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Review

Silicon derivatives of group 1, 2, 11 and 12 elements

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Contents

Abstract

Silyl anions and especially silicon derivatives of group 1, 2, 11 and 12 elements are important and versatile organometallic reagents in synthesis. The best-studied class of silyl anions are the alkali metal silanides that feature monomeric, dimeric and polymeric arrangements as molecular units. Alkali metal silanides have not only become interesting for their molecular structures but have also attracted recent attention due to their synthetic abilities. Recently, alkali metal tri-*tert*-butylsilanides (supersilanides, MSi*t*Bu$_3$) have been used for the synthesis of new main group element clusters and compounds with elements in low coordination states. In contrast to the well-established silanides with alkali metals, few alkaline-earth metal silanides are known. Information regarding the structure and reactivity of these molecules is thus still rather limited. Silyl derivatives of the zinc group are conveniently accessible by metathesis reaction of MX_2 and alkali metal silanides. X-ray

Abbreviations: Ar, aryl; DME, dimethoxyethane; hmpa, hexamethylphosphoramide; Mes, mesityl; Np, neopentyl; Ph, phenyl; *i*Pr, isopropyl; THF, tetrahydrofuran; TMDAP, tetrametyldiaminopropane; TMEDA, tetramethylethylenediamine; Tip, 2,4,6-*i*Pr$_3$C$_6$H$_2$

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crystal structure analyses show that the silanides of zinc, cadmium and mercury (tBu$_3$SiMSitBu$_3$; M = Zn, Cd, Hg) are monomeric, wheras tBu$_3$SiZnBr and tBu$_3$SiHgCl are tetrameric, the former with a regular, the latter with a pronounced irregular cubic M_4X_4 framework. The compound $(Me_3SiMe_2Si)_3Si-Hg-Hg-Si(SiMe_2SiMe_3)_3$ represents the first molecular two-coordinated dinucluear mercury(I) silyl derivative. Contrary to the well-known cuprates with organic ligands, few compounds are known with a Si−Cu bond. In contrast to homoleptic transition metal silanides, a huge number of heteroleptic complexes of transition metals with silyl ligands have been synthesized and structurally characterized. Most of them are prepared by addition of silanes, R_3SiH, to reactive transition metal species.

Keywords: Silyl anion; Alkali metals; Alkaline-earth metals; Transition metals

1. Introduction

Compounds with carbanion character such as lithium alkyls represent an important class of reagents in synthesis. Over the past decade, their heavier homologues, the alkali metal silanides, have also gained a wide area of application. Papers regarding the synthesis and reactivity of silanides $MSiR_3$ were published by Gilman et al. in the 1950s and 1960s [1,2]. The first silanides studied in detail were the triphenylsilanides $MSiPh_3$ (M = Li, Na, K, Rb, Cs) [3]. Early syntheses used hexaphenyldisilane $Ph_3Si-SiPh_3$ as a starting material, which was treated with the respective alkali metal in ammonia solution in the presence of pyridine. However, the amount of by-products such as silazanes and silylated 1,4-dihydropyridine was considerably high with this method [4].

In addition to the well-established tri-*tert*-butylsilyl group ("supersilyl", tBu$_3$Si−) [5] and the tris(trimethylsilyl)-silyl group ("hypersilyl", $(Me_3Si)_3Si-$) [7], this paper presents the di-*tert*-butylphenylsilyl group (tBu$_2$PhSi−) as a new sterically demanding substituent [8,9]. An advantage of the bulky silyl ligands is the good space-filling property, which enables the kinetic stabilization of elements with rare oxidation and coordination numbers. Sterically demanding silyl anions have a strong basicity on account of their electron-donor capacity; metal–metal bonds are thus strengthened. Metathesis reactions can easily be carried out due to the strong nucleophilic power. Bulky silanides are especially suited for cluster synthesis owing to their basicity as well as their nucleophilicity [5].

2. Alkali metal silanides

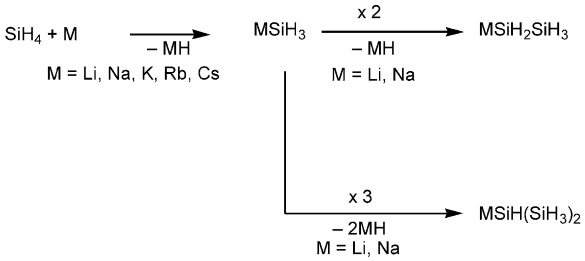
The best-studied class of compounds containing silyl anions are the alkali metal silanides that feature single (monomeric) [5–7,10–14], cyclic (dimeric) [5,7,8] and chain (polymeric) [9] arrangements of molecular units. In addition to the reaction of halosilanes with alkali metals, silanides can be prepared as follows: (i) by transforming a Si−H bond with MH or alkali metals [15,16]; (ii) by cleaving a Si−Si bond using alkali metals, alkoxides ROM (M = Na, K, Cs), alkali metal hydrides MH or lithium alkyls [13,14]; (iii) by methathesis reaction [15,16]; (iv) by metal–metal exchange [7,10].

Alkali metal silanides have not only become interesting on account of their molecular structures but have also attracted recent attention due to their synthetic abilities. However, alkali metal tri-*tert*-butylsilanides (supersilanides), MSitBu$_3$ and tris(trimethylsilyl)silanides (hypersilanides), $MSi(SiMe_3)_3$, have been used in the synthesis of new main group element clusters and compounds with elements in low coordination states. Accordingly, the reaction of sodium supersilanide with thallium(III) chloride produces the supersilylated thallium clusters, $(t\text{Bu}_3\text{Si})_6\text{Tl}_6\text{Cl}_2$ and $(t\text{Bu}_3\text{Si})_4\text{Tl}_3\text{Cl}$ [17], and with $[(Me_3Si)_2N]_2Sn$ leads to the tristannaallene, $(t\text{Bu}_3\text{Si})_2\text{Sn=Sn=Sn}(t\text{Bu}_3\text{Si})_2$ [18].

2.1. Synthesis of alkali metal silanides

2.1.1. Synthesis of silanides by transforming a Si−H bond with alkali metals or MH into a Si−M bond

The hydrogen substituted silanides $MSiH_3$ (M = K, Rb, Cs) are synthesized by the reaction of SiH_4 with alkali metals or alloys of alkali metals such as KNa in monoglyme or diglyme [19–26]. In contrast to $MSiH_3$ (M = K, Rb, Cs), the silanides $MSiH_3$ (M = Li, Na) are formed together with by-products [e.g. $NaSiH_2(SiH_3)$] by the same procedure.



(1)

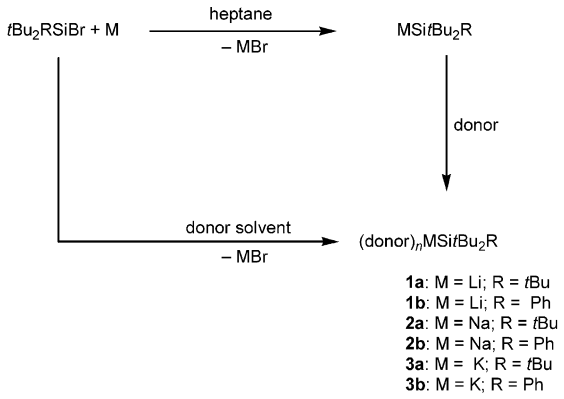
Another synthetic route is the reaction of silanes $HSiR_3$ with alkali metal hydride MH at elevated temperatures to give the appropriate silanides $MSiR_3$ and hydrogen, as shown in Eq. (2):

$$HSiR_3 + MH \xrightarrow[M=Na,K]{-H_2} MSiR_3 \quad (2)$$

The metalation of silanes with MH is a general reaction and has been applied to many silanes with hydrogen, alkyl and aryl substituents [27–29]. Examples of alkali metal silanides synthesized by cleaving a Si−H bond are listed in Table 1.

2.1.2. Synthesis of silanides by reaction of halosilanes with alkali metals

Tri-*tert*-butylsilanides (supersilanides) and di-*tert*-butylphenylsilanides of the alkali metals MSi*t*Bu$_2$R (R = *t*Bu, Ph; M = Li, Na, K) were synthesized from the bromosilanes *t*Bu$_2$RSiBr (R = *t*Bu, Ph) with alkali metals in heptane at moderately elevated temperature as shown in Eq. (3) [5,8,9]:



(3)

The silanides MSi*t*Bu$_2$R (R = *t*Bu, Ph; M = Li, Na, K) are pale yellow compounds that are poorly soluble in alkanes [the potassium silanides KSi*t*Bu$_2$R (R = *t*Bu, Ph) **3a** and **3b** are completely insoluble in alkanes]. Obviously, the intermolecular interactions in the potassium silanides KSi*t*Bu$_2$R (R = *t*Bu, Ph) are stronger than in the silanides of lithium and sodium MSi*t*Bu$_2$R (R = *t*Bu, Ph; M = Li, Na). The resulting silanides MSi*t*Bu$_2$R (R = *t*Bu, Ph; M = Li, Na, K) and alkali metal bromides MBr (M = Li, Na, K) precipitate from alkanes, while the by-products stay in solution. By-products such as the silanes *t*Bu$_3$SiH and *t*Bu$_2$PhSiH or the disilanes *t*Bu$_3$Si−Si*t*Bu$_3$ and *t*Bu$_2$PhSi−Si*Ph*tBu$_2$ are easily separated by filtration from the silanides. However, the solubility of MSi*t*Bu$_2$R (R = *t*Bu, Ph; M = Li, Na, K) in aromatic solvents such as benzene, ethers or tetrahydrofuran is much better than in alkanes. Contrary to tetrahydrofuran, the weaker donor benzene is easily removed from the silanides in vacuo. Therefore, solutions of the silanides MSi*t*Bu$_2$R (R = *t*Bu, Ph; M = Li, Na, K) in benzene are filtered from alkali metal bromide. The pure silanides MSi*t*Bu$_2$R (R = *t*Bu, Ph; M = Li, Na, K) are obtained as residues after removal of benzene [5,8,9].

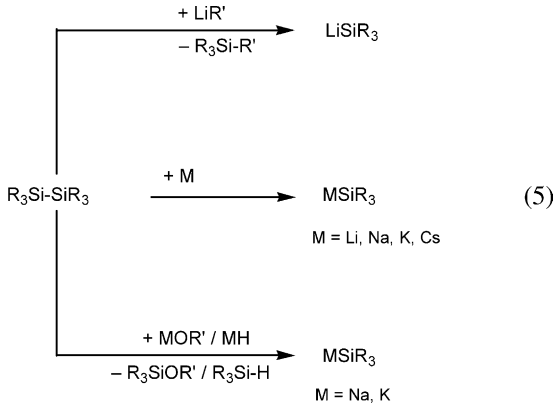
The donor adducts of MSi*t*Bu$_2$R (R = *t*Bu, Ph; M = Li, Na, K) can also be synthesized from the donor-free silanides. Otherwise, the synthesis of MSi*t*Bu$_2$R (R = *t*Bu, Ph; M = Li, Na, K) can be carried out in donor solvents as shown in Eq. (3). On the one hand, the stability of alkali metal arene complexes increases from lithium to potassium. On the other hand, the strength of the adducts of alkali metals with n-donors decreases from lithium to potassium. Other alkali metal silanides with bulky substituents such as MSiR(Si*t*Bu$_3$)$_2$ (R = H, Me; M = Li, Na, K) can be synthesized from the appropriate halosilanes and alkali metals [31]. Examples of alkali metal silanides synthesized by reaction of halosilanes with alkali metals are listed in Table 1.

