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Silicon derivatives of the metals of groups 1 and 2

Paul D. Lickiss, Colin M Smith

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK

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Contents

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Abstract

An account is given of the syntheses, structures and reactions of compounds containing group 1 or 2 elements bonded to silicon. The review concentrates mainly on the group 1 derivatives as these are far more numerous than those of the group 2 elements. Silyllithium compounds are discussed in most detail, particularly Ph_3SiLi and $(Me_3Si)_3SiLi$ for which convenient syntheses are available. The use of silyllithium reagents for organometallic and inorganic synthetic purposes is described and an outline of some of the more important reactions in organic chemistry is given.

Keywords: Silicon derivatives; Group 1 metals; Group 2 metals; Silyllithium compounds

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List of abbreviations

BBN	9-borabicyclo[3.3.1]nonane
BCO	[2.2.2]bicyclooctyl
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
dcpe	bis(dicyclohexylphosphino)ethane
DME	dimethoxyethane
DMI	1,3-dimethyl-2-imidazolidinone
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2-(1*H*)-pyrimidinone
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
HMPA	hexamethylphosphoramide
HMPT	hexamethylphosphorustriamide
MeTHF	2-methyltetrahydrofuran
Nphal	phthalimide
TfO	trifluoromethylsulphonate

thexyl	*tert*-hexyl-1,1,2-trimethylpropyl
THF	tetrahydrofuran
THP	tetrahydropyran
TMDAP	tetramethyldiaminopropane
TMEDA	tetramethylethylenediamine
TMP	2,2,6,6-tetramethylpiperidine
tol	tolyl
Tos	*para*-tolylsulphonyl
TPP	5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin
trityl	triphenylmethyl

1. Introduction

The chemistry of organic derivatives of the elements of groups 1 and 2, particularly organolithium and organomagnesium compounds, has been well established for many years and they are among some of the most useful reagents available to the synthetic chemist today (see for example Ref. [1]). The use of organosilicon compounds in synthetic chemistry is also now widespread both in inorganic and in organic chemistry in which silyl groups may be used for protecting or directing purposes, utilizing both their steric and their electronic properties (see for example Ref. [2]). Despite the existence of these now mature areas of chemistry their combination to give alkali metal derivatives of silicon has been much less widely studied. The use of silyllithium compounds in particular has, however, been increasing rapidly in recent years and it is these compounds that will feature most in the discussion below. The chemistry of silyllithium compounds has been reviewed before [3] and this review will therefore concentrate on work published since 1970 with reference made to important earlier work where necessary.

The relatively slow progress in the field of silylalkalimetal compounds is almost certainly due to the much greater difficulty in their synthesis when compared to their organic counterparts. For example, it is very difficult (indeed several of such compounds are currently unknown as synthetic reagents) to prepare silicon compounds analogous to well-known organic species such as MeLi, *n*-BuLi, PhLi or their organomagnesium (Grignard) analogues. These difficulties have led to a concentration on those compounds that are relatively readily prepared such as Ph_3SiLi and $(Me_3Si)_3SiLi$ and this is reflected throughout the review. It is often not known how many solvent molecules are associated with the alkali metal in R_3SiM species and for convenience, as is usually the case for the organic analogues, the solvent associated with the cation will often be ignored in the text.

To keep this article to a reasonable length and within the general field of organometallic chemistry the use of the compounds discussed for purely synthetic organic purposes will not be described in detail and only illustrative examples of the types of reaction undergone will be given.

2. The synthesis of silyl derivatives of the group 1 metals

Silyl derivatives of the group 1 metals are the biggest class of compound covered in this review and of these silyllithium and potassium reagents are the most commonly prepared. The reasons for the lack of known silylsodium reagents are unclear but this could be because the most convenient early synthesis of silylmetallic reagents was from the cleavage of disilanes which, however, are not cleaved by sodium in the majority of the solvents first investigated. It has also been reported that some silylsodiums react differently to the corresponding silyllithium. For example triphenylsilyllithium reacts with chlorobenzene mainly via metal halogen exchange to give hexaphenyldisilane while triphenylsodium reacts to via substitutions to give mainly tetraphenylsilane [4]. Silyl caesium and rubidium reagents have been prepared but not used extensively owing to the hazards and costs of these metals and, because they are so reactive, they tend to cleave the solvents employed giving low yields of the desired product.

The most readily available silyl–group 1 reagents used are those with at least one aryl ring or an $SiMe_3$ group on the silicon atom as these tend to stabilize the negative charge on the silicon. The most common reagents of this type are $Ph_3SiLi-K$ and $(Me_3Si)_3SiLi$. Much of the important pioneering work on silylmetallic reagents was carried out by Gilman and coworkers in the 1950s and 1960s; this work has been reviewed elsewhere [3–5] and only the more important synthetic points will be discussed here.

Silylmetallic reagents can be prepared in a number of different ways depending on the substituents and the metal. The different reaction types are described below and where possible an indication of the best synthetic method is given. As the silylmetallic reagents are coloured the course of the reactions can often be judged by the colour changes.

2.1. Silicon–silicon bond cleavage

This was the first convenient method for the preparation of silyl derivatives of group 1 metals and is most easily achieved for reagents containing one or more aryl groups on the silicon. This class of compounds can be easily prepared by the cleavage of the parent disilane by the appropriate metal [6,7] (Eq. (1)). This method is useful for the preparation of halide-free solutions of the silylmetallic reagents and is very convenient as many of the disilanes are commercially available.

$$R_3SiSiR_3 + 2M \rightarrow 2R_3SiM \quad (1)$$

The most widely prepared compounds of this type are the triphenylsilyl derivatives which have been prepared for all the group 1 metals except francium. Much of the early work to determine the best reaction conditions for the cleavage of Si—Si bonds was carried out on this system [5]. As the metal is changed from lithium through to caesium the reactivity increases and solubility of the silylmetallic reagent decreases. A whole range of derivatives other than Ph_3Si have been prepared using this method;

examples of these are $Ph_3Me_{3-n}Si-Li,K$ [6,7], Ph_2Bu^tSiK [8], H_3SiK [9,10], PhH_2SiK [10], Ph_2HSiLi [11], (*o*-Tol)$_3$SiLi,K,Cs [12], *p*-TolPh$_2$SiK [12,13]. These reagents are usually a brownish green. The ease of formation decreases with the number of alkyl groups on the silicon and hexaalkyldisilanes are not cleaved by these metals.

Important considerations in these reactions are the choice of solvent and metal used. THF is often the solvent of choice, in which case the reaction proceeds at room temperature in a number of hours to give excellent yields of the silylmetallic reagent. There are, however, some drawbacks to its use at elevated temperatures as the silylmetallic species attack the THF to form compounds of the type $R_3Si(CH_2)_4OH$ derived from ring opening under prolonged refluxing conditions [14]. A range of other solvents such as diethyl ether, DME, dioxane, THP or hydrocarbons have also been investigated but they generally give poorer results. Disilanes are cleaved in ether solutions by lithium or sodium–potassium alloy to give silylmetallic reagents but these silylmetallic reagents tend to be insoluble and slowly cleave the ether [6]. Silylmetallic reagents are readily formed in DME but they are less stable than in THF particularly at elevated temperatures. For example, if a DME solution of triphenylsilylpotassium is refluxed the silylmetallic reagent is consumed in only 1 h so the use of this solvent offers no real advantages and it is not usually employed [15]. In either dioxane or THP the silylmetallic compound is stable but the formation is slow [16,17] and in hydrocarbons the cleavage of the disilane does not occur readily [8]. Liquid ammonia and pyridine have also been used but the silylmetallic reagent formed reacts with the ammonia to form silazanes [19] or with pyridine to give a silyl-1,4-dihydropyridine [20].

The metal purity is also crucial: for example, pure lithium metal is unreactive [21] and so lithium containing 1%–2% sodium must be used; however, higher amounts of sodium are detrimental to the reaction and pure sodium does not cleave the bond in hexaphenyldisilane in ether, xylene or dioxane [6] although it does in THF and DME [15]. This dependence of the reaction on the lithium purity has also been observed in the formation of organolithium reagents [22]. Sodium–potassium alloy is usually employed rather than potassium metal for the formation of silylpotassium reagents [12,13].

The usual reaction conditions employed for the cleavage of disilanes are an excess of the metal stirred in THF with the disilane at room temperature for a few hours or more usually overnight. The yields obtained are excellent but, as they cannot be determined easily for the silylmetallic reagent but only for derivatives, yields will not be generally given. The aryl group is thought to be necessary for stabilization of the negative charge on the silicon in the silylmetallic compound; this stabilization has been attributed to π polarization [23].

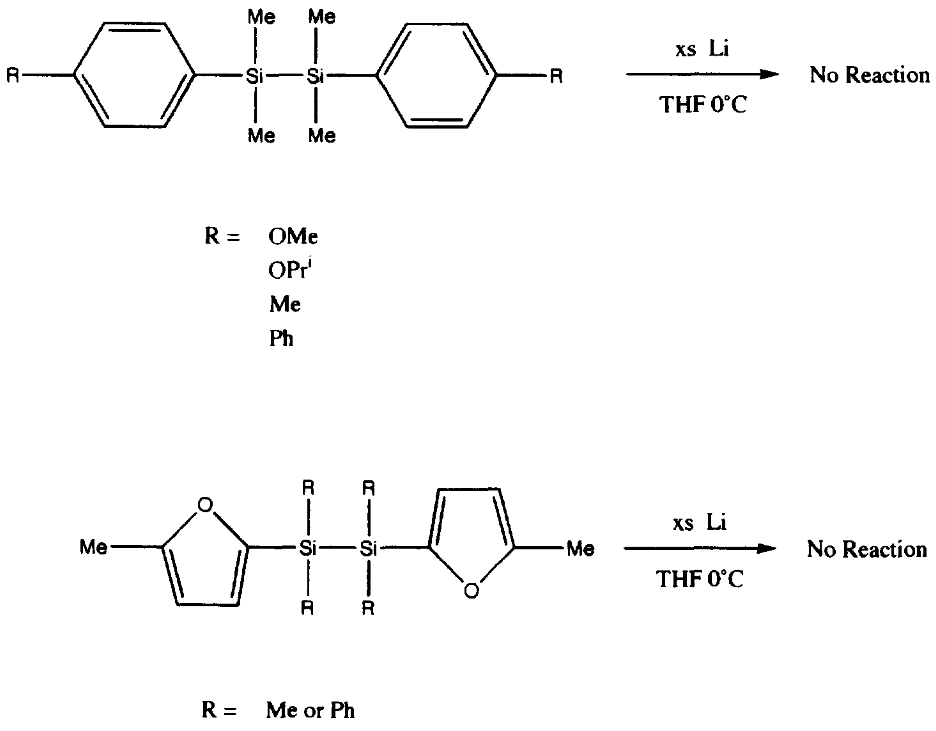
However, not all aryl disilanes can be cleaved with lithium metal in this way as Fleming and coworkers have shown [24]. In an attempt to form silyllithium reagents that would be more reactive towards an organic substrate and then be more easily converted via protodesilyation to alcohols than the widely used $PhMe_2Si$ derivatives they investigated a number of chlorosilanes, such as *p*-TolMe$_2$SiCl, which gave disilanes on treatment with lithium metal. These disilanes were then found not to react with lithium metal in THF at 0 °C; however, under refluxing conditions $(p\text{-TolMe}_2\text{Si})_2$ gave $p\text{-TolMe}_2\text{Si(CH}_2)_4\text{OH}$ in 19% yield presumably via silyllithium formation and then attack on THF [14] (Scheme 1).

As well as simple disilanes, perphenyloligosilanes of the type $\text{Ph}_3\text{Si(SiPh}_2)_n\text{SiPh}_3$ ($n = 1, 2, 3$; for the example $n = 2$ see Eq. (2)) are also cleaved by metals but these compounds tend to give mixtures of products, such as $\text{Ph}_3(\text{SiPh}_2)_x\text{Li}$ ($x = 0, 1, 2$) [25].

$$\text{Ph}_3\text{Si(SiPh}_2)_2\text{SiPh}_3 \xrightarrow{\text{xs Li THF}} \begin{array}{ll} \text{Ph}_3\text{SiLi} & 31\% \\ \text{Ph}_3\text{SiPh}_2\text{SiLi} & 45\% \\ \text{Ph}_3\text{SiPh}_2\text{SiPh}_2\text{SiLi} & 17\% \end{array} \qquad (2)$$

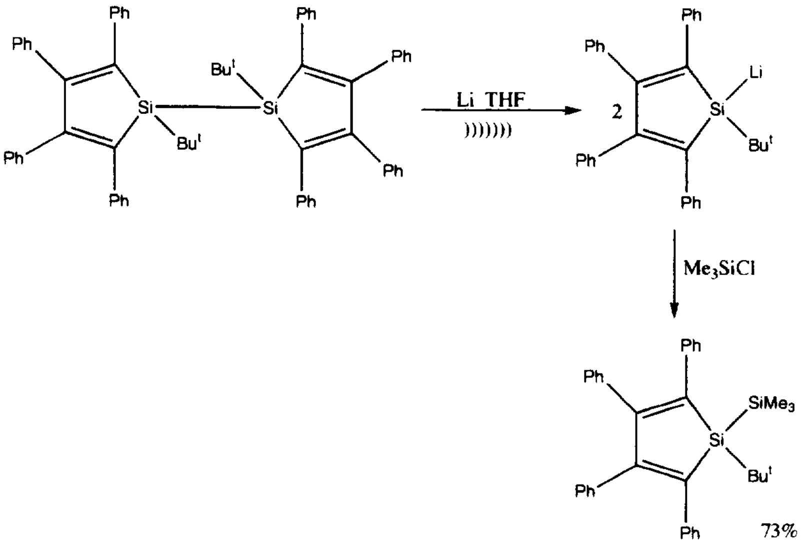
Cyclic perphenyl silanes give silylbimetallic compounds of the type $\text{M(SiPh}_2)_n\text{M}$ when reacted with metals. For example, $\text{Li(Ph}_2\text{Si)}_4\text{Li}$ may be prepared by the reaction of $(\text{Ph}_2\text{Si})_4$ with excess lithium metal [26] (Eq. (3)). The rate and yield of these reactions can be increased by the addition of biphenyl or naphthalene to the reaction [27].

$$cyclo\text{-(SiPh}_2)_4 \xrightarrow{\text{xs Li THF}} \text{LiSiPh}_2\text{SiPh}_2\text{SiPh}_2\text{SiPh}_2\text{Li} \qquad (3)$$



Scheme 1. Non-cleavage of disilanes by lithium metal.

Ultrasonic irradiation is another technique used to promote these type of reactions and has been used extensively by Boudjouk, recently to prepare silole anions [28], which are of interest because of their potential aromatic character. They have been prepared in a number of different ways, for example, by the ultrasound-promoted lithium metal cleavage of disiloles [28] (Eq. (4)) or the reaction of simple silicon substituted silyl siloles with silyllithium reagents [29] (Eq. (5)).



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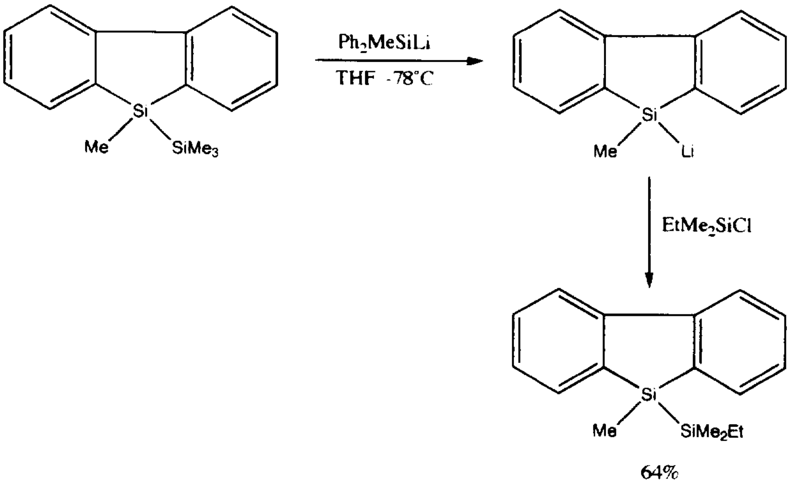


(5)

Trialkylsilylmetallic reagents are less stable than aryl-containing reagents and cannot be readily prepared by the action of metal on the hexaalkyldisilanes [30].

