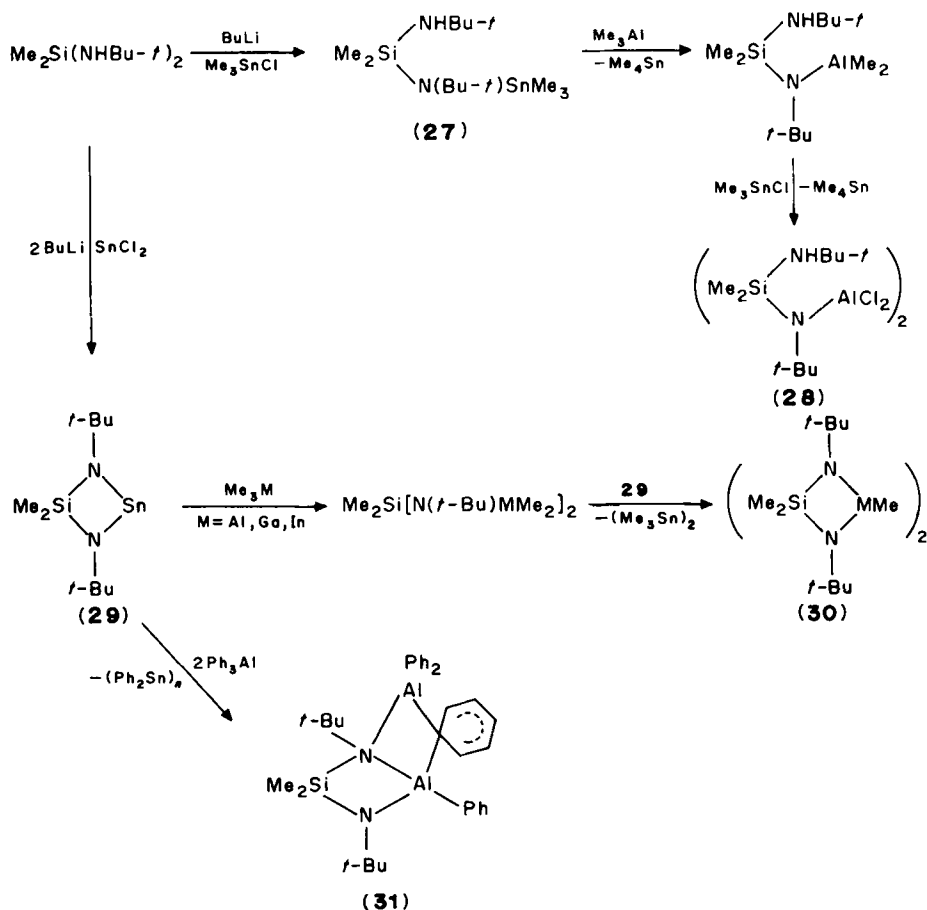
The reaction works well for main group and also transition elements, both titanium and zirconium giving monocyclic ( $\text{M} = \text{Ti}$ , Si–N 176.6 pm) and spiro derivatives ( $\text{M} = \text{Ti}$ , Si–N 174.2 pm;  $\text{M} = \text{Zr}$ , Si–N 175.3 pm), with silicon–nitrogen bond lengths a little longer than those of aminosilanes or disilazanes (equation 47)<sup>76</sup>. Organosilicon dichlorides and silicon tetrachloride behave similarly<sup>77</sup>.



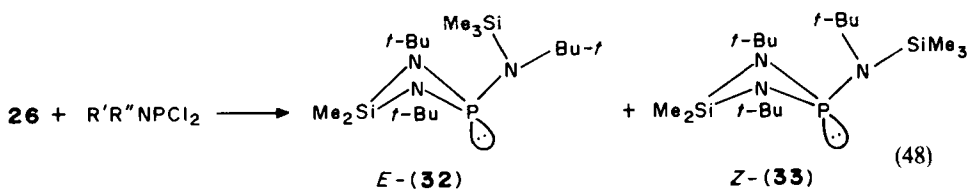
#### A. Boron Group and Phosphorus Derivatives

An extensive variety of group III (13) derivatives results from **26**<sup>78</sup>. The trimethylstannyl derivative **27** reacts with  $(\text{Me}_3\text{Al})_2$ , then trimethyltin chloride to give the aminodichloroalane as a H---Cl hydrogen bonded dimer **28**. The tin(II) heterocycle **29** gives dimeric products **30** on reaction with  $\text{Me}_3\text{M}$ , as confirmed by the steplike structure of the indium derivative. With triphenylaluminium, **31** results in which one aluminium atom bridges both nitrogen atoms, one of its phenyl groups bridging to the other aluminium atom (Scheme 10)<sup>79</sup>.

Condensing **26** with the aminodichlorophosphines  $\text{R}'\text{R}''\text{NPCl}_2$  gives a mixture of two separable isomers **32** and **33**. Their structures indicate planarity at the exocyclic nitrogen atom and longer exocyclic silicon–nitrogen bonds (176.0 and 178.0 pm) than those in the ring (equation 48)<sup>80</sup>.

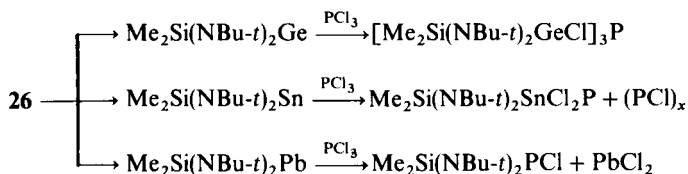


SCHEME 10



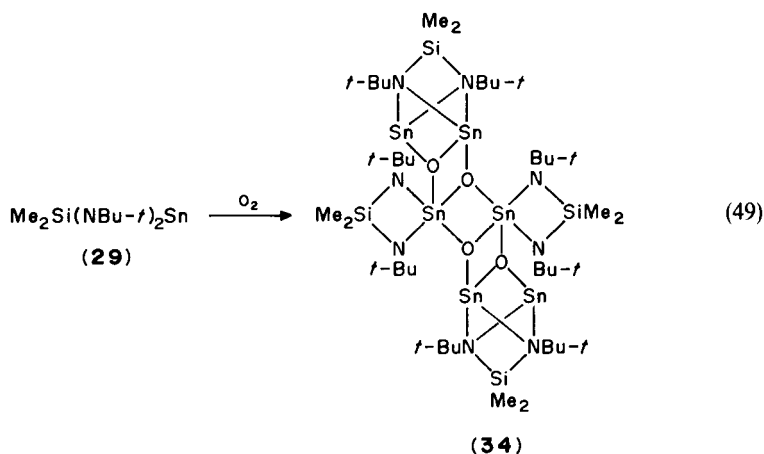
### B. The Tin(II) Derivative and its Reactions

Condensing the bisamidodisilane **26** with the group IV (14) dihalides gives the monomeric heterocycle. All react differently with phosphorus trichloride through oxidation and insertion (Scheme 11)<sup>81</sup>.

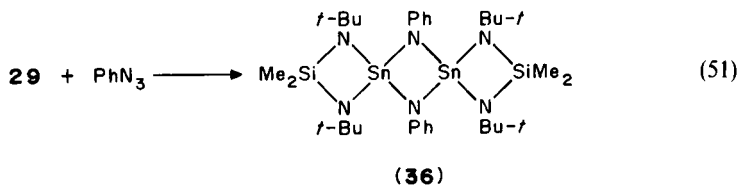
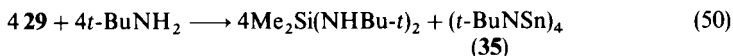


SCHEME 11

The tin derivative **29** has been extensively used as an intermediate for the preparation of a range of adducts and substitution products, many of which are electron-rich cage compounds derived from a cubane-like structure. With oxygen, a complex product  $\text{Sn}_6(\text{Me}_2\text{Si})_4\text{O}_4(\text{NBu-}t)_8$  (**34**) results which comprises two  $\text{SiN}_2\text{Sn}_2\text{O}$  cages coupled to the dispiro unit  $\text{Me}_2\text{Si}(\text{NBu-}t)_2\text{SnO}_2\text{Sn}(t\text{-BuN})_2\text{SiMe}_2$  (equation 49)<sup>82</sup>.

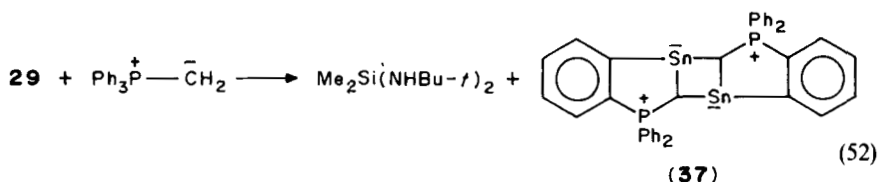


With *t*-butylamine, the initial adduct, which is stabilized by coordination to divalent tin and hydrogen bonding to the nitrogen atoms, subsequently decomposes to eliminate the bisaminosilane and give the cubane-like cage (*t*-BuNSn)<sub>4</sub> (**35**) (equation 50). *i*-Propylamine and *N,N*-dimethylhydrazine react similarly<sup>83</sup>. With phenyl azide, however, oxidation occurs to give the dispiro product **36** analogous to the dispiro unit of **34** (equation 51)<sup>84</sup>.

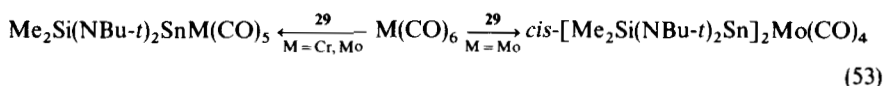


With the phosphorus ylide  $\text{Ph}_3\text{P}^+\text{-CH}_2^-$ , the adduct, which involves coordination to tin, shows a hydrogen bridge between the *o*-carbon atom of the one phenyl ring and

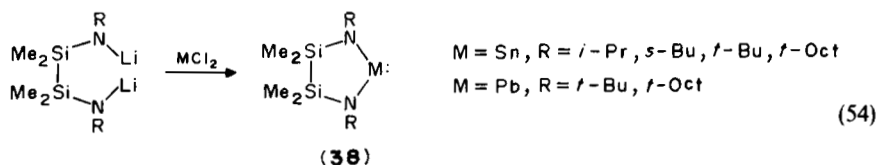
nitrogen. This provides the interaction necessary for the subsequent pyrolysis to the bisaminosilane and pentacyclic  $\text{Sn}_2(\text{CH})_2\text{P}_2(\text{C}_6\text{H}_4)_2\text{Ph}_4$  (**37**) (equation 52)<sup>85</sup>.



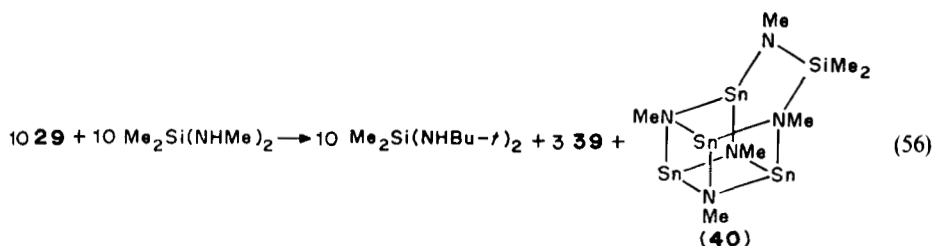
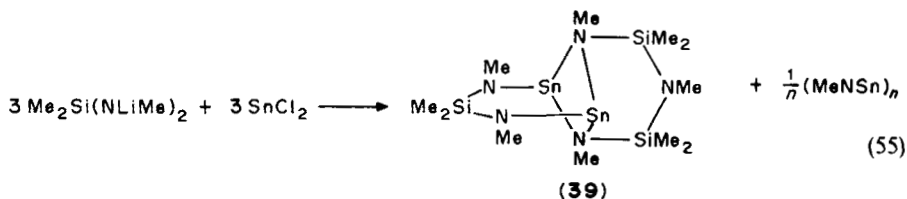
**29** readily coordinates to metal hexacarbonyls on irradiation, giving mono- and disubstituted *cis*-derivatives (equation 53)<sup>86</sup>.



The five-membered tin and lead derivatives **38** can be made by a similar method and, like **29**, are monomeric if the nitrogen substituent is bulky. With  $\text{R} = \text{Me}_3\text{Si}$  ( $\text{M} = \text{Pb}$ ) or  $\text{R} = \text{Et}$  ( $\text{M} = \text{Sn}$ ), however, they are dimeric with metal-metal 'multiple' bonds (equation 54)<sup>87</sup>.

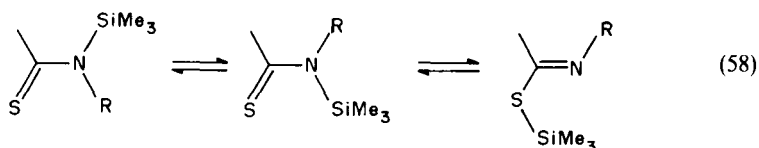


The reaction of  $\text{Me}_2\text{Si}(\text{NLiMe})_2$  with tin(II) chloride gives the polymeric  $(\text{MeNSn})_n$  and the cage  $(\text{Me}_2\text{Si})_3(\text{NMe})_3\text{Sn}_2$  (**39**), which possesses an orthogonal pair of incomplete five-membered rings coupled through a  $\text{Sn}_2\text{N}_2$  ring. It results from **29** and bis(methylamino)dimethylsilane, along with the extended cubane cage **40** (equations 55 and 56)<sup>88</sup>.

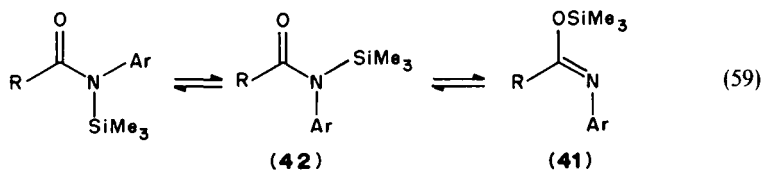


IV. SILYLAMIDES<sup>3a</sup>

Silylation of amides  $RC(O)NH_2$  occurs first at nitrogen, then at oxygen<sup>89</sup>, except with formamide, when the *N,N*-derivative results<sup>90</sup>. *N*-Haloamides<sup>91</sup> and  $\alpha$ -pyridone are silylated at oxygen. Bis(trimethylsilyl)acetamide has been shown by NMR spectroscopy to exist as the iminoether and the similarity of coalescence temperatures (11–15 °C) for both  $Me_3Si$  and  $PhMe_2Si$  shows the aryl group to have little steric or electronic effect. While *N*-alkyl-*N*-silylamides exist as amide, the *N*-aryl derivatives occur as amide–imidate equilibria (equation 57)<sup>89,92</sup>. With silylthioamides, restricted rotation about the C–N bond enables three isomers to be detected (equation 58), but bis(trimethylsilyl)dithioamide crystallizes as the *N,N'*-isomer<sup>93</sup>.

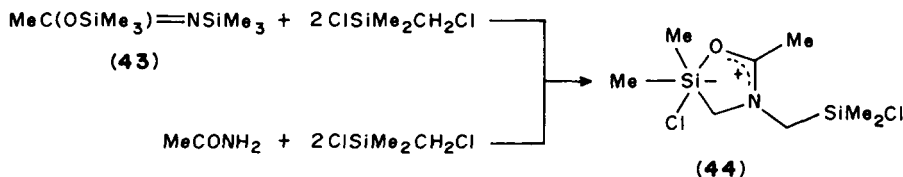


Trimethylsilylanilides occur as amide–imidate mixtures in solution. Low temperature <sup>1</sup>H NMR spectroscopy shows hindered rotation about the carbonyl–nitrogen bond of the amide form, while silyl migration from nitrogen to oxygen gives the imidate isomer **41**. There is no evidence for *syn*–*anti* isomerism with the imidate form (equation 59).



Both isomerization processes occur with formanilides and benzanilides, giving three peaks on cooling, but with acetanilides, only exchange is observed since, even at –60 °C, only two peaks are seen, supporting the presence of only the *syn* amide isomer **42**<sup>94</sup>.

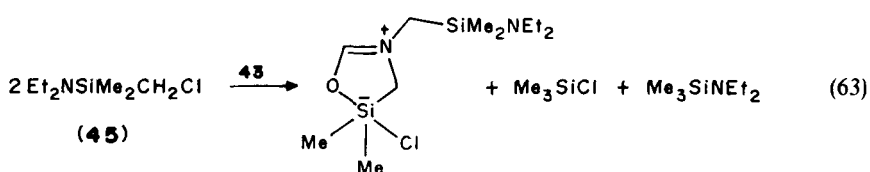
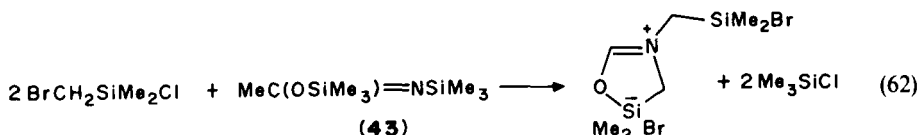
The transsilylation of aminosilanes is a slow reaction (equation 60)<sup>23a</sup>, so it is surprising to find that bis(trimethylsilyl)acetamide (**43**) reacts exothermically with chloromethyl–dimethylchlorosilane to give disubstitution. This occurs at carbon and not silicon. The product **44** has no silicon–nitrogen bonds and a high coalescence temperature for the Si–Me resonances (~140 °C). Indeed, **44** can be prepared directly from acetamide and the chlorosilane in the presence of triethylamine (equation 61)<sup>95</sup>.



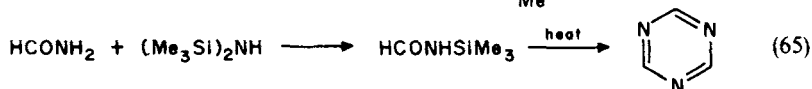
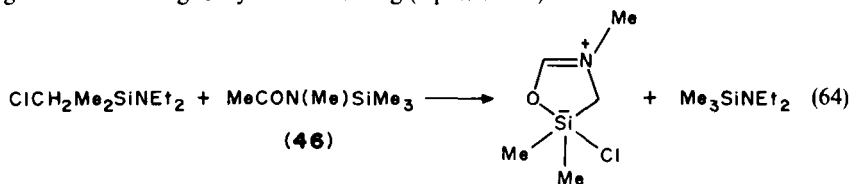
(61)



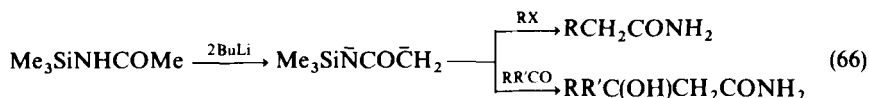
Transsilylation with bromomethyldimethylchlorosilane gives mono- and disubstitution, ring formation occurring as the first step, but halogen exchange also occurs at silicon (equation 62). With the chloromethylaminosilane **45**, only the ring silyl group becomes chlorinated (equation 63).



With *N*-trimethylsilyl-*N*-methylacetamide (**46**), a similar heterocycle results from halomethylsilanes, bromine favouring the ring silicon in the Cl/Br system, but chlorine the ring silicon in the chloromethylaminosilane reaction (equation 64)<sup>96</sup>. *N*-Trimethylsilylformamide results from formamide and hexamethyldisilazane or trimethylsilyl cyanide and gives triazene in good yield on heating (equation 65)<sup>90</sup>.



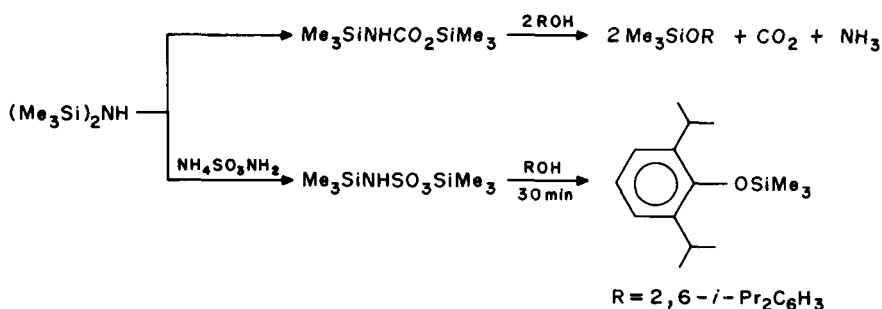
The dianion formed from *N*-trimethylsilylacetamide does not undergo silyl migration, electrophiles yielding the appropriate amides (equation 66)<sup>97</sup>.



## V. PROTECTION OF —OH, >NH AND —SH BONDS<sup>4</sup>

Like hexamethyldisilazane, silylamides have been extensively used as silylating agents in organic and in particular bio-organic synthesis<sup>98</sup>. The silylamidosulphonate is even better than the bis(trimethylsilyl)acetamide. It is prepared as a crystalline solid from ammonium sulphamate<sup>99</sup> and, like *N*-trimethylsilyl imidazole, fully silylates 2,6-diisopropylphenol in 30 min at 30 °C. With the acetamide, only 75% silylation results. Bis(trimethylsilyl)carbamate (7.5%)<sup>100</sup> is little better than hexamethyldisilazane (3.2%),

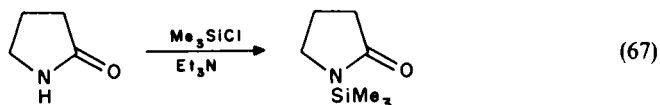
but has the convenience in other syntheses of giving only volatile by-products, ammonia and carbon dioxide (Scheme 12).



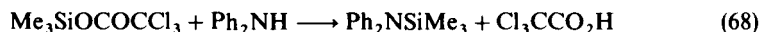
SCHEME 12

In addition to using acetamides for proton protection, ureas have also proved effective. Thus Ph(Me<sub>3</sub>Si)NCONHPh silylates *N,N'*-dimethylurea completely in one minute, whereas hexamethyldisilazane, *N*-trimethylsilylpiperidine and *N*-trimethylsilylaniline give little silylation after 3 days, while *N,N'*-bis(trimethylsilyl)urea, readily prepared from urea and hexamethyldisilazane, is the most effective silylating agent for alcohols and carboxylic acids<sup>101</sup>. *N*-Methyl(*t*-butyldimethylsilyl)acetamide and trifluoroacetamide silylate alcohols, thiols and primary amines in less than one minute at room temperature. Secondary amines take longer. Subsequent ethanolysis regenerates carboxylic acid and thiol groups within 30 min, while *t*-butyldimethylsilylamino groups, which are about 100 times more stable than trimethylsilylamino groups, react with ethanol at 50 C in 15 minutes<sup>102</sup>.

*N*-Trimethylsilyl-2-oxazolidinone, which is readily prepared from oxazolidinone (equation 67), rapidly silylates alcohols in minutes at room temperature, no matter how hindered, if catalysed by a little Me<sub>3</sub>SiCl. It is better at silylating 1,3-dicarbonyl compounds than either bis(trimethylsilyl)formamide or hexamethyldisilazane<sup>103</sup>.



The *t*-butyldiphenylsilyl group is particularly effective at protecting primary amines to chromatography, basic and hydrolytic reagents, and to alkylating and acylating agents. Mild acid or pyridine/HF will smoothly cleave the protecting silyl group<sup>104</sup>. The silyl trichloroacetates RMe<sub>2</sub>SiOCOCCl<sub>3</sub> (R = Me, *t*-Bu) silylate aryl amines in good yield in the presence of dry potassium carbonate and 18-crown-6 on heating to 120°C. Thus diphenylamine can be silylated in 70% yield by this method whereas yields from the chlorosilane or by transamination are poor (equation 68)<sup>105</sup>.



*N*-Tri-isopropylsilylpyrrole is so hindered as to direct electrophilic attack to position 3, subsequent desilylation with Bu<sub>4</sub>NF giving the 3-substituted pyrrole. The ethoxalyl, *p*-toluenesulphonyl, and nitro derivatives result exclusively, but bromination gives a mixture containing 15% of the 2 isomer (equation 69)<sup>106</sup>.





TABLE 3. Molecular parameters for alkali metal disilylamides

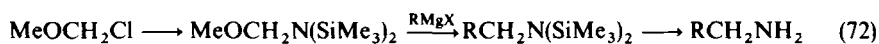
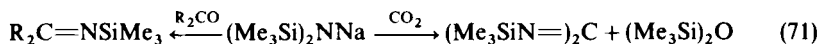
Compound	Si—N (pm)	Si $\hat{N}$ Si (deg)	Metal---nitrogen interaction (pm)	reference
[(Me <sub>3</sub> Si) <sub>2</sub> NLi] <sub>3</sub>	172.9	118.6	200	119
[(Me <sub>3</sub> Si) <sub>2</sub> NNa] <sub>4</sub>	169.0	125.6	235.5	120
(Me <sub>3</sub> Si) <sub>2</sub> NK(dioxan) <sub>2</sub>	164	136.2	270	121
[(Me <sub>3</sub> Si) <sub>2</sub> NLi] <sub>2</sub> <sup>a</sup>	171.2	129.8	199	122
[(Me <sub>3</sub> Si) <sub>2</sub> NLiOEt <sub>2</sub> ] <sub>2</sub>	170.5 (170.5)	121.9 (121.2)	206 (205.5)	123a 123b
[(Me <sub>3</sub> Si) <sub>2</sub> NLiTHF] <sub>2</sub>	168.9	122.3	202.5	124
[(Me <sub>2</sub> Si) <sub>3</sub> N <sub>3</sub> H <sub>2</sub> LiTHF] <sub>2</sub>	169.7	117.7	203.5	125
[(Me <sub>3</sub> Si) <sub>2</sub> NLi(12-crown-4)]	168.1	123.5	196.5	126
[(Ph <sub>3</sub> Si) <sub>2</sub> N <sup>-</sup> (12-crown-4) <sub>2</sub> -Li <sup>+</sup> THF]	163.3	154.9		112b

<sup>a</sup>Electron diffraction study. All others in the table are X-ray diffraction

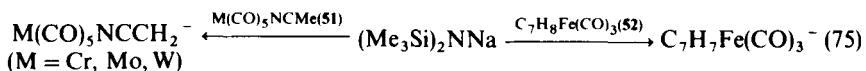
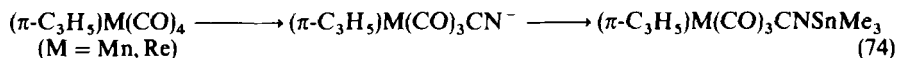
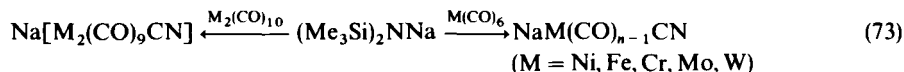
wide Si—N—Si angle, comparable to those of silaimines (see Section XVIII.A). Bond lengths and angles are recorded in Table 3.

## 2. Use in organic synthesis<sup>3,4</sup>

The three amides (Me<sub>3</sub>Si)<sub>2</sub>NM (M = Li, Na, K) have been extensively used in synthesis. The sodium derivative reacts readily with ketones and carbon dioxide to give the imine or carbodiimide (equation 71)<sup>127</sup>, which also results from the silylisocyanate<sup>128</sup>. With chloromethyl methyl ether, the methoxymethylsilylazane results, and can be demethoxylated with a Grignard reagent without cleaving the silicon—nitrogen bond. Subsequent hydrolysis gives the primary amine (equation 72)<sup>129</sup>.

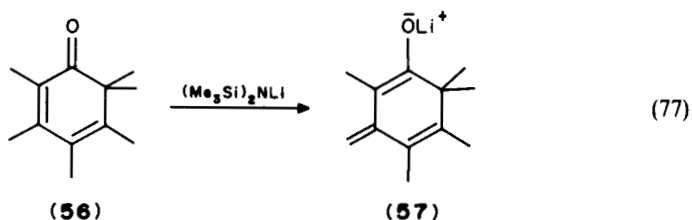
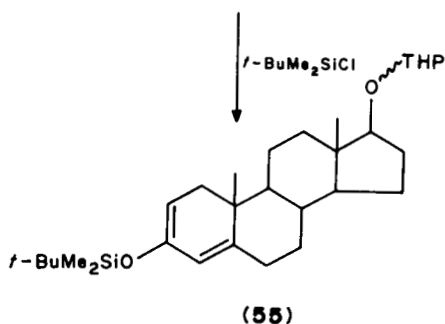
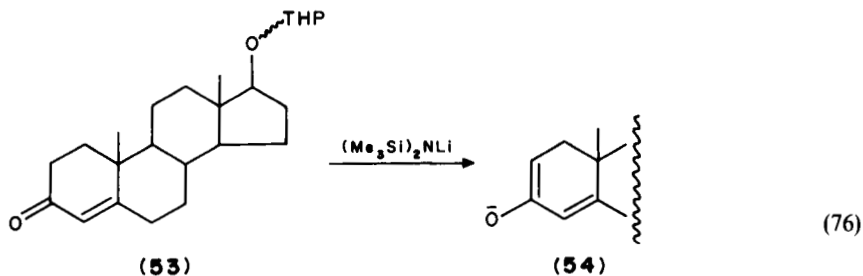


Metal carbonyls are easily converted to the nitrile through nucleophilic attack at the carbonyl group<sup>130</sup>, even with the  $\pi$ -allyl derivative, which can then be stannylated at nitrogen (equations 73 and 74)<sup>131</sup>. With the acetonitrile and heptatriene carbonyl complexes **51** and **52**, however, it functions as a base, in the latter case giving the tropylium complex (equation 75)<sup>132</sup>.

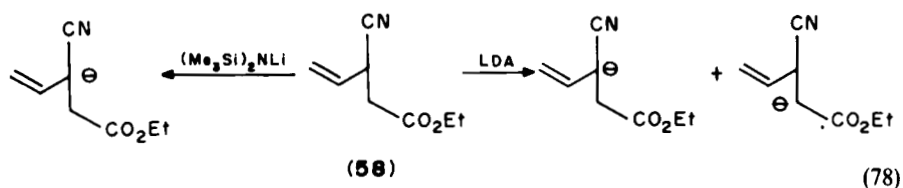


The lithium amide has proved most useful in generating kinetically stable enolates. Enolates formed from the sodium amide are less regioselective. Thus the  $\Delta^4$ -3-keto system of testosterone 17-tetrahydropyranyl ether **53** gives the kinetically controlled  $\Delta^{2,4}$ -homoannular dienolate ion **54** which on silylation and aqueous work up gives the

hitherto unknown homoannular 2,4-dienol silyl ether **55** (equation 76)<sup>133</sup>. With the dienone **56**, the gamma proton is removed exclusively to give the cross-conjugated anion **57** (equation 77)<sup>134</sup>.

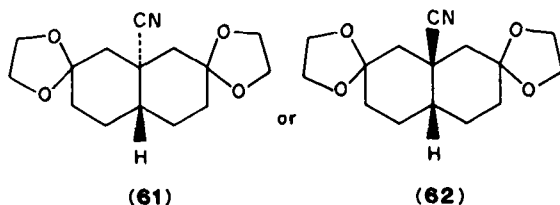
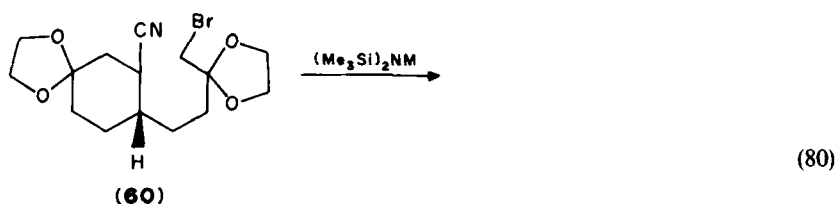
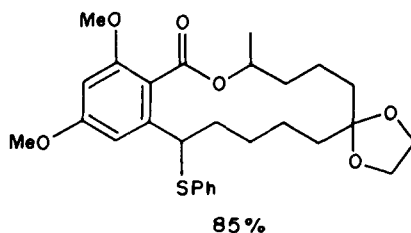
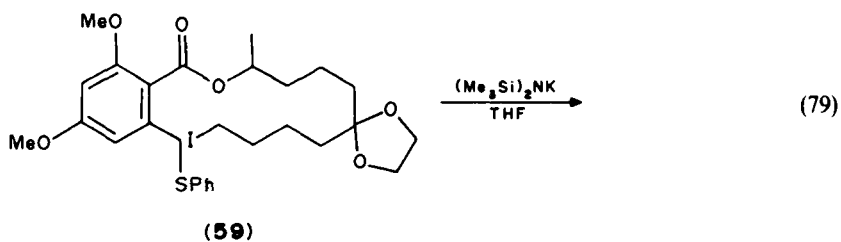


Lithium di-isopropylamide (LDA) gives a mixture of products on deprotonation of **58**, whereas lithium bis(trimethylsilyl)amide exclusively deprotonates alpha to the cyanide (equation 78)<sup>135</sup>.



The potassium amide has been used to cyclize  $\omega$ -iodoalkyl 2-phenylthiomethyl 4,6-dimethoxybenzoate (**59**) to give the macrolide in a high yield, fast synthesis (equation

79)<sup>136</sup>. Indeed, a remarkable contrast in the specificity generated by different cations is illustrated with the cyclization of **60** to the substituted decalins **61** and **62**, the *cis*-isomer dominating if the potassium amide is used, and the *trans*-isomer with the lithium amide (equation 80)<sup>137</sup>.



95%, m. p. 163–164 °C

M = Li

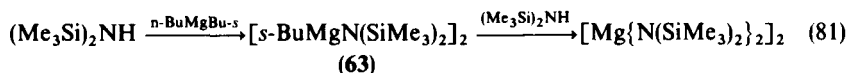
95%, m. p. 108–109 °C

M = K

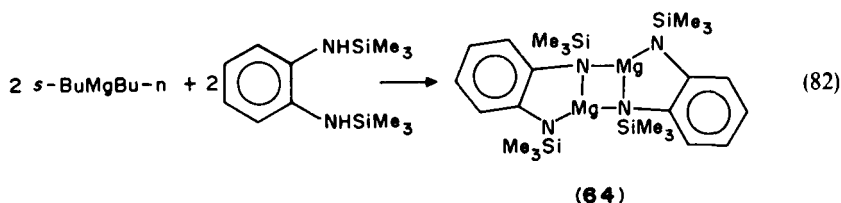
## B. Alkaline Earth Metals

The bisamides of beryllium and magnesium result from the lithium or sodium amide and the appropriate halide. Both are monomeric, volatile liquids. An electron diffraction study on the beryllium derivative (m.p.  $-2^{\circ}\text{C}$ ) shows it to possess  $D_2$  symmetry with the NBeN unit linear and the two BeNSi<sub>2</sub> units planar and perpendicular to each other<sup>138</sup>. The magnesium compound, which also results from hexamethyldisilazane and

the magnesium dialkyl  $n\text{-BuMgBu-s}$ , crystallizes as an etherate but can be readily desolvated. The 1:1 reaction with  $n\text{-BuMgBu-s}$  gives the  $s$ -butyl derivative **63** which shows disorder of the  $s$ -butyl groups in the crystal, and is isomorphous with  $[(\text{Me}_3\text{Si})_2\text{NLiTHF}]_2$ . **63** has Si—N bonds of 174.2 pm and SiNSi angle of  $118.4^\circ$ , showing more covalency at Mg—N and therefore less  $\pi$ -bonding at the silicon–nitrogen bonds than with the lithium amide (equation 81)<sup>124</sup>.

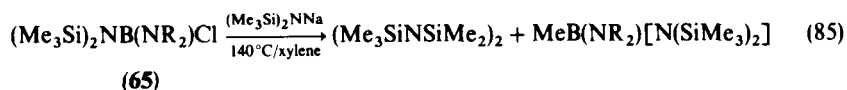
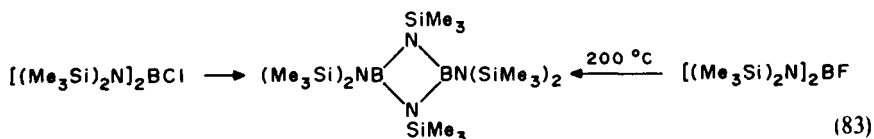


A similar reaction occurs between  $s\text{-BuMgBu-n}$  (formed from  $n\text{-BuMgCl}$  and  $s\text{-BuLi}$ ) and 1,2-bis(trimethylsilylamino)benzene. Butane is eliminated to give the dimeric complex **64** with magnesium solvated and silicon–nitrogen bonds of 171.9 and 177.8 pm (equation 82)<sup>139</sup>.

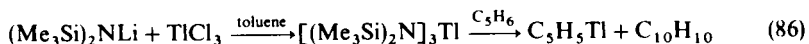


### C. Boron Group Derivatives

The trisamide of boron is not known, though the mono- and bisaminohaloboranes can be prepared, the chlorides condensing with excess sodium silyl amide or on heating to give the diboradiazetane or borazine (equations 83 and 84)<sup>140</sup>. Methyl migration from Si to B occurs with the mixed aminoborane **65** to give the cyclosilazane (equation 85)<sup>141</sup>.



Trisamides of the four group III (13) metals result from the amide and trichloride and are monomeric, low melting solids, with those of aluminium and thallium isomorphous, and having a planar  $\text{MN}_3$  skeleton. The thallium derivative readily oxidizes cyclopentadiene to  $\text{C}_{10}\text{H}_{10}$ , thought to be 9,10-dihydrofulvene (equation 86)<sup>142</sup>.



A series of adducts result from  $\text{Me}_2\text{AlX}$  ( $\text{X} = \text{Me}, \text{Cl}$ ) and  $(\text{R}_3\text{Si})_2\text{NY}$  ( $\text{R} = \text{Me}, \text{Et}$ ;

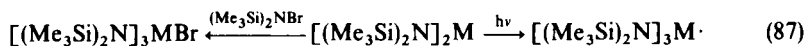


Y = H, Cl, Na) which decompose to give both  $(Et_3Si)_2NAlMe_2$  and  $(Me_3Si)_2NAl_2Me_3$ , the latter possessing chloride and disilylamide bridges between the aluminium atoms<sup>143</sup>.