2.1.3. Synthesis of alkali metal silanides by cleaving a Si−Si bond using alkali metals or strong bases

Reduction of halosilanes R$_3$SiX (X = Cl, Br, I; e.g. R = Me, Ph) with small substituents by alkali metals leads to disilanes as shown in Eq. (4):

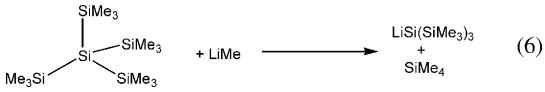
$$2R_3SiX + M \xrightarrow[\substack{M=Li,Na,K\\X=Cl,Br,I}]{-MX} R_3Si{-}SiR_3 \qquad (4)$$

However, many disilanes can be cleaved by alkali metals [32–39] or strong bases such as alkyllithium reagents [40–43], alkali metal alkoxides [44–46,53,54] and alkali metal hydrides [28], as depicted in Eq. (5) (see Table 1 for examples of silanides prepared by this method):



(5)

A convenient method that gives potassium silanides in good yield is the cleavage of disilanes by potassium *tert*-butoxide in polar solvents such as THF or DME (see Table 1 for examples of silanides prepared by cleaving a Si−Si bond) [46]. Treatment of Si(SiMe$_3$)$_4$ with LiMe or alkyllithium reagents produces LiSi(SiMe$_3$)$_3$, as shown in Eq. (6) [40]:



(6)

Interestingly, the potassium supersilanides, KSi*t*Bu$_3$, react with hexamethyldisilane, Me$_3$SiSiMe$_3$, to give the superdisilane, *t*Bu$_3$SiSi*t*Bu$_3$, and the potassium silanide, KSiMe$_3$, as shown in Eq. (7) [47]:

$$Me_3Si{-}SiMe_3 + 2KSi{t}Bu_3 \rightarrow {t}Bu_3Si{-}Si{t}Bu_3 + 2KSiMe_3 \qquad (7)$$

In contrast, few alkali metal silanides have been synthesized by the cleavage of silicon carbon bonds [48,49].

2.1.4. Synthesis of alkali metal silanides by metathesis reaction

Contrary to the syntheses of group 2, 11–14 metal silanides, the metathesis reaction of MX with homologous alkali metal silanides (Eq. (8)) plays only a minor role in the

Table 1
Examples of alkali metal silanides and preparation methods

Silanide	Preparation	References
$MSiH_3$ (M = Na, K, Rb, Cs)	By transforming a Si−H bond (Section 2.1.1)	[19–26,57]
$KSiH_3$	By transforming a Si−H bond (Section 2.1.1)/by Si−Si bond cleavage (Section 2.1.3)	[19–26,57] [35,36]
$NaSi(SiH_3)_3$	By transforming a Si−H bond (Section 2.1.1)	[30]
$KSiH_2Ph$	By Si−Si bond cleavage (Section 2.1.3)	[36]
$KSiHPh_2$	By Si−Si bond cleavage (Section 2.1.3)	[37]
$LiSiMe_3$	By Si−Si bond cleavage (Section 2.1.3)/by metal–metal exchange (Section 2.1.5)	[43] [50]
$MSiMe_3$ (M = Na, K)	By Si−Si bond cleavage (Section 2.1.3)	[28,44–46]
$LiSiEt_3$	By metal–metal exchange (Section 2.1.5)	[51]
$MSiPh_{3-n}Me_n$ (M = Li, K)	By Si−Si bond cleavage (Section 2.1.3)	[32,33]
$MSiPh_3$ (M = Li, K)	By transforming a Si−H bond (Section 2.1.1)/by Si−Si bond cleavage (Section 2.1.3)	[15,16,27] [15,16,46]
$MSiPh_2t$Bu (M = Li, Na, K)	By Si−Si bond cleavage (Section 2.1.3)	[34]
$MSit$Bu$_2$Ph (M = Li, Na, K)	Halosilanes with alkali metal (Section 2.1.2)	[8,9]
$MSit$Bu$_3$ (M = Li, K)	Halosilanes with alkali metal (Section 2.1.2)	[5]
$LiSi(SiMe_3)_3$	By Si−Si bond cleavage (Section 2.1.3)	[57]
$MSi(SiMe_3)_3$ (M = Na, K, Rb, Cs)	By metal–metal exchange (Section 2.1.5)	[7,10]
$LiSiMe_2SiMe_3$	By metal–metal exchange (Section 2.1.5)	[52]
$KSiMe_2SiMe_3$	By Si−Si bond cleavage (Section 2.1.3)	[54]
$MSiR(Sit$Bu$_3)_2$ (M = Li, Na, K; R = H, Me)	Halosilanes with alkali metal (Section 2.1.2)	[31]
$KSiMe_2SiMe_2Ph$	By Si−Si bond cleavage (Section 2.1.3)	[54]

synthesis of silyl derivatives of alkali metals [15,16]:

$$MX + M'SiR_3 \rightarrow M'X + MSiR_3 \quad (8)$$
$$M{=}Li,Na,K;\ M'{=}Rb,Cs;\ X{=}Cl,Br$$

Since the synthesis of cesium or rubidium silanides is more difficult than that of lithium, sodium or potassium, the preparation of alkali metal silanides by metathesis reaction is not very useful.

2.1.5. Synthesis of alkali metal silanides by transmetallation

As shown in Eq. (9), several alkali metal silanides are prepared by the reaction of mercury silanides with alkali metals via metal–metal exchange [15,16]:

$$M + HgSiR_3 \rightarrow Hg + MSiR_3 \quad (9)$$
$$M{=}Li;\ R{=}Me,Et$$
$$M{=}K,Rb,Cs;\ R{=}SiMe_3$$

Examples of alkali metal silanides synthesized by metal–metal exchange are listed in Table 1.

2.2. NMR spectra of alkali metal silanides

The structures of hydrogen substituted silanides (e.g. $NaSiH_2SiH_3$) have been verified with their ^{1}H NMR spectra [25]. Otherwise the ^{29}Si NMR spectra of the silanides and their donor adducts give some evidence of which aggregates are formed in solution. As shown in Table 2, the adducts of $MSit$Bu$_2$Ph (M = Na, K) with benzene and with THF show similar ^{29}Si NMR values. In contrast, the signals of $LiSit$Bu$_2$Ph are shifted to higher field in tetrahydrofuran than in benzene. As shown for supersilanides, a high-field shift of the signals correlates with the observation of monomeric aggregates with more negative charge on the Si center. This indicates that monomeric species of tBu$_2$PhSiLi are probably formed in the stronger donor solvent tetrahydrofuran. Surprisingly, nearly identical shifts of the tetrahydrofuran adducts have been measured in the non-coordinating solvent cyclohexane as well as in the donor solvents tetrahydrofuran or benzene. Obviously, the benzene and the tetrahydrofuran adducts of $MSit$Bu$_2$Ph (M = Na, K) form dimeric species in solution with structures that are similar to those in the solid state [8].

Table 2
^{29}Si{^{1}H} NMR shifts of M(donor)$_n$SitBu$_2$Ph (M = Li, Na, K) [8]

Silanide	Solvent	δ (^{29}Si{^{1}H})
$Li(C_6H_6)Sit$Bu$_2$Ph	C_6D_6	26.8
$Li(THF)_nSit$Bu$_2$Ph	d_8-THF	19.6
$Li(THF)_2Sit$Bu$_2$Ph	C_6D_6	22.5
$Na(C_6H_6)Sit$Bu$_2$Ph	C_6D_6	26.1
$Na(THF)_nSit$Bu$_2$Ph	d_8-THF	28.9
$Na(THF)Sit$Bu$_2$Ph	C_6D_6	26.1
$Na(THF)_2Sit$Bu$_2$Ph	C_6D_6	26.4
$Na(THF)_2Sit$Bu$_2$Ph	C_6D_{12}	26.4
$K(C_6H_6)Sit$Bu$_2$Ph	C_6D_6	26.8
$K(THF)_nSit$Bu$_2$Ph	d_8-THF	23.5
$K(THF)Sit$Bu$_2$Ph	C_6D_6	24.7
$K(THF)_2Sit$Bu$_2$Ph	C_6D_6	25.0
$K(THF)_2Sit$Bu$_2$Ph	C_6D_{12}	23.5

2.3. Structures of alkali metal silanides

The crystal structures of $MSiH_3$ (M = K, Rb, Cs) are of the NaCl type at ambient temperature [21]. At −5 °C the potassium silanide $KSiH_3$ crystallizes from a mixture of DME and *n*-pentane in an orthorhombic modification [24], which shows K−Si distances of 3.64 Å. The strength of agostic interaction between alkali metal centers and H atoms in silanides increases from cesium to lithium and the structure of $LiSiH_3$ has not yet been determined.

Alkali metal silanides normally prefer a pyramidal geometry at the Si center rather than a planar geometry, as the sum of the three CSiC angles is smaller than 330° in structures of the ion-separated silanides $MSi(SiMe_3)_3$ [12]. However, the molecular structure of the non-solvated lithium silanide $LiSi(SitBu_2Me)_3$ features a nearly planar geometry arising from steric strain and intramolecular agostic CH–Li interactions [6]. The sodium di-*tert*-butylphenylsilanide was recently described as a polymeric arrangement of molecular units. The di-*tert*-butylphenylsilyl substituent has the ability to coordinate via both σ bonds (E–Si) and π interactions of the phenyl ring [8,9]. In contrast to the polymeric structure of $NaSitBu_2Ph$ in the solid state, the central framework of the solvent-free supersilanides $MSitBu_3$ (M = Li, Na) [5]

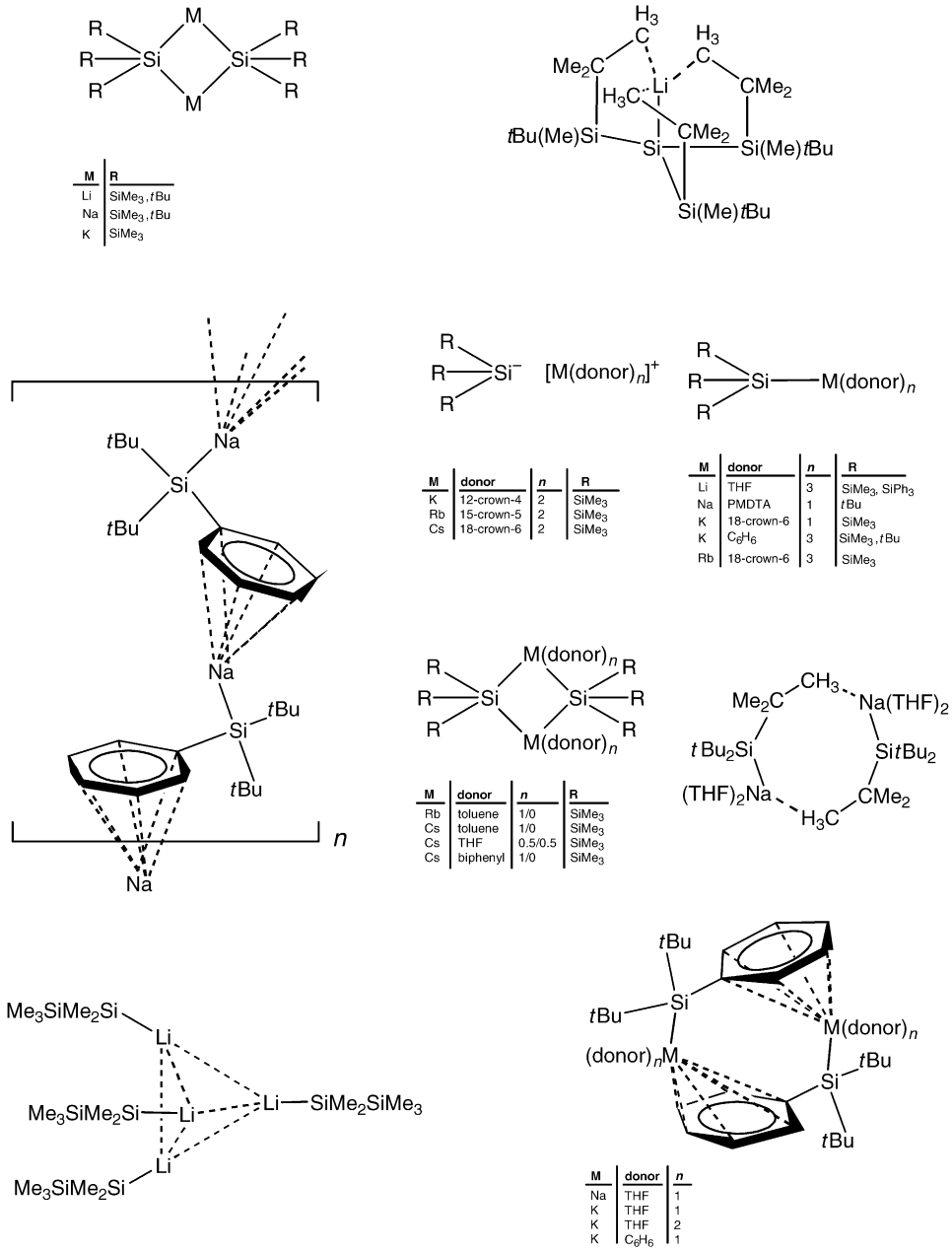


Fig. 1. Molecular structures of alkali metal silanides.