They have, however, been prepared from the cleavage of unsymmetrical disilanes which gave a green solution of both reagents in low yields [31] (Eq. 6) or, as was the case for the first trialkylsilyllithium, Et_3SiLi, by the reaction of triethyl(triphenylgermyl)silane and lithium in ethylamine [31] (Eq. (7)). In this reaction two lithium reagents are formed and when allowed to stand they react with the solvent.

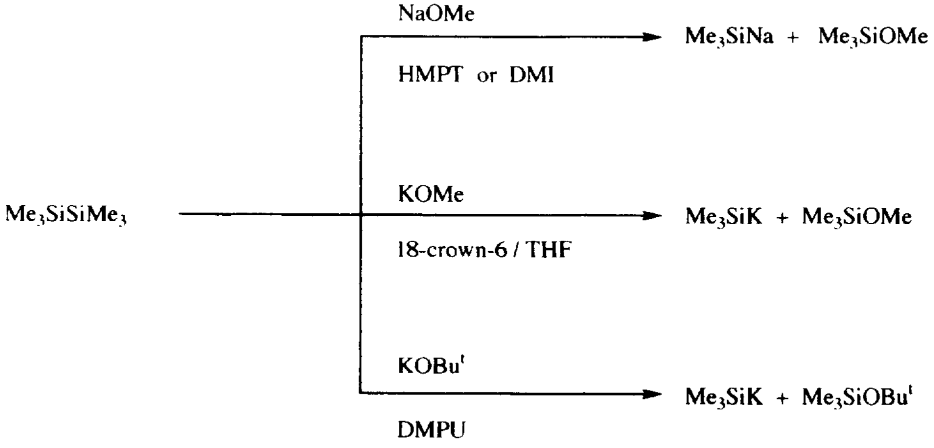
$$Ph_3SiSiEt_3 \xrightarrow[Et_2O]{Na/K} Ph_3SiK + Et_3SiK \tag{6}$$

$$Ph_3GeSiEt_3 \xrightarrow[EtNH_2]{Li} Ph_3GeLi + Et_3SiLi \tag{7}$$

These reactions are not a convenient source of these reagents and a number of alternative methods for their synthesis from disilanes have been developed. The first of these was developed by Still and used the strongly coordinating solvent HMPA to stabilize the trimethylsilyl anion formed from the cleavage of hexamethyldisilane with MeLi in HMPA which gives a deep red solution of Me_3SiLi within 15 min [32] (Eq. (8)).

$$Me_3SiSiMe_3 \xrightarrow[HMPA,\ 0\ ^{\circ}C]{MeLi/Et_2O} Me_3SiLi + Me_4Si \tag{8}$$

Trimethylsilyl sodium and potassium have been prepared in two main ways, the cleavage of the disilane with metal hydrides developed by Corriu and Guerin [33] (Eq. (9)) or by the reaction with sodium and potassium alkoxides in various solvents such as NaOMe in HMPA [34] or DMI [35], KOMe in 18-crown-6–THF [35] and KO^tBu in DMPU [36] (Scheme 2).



Scheme 2. Cleavage of hexamethyldisilane by alkoxides.

$$\mathrm{Me_3SiSiMe_3} \xrightarrow{\mathrm{MH}} \mathrm{2Me_3SiM} \tag{9}$$

$$\begin{array}{llll} \mathrm{M = K} & \mathrm{DME} & 40\,^{\circ}\mathrm{C} & 6\,\mathrm{h} \\ & \mathrm{DME/HMPA(10\%)} & \mathrm{R.T.} & 6\,\mathrm{h} \\ \mathrm{Na} & \mathrm{THF/18\text{-}crown\text{-}6} & \mathrm{R.T.} & 2\,\mathrm{h} \end{array}$$

Other disilanes can also be cleaved by potassium *tert*-butoxide in different solvents, for example hexaphenyldisilane is cleaved in THF or DME but not DMPU [36]; however, the yields of Ph_3SiK from these reactions are quite low, 15%–30%. Unsymmetrical disilanes can also be cleaved using this method which gives the most stable silylmetallic compound, i.e. that with most phenyl groups (Eqs. (10) and (11)); thus, Ph_3SiK is formed in these reactions in yields above 90% [36].

$$\mathrm{Ph_3SiSiPhMe_2} \xrightarrow[\substack{\mathrm{THF\ or\ DME} \\ 0\,^{\circ}\mathrm{C}\ 30\ \mathrm{min}}]{\mathrm{KOBu^t}} \underset{85\text{–}90\%}{\mathrm{Ph_3SiK}} + \mathrm{Me_2PhSiOBu^t} \tag{10}$$

$$\mathrm{Ph_3SiSiMe_3} \xrightarrow[\substack{\mathrm{THF\ or\ DME} \\ 0\,^{\circ}\mathrm{C}\ 30\ \mathrm{min}}]{\mathrm{KOBu^t}} \underset{95\text{–}90\%}{\mathrm{Ph_3SiK}} + \mathrm{Me_3SiOBu^t} \tag{11}$$

The above reactions are very useful in the preparation of trialkylsilylmetallic reagents although the use of HMPA should be avoided if possible as it is a toxic cancer suspect agent and also promotes electron transfer processes [35]. However, as half of the disilane is lost as the silylether the method is less useful for aryl-containing silylmetallic reagents which can be prepared more easily by cleavage of the disilane by the appropriate metal. The only advantage of this method for arylsilylmetallics compared with the metal cleavage of disilanes is the reduced reaction times.

Another method that gives silylmetallic reagents in very short reaction times is the cleavage of disilanes by potassium graphite in oxolane at 0 °C. The silylpotassium reagents formed from this reaction are not isolated but reacted in situ with copper, manganese or vanadium salts and then treated with organic substrates to give the final product. This process is achieved in a matter of minutes for aryl disilanes and gives excellent yields, above 90% (Eq. (12)). The course of the reaction can be monitored by the colour changes from the bronze of potassium graphite to the brown–green of the silylpotassiums through to the red–brown of the transition metal complexes and finally the black precipitate of graphite. However, for alkyldisilanes the reaction takes a number of hours and the yields are low [37].

$$\begin{array}{l} \mathrm{MePh_2SiSiPh_2Me} \xrightarrow[\substack{\mathrm{Oxolane} \\ 5\ \mathrm{min}\ 0\,^{\circ}\mathrm{C}}]{\mathrm{C_8K}} \mathrm{MePh_2SiK} \\ \qquad\qquad\qquad \substack{-70\,^{\circ}\mathrm{C} \\ 80\ \mathrm{min}} \Big\downarrow \substack{\mathrm{i)\ VCl_3} \\ \mathrm{ii)}\ cyclo\text{-}\mathrm{C_6H_{11}COCl}} \\ \qquad\qquad\qquad cyclo\text{-}\mathrm{C_6H_{11}COSiPh_2Me}\quad 80\% \end{array} \tag{12}$$

Branched chain silylmetallic compounds such as $(RMe_2Si)_3SiLi$ (R = H or Me [38]) and $(Me_3M)_3SiLi$ (M = Ge [39] or Sn [40]) can be prepared using the reaction of lithium reagents with the parent tetrasilylated compounds $(RMe_2Si)_4Si$ or $(Me_3M)_4Si$. The most important of these compounds is derived from $(Me_3Si)_4Si$ which gives $(Me_3Si)_3SiLi$ on treatment with silyllithium reagents such as Ph_3SiLi [38] or alkyllithium reagents such as MeLi [41] (Eq. (13)).

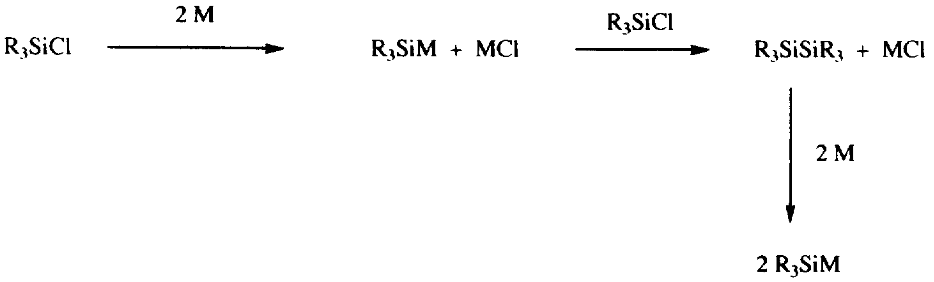
$$(Me_3Si)_4Si \xrightarrow[\text{THF R.T.}]{\text{MeLi/Et}_2\text{O}} \underset{>90\%}{(Me_3Si)_3SiLi} + Me_4Si \qquad (13)$$

The silyllithium reagent $(Me_3Si)_3SiLi$ is obtained in excellent yields above 90% as a yellow solution; from this a white crystalline solid has been isolated. The solid obtained in 92% yield has been formulated as $(Me_3Si)_3SiLi.3THF$ by ^1H nuclear magnetic resonance (NMR) spectroscopy and it can be stored for months under argon without decomposition [42]. This solid reagent $(Me_3Si)_3SiLi.3THF$ can then be dissolved in hydrocarbons to give improved yields of coupling products over those from reactions in THF (see Section 4).

The pentasilane $(Me_3Si)_4Si$ does not react with lithium metal as this would require the formation of Me_3SiLi as well as the stable and readily formed $(Me_3Si)_3SiLi$ reagent. The reaction between the pentasilane and lithium can, however, be achieved if biphenyl is added to the reaction mixture; lithium and biphenyl have also been used to prepare $(Me_3Si)_2MeSiLi$ from $(Me_3Si)_3MeSi$ [42]. Other branched polysilyllithiums of the type $(Me_3Si)_2RSiLi$, R = CD_3 [43], Me [44], Bu^t [44], Ph [44,45], mes [45], $SiMe_2Bu^t$ [46], $SiMe_2SiMe_3$ [47] or $Si(SiMe_3)_3$ [48] have been prepared by the reaction of MeLi with the parent compounds, $(Me_3Si)_3RSi$.

2.2. Silicon–halogen bond cleavage

These reactions presumably proceed via condensation of the halosilane to the disilane which then reacts with the excess metal to form the silylmetallic reagent (Scheme 3). The presence of the disilane can be observed in the ^1H NMR spectrum of the reaction solution [49] and if the reaction is stopped at early stage the disilane can be isolated from the reaction mixture [50]. As the reaction involves Si—Si bond



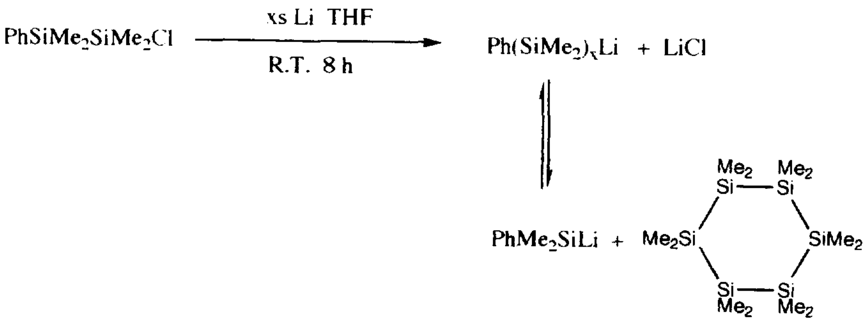
Scheme 3. Preparation of silylmetallics by the reaction of metals with silylchlorides.

cleavage this method only works in general for reagents with at least one aryl group on the silicon atom. Again the correct choice of metal and solvent is important to achieve the best results, and the best synthetic conditions are the same as those used for the cleavage of Si—Si bonds by metals as described earlier in Section 2.1. In practice the reaction is usually carried out with an excess of the metal so that four rather than two equivalents are necessary.

An interesting point about this reaction observed by Gilman is the relative reaction times of this reaction compared with the corresponding disilane cleavage. For example, the cleavage of hexaphenyldisilane by lithium in THF at room temperature takes at least 3 h but the same amount of triphenylsilyllithium can be prepared in 1–2 h by the reaction of triphenylsilylchloride and excess lithium also in THF [50]. This method is the most widely used for aryl-containing silylmetallic reagents owing to the ready availability of the starting materials and the simplicity of the reaction, the only real drawback being the halide content of the final solution. Examples of the range of silylmetallic reagents prepared by this method are $Ph_3Me_{3-n}SiLi$, K, Rb, Cs, $n=0, 1, 2$ [6,50,51], Ph_2Bu^tSiLi [52], $(Bu^n)_2PhSiLi$ [53], $(Et_2N)_nPhSiLi$, $n=1$, 2, and $Et_2NMePhSiLi$ [54], MePhRSiLi, R = *p*-Tol or *cyclo*-C_6H_{12} [55], $(o\text{-}Tol)_3SiLi$, Cs [51], mesPhHSiLi [56], PhR_2SiLi, R = Pr^i or benzyl [57], mes_2HSiLi [58], and $MeCH{=}C(Me)SiPh_2Li$ [59].

As discussed in Section 2.1 Fleming has shown that not all aryl-containing silyl chlorides can be converted to the silyllithium by treatment with lithium in THF; see Scheme 1 in Section 2.1. Some silyl chlorides, such as *p*-$TolSiMe_2SiCl$ or *p*-isopropoxyphenyldimethylsilylchloride, gave the disilanes which are not cleaved by lithium, while *o*-methoxyphenyldimethylsilylchloride does not even give the disilane. Trityldiphenylsilylbromide, Ph_3CSiPh_2Br, on the contrary, gave a red solution on treatment with lithium metal in THF; however, this turned out to be trityllithium, Ph_3CLi [24].

Longer chain silylchlorides such as $Ph(SiMe_2)_2Cl$ can also be treated with lithium metal to give silyllithiums but as Matyjaszewski has shown this is not a simple reaction, and it gives rise to a number of products. The reaction proceeds in four stages. The first involves a short induction period (less than 5 min) in which there is electron transfer from the lithium to the silylchloride which results in the formation of $Ph(SiMe_2)_2Li$. This then couples with the silylchloride to give $Ph(SiMe_2)_4Ph$; the reaction remains colourless during this step. In the second stage (5–125 min) green spots appear on the lithium surface as radical anions are formed via the reaction of $Ph(SiMe_2)_4Ph$ with the lithium metal. These anions then react with the silylchloride to give products of the type $Ph(SiMe_2)_nPh$, $n=2, 3, 4, 5$ and higher, but mainly the tetrasilane $n=4$ (50%) and tri- and pentasilanes, $n=3$ and 5 (25% each). In the third stage (125–250 min), after the consumption of the silylchloride the radical anions formed from the reaction with the lithium metal attack the chain compounds to give *cyclo*-Si_6Me_{12}. This reaction is observed as green streams from the lithium surface which become red at a distance from the metal and fade in the liquid and has been described as bleeding lithium; by the end of this step the solution has gone from pink to red. In the final stage (beyond 250 min) the solution goes from dark red to dark green and the equilibrium is set up as shown in Scheme 4 [60].



Scheme 4. Reaction of 1-chloro-2-phenyl-1,1,2,2-tetramethyldisilane with excess lithium.

