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Sterically overloaded supersilylated main group elements and main group element clusters

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[1] This review summarizes chemical investigations of the following coworkers (in alphabetical order): Kerstin Amelunxen, Harald Auer, Christian Finger, Gerd Fischer, Walter Hochmuth, Edwin Kühnel, Hans-Wolfram Lerner, Wolfgang Niedermayer, Thomas Passler, Klaus Schurz, Harald Schuster and Angelika Wörner.

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Abstract

Supersilyl $t\text{Bu}_3\text{Si}$ behaves as a very bulky, chemically inert group. In fact, it exists (i) as an anion $t\text{Bu}_3\text{Si}^-$ in supersilyl alkaline metals $t\text{Bu}_3\text{SiM}$; (ii) as a short-lived radical $t\text{Bu}_3\text{Si}^\bullet$ after thermolizing $t\text{Bu}_3\text{Si–Si}t\text{Bu}_3$ or photolizing $t\text{Bu}_3\text{Si–Hg–Si}t\text{Bu}_3$; and (iii) as a strongly polarized "cation" in compounds $t\text{Bu}_3\text{Si}^{\delta+}\text{–X}^{\delta-}$ with partners X of weak Lewis basicity. By chemical transfer of these supersilyl species, supersilyl derivatives of almost all main group elements have so far been obtained. These include simple supersilylated compounds $(t\text{Bu}_3\text{Si})_m\text{EX}_n$ ($m=1$, 2; X = halogen and/or hydrogen as well as organyl) of main group elements E which, among others, are characterized by long SiE bond distances and large SiESi and SiEX bond angles. Over and above that, supersilylated compounds of main group element clusters are preparable. These include (i) those of the sixth group like $(t\text{Bu}_3\text{Si})_2\text{E}_n$ (E = S, Se, Te); (ii) those of the fifth group like $(t\text{Bu}_3\text{Si})_2\text{N}_3\text{H}$, $(t\text{Bu}_3\text{Si})_2\text{N}_4\text{H}_2$, $(t\text{Bu}_3\text{Si})_m\text{P}_n$ ($m/n=2/2$, 2/4, 4/6, 2/7, 3/9), $(t\text{Bu}_3\text{Si})_m\text{P}_n\text{Na}_p$ ($m/n/p=2/3/1$, 3/4/1, 2/4/2, 3/5/2, 4/8/4), $(t\text{Bu}_3\text{Si})_4\text{Sb}_4$; (iii) those of the fourth group like $(t\text{Bu}_3\text{Si})_4\text{E}_4$ (E = Si, Ge); and (iv) those of the third group like $(t\text{Bu}_3\text{Si})_4\text{Al}_4$, $(t\text{Bu}_3\text{Si})_4\text{E}_2$ (E = Al, In, Tl), $(t\text{Bu}_3\text{Si})_3\text{Ga}_2$. In general, substitutions of hydrogens in low-valent main group element hydrides by supersilyl lead to a stabilization of the compounds. As a consequence of this, not only the supersilylated clusters mentioned but also unsaturated compounds of the heavier main group elements like $t\text{Bu}_2\text{Si=N–Si}t\text{Bu}_3$ become isolable.

Keywords: Supersilyl $t\text{Bu}_3\text{Si}$; Anions $t\text{Bu}_3\text{Si}^-$; Radicals $t\text{Bu}_3\text{Si}^\bullet$; Cations $t\text{Bu}_3\text{Si}^+$; Supersilylated main group elements; Supersilylated main group element clusters; X-ray structures

1. Introduction

Recently, sterically overloaded substituents have gained increasing significance as stabilizers of main group elements in unusual geometries and low coordination states as well as stabilizers of main group element clusters [1]. Some examples of such groups are "phenyls" like supermesityl with bulky organyls in positions 2, 4 and 6, or "trisyl", "supersilyl" and "hypersilyl" (which in fact is sterically less overloaded than the bulky aryls, the trisyl or the supersilyl group)[2].

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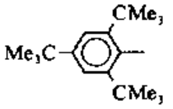
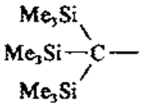
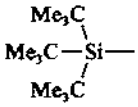
[2] Supermesityl 2,4,6-$t\text{Bu}_3\text{C}_6\text{H}_2$ is derived from mesityl 2,4,6-$\text{Me}_3\text{C}_6\text{H}_2$ by replacing the three methyl groups by tertiary butyls. As the group $t\text{Bu}_3\text{Si}$ is derived from the silyl group Me_3Si in an analogous manner by replacement of the three methyl groups with tertiary butyl ones, it was named supersilyl [2]. The group $(\text{Me}_3\text{Si})_3\text{Si}$ is derived from supersilyl by exchanging all silicon bound carbon atoms by silicon atoms. It contains much more silicon than supersilyl and, therefore, was named hypersilyl. On the other hand, the group $(\text{Me}_3\text{Si})_3\text{C}$ is derived from hypersilyl by exchange of the central silicon by carbon. It is the last member of a row of methyl groups with one ("mono"), two ("di") or three ("tri") silyl substituents bound to carbon: monosyl $(\text{Me}_3\text{Si})\text{CH}_2$, disyl $(\text{Me}_3\text{Si})_2\text{CH}$ (also known as Lappert group [1]) and trisyl $(\text{Me}_3\text{Si})_3\text{C}$.



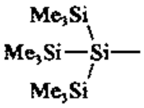
"Supermesityl"



"Trisyl"



"Supersilyl"



"Hypersilyl"

In fact, the supersilyl group has some advantages as an overloaded substituent: It behaves chemically relatively inert as it represents a saturated species and possesses only organyl substituents, whereas the other bulky groups mentioned may be chemically more reactive because of their unsaturation (aryls) or the tendency of silyl groups for migrations (trisyl, hypersilyl). In addition, the supersilyl group is easy to synthesize, and as a strong electron donor stabilizes bonds between electropositive elements as any electron donating group would do.

In the first part of this review I wish to introduce some properties of the supersilyl group which really is a very bulky group – see Fig. 1 – and of its simple compounds with main group elements. In the second part some new results in the field of sterically overloaded supersilylated main group element clusters are reported.

2. The supersilyl group and its simple compounds with main group elements

2.1. Historical background

As already stated, the synthesis of the supersilyl group is easy. Nevertheless, its first preparation took nearly three decades. Thus in the late forties, Taylor, Sommer

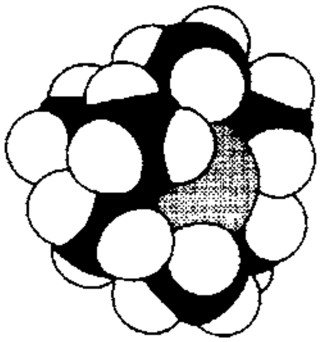
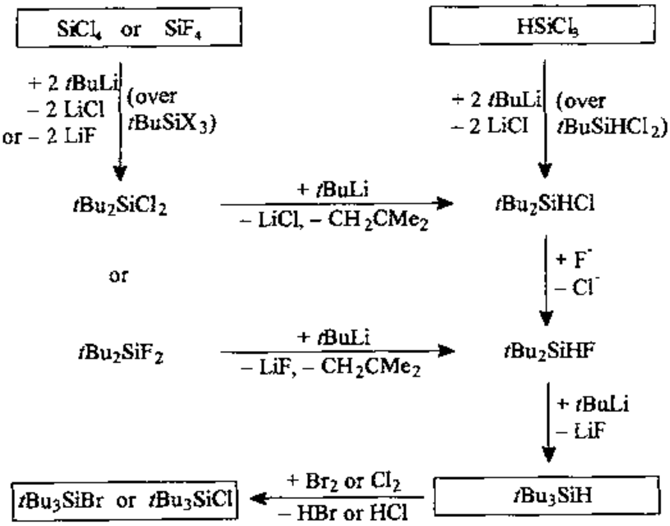


Fig. 1. Space-filling model of the supersilyl group $t\mathrm{Bu}_3\mathrm{Si}$.

and Whitmore [3] succeeded in exchanging up to two chlorines in $SiCl_4$ by tertiary butyl groups (Eq. (1)). Only in 1975, after synthesizing $t\mathrm{Bu_2SiHF}$ by substitution of one halogen atom in $t\mathrm{Bu_2SiX_2}$ (X=Cl, F) by hydrogen and – in the case of $t\mathrm{Bu_2SiHCl}$ – chlorine by fluorine, or by transforming $SiHCl_3$ over $t\mathrm{Bu_2SiHCl}$ into $t\mathrm{Bu_2SiHF}$, were three work groups at the same time (Doyle and West [4], Dexheimer and Spialter [5], Weidenbruch and Peter [6]) able to introduce a third tertiary butyl group in $t\mathrm{Bu_2SiHF}$ and to prepare $t\mathrm{Bu_3SiH}$ as the first supersilyl compound which, over and above that, could easily be transformed into supersilyl chloride or bromide by reaction with chlorine or bromine (cf. Eq. (1)). In fact, the best preparation method for tri-*tert*-butylsilane ("supersilane") $t\mathrm{Bu_3SiH}$ is according to our practical experience: (i) formation of $t\mathrm{Bu_2SiHCl}$ from $SiHCl_3$ and tBuLi in molar ratio 1:2 (refluxing pentane, 83% yield); (ii) formation of $t\mathrm{Bu_2SiHF}$ from $t\mathrm{Bu_2SiHCl}$, KHF_2 and KF in molar ratio 2:2:1 (no solvent, 70 °C, 91% yield); (iii) formation of $t\mathrm{Bu_3SiH}$ from $t\mathrm{Bu_2SiHF}$ and tBuLi in molar ratio 1:1 (refluxing heptane, 86% yield).



(1)

In the following years supersilane, which in fact also may be synthesized from SiF_4 and tBuLi without isolation of intermediate products [7,8] was transformed into many monosupersilylated compounds $t\mathrm{Bu_3SiX}$ with electronegative group X like halogens [9], pseudohalogens [10,11], hydroxide and its derivatives [9,10,12], amine and its derivatives [11], methyl and its derivatives [13,14]. Later on, also disupersilylated compounds $(t\mathrm{Bu_3Si})_2\mathrm{Y}$ like $(t\mathrm{Bu_3Si})_2\mathrm{O}$ or $(t\mathrm{Bu_3Si})_2\mathrm{NH}$ were obtained [15]. On the other hand, trisupersilylated compounds $(t\mathrm{Bu_3Si})_3\mathrm{Z}$ are to date unknown.

Working out good syntheses for supersilyl anions, radicals and "cations" mark important steps not only in the field of the preparation of supersilylated main group elements but also of supersilylated main group element clusters, discussed further below. First of all, I now wish to present supersilyl anions [8,16–20] which have made it possible to open a large door into the area of supersilyl compounds.

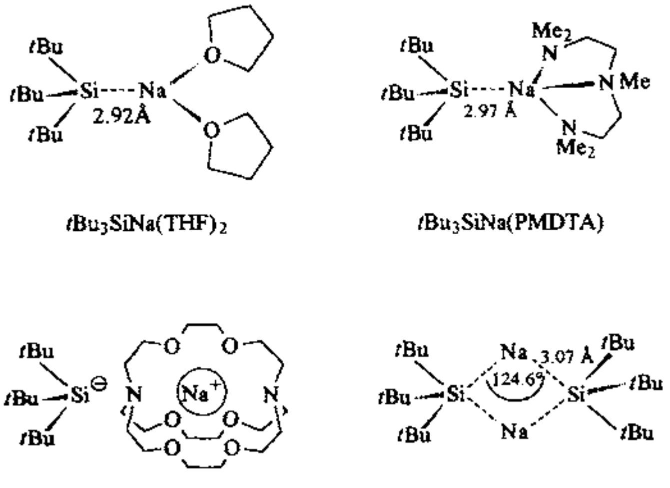
2.2. Supersilyl anions

2.2.1. Syntheses

As we found in 1984 for the first time [18], supersilylated alkaline metals $t\text{Bu}_3\text{SiM}$ which, in fact, contain supersilyl anions $t\text{Bu}_3\text{Si}^-$ are easily obtained by the action of alkaline metals M on supersilyl halides $t\text{Bu}_3\text{SiX}$ in ethers or hydrocarbons above room temperature according to Eq. (2) [8,16–20]. The metallations occur with increasing ease in the series $t\text{Bu}_3\text{SiF} < t\text{Bu}_3\text{SiCl} < t\text{Bu}_3\text{SiBr} < t\text{Bu}_3\text{SiI}$, and $\text{Li} < \text{NaK} < \text{Rb} < \text{Cs}$, and the solvents hydrocarbons < ethers, respectively.

$$t\text{Bu}_3\text{SiX} + 2\text{M} \xrightarrow[(\text{M}=\text{Li,Na,K,Rb,Cs})]{\text{ethers,hydrocarbons}} t\text{Bu}_3\text{SiM} + \text{MX} \qquad (2)$$

Supersilyl sodium $t\text{Bu}_3\text{SiNa}$, for example, is conveniently prepared from supersilyl bromide and sodium in refluxing tetrahydrofuran THF [8,18]. It crystallizes from THF in beautiful yellow needles. X-ray structure analysis shows that the compound contains two molecules of THF, which are bound to sodium as shown in Fig. 2 [20]. In the crystal two such molecules form dimers with $\text{CH}_3\ldots\text{Na}$ contacts. Obviously, the same holds for a Bu_2O adduct of $t\text{Bu}_3\text{SiNa}$, formed from $t\text{Bu}_3\text{SiBr}$ and Na in dibutyl ether at 80 °C [17]. On the other hand, the structure of the adduct with pentamethyldiethylenetriamine PMDTA instead of THF or Bu_2O is monomeric in crystalline phase and contains distorted tetrahedral silicon and sodium atoms (Fig. 2). The SiNa distances amounts to 3 Å and lie in a range which is expected for an ionic bond. Certainly, no covalent connections occur



$t\text{Bu}_3\text{SiNa(THF)}_2$ $t\text{Bu}_3\text{SiNa(PMDTA)}$

$t\text{Bu}_3\text{SiNa(C222)}$ $(t\text{Bu}_3\text{SiNa})_2$

Fig. 2. Structures of $t\text{Bu}_3\text{SiNa(THF)}_2$ (X-ray; H. Nöth, I. Krossing), $t\text{Bu}_3\text{SiNa(PMDTA)}$ (X-ray; H. Nöth, M. Schmidt-Amelunxen), $t\text{Bu}_3\text{SiNa(C222)}$ (assumption) and $(t\text{Bu}_3\text{SiNa})_2$ (X-ray; H. Nöth, M. Schmidt-Amelunxen).

between Si and Na in a reactive adduct of supersilyl sodium and the cryptand C222 (Fig. 2), the crystal structure of which is yet unknown. Supersilyl sodium may also be prepared without donors by reaction of $t\mathrm{Bu_3SiBr}$ with Na in refluxing heptane [20]. According to X-ray structure analysis, the dark yellow crystalline compound is dimeric: as shown in Fig. 2, two supersilyl anions are linked by two sodium cations whereby silicon gains the coordination number 5 and sodium – except for agostic interactions – the coordination number 2. Again, the SiNa distance amounts to 3 Å.