and of the solvent-free hypersilanides $MSi(SiMe_3)_3$ (M = Li, Na, K) [7] forms a four-membered ring. The corners of these rings are alternately occupied by alkali metal and Si atoms [5,7]. According to an X-ray crystal structure analysis $LiSiMe_2SiMe_3$ represents a silanide featuring a tetramer containing a tetrahedron of four Li atoms in the solid state [52].

Contrary to the dimeric structures of $MSitBu_3$ and $MSi(SiMe_3)_3$, the structures of the benzene complexes of the potassium supersilanide $(C_6H_6)_3KSitBu_3$ and the hypersilanide $(C_6H_6)_3KSi(SiMe_3)_3$ involve monomeric units with three benzene molecules coordinated at the potassium atom [5,7]. The silanides $(C_6H_6)_2KSiR(SitBu_3)_3$ (R = H, Me) are monomers in the solid state but in contrast to the structures of potassium supersilanide and hypersilanide, the potassium center is coordinated to only two molecules of benzene [31]. The structures of tetrahydrofuran adducts of the supersilanides and hypersilanides are built of dimeric units connected by σ bonds rather than π interactions as in $(THF)MSitBu_2Ph$ (M = Na, K), as shown in Fig. 1.

The general solid state structural motifs of the silanide donor adducts **2b(THF)**, **3b(C_6H_6)**, **3b(THF)** and **3b(THF)$_2$** features a cycle formed by two silanide molecules [8], in contrast to the polymeric chains of the unsolvated $tBu_2PhSiNa$ [9]. In the silanide donor adducts, the alkali metal centers are coordinated to one silicon atom and to the phenyl ring of a neighboring silyl group in η^6 fashion. The alkali metals are further complexed by solvent molecules, and significant agostic interactions were not observed as already discussed for the structures of the supersilanides and hypersilanides.

The length of alkali metal–silicon bonds and the sum of the CSiC angles on the Si center give evidence of the charge separation in the silanides. Generally, strong donors on the alkali metal center lengthen the Si−M bond and lead to more negative charge on the Si center, so that **3b(C_6H_6)**, involving benzene, adopts a shorter K−Si bond [3.3602(11) Å] than the tetrahydrofuran adduct **3b(THF)** [3.3710(11) Å]. Otherwise the K−Si bond in **3b(THF)** is somewhat shorter than the bond length of 3.405(1) Å estimated for **3b(THF)$_2$**. Likewise the tetrahydrofuran adduct possesses a longer Si−Na bond {**2b(THF)** 2.991(2) Å [8]} than the unsolvated sodium silanide {$NaSitBu_2Ph$ 2.8811(19) Å [9]}. In comparison: the corresponding MSi bonds of the supersilanides {$NaSitBu_3$ 3.067(4) Å [5]} are significantly longer due to steric strain.

Examples of structurally characterized alkali metal silanides are listed in Fig. 1 and Table 3.

3. Alkaline-earth metal silanides

3.1. Synthesis of alkaline-earth metal silanides

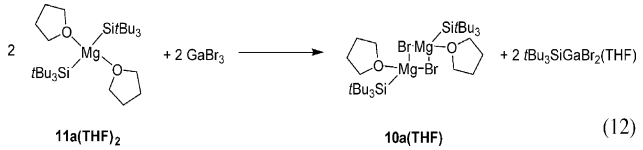
Several routes to alkaline-earth metal silanides are known that are similar to the synthesis of alkali metal silanides discussed in Section 2. The preparation of alkaline-earth metal silanides by the metathesis of MX_2 (M = Be, Mg, Ba; X = Cl, Br, I) with alkali metal silanides is the most preferable method. The Grignard analogous compounds $tBu_3SiMgBr$ and $(Me_3Si)_3SiMgBr$ were produced by reaction of MX_2 with one equivalent of alkali metal silanides, $NaSitBu_3$ and $LiSi(SiMe_3)_3$ [72,73]. Several Grignard analogous compounds have been generated by the same route to the corresponding lithium silanides and magnesium bromide. Most of these compounds have not been isolated, but are used in situ for synthetic purposes:

$$\underset{\substack{R_3Si=tBu_3Si;\,M=Na\\ R_3Si=(Me_3Si)_3Si;\,M=Li}}{R_3SiM} + MgBr_2 \xrightarrow[-MBr]{} \underset{\substack{\mathbf{10}\\ \mathbf{10a}:\,R_3Si=tBu_3Si\\ \mathbf{10b}:\,R_3Si=(Me_3Si)_3Si}}{R_3SiMgBr} \quad (10)$$

Adducts of Me_3SiMgX donor (donor = $Me_2NCH_2CH_2NMe_2$, $MeN(CH_2CH_2NMe_2)_2$; X = Br, I) were synthesized from the halosilanes Me_3SiX with magnesium in toluene at temperatures between 40 and 70 °C in presence of the appropriate donor as shown in Eq. (11) [71]:

$$Me_3SiX + Mg \rightarrow \underset{\substack{\mathbf{10c}:\,X=Br;\,donor=Me_2NCH_2CH_2NMe_2,\ MeN(CH_2CH_2NMe_2)_2\\ \mathbf{10d}:\,X=I;\,donor=Me_2NCH_2CH_2NMe_2,\ MeN(CH_2CH_2NMe_2)_2}}{Me_3SiMgX\,(donor)} \quad (11)$$

Another useful synthetic method for Grignard analogous compounds ($R_3SiMgBr$) is the transformation of $(R_3Si)_2Mg$ with element halides as shown in Eq. (12) [72] for $GaBr_3$ reacted with $(tBu_3Si)_2Mg(THF)_2$ in benzene at ambient temperature. X-ray quality crystals of $tBu_3SiMgBr(THF)$ were grown from a benzene solution [72].

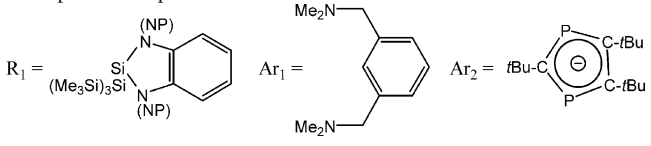


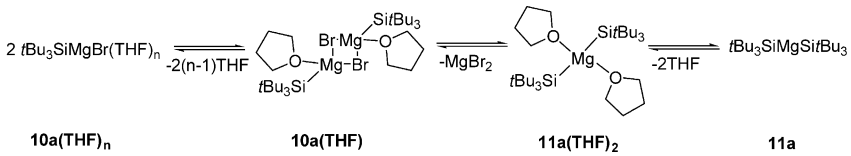
11a(THF)$_2$ **10a(THF)** (12)

Table 3
Alkali metal silanides characterized by X-ray diffraction

Silanide	M−Si (Å)	References
$(LiSiMe_3)_2(TMEDA)_3$	2.70(1)	[62]
$Li(THF)_3SiPh_3$	2.672(9)	[56]
$Li(THF)_3Si(SiMe_3)_3$	2.644(12)/2.669(13)/2.674(13)	[14,56]
$Li(THF)_3Si(SiMe_3)_2(SiMe_2)_2Si(SiMe_3)_3$	2.657(6)	[59]
$Li(THF)_3Si(SiMe_3)_2(SiMe_2tBu)$	2.684(9)	[13]
$Li(THF)_3Si(SiMe_2SiMe_3)_3$	2.760(11)	[63]
$Li(THF)_3(SiPh_2)_4Li(THF)_3$	2.714(10)	[58]
$Li(THF)_3SiPh(NEt_2)_2$	2.627(4)	[61]
$Li(THF)_3SiPh_2(NEt_2)$	2.680(8)	[61]
$Li(THF)_3SiPh_2(NPh_2)$	2.732(7)	[64]
$Li(THF)_2R_1$	2.609(4)	[57]
$Li(THF)SiH(SiMe_2tBu)_2$	2.760(11)	[60]
$[Li(THF)]_2Si(SiiPr_3)_2$	2.549(7)/2.55(1)	[69]
$Li(THF)_2SiiPr_2HgSiiPr_2Li(THF)_2$	2.558(11)	[65]
Li(dioxane)$[Si(Si(Ar_1)_2]_3$Li(dioxane)	2.55(1)	[67]
$Li(THF)[Si(Si(Ar_1)_2]_2Li(THF)_2$	2.542(8)/2.589(8)	[67]
$LiSi(SiMe_3)_3{\cdot}Li(Ar_2)$	2.519(7)	[68]
LiSi(Tip)=$Si(Tip)_2$	2.853(3)	[142]
LiSi(Mes)=Si(SiMetBu)$_2$	2.702(9)	[143]
$LiSi(SiMe_2SiMe_3)_3$	2.711(8)/2.737(7)	[63]
$LiSiMe(SiMe_2Ph)_2$	2.664(5)/2.778(7)	[66]
$LiSiPh(SiMe_3)_2$	2.630(12)/2.775(11)	[66]
$LiSi(SiMe_3)_3$	2.588(4)/2.601(4)	[7]
$LiSi(SiMe_2tBu)_3$	2.531(6)	[6]
$LiSitBu_3$	2.67(1)/2.63(1)	[5]
$[NaSiH_3]_2[NaO_3C_5H_{11}]_6$	3.048	[30]
Na(PMDTA)SitBu_3	2.967(2)	[5]
Na(THF)SiPhtBu_2	2.9910(20)	[8]
$Na(THF)_2SitBu_3$	2.9190(10)	[5]
$NaSiPhtBu_2$	2.8811(19)	[9]
$NaSitBu_3$	3.0670(40)	[5]
$NaSi(SiMe_3)_3$	3.0025(2)/2.993(2)	[7]
$KSiH_3$	3.62(1)/3.64	[21,24]
K(18-crown-6)$Si(SiMe_3)_2Si(SiMe_3)_2$Ph	3.5994(19)	[11]
K(18-crown-6)$Si(SiMe_3)_2(CH_2)_2$ $Si(SiMe_3)_2$K(18-crown-6)	3.4197(12)	[55]
K(18-crown-6)$Si(SiMe_3)_3$	3.447(8)	[12]
$[K(12\text{-crown-}4)_2][Si(SiMe_3)_3]$	*	[12]
K(18-crown-6)$Si(SiMe_3)_2(SiMe_2)_3$ $Si(SiMe_3)_2$K(18-crown-6)	3.568(2)/3.461(4)	[70]
K(18-crown-6)$Si(SiMe_3)_2(SiMe_2)_2$ $Si(SiMe_3)_2$K(18-crown-6)	3.4458(14)	[70]
K(18-crown-6)$Si(SiMe_3)_2SiMe_2$ $Si(SiMe_3)_2$K(18-crown-6)	3.5011(18)/3.5836(18)	[70]
K(toluene)$Si(SiMe_3)_2Si(SiMe_3)_3$	3.3147(12)	[11]
K(benzene)$_3Si(SiMe_3)_3$	3.352(4)	[7]
K(benzene)$_3SitBu_3$	3.3780(10)	[5]
K(benzene)$_2SiH(SitBu_3)_2$	3.306(1)	[31]
K(benzene)$_2SiMe(SitBu_3)_2$	3.351(1)	[31]
K(benzene)Si$PhtBu_2$	3.3602(11)	[8]
K(THF)Si$PhtBu_2$	3.3710(11)	[8]
$K(THF)_2SiPhtBu_2$	3.4050(8)	[5]
$KSi(SiMe_3)_3$	3.4166(9)	[7]
$KSi(SiMe_3)_3{\cdot}KOtBu$	3.487(10)/3.571(10)	[12]
$RbSiH_3$	3.76(1)	[21]
Rb(18-crown-6)$Si(SiMe_3)_3$	3.436(8)/3.452(7)	[12]
$[Rb(18\text{-crown-}6)][Si(SiMe_3)_3]$	(8)/(7)	[12]
$RbSi(SiMe_3)_3{\cdot}(toluene)_{0.5}$	3.616(4)/3.595(4)	[10]
$CsSiH_3$	3.93(1)	[21]
$CsSi(SiMe_3)_3{\cdot}(toluene)_{1.5}$	3.807(2)/3.850(2)	[10]
$CsSi(SiMe_3)_3{\cdot}$(biphenylene)	3.677(2)/3.742(2)	[7]
$CsSi(SiMe_3)_3{\cdot}(THF)_{0.5}$	3.708(1)/3.673(1)/3.732(1)/3.669(1)	[7]
$[Cs(18\text{-crown-}6)][Si(SiMe_3)_3]$	*	[12]