Silylchlorides can also be converted in to silylpotassium reagents by their reaction with two equivalents of potassium graphite in oxolane at 0 °C. The reaction takes only a few minutes and gives excellent yields if there are aryl groups on the silicon but for a trialkylchlorosilane the reaction takes a number of hours and the yields are very low [37]. The very bulky compounds Bu^t_3SiM (M = Na [61] or K [62]) can also be prepared from the $Bu^t_3Si{-}X$ species which are refluxed in a solvent with the metal (Eq. (14)).

$$Bu^t_3SiX \xrightarrow[\text{reflux 6 h}]{\text{xs M}} Bu^t_3SiM + MX \tag{14}$$

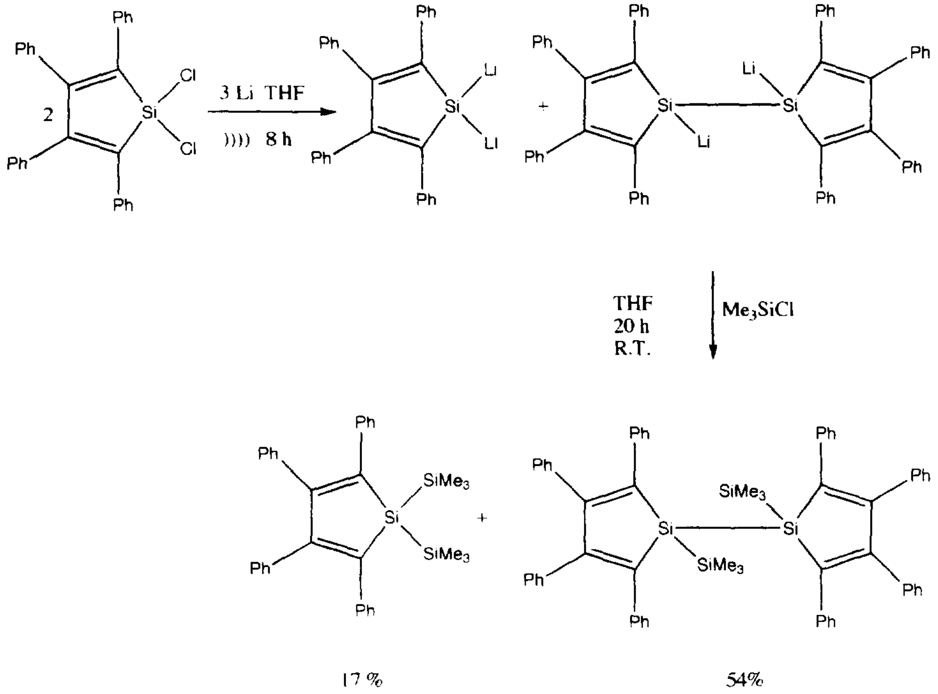
M	X	Solvent
Na	Br	THF
K	I	heptane

Silole anions and dianions have also been prepared by the reaction of silole chlorides and dichlorides with lithium metal [63] (Scheme 5). The dianion is the only product from the reaction of the silole dichloride with lithium but it has not been possible to prepare the disilole dianion without the formation of the silole dianion even with reduced amounts of lithium.

2.3. *Silicon–hydrogen bond cleavage*

Only a limited number of examples of the preparation of silylmetallic reagents by the reactions between silanes and alkali metal are known. The first stable organosilyllithium reagent $(Ph_3Ge)_3SiLi$ was prepared by the reaction of the silane with lithium metal in ethylamine [64]. Triarylsilanes such as triphenylsilane also react with lithium in ether or THF to give triphenylsilyllithium, hexaphenyldisilane and other phenyl-containing products [65].

A much more widely applicable method is the reaction of the silanes with potassium hydrides to give the silylpotassium and hydrogen developed by Corriu and Guerin [33]. This is a very general reaction and has been applied to a wide range of compounds in different solvents [66] (Eqs. (15)–(17)). The reaction is very clean as



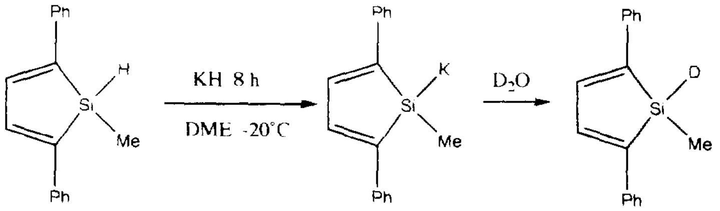
Scheme 5. Preparation of silole dianions and disilole dianions.

hydrogen gas is the sole byproduct and the only potential problem here is the stability of the silylmetallic species in DME at elevated temperatures, although the yields obtained for the products quenched with D_2O are excellent.

$$\mathrm{Ph_3SiH} \xrightarrow{\text{KH 6 h}} \mathrm{Ph_3SiK} + \mathrm{H_2} \xrightarrow{\mathrm{D_2O}} \mathrm{Ph_3SiD} \qquad (15)$$

DME	50 °C	85%
DME/HMPA	R.T.	90%
DME/18-crown-6	R.T.	90%

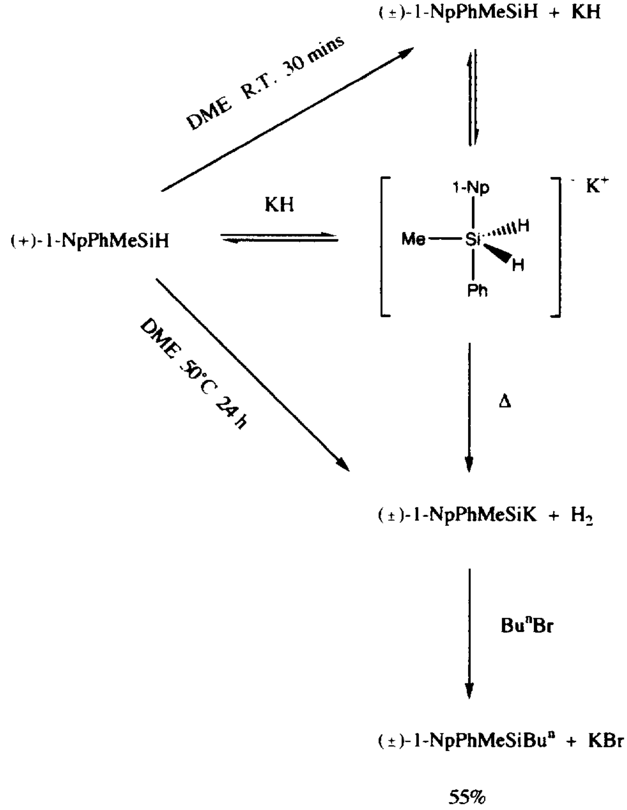
$$\mathrm{Et_3SiH} \xrightarrow[\text{DME 40 °C}]{\text{KH 6 h}} \mathrm{Et_3SiK} + \mathrm{H_2} \xrightarrow{\mathrm{D_2O}} \underset{75\%}{\mathrm{Et_3SiD}} \qquad (16)$$



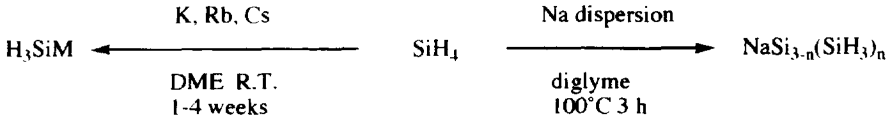
(17)

Corriu and coworkers have investigated the mechanism of this reaction using a chiral silane 1-NapPhMeSiH and suggest that it proceeds via a 5-coordinate intermediate [67]. The reaction giving the silylmetallic species only takes place at elevated temperatures and produces a solution of the racemic silylmetallic reagent. At room temperature the addition of a catalytic amount of potassium hydride quickly gives a racemic mixture of the silane (Scheme 6).

The silyl derivatives, H_3SiK, Rb and Cs, can be prepared by the reaction of the metal with silane in DME, these reactions are quite slow with the potassium being the fastest taking one week and the rubidium the slowest taking three to four weeks [68]. If special conditions are used, i.e. a fresh sodium dispersion made via high speed mixing of sodium in diglyme at 100°C and a continuous flow of silane gas into the reactor maintained at 100°C, then $NaSi(SiH_3)_3$ can be formed in low yield (18%) together with $NaH_{3-n}Si(SiH_3)_n$, $n = 1$–2 [69] (Scheme 7).



Scheme 6. A pentacoordinate silicon intermediate in the reaction of silanes with metal hydrides.



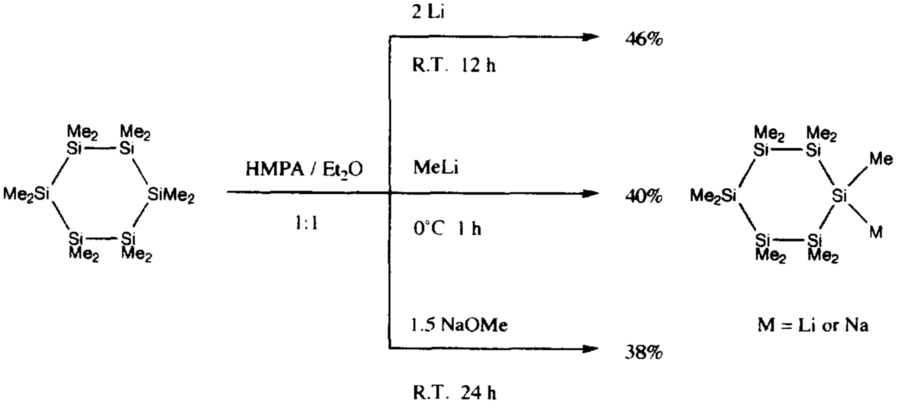
$$H_3SiM \xleftarrow[\text{DME R.T. 1-4 weeks}]{\text{K, Rb, Cs}} SiH_4 \xrightarrow[\text{diglyme } 100^\circ\text{C 3 h}]{\text{Na dispersion}} NaSi_{3-n}(SiH_3)_n$$

Scheme 7. Reaction of silane with alkali metals.

2.4. Silicon–carbon bond cleavage

This is generally not a useful synthetic method for the preparation of silylmetallic reagents as most silicon carbon bonds are stable to attack by group 1 metals. Some specific silicon–carbon bonds may, however, be cleaved by the reaction with the alkali metals but this gives solutions of both silyl and organometallic reagents [4]. An example of this type of synthesis is the reaction of tetraphenylsilane with lithium in THF; this gives both triphenylsilyllithium and phenyllithium. This can be used to prepare solutions of the silyllithium reagent because the phenyllithium formed is insoluble in hydrocarbons and can be removed by filtration. The THF is removed and the solid products are washed with hexane and then filtered to give a hexane solution of the triphenylsilyllithium [70].

A more unusual reaction is that of *cyclo*-Si_6Me_{12} with a number of different reagents such as Li, MeLi or metal alkoxides in at least 20% HMPA solutions which give the *cyclo*-$Si_6Me_{11}M$ reagents by cleavage of a methyl group rather than Si—Si cleavage [71]; the different reactions are shown in Scheme 8. The reaction only occurs in HMPA solutions; for example, if methyllithium in ether is added to *cyclo*-Si_6Me_{12} also in ether no reaction is observed, and if HMPA is then added to this a red colour develops when the solution is 17% HMPA. The course of these reactions is probably governed by the stabilizing effect of the ring compared with the open chain analogue, each silicon atom having two stabilizing silyl substituents if the ring is retained and only one if the ring is cleaved.



Scheme 8. Preparation of *cyclo*-$Si_6Me_{11}M$.

2.5. Silicon–mercury bond cleavage

The reaction of a bis(trialkylsilyl)mercury compound with lithium via metal–metal exchange has been used to prepare the trialkylsilyllithium reagents Me_3SiLi [72] or Et_3SiLi [73] (Eqs. (18) and (19)). The reaction of a bis(silyl)mercury compound with sodium–potassium alloy has been used to prepare *cyclo*-$Si_6Me_{11}K$ in a similar way [74]. However, the slow reaction to give the silylmercury reagent and the use of mercury makes this a less attractive route than those discussed earlier in Sections 2.1 and 2.3. This metal–metal exchange is, however, the only currently available route to the bulky $(Me_3Si)_3SiM$ compounds (M = K, Rb, Cs) [75].

$$(Me_3Si)_2Hg \xrightarrow[\text{THF R.T.}]{\text{2Li 24 h}} 2Me_3SiLi + Hg \tag{18}$$

$$Et_3SiHgEt \xrightarrow[\text{THF R.T.}]{\text{2Li 48 h}} Et_3SiLi + EtLi + Hg \tag{19}$$

2.6. Miscellaneous methods

There are a number of other methods that have been used to prepare specific silylmetallic reagents that do not fit into the above categories and these are described below.

2.6.1. Cleavage of silicon–oxygen bonds

Triarylsilyl ethers can be cleaved by group 1 metals to give the silylmetallic reagents together with the alkoxides [6]. Hexaphenyldisiloxane can also be cleaved by lithium metal in THF, MeTHF or THP to give both the triphenylsilyllithium and triphenylsiloxylithium; hexamethyldisiloxane is not cleaved by sodium–potassium alloy in ether or by lithium in THF [4].

2.6.2. Cleavage of silicon–germanium, tin or lead bonds

As was described above in Section 2.1 the first preparation of triethylsilyllithium was from the cleavage of triethyl(triphenylgermyl)silane with lithium in ethylamine [31]. Other silicon–germanium, tin or lead bonds can be cleaved in the same way in other solvents but all have the same disadvantage, namely the production of solutions containing mixtures of silylmetallic and other metallic reagents [4].

2.7. The preparation of polylithiosilanes

Currently only one organodilithiosilyl compound, $(Me_3Si_2)SiLi_2$, has been prepared; this was formed by the pyrolysis of solid $(Me_3Si)_3SiLi$ (Eq. (20)). When the solid $(Me_3Si)_3SiLi$ was heated under an argon atmosphere to 120 °C it became a yellow–green liquid. The temperature was then raised to 140 °C, with periodic evacuation to remove byproducts of $(Me_3Si)_4Si$, $(Me_3Si)_3SiSi(SiMe_3)_3$ and $Me_3SiSiMe_3$; the liquid became dark orange over the course of 3 h. This orange liquid was cooled down and reacted with C_2H_5OD to give $(Me_3Si)_2SiD_2$ which was isolated in 35% yield [76]. The same group also prepared $SiLi_4$ by the lithium vapour reaction with $SiCl_4$ in 1977 [77].

$$\begin{aligned}(Me_3Si)_3SiLi \xrightarrow[3\,h]{140\text{–}150\ C} & (Me_3Si)_2SiLi_2 \quad 35\% \\ & Me_3SiSiMe_3 + (Me_3Si)_3SiLi \\ & [(Me_3Si)_3Si]_2 + (Me_3Si)_4Si\end{aligned} \qquad (20)$$

3. The structures of silyl derivatives of the group 1 metals

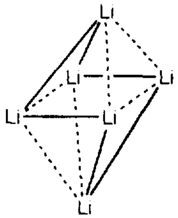
The solid state and solution structures of the organic derivatives of the group 1 metals have been the subject of many studies most of which have involved X-ray crystallography (see for example Refs. [78] and [79] and references therein) or multinuclear NMR investigations. As will be expected from the far smaller number of silicon derivatives available there have been fewer studies carried out although the aims of the work have been the same, to determine the nature of the bonding, ionicity, etc. and to determine the degree of aggregation both in solution and in the solid state.

3.1. *X-ray crystallographic studies*

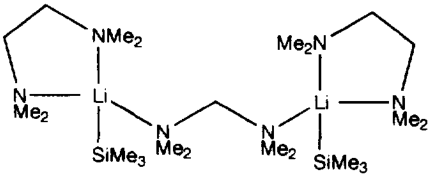
Although there have now been several X-ray crystallographic studies carried out there are too few to make meaningful comparisons either among them as a class of compounds or with their organic analogues. More work needs to be carried out to establish the important factors governing the structures of such compounds. The factors that do seem to be clear from the structures determined so far are that the geometry at silicon is pyramidal and that the Si—Li distance is usually close to that for the sum of the covalent radii for Si and Li of 2.69 Å.

3.1.1. *Me_3SiLi*

The first silyllithium compound to be structurally characterized was Me_3SiLi which was found to be hexameric $(Me_3SiLi)_6$ when crystallized from cyclohexane solution [80,81]. The structure comprises a six-membered ring of lithium atoms in a distorted highly folded chair arrangement (**1**) which may alternatively be viewed as an octahedron distorted so as to form a trigonal antiprism. The six triangular faces of the trigonal antiprism each have two short (2.72(2) Å, the full lines in **1**) and one long (3.25(2) Å, the broken lines in **1**) side and the six Me_3Si groups lie above each of the six faces being closer to the pair of lithium atoms separated by the longer distance (the Si—Li bonds average 2.65 and 2.77 Å) [80,81]. A similar, more regular octahedron of lithium atoms has been found in hexameric cyclohexyllithium $[(C_6H_{11}Li)_6.2C_6H_6]$ [82] and in hexameric 1-lithiomethyl-2,2,3,3-tetramethylcyclopropane [83] in which the alkyl substituents occupy six of the eight triangular faces of the octahedron.