In an analogous manner as for supersilyl sodium, pale to dark yellow supersilyl lithium $t\mathrm{Bu_3SiLi}$ may be obtained as a monomer in ethers at elevated temperatures with donors, coordinated to lithium, or as a dimer in refluxing heptane without donors [20]. On the other hand, the preparation of supersilyl potassium $t\mathrm{Bu_3SiK}$ in hydrocarbons leads to a polymeric product [19,20,60a] (for $t\mathrm{Bu_3SiK(C_6H_6)_3}$ c.f. Ref. [60a]). The same holds for supersilyl rubidium $t\mathrm{Bu_3SiRb}$, and cesium $t\mathrm{Bu_3SiCs}$ [19] which, over and above that, show a high tendency to react with supersilyl halides $t\mathrm{Bu_3SiX}$ under MX elimination (see below). Therefore, both the silyl metals are obtained from $t\mathrm{Bu_3SiI}$ and Rb or Cs in heptane at 100 or 60 °C, respectively, only in small yields (< 10%) besides $t\mathrm{Bu_3SiH}$ and $(t\mathrm{Bu_3Si})_2$.

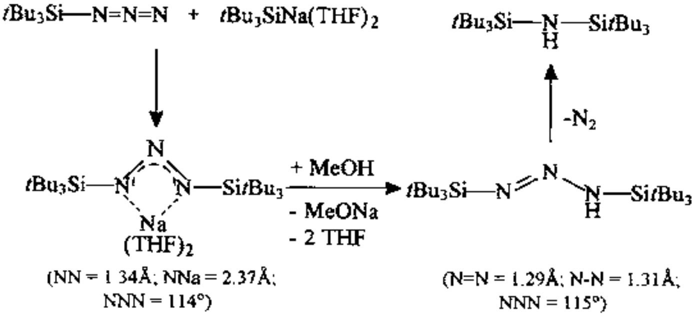
2.2.2. *Reactivity*

The supersilyl anion $t\mathrm{Bu_3Si^-}$ shows a high tendency for delivering electrons. Therefore, the supersilyl alkaline metals act as strong Brönsted bases which – as in Eq. (3) – deprotonate even weak bases RH such as THF or benzene under formation of supersilane [19,20].

$$t\mathrm{Bu_3SiM} + \mathrm{RH}(RH) \xrightarrow[(\mathrm{M=Li,Na,K,Rb,Cs})]{(\mathrm{RH})} t\mathrm{Bu_3SiH} + \mathrm{RM} \tag{3}$$

In fact, as carbon is more electronegative than silicon, silyl alkaline metals are more basic than organyl alkaline metals and should therefore be able to deprotonate hydrocarbon functions. Certainly, the deprotonations may be more or less kinetically hindered, as is shown by the reaction of $t\mathrm{Bu_3SiNa}$ with THF or benzene, respectively, which goes more slowly with THF ($\tau\frac{1}{2} = 175$ h in THF at 85 °C and ca. 60 h in $\mathrm{C_6D_6}$ at 85 °C). With solvent-free supersilyl metals $t\mathrm{Bu_3SiM}$, deprotonation rates obviously increase with the polarity of the SiM bond, that is with increasing atomic number of M.

As expected, the supersilyl anion $t\mathrm{Bu_3Si^-}$ also acts as a strong Lewis base which after Eq. (4) is able to add to Lewis acids such as supersilyl azide [18,21,32], whereby a yellow ditetrahydrofuran adduct of bis(supersilyl)triazenide $(t\mathrm{Bu_3Si})_2\mathrm{N_3Na}$ is formed in THF (X-ray; M. Veith and V. Huch; cf. the additions of phosphanes $\mathrm{PR_3}$ to azides; $t\mathrm{Bu_3P}$ is isoelectronic to $t\mathrm{Bu_3Si^-}$). $(t\mathrm{Bu_3Si})_2\mathrm{N_3Na}$, on the other hand, is easily protonated under formation of bis(supersilyl)triazene $(t\mathrm{Bu_3Si})_2\mathrm{N_3H}$ which at 150 °C eliminates nitrogen under formation of bis(supersilyl) amine $(t\mathrm{Bu_3Si})_2\mathrm{NH}$ (cf. Eq. (4) and Ref. [21]).



(4)

Over and above that, the supersilyl anion $t\mathrm{Bu_3Si}^-$ acts as a strong nucleophile and a reducing agent which may react, for example [19], with halogenides $\mathrm{R}_n\mathrm{EX}$ (R = inorganic or organic substituents) like ClCl, ClSSCl, $\mathrm{PF_3}$, $\mathrm{Me_3SiCl}$, $\mathrm{BF_3}$ and so on by nucleophilic attack at E and X under substitution of X^- (Eq. 5a) and $\mathrm{R}_n\mathrm{E}$ (Eq. 5b), respectively, or by electron transfer under formation of $t\mathrm{Bu_3Si}^\bullet$, X^- and $\mathrm{R}_n\mathrm{E}^\bullet$ Eq. 5c).

$$\mathrm{R}_n\mathrm{E-X} + t\mathrm{Bu_3Si}^- \begin{cases} \xrightarrow{(a)} \mathrm{R}_n\mathrm{E-Si}t\mathrm{Bu_3} + \mathrm{X}^- \\ \xrightarrow{(b)} \mathrm{R}_n\mathrm{E}^- + t\mathrm{Bu_3Si-X} \\ \xrightarrow{(c)} \mathrm{R}_n\mathrm{E}\cdot + \mathrm{X}^- + t\mathrm{Bu_3Si}\cdot \end{cases} \tag{5}$$

Which route is actually selected, depends on steric as well as electronic factors. Certainly, the mechanisms for many reactions of type (5) are not yet exactly known. But it seems reasonable to assume that substitutions of type (5a) occur favorably at unhindered, positively charged centres E, whereas substitutions of type (5b, c) are preferred if the centres E are hindered by bulky groups R. Furthermore, for substitutions of type (5b) an easy attack of X by the nucleophile $t\mathrm{Bu_3Si}^-$ is required (I > Br > Cl > F), whilst for substitutions of type (5c) the inverse probably holds (F > Cl > Br > I).

For instance, the smooth formation of the disilane $t\mathrm{Bu_3Si{-}SiMe_3}$ from $t\mathrm{Bu_3SiNa}$ and $\mathrm{Me_3SiBr}$ according to Eq. (6) [19] obviously proceeds by nucleophilic attack as in Eq. 5a whereas no disilane $t\mathrm{Bu_3Si{-}Si}t\mathrm{Bu_3}$ is found from $t\mathrm{Bu_3SiNa}$ and the more bulky silyl halogenide $t\mathrm{Bu_3SiBr}$. In fact, $t\mathrm{Bu_3SiM}$ formation from $t\mathrm{Bu_3SiX}$ and M (i) without essential secondary condensation of type (6) in the case of silyl metals with M = Li, Na, K and (ii) under marked Wurtz reaction in the case of silyl metals with M = Rb, Cs (see above and Ref. [19]) points to a kinetic hindrance of nucleophilic substitutions (5a) for sterical reasons and facilitation of electron transfers (5c) for electronic reasons (increasing reduction ability with the polarity of $t\mathrm{Bu_3SiM}$; nucleophilic substitutions (5b) lead according to $t\mathrm{Bu_3SiM} + t\mathrm{Bu_3SiX} \rightarrow$

$t\mathrm{Bu_3SiX} + t\mathrm{Bu_3SiM}$ only to identical products):

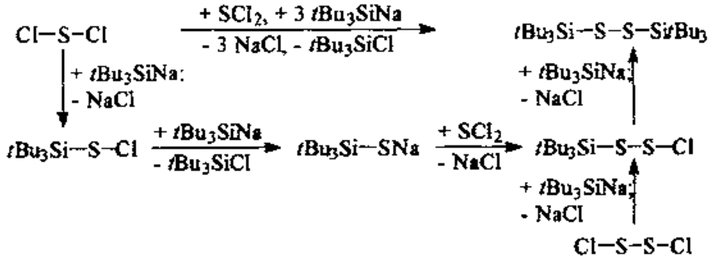
$$t\mathrm{Bu_3SiM} + \mathrm{XSiR_3} \xrightarrow[\mathrm{M=alkaline\ metals}]{\mathrm{X=halogens}} t\mathrm{Bu_3Si-SiR_3} + \mathrm{MX} \tag{6}$$

Obviously, binary main group element halides EX_m primarily react with supersilyl sodium under nucleophilic exchange (5a) of one halogenide by supersilyl under formation of $(t\mathrm{Bu_3Si})\mathrm{EX}_{m-1}$. An exchange of a second halogenide analogous to Eq. 5a then proceeds under formation of $(t\mathrm{Bu_3Si})_2\mathrm{EX}_{m-2}$ if the difference ΔEN of the electronegativity of E and X is not too small. Otherwise the second supersilyl anion reacts faster analogous to Eqs. 5b or 5c. The exchange of a third halogenide by supersilyl has never been observed; instead of this, reactions (5b) or (5c) occur without exception. In fact, the following numbers n of halogen atoms are maximal exchangeable in THF as solvent according to Eq. (7) (see also Section 3).

$$\mathrm{EX}_m + n\ t\mathrm{Bu_3SiNa} \rightarrow (t\mathrm{Bu_3Si})_n\mathrm{EX}_{m-n} + n\mathrm{NaCl} \tag{7}$$

$\mathrm{EX}_m =$	$\mathrm{MgBr_2}$	$\mathrm{AlBr_3}$	$\mathrm{SiF_4}$	$\mathrm{SiCl_4}$	$\mathrm{PCl_3}$	$\mathrm{SCl_2}$
$\Delta\mathrm{EN_{EX}}$	1.51	1.27	2.36	1.09	0.77	0.39
n in Eq. (7)	2	2	2	1	1	1
Ref.	[19]	[22]	[23]	[2]	[24]	[25]

In many cases, the reaction of element halides with supersilyl anions proceeds in a complex manner because the latter react simultanously with the adducts according to Eq. 5a and with the products $(t\mathrm{Bu_3Si})_n\mathrm{EX}_{m-n}$ according to Eq. 5b and/or Eq. 5c to yield secondary products. For example, as in Eq. (8), the reaction of the THF adduct of supersilyl sodium with sulfur dichloride in pentane at room temperature leads to bis(supersilyl)disulfane $(t\mathrm{Bu_3Si})_2\mathrm{S_2}$ [25]. Obviously, the first reaction product, supersilyl sulfur chloride $t\mathrm{Bu_3Si{-}S{-}Cl}$ is transformed according to Eq. (8) via $t\mathrm{Bu_3Si{-}SNa}$ and $t\mathrm{Bu_3Si{-}S{-}S{-}Cl}$ into the disulfane $t\mathrm{Bu_3Si{-}S{-}S{-}Si}t\mathrm{Bu_3}$ which is also prepared by reaction of disulfur dichloride and supersilyl sodium. (For secondary products of the reactions of $t\mathrm{Bu_3SiNa}$ with other element halides like $\mathrm{PCl_3}$, see Section 3.)



(8)

Certainly, substitutions of halogens in halides EX_m by supersilyl are not only influenced by electronic but – not so conspicuously – also by steric effects. Indeed, the latter effect obviously is responsible for the finding that the silane $\mathrm{SiH_2Cl_2}$ may be disupersilylated [2] unlike $\mathrm{SiCl_4}$ which is only monosupersilylated by $t\mathrm{Bu_3SiNa}$.

In connection with the mentioned supersilylation of elemental halides we should consider the supersilyl magnesium compounds $t\mathrm{Bu_3SiMgBr}$ (colorless) and $(t\mathrm{Bu_3Si})_2\mathrm{Mg}$ (colorless) [19]. They are formed from $\mathrm{MgBr_2}$ and $t\mathrm{Bu_3SiNa}$ in the molar ratio 1:1 or 1:2 in THF as THF adducts and really represent examples of supersilylated alkaline earth metals. In an analogous manner colorless to pale yellow supersilyl zinc, cadmium and mercury compounds $t\mathrm{Bu_3SiMX}$ and $(t\mathrm{Bu_3Si})_2\mathrm{M}$ are formed in THF at room temperature according to Eq. (9) by reaction of $\mathrm{ZnBr_2}$, $\mathrm{CdI_2}$ and $\mathrm{HgCl_2}$ with $t\mathrm{Bu_3SiNa}$ [22a]. In fact, $(t\mathrm{Bu_3Si})_2\mathrm{Cd}$ and $(t\mathrm{Bu_3Si})_2\mathrm{Hg}$ are also formed from $\mathrm{Et_2Cd}$ and $\mathrm{Et_2Hg}$ with $t\mathrm{Bu_3SiH}$ [22b].

$$\mathrm{MX_2} \xrightarrow[-\mathrm{NaX}]{+t\mathrm{Bu_3SiNa}} (t\mathrm{Bu_3Si})\mathrm{MX} \xrightarrow[-\mathrm{NaX}]{+t\mathrm{Bu_3SiNa}} (t\mathrm{Bu_3Si})_2\mathrm{M}\,(\mathrm{M} = \mathrm{Mg,Zn,Cd,Hg}) \tag{9}$$

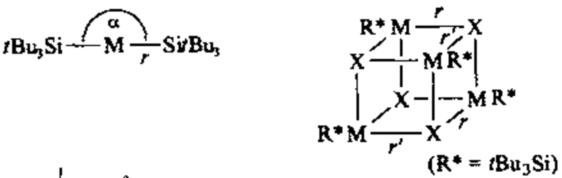
Crystal structure determinations show $t\mathrm{Bu_3SiZnBr}$ and $t\mathrm{Bu_3SiHgCl}$ to be tetrameric of heterocubane type with alternating metal and halogen atoms at the edges of a more or less distorted cube (in $(t\mathrm{Bu_3SiHgCl})_4$ linear $t\mathrm{Bu_3SiHgCl}$ molecules are loosely bound together), and $(t\mathrm{Bu_3Si})_2\mathrm{M}$ with M = Zn, Cd, Hg to be monomeric with the two supersilyl substituents bonded in a linear fashion to the metal (cf. Fig. 3 and [22b]).

Not only element–halogenide groups E–X are subject to nucleophilic cleavage by supersilyl anions but, more generally, element–element groups E–E. This, for instance, is shown by reactions of supersilyl sodium with chalcogens which lead according to Eq. (10) to supersilyl chalcogenides of type $t\mathrm{Bu_3SiY^-}$ (see Section 2.4.2 and Refs. [19,24]).

$$\mathrm{Y}_n + n\ t\mathrm{Bu_3SiNa} \rightarrow n t\mathrm{Bu_3SiYNa} \tag{10}$$

Indeed, $t\mathrm{Bu_3SiONa}$ is better (quantitatively) produced from $\mathrm{N_2O}$ and $t\mathrm{Bu_3SiNa(THF)_2}$ in pentane at room temperature: $\mathrm{N_2O} + t\mathrm{Bu_3SiNa} \rightarrow t\mathrm{Bu_3SiONa} + \mathrm{N_2}$ [26].

Whereas all elements of the seventh and sixth main group are attacked by



M	r [Å]	α [°]
Zn	2.38	180
Cd	2.52	180
Hg	2.50	180

	r [Å]	r' [Å]
R*ZnBr	2.64	2.64
R*HgCl	2.47	3.07

Fig. 3. Crystal structures of $(t\mathrm{Bu_3SiZnBr})_4$ (X-ray; H. Nöth and A. Appel), $(t\mathrm{Bu_3SiHgCl})_4$ (X-ray; H. Nöth and J. Knizek), $(t\mathrm{Bu_3Si})_2\mathrm{Zn}$ (X-ray, K. Polborn), $(t\mathrm{Bu_3Si})_2\mathrm{Cd}$ (X-ray; K. Polborn) and $(t\mathrm{Bu_3Si})_2\mathrm{Hg}$ (X-ray; K. Polborn).

$t\text{Bu}_3\text{Si}^-$, only white phosphorus P_4 and yellow arsenic As_4 from the elements of the remaining fifth to first main groups react with supersilyl sodium (see Section 3.2).