* Separated ion pair.





(13)

While $R_3SiMgBr(THF)_n$ was transformed in non-donor solvents (Schlenk equilibrium) like the related Grignard compounds with carbon centers $R_3CMgBr(THF)_n$, isolation of these Grignard analogous compounds was difficult [72,73]. The supersilyl and hypersilyl compounds, $tBu_3Si-Mg-SitBu_3$ and $(Me_3Si)_3Si-Mg-Si(SiMe_3)_3$ were synthesized by the addition of two equivalents of $NaSitBu_3$ or $LiSi(SiMe_3)_3$ to a tetrahydrofuran solution of $MgBr_2$. Otherwise $tBu_3Si-Mg-SitBu_3$ or $(Me_3Si)_3Si-Mg-Si(SiMe_3)_3$ are obtained when $MgBr_2$ is eliminated from $tBu_3SiMgBr$ (Eq. (13)) [55,72,73].

Solvent-free disilylated magnesium $tBu_3Si-Mg-SitBu_3$ was obtained by heating the solid adduct $(tBu_3Si)_2Mg(THF)_2$ in vacuo and uncomplexed $(tBu_3Si)_2Mg$ was recovered quantitatively from the resulting residue [72].

Another $R_3Si-Mg-SiR_3$ species was prepared by transmetallation, as depicted in Eq. (14). Stirring magnesium powder with $Me_3Si-Hg-SiMe_3$ in donor solvents such as DME for about 1 week led to the formation of the magnesium silanide $Me_3Si-Mg-SiMe_3$ [74,75,76]:

$$Me_3Si-Hg-SiMe_3 + Mg \rightarrow \underset{\mathbf{11c}}{Me_3Si-Mg-SiMe_3} + Hg \quad (14)$$

The supersilylated beryllium compounds $tBu_3Si-Be-SitBu_3$ and $tBu_3SiBeCl$ were synthesized by the addition of one or two equivalents of tBu_3SiNa to $BeCl_2$ in dibutyl ether. The donor-free $(tBu_3Si)_2Be$ was formed when two equivalents of sodium supersilanide reacted with $BeCl_2$ in dibutylether (Eq. (15)). The use of one equivalent sodium supersilanide led to oligomeric $(tBu_3SiBeCl)_n$, which showed broad signals in the ^1H and ^{29}Si NMR spectrum [72]:

$$NaSitBu_3 + BeCl_2 \xrightarrow[-NaCl]{} \underset{\mathbf{12a}}{tBu_3SiBeCl} \xrightarrow[-NaCl]{+NaSitBu_3} \underset{\mathbf{13a}}{tBu_3SiBeSitBu_3} \quad (15)$$

Derivatives of $M[Si(SiMe_3)_3]_2$ (M = Ca, Sr, Ba) have been synthesized recently and characterized by X-ray crystallography [77].

3.2. Structures of alkaline-earth metal silanides

Fig. 2 shows the molecular structures of alkaline-earth metal silanides characterized by X-ray structure analyses. The Si−Be−Si unit is perfectly linear, as for the isoelectronic compound $(tBu_3Si)_2Zn$ [78]. The Be−Si distance of 2.1930(10) Å in the silanide **13a** is a little longer than the Be−Si bond in $CpBeSiMe_3$ (2.185(2) Å) [79] and longer than the sum of the atomic radii (2.10 Å) [80].

The molecule structures of silyl magnesium compounds of type $(R_3Si)_2Mg(donor)_n$ are shown in Fig. 2. An X-ray structure determination of **11a(THF)$_2$** shows that the Si−Mg−Si unit deviates from linearity [**11a(THF)$_2$**: bond angle Si(1)−Mg−Si(2) = 132.82(4)°] due to interactions between Mg and two O atoms from tetrahydrofuran molecules [72]. The Mg−Si distance in **11a(THF)$_2$** is 2.777(2) Å [72], representing a characteristic value for a Mg−Si bond (sum of the atomic radii: 2.77 Å) [80], but longer than in $[(Me_3Si)_3Si]_2Mg(THF)_2$ [75], $(Me_3Si)_2Mg{\cdot}TMEDA$ [76], $(Me_3Si)_2Mg{\cdot}TMDAP$ [74] and $(Me_3Si)_2Mg{\cdot}DME$ [75] (Table 4).

The central framework of the Grignard analogous compound **10a(THF)** forms a planar four-membered ring. The corners of this ring are alternately occupied by Mg and Br atoms (angle of **10a(THF)**: Br−Mg−Br 98.2(2)°, Mg−Si−Mg 81.4(2)°) [72]. In addition to two Br atoms, the Mg atom is surrounded by one Si atom and one molecule of tetrahydrofuran. Contrary to the Mg centers in **10a(THF)** [72] and **10b(THF)$_2$** [73], the Mg atoms in $(Me_3Si)MgBr{\cdot}TMEDA$ [71] is penta-coordinated. The structure of **10a(THF)** features two Mg−Si contacts with a Mg−Si distance of 2.6075(11) Å. However, the Mg−Si distances in **10a(THF)** and **10b(THF)$_2$** are significantly shorter than in **11a(THF)$_2$** and in **11b(THF)$_2$** [72,73]. The Mg−Br bond in **10a(THF)** has a length of 2.5929(9) Å [72], representing a characteristic value for a Mg−Br bond (sum of the ionic radii: 2.53 Å) [80].

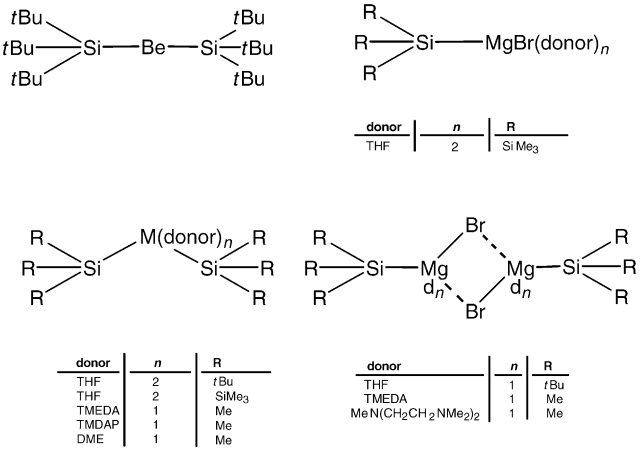


Fig. 2. Molecular structures of alkaline-earth metal silanides.

Table 4
Alkaline-earth metal silanides characterized by X-ray diffraction

Silanide	M−Si (Å)	References
tBu$_3$SiBeSitBu$_3$	2.1930(10)	[72]
CpBeSiMe$_3$	2.185(2)	[79]
Me$_3$SiMgBr(TMEDA)	2.630(4)	[71]
Me$_3$SiMgBr(MeN(CH$_2$CH$_2$NMe$_2$)$_2$	2.651(6)	[71]
tBu$_3$SiMgBr(THF)	2.6075(11)	[72]
(Me$_3$Si)$_3$SiMgBr(THF)$_2$	2.584	[73]
(Me$_3$Si)$_2$Mg(TMEDA)	2.631(4)	[76]
(Me$_3$Si)$_2$Mg(MeN(CH$_2$CH$_2$NMe$_2$)$_2$	2.651(1)	[74]
(Me$_3$Si)$_2$Mg(DME)	2.630(2)	[75]
(tBu$_3$Si)$_2$Mg(THF)$_2$	2.6075(11)	[72]
[(Me$_3$Si)$_3$Si]$_2$Mg(THF)$_2$	2.682(2)	[73]
[(Me$_3$Si)$_3$Si]$_2$Ba(THF)$_4$	3.440(9)	[77]
[(Me$_3$Si)$_3$Si]$_2$Ba(hmpa)$_6$	10.533*	[77]
[((Me$_3$Si)$_3$Si)$_2$Ba(18-crown-6)]-[((Me$_3$Si)$_3$Si)$_2$Ba(hmpa)$_6$]	3.645(4)/11.917*	[77]

* Separated ion pair.