(1)

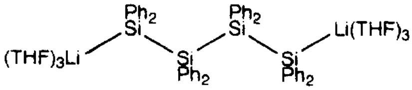


(2)

The structure of the related amine adduct $(Me_3SiLi)_2.3TMEDA$ has no Li—Si—Li interactions, the hexameric nature of the solvent free compound being completely broken down on coordination by the TMEDA. The structure, **2**, comprises two four-coordinate lithium atoms bonded to an Me_3Si group and each chelated by one TMEDA molecule, these two units being bridged by the third TMEDA molecule. The Si—Li distances of 2.70 Å are similar to those found in the uncomplexed hexamer [84].

3.1.2. $Li(Ph_2Si)_4Li$

When crystallized from pentane—THF the tetrasilane $Li(Ph_2Si)_4Li$ crystallizes as discrete centrosymmetric molecules with a planar $Li–Si_4—Li$ arrangement with three molecules of THF coordinated to each lithium atom (**3**). The Si—Li distances are 2.714(10) Å [85], i.e. slightly longer than the value of 2.69 Å for the sum of the covalent radii of Si and Li. It should also be noted that there are similar Si—Li distances in $Li_2Hg(SiMe_2Ph)_4$ of 2.90 and 3.04 Å and those in $Li_2Hg(SiMe_3)_4$ are 2.69–3.60 Å, i.e. the shortest distances are similar to those found in R_3SiLi species [86].



(3)

3.1.3. Ph_3SiLi

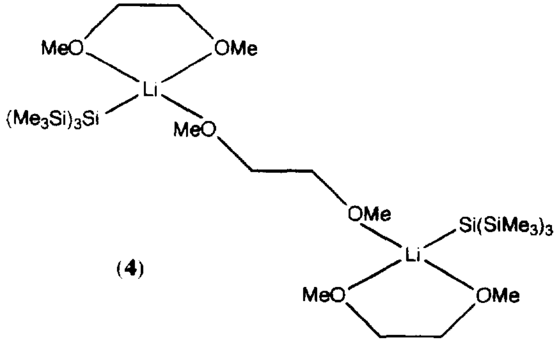
Although it is one of the most readily available silyllithium compounds the structure of Ph_3SiLi was not determined until 1993. On crystallization from a hexane–THF mixture the compound forms a simple solvated species $Ph_3SiLi.3THF$ with a pyramidal geometry at silicon and an Si—Li distance of 2.672(9) Å [87]. The structure of the organometallic analogue $Ph_3CLi.TMEDA$ is also monomeric although in this case there are lithium interactions with three of the aryl carbon atoms as well as with the central methine carbon atom [88].

3.1.4. $(Me_3Si)_3Si—M$ species (M = Li, K, Rb or Cs)

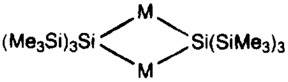
The structure of the commonly used reagent $(Me_3Si)_3SiLi.3THF$ was reported in 1993 to be monomeric with a pyramidal geometry at silicon and an Si—Li distance of 2.669(13) Å [87]. The related compound $(Me_3Si)_3SiLi.1.5DME$ has a bridged dimeric structure $[(Me_3Si)_3SiLi]_2.[DME]_3$ (**4**), similar in overall geometry to $[Me_3SiLi]_2.[TMEDA]_3$, with shorter Si—Li distances of 2.630(5) Å [89].

The silylsilyllithium compound $(Me_3Si)_3SiLi.3THF$ also cocrystallizes with $(Me_3Si)_4Si$ as $[(Me_3Si)_4Si][(Me_3Si)_3SiLi.3THF]_2$, the structure of neither component of the mixing being substantially different from that found for the compounds crystallized independently, the Si—Li distance being 2.674(13) in the mixture and 2.644(12) Å in $(Me_3Si)_3SiLi.3THF$, the corresponding values for average Si—Si—Li angles being 116.4(1)° and 115.8(2)° [90].

The solid state structures of $(Me_3Si)_3SiM$ (M = Rb or Cs) have also been determined as toluene solvates $[(Me_3Si)_3SiRb]_2$.toluene and $[(Me_3Si)_3SiCs]_2$.(toluene)$_3$. Both compounds have structures comprising folded alkali metal bridged dimers (**5**). The rubidium compound has Rb—Si distances of 3.532(4)–3.616(4) Å, angles at Rb of 95.4(1)° and 98.3(1)° and Rb—Si—Rb angles of 74.2(1)° and 74.3°. The corre-



(**4**)



M = Cs or Rb

(**5**)

sponding values for the caesium compound are 3.774(2)–3.850(2) Å, 92.0(1)° and 93.6(1)°, and 80.9(1)° and 80.4(1)°. The fold angles for the Rb and Cs compounds are 139.5° and 143.5° respectively [75].

3.1.5. $MSiH_3$ species

The structure of $KSiH_3$ obtained from monoglyme solution at room temperature was found to be of the cubic NaCl type, containing discrete K^+ and H_3Si^- ions [91]. An orthorhombic form of $KSiH_3$ may also be obtained from monoglyme–pentane at −5 °C; again the structure comprises isolated K^+ and pyramidal SiH_3^- ions with K ··· Si distances of 3.56–3.86 Å [92]. A further study of $MSiH_3$ (M = K, Cs, or Rb) species found that they were all of the NaCl structure with lattice constants *a* of 7.23 Å, 7.52 Å and 7.86 Å respectively. The H_3Si^- ion was estimated to have an effective ionic radius of 2.26 ± 0.04 Å [68].

3.2. Nuclear magnetic resonance

The Si—Si—Si angle of 102.1° in $(Me_3Si)_3SiLi.THF$ in the solid state indicates a pyramidal geometry at the central silicon atom and ionic character for the $(Me_3Si)_3Si$ group. ^7Li and ^{29}Si NMR studies in aromatic solvents, however, show that there is a significant covalent contribution to the Si—Li interaction as a well resolved quartet. $^1J(^{29}Si-^7Li)$ of 38.6 Hz at room temperature from the ^{29}Si spectrum is observed and indicates that the solution species, as in the solid state, is monomeric [90]. The ^{29}Si chemical shift for the central silicon in $(Me_3Si)_3SiLi.3THF$ has been variously reported to be −189.4 ppm at room temperature in $C_7H_8-C_6D_6$ solution [90] and −185.8 in C_6D_6 [89] and also in benzene solution as −187.4 ppm, $^1J(^{29}Si-^{29}Si) =$ 14 Hz, and the ^7Li shift in benzene solution to be 1.28 ppm [93]. The high field ^{29}Si NMR shifts of the central silicon atom suggest a high degree of anionic character and values for $(Me_3Si)_3\underline{Si}M$ are −185.7 ppm, −184.4 ppm and −179.4 ppm respectively for M = K, Rb and Cs in benzene solution [75]. It should be noted that the analogous carbon compound $(Me_3Si)_3CLi$ actually has the formulation $\{[(Me_3Si)_3C]_2Li\}^-[Li(THF)_4]^+$ in the solid state and undergoes complicated exchange processes in solution [94].

At 303 K in THF solution the chemical shift of the SiLi silicons in $Li(SiPh_2)_4Li$ is a single resonance at −28.54 ppm exhibiting no coupling to ^7Li but at 173 K there are three signals at −22.9 ppm, −24.5 ppm and −38.1 ppm with $^1J(^7Li-^{29}Si)$ couplings of 40 Hz, 42 Hz and 32.8 Hz respectively. The ^7Li NMR spectra display two resonances at all temperatures. Thus, although the structure in the solid state is a single symmetrical species, in THF solution there are several exchange processes occurring but it is not clear what the natures of the exchanging species are [85].

The ^{29}Si chemical shift of about −9 ppm for Ph_3Si^6Li does not vary greatly with solvent (THF, 2-MeTHF or DME) or with temperature until at 173 K in MeTHF the single resonance resolves into a triplet with $J^1(^{29}Si-^6Li) = 17$ Hz, implying a monomeric structure (^6Li, $I = 1$), lithium exchange being rapid at higher temperatures and with the better cation solvating solvent DME. On reducing the number of phenyl group substituents the ^{29}Si NMR chemical shift moves upfield to about

−21 ppm and −28 ppm respectively for Ph_2MeSi^6Li and $PhMe_2Si^6Li$ and the rate of exchange decreases such that at 193 K triplets are observed for both species in MeTHF ($J^1(^{29}Si-^6Li)$ = 16 Hz and 18 Hz respectively). Similar chemical shift trends are seen for $Ph_nMe_{3-n}SiK$ (n = 1, 2 or 3) species in THF solution [95]. The similar coupling constants for all three species imply similar Si—Li bonding in all three species. The ^{29}Si NMR spectrum of $PhMe_2Si^7Li$ at 173 K in THF exhibits a quartet (^7Li, $I = 3/2$), $J^1(^7Li-^{29}Si) = 51$ Hz. The ratio of the two couplings involving ^6Li and ^7Li is close to that expected from the ratio of the NMR frequencies for the two nuclei [96]. These NMR studies are thought to show that the solution structures are best described as contact ion pairs. In toluene solution at −80°C the ^{29}Si NMR spectrum of $Ph_3SiLi.3THF$ is a quartet centred at 9.28 ppm with $^1J(^{29}Si-^7Li)$ of 45 Hz. This also suggests that the Si—Li bond is retained in solution and that the species is monomeric [87]. ^{29}Si NMR spectroscopy has also been used to investigate the silylcuprates formed on the reaction between $PhMe_2SiLi$ and copper salts, $PhMe_2SiLi$ having a shift in THF of −28.5 ppm at room temperature [97].

Comparisons of ^{13}C and ^7Li NMR data for $Ph_nMe_{3-n}SiM$ (M = Li or K, n = 1, 2 or 3) in various solvents also suggest that there is significant interaction between Si and M in such systems [23]. Analysis of the ^{13}C chemical shift data for these compounds suggests that the shifts for the aromatic carbon atoms are most significantly affected by π polarizing rather than conjugative effects [23,98] although these data differ from those reported in earlier work [99].

A variable temperature ^7Li NMR study of mixtures of silyllithium species in THF and in MeTHF has, however, provided evidence that the Si—Li interaction is predominantly ionic. At room temperature mixtures of Ph_3SiLi with $Ph_2MeSiLi$ or $PhMe_2SiLi$ give single sharp resonances in the ^7Li spectrum but at −90°C there are two signals resolved in a THF solution of Ph_3SiLi and $PhMe_2SiLi$ and for an MeTHF solution of Ph_3SiLi and $Ph_2MeSiLi$. Together with the fact that the ^7Li chemical shift varies little for the three compounds the data suggest that a bimolecular exchange occurs between the two monomeric compounds which is responsible for the collapse of the ^7Li signals for the two species at high temperatures [100]. It has also been argued that the well-resolved $^{29}Si-^7Li$ coupling at low temperatures is indicative of a mainly ionic bonding mode as significant covalency might be expected to quench coupling by quadrupolar-induced relaxation [100].

A variable temperature ^1H NMR study of $Pr^i_2PhSiLi$ shows that the diastereotopic propyl protons remain inequivalent up to 185°C suggesting a slow inversion at silicon on the NMR timescale with a barrier to inversion of at least 100 kJ mol^{-1} [57].

4. The reactions of silyl derivatives of the group 1 metals

4.1. *With compounds of the p block elements*

The reactions between silyl derivatives of the group 1 elements and metal or metalloid halides are largely what might be anticipated by analogy with organolithium compounds, i.e. substitution of one or more halogen atoms or other good leaving groups by silyl groups at the reactive centre (Eq. (21)). Exceptions to this type of reaction are insertion into the Si—Li bond by the group 16 elements Se and Te to give $(Me_3Si)_3SiELi$ species [101–103], substitution of hydrogen in Si—H containing compounds instead of halogen, for example the formation of $(H_3Si)_3SiK$ from H_3SiK and SiH_4 [104], and the reaction of group 13 alkyls to give addition products in which the group 13 element is four coordinate, e.g. $[(Me_3Si)_3SiAlMe_3][Li(THF)_4]$ from the reaction between $(Me_3Si)_3SiLi$ and Al_2Me_6 [105]. Simple substitution reactions also occur readily with organic acid chlorides to give acyl silanes which have been used as photochemical precursors to silenes (see for example Ref. [106] and others in Table 1).

$$L_mMX_n + nR_3SiLi \rightarrow L_mM(SiR_3)_n + nLiX \tag{21}$$

The products from the reactions of silyl group 1 derivatives to give products of interest in organometallic and inorganic chemistry, their yields and reaction conditions are given in Table 1; a summary of the important features of such reactions is given below.

Perhaps the main constraint on the general reaction given in Eq. (21), apart from the availability of some of the starting materials when compared with the analogous organolithium reaction, is steric. As has been described above, by far the most readily prepared and widely used silyllithium reagents are Ph_3SiLi and $(Me_3Si)_3SiLi.3THF$ both of which are bulky, the latter being the more bulky of the two. This means that a relatively small number of such groups can be attached to an atom when compared with readily available carbon compounds having small substituents such as H_3CLi, *n*-BuLi or PhLi. For example, although it is possible to substitute all four chlorine atoms in $SiCl_4$ for Me, *n*-Bu, or Ph with organolithium reagents it is only possible to attach three Ph_3Si groups (in very low yield) to silicon using $SiHCl_3$ [25] and only one $(Me_3Si)_3Si$ group in the reaction between $(Me_3Si)_3SiLi.3THF$ and $SiCl_4$ [146]. A larger central atom such as tin will, however, accommodate two such groups as for example in $[(Me_3Si)_3Si]_2SnCl_2$ formed in the reaction between $(Me_3Si)_3SiLi.3THF$ and $SnCl_4$ [151,154] and three groups are thought to be attached to lead in $[(Me_3Si)_3Si]_3PbK$ [178]. The geometry around the metal or metalloid is also important and two $(Me_3Si)_3Si$ groups may be attached to trigonal planar boron, e.g. in $[(Me_3Si)_3Si]_2BNMe_2$ [93], or to atoms in which a linear arrangement is to be expected as in $[(Me_3Si)_3Si]_2M$ (M = Zn, Cd, or Hg) [48,166]; see Table 1 for further details. (It should also be noted that the alkyl analogue $(Me_3Si)_3CLi$ is even more sterically demanding and is used widely in the preparation of low coordinate organometallic compounds (see for example Ref. [179] and references therein).) Reaction of a smaller silyllithium does allow tetrasubstitution at silicon, for example the reaction between $PhMe_2SiLi$ and $SiCl_4$ does give a low yield of $(PhMe_2Si)_4Si$ [114]. As long as only one of these large silyl groups is required in the product the yields from reactions of the type shown in Eq. (21) (details in Table 1) are generally good although the solvent THF may be troublesome and reduce yields thus requiring the use of more inert solvents such as toluene or alkanes.

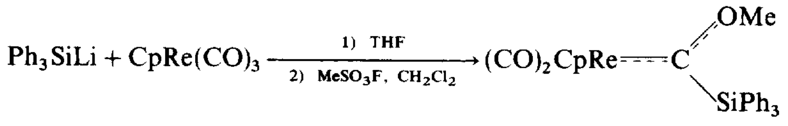
Reactions have often been carried out at low temperature although many reactions have been carried out at room temperature or even at reflux temperatures.

4.2. With compounds of the d and the f block elements

The reactions between the silyl derivatives of group 1 and d or f block metal compounds are generally of the same type as shown for the p block compounds in Eq. (21). Similar reaction conditions may be used and again larger atoms and a suitable geometry at the metal centre may allow the substitution of more than one bulky silyl group. The synthesis of transition metal silyl complexes using alkali metal derivatives of silicon has become popular only relatively recently particularly with the widespread use of $(Me_3Si)_3SiLi$. This synthetic route to transition metal derivatives has to compete with the more established routes of oxidative addition of an Si—H containing compound to a coordinatively unsaturated metal centre and of reaction of a silyl halide with a transition metal anion (for a review of these types of synthesis see Ref. [180] and references therein) both of which are less readily applied to p-block compounds. One of the reasons for the preparation of silyl metal complexes is their interest as intermediates in important catalytic cycles such as hydrosilylation. Table 2 shows a wide range of products derived from the reaction of a silyl group 1 derivative and it is clear that there are many analogies with the reactions shown in Table 1.