2.3. *Supersilyl radicals*

2.3.1. *Syntheses*

Supersilyl radicals $t\text{Bu}_3\text{Si}^\bullet$ are produced according to Eq. (11) by reaction of supersilyl anions $t\text{Bu}_3\text{Si}^-$ (e.g. in the form of $t\text{Bu}_3\text{SiNa}$) with oxidation agents like copper(I), silver(I), tetracyanoethylene [16], or by irradiation of bis(supersilyl) mercury [22a]:

$$2t\text{Bu}_3\text{Si}^- \xrightarrow{-2e^-} 2t\text{Bu}_3\text{Si}^\bullet \xleftarrow[-\text{Hg}]{} (t\text{Bu}_3\text{Si})_2\text{Hg} \tag{11}$$

Over and above that, they are a byproduct of many reactions of supersilyl alkaline metals (cf. Eq. 5c). The radicals so formed dimerize at room temperature and below according to Eq. (12) with formation of colorless, crystalline superdisilane which was synthesized for the first time [16] in this way:

$$2t\text{Bu}_3\text{Si}^\bullet \underset{\Delta}{\rightleftarrows} t\text{Bu}_3\text{Si}-\text{Si}t\text{Bu}_3 \tag{12}$$

The X-ray structure analysis of $t\text{Bu}_3\text{Si–Si}t\text{Bu}_3$ shows a SiSi atom distance of 2.69 Å which is significantly longer than the 2.34 Å bond length in other disilanes [16]. Despite this, the disilane is quite an inactive substance at room temperature and shows no tendency for splitting into two supersilyl radicals. As an explanation of these facts, Weidenbruch and von Schnering have proposed, in another connection, that a sterically determined weakening of SiSi bonds in organopolysilanes might be partly compensated for by van der Waals attractions of peripheral methyl groups [27]. In the case of superdisilane, this idea – according to Bock [27] – is supported by a striking interlocking of the peripheral methyl groups. In fact, the additional attractions force a lowering of the expected symmetry D_{3d} for $t\text{Bu}_3\text{Si–Si}t\text{Bu}_3$ towards D_3.

The reactivity of superdisilane starts at 50 °C and above with the formation of supersilyl radicals (cf. Eq. (12)). Indeed the disilane which is a very convenient source for supersilyl radicals behaves itself like an elastic band which may be considerably expanded until it breaks.

When formed from superdisilane, the radicals are so reactive that up to now their existence could not be proved by ESR spectroscopy. Therefore, its intermediate existence follows from chemical investigations only. It appears that the life-time of the radical is short. Consequently, its concentration remains very small. Our results show that the follow-up reactions of the radical in hydrocarbons or ethers as solvents are primarily the dimerization (Eq. (12)) at lower temperatures and hydrogen abstraction at higher temperatures (see below and Refs. [19,28]). Thus, the disilane thermolyzes in mesitylene at 100 °C in a first order reaction to form quantitative amounts of supersilane ($t\text{Bu}_3\text{SiSi}t\text{Bu}_3 + 2\text{H} \rightarrow 2t\text{Bu}_3\text{SiH}$). As the activation energy for this process which can more or less be equated with the SiSi bond dissociation energy amounts to 160 kJ mol^{-1} [19], the SiSi bond in tBu$_3$Si–SitBu$_3$ is considerably weaker than in normal disilanes, where the SiSi bond dissociation energy amounts to 285 kJ mol^{-1} [29]. In this connection, it should be noted that Mes$_3$Si–SiMes$_3$ is said to dissociate in two radicals Mes$_3$Si$^\bullet$ below 0 °C [29].

2.3.2. *Reactivity*

The supersilyl radical tBu$_3$Si$^\bullet$ shows a high tendency for abstraction of atoms or groups from chemical substances. The hydrogen abstraction has already been mentioned. In fact, the thermolysis of superdisilane in organic solvents RH leads via Eq. (13) to supersilane and to secondary products of the hereby produced radicals R$^\bullet$:

$$\mathrm{RH} \xrightarrow[-t\mathrm{Bu_3SiH}]{+1/2(t\mathrm{Bu_3Si})_2} \mathrm{R}^\bullet \rightarrow \text{secondary products} \qquad (13)$$

For example, the thermolysis of superdisilane in tetrahydrofuran THF, or in dibutyl ether nBu$_2$O, or in cycloheptane C$_7$H$_{14}$, respectively, at 120 °C leads to supersilane and – besides supersilyl-free products – to the following supersilylated compounds [28]: To 1-supersilyl-tetrahydrofuran tBu$_3$SiC$_4$H$_7$O, or to nBu–O–CH(SitBu$_3$)–CH$_2$–CH$_2$–CH$_3$, nBu–O–SitBu$_3$ and tBu$_3$Si–CH$_2$–CH=CH–CH$_3$, or to supersilyl–cycloheptane tBu$_3$SiC$_7$H$_{13}$, respectively. Benzene, obviously, is not attacked by thermolyzing superdisilane, as is shown by the absence of tBu$_3$SiD as a consequence of thermolysis of (tBu$_3$Si)$_2$ in C$_6$D$_6$ at 110 °C. In fact, tBu$_3$SiH and many supersilyl compounds, derived from the reaction of tBu$_3$Si$^\bullet$ with superdisilane (main product (tBu$_3$SiCH$_2$)$_2$C=CH$_2$), are formed [28].

The cleavage of CH bonds by supersilyl radicals is only one example out of the class of main group element bond splittings by tBu$_3$Si$^\bullet$. For example, superdisilane reacts at elevated temperatures according to Eq. (14) with halogens X$_2$ by formation of colorless, waxy supersilylated halogens tBu$_3$SiX [19] which indeed are better produced from tBu$_3$SiH and SbF$_5$, Cl$_2$, Br$_2$, I$_2$ [9], or from tBu$_3$SiBr and KHF$_2$ in refluxing methanol [23]. Unfortunately, it has not yet been possible to obtain crystals of the halogenides which are suitable for X-ray structure analysis.

$$(t\mathrm{Bu_3Si})_2 + \mathrm{X_2} \xrightarrow[(\mathrm{X=F,Cl,Br,I})]{} 2t\mathrm{Bu_3SiX} \qquad (14)$$

Over and above that, superdisilane attacks chalcogens Y$_n$ (Y = S, Se, Te) at temperatures above 100 °C under formation of chalcogenides (tBu$_3$Si)$_2$Y$_n$ (cf. Eq. (15) and Ref. [19]) which are in the case of bis(supersilyl)sulfides colorless to yellow (n = 2–6), in the case of bis(supersilyl)selenides pale to dark red (n = 1–4) and in the case of bis(supersilyl)tellurides pale to dark blue (n = 1, 2). No oxides (tBu$_3$Si)$_2$O$_n$ (n = 1, 2) and no monosulfide (tBu$_3$Si)$_2$S are formed from (tBu$_3$Si)$_2$ and O$_2$ or S$_8$, respectively (see Section 2.4.2).

$$(t\mathrm{Bu_3Si})_2 + n/m\mathrm{Y}_m \xrightarrow[(\mathrm{Y=S,Se,Te})]{} (t\mathrm{Bu_3Si})_2\mathrm{Y}_n \qquad (15)$$

In fact, oxygen reacts with $(t\mathrm{Bu_3Si})_2$ at increased temperatures with the formation of many products, one of which is $t\mathrm{Bu_3SiOH}$.

Whereas all elements of the seventh and sixth main group are attacked at elevated temperatures by superdisilane, only white phosphorus from the elements of the remaining fifth to first main group reacts with $(t\mathrm{Bu_3Si})_2$ (see Section 3.2). For all inactive main group elements only the typical thermolysis products of $t\mathrm{Bu_3Si{-}Si}t\mathrm{Bu_3}$ are formed (see above).

Another important stabilizing reaction of supersilyl radicals is their addition to unsaturated chemical species such as nitrogen monoxide which reacts with superdisilane according to Eq. (16) with formation of bis(supersilyl)hyponitrite [19]:

$$(t\mathrm{Bu_3Si})_2 + 2\mathrm{NO} \rightarrow t\mathrm{Bu_3Si-O-N=N-O-Si}t\mathrm{Bu_3} \tag{16}$$

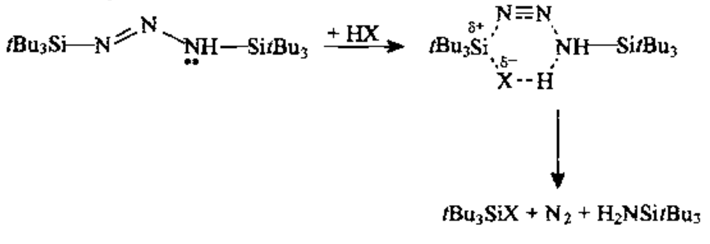
Butadiene $\mathrm{CH_2{=}CH{-}CH{=}CH_2}$, as another example of an unsaturated compound, reacts with superdisilane at 100 °C to form oligomeric to polymeric products [19]. The degree of polymerisation is small if $(t\mathrm{Bu_3Si})_2$ is in excess, but large if butadiene is in excess. In the latter case the disilane acts as a polymerisation starter, transferring butadiene into a colorless glass-like product, sparingly soluble in organic media. Dimethylbutadiene $\mathrm{CH_2{=}CMe{-}CMe{=}CH_2}$, on the other hand, is transformed by $(t\mathrm{Bu_3Si})_2$ in $\mathrm{C_6D_6}$ at 120 °C in three days to *cis*- and *trans*-$t\mathrm{Bu_3Si{-}CH_2{-}CMe{=}CMe{-}CH_2{-}Si}t\mathrm{Bu_3}$ [19].

2.4. *"Supersilyl cations"*

2.4.1. *Syntheses*

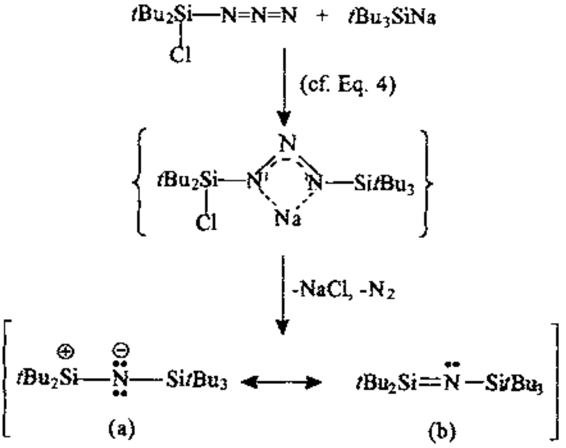
Unlike supersilyl anions which exist as isolable individuals and supersilyl radicals which at least exist as reaction intermediates, supersilyl cations are not, as yet, accessible even as intermediates in the form of species with a planar central silicon atom which is bound to three single bonded neighbors [30]. At best, they exist in a strong polarized form coupled with partners X having weak Lewis basicity. They act then as supersilylation agents (see below).

One such reagent is supersilyltriflate $t\mathrm{Bu_3SiOSO_2CF_3}$ which is easily obtained from $t\mathrm{Bu_3SiH}$ via $t\mathrm{Bu_3SiH} + \mathrm{CF_3SO_3H} \rightarrow \mathrm{H_2} + t\mathrm{Bu_3SiOTf}$ [31]. Furthermore, bis(supersilyl)triazene $(t\mathrm{Bu_3Si})_2\mathrm{N_3H}$ which is formed according to Eq. (4) has proved a special silylation agent for elemental hydrides like $\mathrm{H_2O}$, $\mathrm{H_2S}$, $\mathrm{NH_3}$, $\mathrm{N_2H_4}$ with somewhat acidic hydrogens [25]. The high silylation tendency of the triazene may depend according to Eq. (17) on a marked positivization of the azo bound supersilyl group after interchange of the amino group with the element hydrides XH. This, however, does not result in the liberation of supersilyl cations, as follows from the fact that strong acids give isolable salts with the triazene [25].



(17)

In this connection, it is worth mentioning that the hypothetical supersilyl cation $t\mathrm{Bu_3Si^+}$, after exchanging one of its tBu groups by a $t\mathrm{Bu_3SiN^-}$ anion-radical, becomes an isolable species which according to Eq. (18) was prepared for the first time by reaction of $t\mathrm{Bu_3SiNa}$ with the silylazide $t\mathrm{Bu_2SiClN_3}$ [17] and which gains its metastability by resonance [a ↔ b] (for another route of preparation of the latter compound cf. Ref. [31a]). In fact, this silaneimine $t\mathrm{Bu_2Si{=}N{-}Si}t\mathrm{Bu_3}$ represents – at least in the resonance hybrid form (a) – a silyl cation, because it has a positive charge and a coordination number of three for the planar silicon $\mathrm{C_2SiN}$ (for a homologous silanephosphimin $t\mathrm{Bu_2Si{=}P{-}Si}t\mathrm{Bu_3}$ cf. Ref. [31]).



(Si=N = 1.568Å; N-Si = 1.695Å; SiNSi = 178°)

(18)

2.4.2. Reactivity

2.4.2.1. Supersilyl halides, triflate, triazenide. The more or less positively polarized supersilyl cations in compounds $t\mathrm{Bu_3Si^{\delta+}X^{\delta-}}$ (X = electronegative group) act formally as Lewis acids which are able to combine with Lewis bases. In fact, as in Eq. (19), the reactions of $t\mathrm{Bu_3SiX}$ with the bases which may also be called silylations are nucleophilic substitutions at the supersilyl silicon and, therefore, are somewhat slow, due to steric factors:

$$t\mathrm{Bu_3Si-X+Nu^-}\longrightarrow t\mathrm{Bu_3Si-Nu+X^-} \tag{19}$$

Supersilylhalides $t\mathrm{Bu_3Si{-}Hal}$ are very poor silylating agents [6,9,12,14]. It is mostly the hard and small nucleophiles like fluoride $\mathrm{F^-}$, azide $\mathrm{N_3^-}$ or hydroxide $\mathrm{OH^-}$ which can lead to the desired substitution products (e.g. $t\mathrm{Bu_3Si{-}F}$, $t\mathrm{Bu_3Si{-}N_3}$, $t\mathrm{Bu_3Si{-}OH}$) in reasonable time. On the other hand, amide $\mathrm{NH_2^-}$ does not undergo any reaction even in boiling toluene [11]. In fact, supersilyl amide $t\mathrm{Bu_3Si{-}NH_2}$ was first prepared by the reduction of the azide $t\mathrm{Bu_3Si{-}N_3}$ [11].

A stronger silylating agent, supersilyl triflate $t\mathrm{Bu_3Si{-}OTf}$, reacts much more easily with $\mathrm{NH_2^-}$ to form $t\mathrm{Bu_3Si{-}NH_2}$. The same holds for other element hydride anions like hydroxide OH^-, hydrogensulfide SH^-, dihydrogenphosphide PH_2^-, hydrazide $N_2H_3^-$, which after Eqs. (20), (21) and (22) are supersilylated under formation of tBu$_3$Si–OH, tBu$_3$Si–SH, tBu$_3$Si–PH$_2$, tBu$_3$Si–N$_2$H$_3$ [19,31,32].