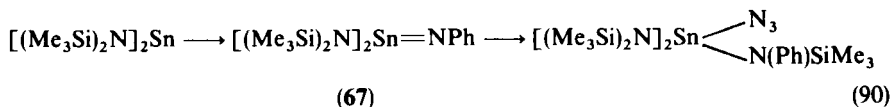
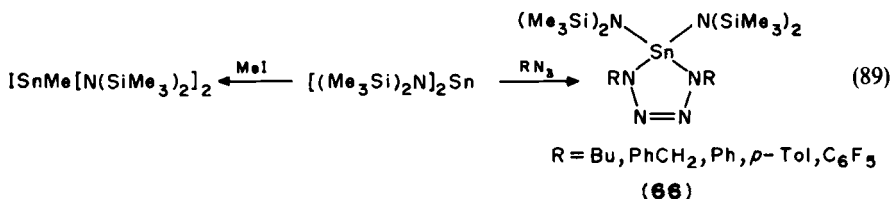
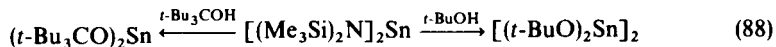
#### D. Divalent Germanium, Tin and Lead Derivatives

The bisamides of germanium, tin and lead can be readily made from the lithium amide and  $MCl_2$  (M = Ge, Sn, Pb). All are thermochromic, low melting crystalline solids, which are monomeric with a bent structure in both the solid and vapour states<sup>144</sup>. The bond angle at M differ by some  $10^\circ$  between the two states, but there is much less difference for other parameters (Table 4)<sup>145</sup>.

All are oxidized by the bromoamine  $(Me_3Si)_2NBr$  and give persistent trisamide radicals (half-life several months) on photolysis, though the lead amide derivative deposits a lead mirror (equation 87)<sup>146</sup>.



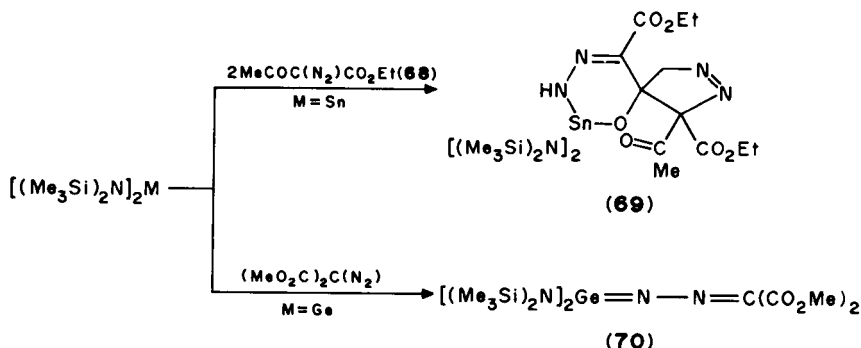
Protic reagents HX regenerate the disilazane and  $MX_2$ , notably with M = Sn, *t*-butanol giving dimeric *trans*- $[Sn(OBu-t)_2]_2$ , with *t*-butoxy bridges, but a monomer with the more hindered alcohol *t*-Bu<sub>3</sub>COH (equation 88)<sup>147</sup>. Organic halides oxidatively add to  $[(Me_3Si)_2N]_2Sn$ <sup>148</sup>, which also reacts with a variety of organic azides to give the heterocycle **66** through addition of the bisamidostannimine (equation 89). Such an intermediate is confirmed through addition of azidotrimethylsilane giving the trisamido-azidostannane **67** (equation 90)<sup>149</sup>.



The tin derivative adds two moles of the diazoester **68** to give the spiro 1:2 adduct **69**, while the germanium analogue is oxidized by the diazo compound to the intermediate germimine **70**, which reacts further if it possesses enolisable protons, but can be isolated for  $(MeO_2C)_2CN_2$  (Scheme 16)<sup>150</sup>.

TABLE 4. Molecular parameters for  $[(Me_3Si)_2N]_2M$  (M = Ge, Sn, Pb)

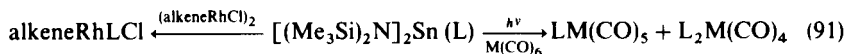
M	M-N (pm)		NMN (deg)		Si-N (pm)	SiNSi (deg)
	X-ray	Gas	X-ray	Gas	X-ray	X-ray
Ge		189		101		
Sn	209	209	104.7	96	174.2	123
Pb	224	220	103.6	91	172.4	126



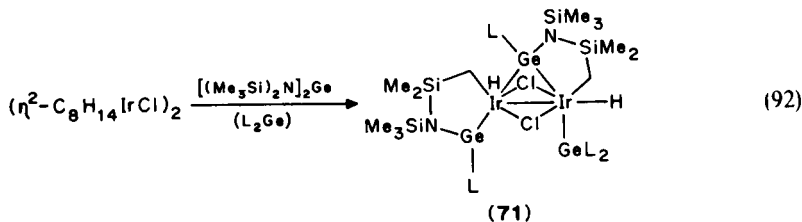
SCHEME 16

## 1. Transition metal derivatives

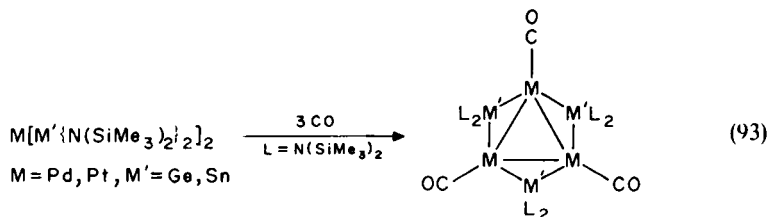
With metal hexacarbonyls, irradiation gives mono and isomeric disubstituted derivatives<sup>151</sup>, while with olefin rhodium chloride dimers, the metal-halogen bond is inserted (equation 91)<sup>152</sup>.



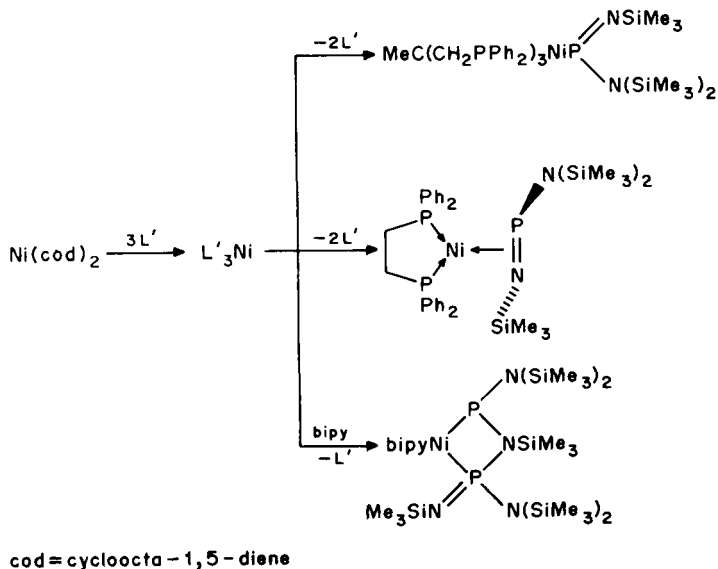
The smaller germylene undergoes a much more complex reaction with [(cyclooctene)<sub>2</sub>IrCl]<sub>2</sub> to give the bimetallic complex **71**, which is formed through olefin displacement, insertion into the C—H bond of Si—Me, and germylene bridging. The three germylene ligands are all different, one solely coordinated, one terminal with C—H insertion and one bridging with C—H insertion (equation 92)<sup>153</sup>.



With (cyclooctadiene)<sub>2</sub>PdCl<sub>2</sub> and (cyclooctadiene)<sub>2</sub>Pt, the germanium(II) and tin(II) amides give three coordinate derivatives which, with CO, form trimetallic clusters (equation 93)<sup>154</sup>.

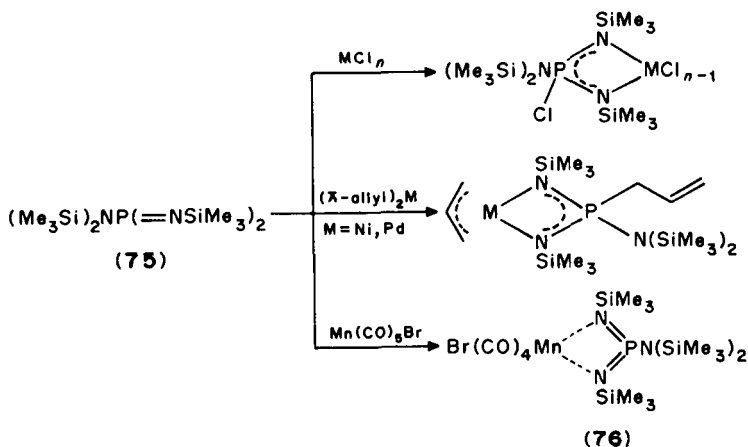






SCHEME 19

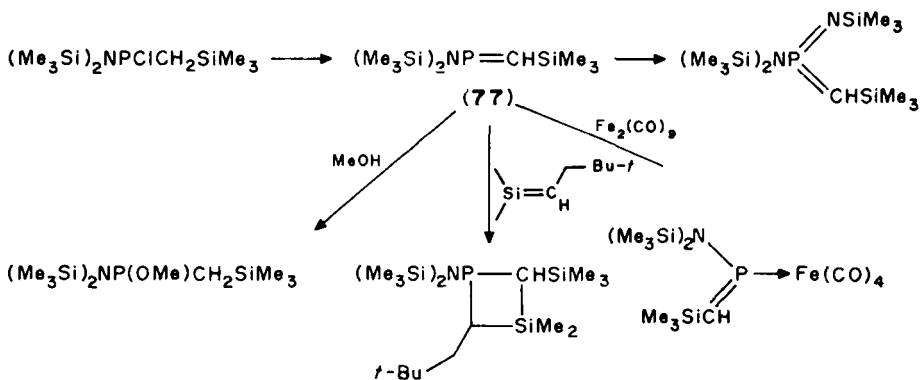
The structure of  $(\text{Me}_3\text{Si})_2\text{NP}=\text{NSiMe}_3$  at  $-130^\circ\text{C}$  shows the imino silicon–nitrogen bond (172.1 pm) to be shorter than the amino ones (177.6 and 179.0 pm)<sup>160</sup>, as is also the case with the aminobis(imino)phosphorane  $(\text{Me}_3\text{Si})_2\text{NP}(=\text{NSiMe}_3)_2$  (**75**)<sup>161</sup>, which results from **73** on oxidation with trimethylsilyl azide<sup>162</sup>. It readily forms chelate complexes with early transition metal chlorides which also undergo chlorine transfer to phosphorus<sup>163</sup>, and reacts with  $(\pi\text{-allyl})_2\text{M}$  ( $\text{M}=\text{Ni}, \text{Pd}$ ) through allyl migration to



SCHEME 20

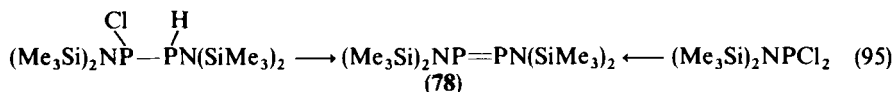
phosphorus. The nickel complex will polymerize ethylene<sup>164</sup>. With  $\text{Mn}(\text{CO})_5\text{Br}$ , a fluconal complex **76** results (Scheme 20)<sup>165</sup>.

The aminophosphane  $(\text{Me}_3\text{Si})_2\text{NP}=\text{CHSiMe}_3$  (**77**) results from  $(\text{Me}_3\text{Si})_2\text{NPCl}-\text{CH}_2\text{SiMe}_3$  and  $(\text{Me}_3\text{Si})_2\text{NLi}$ <sup>166</sup> and, like its imino analogue **73**, adds methanol and silenes, can be oxidized by silyl azide to the phosphorus(V) derivative and complexes as a monodentate ligand on reaction with  $\text{Fe}_2(\text{CO})_9$  (Scheme 21)<sup>167</sup>.

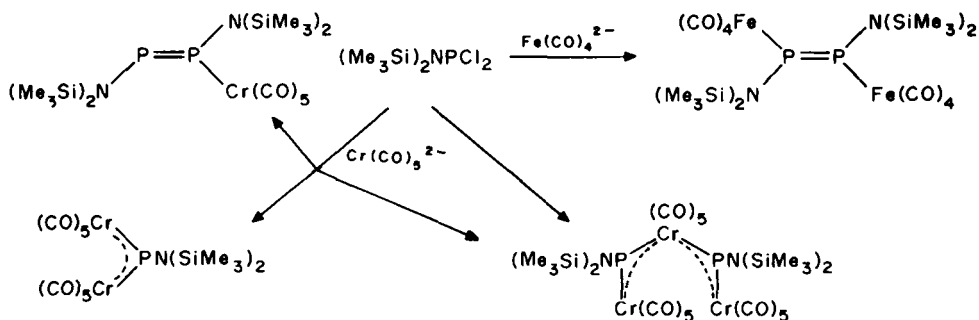


SCHEME 21

The diphosphene **78** results directly from the diphosphine, and also by reductively condensing the aminodichlorophosphine with  $\text{LiAlH}_4$  or  $\text{BuLi}$  (equation 95). **78** slowly dimerises and its structure is *trans* with the  $\text{SiNSi}$  plane at  $77.5^\circ$  to that of  $\text{PPN}$ , in contrast to the coplanar structure of the tetrazene  $(\text{Me}_3\text{Si})_2\text{NN}=\text{NN}(\text{SiMe}_3)_2$  (Section XIII.D)<sup>168</sup>.

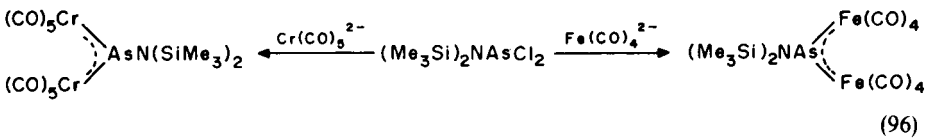


**78** can also be formed by reducing the aminodichlorophosphine with metal carbonyl anions, when  $\sigma$ -bonded complexes of the diphosphene, together with both mono and bisphosphinidene complexes, result (Scheme 22)<sup>169</sup>.



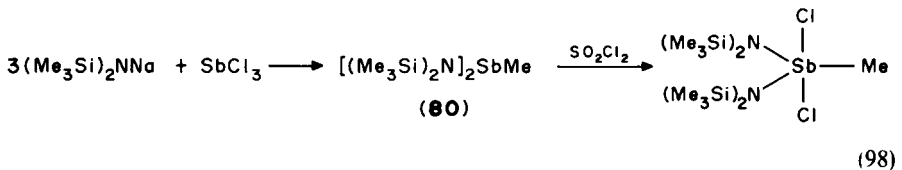
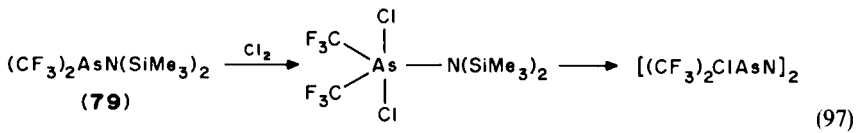
SCHEME 22

Bis(trimethylsilyl)aminodichloroarsine can be similarly reduced (equation 96).



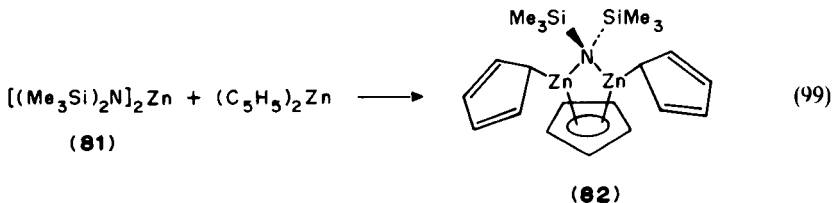
## 2. Arsenic and antimony derivatives

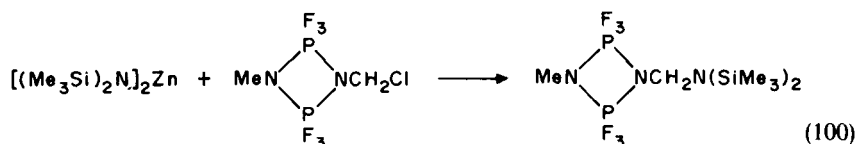
Oxidizing the bisilylaminoarsine **79** with chlorine gives the trigonal bipyramidal adduct which, with excess chlorine, gives the cyclodiarsa-(V)-azane (equation 97)<sup>170</sup>. No tris(bisilylamino)arsine is known, as with phosphorus, and attempts to prepare the antimony analogue from the trichloride and the sodium amide result only in disubstitution and methyl migration to antimony. Oxidation of **80** (using  $\text{SO}_2\text{Cl}_2$ ) gives the adduct with axial chlorine atoms and long Si—N bonds (176.2 and 180.8 pm) and SiNSi angles of  $121 \pm 1^\circ$  (equation 98)<sup>171</sup>.



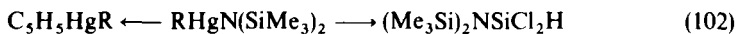
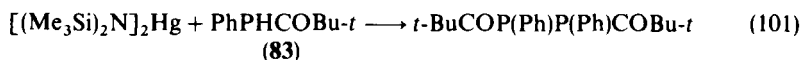
## F. Zinc, Cadmium and Mercury Derivatives

The zinc diamide **81** is monomeric and has a  $D_{2d}$  skeleton structure reduced to  $S_4$  if the methyl groups are included in the symmetry<sup>172</sup>. The silicon–nitrogen bonds average 172.8 pm, but are lengthened to 177 pm in the amide bridged derivative **82** formed from **81** and dicyclopentadienyl zinc (equation 99). **82** provides the first case of a cyclopentadienyl group bridging two metals on the same side of the ring<sup>173</sup>. **81** reacts with the cyclodiphospha-V-azane to substitute at chlorine (equation 100)<sup>174</sup>.



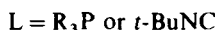
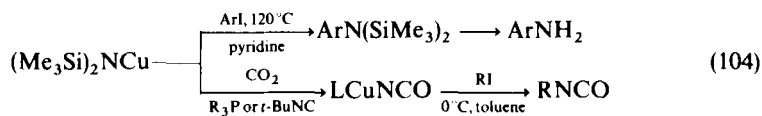
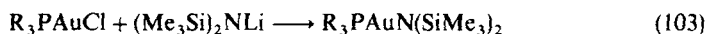


The cadmium and mercury bisamides, like zinc, both have a linear NMN structure, the former readily coordinating with amines<sup>175</sup>, and the latter oxidizing the pivaloyl phosphine **83** to the diphosphine (equation 101) and reacting with phosphines  $\text{R}_2\text{PH}$  to give the diphosphide  $(\text{R}_2\text{P})_2\text{Hg}$ <sup>176</sup>. The mercury monoamides  $\text{RHgN}(\text{SiMe}_3)_2$  can be deaminated by cyclopentadiene, protic reagents and trichlorosilane (equation 102)<sup>177</sup>.



### G. Copper, Silver and Gold Derivatives

Silylamide derivatives of the coinage metals copper, silver and gold are all known. The gold derivatives result as two-coordinate crystalline phosphine and arsine complexes (equation 103)<sup>178</sup>. The uncomplexed silver amide, reported with those of rubidium and caesium, is explosive<sup>179</sup>, and the copper(I) amide, reputedly tetrameric<sup>180</sup>—it has a much higher sublimation temperature than the dimeric manganese(II) and nickel(II) derivatives—has proved a useful synthetic intermediate for the preparation of arylamines or alkyl isocyanates (equation 104)<sup>181</sup>.



### H. Transition Metal Derivatives<sup>10</sup>

The bulky bis(trimethylsilyl)amide ligand (L) has been used extensively to prepare low coordination number transition metal complexes. Neutral trisamides have been synthesized for the metals scandium, titanium, vanadium, chromium and iron. All are trigonal planar, as is the scandium(III) derivative in the vapour, though it is pyramidal as a solid, and apart from the titanium(III) compound, all are volatile<sup>182</sup>. The lanthanide and uranium(III) derivatives are similarly pyramidal, with disordering of the metal ion above and below the plane of ligands, indicating a greater degree of ionic character than with the derivatives of the lighter metals. The silicon–nitrogen bonds are shorter even than those in the planar thallium derivative. The photoelectron spectra of the compounds  $\text{L}_3\text{M}$  ( $\text{M} = \text{Sc, Ti, Cr, Fe, Ga, In}$ ) all support a strong- $I$  mesomeric effect for the disilylamide ligand, indicating  $\text{N} \rightarrow \text{Si } p_\pi\text{-}d_\pi$  bonding<sup>183</sup>. Indeed, a plot of the ionization energies of band A ( $\text{M-N } \pi$ -ionization) in the He-I and He-II photoelectron spectra against band B ( $\text{M-N } \sigma$ -ionization) gives a linear plot with U, Eu and Nd close to  $\text{NaN}(\text{SiMe}_3)_2$  and Hg, Zn and Co near the more covalent  $\text{LiN}(\text{SiMe}_3)_2$ <sup>184</sup>.

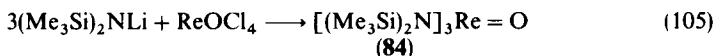
Divalent manganese, cobalt and nickel all give bisilylamide complexes. The former

pairs are dimeric, with metal atoms bridged by amide ligands, which have a smaller angle (112–113°) and longer silicon–nitrogen bonds (177–179 pm) than the terminal amide. The manganese derivative reacts with excess lithium amide to give the THF complex (THF)Li[(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>3</sub>Mn in which manganese is in the plane of the three amide ligands, two of which bridge the lithium cation<sup>185</sup>. With the larger (Ph<sub>2</sub>MeSi)<sub>2</sub>N<sup>-</sup> ligand, the Fe(II) and Co(II) derivatives are monomeric. Both are bent at the metal (NFeN 169.0°, NCoN 147.0°) and short metal–C(phenyl) distances imply the presence of agostic hydrogen atoms. The Si–N bonds are distinctly shorter and the SiNSi angles larger than in {[(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Co}<sub>2</sub><sup>186</sup>.

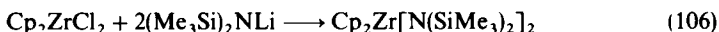
Cobalt forms a pair of monoamide complexes [Li(THF)<sub>4.5</sub>]<sup>+</sup> {Co[N(SiMe<sub>3</sub>)<sub>2</sub>][OC(Bu-*t*)<sub>3</sub>]<sub>2</sub>}<sup>-</sup> and its unsolvated derivative, using the hindered *t*-Bu<sub>3</sub>CO<sup>-</sup> as a second ligand. Structure determinations on both showed a trigonal planar geometry about the metal with silicon–nitrogen bonds shorter, and SiNSi angle wider in the solvated complex, while the lithium ion bridges the two oxygen atoms in the unsolvated one<sup>187</sup>.

The cobalt(II) and nickel(I) complexes [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>CoPPh<sub>3</sub> and (Me<sub>3</sub>Si)<sub>2</sub>NNi(PPh<sub>3</sub>)<sub>2</sub>, like the square planar chromium(II) complex [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Cr(THF)<sub>2</sub>, are paramagnetic<sup>188</sup>. The nitrosyl trisamide complex Cr(NO)[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> and its analogues, however, provided the first examples of low spin tetrahedral complexes<sup>189</sup>.

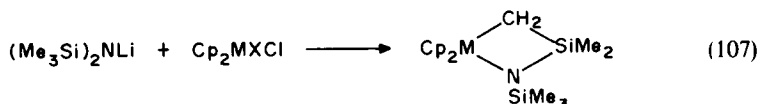
The low oxidation state rhodium(I) and ruthenium(II) derivatives (Me<sub>3</sub>Si)<sub>2</sub>NRh(PPh<sub>3</sub>)<sub>2</sub> [from (Ph<sub>3</sub>P)<sub>3</sub>RhCl] and (Me<sub>3</sub>Si)<sub>2</sub>NRu(H)(PPh<sub>3</sub>)<sub>2</sub> are much less thermally stable than the early transition metal derivatives, the former decomposing at 25 °C with half-life of about 12 h to give hexamethyldisilazane quantitatively. By way of contrast, ReOCl<sub>4</sub> yields the oxytrisamide **84** as an air-stable diamagnetic red sublimable solid (equation 105)<sup>190</sup>.



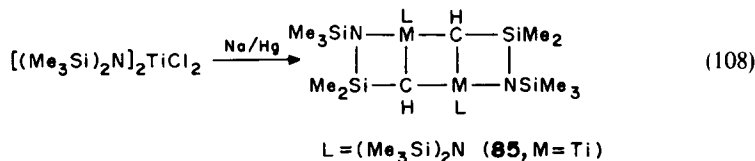
Attempts to synthesize the tetraamides of titanium, zirconium and hafnium from the tetrachloride and excess amide result only in generating the chlorotrisamide [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>3</sub>MCl (M = Ti, Zr, Hf), reflecting the degree of hindrance of this ligand, even with the larger metals<sup>191</sup>. This effect is also manifested with the amides resulting from titanocene and zirconocene dichlorides. The latter will form the bisamide (equation 106), which shows amide non-equivalence at 27 °C. Proton coalescence occurs at 84 °C<sup>192</sup>.



With titanocene dichloride, steric clash induces attack at the methyl group of the amide to give the metallacyclobutane. Cp<sub>2</sub>ZrHCl behaves similarly, no bisamide resulting (equation 107).

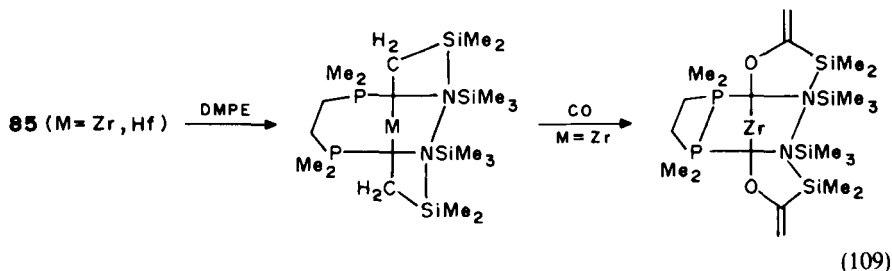


Reducing [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>TiCl<sub>2</sub> with sodium gives the tricyclic metallocycle (**85**, M = Ti) (equation 108). Analogous zirconium and hafnium derivatives result on warming the





amides  $R_2M[N(SiMe_3)_2]_2$  ( $R = Me, Et, Me_3SiCH_2$ ). They add pyridine and complex with bis(dimethylphosphino)ethane (DMPE) to give the bismetallocycle. The hafnium derivative inserts CO under pressure at room temperature (equation 109)<sup>193</sup>.



### I. Lanthanide Derivatives<sup>10</sup>

The trisamide derivatives have been prepared for all the lanthanides except promethium (radioactive<sup>145</sup>Pm half-life 17.7 yr), dysprosium and thulium. The lanthanum and lutetium derivatives are diamagnetic and the others paramagnetic with the gadolinium derivative having a magnetic moment of 7.82 BM (7 unpaired electrons). The structures of the europium and neodymium complexes tend to show pyramidal rather than trigonal geometry, reflecting more ionic character to the bonding than in the d-block complexes<sup>194</sup>. This is also seen in the gas-phase electron diffraction structures of the trisamides of cerium and praeodymium, which show non-planar structures and short silicon–nitrogen bonds<sup>195</sup> (Table 5), though longer than those in the potassium amide derivative (see Table 3).

The lanthanide trisamides form 1:1 adducts with  $Me_3PO$  (La, Pr, Eu, Gd) and  $Ph_3PO$  (La, Eu, Lu) and give the novel peroxy derivatives  $M_2[N(SiMe_3)_2]_4O_2(OPPh_3)_2$  ( $M = La, Pr, Sm, Eu, Lu$ ) using  $(Ph_3PO)_2 \cdot H_2O_2$ . The structure ( $M = La$ ) shows the peroxy group to act as a doubly bridging bidentate ligand in a planar  $La_2O_2$  unit (equation 110)<sup>196</sup>.

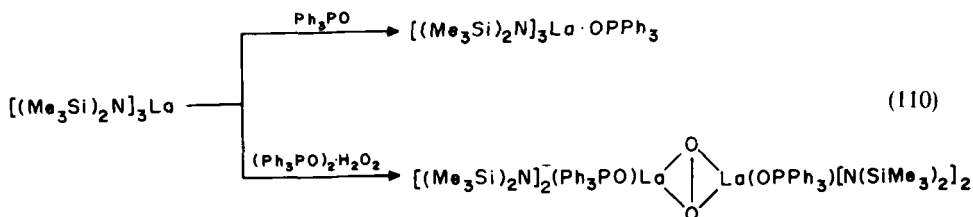
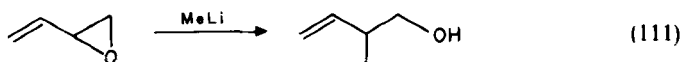


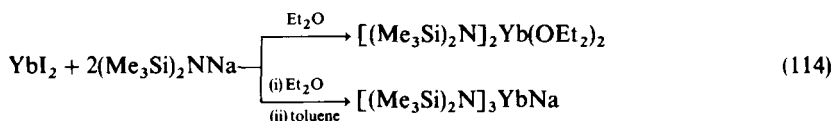
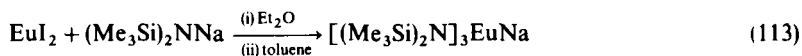
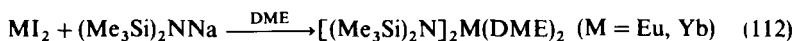
TABLE 5. Molecular parameters for rare-earth amides  $[(Me_3Si)_2N]_3M$

M	Technique	NMN (deg)	Si–N (pm)	SiNSi (deg)
Eu	X ray	116.6	168	129.4
Nd	X ray	117.8	171	126.4
Ce	ED	112	169.6	129
Pr	ED	113	170.5	129

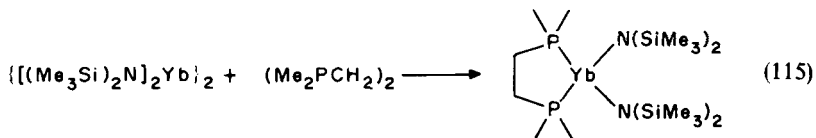
The trisamides of yttrium, samarium and erbium will all catalyse the regiospecific opening of epoxides with MeLi, 2-methyl-3-buten-1-ol resulting from buta-1,3-diene monoxide (equation 111), while from cyclohexane oxide, the *trans*-2-methylcyclohexanol results in excellent yield<sup>197</sup>.



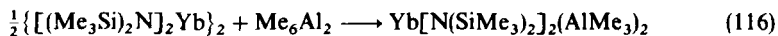
Both europium(II) [4f<sup>7</sup>] and ytterbium(II) [4f<sup>14</sup>] will form bis(silyl)amide derivatives which crystallize as neutral complexes with ether or DME (equations 112 and 114). They also form trisamide anions in the presence of excess sodium silylamide. As with the trisamido manganese(II) complex, two amide groups bridge to the alkali metal ion, but coordination about the lanthanide metal is again pyramidal and the silicon–nitrogen bond lengths are short (<170 pm) (equation 113 and 114)<sup>198</sup>.



The ytterbium(II) amide readily complexes with chelating diphosphines. The amide ligand shows short silicon–nitrogen bonds (~168 pm) and a wide angle at nitrogen (130.5°) because of the greater ionic character of the interaction compared with the d-block complexes. In addition, a weak intramolecular interaction between the metal and a silicon methyl group is present (304 pm), rendering these methyl protons weakly acidic<sup>199</sup>. Such an interaction could provide a pathway for carbanion attack at the metal and cyclization as is observed with titanium and zirconium, uranium and thorium (equation 115).



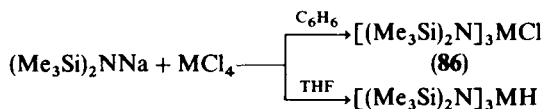
The ytterbium bisamide reacts with trimethylaluminium to give a yellow diamagnetic adduct  $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{AlMe}_3)_2$  in which the alane coordinates with the amide at nitrogen and forms weak Yb---C interactions at 275 (two such interactions), 304 and 320 pm. One methyl group at each silicon is about 305 pm from ytterbium (equation 116)<sup>200</sup>. This complex will polymerize ethylene at room temperature under 12 atmospheres pressure.



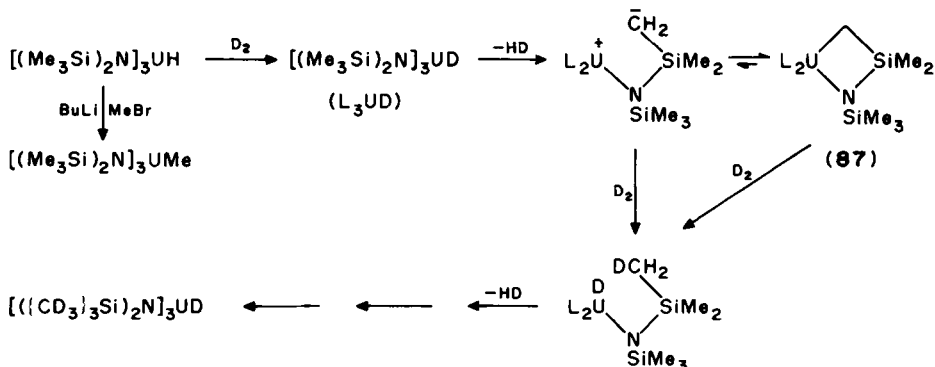
Luminescence studies of the terbium(III) derivative, which involves emission from the excited <sup>5</sup>D<sub>4</sub> state to various <sup>7</sup>F states, shows lifetimes to increase in the presence of coordinating agents [574 μs (pentane) and 1396 μs (Ph<sub>3</sub>PO)]. An increase is observed for olefins, supporting weak adduct formation<sup>201</sup>.

### J. Actinide Derivatives

Uranyl chloride  $\text{UO}_2\text{Cl}_2$  will form the relatively unhindered uranyl bisamide. Trisamides  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{MCl}$  ( $\text{M} = \text{U}, \text{Th}$ ) (**86**) result from  $(\text{Me}_3\text{Si})_2\text{NNa}$  and  $\text{MCl}_4$  in ether, benzene or isooctane, but in THF, the hydride is formed, and also results from **86** and one mole of the sodium amide (Scheme 23)<sup>202</sup>. The thorium hydride is diamagnetic but the uranium one paramagnetic with a pyramidal structure and what are generally regarded as covalently bonded amide groups ( $\text{Si}-\text{N}$  174.0 pm,  $\text{SiNSi}$  125.3°). Both can be methylated using  $\text{BuLi}/\text{MeBr}$  and on pyrolysis eliminate  $\text{H}_2$  to give the metallocycle. In an atmosphere of deuterium the uranium derivative completely exchanges reversibly to give the perdeuterio amidometallocycle through a mechanism involving cleavage of the uranium-carbon bond (Scheme 24)<sup>203</sup>.



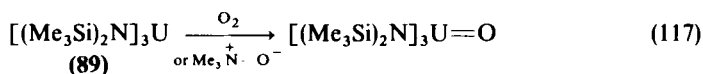
SCHEME 23

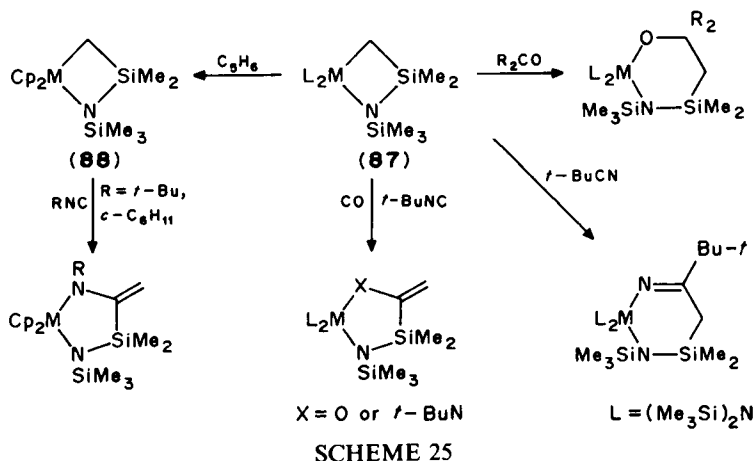


SCHEME 24

The methyl derivative readily inserts ketones to yield the alkoxy derivative and tertiary alcohols on hydrolysis. **87** reacts with alcohols and protic acetylenes to give appropriate trisamido derivatives, while cyclopentadiene forms the dicyclopentadienyl metallocycle **88**. These metallocycles react with nitriles and carbonyls through ring insertion<sup>204</sup>. The amide inserts ketones and *t*-butyl isocyanide to give the six-membered ring, but with  $\text{CO}$  or *t*-butylisocyanide, initial insertion of the  $\text{M}-\text{C}$  bond is followed by insertion into the  $\text{Si}-\text{C}$  bond to give the five-membered exomethylene derivative (Scheme 25)<sup>205</sup>. Similar five-membered ring derivatives result from the dicyclopentadienyl derivative **88** and *t*-butyl or cyclohexyl isocyanides.

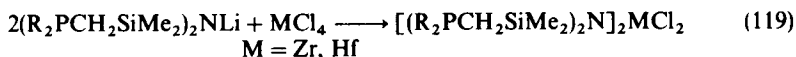
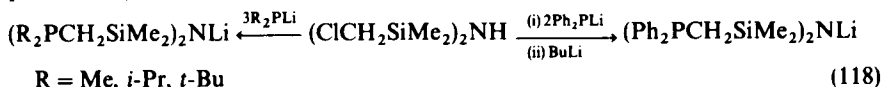
The uranium(III) trisamide **89** results from uranium trichloride and the sodium amide. It is readily oxidized to the oxotrisamide (equation 117) but, unlike its neodymium congener, does not complex with *t*-butyl cyanide or isocyanide<sup>206</sup>.