Silyllithium reagents may also displace a neutral ligand such as CO or COD from a metal centre to give an anionic product as, for example, in Eq. (22) [192] (see also examples in Table 2) although in the case of CO this reaction may have to compete with that of silyl carbene formation resulting from attack of the silyl anion on CO as, for example, in Eq. (23) [218–221]. It should perhaps be noted that R_3Si^- is isolectronic with R_3P and that it is pyramidal and may therefore act in a similar Lewis basic manner in transition metal complexes although this property does not seem to have been widely exploited.

$$Ph_3SiLi + Ni(CO)_4 \xrightarrow{THF} [Li(THF)_2][(CO)_3NiSiPh_3] \quad (22)$$



$$Ph_3SiLi + CpRe(CO)_3 \xrightarrow[2)\ MeSO_3F,\ CH_2Cl_2]{1)\ THF} (CO)_2CpRe{=}C\begin{matrix}OMe\\SiPh_3\end{matrix} \quad (23)$$

4.3. With organic compounds

It is not within the remit of this review to cover in depth the uses of silylmetallic reagents in synthetic organic chemistry which have been covered elsewhere [1,2]. However, this is too important an area to ignore, so an overview of this topic will be included below.

The readily prepared and widely used silylmetallic reagents Ph_3SiLi and $(Me_3Si)_3SiLi$ dominate the inorganic chemistry of silylmetallic reagents. Both of these are extremely bulky when compared with the common organolithium and

Table 1
Selected reaction of silyl derivatives of group 1 metals with main group compounds

Silyl derivative	Main group compound	Conditions	Product	Yield (%)	Reference
Me_3SiLi	BMe_3	Hexane	$Li[Me_3BSiMe_3]$	86	[107]
	BEt_3	Hexane, −78°C	$Li[Et_3BSiMe_3]$	86	[107]
	Me_2BOMe	Hexane, −78°C	$Li[Me_2B(SiMe_3)_2]$	58	[107]
	$MeB(OMe)_2$	Hexane, −78°C	$Li[MeB(SiMe_3)_3]$	60	[107]
	$B(OMe)_3$	Hexane, −78°C	$Li[B(SiMe_3)_4]$	50	[107]
	$Bu^t_2BBBu^t(OMe)$		$Bu^t_2BBBu^t(SiMe_3)$		[108]
	$AlBr_3$	Pentane–hexane, −70°C	$Li[Al(SiMe_3)_4]$	63	[109]
Et_3SiLi	RCl^a		$RSiEt_3$	74	[110]
$PhMe_2SiLi$	$MeMgI$	THF, 0°C	$PhMe_2SiMgMe$		[111]
	Et_2AlCl	THF hexane	$PhMe_2SiAlEt_2$		[111]
	$1\text{-}Br_{10}H_{15}$	C_6H_{12}, 100°C	$1\text{-}(PhMe_2Si)C_{10}H_{15}$	93	[112]
	H_2SiCl_2	2:1 ratio	$(PhMe_2Si)_2SiH_2$		[113]
	$SiCl_4$	THF–Et_2O, −40°C	$(PhMe_2Si)_4Si$	14.6	[114]
	Me_3SiCl	THF	$Me_3SiSiMe_2Ph$		[115]
	Bu^tMe_2SiCl	THF	$Bu^tMe_2SiSiMe_2Ph$	76	[116]
	Me_2SiCl_2	2:1	$(PhMe_2Si)_2SiMe_2$	30	[117,118]
	$(n\text{-}C_6H_{11})_2SiCl_2$	2:1 ratio	$(PhMe_2Si)_2Si(n\text{-}C_6H_{11})_2$		[119]
	$PhMeSiHCl$	THF	$PhMe_2SiSiPhMeH$	49	[120]
	$Me_3SiSiMe_2Cl$	THF	$Me_3SiSiMe_2SiMe_2Ph$	75	[121]
	$Cl(SiMe_2)_nSiMe_2Ph$		$PhMe_2Si(SiMe_2)_nSiMe_2Ph$ ($n = 1–3$)		[122]
	$Cl(SiMe_2)_3Cl$	THF, −70°C	$PhMe_2Si(SiMe_2)_3SiMe_2Ph$		[123]
	$Ph_3SiSiPh_2OTf$	DME, −50°C	$Ph_3SiSiPh_2SiMe_2Ph$		[124]
	$(TfOPh_2Si)_2$	DME, −50°C, 2:1 ratio	$(PhMe_2SiSiPh_2)_2$		[124]
	$(TfOMe_2Si)_2$	2:1 ratio	$(PhMe_2SiSiMe_2)_2$		[125]
	$(TfOPhMeSi)_2$	2:1 ratio	$(PhMe_2SiSiPhMe)_2$		[125]
	$Cp(CO)_2FeGeMe_2Cl$		$Cp(CO)_2FeGeMe_2SiMe_2Ph$	16	[126]
$Ph_2MeSiLi$	Me_2SiHCl	THF	$Ph_2MeSiSiMe_2H$	74	[120]
	$PhMeSiHCl$	THF	$Ph_2MeSiSiPhMeH$	45	[120]
	$MeSi(NEt_2)_2OTf$		$(Et_2N)_2MeSiSiPh_2Me$		[127]

Ph_2Bu^tSiLi	Me_3SiCl	THF, −78°C	$Ph_2Bu^tSiSiMe_3$	86	[128]
	$thexylMe_2SiCl$	THF, −78°C	$Ph_2Bu^tSiSiMe_2thexyl$	85	[128]
	Me_2SiCl_2	THF, −78°C, 2:1 ratio	$(Ph_2Bu^tSi)_2SiMe_2$	56	[128]
	mes_2SiCl_2	THF, room temperature	$mes_2Si(Cl)SiPh_2Bu^t$	74	[129]
Ph_3SiLi	BPh_3	THF	$Li[Ph_3BSiPh_3]$		[130]
	$SiHCl_3$	THF, 3:1 ratio	$(Ph_3Si)_3SiH$	4.4	[25]
	Ph_2SiCl_2	THF, −78°C, 2:1 ratio	$(Ph_3Si)_2SiPh_2$	12.1	[131]
	$Me_2Si(C{\equiv}CPh)OTf$	THF, −78°C	$Me_2Si(S{\equiv}CPh)SiPh_3$		[75,132]
	$Bu^t_2Si(PPh_2)OTf$	THF, −78°C	$Bu^t_2Si(PPh_2)SiPh_3$		[133]
	Ph_2GeCl_2	THF, −78°C, 2:1 ratio	$(Ph_3Si)_2GePh_2$	37	[131]
	$Cp(CO)_2FeGeMe_2Cl$		$Cp(CO)_2FeGeMe_2SiPh_3$	18	[126]
	RCl [a]		$RSiPh_3$	62	[134]
	RCl [b]		$RSiPh_3$	64	[110,134]
	RCl [c]		$RSiPh_3$	31	[134]
	RCl [d]		$RSiPh_3$	30	[134]
$(Me_3Si)_2MeSiLi$	$C_{10}H_{15}C(O)Cl$	Pentane	$(Me_3Si)_2MeSiC(O)C_{10}H_{15}$	51	[44]
$(Me_3Si)_2Bu^tSiLi$	$C_{10}H_{15}C(O)Cl$	THF−pentane	$(Me_3Si)_2Bu^tSiC(O)C_{10}H_{15}$	38	[44]
$(Me_3Si)_2PhSiLi$	$C_{10}H_{15}C(O)Cl$	Pentane	$(Me_3Si)_2PhSiC(O)C_{10}H_{15}$	57	[44]
	$Bu^tC(O)Cl$	Pentane, 0°C	$(Me_3Si)_2PhSiC(O)Bu^t$	81	[44]
	$Et_3CC(O)Cl$	Pentane	$(Me_3Si)_2PhSiC(O)CEt_3$		[44]
	$mesC(O)Cl$	Pentane	$(Me_3Si)_2PhSiC(O)mes$	54	[44]
$(Me_3Si)_3SiLi.3THF$	$MgBr_2$	Et_2O	$(Me_3Si)_3SiMgBr$		[135]
	$Me_3SiMeNBF_2$	Toluene–hexane	$(Me_3Si)_3SiBFNMe(SiMe_3)$	50	[136]
	$Me_3SiEtNBF_2$	Toluene–hexane	$(Me_3Si)_3SiBFNEt(SiMe_3)$	62	[136]
	$Me_3SiPr^iNBF_2$	Toluene–hexane	$(Me_3Si)_3SiBFNPr^i(SiMe_3)$	74	[136]
	$Me_3SiBu^tNBF_2$	Toluene–THF	$(Me_3Si)_3SiBFNBu^t(SiMe_3)$	62	[136]
	$(Me_3Si)_2NBF_2$	Toluene–THF	$(Me_3Si)_3SiBFN(SiMe_3)_2$	51	[136,137]
	Me_2BBr	Toluene, −60°C	$(Me_3Si)_3SiBMe_2$	56.7	[93]
	BBNBBr	Toluene, −60°C	$(Me_3Si)_3SiBBN$	25.4	[93]
	$(Me_2N)_2BCl$	Hexane, −10°C	$(Me_3Si)_3SiB(NMe_2)_2$	81	[93]
	Me_2NBCl_2	Hexane, −75°C	$[(Me_3Si)_3Si]_2BNMe_2$	81	[93]
	$TMPBCl_2$	Toluene–THF	$(Me_3Si)_3SiBClTMP$	13	[136]
	BMe_3	Toluene, −196°C to room temperature	$Li[(Me_3Si)_3SiBMe_3]$		[93]
	Al_2Cl_6	Pentane	$(Me_3Si)_3SiAlCl_2.THF$	60	[105]
		Toluene, −78°C	$[Li(THF)_4][(Me_3Si)_3SiAlCl_3]$		[138]

Table 1 (*continued*)

Silyl derivative	Main group compound	Conditions	Product	Yield (%)	Reference
	Me_2AlCl	Pentane	$(Me_3Si)_3SiAlMe_2.THF$	81	[105]
	Et_2AlCl	Pentane	$(Me_3Si)_3SiAlEt_2.THF$	78	[105]
	$EtAlCl_2$	Pentane	$(Me_3Si)_3SiAlEtCl.THF$	83	[105]
	$AlMe_3$	Pentane	$[Li(THF)_4][(Me_3Si)_3SiAlMe_3]$	88	[105]
	$AlEt_3$		$[Li(THF)_4][(Me_3Si)_3SiAlEt_3]$	80	[105]
	$GaCl_3$	Et_2O, −78°C	$[\{(Me_3Si)_3Si\}_2Ga(\mu\text{-}Cl)_2Li(THF)_2]$		[139]
	$(TMP)_2GaCl$	Et_2O, −78°C	$(Me_3Si)_3SiGa(TMP)_2$	60	[140]
	$InCl_3$	Et_2O, −78°C	$[\{(Me_3Si)_3Si\}_2In(\mu\text{-}Cl)_2Li(THF)_2]$		[139]
	$HC(O)OEt$	Pentane, −78°C	$(Me_3Si)_3SiC(O)H$	20–30	[141]
	$(MeO)_3PO$	THF–Et_2O	$(Me_3Si)_3SiMe$	78	[38]
	MeI	THF	$(Me_3Si)_3SiMe$	87	[43]
		Pentane	$(Me_3Si)_3SiMe$	54	[44]
	CD_3I	THF	$(Me_3Si)_3SiCD_3$	95	[43]
	$BrCH_2CH_2Br$	THF–Et_2O, −70°C	$[(Me_3Si)_3Si]_2$	51	[48]
	CO_2	(1) THF, (2) HCl	$(Me_3Si)_3SiCO_2H$	75,85	[142,143]
	Ethylene oxide		$(Me_3Si)_3SiCH_2CH_2OH$	81	[144]
	Acetone		$Me_3SiCMe_2[(Me_3Si)Si]_2SiLi$		[145]
	$F_3CC(O)Cl$	Pentane, −30 to −40°C	$(Me_3Si)_3SiC(O)CF_3$	90	[106]
	$C_6F_5C(O)Cl$	Pentane, −30 to −40°C	$(Me_3Si)_3SiC(O)C_6F_5$		[106]
	$4\text{-}MeOC_6H_4C(O)Cl$	THF, −70°C	$(Me_3Si)_3SiC(O)C_6H_4OMe\text{-}4$	71	[106]
	$2\text{-}MeOC_6H_4C(O)Cl$	THF, −70°C	$(Me_3Si)_3SiC(O)C_6H_4OMe\text{-}2$	80	[106]
	$3,5\text{-}Me_2C_6H_3C(O)Cl$	THF, −70°C	$(Me_3Si)_3SiC(O)C_6H_3Me_2\text{-}3,5$	50	[106]
	$4\text{-}Bu^tC_6H_4C(O)Cl$	THF, −70°C	$(Me_3Si)_3SiC(O)C_6H_4Bu^t\text{-}4$	60	[106]
	$(BCO)C(O)Cl$	Pentane, −78°C	$(Me_3Si)_3SiC(O)(BCO)$	85	[44]
	$MeSiF_3$	Hexane–toluene, reflux	$(Me_3Si)_3SiSiMeF_2$	80	[146]
	Pr^iSiF_3	Hexane–toluene, reflux	$(Me_3Si)_3SiSiPr^iF_2$	60	[146]
	Bu^tSiF_3	Hexane–toluene, reflux	$(Me_3Si)_3SiSiBu^tF_2$	78	[146]
	$PhSiF_3$	Hexane–toluene, reflux	$(Me_3Si)_3SiSiPhF_2$	55	[146]
	$(Me_3Si)Bu^tNSiF_3$	Hexane–toluene, reflux	$(Me_3Si)_3SiSiNBu^t(SiMe_3)F_2$	58	[146]
	$(Me_3SiMeN)_2SiF_2$	Hexane–toluene, reflux	$(Me_3Si)_3SiSi(NMeSiMe_3)_2F$	35	[146]
	$SiCl_4$	Hexane–toluene, reflux	$(Me_3Si)_3SiSiCl_3$	54	[146]

$MeSiCl_3$	Hexane–toluene, reflux	$(Me_3Si)_3SiSiMeCl_2$	73	[147]
Pr^iSiCl_3	Hexane–toluene, reflux	$(Me_3Si)_3SiSiPr^iCl_2$	74	[146]
Bu^tSiCl_3	Hexane–toluene, reflux	$(Me_3Si)_3SiSiBu^tCl_2$	70	[146]
$PhSiCl_3$	Hexane–toluene, reflux	$(Me_3Si)_3SiSiPhCl_2$	64	[146]
$Bu^tMeSiCl_2$	Hexane–toluene, reflux	$(Me_3Si)_3SiSiBu^tMeCl$	76	[147]
$PhMeSiCl_2$	Hexane–toluene, reflux	$(Me_3Si)_3SiSiPhMeCl$	53	[146]
Ph_2SiCl_2	Hexane–toluene, reflux	$(Me_3Si)_3SiSiPh_2Cl$	40	[146]
$(Me_3Si)_2NMeSiCl_2$	Hexane–toluene, reflux	$(Me_3Si)_3SiSiMeN(SiMe_3)_2Cl$	31	[146]
$(Me_3Si)_3SiCl$	THF – Et_2O, −70°C	$[(Me_3Si)_3Si]_2$	25	[48]
Me_2SiHCl	Toluene	$(Me_3Si)_3SiSiMe_2H$	58	[148]
Bu^t_2SiHCl	Hexane–toluene, reflux	$(Me_3Si)_3SiSiBu^t_2H$	49	[147]
Bu^tPh_2SiCl	THF, −78°C	$(Me_3Si)_3SiSiBu^tPh_2$	25	[128]
$GeCl_2$	Hexane, −78°C	$(Me_3Si)_2\overline{SiSi(SiMe_3)_2Ge}(SiMe_3)_2$	48	[149]
$GeCl_4$	Hexane, −78°C	$[(Me_3Si)_3SiGeCl_2]_2$	49	[150]
		+ all *trans*-$\{[(Me_3Si)_3Si](Cl)Ge\}_4$	19	[151]
	Et_2O, −78°C	$(Me_3Si)_3SiGeCl_3$	20	[152]
Me_2GeCl_2	Hexane, −78°C	$[(Me_3Si)_3SiGeMe_2]_2$	40	[150]
Ph_2GeCl_2	Et_2O, −78°C	$[(Me_3Si)_3SiGePh_2]_2$	32.2	[150]
Me_3GeCl	Et_2O, −78°C	$(Me_3Si)_3SiGeMe_3$	75	[152]
Ph_3GeCl	Et_2O, −78°C	$(Me_3Si)_3SiGePh_3$	79	[152]
cyclo-$C_4Me_4GeCl_2$	C_6H_6, 5°C	*cyclo*-$C_4Me_4GeCl[Si(SiMe_3)_3]$	70	[153]
$SnCl_2$	Et_2O, −78°C	$[(Me_3Si)_3Si]_2Sn.THF$	44	[154]
	2RLi:1$SnCl_2$, Et_2O, −78°C	$[(Me_3Si)_3Si]_2Sn(\mu\text{-}Cl)Li(THF)_3$		[155]
$SnCl_4$	Hexane, −78°C, 4:1	$[(Me_3Si)_3Si]_2SnCl_2$		[151]
$SnCl_4$	Hexane, −78°C, 2:1	$[(Me_3Si)_3Si]_2SnCl_2$	40	[154]
$SnCl_4$	Hexane, −78°C, 1:1	$(Me_3Si)_3SiSnCl_3.THF$	50	[154]
Me_2SnCl_2	Et_2O, −78°C	$[(Me_3Si)_3Si]_2SnMe_2$	70	[154]
Me_3SnCl	Et_2O, −78°C	$(Me_3Si)_3SiSnMe_3$	40	[154]
$Bu^n_2SnCl_2$	Et_2O, −78°C	$[(Me_3Si)_3Si]_2SnBu^n_2$	61	[154]
Bu^n_3SnCl	Et_2O, −78°C	$Me_3Si)_3SiSnBu^n_3$	100	[154]
$PbCl_2$		$[(Me_3Si)_3Si]_2$	100	[156]
Ph_3PbCl	Et_2O, −78°C	$(Me_3Si)_3SiPbPh_3$	80.8	[157]
Ph_2PbCl_2	Et_2O, −78°C	$\{[Me_3Si)_3Si]Ph_2Pb\}_2$	20.7	[157]
		+ $[(Me_3Si)_3Si]_2PbPh_2$	20.9	
NOCl	THF, −78°C	$(Me_3Si)_3SiNO$ [e]		[158]
$Bu^t(Me_3Si)NPF_2$	Toluene–hexane	$(Me_3Si)_3SiPFNBu^t(SiMe_3)$	79	[159]