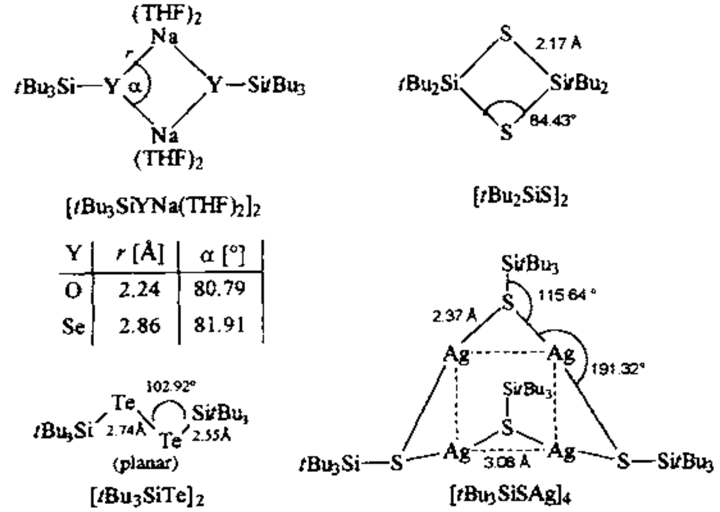
Bis(supersilyl)triazene (tBu$_3$Si)$_2$N$_3$H acts as a stronger silylation agent than the triflate. It plays an excellent role for supersilylations of proton active compounds, even if they are bulky like tBu$_3$Si–OH, tBu$_3$Si–SH, tBu$_3$Si–N$_2$H$_3$ (cf. Eqs. (20), (22) and Ref. [25]).

$$YH^- \xrightarrow[-OTf]{+tBu_3SiOTf} tBu_3Si-YH \xrightarrow[-N_2,\,-tBu_3SiNH_2]{+(tBu_3Si)_2N_3H} tBu_3Si-Y-SitBu_3 \tag{20}$$

$$ZH_2^- \xrightarrow[-OTf]{+tBu_3SiOTf} tBu_3Si-ZH_2\,(Z=N,\ P) \tag{21}$$

$$N_2H_3^- \xrightarrow[-OTf]{+tBu_3SiOTf} tBu_3Si-N_2H_3 \xrightarrow[-N_2,\,-tBu_3SiNH_2]{+(tBu_3Si)_2N_3H} (tBu_3Si)_2N_2H_2 \tag{22}$$

Reactions of type Eq. (20) present for the first time colorless bis(supersilyl)oxide (tBu$_3$Si)$_2$O and light yellow bis(supersilyl)sulfide (tBu$_3$Si)$_2$S which in fact are members of the class of supersilylated chalcogens. As to X-ray structure analysis the former and obviously also the latter compound contain linear SiYSi groups (SiO distance 1.67 Å) [15]. This is a consequence of the bulky supersilyl groups. Even when the angle opening as in bis(supersilyl)amine (tBu$_3$Si)$_2$NH (for preparation see Eq. (4)) is strongly hindered by the hydrogen bound to nitrogen the supersilyl groups bring about surprisingly large bond angles and the compound has almost a T-type structure at nitrogen [15].

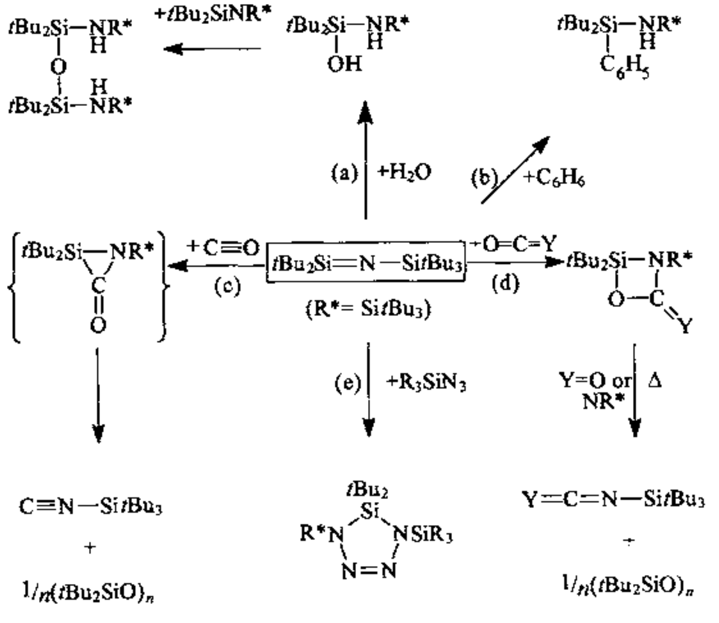


Y	r [Å]	α [°]
O	2.24	80.79
Se	2.86	81.91

Fig. 4. Crystal structures of [tBu$_3$SiONa(THF)$_2$]$_2$ (X-ray; H. Borrmann), [tBu$_3$SiSeNa(THF)$_2$]$_2$ (X-ray; H. Borrmann), (tBu$_2$SiS)$_2$ (X-ray; H. Borrmann), [tBu$_3$SiSAg]$_4$ (X-ray; K. Polborn) and (tBu$_3$Si)$_2$Te$_2$ (X-ray; H. Nöth and J. Knizek).

Besides the mentioned chalcogenides light red bis(supersilyl)selenide $(t\mathrm{Bu_3Si})_2\mathrm{Se}$, light blue bis(supersilyl)telluride $(t\mathrm{Bu_3Si})_2\mathrm{Te}$, yellow bis(supersilyl)disulfide $(t\mathrm{Bu_3Si})_2\mathrm{S_2}$, red bis(supersilyl)diselenide $(t\mathrm{Bu_3Si})_2\mathrm{Se_2}$ and blue bis(supersilyl) ditelluride $(t\mathrm{Bu_3Si})_2\mathrm{Te_2}$ are known (for preparation cf. Eqs. (8), (15), Ref. [19,24]; for X-ray structure analysis of the ditelluride cf. Fig. 4). Also colorless supersilylhydrogenchalcogenides $t\mathrm{Bu_3Si{-}YH}$ of all chalcogens (Y = O, S, Se, Te) exist. They are obtained by hydrolysis of $t\mathrm{Bu_3SiX}$ (cf. Eq. (19) and Ref. [9]) or by protolysis of sodium supersilylchalcogenids $t\mathrm{Bu_3Si{-}YNa}$ with strong acids [25,31] (for preparation of colorless $t\mathrm{Bu_3Si{-}YNa}$ cf. Eq. (10)). X-ray structure analysis of the THF adducts of $t\mathrm{Bu_3Si{-}YNa}$ (Y = O, Se) shows the compounds to be dimeric with planar four-membered YNaYNa rings (cf. Fig. 4 and Ref. [24]). In this connection, I wish to point to a reaction of $t\mathrm{Bu_3Si{-}SNa}$ with AgF which leads to tetrameric $t\mathrm{Bu_3Si{-}SAg}$ (cf. Fig. 4 and Ref. [24]; for $t\mathrm{Bu_3Si{-}PCu_2}$ cf. Ref. [60b]). Over and above that, $t\mathrm{Bu_3Si{-}SH}$ thermolizes in the presence of catalytic amounts of the acid $\mathrm{CF_3SO_3H}$ at elevated temperatures to $(t\mathrm{Bu_2SiS})_2$ with a planar four-memberd SiSSiS-ring (cf. Fig. 4 and Ref. [24]); in fact, the thermolysis belongs to the seldom observed reactions where supersilyl groups are attacked.

2.4.2.2. Silaneimine $t\mathrm{Bu_2Si{=}N{-}Si}t\mathrm{Bu_3}$. It is no wonder that the mentioned silaneimine (Eq. (18)) acts as a strong silylating agent which, as in Eqs. (23)a and b, transforms water even at low temperature into a sterically overloaded disiloxane [17], and silylates benzene. Furthermore, it adds carbon monoxide and dioxide as in Eqs. (23)c and d under formation of supersilyl isocyanide $t\mathrm{Bu_3Si{-}NC}$ [32], supersilyl isocyanate $t\mathrm{Bu_3Si{-}NCO}$ [32] and bis(supersilyl)carbodiimide $t\mathrm{Bu_3Si{-}N{=}C{=}N{-}Si}t\mathrm{Bu_3}$ [32]. The reactions, in a broad sense, may also be classified as silylations. The same holds for the additions of the silaneimine with silyl azides [17] which lead to tetrazolines according to Eq. (23e).



(23)

The mentioned supersilyl isocyanide $t\mathrm{Bu_3Si{-}NC}$ ($\nu_{\mathrm{NC}} = 2068\ \mathrm{cm^{-1}}$) represents an example of supersilylated pseudohalogens. It is an isomer of the longer known supersilyl cyanide $t\mathrm{Bu_3Si{-}CN}$ ($\nu_{\mathrm{NC}} = 2280\ \mathrm{cm^{-1}}$) which is formed, as are other pseudohalides $t\mathrm{Bu_3SiX}$ ($\mathrm{X = NCO, NCS, N_3}$), by silylation of KX with supersilyl halides [10] in the presence of 18-crown-6.

2.5. *The supersilyl group in supersilyl compounds*

By transfer of supersilyl anions, radicals and "cations", supersilyl derivatives of almost all main group elements have so far been obtained. These include supersilylated compounds of elements E^n (n = main group number) of type $t\mathrm{Bu_3SiE^{I}}$, $t\mathrm{Bu_3SiE^{II}X}$, $(t\mathrm{Bu_3Si})_2\mathrm{E^{II}}$, $t\mathrm{Bu_3SiE^{III}X_2}$, $(t\mathrm{Bu_3Si})_2\mathrm{E^{III}X}$, $t\mathrm{Bu_3SiE^{IV}X_3}$, $(t\mathrm{Bu_3Si})_2\mathrm{E^{IV}X_2}$, $t\mathrm{Bu_3SiE^{V}X_2}$, $(t\mathrm{Bu_3Si})_2\mathrm{E^{V}X}$, $t\mathrm{Bu_3SiE^{VI}X}$, $(t\mathrm{Bu_3Si})_2\mathrm{E^{VI}}$, $t\mathrm{Bu_3SiE^{VII}}$ (X = halogen and/or hydrogen as well as organyl; for compounds with element clusters see Section 3). Furthermore, some of these compounds have been structurally characterized.

In this connection, we – among others – were interested in the degree of pyramidalization of supersilyl. In fact, the CSiC angles of supersilyl groups bound to main group elements are, as a rule, within the range of 110 and 112° (cf. Fig. 5). If the additional substituent of supersilyl in supersilyl compounds is as small as hydrogen, then the central supersilyl angles are larger than 112° [33]. On the other hand, they are smaller than 110° if the additional substituents are as bulky as supersilyl [16]. The CSiC angle of $t\mathrm{Bu_3Si}$ in the PMDTA adduct of $t\mathrm{Bu_3SiNa}$ is surprisingly small (cf. Fig. 2). Obviously, the free electron pair of the negatively polarized supersilyl group in supersilyl sodium occupies an s-orbital of silicon which is less strongly involved in silicon–carbon bonds than in supersilyl compounds with positively polarized supersilyl groups. These findings suggest that the value of the CSiC angle in supersilyl compounds is not only determined by sterical effects (spatial expansion of the additional substituent), but also by electronic effects (electronegativity of

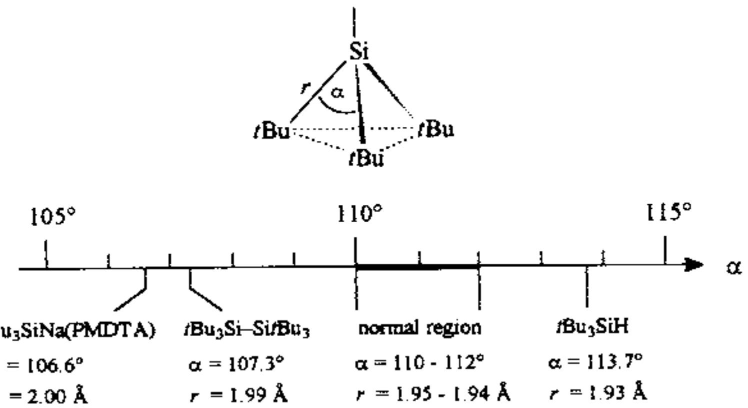


Fig. 5. Geometry of the supersilyl group.

the additional substituent). In this connection, determination of the structures of the supersilylhalides would be valuable. Furthermore, it should be pointed out that the silicon–carbon bond distances in supersilyl decrease as the CSiC angles increase.

To date, the value of the cone angle of supersilyl groups in compounds is not exactly known. In fact, this value is dependent on the distance of the supersilyl silicon to its neighbour. The angle may be in the region of 128–130° if the mentioned distance lies in the region 2.7–2.8 Å (cf. Fig. 8). From this follows the difficulty of synthesizing compounds with three supersilyls, bound to the same atom. On the other hand the coordination number of supersilyl silicon may exceed 4. This is shown with $(t\mathrm{Bu_3SiM})_2$ (cf. Fig. 2). Over and above that, associative nucleophilic substitutions at supersilyl silicon must proceed by way of intermediates with coordination number 5 of silicon.

3. Supersilylated main group element clusters

In the preceding section, supersilylated compounds of elements of the first, second, sixth and seventh main group (cf. Sections 2.2.1, 2.2.2, 2.4.2 and 2.3.2) are discussed in more detail in connection with general remarks about syntheses for supersilyl anions, radicals and "cations". This section is concerned with supersilylated compounds of elements of the third, fourth and fifth main group whereby the attention is especially directed to supersilylated clusters of these elements (for supersilylated clusters of the sixth main group elements cf. Section 2.4.2; supersilylated clusters of second main group elements – including Zn, Cd, Hg – are still unknown).

3.1. Supersilylated elements of the fifth main group

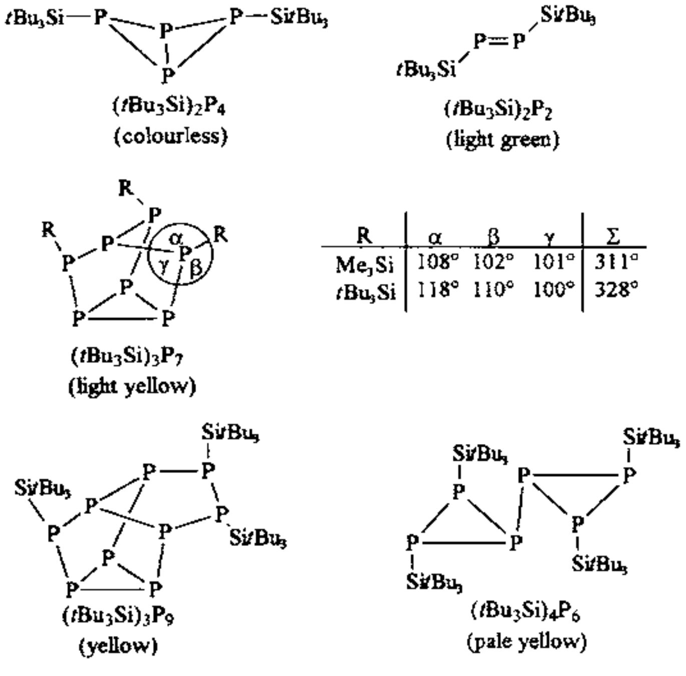
3.1.1. General remarks

Many supersilylated compounds of nitrogen are known. These include simple compounds like $t\mathrm{Bu_3Si\text{-}NH_2}$ and $(t\mathrm{Bu_3Si})_2\mathrm{NH}$ (cf. Eq. (21),(22)) as well as cluster compounds like $t\mathrm{Bu_3Si\text{–}NH\text{–}NH_2}$ and $t\mathrm{Bu_3Si\text{–}NH\text{–}NH\text{–}Si}t\mathrm{Bu_3}$ (cf. Eq. (22); obviously, oxidation under formation of $t\mathrm{Bu_3Si\text{–}N{=}N\text{–}Si}t\mathrm{Bu_3}$ is possible), $t\mathrm{Bu_3Si\text{–}N{=}N\text{–}NH\text{–}Si}t\mathrm{Bu_3}$ (cf. Eq. (4)), $t\mathrm{Bu_3Si\text{–}N{=}N{=}N}$ [10,11], $t\mathrm{Bu_3Si\text{-}NH\text{–}N{=}N\text{–}NH\text{–}Si}t\mathrm{Bu_3}$ (obtained by oxidation of $t\mathrm{Bu_3Si\text{–}N_2H_2Li}$ [32]). In fact, our studies here are still in a state of flux. Up to date, only a few supersilylated compounds of arsenic (obviously analogous to supersilylated compounds of phosphorus, see below), antimony (reaction of $t\mathrm{Bu_3SiNa}$ and $\mathrm{SbCl_3}$ leads to $(t\mathrm{Bu_3SiSb})_4$ [28]) and bismuth exist. Thoroughly studied are, on the other hand, supersilylated compounds of phosphorus which are now discussed in more detail. First of all, reactions of supersilyl radicals with white phosphorus are presented, then reactions of supersilyl anions with white phosphorus and with phosphorus trichloride.