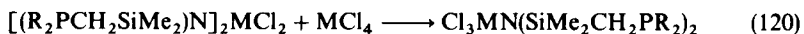


### K. Complexes of Bis(phosphinomethylsilyl)amides

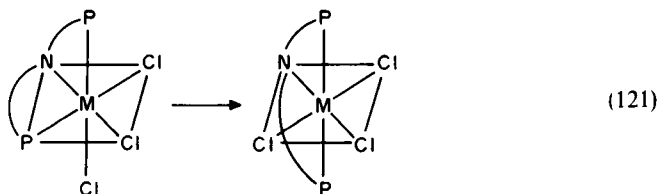
The chloromethyldisilazane (ClCH<sub>2</sub>Me<sub>2</sub>Si)<sub>2</sub>NH gives the bisilylamides (R<sub>2</sub>PCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>NLi (R = Me, *i*-Pr, *t*-Bu) with three moles of phosphide, but the phenyl derivative has to be lithiated separately with BuLi (equation 118). These amides readily disubstitute zirconium and hafnium tetrachlorides to give distorted octahedral bisamide complexes in which the amide is *N,P*-bidentate and not tridentate. The phosphino groups coordinate *cis* and the chlorine groups *trans*, and the complex is chiral due to the *cis* amide ligands interacting as two constrained, 'geared' molecular propellers (equation 119)<sup>207</sup>.



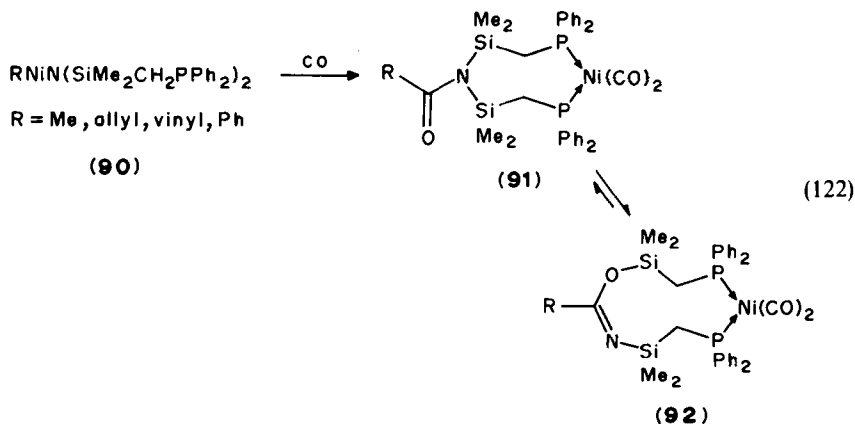
If this reaction is conducted on a 1:1 ratio in toluene, then over a 5-day period, the monosubstituted derivative is formed through conproportionation of the disubstituted one with MCl<sub>4</sub>, probably through interaction of the peripheral phosphine groups (equation 120).



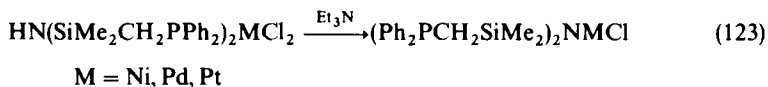
The hafnium derivative with dimethylphosphino groups crystallizes as monoclinic and orthorhombic 6 coordinate *facial* derivatives (allogens). The more hindered diisopropyl phosphino zirconium derivative has a *meridional* configuration and is formed much more quickly. The *fac*-derivatives isomerize in solution. The tendency to form the *mer*-isomer may well be due to the Si<sub>2</sub>NM unit preferring planarity, though with bulky groups, a *fac*-isomer would be more sterically hindered (equation 121)<sup>208</sup>.



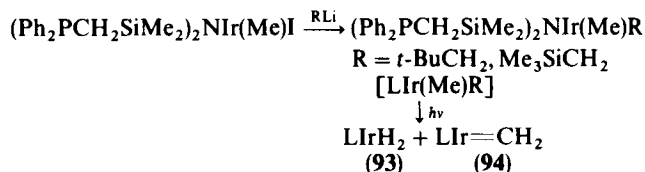
This ligand will stabilize the late transition metals in low oxidation states much more readily than bis(trimethylsilyl)amide. The nickel(II) amide **90** results from the successive substitution of NiCl<sub>2</sub> first with amide, then RMgX. They are crystalline solids which absorb carbon monoxide at atmospheric pressure; this inserting into the nickel-carbon bond gives the acyl derivative, which then undergoes an *N,O*-silatropic rearrangement to give an equilibrium mixture of amide (**91**)-imidate (**92**) diphosphine nickel dicarbonyl (equation 122). The vinyl compound occurs exclusively as the imidate with the vinyl group coordinating to the metal in place of one carbonyl group<sup>209</sup>.



MCl<sub>2</sub> complexes (M = Ni, Pd, Pt) react with one mole of the amide (Ph<sub>2</sub>PCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>NLi to give diamagnetic square planar monochloride complexes, including the first palladium amide. The amine gives a bidentate dichloride (nickel compound tetrahedral) which, with base, forms the metal amides (equation 123)<sup>210</sup>.



Square planar rhodium(I) and iridium(I) derivatives can be formed in the same way from the carbonyl, phosphine, or olefin rhodium(I) or cyclooctene iridium(I) complexes<sup>211</sup>. The iridium complexes readily undergo oxidative addition with MeI to give the 5-coordinate Ir(III) derivatives, which then add H<sub>2</sub> across the Ir-N bond. Alkylation followed by irradiation gives the dihydride and methylene derivatives **93** and **94** (Scheme 26)<sup>212</sup>.



SCHEME 26

### VIII. ALKALI METAL DERIVATIVES OF TRISILAZANES AND TRISAMINOSILANES

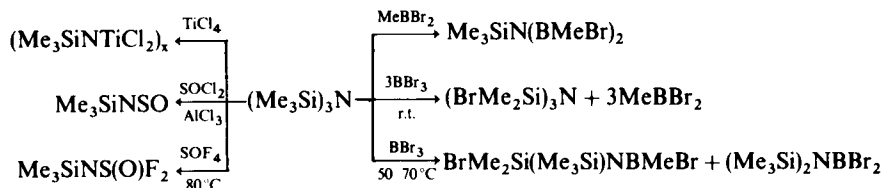
Octamethyltrisilazane (Me<sub>3</sub>SiNH)<sub>2</sub>SiMe<sub>2</sub> form amides with all the alkali metals. The derivatives of lithium and sodium are much more soluble in hydrocarbon solvents than

those of potassium, rubidium or caesium, form stable complexes with ethers and are dimeric in benzene. However, in the solid, the disodium derivative is a trimer. The sodium ions are 2-, 3- and 4-coordinate, nitrogen 4- and 5-coordinate, while the SiNSi angles vary from  $122.6^\circ$  to  $140.0^\circ$ , the largest associated with Si—N bond lengths of 167.1 and 169.4 pm. It is worth noting that the shortest Na---C interaction (265.6 pm) is comparable to the longest Na---N interactions (230.4–260.1 pm)<sup>213</sup>. The largest angle ( $138^\circ$ ) and shortest Si—N bonds (172 pm) for a non-ionic disilazane are found in  $(\text{Ph}_3\text{Si})_2\text{NH}^{112}$ .

The trisaminosilanes  $\text{RSi}(\text{NHR}')_3$  ( $\text{R} = \text{Me}, \text{Ph}, \text{Bu}-t$ ;  $\text{R}' = \text{SiMe}_3$  or  $\text{R} = \text{Ph}$ ;  $\text{R}' = \text{Bu}-t$ ), prepared by appropriate condensation reactions from  $\text{RSiCl}_3$ , all give trilitiated derivatives with  $\text{BuLi}$  which are dimeric in the solid state. The structures all have  $D_{3d}$  symmetry and can be considered as an interconnected pair of trigonal antiprisms of 6 lithium atoms and 6 nitrogen atoms each, each atom interacting with 3 of the other, with the 2 silicon atoms occupying positions on the 3-fold axis. Silicon–nitrogen bonds vary from 168.7 to 174.6 pm and SiNSi angles from  $141^\circ$  to  $131^\circ$  for  $\text{R}' = \text{Me}_3\text{Si}^{214}$ , but for the *t*-butylamino derivative  $\text{PhSi}(\text{NHBu}-t)_3$ , silicon–nitrogen bonds are longer (175 pm)<sup>75</sup>.

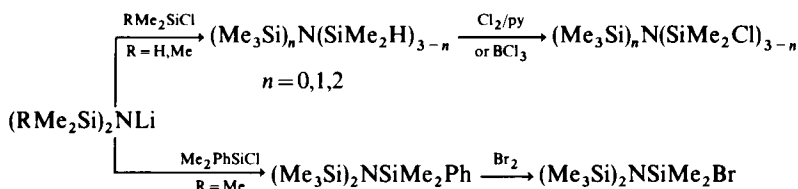
### IX. TRISILYLAMINES<sup>9</sup>

While trisilylamine and tris(methylsilyl)amine can be prepared directly from the chlorosilane and ammonia, tris(trimethylsilyl)amine results from the bisilylamide or lithium nitride and chlorosilane. This is a volatile waxy solid, and though reputedly non-basic, the silicon–nitrogen bond can be cleaved slowly, or under more forcing conditions. Thus with methyl dibromoborane, the trisilylamine can be disubstituted<sup>215</sup>, as it can with sulphur halides<sup>216</sup> and titanium tetrachloride<sup>217</sup>. With boron tribromide, however, only demethylation of the silyl groups occurs at room temperature, though heating induces desilylation (Scheme 27).

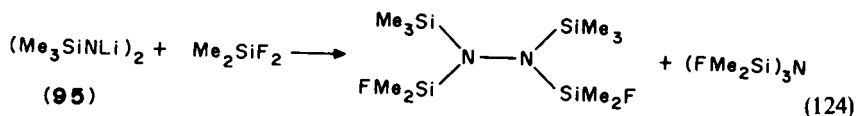


SCHEME 27

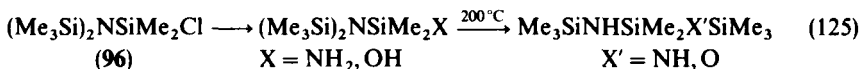
Functionally substituted trisilylamines  $(\text{Me}_3\text{Si})_2\text{NSiMe}_2\text{Ph}$  and  $(\text{Me}_3\text{Si})_n\text{N}(\text{SiMe}_2\text{H})_{3-n}$  ( $n = 0, 1, 2$ ) result from the disilazane anion  $(\text{RMe}_2\text{Si})_2\text{NLi}$  ( $\text{R} = \text{Me}, \text{H}$ ). The Si—H bond can be readily chlorinated using chlorine/pyridine or boron trichloride, and the phenyl groups removed using bromine (Scheme 28)<sup>218</sup>. Remarkably, tris(dimethylfluorosilyl)amine is formed along with the expected fluorosilylhydrazine from the condensation of dimethyldifluorosilane and the 1,2-dilithiodisilyl hydrazine **95** (equation 124)<sup>219</sup>.



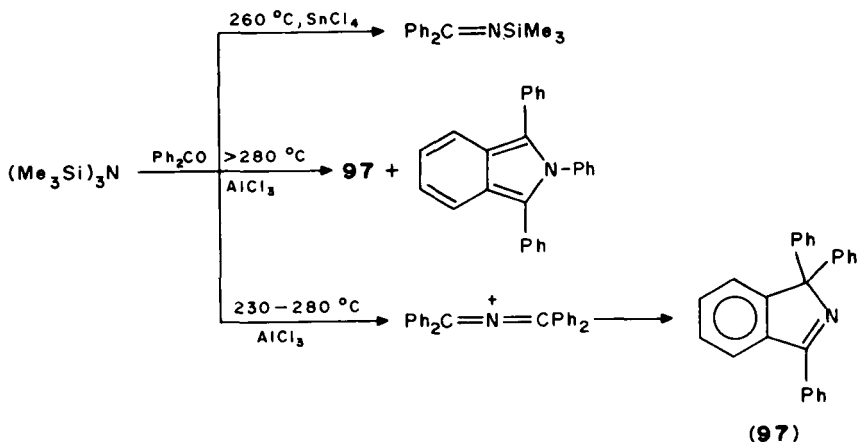
SCHEME 28



Ammonolysis or hydrolysis of the monochlorotrisilylamine **96** gives the thermally labile derivative which undergoes intramolecular rearrangement on heating to give the siloxydisilazane or trisilazane, rather than deamination or dehydration (equation 125)<sup>220</sup>.



The catalysed reaction of tris(trimethylsilyl)amine with diaryl ketones gives the expected *N*-silylketenimine together with the 2-azaallenium cation which condenses on heating to give 1,1,3-triphenyl-1*H*-isoindole (**97**). At temperatures above 280 °C, the acid catalysed pyrolysis of benzophenone and the trisilylamine also gives a small percentage of the *N*-phenyl isomer of **97** (Scheme 29)<sup>221</sup>.



SCHEME 29

Tris(trimethylsilyl)amine and its chlorosilyl derivatives exhibit remarkable behaviour in the solid state. All have a sharp transition temperature some 30 °C below zero and melt over a relatively wide temperature range (up to 5 °C) some one hundred degrees higher. NMR spectral studies confirm 'liquid-like' solid phases for  $(\text{Me}_3\text{Si})_2\text{NSiMe}_n\text{Cl}_{3-n}$ . The wide range for fusion supports a low heat of fusion which allows trace impurities to give a large depression of the freezing point (compare molecular weight determinations in camphor, also a plastic crystal). Changes in molecular geometry determine whether these compounds shall be *meso*-crystalline, the three trisilylamines  $\text{Me}_3\text{SiN}(\text{SiMe}_2\text{X})_2$  ( $\text{X} = \text{H}$  or  $\text{OMe}$ ) and  $(\text{MeOSiMe}_2)_3\text{N}$  melting normally at -48, -55 and -18 °C, respectively<sup>222</sup>.

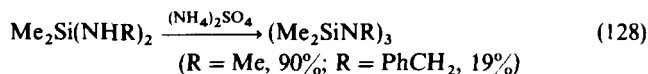
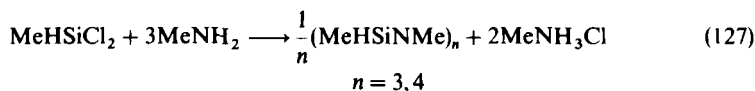
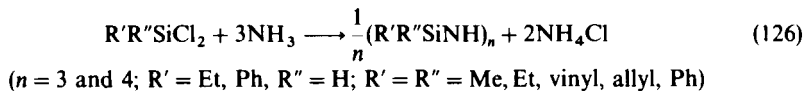
The gas phase structure of  $(\text{MeH}_2\text{Si})_3\text{N}$  shows a planar geometry for the  $\text{Si}_3\text{N}$  unit with Si—N bonds of 172.9 pm, and  $C_s$  symmetry, while in the solid state at 115 K,  $(\text{H}_3\text{Si})_3\text{N}$  has  $C_{3h}$  symmetry and Si—N bonds of 173.0 pm. The nitrogen atoms are stacked above each other, 410 pm apart, supporting lone pair delocalization onto all three silicon atoms<sup>223</sup>.

X. CYCLOSILAZANES<sup>13</sup>

Dichlorosilanes react with ammonia and primary amines to give a variety of products depending on the substituents at both silicon and nitrogen. Bis(amino)silanes  $R_2Si(NH_2)_2$  result as the main product only if at least one substituent is *t*-butyl, and other non-cyclic products include aminodisilazanes. With methylamine, even dimethyldichlorosilane gives mainly the bis(amino)silane, cyclosilazanes resulting only on prolonged heating in the presence of an acid catalyst.

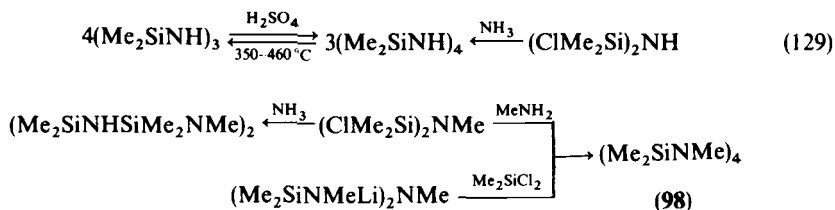
## A. Cyclotrisilazanes and Cyclotetrasilazanes

Condensing  $R_2SiCl_2$  with ammonia gives a mixture of cyclotri- and tetrasilazanes as the main products, though they only result after prolonged acid catalysed (e.g. ammonium sulphate) deamination of the initially formed bisaminosilanes and aminodisilazanes (equation 126). Only methyldichlorosilane and methylamine give cyclotri- and tetrasilazanes directly (equation 127), and yields of these fall as the size of the amine substituent increases (equation 128).



The *N*-methyl cyclotrisilazanes  $(ArMeSiNMe)_3$  result on pyrolysing the bisaminosilane. Two isomers are generated for  $Ar = \text{Ph}$  or *p*-anisyl which can be separated through their different solubilities in petrol. The *trans* isomer in each case shows two methyl resonances in the <sup>1</sup>H NMR spectrum, ratio 2:1, and has the lower melting point. Cyclosiloxanes give similar isomeric mixtures<sup>224</sup>.

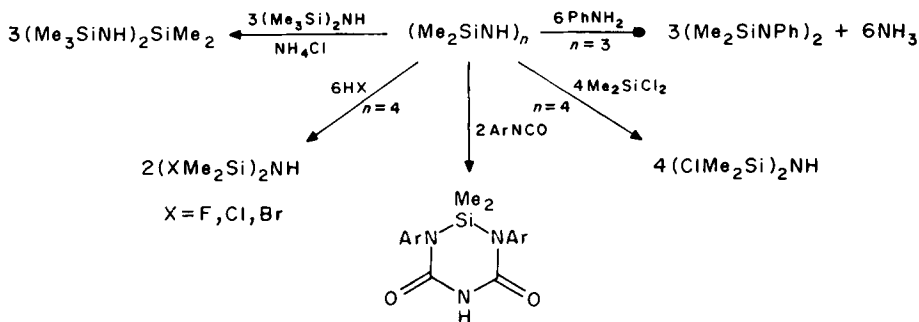
While the methyl cyclotri- and tetrasilazanes can be readily separated by distillation, they, like other examples, can be readily interconverted through acid catalysed ring expansion, or thermal ring contraction (equation 129). The ability to isolate intermediates and to control the degree of amination of the dichlorosilane enables a wide range of cyclosilazanes to be 'tailor-made' from chlorodisilazanes and lithiated aminodisilazanes using the appropriate amine or dichlorosilane. This technique can be expanded to include mono or other polyhalosilanes and halides of other elements to give a most extensive range of heterosubstituted rings (Scheme 30). The permethylcyclotetrasilazane **98** transforms into plastic crystals at 51–52 °C, and subsequently melts at 258–260 °C<sup>225</sup>.



SCHEME 30

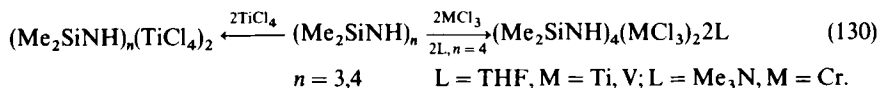


Though cyclosilazanes are relatively stable to water and alkali, in part due to reduced basicity and immiscibility, they are readily cleaved by acid and alcohol. They are easily transaminated to the bisaminosilane by primary amines, though aniline gives the cyclodisilazane. Hydrogen halides will open the rings to give specific halodisilazanes, while ammonium chloride catalyses equilibration of cyclosilazanes with hexamethyldisilazane to form the linear trisilazane. Aryl isocyanates give the 1,3,5-triaza-2-silylcyclohexane-4,6-diones through ring substitution (Scheme 31)<sup>13b</sup>.

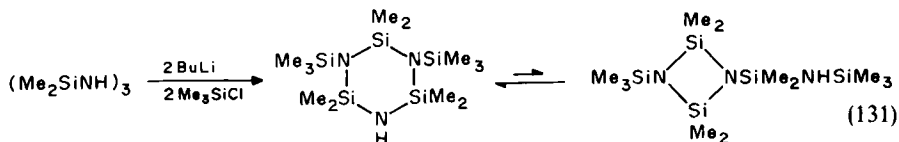


SCHEME 31

Stannic chloride forms sublimable 1:1 complexes with cyclotri- and tetrasilazanes at room temperature, but catalyses ring expansion of the former at 195 °C<sup>226</sup>, while ruthenium or rhodium complexes catalyse the oligomerization of cyclotetrasilazanes<sup>227</sup>. With the trichlorides  $\text{MCl}_3$  ( $\text{M} = \text{Ti, V, Cr}$ ), 1:2 complexes result as with  $\text{TiCl}_4$  (equation 130)<sup>228</sup>.



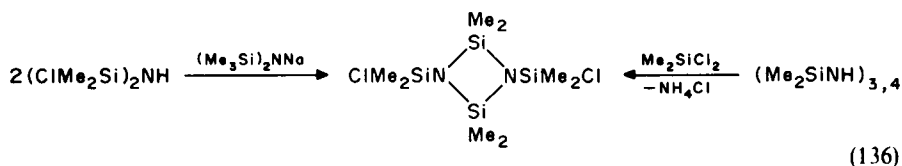
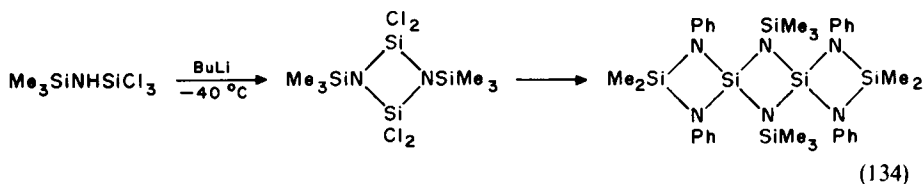
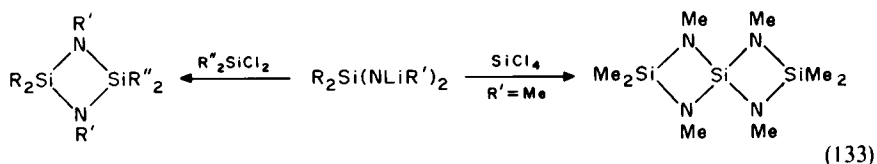
The cyclotrisilazanes  $(\text{R}_2\text{SiNH})_3$  ( $\text{R} = \text{Me, Et, Ph}$ ) all form mono-, di and tri-lithio derivatives. In solution, the methyl derivatives undergo a monomer-dimer equilibrium similar to that of the bisilylamide, and have been used to prepare silyl linked polycyclotrisilazanes using dichlorosilanes. In diglyme at -60 °C, the lithio derivatives of hexamethylcyclotrisilazane can be progressively trimethylsilylated but, at higher temperatures, the lithio derivatives are unstable and ring contract through transannular attack giving cyclodisilazanes (equation 131)<sup>229</sup>.



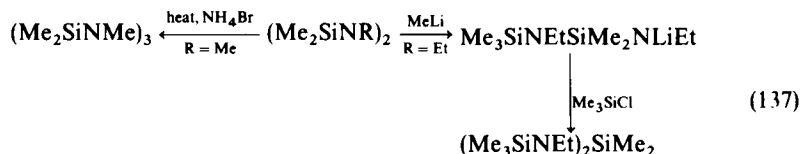
## B. Cyclodisilazanes

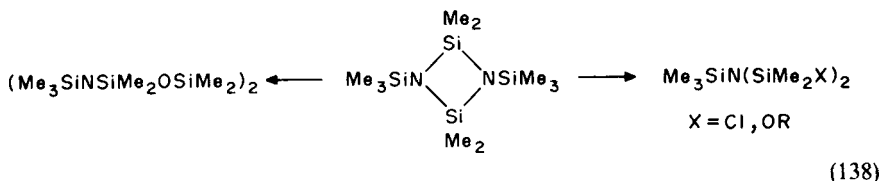
The first cyclodisilazane, silylated at nitrogen, was prepared in 1961 by pyrolysing the cyclotrisilazane (equation 132)<sup>230</sup>. Since then many have been prepared by a wide

range of methods. These include condensation reactions between lithium amides and chlorosilanes (equation 133), and between bis(chlorosilyl)amines and ammonia, primary amines (equations 134 and 135) or sodium bis(trimethylsilyl)amide (equation 136). They also result from the catalysed redistribution reaction of cyclotri- and tetrasilazanes with dimethyldichlorosilane<sup>231</sup>. Their synthesis from lithiated aminosilanes in non-polar solvents (Section II.A.2)<sup>28</sup>, and from the ring contraction of larger cyclosilazanes (last section), has already been described.



Remarkably, the cyclodisilazane ring provides one of the few examples of silicon–nitrogen bond cleavage by organolithium reagents. It also catalytically ring expands to the cyclotrisilazane (equation 137). The relative stability of the exocyclic silicon–nitrogen bonds provides a useful route to mixed trisilylamines, and hence unsymmetrically substituted cyclodisilazanes, and on hydrolysis, the eight-membered cyclosiloxazane (equation 138)<sup>232</sup>.





### C. The Structures of Cyclosilazanes

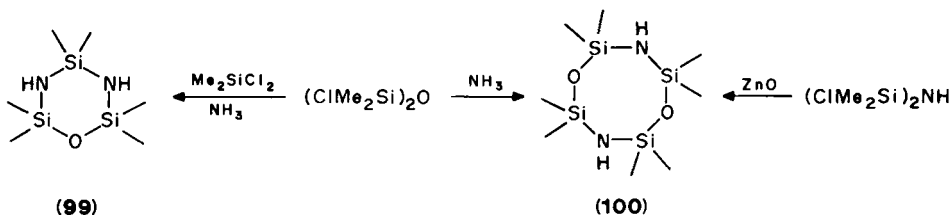
Octamethylcyclotetrasilazane, mp 97 °C,  $(\text{Me}_2\text{SiNH})_4$  has a most noteworthy structure. The crystals possess an ordered arrangement of equal proportions of chair and cradle isomers. The Si—N bond angles are around 131° for both isomers, but while the Si—N bond length varies little for the chair form (173 pm), it does fluctuate a little for the cradle isomer ( $172 \pm 3$  pm)<sup>233</sup>. An early determination of the structure of hexamethylcyclotrisilazane in the vapour showed the ring slightly puckered, with silicon–nitrogen bonds of length  $178 + 3$  pm<sup>234</sup>.

The silylcyclodisilazane  $(\text{Me}_3\text{SiNSiMe}_2)_2$ , the first cyclodisilazane to be prepared, has a planar structure, with exocyclic Si—N bonds of 170.7 pm and ring ones of 172.4 pm<sup>235</sup>. *N,N'*-Dimethyltetramethylcyclodisilazane possesses a planar ring in the vapour state with silicon–nitrogen bond lengths of 173.6 pm<sup>236</sup>.

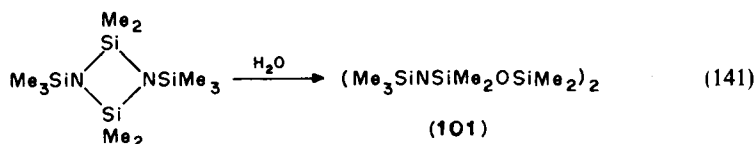
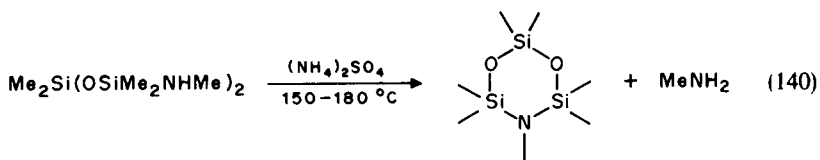
The *N*-aryl derivatives show the aryl group to be twisted out of the  $\text{Si}_2\text{N}_2$  plane for *o*-tolyl and mesityl, but to be in the plane for phenyl, *m*- and *p*-tolyl<sup>237</sup>. Remarkably, the *o*-chlorophenyl derivative has this group in the  $\text{Si}_2\text{N}_2$  plane and possesses a weak interaction between chlorine and silicon (Si---Cl 313.7 pm) which renders the silicon–nitrogen bonds longer (175.6 pm), as also found for those in the pentafluorophenyl derivative  $(\text{Ph}_2\text{SiC}_6\text{F}_5)_2$ , in which the  $\text{C}_6\text{F}_5$  rings are twisted out of the  $\text{Si}_2\text{N}_2$  plane by 16°<sup>238</sup>.

## XI. CYCLOSILOXANES

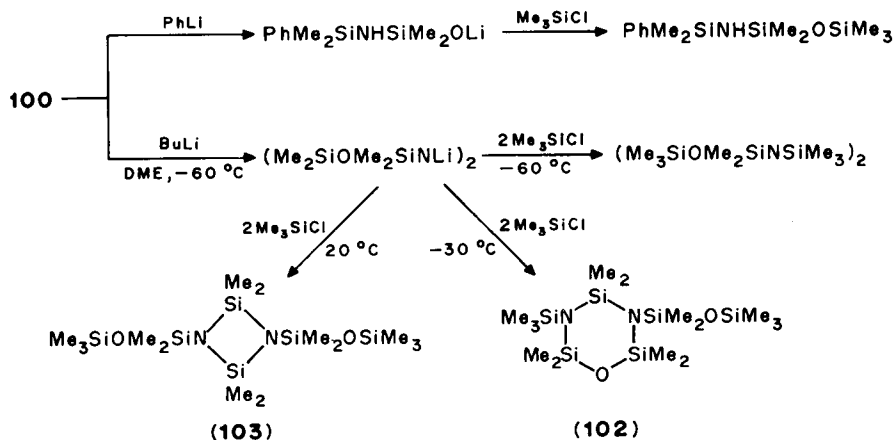
Cyclosiloxane rings contain the SiNSi and SiOSi units as integral parts. They are best prepared by the ammonolysis of chlorosiloxanes (equations 139 and 140), but can be made by hydrolysing cyclodisilazanes (equation 141). The extra bonding site at nitrogen provides for cross-linking in dimethylsilicon polymers, but hydrolytic instability, particularly under acid conditions, restricts their potential. Indeed, the cyclotrisiloxadiazane **99** is less stable to hydrolysis than the cyclotrisilazane, while the *trans*-cyclotetrasilodioxidiazane **100** is more stable to hydrolysis than the cyclotetrasilazane, and the cyclotetrasilodioxidiazane **101** shows remarkable hydrolytic stability<sup>239</sup>. The acid catalysed hydrolysis of the six-membered *N,N'*-diphenylcyclotrisiloxidiazane ring is faster than for the monoaza one, supporting solvent attack at silicon synchronous with protonation at nitrogen<sup>240</sup>.



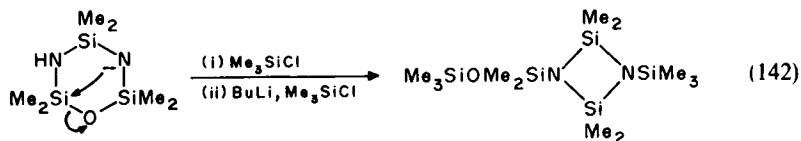
(139)



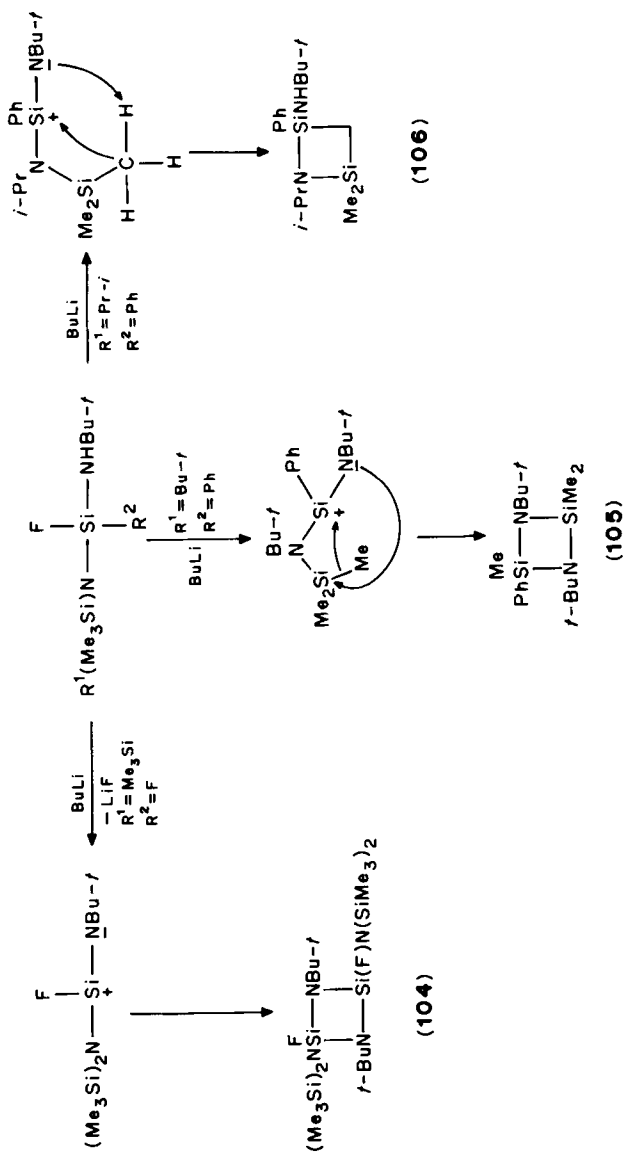
Phenyllithium cleaves the silicon–oxygen bond of **100**, while butyllithium metallates the two nitrogen sites and, as with lithiated cyclosilazanes, undergoes ring contraction on warming. The siloxysilylcyclotrisiloxdiazane **102** results at  $-30^\circ\text{C}$  but, at  $20^\circ\text{C}$ , further contraction to the disiloxysilylcyclodisilazane **103** occurs (Scheme 32). The cyclotrisiloxdiazane **99** ring contracts similarly (equation 142)<sup>239</sup>.



SCHEME 32



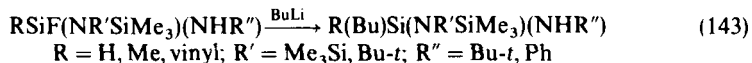
The structures of six- and eight-membered cyclosiloxazanes show Si—O bonds about 10 pm shorter than the Si—N bonds with wider angles at oxygen.  $(\text{Ph}_2\text{SiO})_2\text{Ph}_2\text{SiNEt}$  has a distorted boat conformation, while the eight-membered rings of  $(\text{Me}_2\text{SiOSiMe}_2\text{NC}_6\text{F}_5)_2$  and  $(\text{PhMeSiOSiPhMeNH})_2$  have a chair structure, the latter showing optical activity at silicon, with five possible diastereoisomers<sup>241</sup>.



SCHEME 33

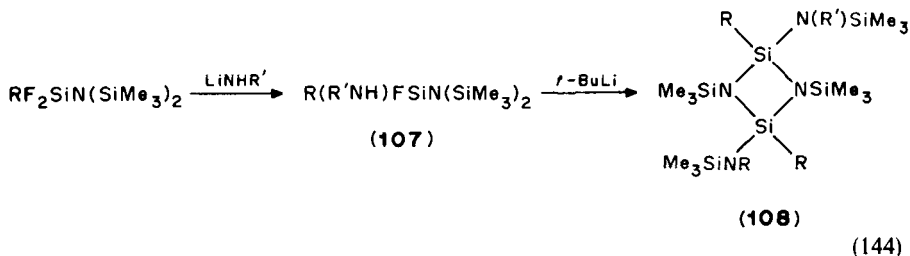
## XII. FLUOROSILYLAMINES

An extensive array of fluorosilylamines and fluorosilylcyclosilazanes have been prepared, primarily to show the influence of bulky groups on reactivity to organolithium reagents, and the mode of decomposition of the amides so formed. However, substitution at fluorine can also occur directly (equation 143)<sup>242</sup>, but lithiation at nitrogen normally results.

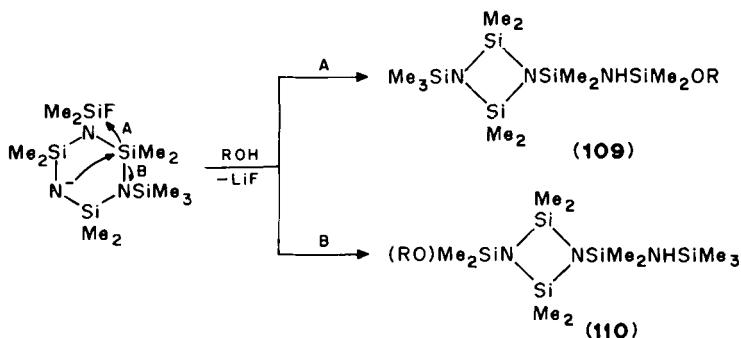


The silylamides formed on lithiation decompose by losing LiF to give the unstable silicon–nitrogen ylide, which can rearrange by three pathways depending on the size and electronic properties of the substituents, and the polarity of the solvents. It can either dimerise to give the cyclodisilazane **104**, cyclise through methanide migration to the cationic silicon site to give the unsymmetrical cyclodisilazane **105** or deprotonate a silyl methyl group with formation of the azadisilacyclobutane **106**<sup>243</sup> [compare the amides of titanium and zirconium, uranium and thorium (Sections VII.H and VII.J)] (Scheme 33).

In addition, the bisaminofluorosilanes **107**, disilylated at nitrogen, which result from amide and difluorosilane, undergo 1,3-silyl migration on heating in the presence of *t*-BuLi to give the *N*-silylated cyclodisilazane **108** (equation 144)<sup>244</sup>.