4. Zinc group metal silanides

4.1. Synthesis of zinc group metal silanides

Compounds containing bonds between silicon and a group 12 metal have been known for many years. All of the known zinc or cadmium silanides and most of the known mercury silanides have the formal oxidation state of 2. The supersilyl and hypersilyl derivatives, tBu$_3$Si−M−SitBu$_3$ [78] and (Me$_3$Si)$_3$Si−M−Si(SiMe$_3$)$_3$ [81] (M = Zn, Cd, Hg) can be synthesized by addition of two equivalents of NaSitBu$_3$ or LiSi(SiMe$_3$)$_3$ to a tetrahydrofuran or ether solution of MX$_2$ (M = Zn, Cd, Hg; X = Cl, Br), as shown in Eq. (16):

$$\underset{\substack{\mathrm{R_3Si}=t\mathrm{Bu_3Si},(t\mathrm{Bu_3Si})_2\mathrm{HSi};\quad \mathrm{M'}=\mathrm{Na};\ \mathrm{X}=\mathrm{Cl,Br}\\ \mathrm{R_3Si}=(\mathrm{Me_3Si})_3\mathrm{Si};\quad \mathrm{M'}=\mathrm{Li};\ \mathrm{X}=\mathrm{Cl,Br}}}{\mathrm{R_3SiM'} + \mathrm{MX_2}} \xrightarrow[-2\mathrm{M'X}]{} \underset{\textbf{14–16}}{\mathrm{R_3Si{-}M{-}SiR_3}} \quad (16)$$

14a: M=Zn; R$_3$Si=tBu$_3$Si
14b: M=Zn; R$_3$Si=(Me$_3$Si)$_3$Si
14c: M=Zn; R$_3$Si=(tBu$_3$Si)$_2$HSi
15a: M=Cd; R$_3$Si=tBu$_3$Si
15b: M=Cd; R$_3$Si=(Me$_3$Si)$_3$Si
15c: M=Cd; R$_3$Si=(tBu$_3$Si)$_2$HSi
16a: M=Hg; R$_3$Si=tBu$_3$Si
16b: M=Hg; R$_3$Si=(Me$_3$Si)$_3$Si
16c: M=Hg; R$_3$Si=(tBu$_3$Si)$_2$HSi

The supersilylated silanides of the type R$_3$SiMX, such as tBu$_3$SiZnBr, tBu$_3$SiCdBr and tBu$_3$SiHgCl are prepared by metathesis reaction of one equivalent of NaSitBu$_3$ with one equivalent of MX$_2$ or by transformation of tBu$_3$Si−M−SitBu$_3$ (M = Zn, Cd, Hg) with element halides, as shown in Eq. (17) [78]:

$$\underset{\textbf{14a–16a}}{t\mathrm{Bu_3Si{-}M{-}Si}t\mathrm{Bu_3}} + \mathrm{EX_3} \rightarrow \underset{\textbf{17a–19a}}{t\mathrm{Bu_3SiMX}} + t\mathrm{Bu_3SiEX_2} \quad (17)$$

E=Al, Ga
X=Cl, Br

In addition to the metathesis reactions shown in Eq. (16), silanides of zinc group metals can be prepared as follows: (i) by transforming a Si−H bond with MR$_2$ [82,83] or (ii) by transmetallation [84].

The first molecular two-coordinated dinuclear mercury(I) derivative (Me$_3$SiMe$_2$Si)$_3$Si−Hg−Hg−Si(SiMe$_2$SiMe$_3$)$_3$ has been synthesized from the silane (Me$_3$SiMe$_2$Si)$_3$SiH and HgtBu$_2$, as shown in Eq. (18) [85]:

$$(\mathrm{Me_3SiMe_2Si})_3\mathrm{SiH} + \mathrm{Hg}t\mathrm{Bu_2} \rightarrow (\mathrm{Me_3SiMe_2Si})_3\mathrm{Si{-}HgHg{-}Si(SiMe_2SiMe_3)_3} \quad (18)$$

Several lithium mercury metallates, Li$_2$Hg(SiR$_3$)$_4$, have been synthesized, as depicted in Eq. (19) [86,87]:

$$2\mathrm{Li} + 2\mathrm{Hg(SiR_3)_2} \rightarrow \underset{\substack{\textbf{20a}:\ \mathrm{R_3Si}=\mathrm{Me_3Si}\\ \textbf{20b}:\ \mathrm{R_3Si}=\mathrm{PhMe_2Si}}}{\mathrm{Li_2[Hg(SiR_3)_4]}} + \mathrm{Hg} \quad (19)$$

Examples of synthesized and structurally characterized lithium and magnesium mercury metallates, Li$_2$Hg(SiR$_3$)$_4$ and Mg[Hg(SiR$_3$)$_3$]$_2$, are listed in Fig. 3 and Table 5 [86–88].

4.2. Structures of zinc group metal silanides

X-ray crystal structure analyses show that the disilylated zinc group metal derivatives R$_3$SiMSitBu$_3$ (M = Zn, Cd, Hg, R$_3$Si = tBu$_3$Si; M = Zn, R$_3$Si=(Me$_3$Si)$_3$Si) are monomeric in the solid state [78,81,84]. The Si−M−Si units in **14a**, **15a**, **16a** and **14b** are perfectly linear (Fig. 3). In contrast, the Si−M−Si units in **14c**, **15c** and **16c** deviates somewhat from linearity (bond angle Si−M−Si in **14c**, **15c** and **16c** M = Zn: 170.72(8)°/172.46(9)°; M = Cd: 174.20(8)°; M = Hg: 174.40(7)°) due to weak agostic interactions between the metals M (M = Zn, Cd, Hg) and H [89]. The Si−M distances in **14a**–**16a** are significantly longer than the sums of the atomic radii [78]. The X-ray crystal structure of (Me$_3$SiMe$_2$Si)$_3$Si−Hg−Hg−Si(SiMe$_2$SiMe$_3$)$_3$ shows that the Si−Hg−Hg−Si unit is linear with a Hg−Hg bond length of 2.6569(1) Å [85], which is longer than in Hg$_2$X$_2$ (X = F, Cl, Br), but slightly shorter than in Hg$_2$I$_2$.

The silanides tBu$_3$SiZnBr and tBu$_3$SiHgCl are tetrameric in the solid state, the former with a regular, the latter with a pronounced irregular cubic M$_4$X$_4$ framework [78]. The M−Si distances in **17a** and **19a** are somewhat shorter than in **14a** and **16a**. The Hg atoms in the lithium mercury metallates **20a** and **20b** are coordinated by four Si atoms, forming a distorted tetrahedron. The structures of **20a** and **20b** feature short Li−Hg contacts with average Hg−Li distances of 2.566(13) and 2.58(1) Å, respectively [86]. Selected Si−M bond lengths of the silyl derivatives of metal of the zinc group are listed in Table 5.

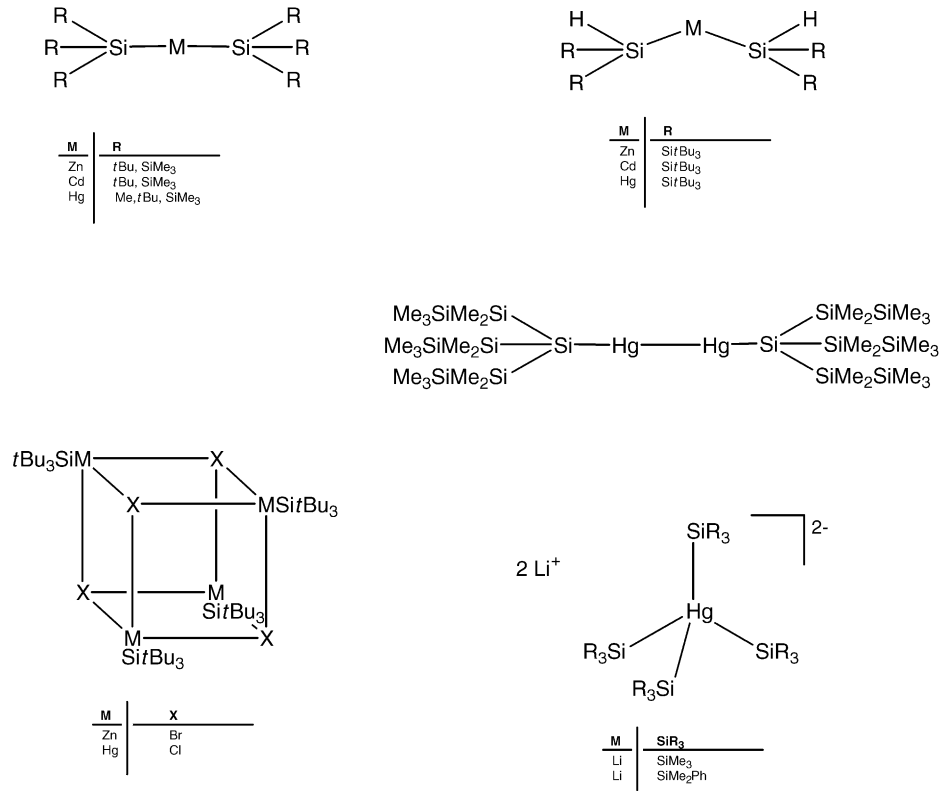


Fig. 3. Molecular structures of zinc group metal silanides.

Table 5
Silyl derivatives of the zinc, cadmium and mercury characterized by X-ray diffraction

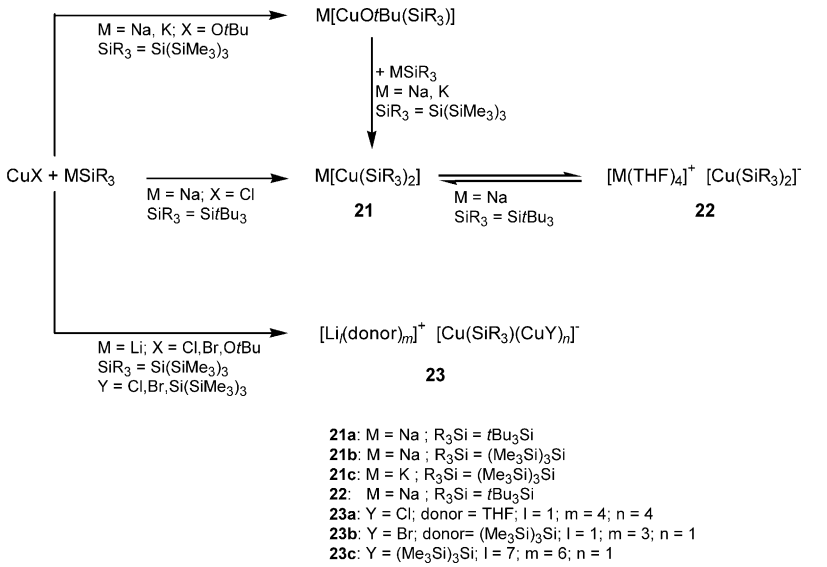
Silanide	M−Si (Å)	References
tBu$_3$SiZnSitBu$_3$	2.384(1)	[78]
[(Me$_3$Si)$_3$Si]$_2$Zn	2.342(4)	[81]
(tBu$_3$Si)$_2$HSiZnSiH(SitBu$_3$)$_2$	2.449(2)/2.425(2)	[89]
tBu$_3$SiCdSitBu$_3$	2.524(2)	[78]
[(Me$_3$Si)$_3$Si]$_2$Cd	2.510(4)	[84]
(tBu$_3$Si)$_2$HSiCdSiH(SitBu$_3$)$_2$	2.609(2)/2.599(3)	[89]
Me$_3$SiHgSiMe$_3$	2.500(5)	[92]
Ph$_3$SiHgSiPh$_3$	2.505(4)	[91]
Hg[SiMe$_2$SiCH$_2$Me$_2$Si]$_2$Hg	2.503(4)	[91]
tBu$_3$SiHgSitBu$_3$	2.495(2)	[78]
[(Me$_3$Si)$_3$Si]$_2$Hg	2.467(2)	[84]
Li(THF)$_2$SiiPr$_2$HgSiiPr$_2$Li(THF)$_2$	2.4795(13)	[65]
(tBu$_3$Si)$_2$HSiHgSiH(SitBu$_3$)$_2$	2.563(2)/2.561(2)	[89]
(Cp*$_2$SiBr)$_2$Hg	2.466(3)/2.479(3)	[90]
tBu$_3$SiZnBr	2.369(4)/2.372(2)	[78]
tBu$_3$SiHgCl	2.437(3)/2.439(3)	[78]
(Cp*$_2$SiCl)HgCl	2.4076(16)	[90]
Li$_2$[Hg(SiMe$_3$)$_4$]	2.539(2)/2.548(2)	[86]
Li$_2$[Hg(SiPhMe$_2$)$_4$]	2.493(2)/2.549(2)	[86,87]
Mg[Hg(SiPhMe$_2$)$_3$]$_2$	2.516 av	[88]
(Me$_3$SiMe$_2$Si)$_3$SiHgHgSi(SiMe$_2$SiMe$_3$)$_3$	2.485(2)	[85]

5. Silyl derivatives of copper—cuprates

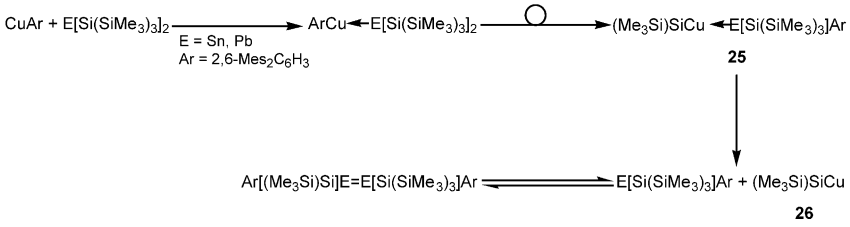
5.1. Synthesis of silyl derivatives of copper

Lithium alkyl cuprates are important and versatile organometallic reagents in organic synthesis [93]. Various details of their reaction mechanisms and molecular structures are, however, still not fully elucidated and therefore subject to current investigations [94,95]. NMR spectroscopy and ebullioscopic measurements on cuprates with small organic ligands showed that in many cases oligonuclear aggregates are formed, their structures depend on the solvent and on the stoichiometry of the reaction mixture [96–98]. Monomeric cuprates can be obtained by: (i) complexation of their alkali metal counterions with appropriate crown ethers [99]; and by (ii) employing sterically demanding ligands that kinetically stabilize these reactive species [100,101].