3.1.2. Reactions of supersilyl radicals with white phosphorus

After heating equimolar quantities of superdisilane as a source for supersilyl radicals with white phosphorus for two days in THF at 100 °C, it is found that both colorless, thermostable, oxygen sensitive bis(supersilyl)tetraphosphane $(t\mathrm{Bu_3Si})_2\mathrm{P_4}$ and light yellow, thermo- and oxygen stable tris(supersilyl)heptaphosphane $(t\mathrm{Bu_3Si})_3\mathrm{P_7}$ are formed in the molar ratio of 3:4 [19,24,34]. According to the ^{31}P-NMR spectra the phosphanes have a bicyclo-tetraphosphane and a tricyclo-heptaphosphane structure (the latter with nortricyclan framework), shown in Fig. 6. An X-ray structure analysis of $(t\mathrm{Bu_3Si})_3\mathrm{P_7}$ confirmed the nortricyclan structure. Obviously, supersilyl radicals which are in equilibrium with superdisilan at 100 °C, attack white phosphorus under cleavage of a PP bond. The supersilyl phosphorus radical $t\mathrm{Bu_3SiP_4^{\bullet}}$ so formed then stabilizes by addition of a second supersilyl radical. The mechanism of the heptaphosphane is less straight forward.

Of particular interest was an answer to the question: how does the long known structure of $(\mathrm{Me_3Si})_3\mathrm{P_7}$ [35] change after substitution of trimethylsilyl by supersilyl groups? In fact, as is shown in Fig. 6, the silyl group exchange does not lead to any fundamental change (for example compression) of the cage structure (no change of angle γ) but the supersilyl groups, all of which are similarly directed, win space by



R	α	β	γ	Σ
Me₃Si	108°	102°	101°	311°
tBu₃Si	118°	110°	100°	328°

Fig. 6. Structures of polyphosphanes $(t\mathrm{Bu_3Si})_m\mathrm{P}_n$: $(t\mathrm{Bu_3Si})_2\mathrm{P_2}$ and $(t\mathrm{Bu_3Si})_2\mathrm{P_4}$ (NMR; K. Karaghiosoff), $(t\mathrm{Bu_3Si})_3\mathrm{P_7}$ (X-ray; D. Fenske, G. Baum), $(t\mathrm{Bu_3Si})_3\mathrm{P_9}$ (NMR; K. Karaghiosoff), $(t\mathrm{Bu_3Si})_4\mathrm{P_6}$ (NMR, K. Karaghiosoff).

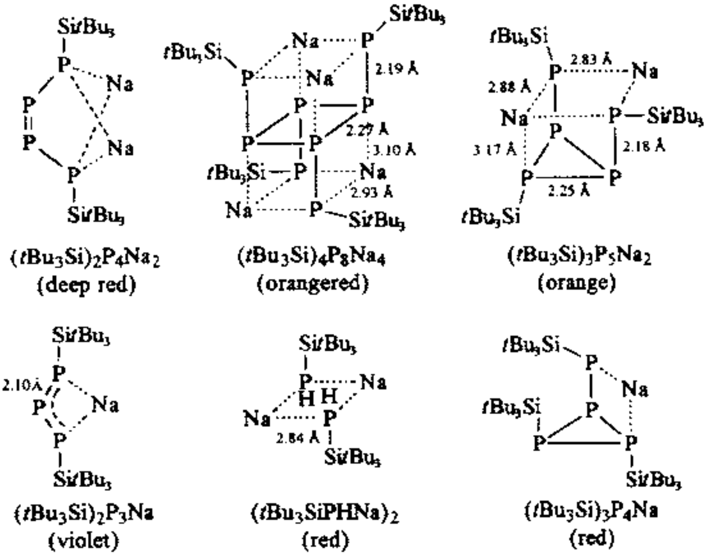
reduction of the pyramidalization of phosphorus, bound to supersilyl (increasing angles α and β).

The tetraphosphane $(t\mathrm{Bu_3Si})_2\mathrm{P_4}$ reacts according to: $(t\mathrm{Bu_3Si})_2\mathrm{P_4}+2e^- \rightleftarrows (t\mathrm{Bu_3Si})_2\mathrm{P}_4^{2-}$ with sodium as reduction agent to bis(supersilyl)tetraphosphide $(t\mathrm{Bu_3Si})_2\mathrm{P_4Na_2}$ (cf. Section 3.1.3) and according to: $(t\mathrm{Bu_3Si})_2\mathrm{P_4}+t\mathrm{Bu_3SiNa} \rightarrow (t\mathrm{Bu_3Si})_3\mathrm{P_4Na}$ with supersilyl sodium as Lewis base to the red THF adduct of the tris(supersilyl)tetraphosphide $(t\mathrm{Bu_3Si})_3\mathrm{P_4Na}$ [24]. The latter compound may also be synthesized by reaction according to $(t\mathrm{Bu_3Si})_3\mathrm{P_7}+2t\mathrm{Bu_3SiNa} \rightarrow (t\mathrm{Bu_3Si})_2\mathrm{P_3Na}+(t\mathrm{Bu_3Si})_3\mathrm{P_4Na}$ [24]. The tris(supersilyl)tetraphosphide represents a sodium salt of 1-(supersilylphosphanyl)-*trans*-bis(supersilyl)-cyclotriphosphane $(t\mathrm{Bu_3SiPH})(t\mathrm{Bu_3Si})_2\mathrm{P_3}$ as shown by ^{31}P-NMR spectra (cf. Fig. 7 and for bis(supersilyl)triphosphide Eq. (27)).

3.1.3. *Reactions of supersilyl anions with white phosphorus*

The reaction of supersilyl sodium as a source for supersilyl anions with white phosphorus proceeds in THF much faster than the reaction with superdisilane (see above), that is at lower temperatures. In fact, supersilyloligophosphides of the general formula $(t\mathrm{Bu_3Si})_m\mathrm{P}_n\mathrm{Na}_p$ are formed, the numbers m, n and p of which are essentially determined by the stoichiometry of the educts, $t\mathrm{Bu_3SiNa}$ and $\mathrm{P_4}$, as well as the reaction temperature and the solvent used [24].

For example, as in Eq. (24), reaction of $\mathrm{P_4}$ in THF or DME (dimethoxyethane) with $t\mathrm{Bu_3SiNa}$ in molar ratio 1:2 at −78 °C leads quantitatively to deep red, air-



$(t\mathrm{Bu_3Si})_2\mathrm{P_4Na_2}$ (deep red) **$(t\mathrm{Bu_3Si})_4\mathrm{P_8Na_4}$ (orangered)** **$(t\mathrm{Bu_3Si})_3\mathrm{P_5Na_2}$ (orange)**

$(t\mathrm{Bu_3Si})_2\mathrm{P_3Na}$ (violet) **$(t\mathrm{Bu_3SiPHNa})_2$ (red)** **$(t\mathrm{Bu_3Si})_3\mathrm{P_4Na}$ (red)**

Fig. 7. Structures of donor adducts of polyphosphides $(t\mathrm{Bu_3Si})_m\mathrm{P}_n\mathrm{Na}_p$ (donor molecules not shown): $(t\mathrm{Bu_3Si})_2\mathrm{P_4Na_2}$ (NMR; K. Karaghiosoff), $(t\mathrm{Bu_3Si})_4\mathrm{P_8Na_4}$ (X-ray; D. Fenske), $(t\mathrm{Bu_3Si})_3\mathrm{P_5Na_2}$ (X-ray; H. Nöth), $(t\mathrm{Bu_3Si})_2\mathrm{P_3Na}$ (X-ray; D. Fenske),$(t\mathrm{Bu_3Si})_2\mathrm{H_2P_2Na_2}$ (X-ray; H. Nöth and H. Schwenk), $(t\mathrm{Bu_3Si})_3\mathrm{P_4Na}$ (NMR; K. Karaghiosoff).

sensitive THF or DME adducts of the tetraphosphide $(t\mathrm{Bu_3Si})_2\mathrm{P_4Na_2}$ whereas the product of the reaction of $\mathrm{P_4}$ in TBME (*tert*-butylmethyl ether) with two moles of $t\mathrm{Bu_3SiNa}$ at −78 °C is an orange-red, air-sensitive TBME adduct of the octaphosphide $(t\mathrm{Bu_3Si})_4\mathrm{P_8Na_4}$ [36]. There exists an equilibrium between the tetra- and the octaphosphide: after exchanging the solvent of the tetraphosphide in THF by TBME or of the octaphosphide in TBME by THF or DME the octaphosphide is formed in the first case and the tetraphosphide in the second case. In DME/benzene or DME/pentane, mixtures of the tetra- and octaphosphide exist.

$$\begin{tikzcd}
 & \mathrm{P_4} + 2\,t\mathrm{Bu_3SiNa} \arrow[dl, "\text{(THF, or DME)}"'] \arrow[dr, "\text{(TBME)}"] & \\
\begin{array}{c}(t\mathrm{Bu_3Si})_2\mathrm{P_4Na_2}\\ \text{(as donor adduct)}\end{array} \arrow[rr, shift left, "\text{(TBME)}"] & & \begin{array}{c}\tfrac{1}{2}\,(t\mathrm{Bu_3Si})_4\mathrm{P_8Na_4}\\ \text{(as donor adduct)}\end{array} \arrow[ll, shift left, "\text{(THF)}"]
\end{tikzcd} \qquad (24)$$

According to ^{31}P-NMR spectra, the THF or DME adducts of the tetraphosphide (number of donor molecules yet unknown) have the structure shown in Fig. 7. It follows from this, that the tetraphosphide is a sodium salt of bis(supersilyl)-*cis*-2-tetraphosphene $t\mathrm{Bu_3Si{-}PH{-}P{=}P{-}PH{-}Si}t\mathrm{Bu_3}$ (see above for a homologous nitrogen compound). On the other hand, the DME adduct of the octaphosphide which crystallizes from DME/pentane at −25 °C represents, after X-ray structure analysis, a sodium salt of tetrakis(supersilylphosphanyl)cyclotetraphosphane $(t\mathrm{Bu_3SiPH})_4\mathrm{P_4}$ (cf. Fig. 7). It contains a $\mathrm{P_8Na_4}$ skeleton which forms a double cube with four P atoms in the second layer and two P and two Na atoms in alternating positions in the first and in the third layer (the Na atoms are coordinated with three phosphorus atoms each and, over and above that, with two oxygen atoms of an DME donor; see Fig. 7).

Obviously, the octaphosphide is a [2+2] cycloadduct of the tetraphosphide, whereby the formation tendency of the octaphosphide, which has a four membered ring of phosphorus atoms normally not preferred by phosphorus [37], may be due to building up a mixed cluster of phosphorus and sodium atoms. Nevertheless, in the course of [2+2] cycloaddition, both tetraphosphide molecules which take part in the reaction must change their configuration.

Oxidation of the bis(supersilyl)tetraphosphide and the tetrakis(supersilyl)octaphosphide with $(\mathrm{NC})_2\mathrm{C{=}C(CN)_2}$ (TCNE) in THF at room temperature leads to bicyclic $(t\mathrm{Bu_3Si})_2\mathrm{P_4}$ in the former case (cf. Fig. 6), and to a polyphosphane with unknown structure in the latter case [36]. The nature of products formed by protolysis of the tetraphosphide, on the other hand, depends strongly on the reaction conditions [24]. If a solution of the acid $\mathrm{CF_3SO_3H}$ in pentane is dropped slowly into a solution of twice the amount of the bis(supersilyl)tetraphosphide in THF at −78 °C, then, according to Eq. (25), a THF adduct of the orange pentaphosphide $(t\mathrm{Bu_3Si})_3\mathrm{P_5Na}$ as well as a red THF adduct of $t\mathrm{Bu_3SiPHNa}$ and other products are formed. Giving a solution of the tetraphosphide in THF to a solution of twice the amount of the acid $\mathrm{CF_3SO_3H}$ in pentane at −78 °C, yields the yellow nonaphosphane $(t\mathrm{Bu_3Si})_3\mathrm{P_9}$ as well as $t\mathrm{Bu_3SiPH_2}$ according to Eq. (26):

$$2(t\mathrm{Bu_3Si})_2\mathrm{P_4Na_2} \xrightarrow[-\text{“}\mathrm{P_2}\text{”},\,-\mathrm{Na^+}]{+\mathrm{H^+}} (t\mathrm{Bu_3Si})_3\mathrm{P_5Na_2} + t\mathrm{Bu_3SiPHNa} \qquad (25)$$

$$3(t\mathrm{Bu_3Si})_2\mathrm{P_4Na_2} \xrightarrow[-6\mathrm{Na^+}]{+6\mathrm{H^+}} (t\mathrm{Bu_3Si})_3\mathrm{P_9} + 3t\mathrm{Bu_3SiPH_2} \qquad (26)$$

In fact, the pentaphosphide is also obtained from the reaction of $\mathrm{P_4}$ and $t\mathrm{Bu_3SiNa}$ (molar ratio 1:2) in THF/toluene at room temperature [24]. As to X-ray structure analysis of a THF adduct, the pentaphosphide represents a sodium salt of bis(supersilylphosphanyl)(supersilyl)cyclotriphosphane $(t\mathrm{Bu_3SiPH})_2(t\mathrm{Bu_3Si})\mathrm{P_3}$ (cf. Fig. 7). Obviously, it contains a three-membered ring of three phosphorus atoms, the substituents of which are two $t\mathrm{Bu_3SiPNa}$ groups in the *cis* position and a $t\mathrm{Bu_3Si}$ group in the *trans* position to these (the Na atoms are coordinated to two or three P atoms, respectively, and each also with the O atoms of two THF molecules). So far the phosphorus skeleton looks as if it is built up by [1+2] cycloaddition of the phosphanidene $t\mathrm{Bu_3SiP}$ with the mentioned bis(supersilyl)tetraphosphide.

The sodium salt $t\mathrm{Bu_3SiPHNa}$ of supersilylphosphane $t\mathrm{Bu_3SiPH_2}$ (cf. Eq. (21)) which is also obtained by reaction of $t\mathrm{Bu_3SiPH_2}$ and $t\mathrm{Bu_3SiNa}$ in THF crystallizes from THF at −25 °C [24]. As to X-ray structure analysis, it contains a four-membered ring with alternating P and Na atoms (cf. Fig. 7; the Na atoms are coordinated with two P atoms and O atoms of two THF molecules).

Further, from the ^{31}P-NMR spectra, nonaphosphane has probably the cage structure, shown in Fig. 6, and therefore represents a supersilyl derivative of nonaphosphane $\mathrm{P_9H_3}$ which is said to have the very stable deltacyclan skeleton [37]. Possibly its formation from the tetraphosphide goes via the protonation product of $(t\mathrm{Bu_3Si})_2\mathrm{P_4Na_2}$, namely $t\mathrm{Bu_3Si{-}PH{-}P{=}P{-}PH{-}Si}t\mathrm{Bu_3}$, which transforms, under elimination of $t\mathrm{Bu_3Si{-}PH_2}$, into the “phosphaazide” $t\mathrm{Bu_3Si{-}P{=}P{=}P}$. The latter, then, may polymerize by way of the hexaphosphane $(t\mathrm{Bu_3SiP_3})_2 = (t\mathrm{Bu_3Si})_2\mathrm{P_6}$ under formation of the nonaphosphane $(t\mathrm{Bu_3SiP_3})_3 = (t\mathrm{Bu_3Si})_3\mathrm{P_9}$.