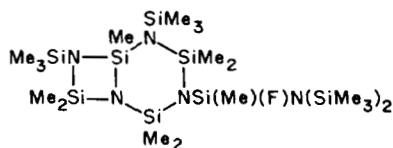
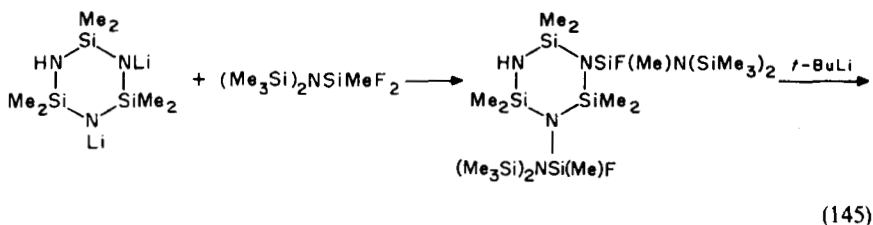


Lithiated fluorosilylcyclotrisilazanes undergo ring contraction, alcoholysis leading not only to substitution, but to two cyclodisilazanes **109** and **110**, through ring opening on both sides of the attacked site (Scheme 34)<sup>245</sup>.

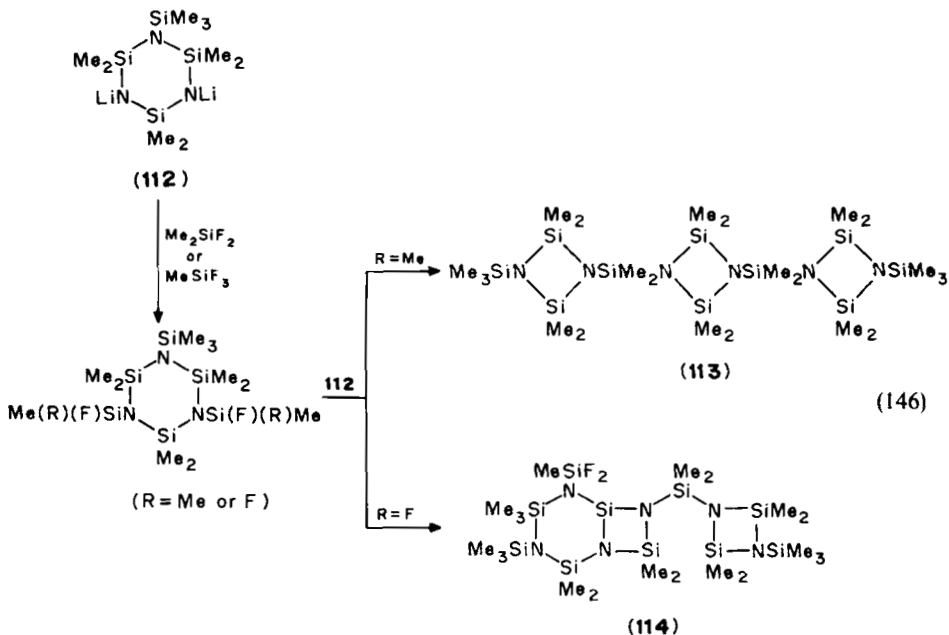


SCHEME 34

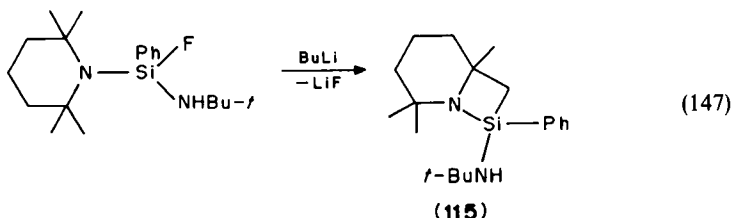
Such ring contractions also occur on the condensation of fluorosilanes with lithiated cyclotrisilazanes<sup>246</sup>, but methyl exchange can also result, for instance, to give the bicyclo[4.2.0]octane **111** (equation 145), which possesses a planar four-membered ring which induces a boat conformation in the six-membered one. The cyclotrisilazane ring in **111** is forced out of planarity by the fused cyclodisilazane and the bulky substituents. This boat conformation is also found in the monocyclic trisilyl derivative  $(\text{Me}_3\text{SiNSiMe}_2)_3$ <sup>247</sup>.

**(111)**

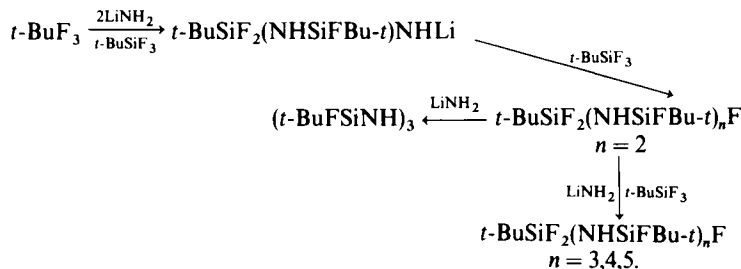
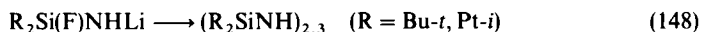
Condensing **112** with  $\text{Me}_2\text{SiF}_2$  or  $\text{MeSiF}_3$  gives the trisilylcyclotrisilazanes, which further condense with more **112** to give either the coupled triscyclodisilazane **113** through ring contraction, or the bicyclo[4.2.0]octane **114** through both ring contraction and



methyl migration (equation 146)<sup>248</sup>. With the 2,2,6,6-tetramethylpiperidine, deprotonation occurs at the methyl group to give the bicyclo[4.2.0]octane **115** (equation 147)<sup>249</sup>.

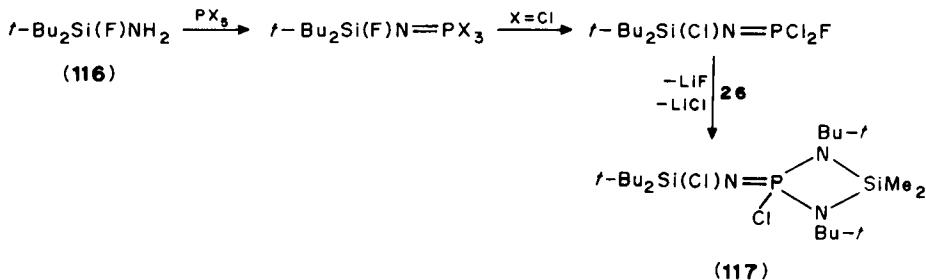


Condensing  $\text{R}_2\text{SiF}_2$  ( $\text{R} = i\text{-Pr}, t\text{-Bu}$ ) and  $\text{LiNH}_2$  gives both the cyclodi- and trisilazanes (equation 148)<sup>250</sup>,  $(t\text{-Bu}_2\text{SiNH})_3$  showing a planar structure with silicon–nitrogen bonds of 172.7 pm and SiNSi angles of 135.9°<sup>251</sup>. With  $t\text{-BuSiF}_3$ , a series of chain oligomers can be readily made by stepwise reaction, together with both *cis*- (mp 242 °C) and *trans*-( $t\text{-BuFSiNH}$ )<sub>3</sub> (mp 114 °C) (Scheme 35), which can be separated from a methylene chloride solution by adding hexane, since the *cis* compound is less soluble in non-polar solvents. Both show a planar ring structure with silicon–nitrogen bonds of 169.5 pm and angles at nitrogen of 133°<sup>252</sup>. The derivative  $(\text{FPhSiNMe})_3$  is almost planar, but tending towards a chair conformation, with silicon–nitrogen bond lengths similar ( $170.0 \pm 0.6$  pm), and the SiNSi angles 129.8°<sup>253</sup>.



SCHEME 35

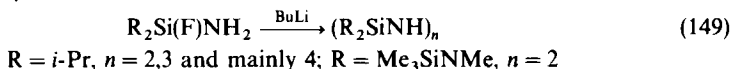
The aminofluorosilane **116** condenses with  $\text{PX}_5$  ( $\text{X} = \text{F}, \text{Cl}$ ) to give the phosphinimine, which undergoes halogen exchange between silicon and phosphorus if  $\text{X} = \text{Cl}$ , and condenses with the bisamidodisilane  $(t\text{-BuNLi})_2\text{SiMe}_2$  to give the cyclophosphasiladiazane **117** (Scheme 36)<sup>254</sup>.



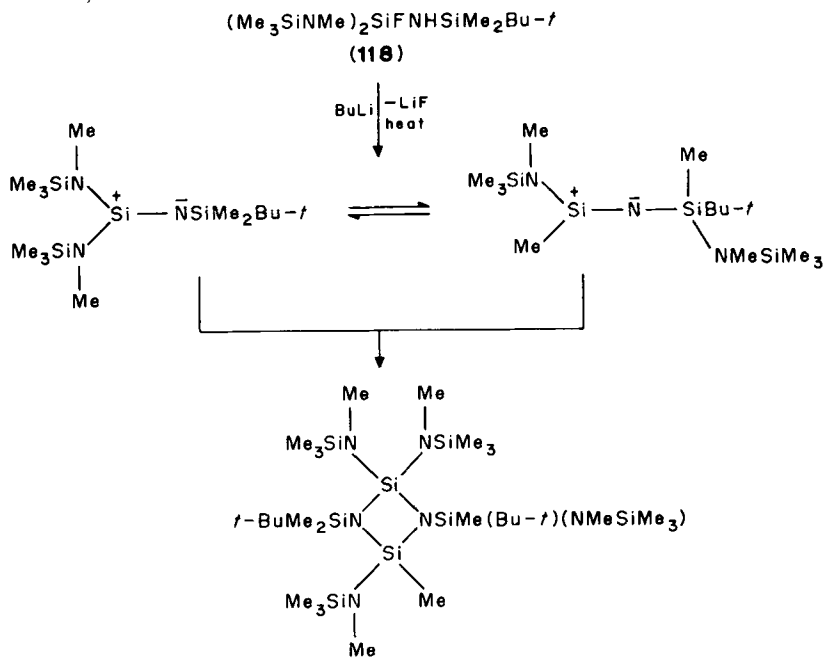
SCHEME 36



If the intermediate  $R_2Si(F)(NH_2)$  is condensed with BuLi, then the cyclotetrasilazane dominates the products for  $R = i\text{-Pr}$ , but the cyclodisilazane results for  $R = Me_3SiNMe$  (equation 149)<sup>255</sup>.

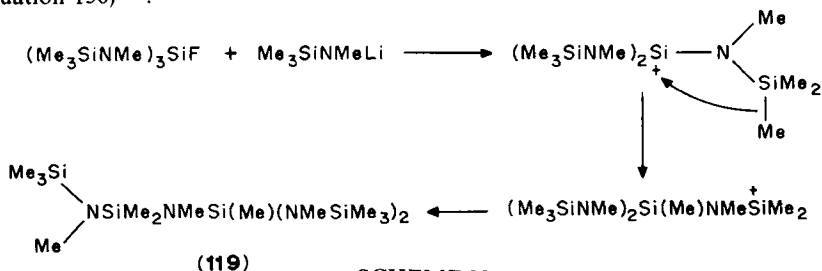


Lithiation of the more hindered trisaminofluorosilane **118** results in methyl migration, the equilibrating ylides coupling to form the unsymmetrical cyclodisilazane (Scheme 37)<sup>256</sup>.

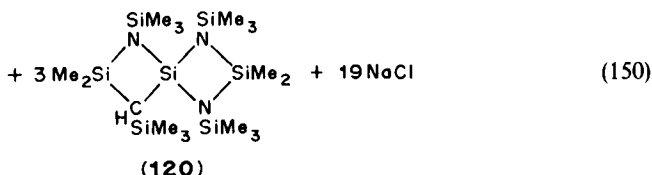
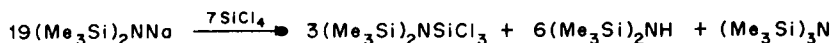


SCHEME 37

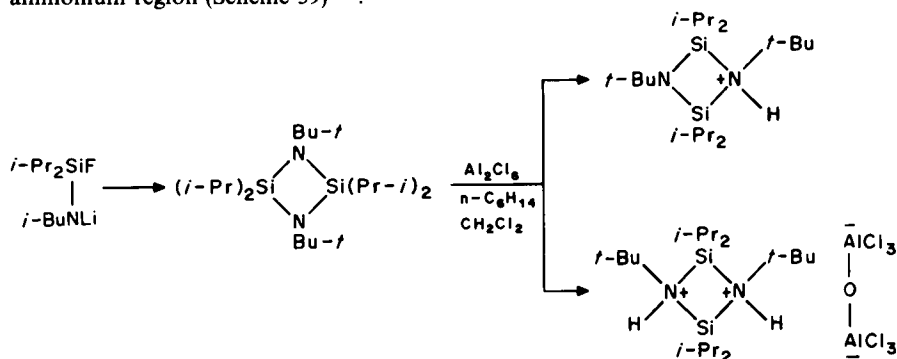
Indeed attempts to prepare the tetra(silylamino)silane from  $(Me_3SiNMe)_3SiF$  and  $Me_3SiNMeLi$  result again in methyl migration and formation of the linear isopentasilatetrazane **119** in 45% yield (Scheme 38)<sup>257</sup>. Slowly adding  $SiCl_4$  to  $(Me_3Si)_2NNA$  at  $200^\circ C$  gives a series of products including the trisilatriazaspiro[3.3]-heptane **120**, again indicating attack at a methyl group which then itself attacks at silicon (equation 150)<sup>258</sup>.



SCHEME 38

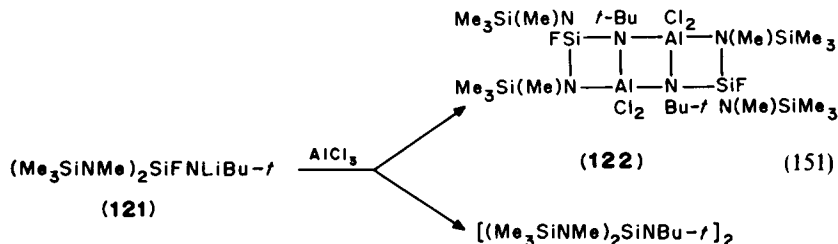


The hindered cyclodisilazane (*i*-Pr<sub>2</sub>SiN*t*-Bu)<sub>2</sub> can be prepared successfully by condensing the fluorosilylamide with ring parameters comparable to those of the unhindered cyclodisilazanes (Si—N 174.4 pm)<sup>259</sup>. It reacts with aluminium trichloride to give the first examples of stable bis-silyl substituted ammonium salts (equation 27 for a monosilyl one). Methylene chloride appears essential with adventitious water providing for the diprotonated salt. A structure determination NMR shows the silicon–nitrogen bonds to be significantly longer (179.2 pm) and the <sup>15</sup>N NMR signal to appear in the ammonium region (Scheme 39)<sup>260</sup>.



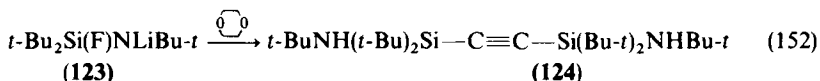
SCHEME 39

Aluminium readily stabilizes silicenium ylids as a 5-coordinate complex. Adding AlCl<sub>3</sub> in Et<sub>2</sub>O to the amide **121** gives the dimeric silylamino-dichloroalane **122** along with a little of the cyclodisilazane (equation 151)<sup>261</sup>.

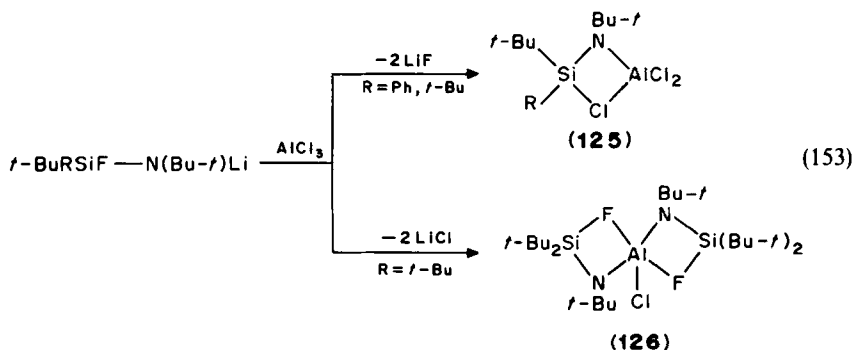


Attempts to prepare the fully *t*-butylated cyclodisilazane have proved unsuccessful to date, though the analogous *t*-butyl substituted Si—P ring has been made (see chapter 5,

Section VII, Scheme 21). The intermediate amidofluorosilane **123** is sufficiently stable to be purified by sublimation at 120°C/0.1 mm Hg or recrystallized from hexane, and gives a particularly high-field  $^{19}\text{F}$ NMR resonance signal<sup>262</sup>. However, while it is thermally quite stable, remarkably, it attacks dioxan to form the substituted acetylene **124** (equation 152)<sup>263</sup>:



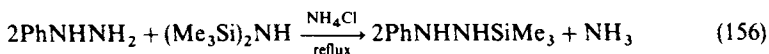
With aluminium trichloride, **123** reacts in petrol to give a 1:1 derivative **125** with 4 coordination, but with excess amide to THF, the 5-coordinate complex **126** results (Si—N 169.8 and 169.5 pm) in which halogen exchange has occurred. Angles at fluorine are about 93°, in sharp contrast to those found in  $(\text{Et}_3\text{AlFAlEt}_3)^-$  (180°) and  $(\text{Me}_2\text{AlF})_4$  (148°) (equation 153)<sup>264</sup>.



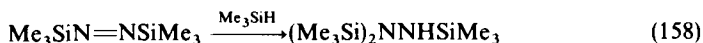
### XIII. POLYAZO COMPOUNDS<sup>16</sup>

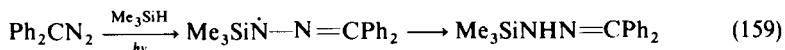
#### A. Silylhydrazines<sup>11,13a</sup>

The synthetic routes to silylhydrazines use the methods employed for aminosilanes, disilazanes and trisilylamines. Successive substitution increases hindrance and so necessitates the use of amide intermediates in order to fully substitute at both nitrogen atoms. Hydrazine and methylhydrazine substitute 1,2- without recourse to metallation, but phenylhydrazine is only monosilylated (equations 154–156).

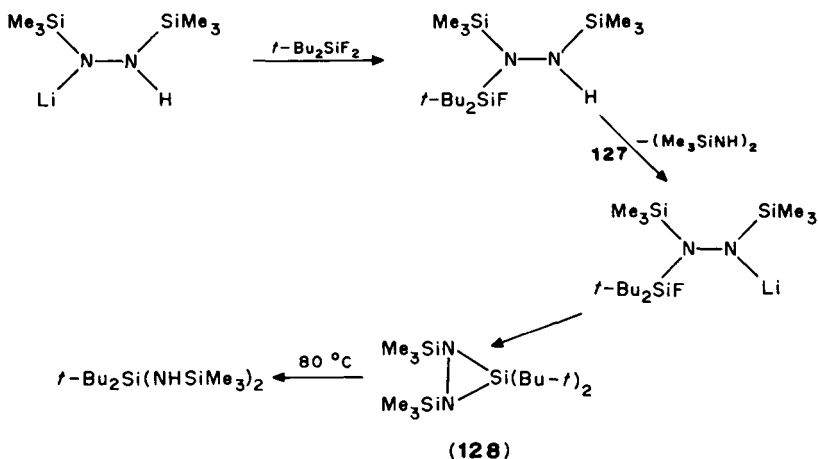


Hydrosilylation of azobenzenes and of bis(trimethylsilyl)diazene gives the substituted hydrazine, while diphenyldiazomethane forms the hydrazone photolytically (equations 157–159)<sup>265</sup>.

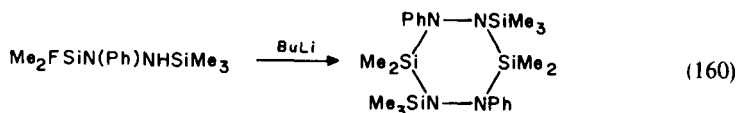




The siladiazacyclopropane **128** results from the monolithiobis(silyl)hydrazine **127** on silylation with di(*t*-butyl)difluorosilane, and is a crystalline solid which shows a large upfield shift for the ring silicon atom in the  $^{29}\text{Si}$  NMR spectrum relative to the trimethylsilyl groups. The strain in the ring is reflected in the thermal instability of the compound giving the linear trisilazane on warming to  $80^\circ\text{C}$  (Scheme 40)<sup>266</sup>. This route is normally used to prepare the six-membered ring derivatives and can be also used for five-membered ones (equation 160)<sup>267</sup>.



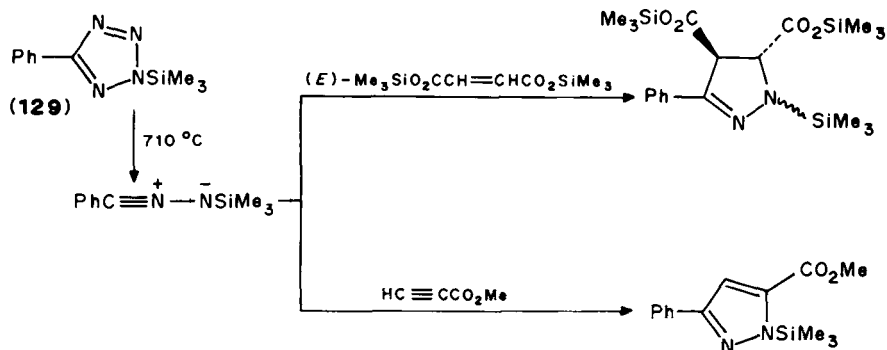
SCHEME 40



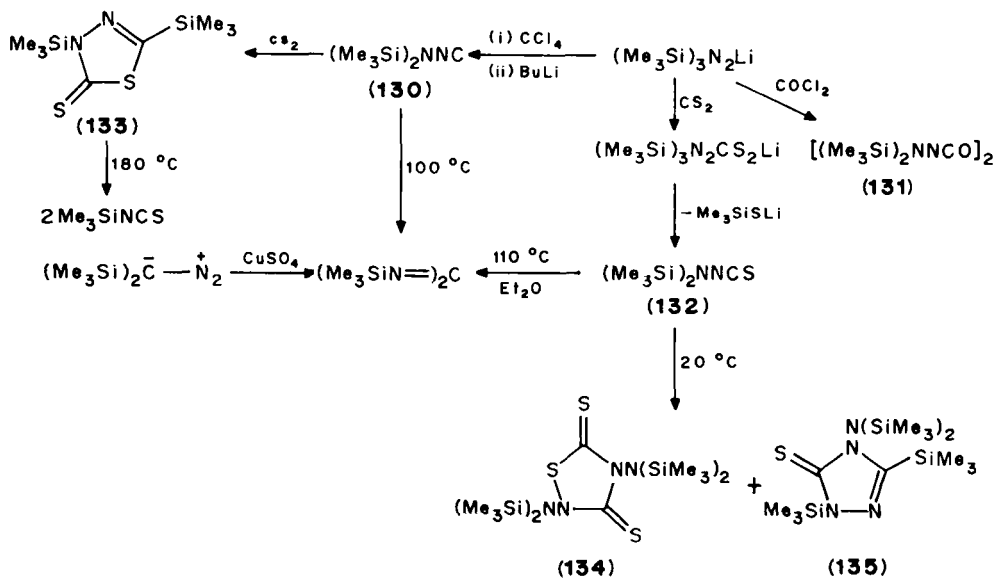
Flash vacuum pyrolysis of *C*-phenyl-2-trimethylsilyltetrazole (**129**) gives the *C*-phenyl-*N*-trimethylsilylnitrile imine intermediate, characterized by  $\nu_{\text{asym}}\text{CNN}$  at  $2230\text{ cm}^{-1}$ . This gives cyclic adducts with (*E*)-bis(trimethylsilyl)fumarate or methyl propiolate (Scheme 41)<sup>268</sup>.

The lithiated derivative of tris(trimethylsilyl)hydrazine is the intermediate in the preparation of bis(silylamino) isocyanide (**130**), isocyanate (**131**) and isothiocyanate (**132**). The isocyanate results from phosgene and is stable as a dimer, but the isocyanide and isothiocyanate are monomeric and thermally unstable, both decomposing at about  $100^\circ\text{C}$  into the carbodiimide. With  $\text{CS}_2$ , the isocyanide reacts to give the 1,2-diazathiazole (**133**) which decomposes at  $180^\circ\text{C}$  to trimethylsilylisothiocyanate. At  $20^\circ\text{C}$ , the isothiocyanate **132** associatively condenses to give a mixture of the two heterocycles **134** and **135** (Scheme 42)<sup>269</sup>.

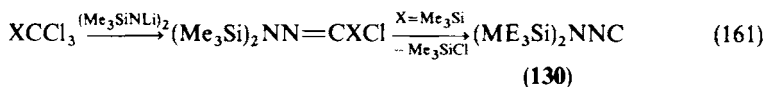
The aminoisocyanide **130** is also formed from  $\text{Me}_3\text{SiCCl}_3$  and the dilithium hydrazide, while  $\text{CCl}_4$  gives the aminocarbonimidic dichloride (equation 161)<sup>270</sup>. The bis(silyl)diazene  $\text{Me}_3\text{SiN}=\text{NSiMe}_3$  results as an intermediate with  $\text{CBr}_4$  or  $\text{SnCl}_4$ .



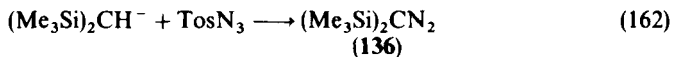
SCHEME 41



SCHEME 42



A third isomer of the aminoisocyanide **130** is the diazomethane derivative **136**, which results from  $(\text{Me}_3\text{Si})_2\text{CH}^-$  and  $\text{TosN}_3$  (equation 162) and, like the isocyanide, decomposes to the carbodiimide<sup>271</sup>. It also results from the decomposition of the silene adduct with  $\text{Me}_3\text{SiN}_3$  (Section XVIII.A, equation 197)<sup>272</sup>.



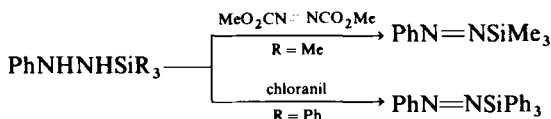
Successive lithiation and methylation of 1,1-bis(trimethylsilyl)hydrazine gives a mixture of isomeric tetrasubstituted hydrazines (equation 163). This is thought to result through amide equilibration via a five-coordinate state, and so is not subject to the orbital



by phenyl substitution at nitrogen. The  $^{19}\text{F}$  NMR spectrum of the difluorosilyl hydrazine  $(\text{MeF}_2\text{Si})\text{PhNNPh}(\text{SiF}_2\text{Me})$  shows coalescence of the two fluorine signals only at  $170^\circ\text{C}$ , indicating restricted rotation about the silicon–nitrogen bond<sup>276</sup>.

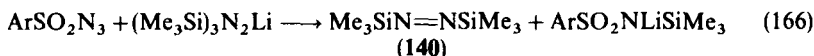
### B. Silyldiazenes<sup>16a,b</sup>

The phenyl(silyl)diazenes  $\text{PhN}=\text{NSiR}_3$  ( $\text{R} = \text{Me}, \text{Ph}$ ) are formed by the mild oxidation of the *N*-phenyl-*N'*-silylhydrazine using dimethyl diazenedicarboxylate ( $\text{R} = \text{Me}$ ) or chloranil, tetrachloro-*p*-quinone ( $\text{R} = \text{Ph}$ ). They are blue and act as a useful source of phenyldiazene and the phenyl anion (Scheme 45)<sup>277</sup>.

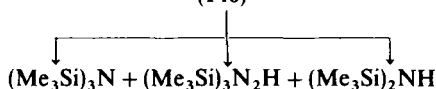
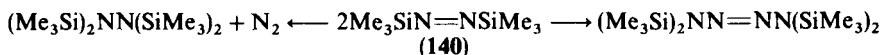


SCHEME 45

The bisilyldiazene (or diimine) **140** results from the oxidation of the lithio trisilylhydrazine with arylsulphonyl azide (equation 166). The blue colour is attributed to the tail of a weak, forbidden  $n \rightarrow \pi^*$  transition at  $12750\text{ cm}^{-1}$ . This is of a much longer wavelength than the yellow and red derivatives *t*-BuN=NBu-*t* ( $27200\text{ cm}^{-1}$ ) and *t*-BuN=NSiMe<sub>3</sub> ( $20000\text{ cm}^{-1}$ )<sup>278</sup>. It possesses a *trans* structure at  $-130^\circ\text{C}$  with long silicon–nitrogen bonds (181 pm) and a short nitrogen–nitrogen distance (117 pm)<sup>279</sup>.



While azoalkanes thermolyse to alkanes, no hexamethyldisilane results when **140** is heated. Instead, five silicon–nitrogen derivatives form through routes involving disproportionation, dimerisation and a radical chain mechanism (Scheme 46)<sup>280</sup>.

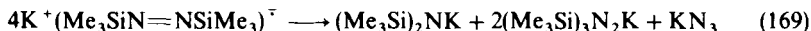


SCHEME 46

Bis(trimethylsilyl)diazene reduces stannic chloride and adds trimethylsilane across the double bond (equation 167).

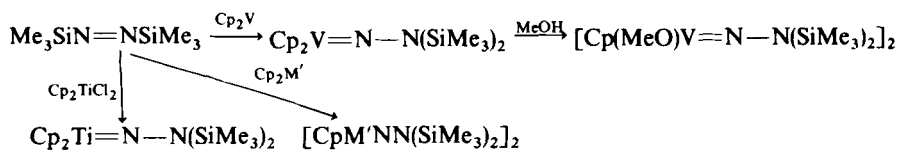


Reactions with alkali metals are more complex. The dianions are stable, but the radical anions decompose giving products dependent upon the metal used. With lithium, amides dominate the products but potassium gives polyazo derivatives, particularly at low temperature. This has been attributed to the greater polarizing power of lithium (equations 168 and 169)<sup>281</sup>.



Both titanocene dichloride and vanadocene react with the disilyldiazene to give the

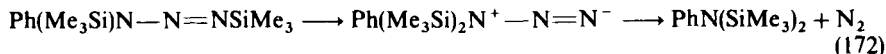
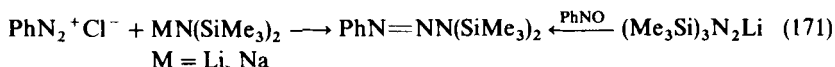
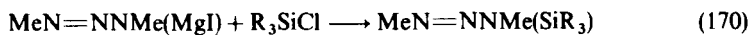
isodiazene complex  $\text{Cp}_2\text{M}=\text{N}-\text{N}(\text{SiMe}_3)_2$  ( $\text{M}=\text{Ti}, \text{V}$ ). The vanadium derivative has  $\text{C}_2$  symmetry with a linear VNN skeleton, long Si—N bonds and a wide SiNSi angle ( $136.7^\circ$ ). With methanol, the paramagnetic vanadium derivative loses cyclopentadiene rather than be desilylated. With the metallocenes  $\text{Cp}_2\text{M}'$  ( $\text{M}'=\text{Cr}, \text{Mn}$ ) and the disilyldiazene, each loses cyclopentadiene to give the diamagnetic isodiazene bridged dimer, the structure of the manganese compound having a very short Mn—Mn bond (239.3 pm), Si—N bonds of 174 pm and SiNSi angle of  $128.9^\circ$  (Scheme 47)<sup>282</sup>.



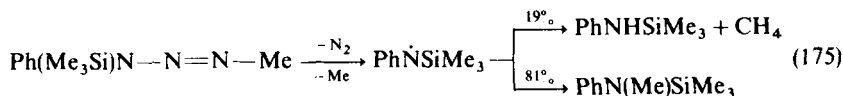
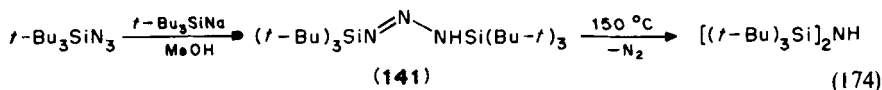
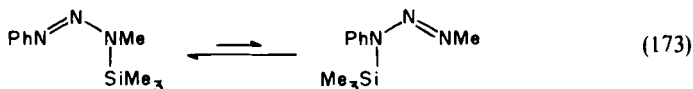
SCHEME 47

### C. Silyltriazenes<sup>16c,d</sup>

Mono and disilyl triazenes can be made by substituting the triazene skeleton, by coupling diazonium salts with a bisilylamide or by condensing a hydrazide with nitrosobenzene (equations 170 and 171). The monosilyl derivatives are colourless distillable liquids, but the red disilyl compounds are thermally unstable, decomposing to nitrogen and the *N*-aryldisilazane through a zwitterionic intermediate (equation 172)<sup>283</sup>.



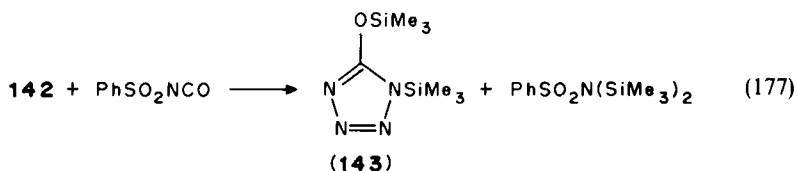
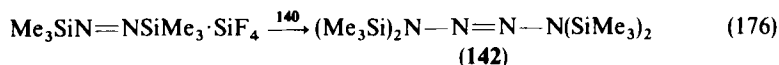
Monosilyl triazenes undergo 1,3-silyl migrations, the rate increasing with the electronegativity of the silyl substituent and decreasing with its size (equation 173). Consequently the bisilyl triazene **141**, which results on reducing the azide with the sodium silyl, shows inequivalence of the *t*-butyl groups up to  $55^\circ\text{C}$  in THF, when coalescence of the proton NMR signals occurs. The free energy of activation of this 1,3-proton shift is  $78\text{ kJ mol}^{-1}$  at  $55^\circ\text{C}$ , corresponding to an average lifetime of the tautomers of  $1/8$  of a second. At  $150^\circ\text{C}$ , the triazene decomposes to disilazane and nitrogen (equation 174)<sup>284</sup>. The monosilyl triazenes decompose by a radical pathway to give aniline derivatives (equation 175)<sup>283</sup>.



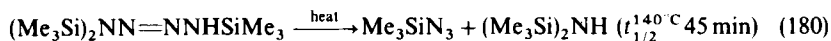
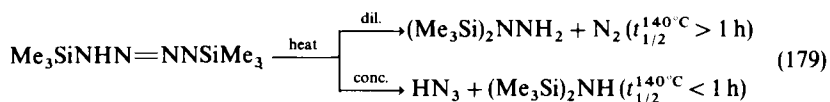
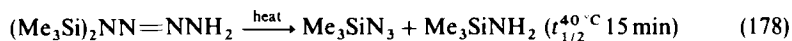


**D. Silyltetrazenes and Cyclosilatetrazenes<sup>16c,d</sup>**

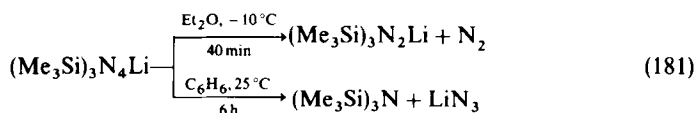
Tetrakis(trimethylsilyl)tetrazene (**142**) is a decomposition product of bis(trimethylsilyl)-diazene. However, it is more conveniently made through the intermediacy of its complex with silicon tetrafluoride (equation 176)<sup>285</sup>. The Si<sub>4</sub>N<sub>4</sub> skeleton of **142** is planar with the N<sub>4</sub> unit *trans*. Both the Si—N (178 pm) and N=N (127 pm) bonds are long, and the N—N bonds are short (139 pm), supporting a  $\pi$ -delocalized system<sup>286</sup>. Remarkably, the compound is stable to water and thermally decomposes only above 150 °C, yielding trisilylamine and silyl azide. It is protonated by trifluoroacetic acid, the parent tetrazene reacting *in situ* with germyl and stannyl amines Me<sub>3</sub>MNEt<sub>2</sub> (M=Ge, Sn) to give full substitution. With benzenesulphonyl isocyanate, the silylated tetrazole **143** results (equation 177)<sup>285</sup>.

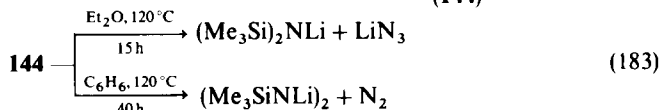
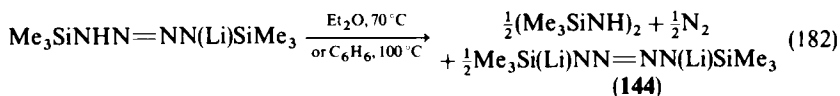


The decomposition products of silyl tetrazenes depend on the degree of protonation and on the concentration and temperature. Thus at 40 °C, the 1,1-disilyltetrazene gives silyl azide and aminosilane (half-life 30 min) (equation 178), but at 140 °C, it isomerizes to the 1,4-disilyl derivative, which forms the 1,1-disilylhydrazine and nitrogen if dilute (half-life greater than 1 hour) but hydrazoic acid and disilazane if concentrated (half-life less than 1 hour) (equation 179). At 140 °C the trisilyltetrazene gives silylazide and disilazane only (half-life 45 min) (equation 180)<sup>287</sup>. The tetrasilyltetrazene can be readily

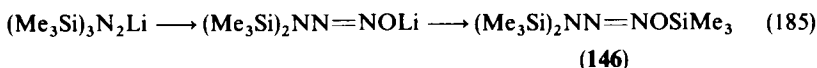
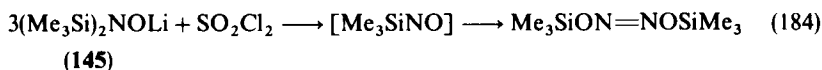


protonated and hence lithiated. The decomposition of lithium silyl tetrazenes is equally complex. With the trisilyl derivative, nitrogen and hydrazide result at -10 °C in ether, but azide and trisilylamine in benzene at 25 °C (equation 181). The lithio 1,4-disilyl-tetrazene gives 1,2-disilyl hydrazine, nitrogen and 1,4-dilithio-1,4-disilyltetrazene (**144**) in ether at 70 °C, and in benzene at 100 °C (equation 182). At 120 °C, in ether, **144** gives disilylamide and lithium azide, while in benzene, the 1,2-dilithio hydrazide and nitrogen form (equation 183)<sup>288</sup>.