In contrast to the well-established cuprates with organic ligands, few compounds are known with a Si−Cu bond. Information regarding the structure and reactivity of these silyl cuprates is thus still rather limited. Most of these silyl copper compounds are produced by reaction of alkali metal silanides, MSiR$_3$, with copper(I)halides, CuX (X = Cl, Br, I), or copper(I)alkoxides, CuOR (R = tBu), as shown in Eq. (20) [100–106].



(20)



(21)

The synthesis of the supersilylated sodium cuprate $Na[Cu(SitBu_3)_2]$ was carried out from sodium supersilanide $NaSitBu_3$ and copper(I)chloride CuCl in tetrahydrofuran at −78 °C. Removal of the solvent in vacuo gave a solid residue, which was first extracted with heptane and then with toluene. The heptane extract yielded bright yellow crystals of the cuprate **21a**, while the solvent separated ion pair **22** crystallized from the toluene filtrate [102]. The silyl derivatives of copper **25** and **26** were prepared by the reaction of stannanediyl or plumbanediyl $E[Si(SiMe_3)_3]_2$ (E = Sn, Pb) with aryl copper CuAr (Ar = 2,6-$Mes_2C_6H_3$), as depicted in Eq. (21) [105].

Examples of synthesized and structurally characterized compounds with a Si−Cu bond are listed in Table 6. The supersilylated cuprates **21a** and **22** are sensitive to air and moisture and the supersilane tBu_3SiH is produced quantitatively when solutions of **21a** and **22** are treated with a small amount of water. When exposed to air, oxidation of the supersilylated cuprates **21a** and **22** proceeds with the formation of superdisilane $tBu_3Si{-}SitBu_3$ [102].

5.2. Structures of silyl derivatives of copper

The heterocuprates $M[CuOtBuSi(SiMe_3)_3]$ (M = Na, K, Cs) consist of dimers [104] while the homoleptic cuprates **21** and **22** are monomers in the solid state [102,104]. The central core of lithium cuprate $Li[Cu_5Cl_4\{Si(SiMe_3)_3\}_2]$ possesses a distorted tetrahedron structure of four Cu atoms [100] with short distances resulting from bridging chlorine atoms.

The crystal structure of **21a** is shown in Fig. 4 [102]. The Si−Cu−Si unit deviates somewhat from linearity [bond angle Si(1)−Cu−Si(2) = 175.26(5)°] due to weak interactions between Cu and Na. The distance between the Cu and Na atom is 2.7393(18) Å. The structure of **21a** features three short CH_3−Na− contacts with an average H−Na distance of 2.576 Å. In addition, the Na atom is coordinated by one Cu atom and two molecules of tetrahydrofuran. Fig. 5 shows the molecular structure of **22** in the crystal lattice [102]. Similar to the isoelectronic compound $(tBu_3Si)_2Zn$ [78], the Si−Cu−Si unit is perfectly linear. The Cu−Na distance of 7.06 Å in the solvent separated ion pair **22** is significantly longer than the sum of the atomic radii [80]. The Na atom is coordinated by four O atoms, forming a slightly distorted tetrahedron [102].

Only three neutral compounds with a Si−Cu bond have been characterized by X-ray crystallography. The phosphane adduct $Ph_3SiCu(PMe_3)_3$ and the stannylene adduct $(Me_3Si)_3SiCuSn[Si(SiMe_3)_3]Ar$ (Ar = 2,6-$Mes_2C_6H_3$) are monomers while $CuSi(SiMe_3)_3$ forms a three-membered ring with average Cu−Cu distances of 2.4021(7) Å [105]. The Cu−Si bond lengths of structurally characterized silyl derivatives of copper are listed in Table 6.

Table 6
Silyl derivatives of copper characterized by X-ray diffraction

Silanide	Cu−Si (Å)	References
$Na[Cu(SitBu_3)_2]_2$	2.3581(3)/2.3638(13)	[102]
$Na[Cu(Si(SiMe_3)_3)_2]$	2.2863(14)/2.2809(14)	[104]
$K[Cu(Si(SiMe_3)_3)_2]$	2.2988(13)/2.3001(13)	[104]
$Na[Cu(Si(SiMe_3)_3)OtBu]$	2.2347(11)	[104]
$K[Cu(Si(SiMe_3)_3)OtBu]$	2.2259(2)	[104]
$Cs[Cu(Si(SiMe_3)_3)OtBu]$	2.230(2)	[104]
$[Na(THF)_4][Cu(SitBu_3)_2]_2$	2.307(2)	[102]
$Ph_3SiCu(PPh_3)_3$	2.340(4)	[103]
$[(Me_3Si)_3SiCu]_3$	2.350 av/2.492 av	[105]
$[Li][Cu_2(Si(SiMe_3)_3)_3]$	2.3551(12)/2.3033(13)	[106]
$[(2,6\text{-}Mes_2C_6H_3)((Me_3Si)_3Si)Sn]$-$[CuSi(SiMe_3)_3]$	2.22727(11)	[105]
$[Li(THF)_4][Cu_5Cl_4(Si(SiMe_3)_3)_2]$	2.341 av	[100]
$[Li(THF)_3][Cu_2Br(Si(SiMe_3)_3)_2]$	2.266/2.406	[101]
$[Li_7(OtBu)_6][Cu_2(Si(SiMe_3)_3)_3]$	2.313(3)/2.315(3)	[106]
$[Li][Cu_2(Si(SiMe_3)_3)_3]$	2.3551(12)/2.3033(13)	[106]

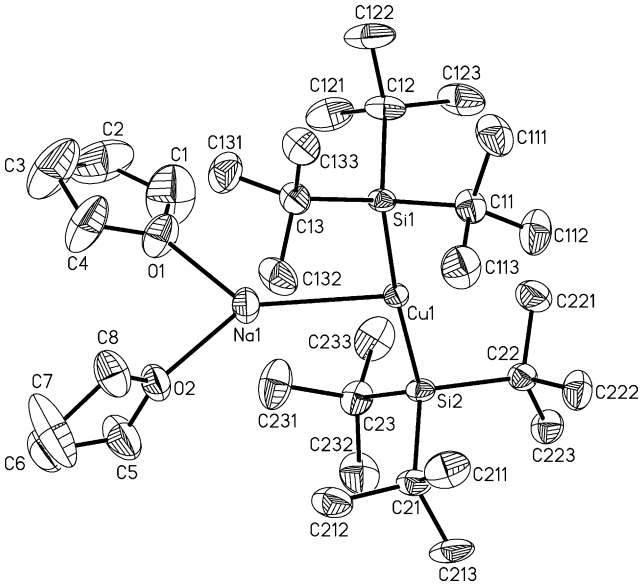
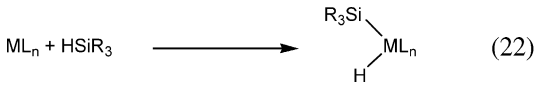


Fig. 4. ORTEP drawing of **21a**.

6. Silyl derivatives of transition metals

A huge number of hetereoleptic transition metal complexes with silyl ligands are known [107]. Most of these compounds are synthesized by addition of silanes, R_3SiH, to reactive transition metal species (Eq. (22)). In contrast, few monoleptic transition metal complexes with M−Si bonds have been structurally characterized [140]. Many reviews have been devoted to hetereoleptic transition metal complexes with silyl ligands [107].



(22)

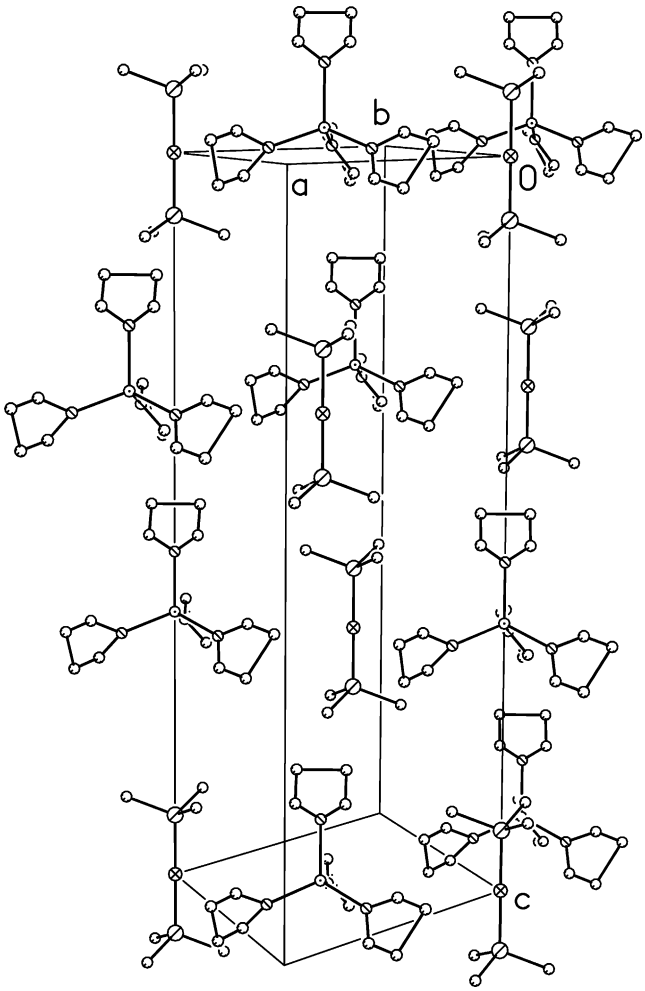


Fig. 5. Packing diagram of **22**.

7. Reactivity of silanides

The reactivity of silyl anions will be exemplified by the silanides $MSitBu_2R$ (R = *t*Bu, Ph) in the sections that follow.

7.1. Basicity

The alkali metal and alkaline-earth metal silanides $MSitBu_2R$ (R = *t*Bu, Ph; M = Li, Na, K, Mg, Be) and their donor adducts are extremely sensitive to air and moisture. When solutions of the alkali metal and alkaline-earth silanides $MSitBu_2R$ (R = *t*Bu, Ph; M = Li, Na, K, Mg, Be) in benzene are treated with a small amount of water, the alkali metal or alkaline-earth metal cation is substituted cleanly by protons [5,8,9].

In the thermolysis of the sodium and potassium silanides $(THF)_2NaSitBu_2Ph$ and $(THF)KSitBu_2Ph$ in D_{12}-cyclohexane at 100 °C, NMR spectroscopy shows the silane tBu_2PhSiH to be the main product (66%), while the formation of tBu_2PhSiD was not observed [8].