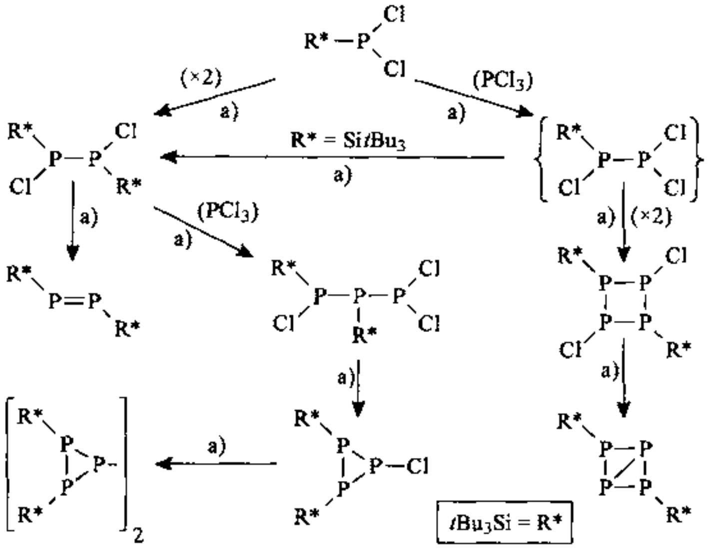
Obviously, the depolymerization of the nonaphosphane is brought about with supersilyl sodium in THF [24] which transforms $(t\mathrm{Bu_3SiP_3})_3$ quantitatively into the violet triphosphide $(t\mathrm{Bu_3Si})_2\mathrm{P_3Na}$ according to Eq. (27):

$$(t\mathrm{Bu_3Si})_3\mathrm{P_9} + 3t\mathrm{Bu_3SiNa} \rightarrow 3(t\mathrm{Bu_3Si})_2\mathrm{P_3Na} \qquad (27)$$

In fact, the triphosphide is also obtained from the reaction of $\mathrm{P_4}$ and $t\mathrm{Bu_3SiNa}$ in THF at room temperature [24]. As to X-ray structure analysis, the THF adduct of the triphosphide represents a sodium salt of bis(supersilyl)triphosphene $t\mathrm{Bu_3Si{-}P{=}P{-}PH{-}Si}t\mathrm{Bu_3}$ which is a homologue of $t\mathrm{Bu_3Si{-}N{=}N{-}NH{-}Si}t\mathrm{Bu_3}$ (cf. Eq. (4)). It contains a four-membered ring with three P and one Na atoms (equal PP-distances; the Na atoms are coordinated with two P atoms and O atoms of four THF molecules). For preparation of a tris(supersilyl)tetraphosphide $(t\mathrm{Bu_3Si})_3\mathrm{P_4Na}$ cf. Section 3.1.2.

3.1.4. Reactions of supersilyl anions with phosphorus trichloride

The reaction of donor-free supersilyl sodium as a source of supersilyl anions with PCl_3 is very complex [24]. Nevertheless, supersilylphosphorus dichloride $t\mathrm{Bu_3SiPCl_2}$ is formed according to Eq. (7) as a first reaction product (high yields of the dichlorophosphane are obtained by supersilylation of PCl_3 in heptane with $(t\mathrm{Bu_3Si})_2\mathrm{Zn}$). Then, $t\mathrm{Bu_3SiPCl_2}$ obviously reacts like $t\mathrm{Bu_3SiSCl}$ (cf. Eq. (8)) with $t\mathrm{Bu_3SiNa}$ under formation of element–element bonds. Certainly, there are more possibilities of reaction of tervalent phosphorus than of divalent sulfur. Up to date, some polyphosphanes $(t\mathrm{Bu_3Si})_m\mathrm{P}_n$, namely $(t\mathrm{Bu_3Si})_2\mathrm{P_2}$ (best prepared from $t\mathrm{Bu_3SiPCl_2}$ and Na in refluxing heptane), $(t\mathrm{Bu_3Si})_2\mathrm{P_4}$ (best prepared from P_4 and $(t\mathrm{Bu_3Si})_2$ in THF at 100 °C) and $(t\mathrm{Bu_3Si})_4\mathrm{P_6}$ (cf. Fig. 6), as well as some halogenated polyphosphanes, namely $(t\mathrm{Bu_3Si})_2\mathrm{P_2Cl_2}$, $(t\mathrm{Bu_3Si})_2\mathrm{P_3Cl}$ and $(t\mathrm{Bu_3Si})_2\mathrm{P_4Cl_2}$ could be identified by ^{31}P-NMR. Taking into consideration the reaction of SCl_2 and $t\mathrm{Bu_3SiNa}$ (Eq. (8)), the way of their formation from $t\mathrm{Bu_3SiPCl_2}$ under dehalogenation may be as in Eq. (28).



(28)

a) In each case: + R*Na. PP formation after to: >P–Cl + Cl–P< + R*Na → >PNa + Cl–P< + R*Cl → >P–P< + NaCl + R*Cl.

3.2. Supersilylated elements of the third main group

3.2.1. General remarks

To date, only a few supersilylated compounds of elements of the third main group are known. These include for boron only simple compounds such as $(t\mathrm{Bu_3Si})_2\mathrm{BF}$, $t\mathrm{Bu_3SiBBr_2}$, $t\mathrm{Bu_3SiBBr_2(py)}$ [38], whereas for aluminium, gallium, indium and thallium, compounds with element clusters are also known. They are now discussed in more detail. In fact, donor-free uncharged molecular compounds

$(RM)_n$ and $(R_2M)_2$ (R = organic or inorganic substituent) with clusters of the boron homologues M have been known for only about ten years. In general, clusters of type $(RM)_n$ and $(R_2M)_2$ disproportionate as to Eq. (29).

$$6RM \rightarrow 3R_2M + 3M \rightarrow 2R_3M + 4M \tag{29}$$

However, this process can be stopped at the $(RM)_n$ or the $(R_2M)_2$ stage by using more or less bulky substituents. Known examples of $(RM)_4$ are those with $R = C_5Me_5$, $C(SiMe_3)_3$, $Si(SiMe_3)_3$, $Si(CMe_3)_3$, known examples of $(R_2M)_2$ are those with $R = CH(SiMe_3)_2$, 2,4,6-iPr$_3$C$_6$H$_2$, 2,4,6-$(CF_3)_3C_6H_2$, $Si(SiMe_3)_3$, $Si(CMe_3)_3$ [39].

3.2.2. *Supersilylated aluminium and gallium*

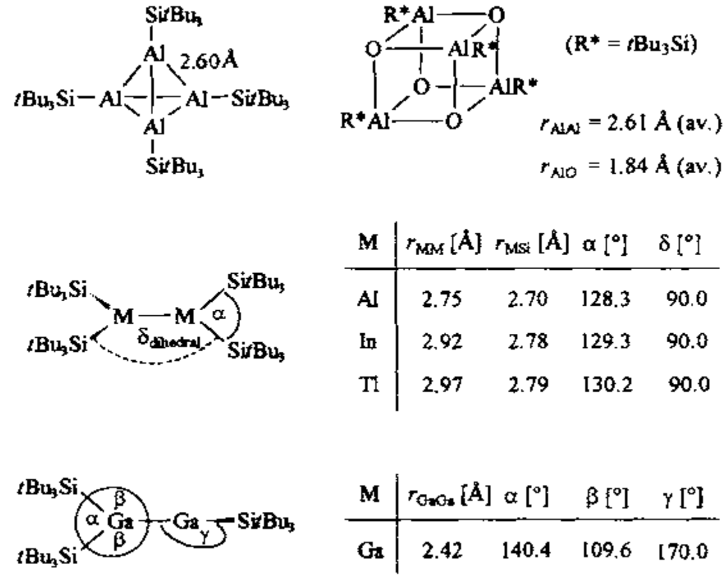
On warming a solution of equimolar amounts of AlCl in toluene/Et_2O and tBu$_3$SiNa in Bu_2O from −78 °C, the solution becomes dark red at about 0 °C [2,40]. According to MS, NMR and ESR, tetrameric supersilylaluminium tBu$_3$SiAl has been formed according to Eq. (30), as well as other products and traces of a radical which contains Al.

$$4AlX + 4tBu_3SiNa \xrightarrow[-4NaX]{} (tBu_3SiAl)_4 \tag{30}$$

The supersilylaluminium $(tBu_3SiAl)_4$, obtained in this way, could so far not be isolated by crystallisation but by sublimation at 180 °C under high vacuum as a deep violet, X-ray amorphous, pentane-soluble, oxygen- and moisture-sensitive solid [40]. It has the same tetrahedral structure as tetrameric pentamethylcyclopentadienyl aluminium $(C_5Me_5Al)_4$ [41] and represents tetrakis(supersilyl)-tetrahedrotetraalane (cf. below Fig. 8; for $(tBu_3SiGa)_4$ cf.).

Ab-initio calculations [41a] clearly confirm the tetrahedral structure of the tetrameric supersilyl aluminium. According to these calculations, an electron pair is ascribed to every surface of the Al_4 tetrahedron which formally occupies a three-center bonding molecular orbital. The energy of every AlAl bond amounts to about 100 kJ mol^{-1}. Indeed, the bonds are much stronger than those in the tetrameric cyclopentadienyl aluminium. As a consequence, the latter compound, according to X-ray structure analysis, has comparably long AlAl bonds of 2.77 Å and, with AlAl bond energies of only about 25 kJ mol^{-1}, is not very thermostable whereas the supersilyl derivative contains, from *ab-initio* calculations, short AlAl bonds of about 2.60 Å and does not decompose below 180 °C. As expected, supersilyl substituents stabilize the AlAl bonds of the tetraalatetrahedrane.

The tetrameric supersilyl aluminium may also be prepared analogous to Eq. (30) on warming a cooled solution of $[AlI(NEt_3)]_4$ [42] and tBu$_3$SiNa in heptane/toluene. Thereby, reaction takes place at about 0 °C under formation of a violet solution from which, after exchanging the solvent by heptane and separation of unsoluble NaI, violet, very oxygen-sensitive $(tBu_3SiAl)_4$ crystallizes at −23 °C [43]. As to X-ray structure analysis, it has the terahedrane structure, shown in Fig. 8. It is extremely sensitive to oxygen O_2 by which it is transformed into $(tBuSiAlO)_4$ (there



M	r_{MM} [Å]	r_{MSi} [Å]	α [°]	δ [°]
Al	2.75	2.70	128.3	90.0
In	2.92	2.78	129.3	90.0
Tl	2.97	2.79	130.2	90.0

M	r_{GaGa} [Å]	α [°]	β [°]	γ [°]
Ga	2.42	140.4	109.6	170.0

Fig. 8. Structures of clusters $(t\mathrm{Bu_3Si})_m\mathrm{M}_n$ of the heavier third main group elements: $(t\mathrm{Bu_3SiAl})_4$ (X-ray; H. Schnöckel and A. Purath), $(t\mathrm{Bu_3SiAlO})_4$ (X-ray; H. Nöth and H. Schwenk), $(t\mathrm{Bu_3Si})_4\mathrm{Al}_2$ (X-ray, H. Nöth and I. Krossing), $(t\mathrm{Bu_3Si})_4\mathrm{In}_2$ (X-ray; H. Nöth and M. Schmidt), $(t\mathrm{Bu_3Si})_4\mathrm{Tl}_2$ (X-ray; H. Nöth and H. Schwenk), $(t\mathrm{Bu_3Si})_3\mathrm{Ga}_2$ (X-ray; H. Nöth and H. Schwenk).

appear to be no partly oxidized species [43]). Obviously, there is no change of the geometry of the $\mathrm{Al_4}$ tetrahedron in the course of $(t\mathrm{Bu_3SiAl})_4$ oxidation, that is by setting up oxygen atoms on the $\mathrm{Al_3}$ surfaces of the $\mathrm{Al_4}$ tetrahedron (cf. Fig. 8).

As supersilyl sodium works as an agent for exchanging halogenide by supersilyl and, over and above that, as a dehalogenation reagent, it was sensible to study the reactions of $t\mathrm{Bu_3SiNa}$ with aluminium trihalides which could lead to tetrameric supersilyl aluminium according to: $4\mathrm{AlX_3} + 8t\mathrm{Bu_3SiNa} \rightarrow (t\mathrm{Bu_3SiAl})_4 + 4t\mathrm{Bu_3SiX} + 8\mathrm{NaX}$. In fact, supersilyl sodium $t\mathrm{Bu_3SiNa}$ (donor-free or as an adduct with two THF) transforms $\mathrm{AlCl_3(THF)}$ or $\mathrm{AlBr_3(NEtMe_2)}$ in heptane at room temperature into colorless donor adducts of mono(supersilyl)aluminium dihalides $t\mathrm{Bu_3SiAlX_2}$ (X = Cl, Br), and also $\mathrm{AlCl_3}$ or $\mathrm{AlBr_3}$ in heptane at elevated or at room temperature directly into colorless bis(supersilyl)aluminum monohalides $(t\mathrm{Bu_3Si})_2\mathrm{AlX}$ (X = Cl, Br), even though the molar ratio of the adducts amounts to 2:1 in the former and 1:1 in the latter case [22]. The same holds, obviously, for donor adducts and donor-free $\mathrm{GaCl_3}$ as well as $\mathrm{GaBr_3}$ [22]. Bis(supersilyl)aluminum chloride may be further attacked by $t\mathrm{Bu_3SiNa}$ under formation of red tetrakis(supersilyl)dialane $(t\mathrm{Bu_3Si})_4\mathrm{Al_2}$, the structure of which, from the X-ray structure analysis, is shown in Fig. 8. In all, the latter compound is formed from a $\mathrm{Et_2O}$ adduct of $\mathrm{AlCl_3}$ and $t\mathrm{Bu_3SiNa}$ in heptane at about 40 °C via Eq. (31) and crystallizes from pentane at −23 °C [22].

$$2\mathrm{AlCl_3} + 6t\mathrm{Bu_3SiNa} \rightarrow (t\mathrm{Bu_3Si})_4\mathrm{Al_2} + (t\mathrm{Bu_3Si})_2 + 6\mathrm{NaCl} \qquad (31)$$

Unexpectedly, $\mathrm{GaCl_3}$ as well as $(t\mathrm{Bu_3Si})_2\mathrm{GaCl}$ reacts with supersilyl sodium in heptane at room temperature according to Eq. (32) under formation of dark blue tris(supersilyl)digallyl $(t\mathrm{Bu_3Si})_3\mathrm{Ga_2}$, the X-ray structure of which is shown in Fig. 8 [44] (for $(t\mathrm{Bu_3SiGa})_4$ and $(t\mathrm{Bu_3Si})_3\mathrm{Ga_2Na}$ cf. Ref [60c]).

$$2\mathrm{GaCl_3} + 6t\mathrm{Bu_3SiNa} \rightarrow (t\mathrm{Bu_3Si})_3\mathrm{Ga}_2^{\bullet} + 1.5(t\mathrm{Bu_3Si})_2 + 6\mathrm{NaCl} \qquad (32)$$

3.2.3. *Supersilylated indium and thallium*

To our surprise, the reactions of InBr and TlBr with $t\mathrm{Bu_3SiNa}$ in THF at −78 °C did not lead – as in case of reactions of AlCl or AlI with $t\mathrm{Bu_3SiNa}$ (see above) – to tetrahedranes $(t\mathrm{Bu_3SiM})_4$ (M = In, Tl) but gave deep violet tetrakis(supersilyl)diindane $(t\mathrm{Bu_3Si})_4\mathrm{M_2}$ and black-green tetrakis(supersilyl)dithallane $(t\mathrm{Bu_3Si})_4\mathrm{Tl_2}$ according to Eq. (33), as well as $t\mathrm{Bu_3SiH}$, $t\mathrm{Bu_3SiBr}$ and $(t\mathrm{Bu_3Si})_2$. Traces of a radical which contain In or Tl are also found by ESR spectra (cf. $(t\mathrm{Bu_3Si})_3\mathrm{Ga_2}$, Eq. (32)).

$$4\mathrm{MBr} + 4t\mathrm{Bu_3SiNa} \rightarrow (t\mathrm{Bu_3Si})_4\mathrm{M_2} + 2\mathrm{M} + 4\mathrm{NaBr} \qquad (33)$$

$$(\mathrm{M} = \mathrm{In, Tl})$$

The compounds (crystals from pentane), the structures of which are shown in Fig. 8, [39] thermolyze at about 125 °C (In) or 52 °C (Tl). The diindane reacts with $\mathrm{AgF_2}$ in heptane at room temperature to give among others the bis(supersilyl)indium halide $(t\mathrm{Bu_3Si})_2\mathrm{InF}$, which decomposes in $\mathrm{C_6D_6}$ at 40 °C under formation of $t\mathrm{Bu_3SiF}$, $(t\mathrm{Bu_3Si})_2$ and In. The dithallan, on the other hand, is transformed by $\mathrm{AgF_2}$ directly into $t\mathrm{Bu_3SiF}$, $(t\mathrm{Bu_3Si})_2$ and Tl. This suggests from this an instability of the bis(supersilyl)thallium halide $(t\mathrm{Bu_3Si})_2\mathrm{TlF}$.