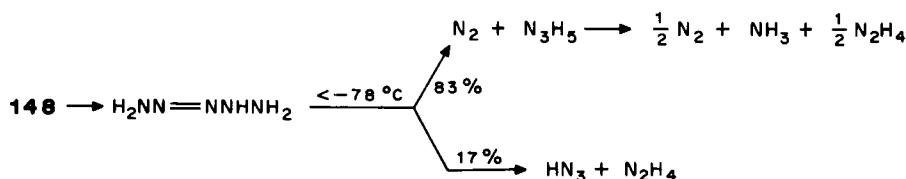
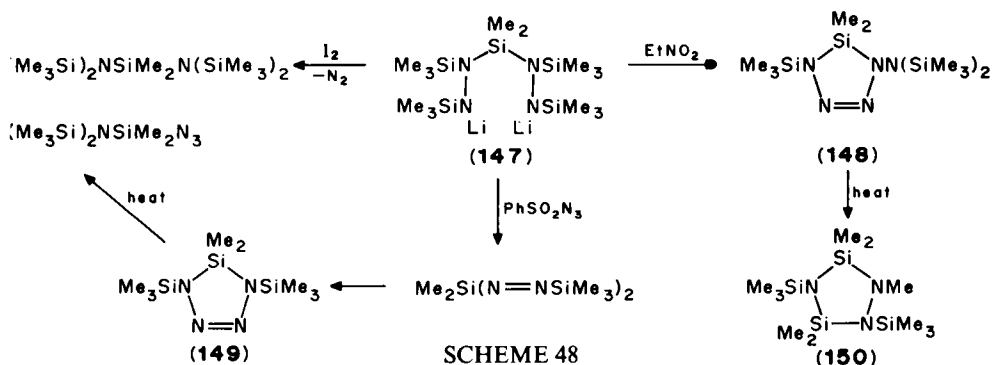




The tetrazeno can be considered as the bis-amide of *trans*-hyponitrous acid. The silylated derivative of this acid results on silylation of the silver salt or oxidation of the lithiated hydroxylamine **145** (equation 184). It is a sublimable solid, m.p.  $35^\circ\text{C}$ , that decomposes to nitrogen and silanol on heating. The monoamide, siloxytriazene **146** is formed by oxidizing the trisilylhydrazide with *i*-amyl nitrite. It decomposes at  $65^\circ\text{C}$  into disiloxane and azide (equation 185)<sup>289</sup>.



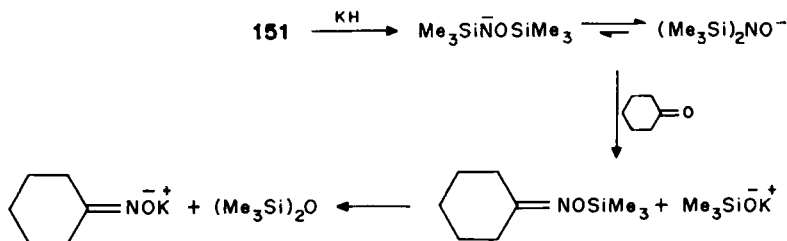
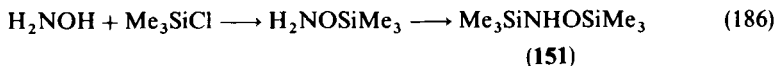
Oxidation of the lithiated bis(silylhydrazino)silane **147** gives a linear pentasilazane if iodine is used, but substituted cyclosilatetrazenes **148** and **149** with ethyl nitrite or benzenesulphonyl azide, the former also containing the pentazene unit. Heating induces isomerization to azidosilyldisilylamine or nitrogen loss and methyl migration to give the tetrahydrotriazole derivative **150** (Scheme 48). Reaction of **148** with trifluoroacetic acid below  $-78^\circ\text{C}$  gives the parent pentazene  $\text{H}_2\text{NN}=\text{NNHNH}_2$  which decomposes 17% to hydrazine and hydrazoic acid, and 83% to nitrogen and triazene, which itself gives nitrogen, ammonia and hydrazine (Scheme 49)<sup>290</sup>.



SCHEME 49

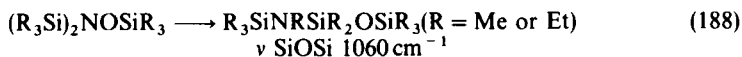
XIV. SILYLHYDROXYLAMINES<sup>14</sup>

Hydroxylamine can be readily silylated consecutively at oxygen, then nitrogen to give the N,O-derivative **151**, which rearranged on heating at 120 °C, as established with different substituents on silicon (equation 186)<sup>291</sup>. This can be metallated at nitrogen, the anion so formed isomerizing to give an equilibrium mixture of amide and oxide<sup>292</sup>, and reacts with aldehydes and ketones to give the oximate in high yield (Scheme 50)<sup>293</sup>.

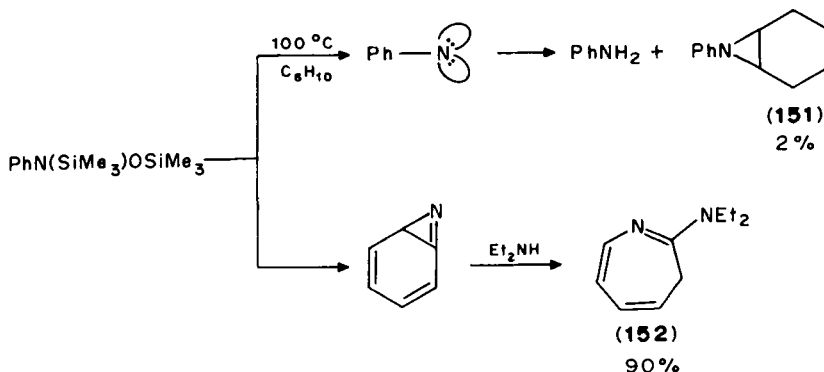


SCHEME 50

**151** reacts with BuLi/Me<sub>3</sub>SiCl to give the trisilyl derivative, which with organic acid chlorides gives hydroxamic acids in good yield on exposure to moist air (equation 187)<sup>294</sup>. Pyrolysis at 200 °C results in the intramolecular rearrangement to the siloxy-disilazane (equation 188)<sup>14,295</sup>.



With the *N*-phenyl bis(trimethylsilyl)hydroxylamine, pyrolysis at 100 °C in the presence of cyclohexene gives disiloxane, 53% of aniline and 2% of 7-phenyl-7-azabicyclo[4.1.0]-heptane, **151**, indicating nitrene formation. In the presence of secondary amines, high yields of the aminoazepine **152** result (Scheme 51)<sup>296</sup>.



SCHEME 51

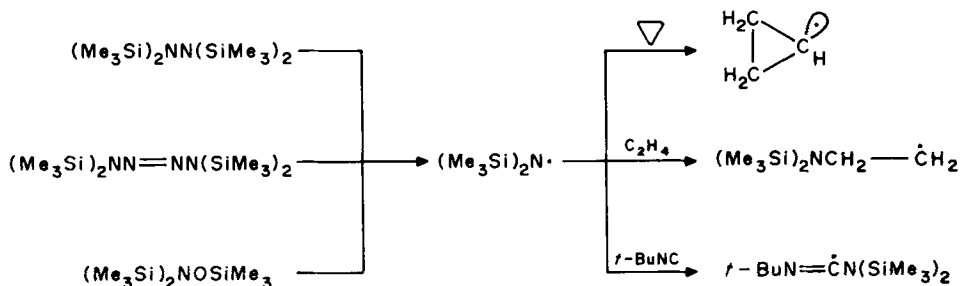
Methylhydroxamic acid can be readily silylated with  $(\text{Me}_3\text{Si})_2\text{NH}$ , the bissilyl product being present as an equilibrium mixture dominated by the keto isomer (equation 189)<sup>297</sup>.



The ESR spectrum of the radical  $(\text{Me}_3\text{Si})_2\text{NO}^\cdot$ , formed by oxidizing the anion, shows a low hyperfine splitting attributed to strong  $\text{N} \rightarrow \text{Si} \pi$ -bonding<sup>292</sup>, while the facile cleavage of the  $\text{C}-\text{O}$  bonds in the mass spectra of  $(\text{Me}_3\text{Si})_2\text{NOR}$  ( $\text{R} = \text{PhCH}_2$ , allyl) results through anchimeric assistance in  $\text{N} \rightarrow \text{O}$  migration of the silyl group<sup>298</sup>.

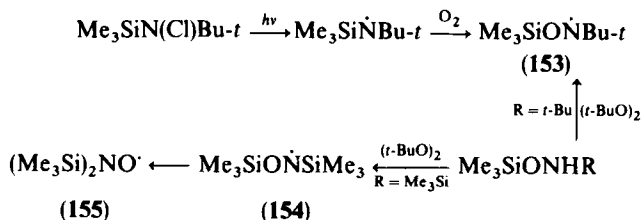
### XV. SILYLAMINYL RADICALS

Photolysing the tetrasilylhydrazine  $(\text{Me}_3\text{Si})_4\text{N}_2$  or tetrazene  $(\text{Me}_3\text{Si})_4\text{N}_4$ , or the trisilylhydroxylamine  $(\text{Me}_3\text{Si})_2\text{NOSiMe}_3$  gives the bis(trimethylsilyl)aminyll radical. This appears much more reactive than dialkylaminyll radicals, deprotonating propene and cyclopropane, but adding to ethylene and to *t*-butyl isocyanide (Scheme 52). The bis(triethylsilyl)aminyll radical behaves similarly<sup>299</sup>.



SCHEME 52

The *t*-butyl(silyl)aminyll radical, which results from the chloramine on photolysis, is readily oxidized to the siloxyaminyll radical **153**, which can also be prepared directly from the hydroxylamine. The siloxy(silyl)aminyll radical **154**, prepared similarly, rearranges to the nitroxide radical **155** (Scheme 53).

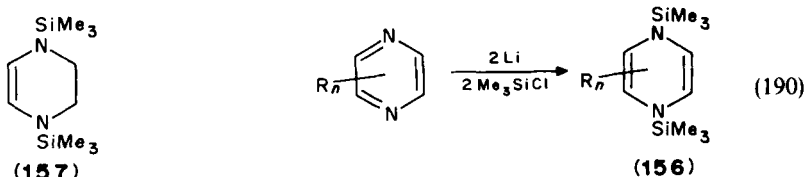


SCHEME 53

### XVI. SUBSTITUTED DIHYDROPYRAZINES

Reducing pyrazine gives the conjugated 1,2-dihydropyrazine and not the symmetrical 1,4-isomer. However, reductive silylation of pyrazines provides a route to the highly reactive 1,4-bissilyl-1,4-dihydropyrazines **156** which are pale yellow liquids or solids (equation 190). The silyl substituents at nitrogen encourage the unfavourable  $8\pi$ -electron conjugation by forcing the nitrogen atom towards a planar configuration and hence a

triplet HOMO and a diradical. This is reflected in the 'antiaromatic' upfield shift of the hydrogen atoms of the ring of **156** ( $R = H$ ) compared with mono- and dimethyl isomers, and the tetrahydropyrazine **157**.



In addition, the low first ionization energy of **156** ( $R = H$ ) of 6.16 eV compared to **156** ( $R = Me$ ) of 6.48 eV reflects the instability of the planar  $8\pi$ -electron system, while the bis(trimethylgermyl) derivative ( $R = H$ ) shows an even lower first ionization energy of 5.87 eV. Indeed, methyl substitution of the ring would be expected to lower the ionization energy, but steric repulsion leads to ring distortion from planarity and a lowering of the HOMO relative to the LUMO. This is accompanied by a change in colour from yellow for **156** ( $R = H$ ) to colourless for the tetramethyl derivative<sup>300</sup>.

Structure determinations for **156** ( $R = H$ ) and its trimethylgermyl derivative show both to have planar rings, and the tetramethyl compound **156** ( $R = Me$ ) to have a boat conformation. The silicon–nitrogen bond lengths are similar for each (174.4–175.4 pm)<sup>301</sup>.

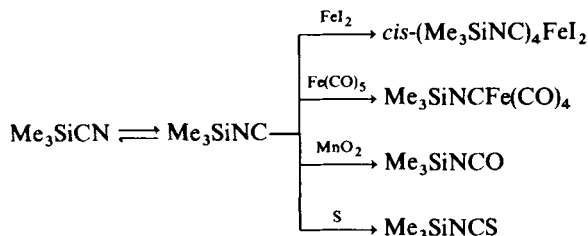
These silylated 1,4-dihydropyrazines form very persistent radical cations, so it is not surprising that the unpaired electron density of the 1,5-dihydroflavins and certain luciferin radical cations is in this ring.

## XVII. SILYL PSEUDOHALIDES<sup>5-7</sup>

Organosilicon pseudohalides are conveniently prepared in good yield from chlorosilanes and a salt using a polar solvent. However, high yields of the trimethylsilyl derivatives result from the silyl sulphate using *N*-methylpyrrolidone as solvent<sup>302</sup>. The azides are best prepared in HMPT<sup>303</sup>. The methyl derivatives are readily distillable liquids—even the azides. The tri-*t*-butyl derivatives are best made in the presence of 18-crown-6<sup>304</sup>.

The vapour-phase structure determinations of  $\text{Me}_3\text{SiX}$  ( $X = \text{N}_3, \text{NCO}, \text{NCS}$ ) show the pseudohalide group to be linear, with the  $\text{SiNX}$  angle much less for the azide<sup>305-307</sup>. Dimethylsilylisocyanate and isothiocyanate are similar<sup>309</sup>, while the X-ray structure of  $\text{Ph}_3\text{SiN}_3$ <sup>311</sup> also shows a much smaller  $\text{SiNN}$  angle than the  $\text{SiNC}$  angle in  $\text{Ph}_3\text{SiNCS}$  (Table 6)<sup>312</sup>.

The nitrile  $\text{Me}_3\text{SiCN}$  appears to exist predominantly as the C-bonded isomer, but reacts with  $\text{FeI}_2$  to give the 6-coordinate silyl isocyanide complex  $\text{cis}-(\text{Me}_3\text{SiNC})_4\text{FeI}_2$ <sup>313</sup>. It also substitutes  $\text{Fe}(\text{CO})_5$  as the *iso*-isomer and is oxidized by  $\text{MnO}_2$  or sulphur to the isocyanate and isothiocyanate respectively (Scheme 54)<sup>314</sup>.



SCHEME 54

TABLE 6. Molecular parameters for silyl pseudohalides

Compound	Technique	Si-N (pm)	Si-N-X (deg)	Reference
Me <sub>3</sub> SiN <sub>3</sub>	ED	173.4	128	305b
Me <sub>3</sub> SiNCO	ED	174.0	156.9	306
Me <sub>3</sub> SiNCS	ED	178	154	307
Me <sub>3</sub> SiN=PMe <sub>3</sub>	ED	170.5	144.6	308
Me <sub>2</sub> HSiNCO	ED	171.9	153.5	309
Me <sub>2</sub> HSiNCS	ED	172.3	154.7	309
H <sub>3</sub> SiNCO	ED	169.9	152	310
H <sub>3</sub> SiNCS	ED	171.4	164	310
Ph <sub>3</sub> SiN <sub>3</sub>	X ray	174	120.5	311
Ph <sub>3</sub> SiNCS	X ray	173.5	170.7	312

All silyl cyanates and thiocyanates occur as the N-bonded *iso* derivatives. However the *O*- and *S*-bonded isomer can be made for the highly hindered trisilylmethylsilyl derivatives. The tris(trimethylsilyl)methylsilyl iodides TsiSiR<sub>2</sub>I [Tsi = (Me<sub>3</sub>Si)<sub>3</sub>C, R<sub>2</sub> = Me<sub>2</sub>, Me(MeO), Ph<sub>2</sub>] all give the *O*-bonded cyanate with silver cyanate, the last, (Me<sub>3</sub>Si)<sub>2</sub>C(SiPh<sub>2</sub>Me)SiMe<sub>2</sub>OCN, through rearrangement. Heating causes isomerization to the *N*-bonded isomer with infrared bands at 2240 cm<sup>-1</sup> and 1160 cm<sup>-1</sup> replaced by one at 2280 cm<sup>-1</sup> (equation 191). The less hindered TsiSiPh(H)I gives the isocyanate directly<sup>315</sup>.

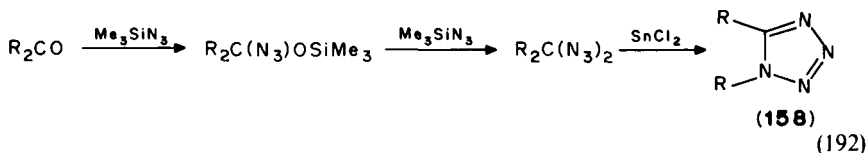


With silver thiocyanate, the *S*-bonded thiocyanate results from (Me<sub>3</sub>Si)<sub>2</sub>C(SiMe<sub>2</sub>OMe)-SiMe<sub>2</sub>Cl, the only significant differences in physical properties with the *N*-bonded isomer being in the NMR spectra. The m.p. and IR peaks are virtually identical, but the *S*-bonded isomer is several thousand times more reactive to solvolysis<sup>316</sup>. With MeH<sub>2</sub>SiBr and the silver pseudohalide, the *N*-bonded isomer results<sup>317</sup>. The *t*-butyl derivatives are *N*-bonded<sup>304</sup>.

## A. Reactions of Silyl Azides

### 1. In organic synthesis<sup>6a,6b,318</sup>

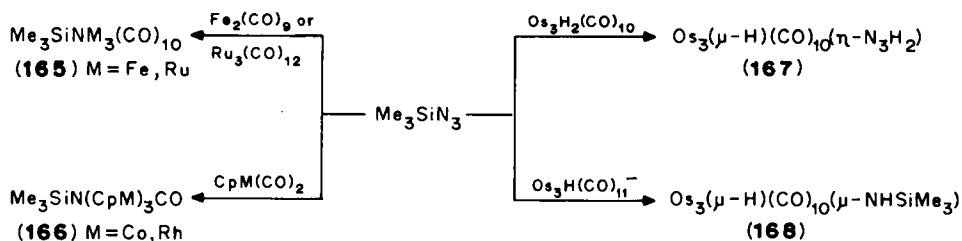
Azidotrimethylsilane readily converts benzyl halides to the azide in HMPA<sup>319</sup>, and acyl or aroyl chlorides in the presence of either 18-crown-6 or zinc iodide<sup>320</sup>, while epoxides are ring opened both regio- and stereoselectively in the presence of catalysts<sup>321</sup>. Acetals yield azido derivatives<sup>322</sup>, diazides yielding the tetrazole **158** in the presence of stannous chloride (equation 192)<sup>323</sup>.



The tetrazoles **159** and **160** result from silylazide and aryl cyanide or isocyanate (equation 193)<sup>318,324</sup>, while in the presence of zinc chloride, aryl aldehydes react with silyl azide to give nitrile through silanol loss (equation 194)<sup>325</sup>.



$\text{Ru}_3(\text{CO})_{12}$  or  $\text{CpM}(\text{CO})_2$  ( $\text{M} = \text{Co}, \text{Rh}$ ). The silicon–nitrogen bond in the iron compound is 177.9 pm long<sup>332</sup>. With the two triosmium compounds, two products result, neither of which involves the triple metal bridging of the smaller iron, cobalt or rhodium triangles. **167** has the  $\text{N}_3\text{H}_2$  ligand and **168** has  $\text{Me}_3\text{SiNH}$  ( $\text{Si}-\text{N}$  166 pm), both edge-bridging two metal atoms (Scheme 57)<sup>333</sup>.



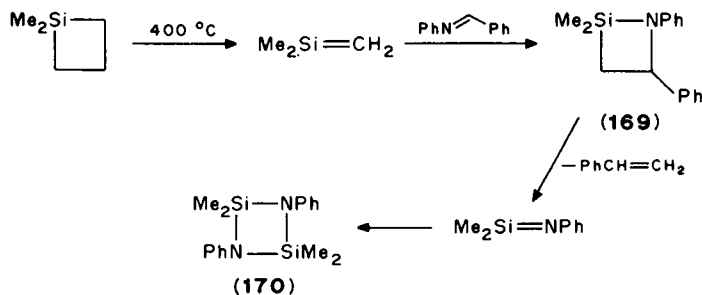
SCHEME 57

### XVIII. THE SILICON–NITROGEN MULTIPLE BOND<sup>15</sup>

The considerable variation in the silicon–nitrogen single bond length supports the suggestion, now generally recognized, that the nitrogen lone-pair electrons are delocalized into either the silicon d-orbitals or the  $\sigma^*$ -orbitals of the  $\text{Si}-\text{C}$  bond. The diagnostic test for this has still to be designed<sup>73</sup>. Trisilylamines are trigonal planar and not pyramidal like trimethylamine, and silylamines do not readily form silylammonium salts unlike the more basic organic amines (but see equation 27 and Scheme 39).

#### A. Silaimines

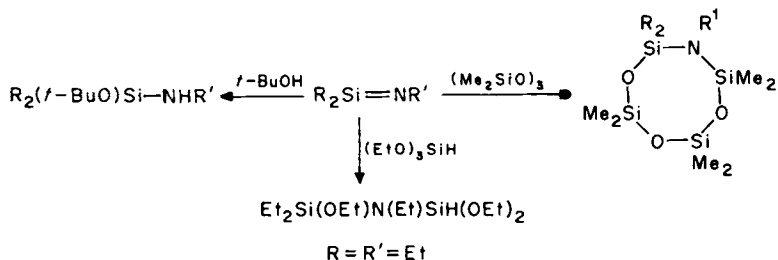
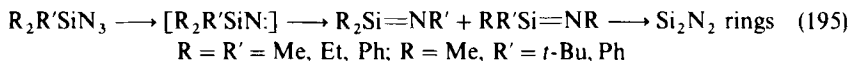
For many decades it was thought that  $\pi$ -bonding of the type encountered in imines and cyanide would not be possible for silicon, but in 1974 the first conclusive evidence for the transient existence of a silicon–nitrogen intermediate  $\text{R}_2\text{Si}=\text{NR}'$  was presented. Pyrolysing 1,1-dimethyl-1-silacyclobutane at 400 °C with imines gives the intermediate azasilacyclobutane **169**, which decomposes to the cyclodisilazane **170** via the silaimine (Scheme 58)<sup>334</sup>.



SCHEME 58

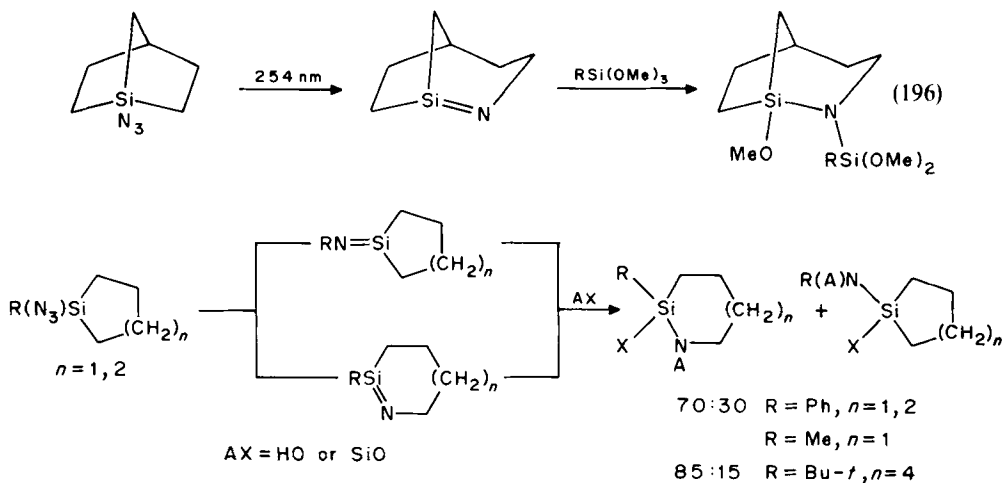
Silaimines are better generated through photolytic nitrogen loss and alkyl migration of azidosilanes (equation 195). The product can be readily trapped by insertion into cyclosiloxanes, adds *t*-butanol, and inserts into the silicon–oxygen bond of triethoxysilane, showing the silaimine to be a polar rather than radical intermediate (Scheme 59)<sup>335</sup>.





SCHEME 59

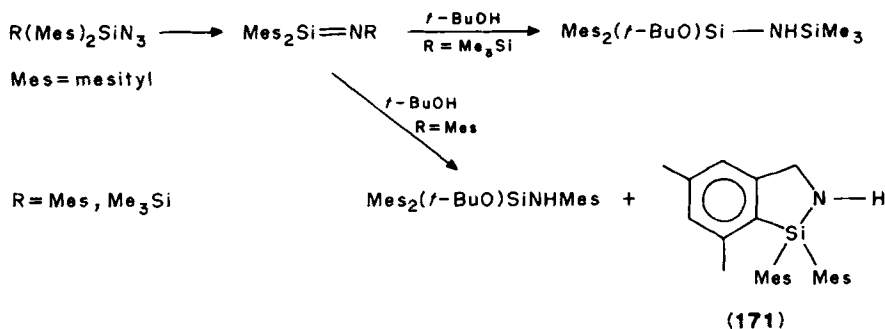
Photolysing 1-azido-1-silabicyclo[2.2.1]heptane or its [2.2.2]octane analogue generates the bridgehead silaimine, which can be trapped as a methoxysilane adduct. No product resulted through silaimine incorporation in the methylene link (equation 196). With the photolysis of monocyclic azidosilanes, adducts indicate both endo- and exocyclic silaimine intermediates (Scheme 60)<sup>336</sup>.



SCHEME 60

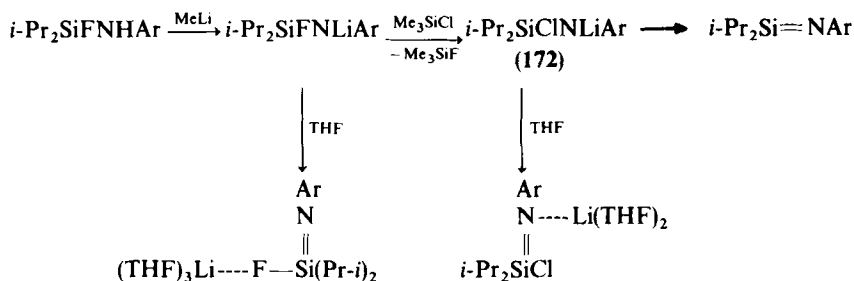
The azidosilanes  $R_2R'SiN_3$  ( $R = \text{mesityl}; R' = \text{mesityl, Me}_3\text{Si}$ ) photolyse in matrix at low temperature to give the orange silaimine  $R_2Si=NR'$  which gives  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions at 272 and 474 nm ( $R' = \text{Me}_3\text{Si}$ ) or 296 and 444 nm ( $R' = \text{mesityl}$ ). Both silaimines add *t*-butanol and the latter decomposes above  $-120^\circ\text{C}$  to give the dihydro-1-silaisoindole **171** through C—H insertion (Scheme 61)<sup>337</sup>.

Condensing di-isopropyldifluorosilane with the lithium derivative of 2,4,6-tris(*t*-butyl)-aniline gives the *N*-fluorosilylaniline which on further lithiation and F/Cl exchange yields



SCHEME 61

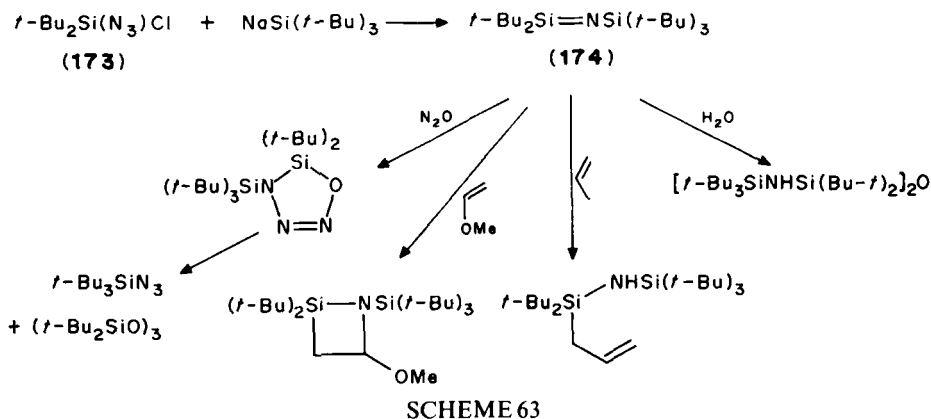
**172**, which eliminates LiCl on heating to give the free silimine as an orange solid, m.p. 97–99 °C. It shows little tendency to dimerise and has a low-field  $^{29}\text{Si}$  NMR absorption typical of silenes and disilenes. The THF complex of the fluoro derivative of **172** has a very short silicon–nitrogen bond (161.9 pm), with the SiNC angle (172.1°) a typical imine value. The LiFSi angle is 162° with the Si—F bond long (168.6 pm). The chloro derivative, where cation interaction occurs at nitrogen, and probably with an agostic hydrogen on a *t*-butyl group (Li—C 274.7 pm), has a longer Si—N bond of 164.2 pm and a SiNC angle of 138.7° (Scheme 62)<sup>338</sup>.



SCHEME 62

Reacting the chloroazide **173** with tri(*t*-butyl)silylsodium gives the silimine **174** as a pale yellow solid, silicon–nitrogen bond lengths 156.8 and 169.5 pm, and an SiNSi angle of 177.8°, supporting a silicon–nitrogen double bond. THF readily complexes with **174** at silicon and is difficult to remove. **174** reacts with protic reagents and adds to electron-rich systems (Scheme 63)<sup>339</sup>.

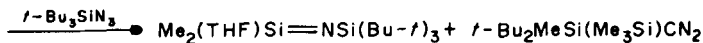
Silimines **175** can also be made by the novel ene exchange between THF complexed silaethene **176** and azidosilanes. The bissilyl diazomethane is the other product (equation 197). Adducts result with  $\text{Et}_3\text{N}$  and  $\text{Me}_3\text{SiX}$ , while  $\text{Ph}_2\text{CO}$  gives imines (Scheme 64)<sup>340</sup>. A structure determination on the THF silimine complex **175** prepared this way shows two independent molecules in equal proportions in the crystal, with silicon–nitrogen bond lengths 158.9 and 157.4 pm for the ‘double’ bond, a little longer than in **174**, and



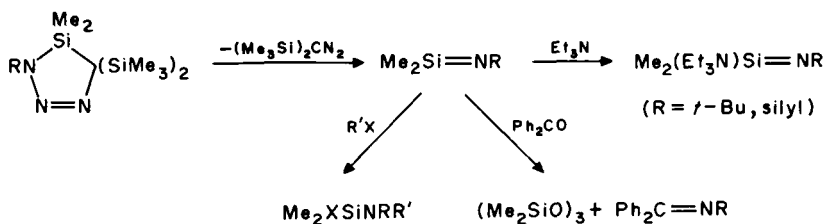
'single' bond lengths of 165.4 and 166.7 pm, slightly shorter than in **174**, in accordance with a zwitterionic description of **175**. The angle at nitrogen is  $161^\circ.339$ .



(176)



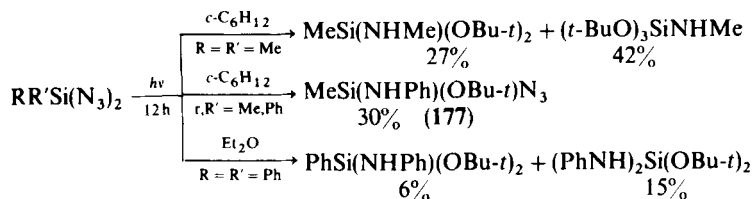
(175)



SCHEME 64

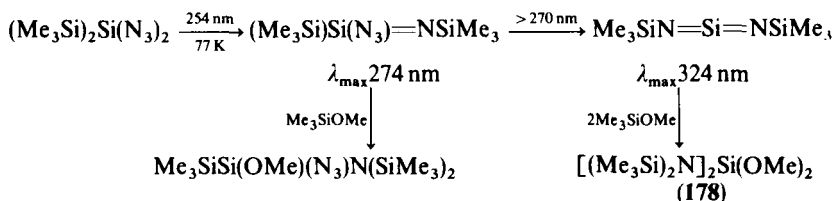
## B. Siladliimides

Photolysing the three diazides  $\text{RR}'\text{Si}(\text{N}_3)_2$  in the presence of *t*-butanol gave products supporting the possible intermediacy of the siladiimide  $\text{RN}=\text{Si}=\text{NR}'$  as well as the silaimine (Scheme 65). However, the isolation of the *t*-butoxyzide **177** indicates that the decomposition may be a stepwise reaction<sup>341</sup>.



SCHEME 65

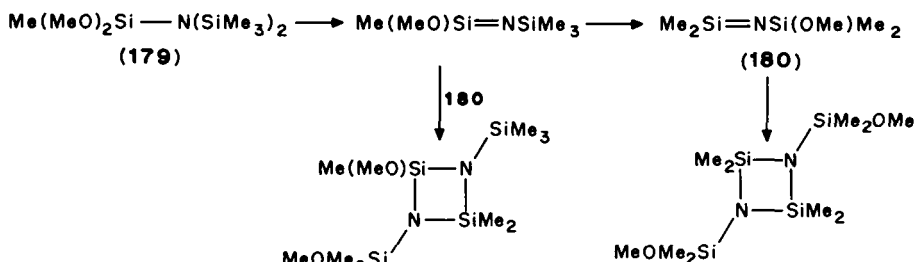
Evidence for the formation of such a siladiimide analogue arises from the photolysis of the diazidosilane  $(\text{Me}_3\text{Si})_2\text{Si}(\text{N}_3)_2$  at 254 nm which generates two new bands at 274 and 324 nm. Their growth at different rates show them to be due to different species, and irradiating at longer wavelength reduces the 274 nm band and increases the 324 nm band (Scheme 66). This, together with a linear relationship observed between the absorbance of this band and the amount of methoxysilane adduct **178** formed, indicates that the siladiimide is produced, but suggests that stepwise addition occurs in the presence of protic reagents<sup>342</sup>.



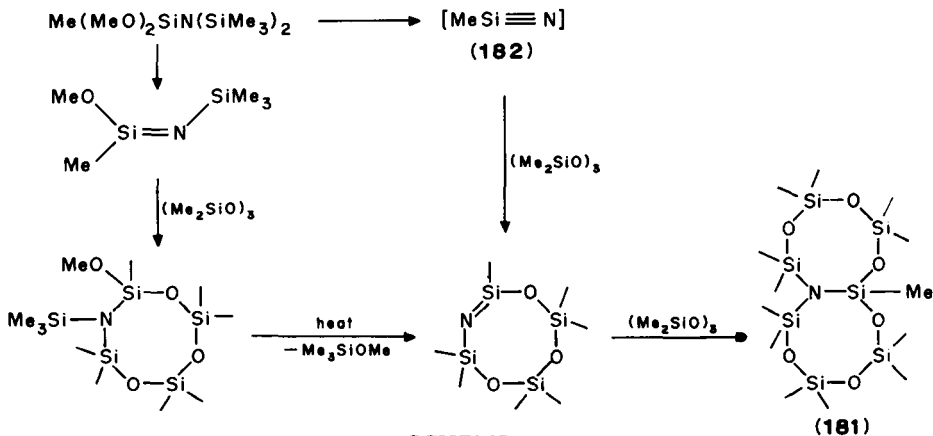
SCHEME 66

### C. The Silicon–Nitrogen Triple Bond

Silamines can also be formed by the pyrolysis of methoxy(silylamino)silanes **179**, the silamine so formed isomerizing to **180** since a mixture of isomeric cyclodisilazanes results (Scheme 67). They insert cyclotrisiloxanes, and the isolation also of the bicyclosiloxane **181** indicates either a stepwise elimination of methoxysilane or the intermediacy of the silaacetonitrile **182** (Scheme 68)<sup>343</sup>. Pyrolysing phenylsilicon triazide at 1100 K



SCHEME 67



SCHEME 68

gives the phenyl silaisocyanide and not the cyanide. Calculations suggest the former to be the more stable by some 400 kJ mol<sup>-1</sup>, with a Si—N bond length of 152 pm (equation 198)<sup>344</sup>.



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# Appendix to 'Organosilicon nitrogen compounds'<sup>†</sup>

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<sup>†</sup>The material in this Appendix is divided in the same manner as in the main chapter (Chapter 11). Section number in the Appendix are preceded by an asterisk. The number of structures, equations, tables, schemes and references run continuously in Chapter 11 and this Appendix.

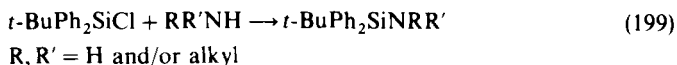
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This Appendix covers the literature from mid-1987 to mid-1990. While it has been possible to make the sulphur and phosphorus group chapters and their appendices reasonably comprehensive, this has not been possible for the nitrogen chapter nor for its appendix. A fairly extensive list of references will be found in the Royal Society of Chemistry's Specialist Periodical Reports on Organometallic Chemistry<sup>345</sup>, where the barest descriptive detail is given. Since their last three years include over 300 references on silicon-nitrogen bond alone, as many as in the main chapter here, the appendix will extend the sections in the main chapter and include new areas under current section headings. Many of the papers using Si-N compounds as intermediates in the synthesis of inorganic products not containing silicon will be excluded.