7.2. Redox behaviour

The alkali metal silanides and their donor adducts are strong reducing agents, whereas alkaline-earth silanides are slightly weaker reducing agents. When exposed to air, oxidation of $MSitBu_2R$ (R = *t*Bu, Ph; M = Li, Na, K, Mg) proceeds with the formation of the disilanes $tBu_2RSi{-}SiRtBu_2$ (R = *t*Bu, Ph) and the silanolates (siloxides) $MOSitBu_2R$ (R = *t*Bu, Ph; M = Li, Na, K, Mg), according to Eq. (23) [8,9,108]:

$$10MSitBu_2R + 6O_2 \xrightarrow[-2MO_2]{} 8MOSitBu_2R + tBu_2RSi{-}SiRtBu_2 \quad (23)$$

The disilanes $tBu_2RSi{-}SiRtBu_2$ (R = *t*Bu, Ph) are more readily synthesized by oxidation, as shown in Eq. (24):

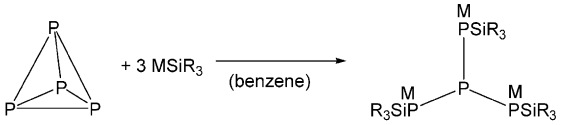
$$2MSitBu_2R + TCNE \text{ or } 2Ag^+ \xrightarrow[-TCNE^{2-} \text{ or } 2Ag]{} tBu_2RSi{-}SiRtBu_2 \quad (24)$$

Oxidation of the silanides $MSitBu_2R$ (R = *t*Bu, Ph; M = Li, Na, K) with $AgNO_3$ or TCNE proceed with the formation of the corresponding disilanes $tBu_2RSi{-}SiRtBu_2$ (R = *t*Bu, Ph) [5,8,9,109]. EPR spectroscopy measurements (Fig. 6) on solutions of the sodium silanides $NaSitBu_3$ in tetrahydrofuran that were exposed to dry air showed the presence of the supersilyl radical tBu_3Si [110].

Up to now it has not been possible to determinate the redox potentials of $MSitBu_2R$ (R = *t*Bu, Ph; M = Li, Na, K, Mg).

7.3. Nucleophilic addition

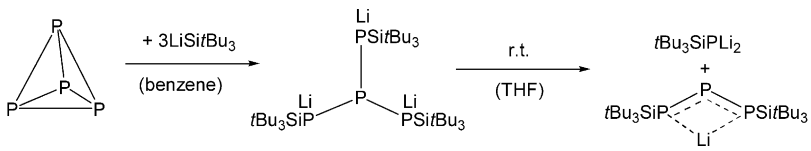
One of the most interesting features of alkali silanides is their nucleophilicity. Silanides are isoelectronic with phosphines. Promising results have already been obtained in the degradation of P_4 with the silanides $MSitBu_3$ (M = Li, Na) and $NaSitBu_2Ph$. The reaction of P_4 with the silanides $MSitBu_3$ (M = Li, Na) and $NaSitBu_2Ph$ at a 1:3 stoichiometry led cleanly to the tetraphosphides $(tBu_3Si)_3P_4M_3$ (M = Li, Na) and $(tBu_2PhSi)_3P_4Na_3$ (Eq. (25)) [111]:



(25)

27a: R_3Si = tBu_3Si, M=Li, Na
27b: R_3Si = tBu_2PhSi, M=Na

However, the tetraphosphide $(tBu_3Si)_3P_4Li_3$ features a dimer in the solid state and can be transformed into the unsaturated triphosphide $(tBu_3Si)_2P_3Li$ and the monophosphide tBu_3SiPLi_2 (Eq. (26)):



(26)

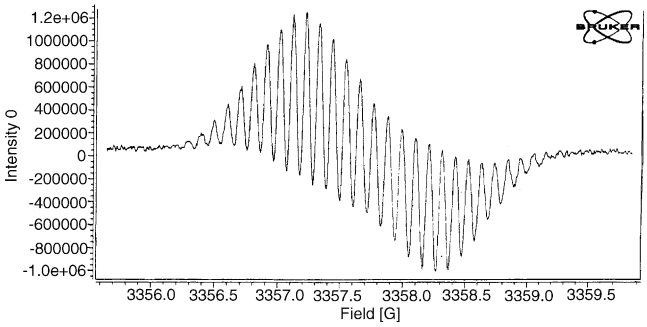
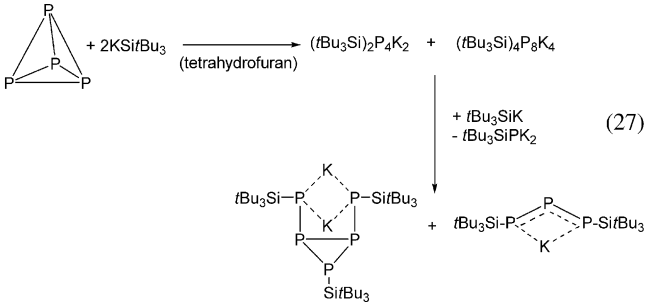


Fig. 6. EPR spectrum of the supersilyl radical tBu_3Si.

Otherwise, the reaction of P_4 with $MSitBu_3$ (M = Li, Na) and $NaSitBu_2Ph$ in a molar ratio of 1:2 leads to the tetraphosphides **28** $(tBu_3Si)_2P_4Na_2$ (M = Li, Na) and $(tBu_2PhSi)_2P_4Na_2$,which dimerize in weak-polar solvents to the sodium octaphosphides **31** $(tBu_3Si)_4P_8M_4$ (M = Li, Na) and $(tBu_2PhSi)_4P_8Na_4$ [112,113].

In contrast, when P_4 was treated with three equivalents $KSitBu_3$ in tetrahydrofuran, the tetraphosphide $(tBu_3Si)_2P_4K_2$ and the octaphosphide $(tBu_3Si)_4P_8K_4$ were first formed as main products rather than the tetraphosphide $(tBu_3Si)_3P_4K_3$. Surprisingly, after the reaction mixture had been stored at ambient temperature for 3 weeks, the resonances of $(tBu_3Si)_2P_4K_2$ and $(tBu_3Si)_4P_8K_4$ were no longer observable in the ^{31}P NMR spectrum and new signals were assigned to the pentaphosphide $(tBu_3Si)_3P_5K_3$ (34% of P atoms), the triphosphide $(tBu_3Si)_2P_3K$ (42% of P atoms) and the monophosphide tBu_3SiPK_2 (24% of P atoms). Obviously, the potassium silanide tBu_3SiK transforms slowly to the tetraphosphide $(tBu_3Si)_2P_4K_2$ and the octaphosphide $(tBu_3Si)_4P_8K_4$ transforms into $(tBu_3Si)_2P_3K$ and $(tBu_3Si)_3P_5K_2$ [114].



(27)

As shown in Eq. (27), the silanide $KSitBu_3$ decomposes to both phosphides $(tBu_3Si)_2P_4K_2$ and $(tBu_3Si)_4P_8K_4$ by the formation of the monophosphide tBu_3SiPK_2, the triphosphide $(tBu_3Si)_2P_3K$, and the pentaphosphide $(tBu_3Si)_3P_5K_2$. Contrary to the lithium tetraphosphide $(tBu_3Si)_3P_4Li_3$ [111], the potassium tetraphosphide $(tBu_3Si)_3P_4K_3$ is unknown and

the triphosphide $(t\mathrm{Bu_3Si})_2\mathrm{P_3K}$ may be produced via an intermediary tetraphosphide such as $(t\mathrm{Bu_3Si})_2\mathrm{P_3Li}$.

$$\mathrm{MSiR_3} + \mathrm{N_2O} \xrightarrow[-\mathrm{N_2}]{} \mathrm{MOSiR_3} \quad (28)$$
32a : $\mathrm{R_3Si} = t\mathrm{Bu_3Si}$
32b : $\mathrm{R_3Si} = t\mathrm{Bu_2PhSi}$

Treatment of $\mathrm{N_2O}$ with one equivalent of $\mathrm{MSi}t\mathrm{Bu_2R}$ (R = *t*Bu, Ph; M = Li, Na, K) leads to the addition products that were thermolized quantitatively into $\mathrm{N_2}$ and $\mathrm{MOSi}t\mathrm{Bu_2R}$ (R = *t*Bu, Ph; M = Li, Na, K). Therefore, the synthesis of $\mathrm{MOSi}t\mathrm{Bu_2R}$ (R = *t*Bu, Ph; M = Li, Na, K) according to Eq. (28) is preferable to the oxidation of $\mathrm{MSi}t\mathrm{Bu_2R}$ (R = *t*Bu, Ph; M = Li, Na, K) with air because the siloxides $\mathrm{MOSi}t\mathrm{Bu_2R}$ (R = *t*Bu, Ph; M = Li, Na, K) are obtained in high purity and very good yield without disilane $t\mathrm{Bu_2RSi{-}SiR}t\mathrm{Bu_2}$ (R = *t*Bu, Ph) as a side product [105].

$$\mathrm{NaSi}t\mathrm{Bu_3} + \mathrm{R_3SiN_3} \rightarrow \mathrm{R_3Si{-}N{=}N{-}NNaSi}t\mathrm{Bu_3}$$
$$\xrightarrow[-\mathrm{N_2}]{} \mathrm{NaN(SiR_3)(Si}t\mathrm{Bu_3)} \quad (29)$$
33a : $\mathrm{R_3Si} = t\mathrm{Bu_3Si}$
33b : $\mathrm{R_3Si} = t\mathrm{Bu_2MeSi}$
33c : $\mathrm{R_3Si} = t\mathrm{BuMe_2Si}$

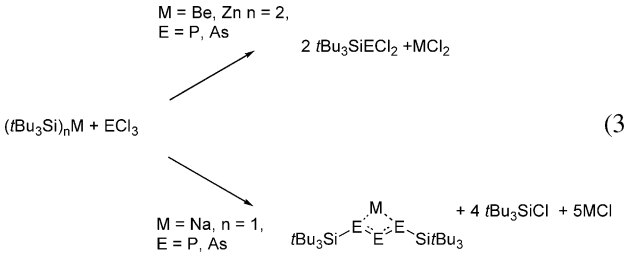
In a similar way, the silyl amides **33a**–**33c** can be obtained almost quantitatively via triazenides $\mathrm{R_3SiN{=}N{-}NNaSi}t\mathrm{Bu_3}$ from the reaction of sodium silanide $\mathrm{NaSi}t\mathrm{Bu_3}$ with silyl azides $\mathrm{R_3SiN_3}$ (Eq. (29)) [115]. This type of reaction is known as the Staudinger reaction in the chemistry of isoelectronic phosphines.