3.3. *Supersilylated elements of the fourth main group*

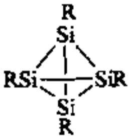
3.3.1. *General remarks*

To date, only a few supersilylated compounds of carbon are known. These include compounds such as $t\mathrm{Bu_3Si{-}CH}_{3-n}\mathrm{Br}_n$, $t\mathrm{Bu_3Si{-}CHX{-}CHX{-}Si}t\mathrm{Bu_3}$ (X = H, Cl, Br) and $t\mathrm{Bu_3Si{-}CX{=}CX{-}Si}t\mathrm{Bu_3}$ [9,14,32]. Certainly, a very large number of supersilyl carbon compounds are preparable. For silicon, germanium, tin and lead, many "simple" compounds of the types $t\mathrm{Bu_3SiEX_3}$, $(t\mathrm{Bu_3Si})_2\mathrm{EX_2}$ and $t\mathrm{Bu_3SiEX_2{-}EX_2Si}t\mathrm{Bu_3}$ exist (E = Si, Ge, Sn, Pb; X = H, organyls, halogens) [23,28,45,46]. In general, they were prepared (i) by supersilylation of element halides (e.g. $t\mathrm{Bu_3SiNa} + \mathrm{SiH_2Cl_2} \rightarrow t\mathrm{Bu_3SiSiH_2Cl} + \mathrm{NaCl}$), (ii) by condensation of supersilylated element halides (e.g. $2t\mathrm{Bu_3SiH_2Cl} + 2\mathrm{Na} \rightarrow t\mathrm{Bu_3SiSiH_2SiH_2Si}t\mathrm{Bu_3} + 2\mathrm{NaCl}$), (iii) by halogenation of supersilylated element hydrides or organyls (e.g. $t\mathrm{Bu_3SiSiH_2SiH_2Si}t\mathrm{Bu_3} + 4\mathrm{Br_2} \rightarrow t\mathrm{Bu_3SiSiBr_2SiBr_2Si}t\mathrm{Bu_3}$; $t\mathrm{Bu_3SiSnMe_2SnMe_2Si}t\mathrm{Bu_3} + 4\mathrm{SnCl_4} \rightarrow t\mathrm{Bu_3SiSnCl_2SnCl_2Si}t\mathrm{Bu_3} + 4\mathrm{MeSnCl_3}$); $t\mathrm{Bu_3SiSnPh_3} + 3\mathrm{HBr} \rightarrow t\mathrm{Bu_3SiSnBr_3} + 3\mathrm{PhH}$), and (iv) by hydrogenation of supersilylated element halides ($t\mathrm{Bu_3Si{-}GeCl_3} + 3\mathrm{H^-}$ from $\mathrm{LiAlH_4} \rightarrow t\mathrm{Bu_3Si{-}GeH_3} + 3\mathrm{Cl^-}$).

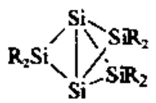
Now, supersilylated tetrahedranes of silicon and germanium are discussed in more detail.

3.3.2. Tetrakis(supersilyl)-tetrahedro-tetrasilane and -tetragermane

"The greatest challenges for silicon chemists are currently the syntheses of a tetrasilatetrahedrane $(RSi)_4$, a disilyne $(RSi)_2$ and a pentasila[1.1.1]propellane R_6Si_5," this was stated in a review from 1991 on cluster chemistry of the heavier elements of the fourth main group. In 1993, we then succeeded in preparing the first molecular tetrasilatetrahedrane [47].



$R-Si\equiv Si-R$



As a tetrasilatetrahedrane should be more stable than any larger cluster with the same total formula if it has sterically demanding substituents, we tried to synthesize a Si_4 cluster with supersilyl substituents $R = SitBu_3$. In fact, the synthesis of tetrakis (supersilyl)tetrasilatetrahedrane $(tBu_3Si)_4Si_4$ is simple: one adds the twofold quantity of supersilyl sodium in THF to a THF solution of the bis(supersilyl)disilane $tBu_3Si–SiBr_2–SiBr_2–SitBu_3$ at −20 °C in 10 min, and the tetrakis(supersilyl)tetrasilatetrahedrane forms quantitatively according to Eq. (34) during warm up of the solution.

$$2tBu_3Si-EX_2-EX_2-SitBu_3 \xrightarrow[-4tBu_3SiX,\ -4NaX]{+4tBu_3SiNa} (tBu_3SiE)_4 \tag{34}$$

(E/X = Si/Bv, Ga/Cl)

The cluster $(tBu_3SiSi)_4$ which forms yellow-orange crystals, is very thermostable. An X-ray structure analysis of the compound (cf. Fig. 10 and Ref. [47]), shows no peculiarities: the lengths of the *endo*- and *exo*cyclic SiSi bonds lie in the typical single bond region. The crystals display high thermo- and photostability and are stable to water and air. On the other hand, in solution the tetrahedrane is slowly oxidized by air and reacts with oxidants like Br_2 or TCNE. Reduction of the cluster in benzene with sodium is not observed.

By an analogous route as the Si_4 tetrahedron, tetrakis(supersilyl)tetragermatetrahedrane $(tBu_3Si)_4Ge_4$ is obtained from $tBu_3Si–GeCl_2–GeCl_2–SitBu_3$ and tBu_3SiNa in THF according to Eq. (34) in low yield together with other supersilyl-containing products [48]. It is also produced in better yields according to Eq. (35) by reaction of $GeCl_2$(dioxane) at room temperature.

$$4GeCl_2 + 6tBu_3SiNa \rightarrow (tBu_3SiGe)_4 + 2tBu_3SiCl + 6NaCl \tag{35}$$

Initially, only trichloro-tris(supersilyl)cyclotrigermane $(tBu_3SiGeCl)_3$ (cf. Fig. 9) forms together with $(tBu_3Si)_2GeCl_2$ as a pale yellow, oxidation-sensitive, hydrolysis-

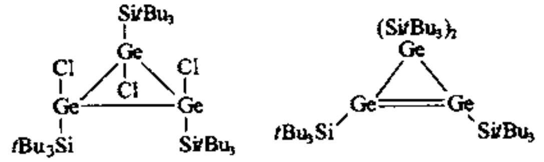


Fig. 9. Two products of the reaction of $GeCl_2$(dioxane) with tBu$_3$SiNa in THF (for (tBu$_3$SiGe)$_4$, also formed, see Fig. 10).

stable product (characterization by NMR) [48]. In the further course of the reaction, an unidentified product, the Ge_4 tetrahedron and a substance whose NMR shifts resemble those of tetrakis(supersilyl)cyclotrigermene (tBu$_3$Si)$_4$Ge$_3$, obtained recently from $GeCl_2$(dioxane) and tBu$_3$SiNa in THF (characterisation by X-ray structure analysis; cf. Fig. 9 and Ref. [49], [60d]), are found.

The cluster (tBu$_3$SiGe)$_4$ forms intense red crystals which hydrolyze slowly, and are rapidly oxidized by air. It can be reduced with sodium; among the products of the reaction is tBu$_3$SiNa. An X-ray structure analysis of the compound (cf. Fig. 10 and Ref. [48]) shows no peculiarities: the GeGe and GeSi distances lie in the typical single bond region.

Now, with the exception of N_4 and of (RSn)$_4$, compounds with a tetrahedral framework, constructed of atoms of one element, exist not only for silicon and germanium (see above), but for all next elements near Si and Ge in the periodic table, namely carbon [50], boron [51], aluminum (see Section 2.3.2), gallium [52, 60c], indium [53], antimony (Sb_4), arsenic (As_4) and phosphorus (P_4). This is shown in Fig. 10, from which it is also seen that the colors of the compounds shift from blue through red and yellow to colorless by going up a group of elements or along a period of elements from left to right. In the same directions the element–element bond distances decrease.

3.3.3. *Mechanism of the formation of tetrakis(supersilyl)-tetrahedro-tetrasilane*

The high yield of the tetrasilatetrahedrane from the reaction of tBu$_3$Si–SiBr$_2$–SiBr$_2$–SitBu$_3$ and tBu$_3$SiNa in THF points to a unique mechanism of its formation. Therefore, the question arises whether the cluster may be formed, according to Eq. (36), by [2+2] cycloaddition of two molecules of bis(supersilyl)disilyne which itself may be the product of debromination of the educt bis(supersilyl)-tetrabromodisilane.

$$(t\mathrm{Bu_3Si-SiBr_2})_2 \xrightarrow[-4\mathrm{Br}]{?} t\mathrm{Bu_3Si-Si{\equiv}Si-Si}t\mathrm{Bu_3} \xrightarrow{\times 2} (t\mathrm{Bu_3SiSi})_4 \qquad (36)$$

In order to get more insight into the mechanism of the formation of the tetrasilatetrahedrane, we first of all reacted partially brominated 1,2-bis(supersilyl)disilanes with supersilyl sodium because in the latter case the debromination should stop at earlier stages of cluster formation.

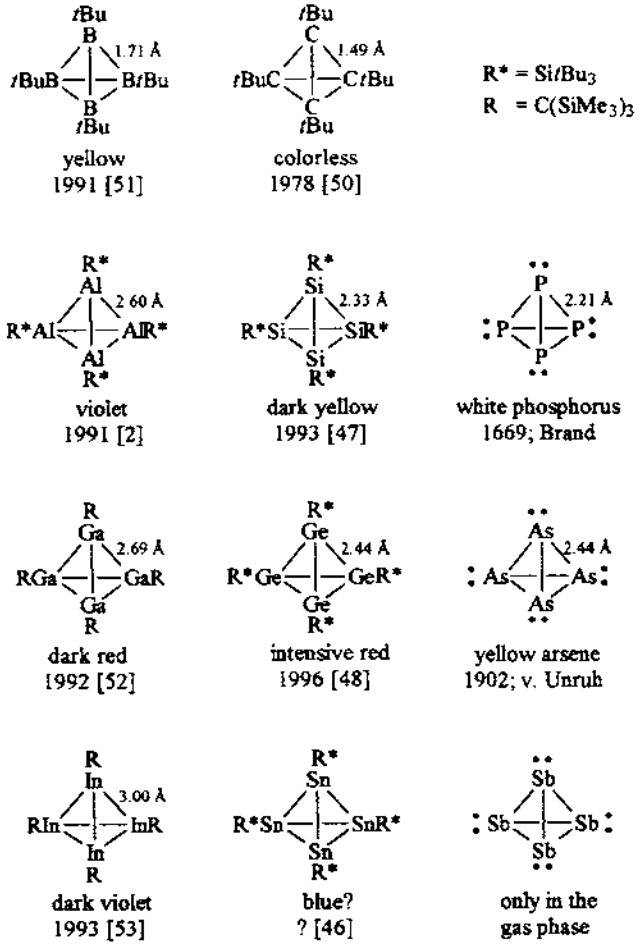
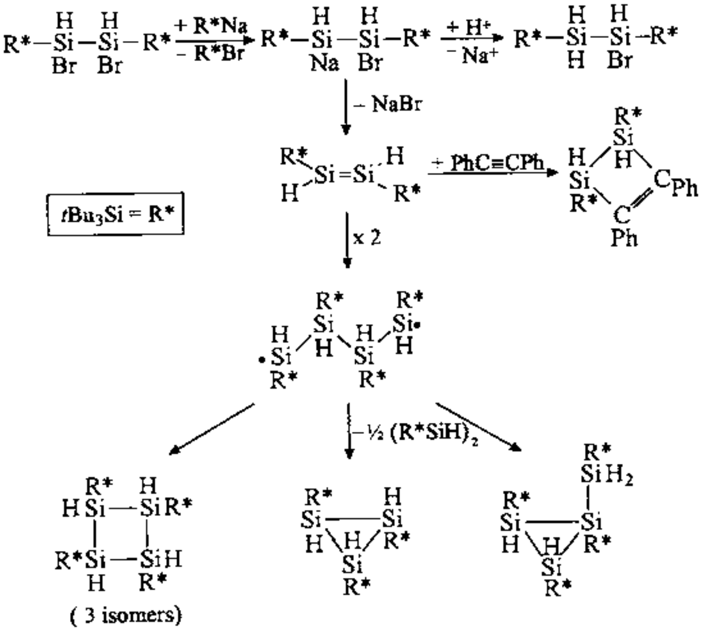


Fig. 10. Compounds (first preparation) with a tetrahedral framework of third, fourth and fifth main group elements ($[(Me_3Si)_3CTl]_4$ could also be prepared [54]; Bi_4 exists in the liquid phase).

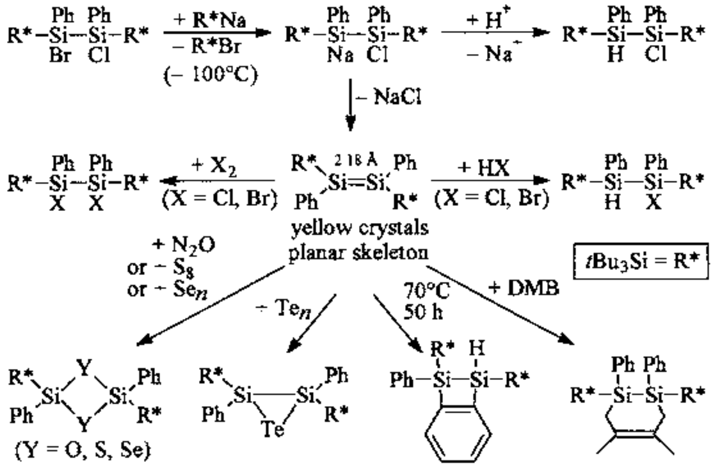
3.3.3.1. Debromination of tBu$_3$Si–SiHBr–SiHBr–SitBu$_3$. Reaction of tBu$_3$Si–SiHBr–SiHBr–SitBu$_3$ with an equimolar amount of tBu$_3$SiNa at −78 °C in THF with subsequent warming to room temperature leads to a 1:3 mixture of cyclotetrasilanes (three isomers) and cyclotrisilanes (two compounds; cf. Eq. (37) and Ref. [55]). The relative yields of the cyclotetra- and cyclotrisilane products are almost independent of reaction temperature, whereas the yield of the cyclotrisilane with a handle increases at the cost of the yield of the cyclotrisilane without handle with increasing temperature: at −78 °C the latter compound is mainly produced, at 65 °C the former.