A review covers the structure of 'covalent' versus 'dative' bonds in main group metal and metalloid amine derivatives, and provides some useful distinctions in silicon-nitrogen compounds<sup>346</sup>. 'Dative' bonds from nitrogen to silicon are included in Section \*II.B.

## I. THE GENERAL SYNTHESIS OF AMINOSILANES, DISILAZANES AND TRISILYLAMINES

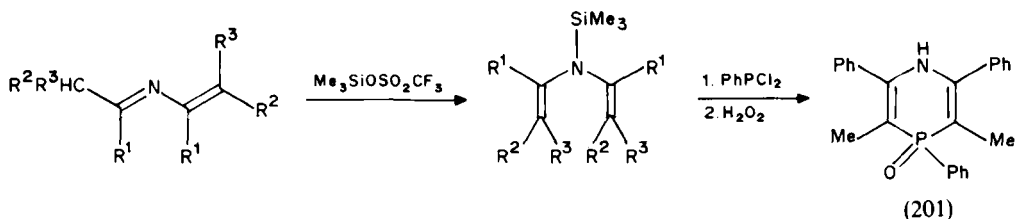
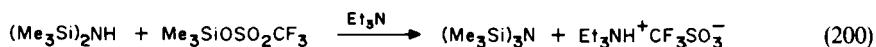
*t*-Butyldiphenylchlorosilane is now used extensively as a protecting group. It reacts readily with ammonia, primary and secondary amines to give the aminosilane which is stable to hydrolysis (equation 199)<sup>347</sup>.



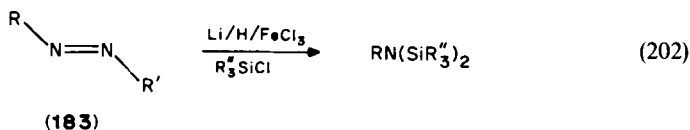
Me<sub>3</sub>SiOSO<sub>2</sub>CF<sub>3</sub> silylates hexamethyldisilazane in the presence of Et<sub>3</sub>N, to give the trisilylamine in good yield (equation 200)<sup>348</sup>. It also silylates 2-aza-1,3-dienes to give the first examples of *N*-trimethylsilyl divinylamines (R' = Ar, alkyl, H; R<sup>2</sup> = alkyl; R<sup>3</sup> = H, Me)<sup>32</sup>. These alkyl- and aryl-substituted amines are thermally stable and condense with PhPCl<sub>2</sub> to give azaphosphinines (R' = Ph; R<sup>2</sup> = Me, R<sup>3</sup> = H) (equation 201)<sup>349</sup>.

Reducing the azo compounds **183** (R = R' = aryl; R = R' = alkyl; R = Ph, R' = Me<sub>3</sub>Si)





with lithium in the presence of a transition metal catalyst, followed by silylation with  $\text{R}''_3\text{SiCl}$ , gives the disilazane, generally in good yield. With  $\text{R}'' = \text{Me}_3\text{Si}$ ,  $\text{PhN}(\text{SiMe}_3)_2$  results in 37% yield and the trisilylamine in 25% yield. With *t*-BuMe<sub>2</sub>SiCl and azobenzenes, the aminosilane *t*-BuMe<sub>2</sub>SiNHPh results, the disilazane only forming on prolonged heating to 66 °C (equation 202)<sup>350</sup>.



## \*II. AMINOSILANES

### \*B. Substitution at Silicon

Chloromethylchlorosilanes give 1-[2-pyridone-(2'-pyridyl)imine]methylsilanes (**184**) with *N*-trimethylsilyl-2,2'-dipyridylamine (equation 203). The complexes show structural features indicative of an equilibrium favouring four-coordinate silicon at high temperature and an ionic form at low temperature (equation 204). Increasing methylation at Si also reflects an increase in the ease of ionization of chlorine (Table 7)<sup>351</sup>. The aminomethyl-substituted arylsilane (**185**) shows a distorted trigonal bipyramidal structure with nitrogen and fluorine atoms apical. The Si—N distance is 234.6 pm, longer than those reported in Tables 1 and 7<sup>352</sup>.

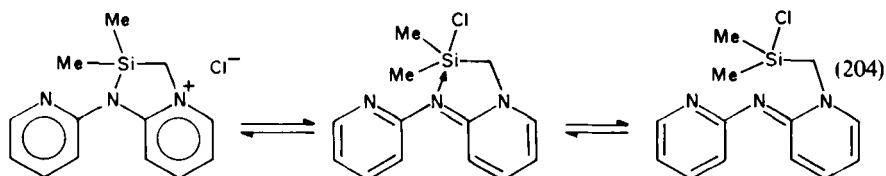
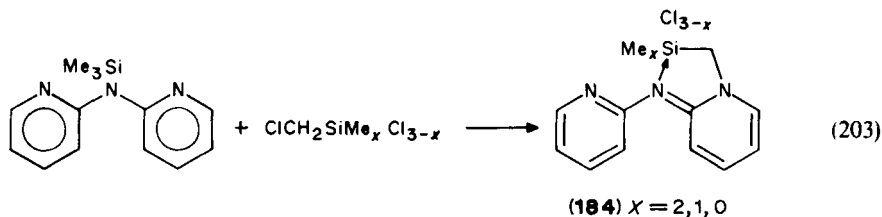
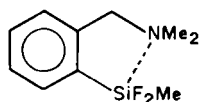


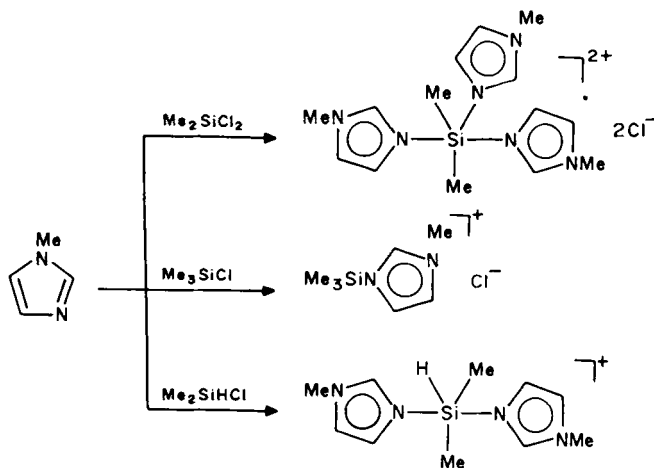
TABLE 7. Bond lengths in pyridylmethylsilanes

	Distances	
	Si-N (pm)	Si-Cl (pm)
<b>184</b> , $x = 2$	189.8	259.8
<b>184</b> , $x = 0$	190.1	223.8

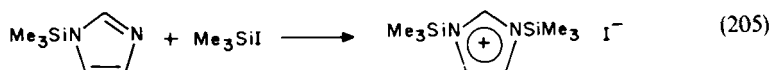


(185)

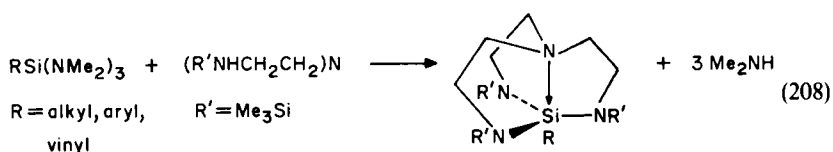
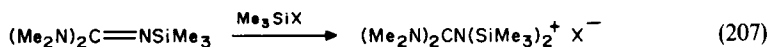
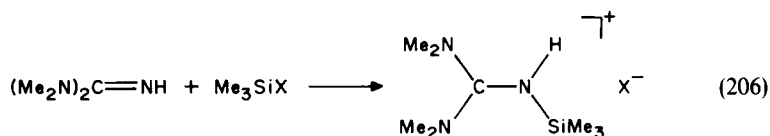
$\text{Me}_3\text{SiCl}$  forms a 1:1 ionic adduct with *N*-methylimidazole through substitution at the other ring nitrogen atom.  $\text{Me}_2\text{SiHCl}$  gives a 1:2 adduct with nitrogen atoms axial (Si-N 200.5 and 203.4 pm), while the 1:3 adduct with  $\text{Me}_2\text{SiCl}_2$  has both chlorine atoms ionic with the cation  $\text{Me}_2\text{Si}(\text{NC}_3\text{H}_3\text{NMe})_3^{2+}$  having two imidazole groups axial (Si-N 198.3 and 202.3 pm) and one equatorial (Si-N 181.7 pm) (Scheme 69)<sup>353</sup>.  $\text{Me}_3\text{SiI}$  forms a similar ionic 1:1 adduct with *N*-trimethylsilyl imidazole, with Si-N bonds 177.2 pm (equation 205)<sup>354</sup>.



SCHEME 69



The guanidines  $(\text{Me}_2\text{N})_2\text{C}=\text{NH}$  and  $(\text{Me}_2\text{N})_2\text{C}=\text{NSiMe}_3$  also give guanidinium adducts with  $\text{Me}_3\text{SiX}$  (X = Cl, Br, I) but not with  $\text{Me}_3\text{SiF}$ . The bisilyl salts are less stable than the monosilyl ones, with iodides the most thermally stable (equations 206 and 207)<sup>355</sup>. Azasilatranes, 2,5,8,9-tetraaza-1-silatricyclo[3.3.3.0<sup>1,5</sup>]undecanes, result from  $\text{RSi}(\text{NMe}_2)_3$  and the tris( $\beta$ -aminoethyl)amine (equation 208)<sup>356</sup>. Increasing silylation at

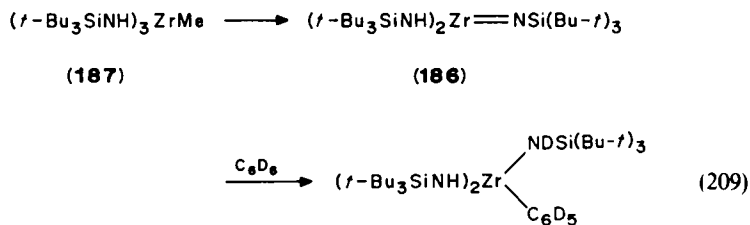


nitrogen weakens the transannular interaction<sup>357</sup>. Thus for R = Ph, R' = H, the distance is 213.2 pm, which agrees closely with that found in the  $\gamma$ -modification of the silatrane PhSi(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N, and is significantly shorter than those of the other two modifications<sup>358</sup>. For R = Me, R' = Me<sub>3</sub>Si, it is 277.5 pm, the longest N → Si coordinated bond reported but still some 24% shorter than the van der Waals interaction distance of 365 pm. Methylation at this axial nitrogen atom occurs using CF<sub>3</sub>O<sub>2</sub>SOMe. The <sup>29</sup>Si NMR spectra also support deshielding<sup>359</sup>.

### \*C. Properties of Aminosilanes

#### \*2. Transition metal derivatives

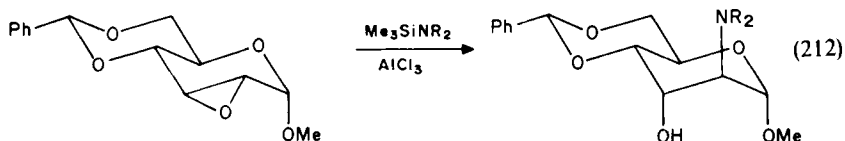
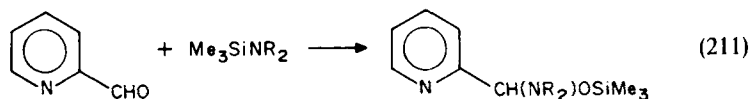
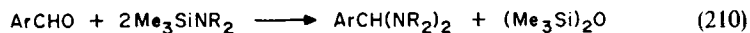
A number of silylamino derivatives of transition metals have been made, particularly for vanadium<sup>360</sup>. Among the more remarkable is the *t*-butylsilylamino zirconium complex (186), which results transiently from the pyrolysis of 187, and activates C—H and C—D bonds, C—D adding across the Zr=N double bond (equation 209)<sup>361</sup>.



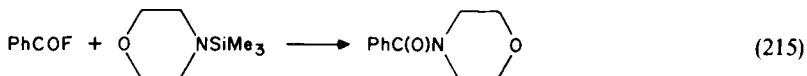
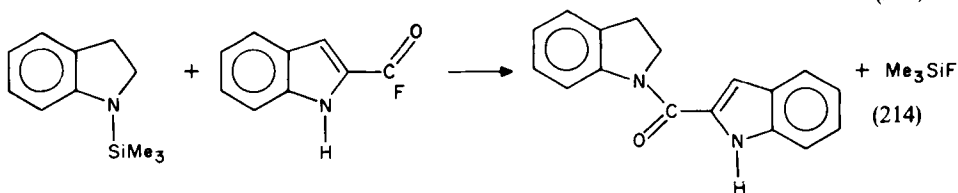
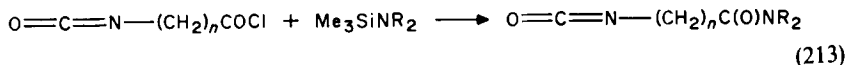
#### \*3. Use in organic synthesis

In the presence of trimethylsilyl triflate and fluoride, aminosilanes add to RCHO to give bis(amino) derivatives in excellent yield (equation 210). With 2-pyridine carboxaldehydes, the intermediate hemiacetals can be isolated (equation 211)<sup>362</sup>.

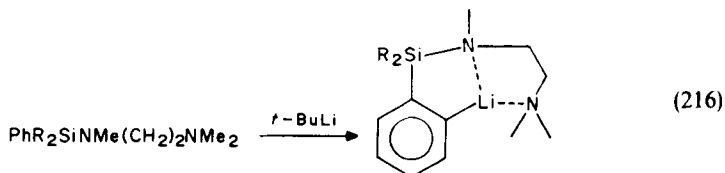
Me<sub>3</sub>SiNR<sub>2</sub> (R = Me, Et) *trans*-diaxially cleaves the oxirane ring in 2,3-anhydro sugars to give regioisomerically pure aminodeoxy sugars, using AlCl<sub>3</sub> catalyst under mild conditions (equation 212)<sup>363</sup>. Isocyanato alkane carboxylic acid amides (and esters) result from the acid chloride and aminosilane (or alkoxysilane) (equation 213)<sup>364</sup>, while acyl and



benzoyl fluorides cleave the Si—N bond of silyl-substituted heterocycles to give the amide in excellent yield (equations 214 and 215)<sup>365</sup>.  $\text{Me}_3\text{SiN}(\text{Li})\text{CH}_2\text{Ph}$  adds 1,4- to crotonates,

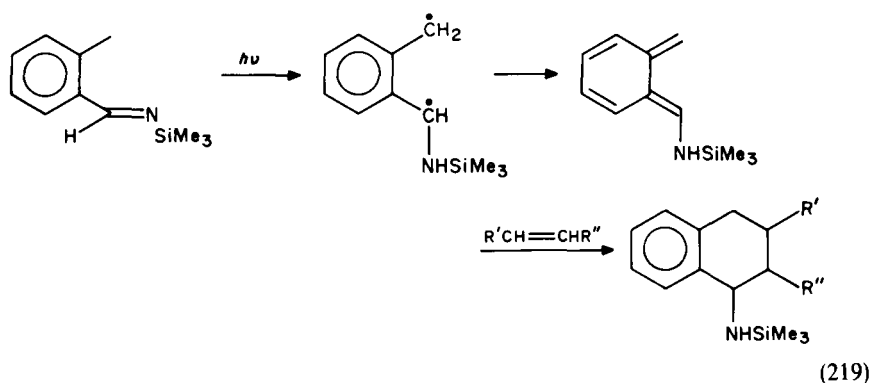
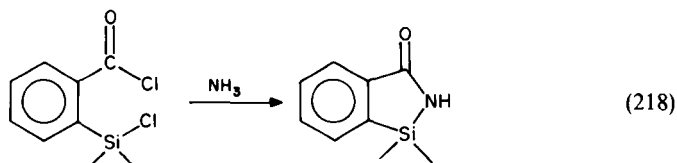
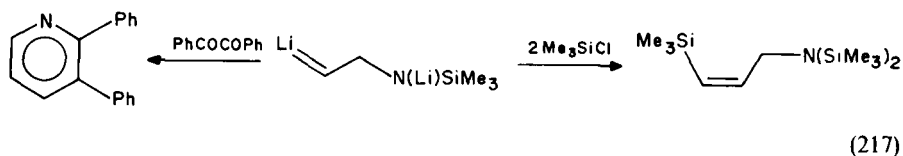


in contrast to non-silylated amides, and  $\beta$ -aminoethylamino(phenyl)silanes undergo ready *ortho*-lithiation, providing a new route to *ortho*-substituted phenylsilane derivatives (equation 216)<sup>366</sup>. *t*-Bu( $\text{R}_3\text{Si}$ )NLi deprotonates a series of unsymmetrical ketones with

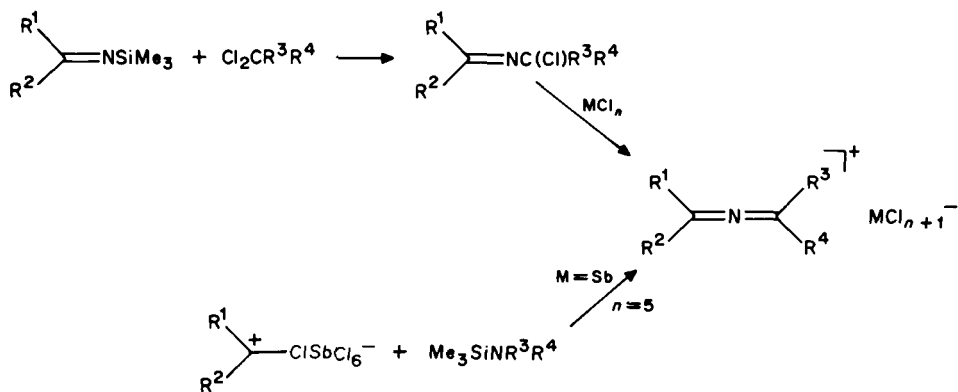


equal or greater regioselectivity to *i*-Pr<sub>2</sub>NLi. The dilithio derivatives of substituted allylaminosilanes and arylaminosilanes give a series of *N,N,C*-tris(trimethylsilyl)amines while notably that of trimethylsilyl(allyl) amine has been used to prepare a range of pyrroles and pyridines (equation 217)<sup>367</sup>.

Aminating 2-( $\text{ClMe}_2\text{Si}$ ) $\text{C}_6\text{H}_4\text{COCl}$  gives 1-silaisoindolinone, a saccharin analogue in which  $>\text{SiMe}_2$  replaces  $>\text{SO}_2$ , and is found not to be sweet (equation 218)<sup>368</sup>. Irradiating *o*-(*N*-trimethylsilyliminomethyl)toluene induces  $\gamma$ -H transfer to give the *o*-quinodimethane intermediate, which then gives a series of tetrahydronaphthalene derivatives using



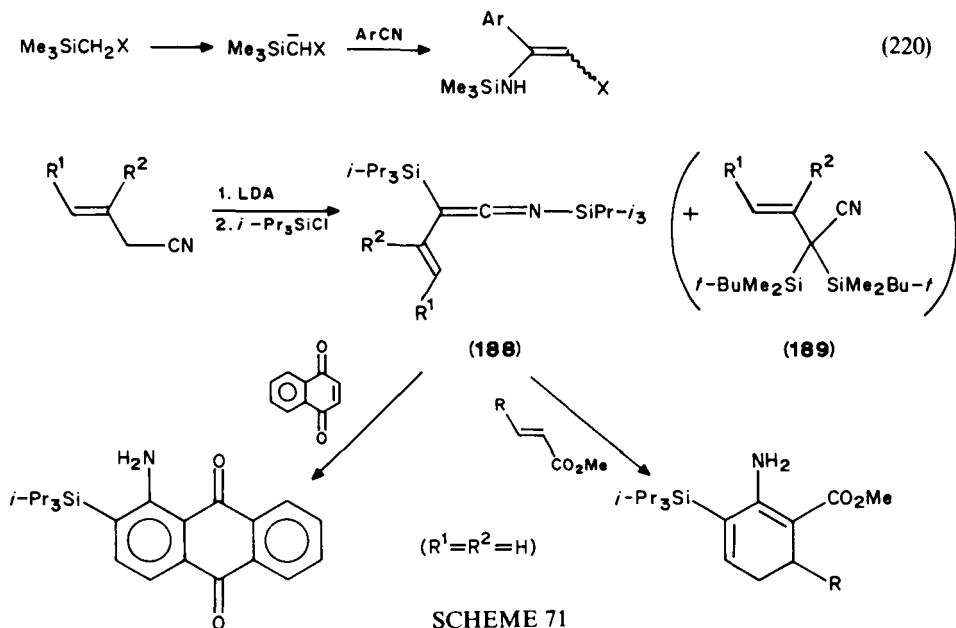
electron-rich alkenes (equation 219)<sup>369</sup>. Diaryldichloromethanes and *N*-silylated benzenonimines give *N*-chloromethyl imines which, with a halide ion acceptor, form the 2-azoniaallene salts. These salts also result using *N*-silyl imines substituted with electron-rich groups, and chlorocarbenium salts at low temperature (Scheme 70)<sup>370</sup>.



$R^1, R^2 = \text{Me}_2\text{N}$  and/or aryl;  $R^3, R^4 = \text{Me}_2\text{N}, \text{EtO}, \text{MeS}$  or Ph

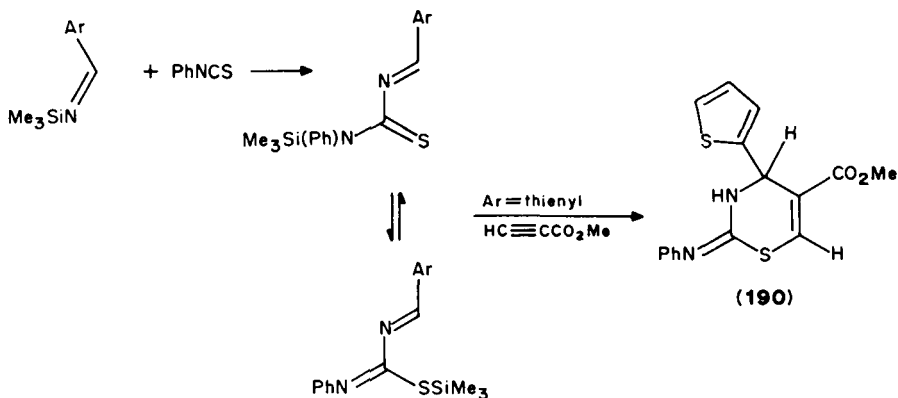
SCHEME 70

While  $\alpha$ -silyl carbanions add to aryl nitriles to yield the *N*-silyl enamine (equation 220)<sup>371</sup>, allylic cyanides lithiated with LDA give the alkenyl ketenimine **188** exclusively with *i*-Pr<sub>3</sub>SiCl, but as the major part of a mixture with **189** using *t*-BuMe<sub>2</sub>SiCl (Scheme 71)<sup>372</sup>. While *N*-silyl imines ArCH=NSiMe<sub>3</sub> add 1,2- to PhNCS across both

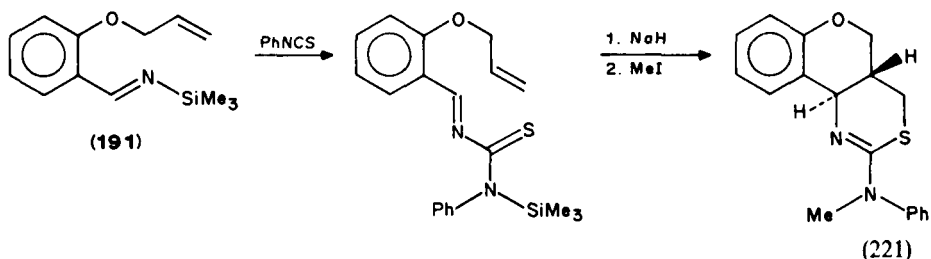


SCHEME 71

C=N and C=S bonds, subsequent [4 + 2] addition of electron-poor dienophiles gives the phenyl imine derivative **190** through exclusive addition to the thione (Scheme 72)<sup>373</sup>. The imine **191** adds RNCS to give the 1-thia-3-azabutadiene, which itself undergoes [4 + 2] Diels-Alder cycloaddition to give, for example, functionalized indolizines in one step from silyl imines (equation 221)<sup>374</sup>.



SCHEME 72

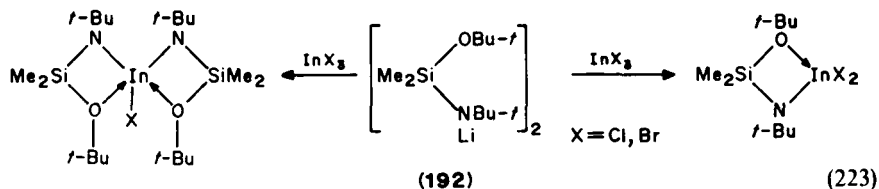
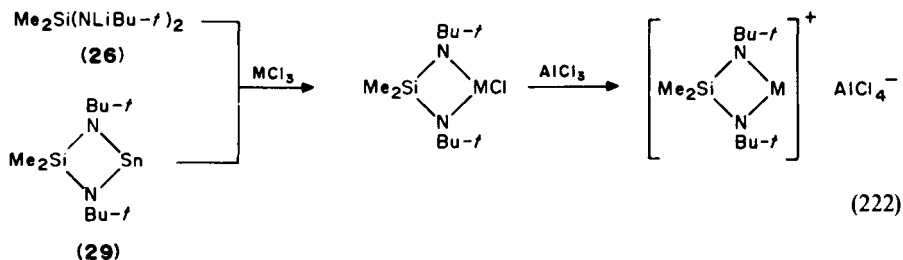


### \*III. BISAMINOSILANES

A more extensive range of compounds derived from  $\text{Me}_2\text{Si}(\text{NLiBu-}t)_2$  (26) has now been made and includes the phosphorus group metalloids, as well as those included in Section IIIA of the main chapter. In addition, germanium(II) and lead(II) derivatives have been prepared in addition to the tin(II) derivatives.

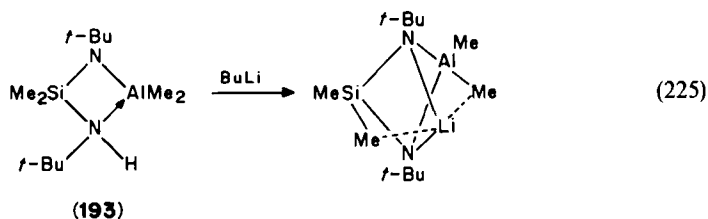
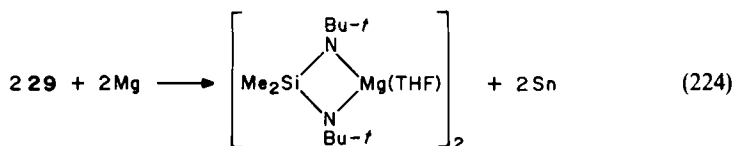
#### \*A. Boron Group and Phosphorus Derivatives

Condensing 26 with one mole of  $\text{MCl}_3$  ( $M = \text{As, Sb, Bi}$ ) gives the four-membered heterocycle. That with arsenic is a very weakly associated dimer, but the antimony and bismuth derivatives are one-dimensional chloride-bridged polymers. They can also be prepared from the tin(II) heterocycle 29 and react with  $\text{AlCl}_3$  to give the formally two-valent cationic derivatives of the phosphorus group elements.  $\text{PCl}_3$  reduced by 29 (equation 222)<sup>375</sup>. The dimeric *t*-butoxy derivative 192 also couples with halides of gallium and indium, chelation being more pronounced with gallium (equation 223)<sup>376</sup>.

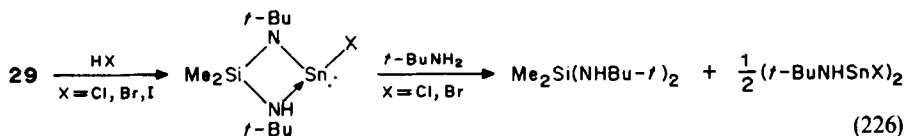


#### \*B. The Tin(II) Derivative and Its Reactions

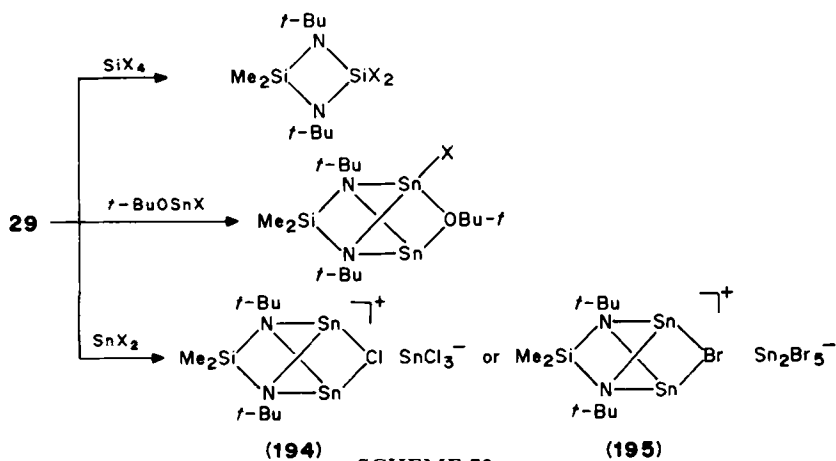
Reacting 29 with magnesium in THF gives the dimeric THF complex through metal exchange (equation 224), while the aluminium derivative 193 can be readily metallated at



the N—H group by lithium, sodium and magnesium (equation 225)<sup>377</sup>. **29** readily adds HX (X = Cl, Br, I) to the Sn—N bond, the adduct reacting with excess *t*-BuNH<sub>2</sub> through detachment of the Sn(II) residue as (*t*-BuNHSnX)<sub>2</sub> (equation 226)<sup>378</sup>. **29** also adds *t*-

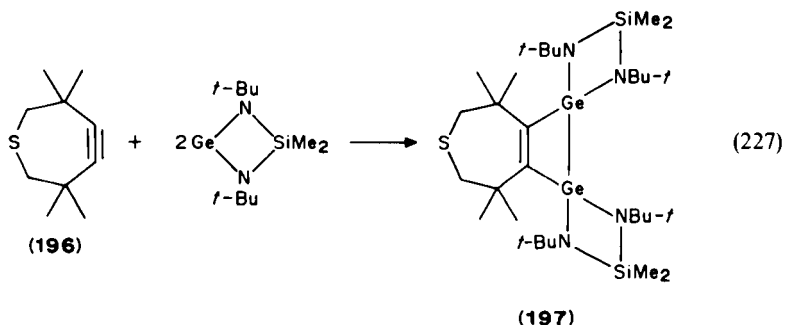


BuOSnCl, gives a 1:2 adduct with SnCl<sub>2</sub> (**194**), a 1:3 adduct with SnBr<sub>2</sub> (**195**), is substituted by SiX<sub>4</sub> (X = Cl, Br, I) to give the cyclodisilazane, and reduces 1,2-dihaloalkanes to the alkene (Scheme 73)<sup>379</sup>. While the germanium analogue of **29** is coupled by the



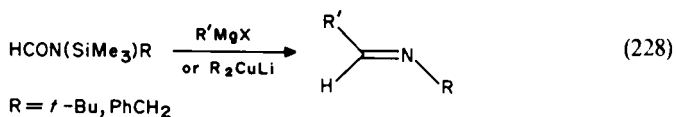
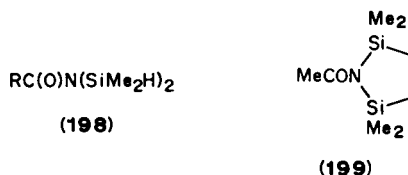
thiacycloalkyne **196** to give the dimetallacyclobutene **197** (equation 227)<sup>380</sup>, the *N*-*i*-Pr derivative of **29** and the lead(II) derivatives are dimeric and show dynamic behaviour that can be interpreted through maintaining the identity of the four-membered rings<sup>381</sup>.



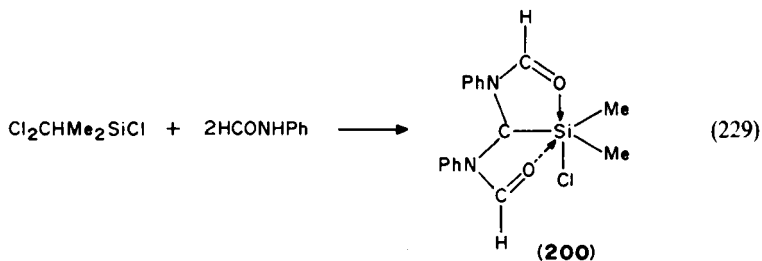


#### \*IV. SILYLAMIDES

While bis(trimethylsilyl)amides exist in the imidate form (except for formamide), bis(dimethylsilyl)amides exist solely in the amide form **198** and **199**<sup>382</sup>. *N*-Silylated formamides will add the Grignard reagent or cuprates, to give imines (equation 228)<sup>383</sup>.

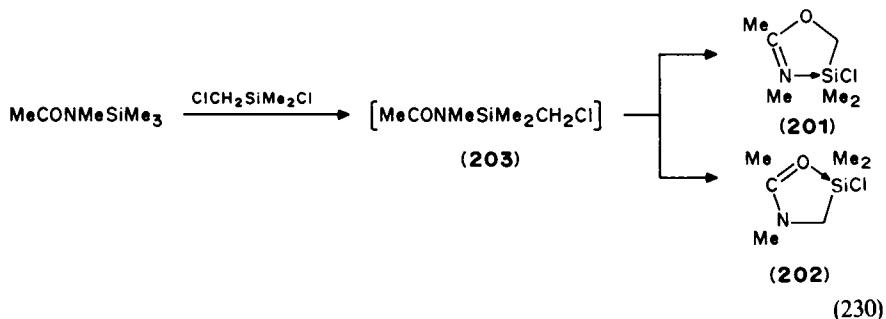


Both triorganosilyl formamides and dimethylsilyl acetanilides exist as an amide-imidate tautomers, while the attempted preparation of dichloromethyldimethylsilyl formamide led to substitution at carbon. The product **200** showed a distorted trigonal bipyramidal structure with non-equivalent coordination from the amide carbonyl groups (equation 229)<sup>384</sup>.

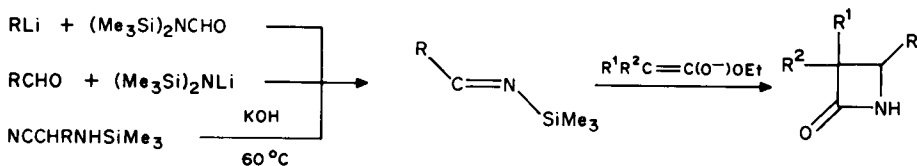


The complex reaction of  $\text{ClCH}_2\text{Me}_2\text{SiCl}$  with *N*-trimethylsilyl amides and lactams has been monitored by NMR spectroscopy and starts with *trans*-silylation. This is followed by

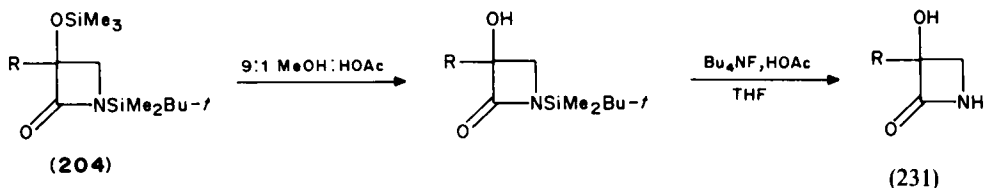
silyl methylation of the unstable amide or lactam to give the kinetically favoured product **201** or thermodynamically favoured **202**, depending on the conditions chosen, with **203** detected for the first time (equation 230)<sup>385</sup>.



Bis(trimethylsilyl)formamide reacts with RLi to give *N*-silyl aldimines, which also result from RCHO and (Me<sub>3</sub>Si)<sub>2</sub>NLi, or by pyrolysing silylated α-aminonitriles in the presence of KOH. With the lithium enolates of esters, the β-lactam results (Scheme 74)<sup>386</sup>. The *N*-silyl-3-siloxyazetidin-2-one (**204**) has been used as a precursor for various C-substituted β-lactams (equation 231)<sup>387</sup>.



SCHEME 74



#### \*V. PROTECTION OF —OH, >NH AND —SH BONDS

(Me<sub>3</sub>Si)<sub>2</sub>NH with a trace of Me<sub>3</sub>SiCl is used for the protection of —OH, with primary preferential to secondary preferential to tertiary. With secondary and tertiary alcohols, equimolar quantities of Me<sub>3</sub>SiCl are used. The mixture also preferentially substitutes primary alcohols to secondary amines, and protects organic acids<sup>388</sup>.

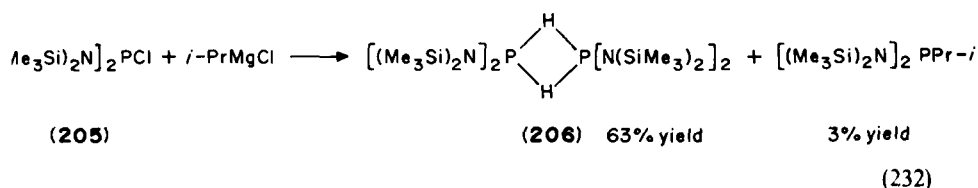
#### \*VI. HEXAMETHYLDISILAZANE [BIS(TRIMETHYLSILYL)AMINE]

The structures of a further range of disilazanes have been determined, with those more hindered at silicon showing wider SiNSi bond angles, in contrast to those more hindered at nitrogen (Table 8; see also Table 2, Chapter 11). The silyl amines (H<sub>3</sub>Si)<sub>2</sub>NR are coplanar at nitrogen.