7.4. Nucleophilic substitution

Nucleophilic substitution reactions of alkali metal supersilanides on element halides $\mathrm{EX_3}$ (E = Al, Ga, In, Tl) often occur with a reduction of E and the formation of E−E bonds [116–118]. However, the reactions between $t\mathrm{Bu_2PhSiNa}$ and $\mathrm{EBr_3}$ (E = Al, Ga) give substitution reactions only [119]:

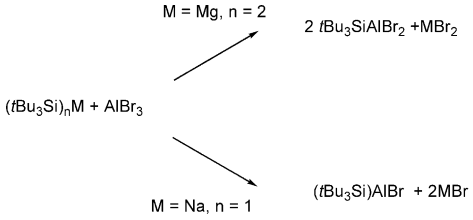
$$\mathrm{NaSiPh}t\mathrm{Bu_2} + \mathrm{ClSiR_3} \xrightarrow[-\mathrm{NaCl}]{} t\mathrm{Bu_2PhSi{-}SiR_3} \quad (30)$$
R=Cl,Me

The reactions between $t\mathrm{Bu_2PhSiNa(THF)_2}$ and $\mathrm{SiCl_4}$, as well as $\mathrm{Me_3SiCl}$ lead cleanly to the disilanes $t\mathrm{Bu_2PhSiSiCl_3}$ and $t\mathrm{Bu_2PhSiSiMe_3}$, as shown in Eq. (30) [8]. Surprisingly, the reaction of $t\mathrm{Bu_3SiNa(THF)_2}$ with $\mathrm{ECl_3}$ (E = P, As) leads to the sodium disupersilyltriphosphenide, $t\mathrm{Bu_3Si(Na)P{-}P{=}PSi}t\mathrm{Bu_3}$ [120], and the disupersilyltriarsenide, $t\mathrm{Bu_3Si(Na)As{-}As{=}AsSi}t\mathrm{Bu_3}$ [109], as shown in Eq. (31):

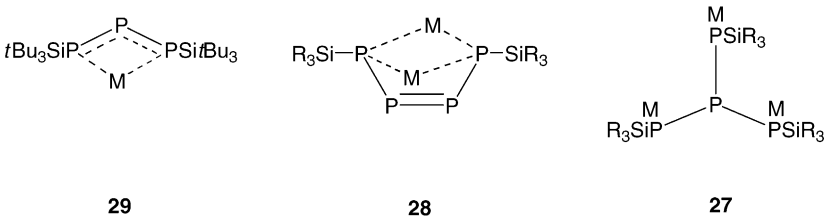


(31)

This result demonstrates the high reduction potential of alkali metal supersilanides. On the other hand, $(t\mathrm{Bu_3Si})_2\mathrm{Be}$ and $(t\mathrm{Bu_3Si})_2\mathrm{Zn}$ react with element trichlorides $\mathrm{EX_3}$ (E = P, As; X = Cl, Br) to produce $t\mathrm{Bu_3SiEX_2}$ in high yield [121,122]:



(32)



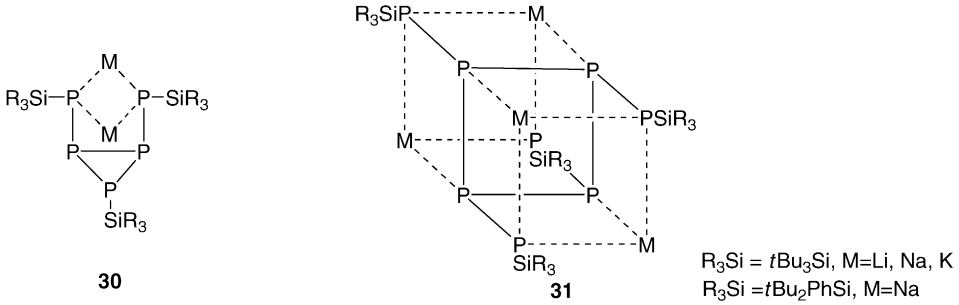
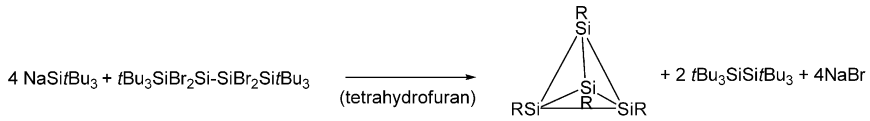
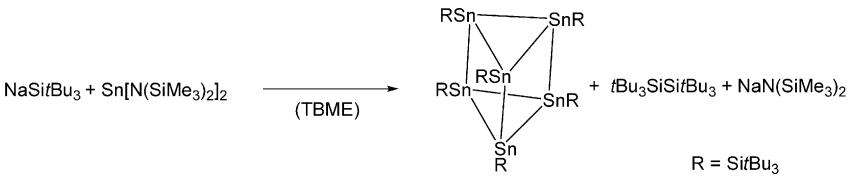


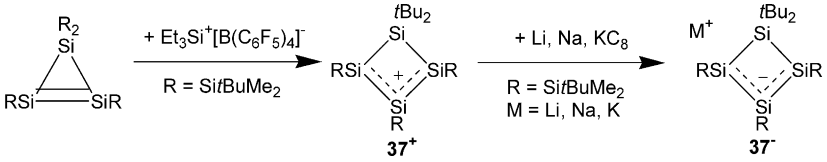
Fig. 7. Supersilyl and di-*tert*-butylsilyl phosphanides.



(33)



(34)



(35)

The reaction of sodium supersilanide with triel (group 13 element) [141] halides, EX_3, does not depend on the Si:M ratio (1:1 or 2:1) and always produces the disupersilylated compounds, $(t\mathrm{Bu_3Si})_2EX$ [116]. However, one equivalent of the silanide $(t\mathrm{Bu_3Si})_2\mathrm{Mg(THF)_2}$ reacts with EBr_3 (E = Al, Ga) to give $t\mathrm{Bu_3SiEX_2}$ as depicted in Eq. (32). Only the monosupersilylated compounds $t\mathrm{Bu_3SiEBr_2}$ (E = Al, Ga) are formed. $t\mathrm{Bu_3SiAlBr_2}$ was isolated as the $MgBr_2$ adduct [116] and $t\mathrm{Bu_3SiGaBr_2}$ as the THF adduct [72].

On the one hand, it is an advantage to synthesize silylated compounds of the type $(t\mathrm{Bu_3Si})_lEX_{n-l}$ by reaction of group 2 or group 12 metal silanides with the appropriate element halides EX_n. On the other hand, reduction reactions of element halides, alkoxides, or amides should be carried out with alkali metal silanides, as shown in Eqs. (33) and (34) [123,124] (Fig. 7):

8. Cyclic compounds with negatively charged Si centers

The first silole dianion salt was reported in 1990 [125]. As shown in Fig. 8, several silole dianions with different counter ions have been structurally characterized. Also the silaindenyl **35** and the silafluorenyl dianions **36a** and **36b** have been synthesized.

NMR spectroscopy and theoretical studies on silole dianions showed delocalization of the ring and equalization of CC bonds in the ring. Silole dianions undergo nucleophilic reactions, single electron-transfer reactions, and polymerization to form polymers and copolymers with fluorescent and electroluminescent properties [125–134].

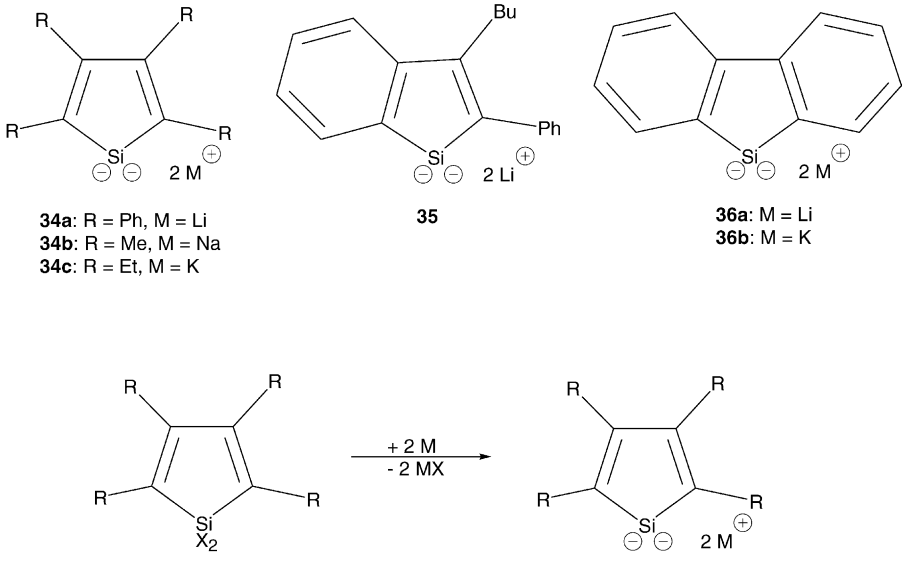
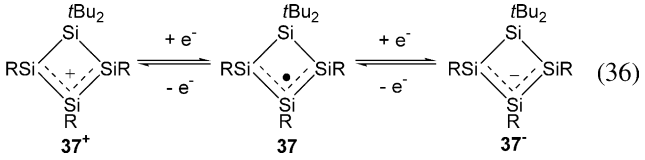


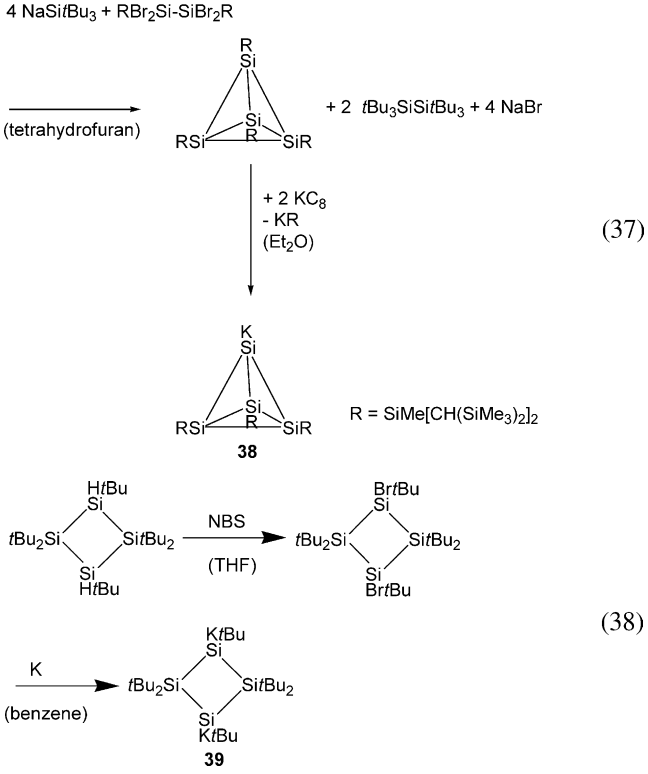
Fig. 8. Silole dianions.

Moreover, several anionic ring systems with more than one Si center have been studied in detail recently. According to X-ray diffraction analysis, the cyclotetrasilenide $\mathbf{Li^+ \cdot 37^-}$ contains a non-planar Si_4-ring with η^3-coordination of a Li cation [135]. The cyclotetrasilenide $\mathbf{Li^+ \cdot 37^-}$ undergoes one electron oxidation by $Et_3Si^+[B(C_6F_5)_4]^-$ to form **37** which also reacts with $Et_3Si^+[B(C_6F_5)_4]^-$ to give the cation $\mathbf{37^+}$, as shown in Eq. (36) [135]:



(36)

Recently, the isolable radical anion $[Si\{1,2\text{-}(NEt)_2C_6H_4\}]_4^-$ and the dianion $[Si\{1,2\text{-}(NEt)_2C_6H_4\}]_4^{2-}$ have been synthesized as potassium salts [136].

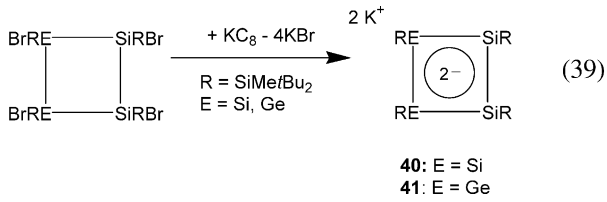


(37)

(38)

As shown in Eq. (37), the potassium tetrasilatetrahedranide **38** was obtained by reaction of the appropriate tetrasilatetrahedrane with potassium graphite via cleavage of an exocyclic bond [137].

The cyclic silanide **39** was prepared as depicted in Eq. (38). The molecular structure of **39** features a completely planar Si ring [138].



(39)

Very recently the cyclobutadiene dianion derivatives **40** and **41** have been isolated and characterized by X-ray crystallography [139].

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