Table 1 (*continued*)

Silyl derivative	Main group compound	Conditions	Product	Yield (%)	Reference
	$C_{10}H_{15}(Me_3Si)NPF_2$	Toluene–hexane	$(Me_3Si)_3SiPFNC_{10}H_{15}(SiMe_3)$	46	[159]
	$mes(Me_3Si)NPF_2$	Toluene–hexane	$(Me_3Si)_3SiPFNmes(SiMe_3)$	60	[159]
	$(Me_3Si)_2NPF_2$	Toluene–hexane	$(Me_3Si)_3SiPFN(SiMe_3)_2$	48	[159]
	$(TMP)PF_2$		$(Me_3Si)_3SiPF(TMP)$	58	[147]
	PCl_3		Phosphorus polymer		[160]
	$MePCl_2$	THF, −50°C	$(Me_3Si)_3SiP(Me)Cl$ [f]		[160]
	Bu^tPCl_2	THF–Et₂O, −23°C	$(Me_3Si)_3SiP(Bu^t)Cl$		[160]
	$ArPCl_2$	THF, −70°C	$(Me_3Si)_3SiP(Ar)Cl$ [g]		[161]
	$ArP{=}PCl$	−50 to −30°C	$(Me_3Si)_3SiP{=}PAr$ [h]	High	[162]
	$Pr^i_2NPCl_2$		$(Me_3Si)_3SiPClNPr^i_2$		[147]
	$(TMP)PCl_2$		$(Me_3Si)_3SiPCl(TMP)$	42	[147]
	$RPCl$	Pentane, −78°C	$(Me_3Si)_3SiPR$ [i]		[163]
	Se	THF	$[(Me_3Si)_3SiSeLi.2THF]_2$		[101]
	Te	THF	$[(Me_3Si)_3SiTeLi.2THF]_2$	82	[164,165]
	I_2	THF–Et₂O, −70°C	$[(Me_3Si)_3Si]_2$	19.5	[48]
	$ZnCl_2$	Et_2O	$[(Me_3Si)_3Si]_2Zn$	81	[166]
	$CdCl_2$	Et_2O	$[(Me_3Si)_3Si]_2Cd$	74	[166]
	$HgCl_2$	THF–Et₂O, room temperature	$[(Me_3Si)_3Si]_2$	5.3	[48]
	$HgBr_2$	Et_2O	$[(Me_3Si)_3Si]_2Hg$	56	[166]
$(Me_3Si)_3SiLi.1.5DME$	Te		$[(Me_3Si)_3SiTeLi.DME]_2$		[102,103]
$Me_3SiCMe_2[(Me_3Si)_2Si]_2SiLi$	H_2O or D_2O		$Me_3SiCMe_2[(Me_3Si)_2Si]_2SiH/D$		[145]
	Me_3SiCl		$Me_3SiCMe_2(Me_3Si)_2SiSi(SiMe_3)_3$		[145]
$(Me_3Si)_2SiLi_2$	MeI		$(Me_3Si)_2SiMe_2$	27	[76]
Bu^t_3SiNa	$Bu^t_3Si(SiBr_2)_2SiBu^t_3$	THF, −20°C	$[Bu^t_3SiSi]_4$	57	[167]
	$Bu^t_2SiCl(N_3)$	Bu₂O, −50°C	$Bu^t_2Si{=}NSiBu^t_3$	60	[168,169]
	Me_3SiN_3		$Na[Bu^t_3Si{-}N{-}N{=}N{-}SiMe_3]$		[170]
	$Bu^t_3SiN_3$		$Na[Bu^t_3Si{-}N{=}N{-}N{-}SiBu^t_3]$		[171]
Ph_3SiNa	Me_3GeCl	THF, 0°C	$Ph_3SiGeMe_3$		[172]
$(H_3Si)_3SiNa$	$p\text{-}MeC_6H_4SO_3Me$		$(H_3Si)_3SiMe$		[69]
H_3SiK	SiH_4		H_3SiSiH_2K,$(H_3Si)_2SiHK$,		[104]

	$CsGeCl_3$		$K,CsGe(SiH_3)_3$		[69]
Me_3SiK	$PhCH_2Cl$	HMPT, 0°C	Me_3SiCH_2Ph	20	[66]
	Bu^nCl	HMPT, 0°C	Me_3SiBu^n	25	[66]
		DME, 18-crown-6, 0°C		75	[66]
	Ph_3GeBr	HMPT, 0°C	$Me_3SiGePh_3$	80	[66]
Et_3SiK	Me_3SiCl	DME, room temperature	$Et_3SiSiMe_3$	75	[66]
Ph_3SiK	$PhCH_2Cl$	DME, 0°C	Ph_3SiCH_2Ph	70	[66]
	Ph_2SiF_2	Et_2O, −50°C	$Ph_3SiSiPh_2F$	85	[173]
	$SiCl_4$		$Ph_3SiSiCl_3$	82	[174]
	$SiHCl_3$	Et_2O	$Ph_3SiSiCl_3$	27	[12]
		Et_2O, −70°C, 2:1 ratio	$(Ph_3Si)_2SiHCl$	31	[175]
	$ISiH_3$		Ph_3SiSiH_3	59	[174]
	$PhSiCl_3$	Et_2O	$Ph_3SiSiPhCl_2$	34	[12]
	$Ph_3GeSiPh_2Cl$	Et_2O, −78°C	$Ph_3GeSiPh_2SiPh_3$	41	[131]
	$PhSiBr_3$	Et_2O	$(Ph_3Si)_2SiPhBr$	25	[176]
	Ph_2GeCl_2	Et_2O, −78°C	$Ph_3SiGePh_2Cl$	35.4	[131]
$(p\text{-tol})_3SiK$	$SiCl_4$		$(p\text{-tol})_3SiSiCl_3$		[177]
	$ISiH_3$		$(p\text{-tol})_3SiSiH_3$	11	[174]
$cyclo\text{-}Si_6Me_{11}K$	Me_2SiCl_2	THF, 2:1 ratio	$(cyclo\text{-}Si_6Me_{11})_2SiMe_2$	59.8	[74]
1-Me-1-silafluorenylK	Me_3SiCl	DME, room temperature	1-Me-1-(Me_3Si)-1-silafluorene	100	[66]
$(Me_3Si)_3SiK$	$[(Me_3Si)_3Si]_2Pb$		$[(Me_3Si)_3Si]_3PbK$		[178]
$(Me_3Si)_3SiCs$	$[(Me_3Si)_3Si]_2Pb$		$[(Me_3Si)_3Si]_3PbCs$		[178]
$(Me_3Si)_3SiRb$	$TlN(SiMe_3)_2$	Pentane toluene, −30°C	$(Me_3Si)_3SiTlTlSi(SiMe_3)_3$	47	[178]

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[a] R = 1,3-di-*t*-butyl-1,3,2-diazaphosphorinane.

[b] R = 1,3-di-*s*-butyl-1,3,2-diazaphosphorinane.

[c] R = 1,3-dibenzyl-1,3,2-diazaphosphorinane.

[d] R = 1,3-diphenyl-1,3,2-diazaphosphorinane.

[e] Unstable above −10°C.

[f] Unstable at room temperature.

[g] Ar = 2,4,6-$Bu^t_3C_4H_2$, product rapidly loses $(Me_3Si)_3SiCl$ to give ArP=PAr.

[h] Ar = 2,4,6-$Bu^t_3C_6H_2$.

[i] R = PhC = CBu^t.

Table 2
Selected reactions of silyl derivatives of group 1 metals with transition metal compounds

Silyl derivative	Metal compound	Conditions	Product	Yield (%)	Reference
Me_3SiLi	$(TPP)FeCl$	THF, −78°C	$(TPP)FeSiMe_3$		[181]
	$Cp_2Lu(\mu\text{-}Cl)_2Na(DME)_2$	DME–pentane, −78°C, 2:1	$[Li(DME)_3][Cp_2Lu(SiMe_3)_2]$	29	[182]
	$Cp_2Sm(\mu\text{-}Cl)_2Na(DME)_2$	DME–pentane, −78°C, 2:1	$[Li(DME)_3][Cp_2Sm(SiMe_3)_2]$	20	[183]
$PhMe_2SiLi$	*cis*-$(Ph_2MeP)_2PtCl_2$	THF, room temperature	*cis*-$(Ph_2MeP)_2Pt(SiMe_2Ph)_2$	60	[184]
	cis-$(Et_3P)_2PtCl_2$	THF, room temperature	*cis*-$(Et_3P)_2Pt(SiMe_2Ph)_2$	21	[185]
	$Cp_2Sm(\mu\text{-}Cl)_2Na(DME)_n$	DME–pentane, −78°C, 2:1	$[Cp_2Sm(SiMe_3)_2][Li(DME)_3]$	20	[186]
	$Cp_2Dy(\mu\text{-}Cl)_2Na(DME)_n$	DME–pentane, −78°C, 2:1	$[Cp_2Dy(SiMe_3)_2][Li(DME)_3]$	35	[186]
	$Cp_2Ho(\mu\text{-}Cl)_2Na(DME)_n$	DME–pentane, −78°C, 2:1	$[Cp_2Ho(SiMe_3)_2][Li(DME)_3]$	44	[186]
	$Cp_2Er(\mu\text{-}Cl)_2Na(DME)_n$	DME–pentane, −78°C, 2:1	$[Cp_2Er(SiMe_3)_2][Li(DME)_3]$	35	[186]
	$Cp_2Tm(\mu\text{-}Cl)_2Na(DME)_n$	DME–pentane, −78°C, 2:1	$[Cp_2Tm(SiMe_3)_2][Li(DME)_3]$	15	[186]
	$Cp_2Lu(\mu\text{-}Cl)_2Na(DME)_n$	DME–pentane, −78°C, 2:1	$[Cp_2Lu(SiMe_3)_2][Li(DME)_3]$	42	[186]
$Ph_2MeSiLi$	*cis*-$(PhMe_2P)_2PtCl_2$	THF, room temperature	*cis*-$(PhMe_2P)_2Pt(SiMePh_2)_2$	67	[184]
	$dppePtCl_2$	THF, C_6H_6, room temperature	$dppePt(SiMePh_2)_2$	34	[184]
	$PhNCAuCl$	THF	$PhNCAuSiPh_2Me$	3–5	[187]
	$dppm(AuCl)_2$	THF, −78°C, 2: ratio	$dppm[AuSiPh_2Me]_2$	15	[188]
$Ph_2Bu^tSiLi.3THF$	$[Cp_2ScCl]_2$	Toluene	$Cp_2Sc[SiPh_2Bu^t]Cl$	37	[189]
$Ph_3SiLi.3THF$	$[Cp_2ScCl]_2$	Pentane	$Cp_2Sc[SiPh_3]Cl$	36	[189]
	Cp_2NbCl_2		$Cp_2Nb(SiPh_3)_2$	38	[190]
	$Mo_2Cl_2(NMe_2)_4$	2:1 ratio	$Mo_2(SiPh_3)_2(NMe_2)_4$	49	[191]
	$W_2Cl_2(NMe_2)_4$	2: ratio	$W_2(SiPh_3)_2(NMe_2)_4$	36	[191]
	$Ni(CO)_4$	THF	$[Li(THF)_2][(CO)_3NiPh_3]$		[192]
	$CuCl + PMe_3$	THF, −78°C	$(PMe_3)_3CuSiPh_3$	65	[193]
	$AgCl + 3PhMe_2P$	THF	$(PhMe_2P)_3AgSiPh_3$	7	[194]
	$Ph_2tolPAgCl + 2Ph_2tolP$	THF	$(Ph_2tolP)_3AgSiPh_3$	23	[194]
	$(Ph_2Me)_3PAgCl$	THF	$(Ph_2MeP)_3AgSiPh_3$	55	[194]
	$dppm(AgNO_3)_2$	THF, 2:1 ratio	$dppm[AgSiPh_3]_2$	19	[194]
	$dppe(AgNO_3)_2$	THF, 2:1 ratio	$dppe[AgSiPh_3]_2$	18	[194]
	$PhMe_2PAuCl$	THF	$PhMe_2PAuSiPh_3$	26	[187]
	$Ph_2MePAuCl$	THF	$Ph_2MePAuSiPh_3$	47	[187]