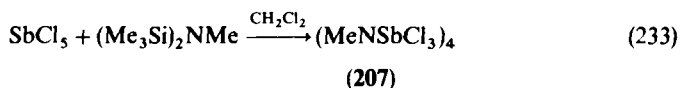
TABLE 8. Structural parameters for disilazanes

	Technique	Si—N (pm)	SiNSi	Reference
(H <sub>3</sub> Si) <sub>2</sub> NMe	ED	172.3	125.2	389
(H <sub>3</sub> Si) <sub>2</sub> NEt	ED	172.6	123	389
(H <sub>3</sub> Si) <sub>2</sub> NPr- <i>i</i>	ED	172.7	121.6	390
(H <sub>3</sub> Si) <sub>2</sub> NBu- <i>t</i>	ED	173.5	118.4	390
(MePh <sub>2</sub> Si) <sub>2</sub> NH	X-ray	172.0	131.6	391
(Ph <sub>3</sub> Si) <sub>2</sub> NH	X-ray	172.2	136.1	391
( <i>t</i> -Bu <sub>3</sub> Si) <sub>2</sub> NH	X-ray	176	167	392

The silylaminophosphine **206** results as the main product (63%) of the alkylation of the chlorophosphine **205** using *i*-PrMgCl, the alkylated phosphine resulting in only 3% yield. It is dimeric, with a remarkable hydrogen bridge (equation 232)<sup>393</sup>. The arsenic analogue is a monomer.



(Me<sub>3</sub>Si)<sub>2</sub>NMe condenses under very dilute conditions with SbCl<sub>5</sub> to give the cubane-like derivative **207** (equation 233)<sup>394</sup>. MoO<sub>3</sub> reacts with (Me<sub>3</sub>Si)<sub>2</sub>NH to give the complexes Mo<sub>2</sub>N<sub>2</sub>(OSiMe<sub>3</sub>)<sub>6</sub>(NH<sub>3</sub>)<sub>2</sub> and [Mo<sub>4</sub>N<sub>4</sub>O<sub>2</sub>(OSiMe<sub>3</sub>)<sub>8</sub>py<sub>4</sub>]·2py. The former contains terminal nitride and bridging siloxy ligands and the latter an eight-membered Mo<sub>4</sub>N<sub>4</sub> ring bridged by the oxide ligands<sup>395</sup>.



## \*VII. METAL DERIVATIVES OF HEXAMETHYLDISILAZANE

### \*A. Alkali Metals

#### \*1. Structures

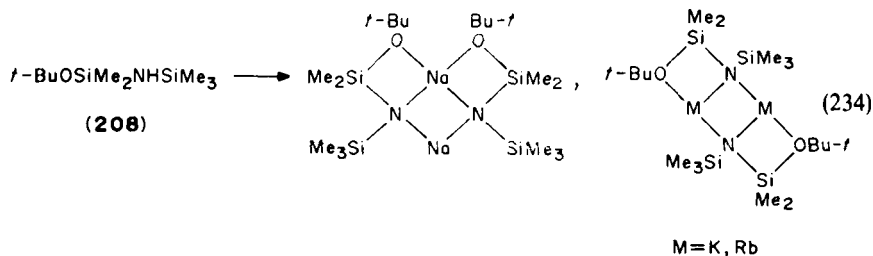
Further studies on solvated derivatives of lithium disilylamides tend to show a widening of the SiNSi angle as the ion pair lithium—nitrogen interaction distance increases (Table 9; see also Table 3, Chapter 11).

TABLE 9. Structural parameters for alkali metal derivatives of disilazanes

	Si—N (pm)	SiNSi	Li—N (pm)	Reference
(Ph <sub>2</sub> MeSi) <sub>2</sub> NLi(THF) <sub>2</sub>	167.1	132.3°	194.9	391
(Ph <sub>3</sub> Si) <sub>2</sub> NLi(THF) <sub>2</sub>	166.6	140.5°	199.8	391
(Ph <sub>2</sub> MeSi) <sub>2</sub> N <sup>-</sup> Li(12-crown-4) <sup>+</sup>	166.7	133.9°	206.4	391

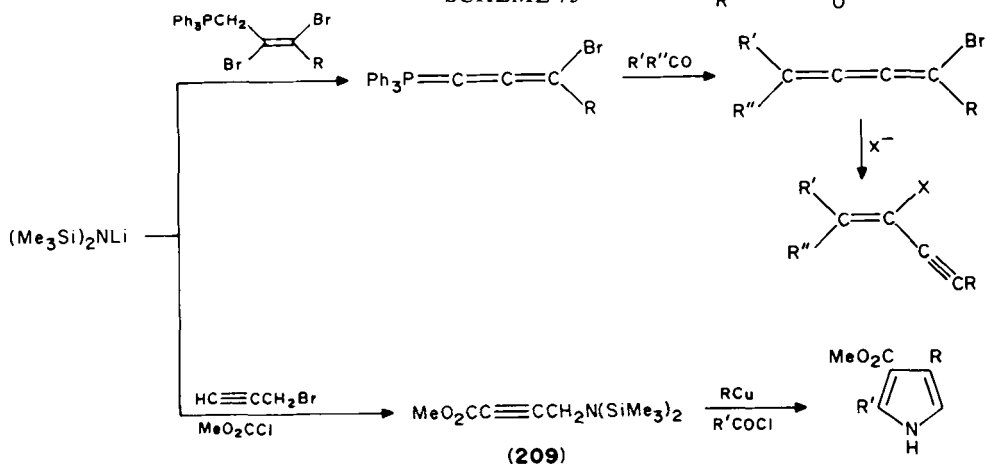
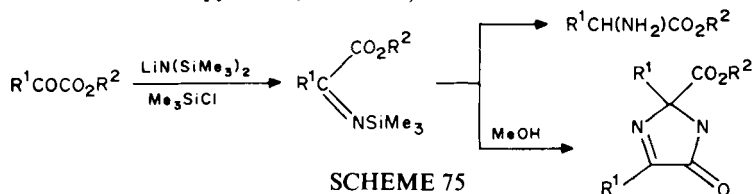
The unsolvated  $(\text{Me}_3\text{Si})_2\text{NK}$  crystallizes from hexane as a dimeric ion pair with the  $\text{K}_2\text{N}_2$  bridge almost square and containing two-coordinate potassium ions. The silicon–nitrogen bonds (168.2 pm) are longer and the  $\text{SiNSi}$  angle smaller ( $129^\circ$ ) than in the dimeric toluene solvate (167.4 pm and  $133.8^\circ$ ) or in the bis(dioxan) adduct (164 pm and  $136^\circ$ ). The reactivities of this and other silylamides vary with solvent<sup>396</sup>.

The alkali metal derivatives of the *t*-butoxy disilazane **208** are all dimeric in solution and in the solid, the sodium derivative showing 4- and 2-coordination, whereas the potassium and rubidium derivatives are 3-coordinate for each metal ion (equation 234)<sup>397</sup>.



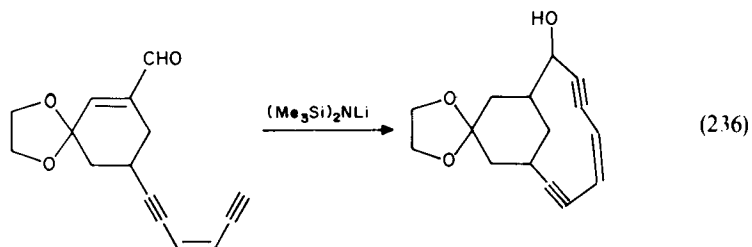
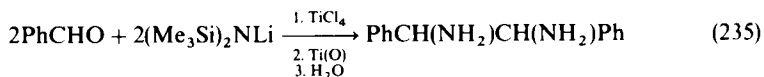
## \*2. Use in organic synthesis

$(\text{Me}_3\text{Si})_2\text{NLi}$  is used to convert  $\alpha$ -keto esters into  $\alpha$ -(*N*-trimethylsilyl)imino esters for use in the synthesis of  $\alpha$ -amino esters and 2-alkoxycarbonylimidazol-4(2*H*)-ones (Scheme 75)<sup>398</sup>. Haloenynes result from the novel regioselective halide displacement of allylic phosphonium salts and the requisite ketone in the presence of  $(\text{Me}_3\text{Si})_2\text{NLi}$ , while the aminomethyl propiolate **209**, which results from  $\text{HC}\equiv\text{CCH}_2\text{Br}$  and  $(\text{Me}_3\text{Si})_2\text{NLi}$ , can be cyclized to the functional pyrroles (Scheme 76)<sup>399</sup>.

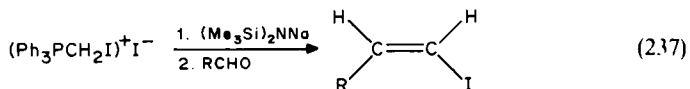


SCHEME 76

PhCHO couples with  $(\text{Me}_3\text{Si})_2\text{NLi}$  to give the 1,2-diphenylethylene diamine<sup>400</sup>, while the enediyne aldehyde undergoes intramolecular acetylide cyclization to the epimeric carbinol (equations 235 and 236)<sup>401</sup>.  $(\text{Me}_3\text{Si})_2\text{NM}$  ( $\text{M} = \text{Li}, \text{Na}$ ) generates enolates

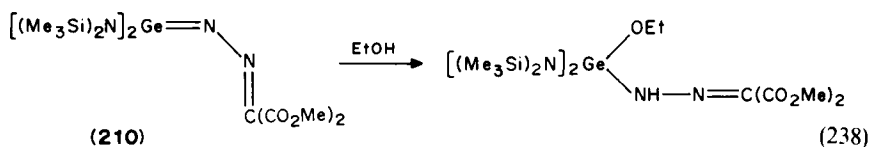


from chiral glycinates which alkylate with a high degree of diastereoselectivity, while  $(\text{Me}_3\text{Si})_2\text{NNa}$  deprotonates ketones regio- and stereoselectively, and couples  $\text{ICH}_2\text{PPh}_3^+\text{I}^-$  with aldehydes to give (*Z*)-1-iodo-1-alkenes (equation 237)<sup>402</sup>.



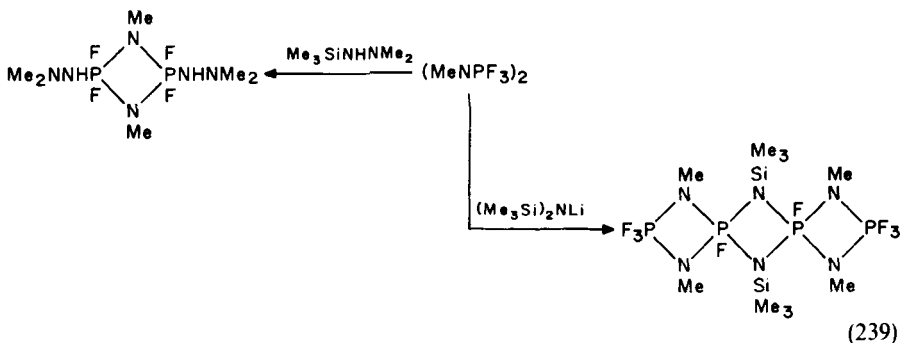
#### \*D. Divalent Germanium, Tin and Lead Derivatives

The  $(\text{Me}_3\text{Si})_2\text{N}$  group stabilizes the germaine **210**, which results from  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}$ : and  $(\text{MeO}_2\text{C})_2\text{CN}_2$ , and exists as cisoid and transoid forms in solution, with calculations supporting greater stability of the former for  $[(\text{H}_3\text{Si})_2]_2\text{Ge}=\text{NN}=\text{C}(\text{CO}_2\text{Me})_2$ . 1,2-Addition of  $\text{HX}$  occurs across the  $\text{Ge}=\text{N}$  double bond (equation 238)<sup>403</sup>.



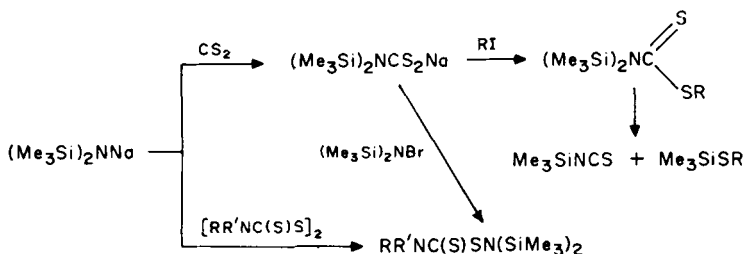
#### \*E. Phosphorus and Sulphur Group Derivatives

$(\text{Me}_3\text{Si})_2\text{NLi}$  couples  $(\text{MeNPF}_3)_2$  to give the dispiro derivative while silyl hydrazines substitute at phosphorus (equation 239)<sup>404</sup>.  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{S}$ , mp  $66^\circ\text{C}$ , results from  $(\text{Me}_3\text{Si})_2\text{NLi}$  and  $\text{SCl}_2$ , and shows some variation within the  $\text{Si}-\text{N}$  bond lengths (171.6 to 176.5 pm) and  $\text{SiNSi}$  bond angles ( $114^\circ$  to  $124^\circ$ )<sup>405</sup>. The first aryltellurium(II) amides to be characterized result from the iodide and  $(\text{Me}_3\text{Si})_2\text{NLi}$ , and show a  $^{125}\text{Te}$  NMR signal at about 1200 Hz. The 2-naphthyl derivative melts at  $63-65^\circ\text{C}$  and is stable in argon at room temperature, unlike the phenyl derivative, an oil (equation 240)<sup>406</sup>.



Ar = Ph, 2-naphthyl

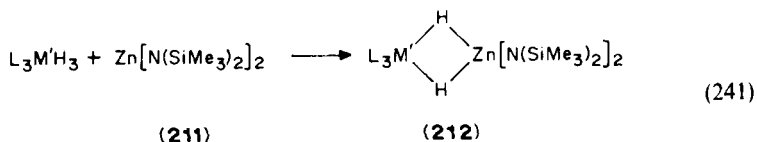
$(\text{Me}_3\text{Si})_2\text{NM}$  ( $\text{M} = \text{Na}, \text{K}$ ) adds to  $\text{CS}_2$  giving the dithiocarbamate salt, which can be hydrolysed to the acid, esterified with  $\text{RI}$ , the esters decomposing to  $\text{Me}_3\text{SiNCS}$  and thiosilane, while the *S*-bis(trimethylsilyl)amino ester of dithiocarbamic acid results from the *S*—*S* cleavage of the disulphide, and by coupling the dithiocarbamate with the bromodisilazane (Scheme 77). Structural determinations show the  $\text{C}_3\text{NC}(\text{S})\text{SN}$  skeleton to be planar, and for  $\text{R} = \text{R}' = \text{Me}$ , the rotational barrier at  $-2^\circ\text{C}$  about the  $\text{C}—\text{N}$  bond is  $58 \text{ kJ mol}^{-1}$ <sup>407</sup>.



SCHEME 77

### \*F. Zinc, Cadmium and Mercury Derivatives

Calorimetric measurements on the heats of hydrolysis of the amides  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}$  ( $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$ ) at  $25^\circ\text{C}$  in sulphuric acid give bond enthalpies for the  $\text{M}—\text{N}$  bonds of 209 (Zn), 144 (Cd) and  $108 \text{ kJ mol}^{-1}$  ( $\text{Hg}$ )<sup>408</sup>. The zinc amide **211** reacts with the hydrides  $\text{L}_3\text{M}'\text{H}_3$  [ $\text{M}' = \text{Rh}, \text{Ir}$ ;  $\text{L}_3 = (\text{PhMe}_2\text{P})_3$  or  $\text{MeC}(\text{CH}_2\text{PR}_2)_3$ ] to give the hydride bridged complex **212**, which shows non-rigidity in solution (equation 241)<sup>409</sup>.



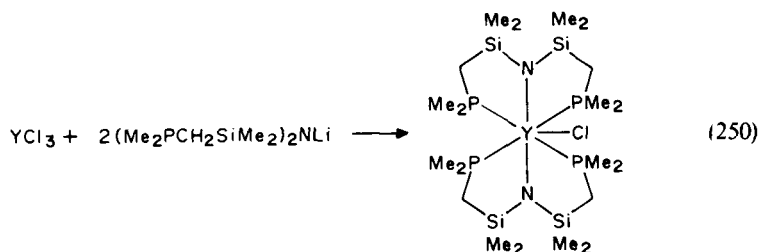




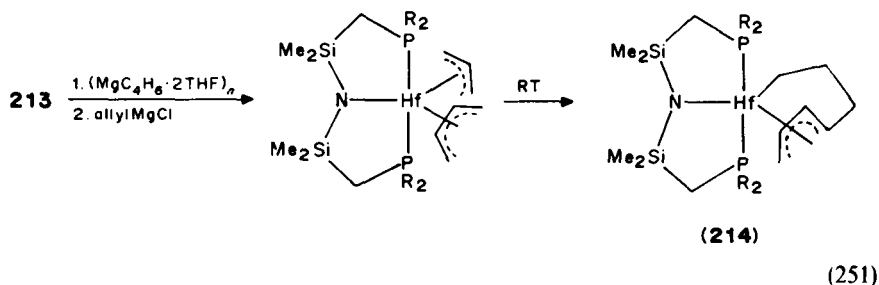


**\*K. Complexes of Bis(phosphinomethylsilyl)amides**

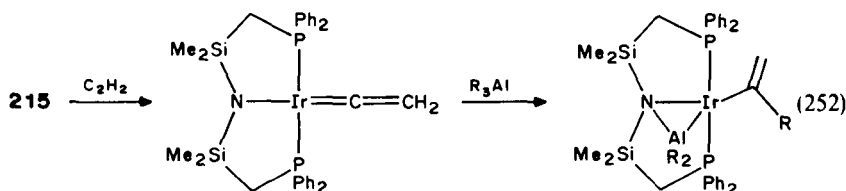
The trivalent yttrium complex  $\text{ClY}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2]_2$ , the first phosphine complex of yttrium, results from  $\text{YCl}_3$  and two moles of the bissilylamide. It is 7-coordinate and, at 25 °C, the  $^{31}\text{P}$  NMR spectrum shows a doublet due to  $^{89}\text{Y}$  splitting. Cooling causes splitting, suggesting fluxionality in solution, and a structure with the four phosphino groups and chlorine atom in the equatorial plane and the amide nitrogen atoms apical. This complex can be phenylated and benzylated at chlorine (equation 250)<sup>422</sup>.



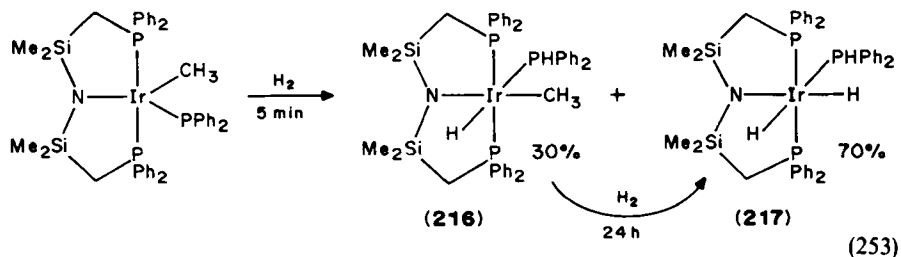
The meridional hafnium complex  $(\text{R}_2\text{PCH}_2\text{Me}_2\text{Si})_2\text{NHfCl}_3$  (**213**) gives a butadiene complex with  $(\text{MgC}_4\text{H}_6 \cdot 2\text{THF})_n$  in THF and the third chlorine atom can be further replaced by  $\pi$ -allyl using allylMgCl. These two organic ligands couple at room temperature to give the  $\eta^5$ - $\text{C}_7\text{H}_{11}$  complex **214** (equation 251)<sup>423</sup>.



The square-planar  $\eta^2$ -cyclooctene complex  $\text{Ir}(\eta^2\text{-C}_8\text{H}_{14})[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  (**215**) with excess buta-1,3-diene gives the 5-coordinate diene complex, which has the amide ligand bonding quasi-facial while the butadiene ligand shows no fluxional behaviour<sup>424</sup>. With ethyne, the vinylidene complex results, which adds  $\text{R}_3\text{Al}$ , probably through oxidative addition, the  $\text{R}_2\text{Al}$  group then interacting with nitrogen (equation 252)<sup>425</sup>.

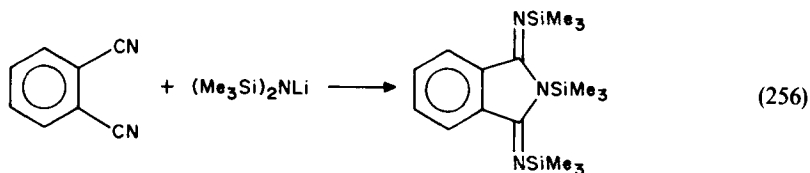
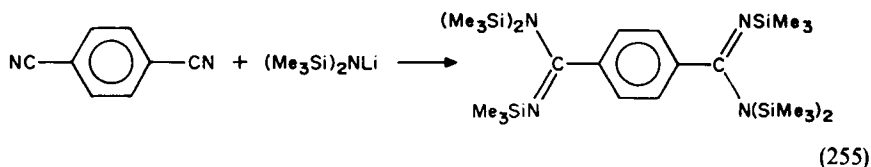
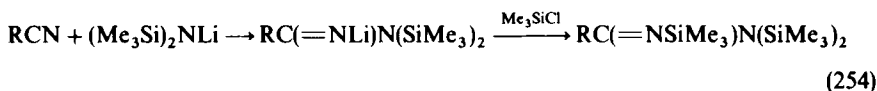


The 5-coordinate methyl phosphido complex  $\text{IrMe}(\text{PPh}_2)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  reacts with  $\text{H}_2$  to give the 6-coordinate mono- and dihydrides **216** and **217** in the ratio 3:7 (equation 253)<sup>426</sup>. Using  $\text{D}_2$  and the  $\text{CD}_3$  substituted starting material gives products suggesting that the phosphido group abstracts a proton from the methyl group. This suggests an  $\text{Ir}=\text{CH}_2$  intermediate.



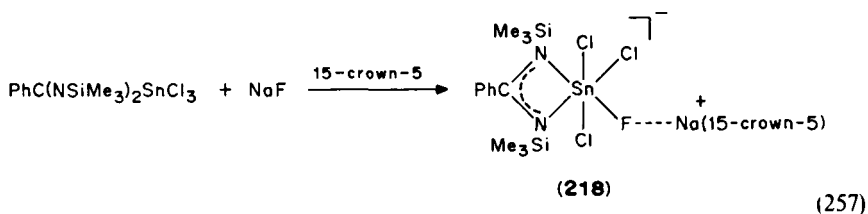
### L. Derivatives of Amidines

*N,N,N'*-Tris(trimethylsilyl)amidines  $\text{RC}(=\text{NSiMe}_3)\text{N}(\text{SiMe}_3)_2$  ( $\text{R} = p$ -substituted phenyl and  $\text{CF}_3$ ) result from the nitrile and  $(\text{Me}_3\text{Si})_2\text{NLi}\cdot\text{OEt}_2$  after silylation (equation 254)<sup>427</sup>. 1,4-Dicyanobenzene gives the persilyl 1,4-diamidine in which the imino-silicon bonds are shorter (172.3 pm) than the amino-silicon ones (176.6 and 177.6 pm) (equation 255). With 1,2-dicyanobenzene, however, the bis(imino)-1,3-dihydroisindole results with a greater difference in the two types of  $\text{Si}-\text{N}$  bond length ( $\text{Si}-\text{N} = 171.4$  and 170.9 pm;  $\text{Si}-\text{N} < 180.2$  pm) (equation 256)<sup>428</sup>.

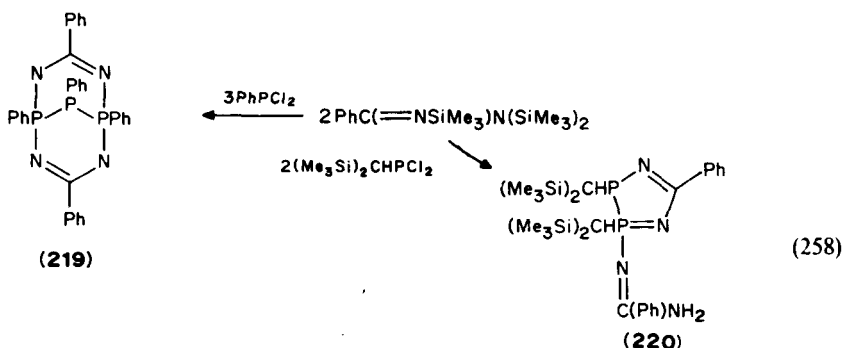


The phenylamidine forms a 1:1 adduct with  $\text{BF}_3$  without  $\text{B}-\text{F}$  cleavage, but is monodesilylated by a wide range of main group and transition metal halides to give monomeric and associated products depending on the steric and coordination number demands of the metal(loid) with which the amidine chelates. These include halides of the boron and silicon groups, and a range of transition metals<sup>429</sup>.

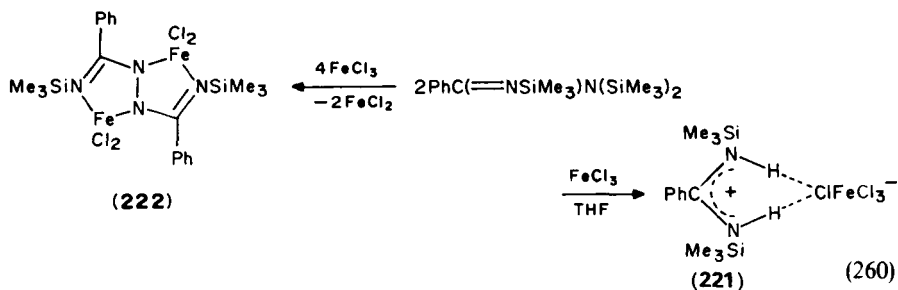
$\text{PhC}(\text{NSiMe}_3)_2\text{SnCl}_3$  reacts with  $\text{NaF}$  in 15-crown-5 to give the 6-coordinate ion pair **218** (equation 257)<sup>430</sup>. With  $\text{PhPCl}_2$  and  $(\text{Me}_3\text{Si})_2\text{CHPCl}_2$ , complete desilylation of the



amidine occurs, together with disproportionation, to give the cyclic derivatives **219** and **220** containing phosphorus in both of its common oxidation states (equation 258)<sup>431</sup>.  $\text{SbCl}_3$  and  $\text{TeCl}_4$  give the expected substitution products through monodesilylation<sup>432</sup>, but  $\text{SCl}_2$  forms the dithiadiazolium salt through complete desilylation (equation 259)<sup>433</sup>.



While Ti, Zr<sup>434</sup>, Ta<sup>435</sup>, Cu<sup>436</sup>, Au<sup>437</sup> and U<sup>438</sup> give monodesilylated products analogous to those of the main group elements, Mo(VI) chlorides give C—N cleavage<sup>439</sup>, and  $\text{FeCl}_3$  forms both salt **221** and the centrosymmetric hydrazine derivative **222** (equation 260)<sup>440</sup>.



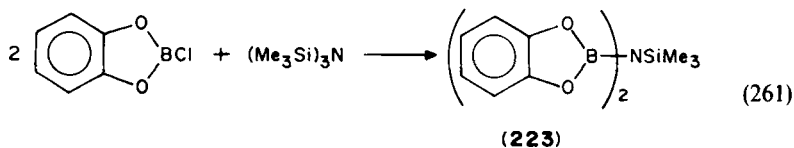
#### \*VIII. DERIVATIVES OF POLYSILAZANES AND POLYAMINOSILANES

Coammonolysis of  $\text{RMe}_2\text{SiCl}$  ( $\text{R} = \text{Me, Et, n-Bu, Ph, PhCH}_2$ ) and  $\text{Me}_{3-n}\text{Cl}_n\text{SiH}$  gives a range of polysilazanes  $\text{Me}_{3-n}(\text{Me}_3\text{SiNH})_n\text{SiH}$  ( $n = 1 - 3$ ) and  $(\text{RMe}_2\text{SiNH})_3\text{NH}$ , spectral studies showing  $\nu\text{Si-H}$  to increase with  $\sigma^*$  of R, and the methyl polysilazanes to have

similar basicity to  $(\text{Me}_3\text{Si})_2\text{NH}^{441}$ . A spectral study of the lithiated derivatives of the n-butylamino silanes  $(\text{Me}_{4-x})\text{Si}(\text{NHBU-n})_x$  and their amine complexes enables a provisional correlation of  $^7\text{Li}$  NMR shifts with solvent, and hence an opportunity to possibly predict the behaviour of  $\text{Si}(\text{NLiBu-n})_4^{442}$ .

### \*IX. TRISILYLAMINES

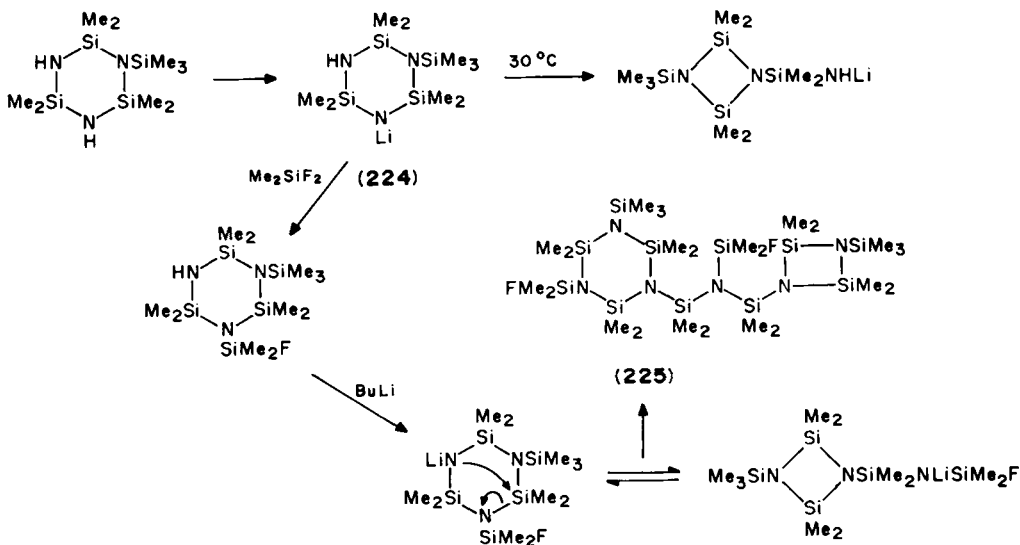
An electron diffraction study of the structure of  $(\text{Me}_3\text{Si})_3\text{N}$  shows the  $\text{Si}_3\text{N}$  unit planar, with  $\text{Si}-\text{N}$  bonds of 175.5 pm, some 2.6 pm longer than those of  $(\text{MeH}_2\text{Si})_3\text{N}$ . The twisting of the  $\text{Me}_3\text{Si}$  groups by  $5.2^\circ$  reduces the symmetry from  $C_{3h}$  to  $C_3^{443}$ .  $(\text{Me}_3\text{Si})_3\text{N}$  can be mono- and disubstituted by a series of monochloroboranes, a structure determination on **223** showing trigonal planar geometry at nitrogen and a particularly long  $\text{Si}-\text{N}$  bond of 178.3 pm (equation 261)<sup>444</sup>.



### \*X. CYCLOSILAZANES

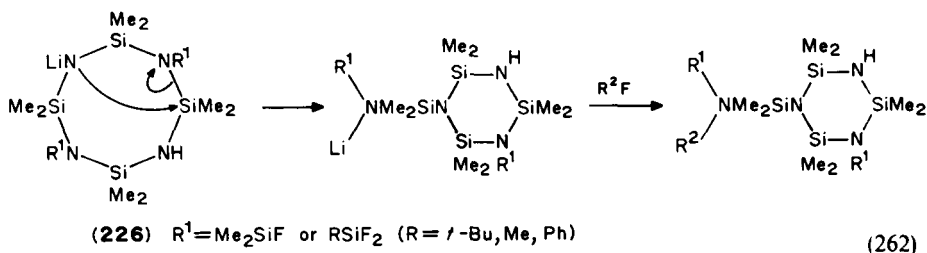
#### \*A. Cyclotrisilazanes and Cyclotetrasilazanes

The lithiated cyclotrisilazane **224** can be further silylated with  $\text{Me}_2\text{SiF}_2$  but ring-contracts above  $30^\circ\text{C}$ . Further lithiation leads to an equilibrium with the ring-contracted product which then condenses to the coupled product **225** (Scheme 78)<sup>445</sup>. The

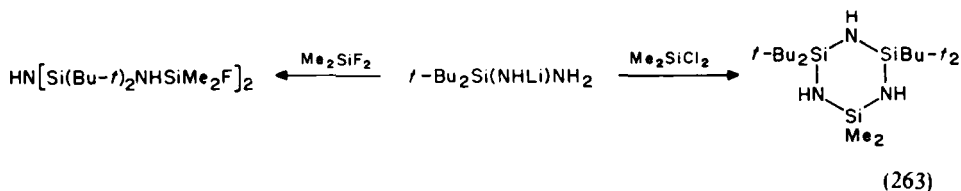
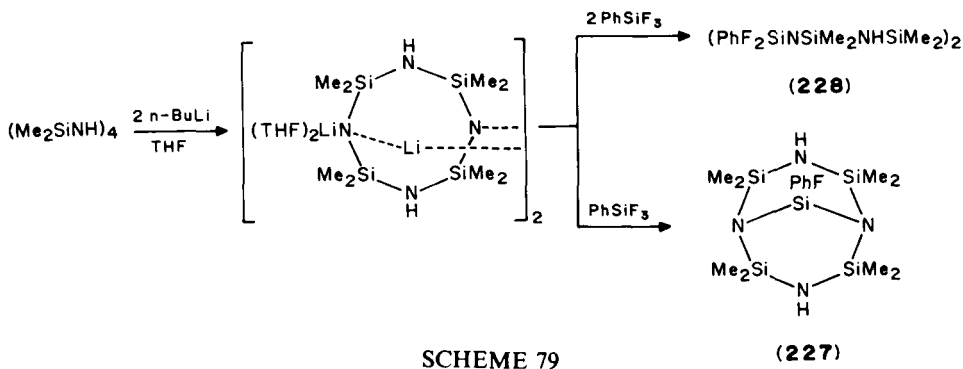


SCHEME 78

cyclotetrasilazane **226** undergoes a similar ring contraction on lithiation (equation 262)<sup>446</sup>.

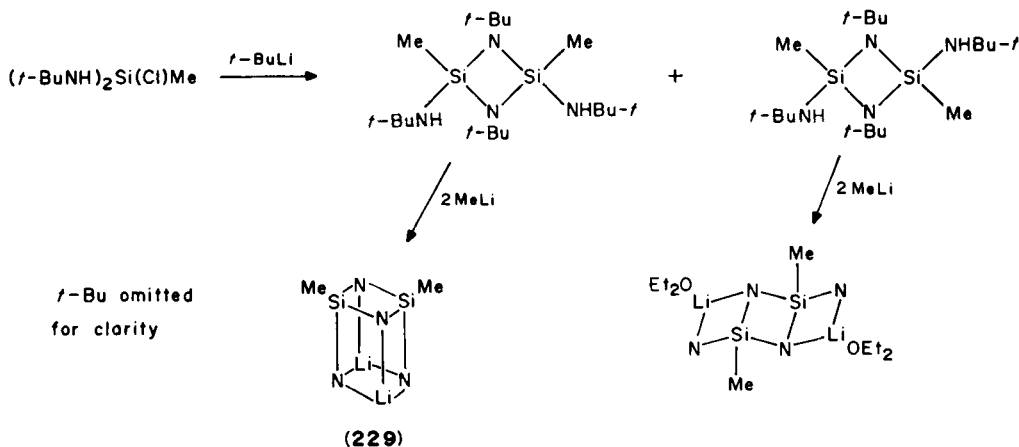
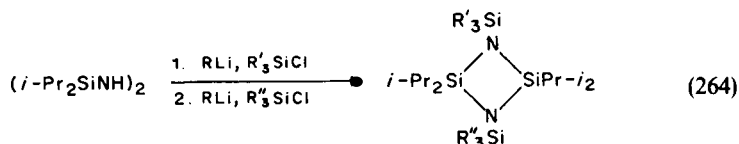


The dilithio derivative of  $(\text{Me}_2\text{SiNH})_4$  is dimeric through one lithium ion bridging both nitrogen atoms of the monomer, then bridging through a  $\text{Li}_2\text{N}_2$  bridge. With one mole of  $\text{PhSiF}_3$ , the ring is bridged, giving 1,3,5,7-tetraaza-2,4,6,8,9-pentasilabicyclo-[3.3.1]nonane **227**, but with two moles of  $\text{PhSiF}_3$ , the expected **228** results (Scheme 79)<sup>447</sup>. Coupling  $t\text{-Bu}_2\text{Si}(\text{NHLi})\text{NH}_2$  with  $\text{Me}_2\text{SiCl}_2$  or  $\text{Me}_2\text{SiF}_2$  gave respectively the cyclotrisilazanes and linear tetrasilazanes (equation 263)<sup>448</sup>.