(37)

The mechanism of product formation may be as follows: At first bromine is exchanged by sodium under formation of a silyl sodium compound, the existence of which becomes visible by derivatisation. Then, the silyl sodium compound eliminates NaBr under formation of a disilene, the intermediacy of which was proved by trapping it with diphenylacetylene at 65 °C. As the supersilyl groups of this product are *trans*-configured, the same must apply for the supersilyl groups of the disilene. Finally, the intermediately formed disilene disappears by reaction with itself. Certainly, a synchronous [2+2] cycloaddition is forbidden by rules of the conservation of orbital symmetry. On the other hand, a dimerization of two molecules of disilene under formation of a diradical is an allowed process. It may transform into the end products in three ways: (i) cyclisation with formation of cyclotetrasilanes; (ii) cyclisation with formation of a cyclotrisilane and a silylene which itself dimerizes; (iii) cyclisation with formation of a cyclotrisilane with handle by intramolecular hydrogen migration.

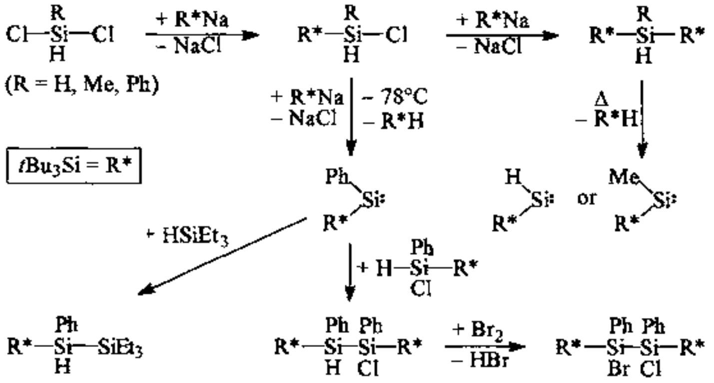
3.3.3.2. Incidental remarks: the disilene (tBu_3Si)PhSi=SiPh($SitBu_3$) and the silylenes (tBu_3Si)RSi (R = H, Me, Ph, $SitBu_3$). The above-mentioned bis(supersilyl)disilene is not isolable. The same applies for a bis(supersilyl)disilene with bulkier methyl groups instead of the silicon bound hydrogen atoms, but not for a bis(supersilyl)disilene with even bulkier silicon bound phenyl groups. In fact, the reaction of 1,2-bis(supersilyl)-1,2-diphenyl-bromochlorodisilane with an equimolar amount of *t*Bu$_3$SiNa at −78 °C in THF with subsequent warming to room temperature leads to a solution which – after exchanging THF by pentane – gives yellow crystals. As to X-ray structure analysis, the latter are composed of molecules of *trans*-1,2-bis(supersilyl)-1,2-diphenyldisilene (cf. Eq. (38) and Ref. [56]). The compound contains a planar central skeleton and the length of the SiSi bond amounts to 2.18 Å, that is a slightly elongated SiSi double bond. The compound slowly stabilizes itself at 70 °C by intramolecular isomerization.



(38)

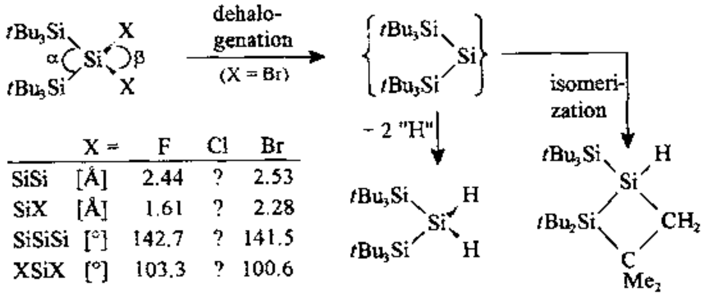
The disilene is very active against reactants which are not too bulky. For example, it adds halogens or hydrogen halides. Dinitrogenoxide, elemental sulfur, selenium or tellurium attack it with cleavage of the SiSi double bond, and 2,3-dimethylbutadiene forms a Diels–Alder adduct with it [23].

As demonstrated with Eq. (38), the disilene is produced from (*t*Bu$_3$Si)PhSiBr–SiClPh(Si*t*Bu$_3$). The synthesis of the latter compound has some unexpected aspects. As is shown with Eq. (39), the reaction of RSiHCl$_2$ (R = H, Me, Ph) with supersilyl sodium proceeds in THF by way of mono- and disupersilylation. Surprisingly, the disupersilylated products eliminate supersilyl hydride with formation of silylenes [23]. Obviously, sterical reasons are the driving force for these decompositions, which occur at high, medium and low temperature in the case of (*t*Bu$_3$Si)$_2$SiH$_2$, (*t*Bu$_3$Si)$_2$SiHMe and (*t*Bu$_3$Si)$_2$SiHPh, respectively. The intermediate existence of the mono(supersilyl)silylenes (*t*Bu$_3$Si)HSi, (*t*Bu$_3$Si)MeSi and (*t*Bu$_3$Si)PhSi can be demonstrated by trapping these with triethylsilane, as is shown in Eq. (39) for supersilylphenylsilylene. In the latter case, also supersilylphenylchlorosilane, an intermediate of the supersilylation, works as trap like triethylsilane and gives (*t*Bu$_3$Si)PhSiH–SiClPh(Si*t*Bu$_3$) in high yields. Its bromination leads to the precursor of the mentioned disilene.



(39)

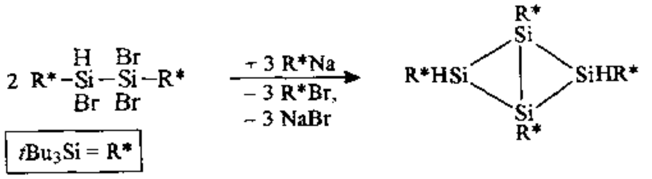
Worth mentioning in this connection are the dehalogenations of the dihalosilanes $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{SiX}_2$ (prepared from SiF_4 and $t\mathrm{Bu}_3\mathrm{SiNa}$, or by chlorination and bromination of $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{SiH}_2$ prepared from $\mathrm{SiH}_2\mathrm{Cl}_2$ and $t\mathrm{Bu}_3\mathrm{SiNa}$; X-ray for $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{SiF}_2$: D. Fenske and G. Baum; for $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{SiBr}_2$: K. Polborn). In fact, the reactions of $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{SiBr}_2$ with sodium in benzene or with $t\mathrm{Bu}_3\mathrm{SiNa}$ in THF lead to exchange of the two bromine atoms by hydrogens to $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{SiH}_2$ according to Eq. (40) [2,57]. In addition, the dihalosilane produces a disilacyclobutane derivative. Therefore, it appears plausible that the dehalogenations proceed with a primary formation of bis(supersilyl)silylene $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{Si}$ which may, as a consequence of the bulky supersilyl substituents, exist in a triplet state.



	X =	F	Cl	Br
SiSi	[Å]	2.44	?	2.53
SiX	[Å]	1.61	?	2.28
SiSiSi	[°]	142.7	?	141.5
XSiX	[°]	103.3	?	100.6

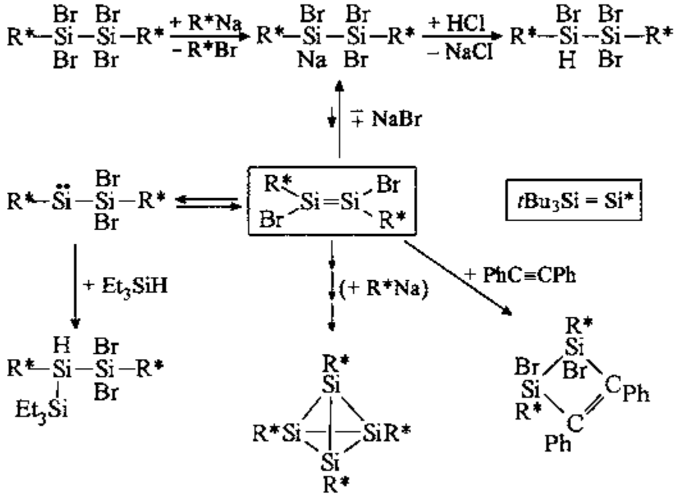
(40)

3.3.3.3. Debromination of tBu₃Si–SiHBr–SiBr₂–SitBu₃. Reaction of $t\mathrm{Bu}_3\mathrm{Si}$–SiHBr–$\mathrm{SiBr}_2$–$\mathrm{Si}t\mathrm{Bu}_3$ with $t\mathrm{Bu}_3\mathrm{SiNa}$ (molar ratio 1:1.5) in THF at −78 °C with subsequent warming to room temperature leads to a 1:4 mixture of a substance with unknown structure (obviously a partly brominated cyclotetrasilane $(t\mathrm{Bu}_3\mathrm{SiSiH})_4$)) and the colorless bicyclo-tetrasilane, shown in Eq. (41), the structure of which was solved by NMR and X-ray structure analysis [58].



(41)

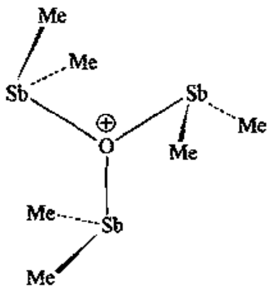
3.3.3.4. Debromination of $tBu_3Si–SiBr_2–SiBr_2–SitBu_3$. As in the case of tBu$_3$Si–SiHBr–SiHBr–SitBu$_3$, already mentioned (Eq. (37)), the reaction of tBu$_3$Si–SiBr$_2$–SiBr$_2$–SitBu$_3$ with tBu$_3$SiNa at low temperatures in THF leads primarily to a silyl sodium compound under exchange of bromine by sodium (cf. Eq. (42)). The existence of this again became visible by derivatisation. Then, the silyl sodium compound eliminates NaBr with formation of a disilene, the intermediacy of which was proved by trapping it with diphenylacetylene at room temperature with formation of a [2+2] cycloadduct [55]. In the X-ray structure, the supersilyl groups of the adduct are *trans*-configured [55]; therefore, the same must apply to the disilene. In fact, a solution of the silyl sodium compound, produced from equimolar amounts of tBu$_3$Si–SiBr$_2$–SiBr$_2$–SitBu$_3$ and tBu$_3$SiNa is metastable up to −20 °C and, obviously, at higher temperatures contains also the disilene and a silylene in small equilibrium concentrations. The intermediacy of the silylene was proved by trapping it with triethylsilane [59].



(42)

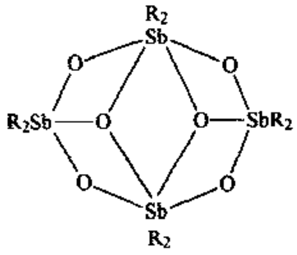
Now what fate does the immediate disilene suffer next? To date it is not possible to answer this question definitively. But it is now certain that the reaction scene is strongly influenced by the reaction conditions. Our present investigations also demonstrate that the reaction of tBu$_3$Si–SiBr$_2$–SiBr$_2$–SitBu$_3$ with tBu$_3$SiNa in THF is independent of the stoichiometry of the educts at temperatures below −30 °C. By further warming up to room temperature, solutions obtained from equimolar amounts of educts give a mixture of compounds which after addition of a second equivalent of supersilyl sodium do not transform into the tetrasilatetrahedrane but to new, unidentified substances. On the other hand, by warming up a solution, obtained from the tBu$_3$Si–SiBr$_2$–SiBr$_2$–SitBu$_3$ and tBu$_3$SiNa in molar ratio 1:2, only the tetrasilatetrahedrane is formed [59].

These latter results are summarized in Eq. (43). In the absence of tBu$_3$SiNa, the disilene (tBu$_3$Si)BrSi=SiBr(SitBu$_3$) transforms into still unidentified products, in the presence of an additional equivalent supersilyl sodium, tetrasupersilyl-tetrasilatet-

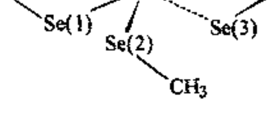


Sb-O 211.6(1) Sb-O-Sb 119.9(1)°

Derivatives of the type $[(R_2Sb)_2E_3]_2$ (R = Ph, *o,p*-Tol) have been obtained by air oxidation of distibines or by a rearrangement process during the oxidation of $RSb(SiMe_3)_2$ [62]. The crystal structure consists of polynuclear molecules: The analogous phenyl compound has been obtained before by the reaction of Ph_3Sb with H_2O_2 [63].



A compound of the type $Sb(ER)_3$ has been prepared by reaction of elemental antimony with dimethyldiselenide. In the crystals of $Sb(SeMe)_3$ [64] the molecules have a trigonal pyramidal skeleton formed by the heavy atoms. They are associated through short intermolecular Sb···Se contacts with distances of 355–366 pm.



Sb-Se 256.8(1) - 258.8(1) pm Se-Sb-Se 82.5(1)-102.1(1)°

Compounds of the type Me_2SbEMe (E = S, Se, Te) are formed by exchange reaction of MeEEMe with $Me_2SbSbMe_2$. The molecular structure of two of these derivatives (E = S, Se) has been determined by gas phase electron diffraction [65]. The data show that the predominant conformer is one where the dihedral angle ϕ defined by the E–C bond, the Sb–E bond and the presumed direction of the lone methylsilyl)methyl group $(Me_3Si)_2CH$ ("Lappert group"; [1]) by exchanging the trimethylsilyl against supersilyl groups.

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[60] *Remarks added in proof:*

(a) Yellow $t\mathrm{Bu_3SiK}$, unsoluable in heptane, gives red solutions in benzene, from which it crystallizes as $t\mathrm{Bu_3SiK(C_6H_6)_3}$. In the latter compound potassium is bound to a supersilyl group and three centrically coordinated benzene molecules [20].

(b) In light brown $[t\mathrm{Bu_3SiPCu_2}]_6$ (from CuI and $t\mathrm{Bu_3SiPLi_2}$) the Cu atoms are located at the corners of a regular cuboctahedron, the six square planes of which are bridged by $t\mathrm{Bu_3SiP}$ groups.

(c) $(t\mathrm{Bu_3Si})_3\mathrm{Ga}_2^{\bullet}$ transforms at 80°C in heptane under elimination of supersilyl radicals into violet oxygen sensitive tetrakis(supersilyl)-*tetrahedro*-tetragallane $(t\mathrm{Bu_3SiGa})_4$ (r_{GaGa} ca. 2.60 Å). Over and above that, it is reduced by sodium at room temperature in THF to a sodium salt $(t\mathrm{Bu_3Si})_3\mathrm{Ga_2Na(THF)_3}$ of tris(supersilyl)trigallanide ($t\mathrm{Bu_3Si_3Ga}_2^-$ ($r_{\mathrm{GaGa}} = 2.38$ Å). N. Wiberg, K. Amelunxen, H.-W. Lerner, H. Nöth, H. Schwenk, J. Knizek, unpublished results.

(d) The reaction of $(t\mathrm{Bu_3Si})_4\mathrm{Ge_3}$ with $\mathrm{Ph_3C^+BPh_4}$ in benzene produces a yellow salt with the cyclotrigermylium cation $(t\mathrm{Bu_3Si})_3\mathrm{Ge}_3^+$, which in fact is a 2π-electron system ($r_{\mathrm{GeGe}} = 2.33$ Å).