	$Ph_2tolPAuCl$	THF	$Ph_2tolPAuSiPh_3$	27	[187]
	$[Ph_2tolPAu][BF_4]$	THF–toluene	$Ph_2tolPAuSiPh_3$	28	[187]
	$dppm(AuCl)_2$	THF, −78°C, 2:1 ratio	$dppm[AuSiPh_3]_2$	47	[188]
	$dppe(AuCl)_2$	THF, −78°C, 2:1 ratio	$dppe[AuSiPh_3]_2$	44	[188]
	$PhNCAuCl$	THF	$PhNCAuSiPh_3$	3–5	[187]
	UCp_3Cl	THF, −30°C	UCp_3SiPh_3		[70]
$Ph_2tolSiLi$	$AgCl + 3Ph_2MeP$	THF	$(Ph_2MeP)_3AgSiPh_2tol$	21	[194]
	$AgCl + 3Ph_3P$	THF	$(Ph_3P)_3AgSiPh_2tol$	19	[194]
	Ph_3PAgCl	THF	$Ph_3PAgSiPh_2tol$	9	[194,195]
	$Ph_3PAgI + 2Ph_3P$	THF	$(Ph_3P)_3AgSiPh_2tol$	27	[194]
	$(Ph_2MeP)_2AgCl + Ph_3P$	THF	$(Ph_2MeP)_3AgSiPh_2tol$	13	[194]
	$(Ph_2MeP)_2AgCl$	THF	$(Ph_2MeP)_2AgSiPh_2tol$	15	[194,195]
	$(Ph_2Me)_3PAgCl$	THF	$(Ph_2MeP)_3AgSiPh_2tol$	39	[194,195]
	$dppm(AgNO_3)_2$	THF, 2:1 ratio	$dppm[AgSiPh_2tol]_2$	30	[194]
	$dppe(AgNO_3)_2$	THF, 2:1 ratio	$dppe[AgSiPh_2tol]_2$	12	[194]
	$Ph_2tolPAuCl$	THF	$Ph_2tolPAuSiPh_2tol$	26	[187]
	$[Ph_2tolPAu][BF_4]$	THF–toluene	$Ph_2tolPAuSiPh_2tol$	20	[187]
	$Ph_2MePAuCl$	THF	$Ph_2MePAuSiPh_2tol$	51	[187]
	$dppm(AuCl)_2$	THF, −78°C, 2:1 ratio	$dppm[AuSiPh_2tol]_2$	14	[188]
	$dppe(AuCl)_2$	THF, −78°C, 2:1 ratio	$dppe[AuSiPh_2tol]_2$	30	[188]
	$PhNCAuCl$	THF	$PhNCAuSiPh_2tol$	3–5	[187]
$Ph(tol)_2SiLi$	$Ph_2tolPAuCl$	THF	$Ph_2tolPAuCl$	29	[187]
mes_2HSiLi	$Cp_2Zr(Me)Cl$	Toluene	$Cp_2Zr(SiHMes_2)Me$	72	[196]
	$Cp_2^*Zr(Me)Br$	Toluene	$Cp_2^*Zr(SiHmes_2)Me$	84	[196]
$(Me_3Si)_2MeSiLi$	$BrMn(CO)_5$	THF, −80°C	$(Me_3Si)_2MeSiMn(CO)_5$	30	[42]
$(Me_3Si)_2PhSiLi.3THF$	$[Cp_2SeCl]_2$	Pentane	$Cp_2Sc[SiPh(SiMe_3)_2]Cl$	61	[189]
	$dcpePtCl_2$	THF	$dcpePt[SiPh(SiMe_3)_2]Cl$		[197]
$(Me_3Si)_3SiLi.3THF$	$[Cp_2ScCl]_2$		$Cp_2Sc[Si(SiMe_3)_3]Cl$		[198]
	$[Cp_2ScCl]_2$	Pentane	$Cp_2Sc[Si(SiMe_3)_3]Cl$	75	[189]
	$(Me_2N)_3TiCl$	Hexane, 20°C	$(Me_3Si)_3SiTi(NMe_2)_3$	40	[199]
	Cp^*ZrCl_3	Et_2O, −78°C	$Cp^*Zr[Si(SiMe_3)_3]Cl_2$	71	[200]
	$CpCp^*ZrCl_2$	Benzene, room temperature	$CpCp^*Zr[Si(SiMe_3)_3]Cl$	62	[141,201]
	$(Bu^tCH_2)_3ZrCl$		$(Bu^tCH_2)_3ZrSi(SiMe_3)_3$		[202]
	$(Bu^tO)_3ZrCl$	Et_2O	$(Bu^tO)_3ZrSi(SiMe_3)_3$	60–70	[203]
	Cp^*HfCl_3	Et_2O, −78°C	$Cp^*Hf[Si(SiMe_3)_3]Cl_2$	75	[200]
	$CpCp^*HfCl_2$	Et_2O	$CpCp^*Hf[Si(SiMe_3)_3]Cl$	67	[204]
	$CpCp^*HfBr_2$		$CpCp^*Hf[Si(SiMe_3)_3]Br$		[204]

Silyl derivative	Metal compound	Conditions	Product	Yield (%)	Reference
	$(Bu^tO)_3HfCl$	Et_2O	$(Bu^tO)_3HfSi(SiMe_3)_3$	60–70	[203]
	$Bu^tN{=}VCp(NHBu^t)Cl$	Pentane, −78°C	$Bu^tN{=}VCp(NHBu^t)Si(SiMe_3)_3$	79	[205]
	$Bu^tN{=}VCp(OBu^t)Cl$		$Bu^tN{=}VCp(OBu^t)Si(SiMe_3)_3$	64	[205]
	$(Bu^tCH_2)_3TaCl_2$	2:1 ratio	$(Bu^tCH_2)_2Ta{=}CHBu^t[Si(SiMe_3)_3]$		[202]
	$CrCl_3$	Et_2O, 2:1 ratio	$[Li(THF)_3][\{(Me_3Si)_3Si\}_2CrCl]$	80	[206]
	$Mo_2Cl_2(NMe_2)_4$		$Mo_2[(Me_3Si)_3Si]_2(Me_2N)_4$	22.8	[207]
	$W_2Cl_2(NMe_2)_4$		$W_2[(Me_3Si)_3Si]_2(Me_2N)_4$	25.3	[207,208]
	$Cp_2W(H)Cl$	Benzene	$Cp_2W(H)Si(SiMe_3)_3$	73	[209,210]
	Cp_2WCl_2	Benzene, 2:1 ratio	$[C_4H_4Si(SiMe_3)_3]_2WH_2$	56	[209,210]
	$(Bu^tCH_2)_2W(Cl){\equiv}CBu^t$		$(Bu^tCH_2)_2W[Si(SiMe_3)_3]{\equiv}CBu^t$		[202]
	$MnCl_2$	DME, 2:1 ratio	$[Li(DME)_2][\{(Me_3Si)_3Si\}_2MnCl]$	85	[206]
	$BrMn(CO)_5$	THF, −80°C	$(Me_3Si)_3SiMn(CO)_5$	41	[42]
	$BrMn(CO)PPh_3$	THF, −80°C	$(Me_3Si)_3SiMn(CO)_4PPh_3$	8	[42]
	$BrRe(CO)_5$		$(Me_3Si)_3SiRe(CO)_5$		[211]
	$FeCl_2$	DME, 2:1 ratio	$[Li(DME)_2][\{(Me_3Si)_3Si\}_2FeCl]$	76	[206]
	$Cp(CO)_2FeBr$	THF	$Cp(CO)_2FeSi(SiMe_3)_3$	8	[212]
	$Cp(CO)Ph_3PFeBr$	THF	$Cp(CO)Ph_3PFeSi(SiMe_3)_3$	10	[212]
	$dcpePtCl_2$	THF	$dcpePt[Si(SiMe_3)_3]Cl$		[197]
	$CuCl$	THF–pentane, −78°C, 1:2.5	$[Li(THF)_4][Cu_5Cl_4\{Si(SiMe_3)_3\}_2]$	20	[138]
	$CuBr$	THF, −78°C	$\{Cu_2[Si(SiMe_3)_3]_2BrLi(THF)_3\}$	23	[213]
	$CuCl[MeC(CH_2PPh_2)_3]$	THF	$Cu[Si(SiMe_3)_3][MeC(CH_2PPh_2)_3]$	76	[214]
	$(Ph_2MeP)_2AgCl$	THF	$(Ph_2MeP)_2AgSi(SiMe_3)_3$	36	[195,215]
	Ph_3PAgCl	THF	$Ph_3PAgSi(SiMe_3)_3$	17	[195,215]
	$Ph_2tolPAgCl$	THF	$Ph_2tolPAgSi(SiMe_3)_3$	9	[215]
	$(Ph_2tolP)_2AgCl$	THF	$(Ph_2tolP)_2AgSi(SiMe_3)_3$	12	[215]
	$dppm(AgNO_3)_2$	THF, 2:1 ratio	$dppm[AgSi(SiMe_3)_3]_2$	18	[215]
	$dppe(AgNO_3)_2$	THF, 2:1 ratio	$dppe[AgSi(SiMe_3)_3]_2$	16	[215]
	$Ph_2MePAuCl$	THF	$Ph_2MePAuSi(SiMe_3)_3$	32	[187]
	$Ph_2tolPAuCl$	THF	$Ph_2tolPAuSi(SiMe_3)_3$	20	[187]
	$dppm(AuCl)_2$	THF, −78°C, 2:1 ratio	$dppm[AuSi(SiMe_3)_3]_2$	28	[188]
	$dppe(AuCl)_2$	THF, −78°C, 2:1 ratio	$dppe[AuSi(SiMe_3)_3]_2$	27	[188]
	$LaCl_3$	Et_2O, −78°C, 3:1 ratio	$[(Me_3Si)_3Si]_2LaCl.THF$		[151]
$(Me_3Sn)_3SiLi.3THF$	$[NEt_4][(CO)_5CrCl]$	THF	$[NEt_4][(CO)_5CrSi(SnMe_3)_3]$	43.9	[40]
$(Me_3Sn)_3SiLi.3THF$	$[NEt_4][(CO)_5MoCl]$	THF	$[NEt_4][(CO)_5MoSi(SnMe_3)_3]$	23	[40]
$(Me_3Sn)_3SiLi.3THF$	$[NEt_4][(CO)_5WCl]$	THF	$[NEt_4][(CO)_5WSi(SnMe_3)_3]$	70.7	[40]
H SiK	CpFe(CO) Br	DME, 40°C	CpFe(CO) SiH	13	[216]

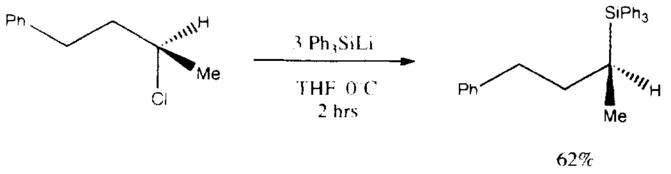
Grignard reagents usually employed in synthetic organic chemistry. So it is the much smaller, although still not small, silylmetallic reagents such as trimethylsilyllithium, used by Still [32], or dimethylphenylsilyllithium, used by Ager and Fleming [222], which are by far the most widely employed in the field of organic chemistry. The bulky reagents, such as Ph_2Bu^tSiLi [223], Ph_3SiLi and $(Me_3Si)_3SiLi$ [224], have been investigated and have been found to have different reactivity to the reagents with the smaller substituents.

Silylmetallic reagents have been used in the same basic type of reactions as the related organolithium reagents such as methyl, butyl, phenyl etc. have been used, i.e. mainly in reactions with unsaturated compounds or organic halides. The silyllithium reagent is most often employed in conjunction with a metal salt, such as those of copper, magnesium, aluminium, zinc, manganese or vanadium to give reagents formulated as R_3SiCu [224,225], $(R_3Si)_2CuLi$ [223,226], $(R_3Si)_2CuLi.LiX$ [222,226], $(R_3Si)_3CuLi_2$ [226], $(R_3Si)R'CuLi$ [227], R_3SiMgX [228–231], R_3SiMgR [230,231], R_3SiAlR_2 [230,231], R_3SiAlR_3Li [232], R_3SiZnR_2Li [232,233], $(R_3Si)_3ZnMgMe$ [232], $(R_3Si)_3MnMgMe$ [234]. These reagents, especially those containing aluminium or zinc, are quite often used in conjunction with transition metal catalysts, such as CuCN, CuI, $Pd(PPh_3)_4$, $PdCl_2(P\textit{o}\text{-}Tol)_2$, $CoCl_2(PPh_3)_2$ or $PtCl_2(PBu^n_3)_2$ [232,234]. These reagents produced by the reaction with metal salts are very widely employed to introduce the R_3Si group; the metal salts modify the reactivity to give the desired regio- and stereochemical control of the final product. Those reagents that contain magnesium will be discussed in more detail in Section 7.

The general reaction types of the various silylmetallic reagents with organic substrates are discussed briefly below. Examples are given in which the intermediate has usually been quenched with aqueous NH_4Cl; however, other reagents can be added to give further substitution. The silyl group can also be removed by protodesilylation to give an alcohol [59].

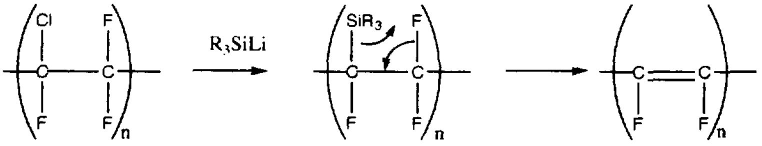
4.3.1. *Reaction with organic halides*

Silylmetallic reagents react with organic halides to give the substitution products with inversion of stereochemistry at the carbon via a normal S_N2 pathway [235–237] (Eq. (24)).



(24)

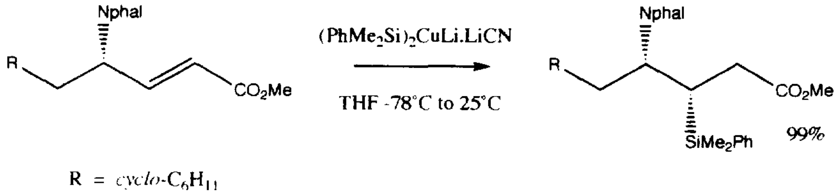
Silyllithium reagents also react with the halides in poly(chlorotrifluoroethane) and unlike alkyllithiums which give the substitution products by reaction with the chloride silylmetallics react probably via nucleophilic substitution followed by an elimination to give carbonization of the polymer backbone (Eq. (25)). This is observed as blackening and pitting of the polymer surface; alkyllithiums and Grignards react to give a brown-coloured surface with pitting only in the case of the lithium reagents. Silylmetallics are also reactive enough to attack PTFE again probably by a nucleophilic substitution followed by an elimination to give carbonization of the PTFE which explains the black magnetic stirrer bars found in laboratories working with silyllithium reagents [238].



(25)

4.3.2. Reaction with double bonds

Silylmetallic compounds react to give the addition products from the double bond usually from the least hindered end [239–242] (Eq. (26)) or if leaving groups are present to give a new double bond by its elimination [243–245] (Eq. (27)), although in some cases they have been shown to react to give the substitution product [243,246–248] (Eq. (28)). Silylmetallics attack allenes either by addition at the centre or at the terminal carbon atom depending on the particular reagent and conditions used [223,249].



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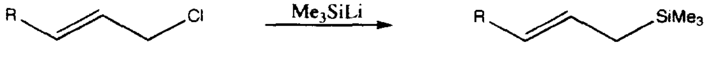

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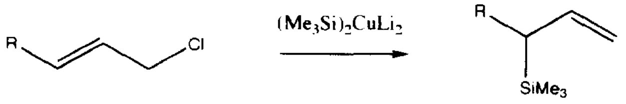
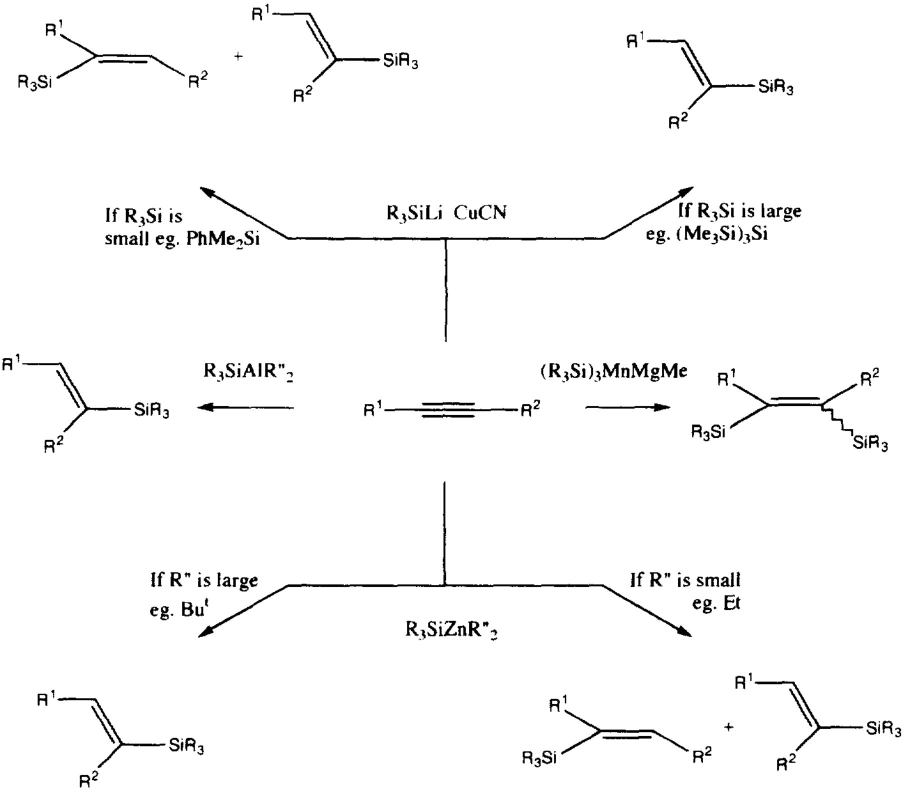


(28)

4.3.3. Reaction with triple bonds

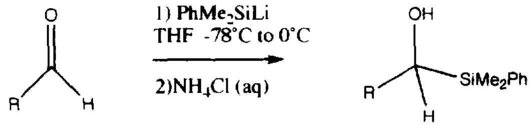
Silylmetallic compounds attack triple bonds to give the addition products via attack at the least hindered side; however, this regioselectivity can be altered by the addition of different metal salts [224,231,232,250–252] (Scheme 9).