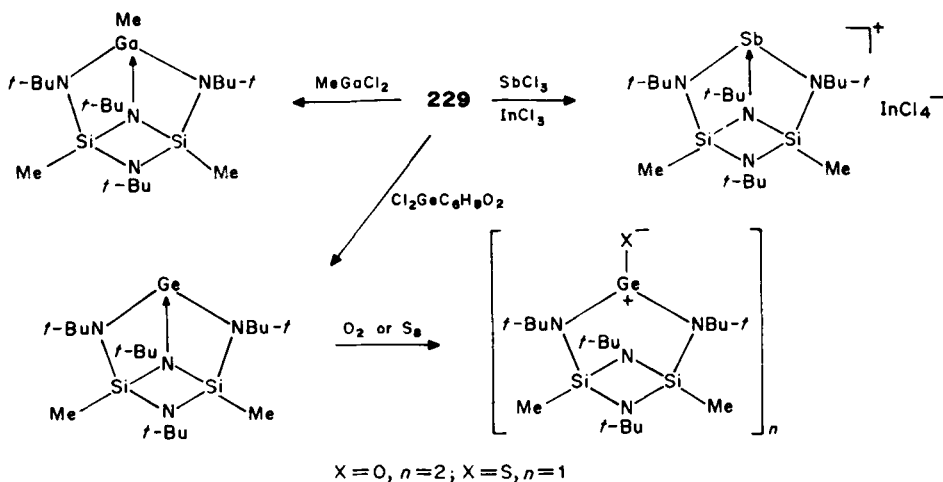
### \*B. Cyclodisilazanes

Stepwise lithiation of  $(i\text{-Pr}_2\text{SiNH})_2$  leads to mono- and disilyl-substituted cyclodisilazanes (equation 264)<sup>448</sup>. Condensing  $(t\text{-BuNH})_2\text{Si}(\text{Cl})\text{Me}$  using  $t\text{-BuLi}$  gives the cyclodisilazane as both *cis* and *trans* isomers, subsequent lithiation leading to a cubane-like derivative of the *cis*-cyclodisilazane, with  $\text{Li}-\text{N}$  217.8 to 206.0 pm and  $\text{Si}-\text{N}$  168.3 to 177.3 pm, and a ladderane complex of the *trans* isomer. The *cis* derivative **229** reacts with  $\text{TlCl}$  giving the  $\text{Tl}$  derivative with a structure similar to that of its



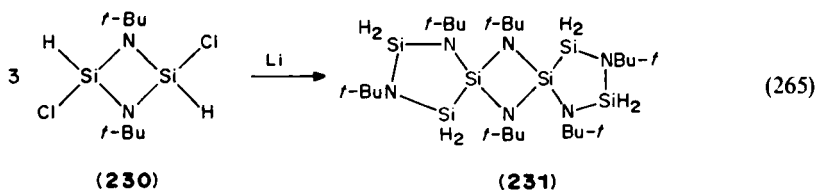
SCHEME 80

precursor, with Tl—N bonds in the range 252–273 pm (Scheme 80)<sup>449</sup>. The *cis* isomer can also be readily metallated at the amino group to give a range of cubane-like fragments with a metal ion substituting at each *cis*-NH group. The MeGa and Sb fragments will bridge both sites as does Ge(II). This reacts with oxygen to give the cyclic oxide dimer and with sulphur to give the monomer with a Ge—S double bond (Scheme 81)<sup>450</sup>.

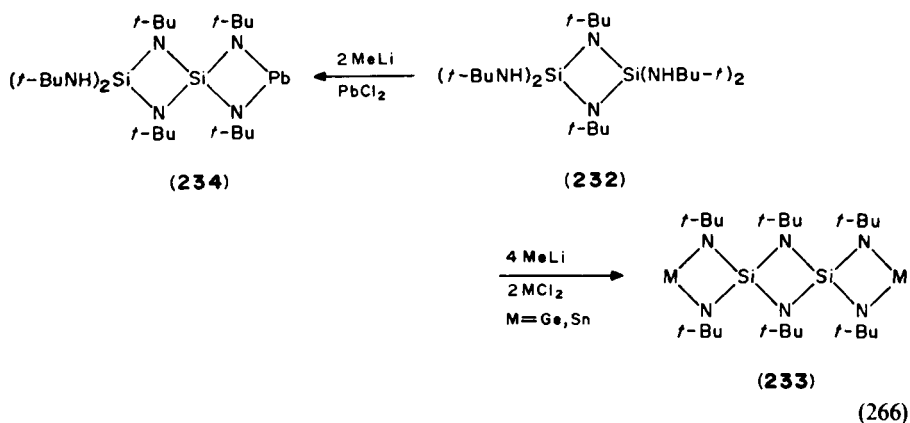


SCHEME 81

The amino(chloro)silanes  $\text{RSiCl}_2\text{NHBu-}t$  ( $\text{R} = \text{Cl, H}$ ) result from the chlorosilane and amide and  $\text{HSiCl}_2\text{N(Bu-}t\text{)SiMe}_3$  similarly.  $\text{HSiCl}_3$  and  $\text{Me}_3\text{SiN(Li)Bu-}t$ , however, condense to give the cyclodisilazane  $(\text{HClSiNBu-}t)_2$  (**230**). **230** condenses with lithium to give the remarkable dispirotricyclic derivative 1,3,6,8,10,12-hexaaza-2,4,5,7,9,11-hexasiladispiro[4.1.4.1]dodecane **231** (equation 265)<sup>451</sup>. The amino-substituted cyclodisila-

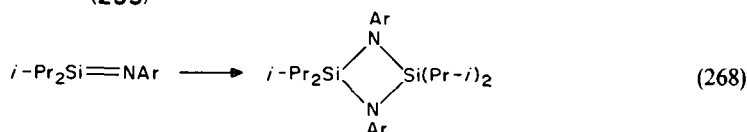
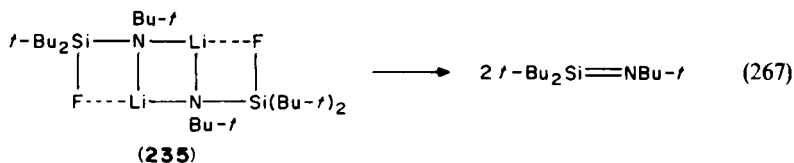


zane **232**, on full lithiation, condenses with  $\text{GeCl}_2$  and  $\text{SnCl}_2$  to give **233**, and on dilithiation at one end only to give the lead derivative **234** (equation 266)<sup>452</sup>.

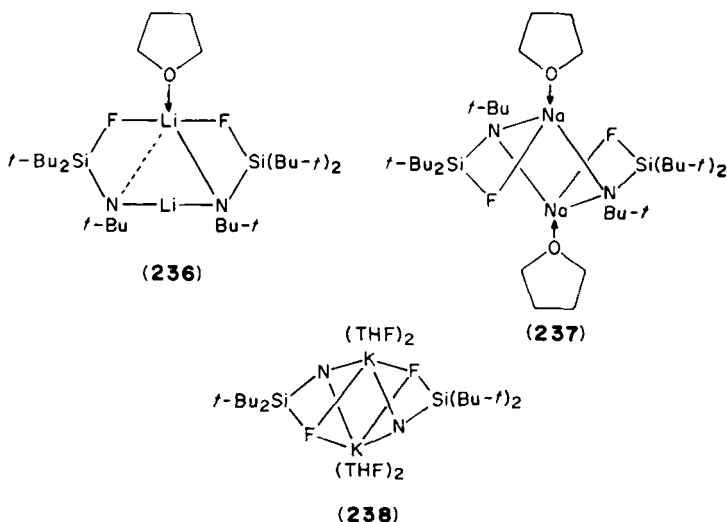


### \*XII. FLUOROSILYLAMINES

Unsolvated  $t\text{-Bu}_2\text{FSiN(Li)Bu-}t$  (**235**) is dimeric with a tricyclic ladderane-type structure (equation 267). Heating eliminates  $\text{LiF}$  to give the silimine, which dimerises if the substituents are  $i\text{-Pr}$  and  $\text{Ar}$  (equation 268)<sup>453</sup>.



While the THF derivatives of the alkali metal derivatives of this fluorosilylamine are also dimeric, all have structures which differ through the influence of coordination number at the alkali metal ion. The lithium derivative **236** possesses one molecule of THF per dimer and is fluxional in solution with the nitrogen atoms equivalent. A crystal structure shows Li with 4- and 2-coordination possessing Si—N bond lengths of 162.7 and 168.1 pm<sup>454</sup>.

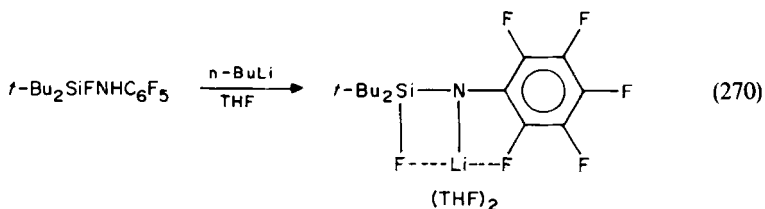


The sodium derivative **237** shows both sodium ions 4-coordinate and equivalent in the solid, with one molecule of THF coordinated to each metal ion, and Si—N bonds of 165.5 pm. The potassium derivative **238** is 6-coordinate at potassium with two molecules of THF per metal ion and Si—N bonds of 166.7 pm<sup>455</sup>.

The lithium derivative of  $t\text{-Bu}_2\text{Si}(\text{F})\text{NH}_2$  gives the mixed silylstannyl amine with  $\text{Me}_3\text{SnCl}$ . At 100 °C, it disproportionates to give the silyl bisstannyl amine, which is thermally stable. A structure determination shows planarity at nitrogen and NMR spectroscopy shows restricted rotation about the Si—N bond (equation 269)<sup>456</sup>.

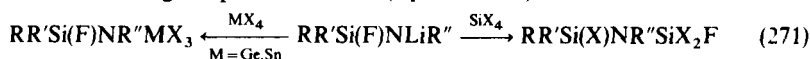


The fluorosilyl pentafluoroanilines  $\text{R}_2\text{FSiNHC}_6\text{F}_5$  ( $\text{R} = t\text{-Bu}, i\text{-Pr}$ ) result from  $\text{R}_2\text{SiF}_2$  and  $\text{C}_6\text{F}_5\text{NHLi}$ . Their doubly solvated Li derivatives result using  $n\text{-BuLi}$ , the  $t\text{-Bu}$  derivative crystallizing from THF with short Li contacts with fluorine atoms at both Si and the *ortho* position of the phenyl ring of 227.3 and 238.6 pm, respectively (equation 270)<sup>457</sup>. In solution, the  $i\text{-Pr}$  derivative shows fluxionality between these two sites.

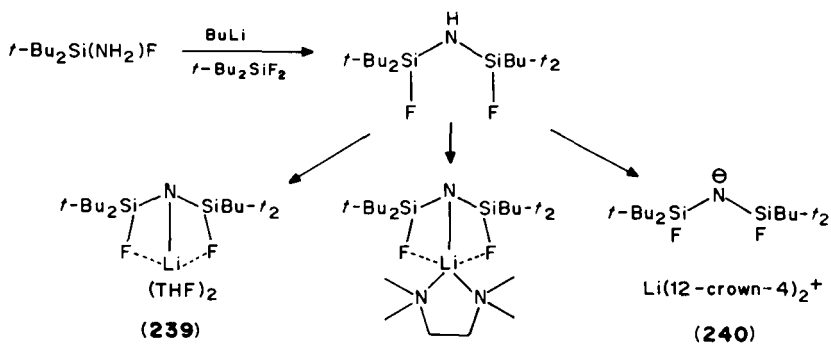




The hindered aminofluorosilanes  $RR'Si(F)NHR''$  lithiated at nitrogen condense with  $MX_4$  ( $M = Si, Ge, Sn$ ;  $X = Cl, Br$ ) to give the  $MX_3$  derivatives, which also undergo halogen/fluorine exchange in particular cases (equation 271)<sup>458</sup>.



The lithiated disilazane ( $t-Bu_3FSi$ )<sub>2</sub>NLi(THF)<sub>2</sub> occurs as an ion pair **239** with an almost linear SiNSi skeleton (SiNSi 176.7°) and equal Si—N bonds of 163.6 pm. These show considerable multiple-bond character as do those in the ionic 12-crown-4 derivative **240**, where the angle at nitrogen is less linear, but the Si—N bonds a little shorter (160.6 and 163 pm) (Scheme 82)<sup>459</sup>.

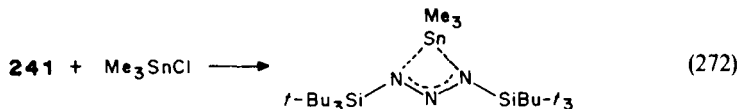


SCHEME 82

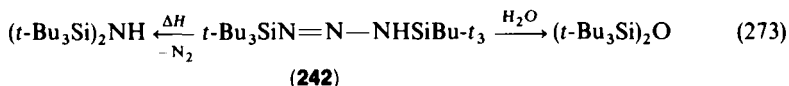
## \*XIII. POLYAZO COMPOUNDS

## \*C. Silyltriazenes

The yellow anion of  $[t-Bu_3SiNNSiBu-t_3]^- Na(THF)_3^+$  (**241**), which results from  $t-Bu_3SiN_3$  and  $t-Bu_3SiNa$ , slowly loses  $N_2$  above 200°C giving the sodium amide. It forms protic and stannyl derivatives, which show fluctuonality in solution and a planar zigzag configuration for the SiNNSi skeleton in the solid. The Si—N bond lengths in both are long (180 pm for the hydrogen derivative and 177–187 pm for the tin derivative) with the latter containing 5-coordinate tin (equation 272)<sup>460</sup>. The yellow triazene

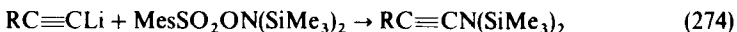


$t-Bu_3SiN=N-NHSiBu-t_3$  (**242**) hydrolyses to the disiloxane and, on heating, gives the disilazane. The disiloxane possesses a linear SiOSi skeleton while that of the disilazane is within 13° of linearity, despite the proton attached (equation 273)<sup>392</sup>.

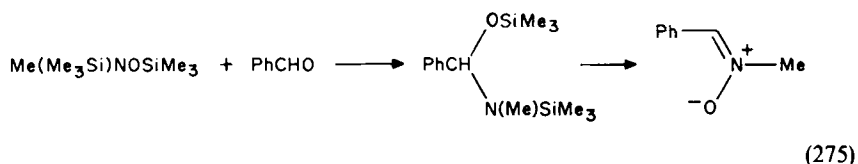


**\*XIV. SILYLHYDROXYLAMINES**

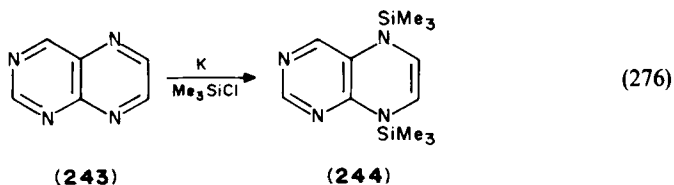
*O,N*-Bis(trimethylsilyl)hydroxylamine reacts with mesitylsulphonyl chloride to give the silylated hydroxylamine sulphonate. This condenses with  $RC\equiv CLi$  to form the bisilyl ynamine (equation 274)<sup>461</sup>.



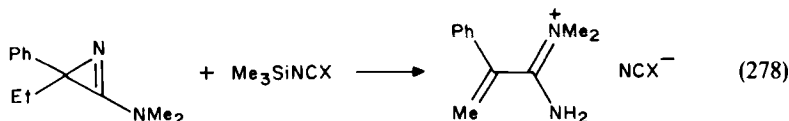
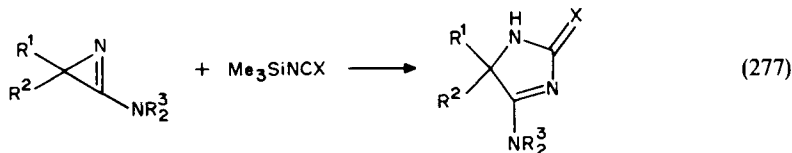
The *N*-methyl homologue, which results from *N*-methyl hydroxylamine hydrochloride in the presence of base and  $Me_3SiCl$  or  $Me_6Si_2$ , adds to aldehydes which lose siloxane to give the nitron (equation 275)<sup>462</sup>.

**\*XVI. SUBSTITUTED DIHYDROPYRAZINES**

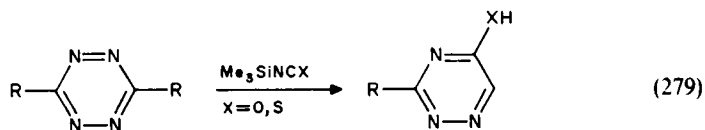
The reductive silylation of pteridine (243) and its 1- and 3-deaza derivatives 1,4,6- and 1,4,5-triazanaphthalene, and of the 1,3-dideaza derivative quinoxaline, give the *N*-silylated 1,4-dihydro-1,4-diazine ring with a  $8\pi$ -conjugated electron system (equation 276). The deaza derivatives prove less electron-rich than the silylated 5,8-dihydropteridine (244), despite increase in electron density in the aromatic non-1,4-diazine ring<sup>463</sup>.

**\*XVII. SILYL PSEUDOHALIDES**

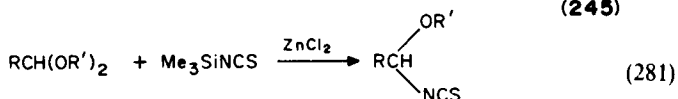
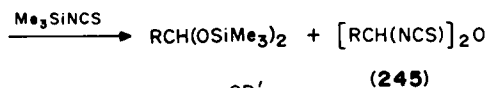
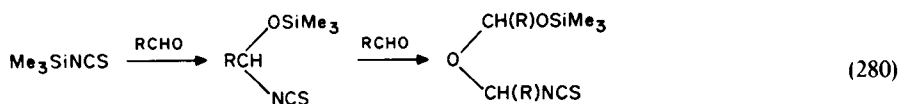
A continuation of structural studies shows those of  $MeH_2SiNCO$  and  $MeH_2SiNCS$  to have Si—N bond lengths (171.8 and 172.4 pm) and SiNC angles ( $151.7^\circ$  and  $156.4^\circ$ ) close to those of the dimethylsilyl derivatives (Table 6)<sup>464</sup>. The PES and CNDO/S semiempir-



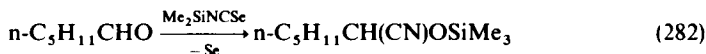
ical quantum-chemical calculations support a linear SiNCX skeleton for  $\text{Me}_n\text{Si}(\text{NCX})_{4-n}$  ( $n = 0-3, X = \text{O}, \text{S}$ )<sup>465</sup>.  $\text{Me}_3\text{SiNCX}$  ( $X = \text{O}, \text{S}$ ) both react with aziridines to give imidazolinones and thiones (equation 277) or amidinium salts (equation 278)<sup>466</sup>. They also convert 1,2,4,5-tetrazines into 1,2,4-triazin-5-ols and thiols (equation 279)<sup>467</sup>.



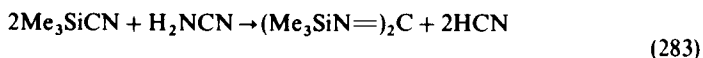
$\text{Me}_3\text{SiNCS}$  couples aldehydes to give the ethers **245** in excellent yield, while acetals are monosubstituted (equations 280 and 281)<sup>468</sup>.  $\alpha\text{-P}_4\text{S}_3\text{I}_2$  is mono- and disubstituted by



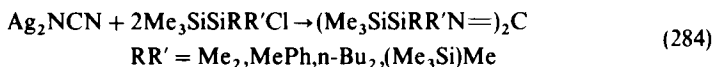
$\text{Me}_3\text{SiNCS}$ , collapse of the  $^{31}\text{P}$  spectra on substitution being due to  $^{14}\text{N}$  relaxation and not to chemical exchange<sup>469</sup>. While  $\text{R}_3\text{SiNCSe}$  exists solely as the iso-isomer ( $\text{R} = \text{alkyl}$ ),  $\text{Ph}_2\text{HSiNCSe}$  exists as a mixture with the selenocyanate isomer.  $\text{Me}_3\text{SiNCSe}$  adds to carbonyl compounds with high chemoselectivity to give the *O*-silylated cyanohydrins in high yield with loss of elemental selenium. Alkyl aldehydes are much more reactive than aryl aldehydes, crotonaldehyde or methyl ketones (equation 282)<sup>470</sup>.



The preparation of *N,N'*-bis(trimethylsilyl)carbodiimide normally requires forcing conditions, but  $\text{Me}_3\text{SiCN}$  reacts with cyanamide at room temperature to give the carbodiimide in 90% yield within one minute. The HCN by-product was vented and trapped in alkali (equation 283)<sup>471</sup>.



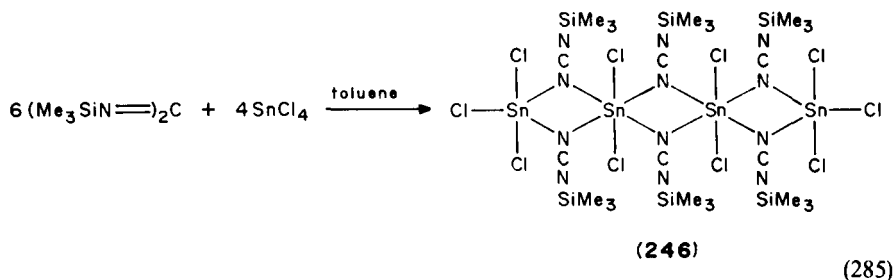
A range of di- and trisilylcarbodiimides result from silver cyanamide and the chloropolysilane (equation 284)<sup>472</sup>.



Stannic chloride reacts with  $(\text{Me}_3\text{SiN}=\text{C})_2$  to give the thermally unstable complex  $\text{Cl}_{10}\text{Sn}_4(\text{NCNSiMe}_3)_6$  (toluene) (**246**), which possesses a bridged-chain structure of 5- and 6-coordinate tin (equation 285)<sup>473</sup>.

The two hindered azidosilanes  $\text{Me}_3\text{SiN}_3$  and *t*-BuPh<sub>2</sub>SiSiMe<sub>2</sub>N<sub>3</sub> show both N-N

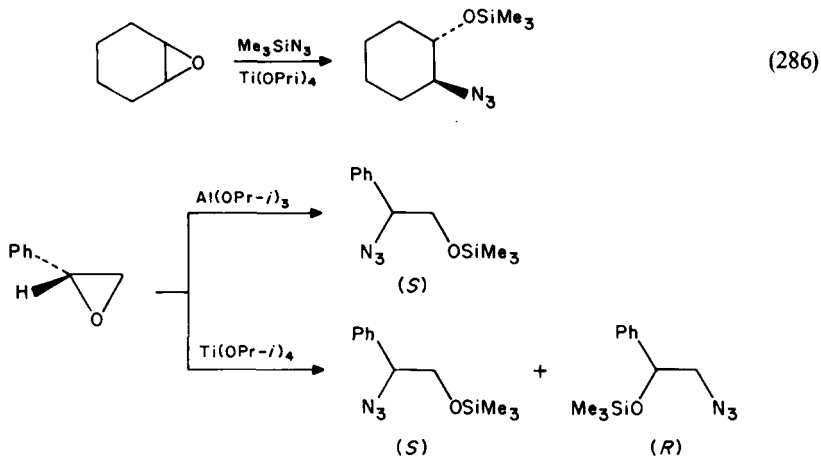
bonds in each to be similar in length, with the terminal one slightly shorter in the latter, and Si—N bonds (181.4 and 178.1 pm, respectively) longer than in  $\text{Ph}_3\text{SiN}_3$ . In organic azides, the terminal N—N bond is much the shorter<sup>474</sup>. The ESR spectrum of the radical cation of trimethylsilyl azide shows the unpaired electron density to be unsymmetrically distributed over the three nitrogen atoms, with the highest spin density on the silicon-substituted nitrogen. Calculations indicate  $\pi$ -delocalization of about 14% onto the  $\text{Me}_3\text{Si}$  group<sup>475</sup>.



### \*A. Reactions with Silyl Azides

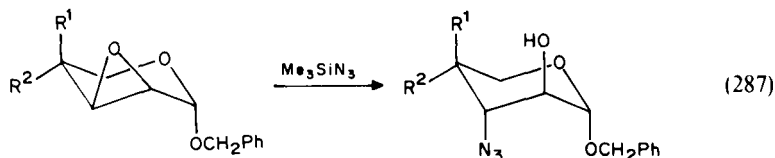
#### \*1. In organic synthesis

The  $\text{Me}_3\text{SiN}_3$  ring opens the epoxide of cyclohexene to give the *trans*-2-azidocyclohexanol with 24% enantiomeric excess with  $\text{Ti}(\text{OPr-}i)_4$  (equation 286)<sup>476</sup>, while (*R*)-epoxystyrene gives (*S*)-silylated azidoalcohol in the presence of  $\text{Al}(\text{OPr-}i)_3$  in > 76% e.e. With  $\text{Ti}(\text{OPr-}i)_4$ , however, enantiodivergent opening occurs, the proportion of (*R*) and (*S*) isomers depending on the solvent used (Scheme 83)<sup>477</sup>. Lewis acids catalyse the reaction

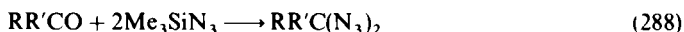


SCHEME 83

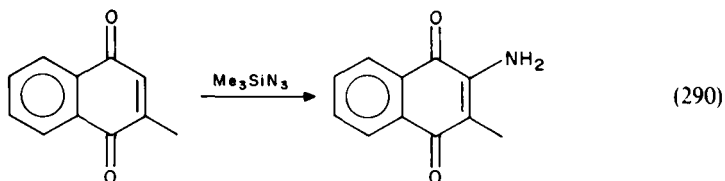
of  $\text{Me}_3\text{SiN}_3$  with anhydro sugars to give isomeric mixtures of the corresponding unsilylated azidodeoxy sugar under mild conditions, such that nucleophile-sensitive groups are not displaced (equation 287)<sup>478</sup>. *Gem* diazides result from  $\text{Me}_3\text{SiN}_3$  and



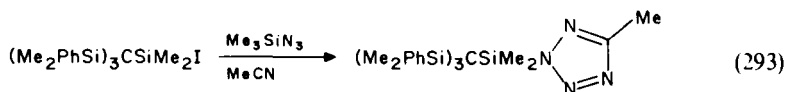
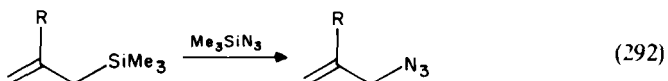
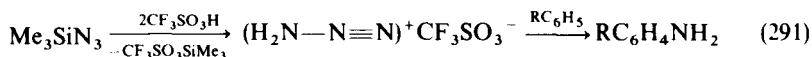
aldehydes or ketones in the presence of  $\text{SnCl}_2$  or  $\text{ZnCl}_2$ . With catalytic amounts of  $\text{NaN}_3/15\text{-crown-5}$ , the  $\alpha$ -siloxy azides resulted exclusively (equations 288 and 289)<sup>479</sup>.



Aminonaphthoquinones result from the reaction of 1,2- and 1,4-naphthoquinones with  $\text{Me}_3\text{SiN}_3$  (equation 290)<sup>480</sup>.



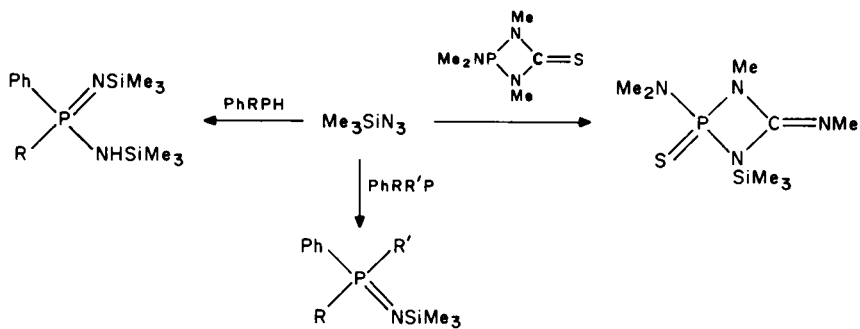
In the presence of triflic acid,  $\text{Me}_3\text{SiN}_3$  provides a useful source of the electrophilic aminating intermediate  $\text{H}_2\text{N}-\text{N}_2^+$ , which has been used to aminate arenes to give the substituted aniline in  $> 90\%$  yield. In the presence of  $\text{PhIO}/\text{F}_3\text{B}\cdot\text{OEt}_2$ ,  $\text{Me}_3\text{SiN}_3$  cleaves allylsilanes to form the allyl azide in good yield (equations 291 and 292)<sup>481</sup>. The highly hindered silane  $(\text{Me}_2\text{PhSi})_3\text{CSiMe}_2\text{I}$  condenses with  $\text{NaN}_3$  in  $\text{MeCN}$  to give the crystalline silyl-substituted tetrazole **247** (equation 293)<sup>482</sup>.



**(247)** m. p.  $161^\circ\text{C}$

## \*2. With main group compounds

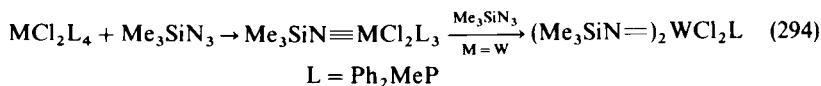
Boranes  $\text{R}_3\text{B}$  can be converted to primary amines in neutral protic media using  $\text{Me}_3\text{SiN}_3$ , which also exchanges with  $(\text{Me}_3\text{Ge})_2\text{O}$  to give the germyl azide<sup>483</sup>.  $\text{Me}_3\text{SiN}_3$  oxidizes a wide variety of substituted phosphines, giving the silyl-substituted phosphimine, notably with H and S migration (Scheme 84)<sup>484</sup>.



SCHEME 84

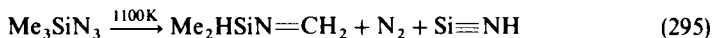
### \*3. With transition metal compounds

Mo(II) and W(II) chloride phosphine complexes can be oxidized stepwise by  $\text{Me}_3\text{SiN}_3$  to the M(IV) and M(VI) imide derivatives (equation 294). The former are 6-coordinate and the latter 5, with the imido groups equatorial<sup>485</sup>.

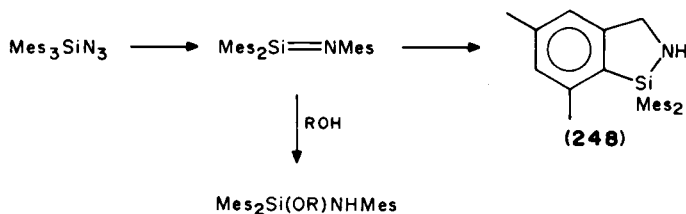


## \*XVIII. THE SILICON-NITROGEN MULTIPLE BOND

The gas-phase thermal fragmentation of  $\text{Me}_3\text{SiN}_3$ , with calculations for support, indicates equimolar production of the silaisocyanide and *N*-silylated imine (equation 295), whereas  $\text{Me}_3\text{GeN}_3$  gives only the germaisocyanide<sup>486</sup>.

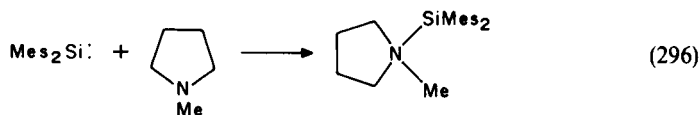


While trimesitylazidosilane photolyses at 77 K in glassy 3-methylpentane or in solution at  $-140^\circ\text{C}$  to  $\text{Mes}_2\text{Si}=\text{NMe}$  and its CH insertion product **248** (Scheme 85), the three azidosilanes  $\text{R}_2\text{ArSiN}_3$  ( $\text{R} = \text{Mes}$ ,  $\text{Ar} = \text{Ph}$ ;  $\text{R} = \text{Me}$ ,  $\text{Pr}$ ,  $\text{Ar} = \text{Mes}$ ) all give the silaimine only. If photolysed in the presence of alcohols, all yield alkoxyaminosilanes<sup>487</sup>.



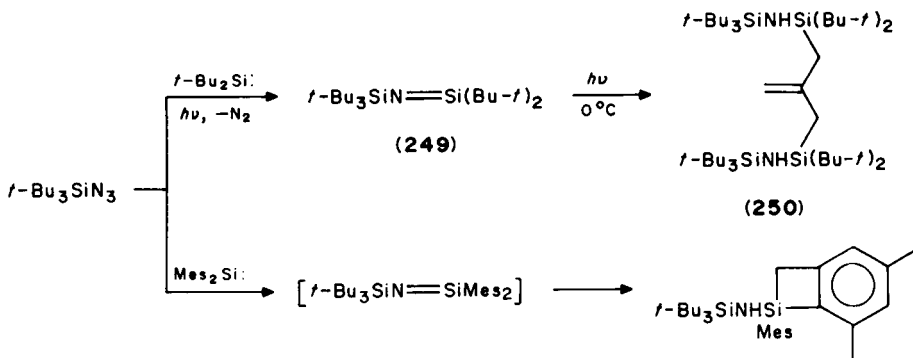
SCHEME 85

Dimesitylsilylene  $\text{Mes}_2\text{Si}$ , generated by the photolysis of the trisilane  $(\text{Me}_3\text{Si})_2\text{SiMes}_2$ , gives a silaylide with *N*-methylpyrrolidine at 77 K, the UV spectra supporting the formation of the ylide at low temperature. Bands for the disilene  $\text{Mes}_2\text{Si}=\text{SiMes}_2$



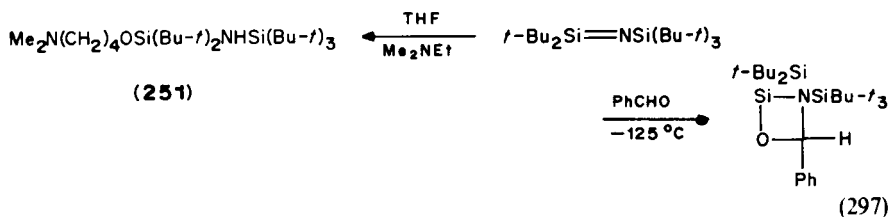
appeared on warming (equation 296)<sup>488</sup>. Photochemically generated *t*-Bu<sub>2</sub>Si: reacts with *t*-Bu<sub>3</sub>SiN<sub>3</sub> to give the silimine **249** and its decomposition product **250** (Scheme 86).

With Mes<sub>2</sub>Si:, however, the silimine formed spontaneously rearranges to the isomeric silacyclobutene (Scheme 86)<sup>489</sup>. The structure of **249** has a SiNSi skeleton that is almost

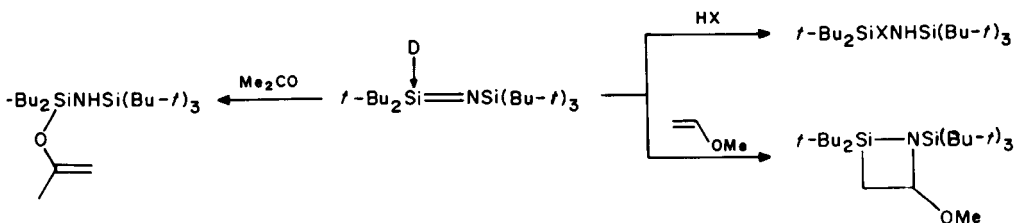


SCHEME 86

linear with Si—N bond lengths of 156.8 and 169.5 pm. The complexes with Ph<sub>2</sub>CO and THF show the SiNSi angle to decrease and Si—N bonds to become more similar in length compared with the uncoordinated species (Ph<sub>2</sub>CO 169.3°, 160.1 and 167.8 pm; THF 161.5°, 158.8 and 165.4 pm), and for coordination to be exclusively to the unsaturated Si atom<sup>490</sup>. With PhCHO at -125°C, the four-membered heterocyclic adduct results while, with EtNMe<sub>2</sub>, the THF adduct gives the linear product **251** (equation 297)<sup>491</sup>.

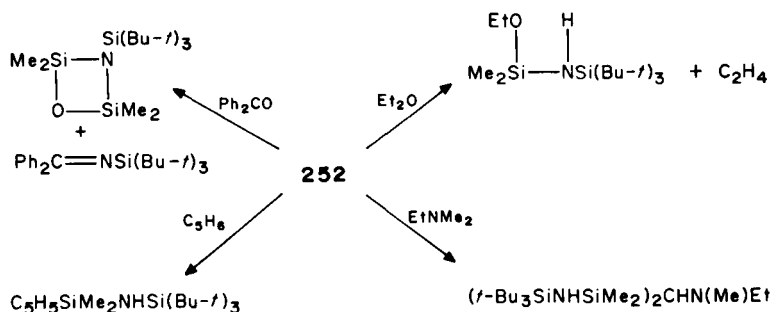


*t*-Bu<sub>2</sub>Si=NSi(Bu-*t*)<sub>3</sub> forms adducts with oxygen and nitrogen donors D, and readily adds protic reagents across the Si=N double bond, including alkenes (Scheme 87)<sup>491</sup>.



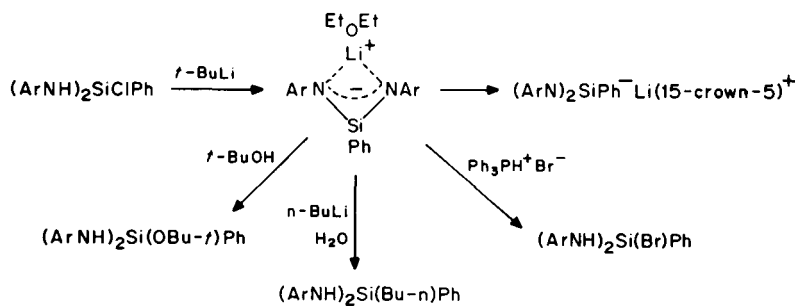
SCHEME 87

With  $\text{Me}_2\text{Si}=\text{NSi}(\text{Bu}-t)_3$  (**252**), a similar range of donor complexes form, but decompose with olefin elimination, C—H addition or silylimine extrusion (Scheme 88)<sup>492</sup>.



SCHEME 88

The first silaamidide results from the hindered bis(amino)silane  $(\text{ArNH})_2\text{SiClPh}$  with *t*-BuLi in ether. The 15-crown-5 ether complex gives an intense IR band at  $1304\text{ cm}^{-1}$ , ascribable to the  $\nu_{\text{as}}\text{NSiN}$ , the region for multiple Si—N bonds, and adds *t*-BuOH, HBr (as  $\text{Ph}_3\text{PH}^+\text{Br}^-$ ) and *n*-BuLi/ $\text{H}_2\text{O}$  (Scheme 89)<sup>493</sup>.



SCHEME 89

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