Scheme 9. Addition of silylmetallics to triple bonds (where R^1 is larger than R^2).

4.3.4. Reaction with carbonyls

Silylmetallics attack carbonyls to give after an aqueous work-up the simple addition products [249,253,254] (Eq. (29)). The intermediate in this reaction can undergo a Brook rearrangement to give the silylether [255–257] (Eq. (30)).



(29)

R	%
n-C_5H_{11}	73
n-C_7H_{15}	70
Ph	92
cyclo-C_6H_{11}	67

(30)

Silylmetallics react with acid chlorides [258], esters, amides [259] or anhydrides [261] to give the substitution products from the displacement of the chloride etc. In the reaction with α,β-unsaturated ketones, silyllithium reagents in general attack via 1,2 addition [256,261,262] but trimethylsilyllithium [263,264], silylcuprates [222,265,266] or silylzincates [267] attack via 1,4 addition (Scheme 10). The products of the 1,4 attack have been used to protect–mask α,β-unsaturated ketones as the silyl group can be removed by desilylbromination to regenerate the double bond [222,268].

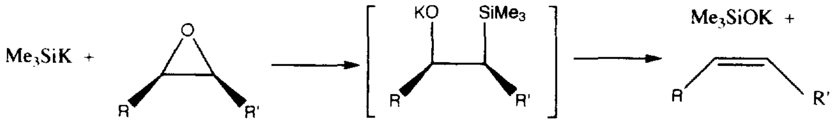
4.3.5. Other reactions

The bulky reagent Ph_2Bu^tSiLi has been used by Baldwin et al. to convert isocyanates into isonitriles [269] (Eq. (31)). As an intermediate they isolated $Ph_2Bu^tSiC(O)NH$-*cyclo*-C_6H_{12}, the first carboxylamide [270].

$$R-N=C=O \xrightarrow[\text{THF 0 C}]{Ph_2Bu^tSiLi} R-N=C + Ph_2Bu^tSiOLi \qquad (31)$$

R	%
Ph	65
1-Np	79
cyclo-C_6H_{11}	73

Trimethylsilylpotassium has been used to deoxygenated epoxides to give the alkene [271,272] (Eq. (32)).



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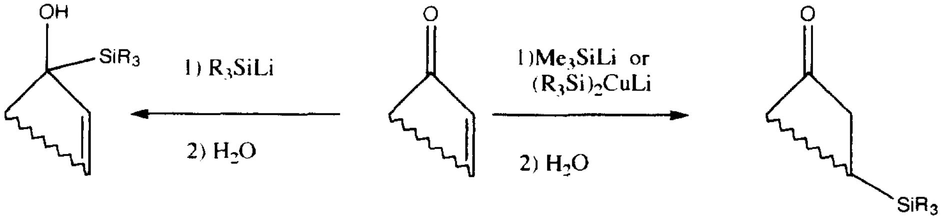


Scheme 10. Reaction of silylmetallics with α,β-unsaturated ketones.

As well as these reactions the trimethylsilyl derivatives, Me_3SiNa and K, have been used as single-electron transfer agents to produce radical anions that are not readily available; these have then been studied by electron spin resonance [34,35,273,274].

A point about reactivity in different solvents is shown by the trimethylsilyllithium adduct with TMEDA, $(Me_3SiLi)_2.(TMEDA)_3$; this adduct will react with compounds such as benzene, toluene, xylenes, mesitylene etc. while the free lithium reagent can be stored in these solvents for months with no reaction [275].

5. The synthesis of silyl derivatives of the group 2 metals

Despite the ready availability and wide applicability of Grignard reagents, RMgX, for many years analogous silicon compounds R_3SiMgX and $(R_3Si)_2Mg$ species were very rare. Attempts to prepare silyl Grignard reagents are hampered by the lack of ready reaction between magnesium and chlorosilanes (bromo- and iodosilanes being less readily available than their carbon counterparts) and by the Wurtz coupling reaction to form disilanes when highly reactive metals are used (see for example Sections 2.1 and 2.2). Silyl derivatives of either beryllium or the lower group 2 elements are almost unknown.

Although there were many unsuccessful early attempts at the synthesis of silyl Grignard reagents in recent years there have been a number of investigations that suggest that R_3SiMgX, R_3SiMgR' (R' = alkyl group) and $(R_3Si)_2Mg$ do exist in solution and even a few examples of disilylmagnesium species being characterized by X-ray crystallography.

5.1. R_3SiMX species

The first report of a reaction involving an R_3SiMgX species as a probable intermediate was that of Selin and West in 1959 who found that the reaction between Ph_3SiCl and *cyclo*-$C_6H_{11}MgBr$ gave $Ph_3SiSiPh_3$ in 67% yield and that a mixture of Ph_3SiCl and Me_3SiCl with the same Grignard reagent gave $Ph_3SiSiMe_3$ [276]. In each case the formation of $Ph_3SiMgBr$ was invoked which then reacted, as does Ph_3SiLi, with the excess chlorosilane present to give the disilane product. George et al. found that there was a slow reaction between magnesium turnings in THF solution to give $Ph_3SiSiPh_3$. Again the formation of $Ph_3SiMgCl$ was reasonably invoked which, as would be expected, reacted with Ph_3SiCl to give the disilane [51].

Further evidence for the formation of silyl "Grignard" compounds was reported by Colomer and Corriu who found that the reaction between $[(CO)_4CoSiPh_3]$ with RMgX reagents (R = Me, Et, or allyl) gave an intermediate which reacted as if it were $Ph_3SiMgBr$ with H_2O, Me_3SiCl and $PhCH_2Cl$, giving Ph_3SiH, $Ph_3SiSiMe_3$ and Ph_3SiCH_2Ph respectively. A similar reaction between $[(CO)_4CoSiMePh(\alpha\text{-naphth})]$ and MeMgBr gave $MePh(\alpha\text{-naphth})SiMgBr$ which reacted with water with retention of configuration at silicon [277].

Although the reaction between Me_3SiCl and Mg turnings in THF does not appear to proceed at any appreciable rate in THF, in HMPT solutions an intermediate formulated as $Me_3SiCl.xHMPT$ does seem to form and further reaction with Me_3SiCl affords $Me_3SiSiMe_3$. The use of highly reactive "Rieke" magnesium in THF does, however, lead to the formation of $Me_3SiSiMe_3$, again presumably as a result of the reaction between the intermediate $Me_3SiMgCl$ and Me_3SiCl [278]. The cocondensation of Mg with $PhMe_2SiCl$ at 77 K is also reported as a synthesis of $PhMe_2SiMgCl$ [279].

More recently several silyl "Grignards" have been prepared by the addition of a silyllithium reagent to magnesium bromide. Thus $Ph_3SiMgBr$ has been generated from Ph_3SiLi and $MgBr_2$ [280], the addition of $MgBr_2$ to $(Me_3Si)_3SiLi.3THF$ affords $(Me_3Si)_3SiMgBr$ [281], and $PhMe_2SiLi$ and $MgBr_2$ in THF solution at 0°C give $PhMe_2SiMgBr$ [228]. These silylmagnesium compounds have not been isolated but used in situ for synthetic purposes. It would clearly be of interest to isolate and structurally characterize such compounds.

The reaction of highly reactive calcium using the metal vapour synthesis technique with chlorosilanes is reported to give $R_3SiCaCl$ species ($R_3 = Me_3$, Et_3, or $PhMe_2$) which may be derivatized with, for example, H_2O or PhBr to give R_3SiH and R_3SiPh respectively. Little further work on these interesting compounds seems to have been carried out [282].

5.2. $(R_3Si)_2M$ species

The first $(R_3Si)_2Mg$ species, $(Me_3Si)_2Mg$, was prepared and characterized independently by two groups in 1977 as the DME adduct [283,284]. Stirring magnesium powder with $(Me_3Si)_2Hg$ in DME for about 8 days affords a volatile product that ignites in air and forms colourless needles when crystallized from pentane. The compound was formulated as $(Me_3Si)_2Mg.DME$ using ^1H NMR spectroscopic data and mass spectrometry [283]. Another synthesis using magnesium turnings gave the same product after 4–5 weeks as a pink crystalline material. If carried out in THF solution the product appears to be $(Me_3Si)_2Mg.2THF$ but this rapidly loses one THF molecule to give $(Me_3Si)_2Mg.THF$ which is thought to be either a THF or an Me_3Si bridged dimer [284]. More recently the synthesis of $(Me_3Si)_2Mg.DME$ has been greatly improved by carrying out the reaction using magnesium powder in an ultrasonic bath which is known to accelerate the synthesis of organic Grignard reagents owing to the cleaning of the metal surface and improvement in the transport of reactive species to and from the metal surface. Thus, the disilylmagnesium compound may be made in 80% yield in four days at 30 °C using a 14-fold excess of magnesium over $(Me_3Si)_2Hg$ [285].

The reaction between $(Me_3Si)_2Mg.DME$ and excess TMEDA in hydrocarbon solvent gives $(Me_3Si)_2Mg.TMEDA$ as colourless needles in 66% yield [286]. The $Me_2N(CH_2)_3NMe_2$ (TMDAP) adduct of $(Me_3Si)_2Mg$ has been prepared in several ways. A slow, low yielding (3%) reaction occurs in the direct synthesis using Mg powder and Me_3SiCl in TMDAP with Hg present as a catalyst. Much better routes are the reaction between Mg and $(Me_3Si)_2Hg$ in TMDAP—Et_2O (85% yield) and the displacement of DME from $(Me_3Si)_2Mg.DME$ using TMDAP in a manner similar to that used for the TMEDA adduct [287].

Although calcium, strontium and barium do not react in THF solution with $(Ph_3Si)_2$, if liquid ammonia is used as solvent they are reported to give $(Ph_3Si)_2M$ species but only the barium compound is sufficiently stable towards ammonolysis to be isolated [288].

5.3. R_3SiMgR' species ($R' = alkyl$)

The preparation of $PhMe_2SiMgMe$ from $PhMe_2SiLi$ and MeMgI occurs readily in THF solution at 0 °C [111,289,290] but it does not seem to have been isolated but rather used as generated in situ usually together with a transition metal catalyst. The use of $Et_3SiMgEt$ has been reported but it is unclear how the reagent was prepared [291]; presumably the reaction of Et_3SiLi with an ethyl Grignard would lead to the species in the same manner as for $PhMe_2SiMgMe$.

6. The structures of silyl derivatives of the group 2 metals

The majority of silyl derivatives of the group 2 elements are rarely isolated as solids and so their structural characterization, particularly by X-ray crystallography, is very limited. Few detailed NMR studies on the equilibria between solution species appear to have been carried out.

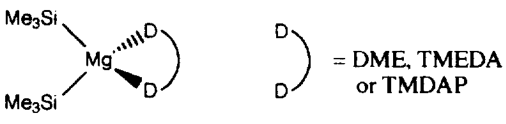
6.1. R_3SiMgX species

No structural data appear to be available for R_3SiMgX species but if the addition of MgX_2 to R_3SiLi to give such compounds is general then further work in this area should give compounds that may be structurally characterized.

6.2. $(R_3Si)_2Mg$ species

The X-ray crystal structure of $(Me_3Si)_2Mg.DME$ (**6**) exhibits a distorted tetrahedral arrangement at Mg with Mg—Si distances of 2.630(2) Å and Si—Mg—Si and O—Mg—O angles of 125.2(1)° and 76.3(2)° respectively. The Si—Mg—Si angle is thought to be large owing to steric repulsion between the two Me_3Si groups and the O—Mg—O angle is small owing to the DME chelate ring [284].

The structure of $(Me_3Si)_2Mg.TMEDA$ is similar to that of the DME adduct (**6**)



(**6**)

and has an Mg—Si distance of 2.627 Å and Si—Mg—Si and N—Mg—N angles of 115.3(1)° and 82.8(4)° respectively. The closing up of the Si—Mg—Si angle relative to that in the DME adduct has been attributed to TMEDA being a weaker base than DME and the methyl groups interfering with the positioning of the Me_3Si groups [286]. The structure of $(Me_3Si)_2Mg$.TMDAP is again similar (**6**), with Si—Mg distances averaging 2.66 Å and Si—Mg—Si and N—Mg—N angles of 119.7(1)° and 93.1(1)° respectively [287].

6.3. *R_3SiMgR' species*

Although several such species have been prepared in solution no detailed NMR studies seem to have been carried out on them and none seem to have been isolated as solids.

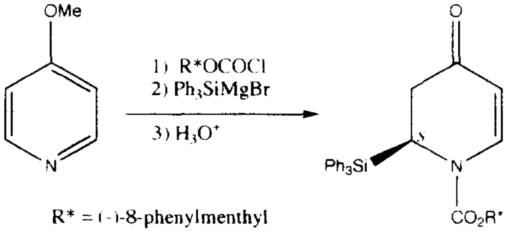
7. The reactions of silyl derivatives of the group 2 metals

The use of silyl derivatives of the group 2 elements for synthetic purposes has received little attention especially when compared with their organic counterparts. This is probably largely due to their relatively difficult syntheses and because many of the reactions that they might be expected to undergo may be readily achieved using other, more readily available organic reagents. The few studies on the reactivity of silyl magnesium compounds carried out so far suggests that although they often give the same products that would be found from the silyllithium reagents they may give products with different regio- or stereoselectivity.

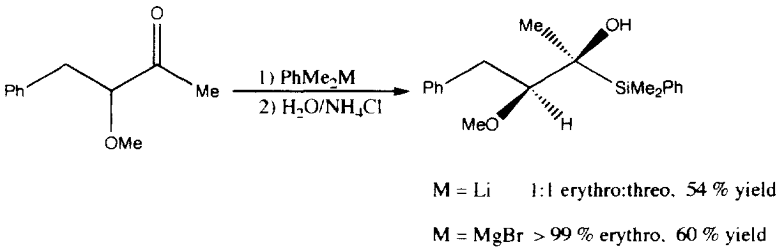
7.1. *R_3SiMgX species*

There appear to have been few studies using such species for synthetic purposes although as noted above in Section 5.1 if they are generated in a solution containing a chlorosilane they do appear to react, as would be expected, to give disilane products. Several other reactions of R_3SiMgX-type species thought to be reaction intermediates are also described in Section 5.1.

More recently several silyl "Grignards" have been used in synthetically useful preparations. Thus $Ph_3SiMgBr$ adds stereoselectivity to chiral 1-acyl-4-methoxypyridinium salts but the absolute configuration of the dihydropyridones formed (Eq. (33)) is opposite to that formed from analogous reactions with alkyl Grignards [280], whereas the bulky silylmagnesium compound $(Me_3Si)_3SiMgBr$ reacts in the manner expected for a Grignard reagent with mesCHO to give $(Me_3Si)_3SiCH(OH)$mes in 66% yield [281]. The use of $PhMe_2SiMgBr$ in the chelation-controlled addition of an α-alkoxy carbonyl compound gives a significantly different ratio of diastereomers of the expected α-silyl alcohols compared with the corresponding lithium reagent $PhMe_2SiLi$ (Eq. (34)) [228].



(33)



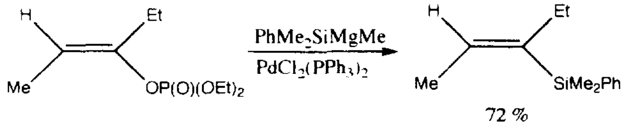
(34)

7.2. *($R_3Si)_2Mg$ species*

The use of $(Me_3Si)_2Mg.DME$ as an Me_3Si transfer reagent has been rather limited but it has been used in the synthesis of silyl derivatives of lead [292], phosphorus [293], and arsenic [294] as shown in Scheme 11. The synthesis of $(Me_3Si)_3Fe$ using $(Me_3Si)_2Mg.DME$ has also been reported briefly [293]. The barium silyl $(Ph_3Si)_2Ba$ reduces silver nitrate to silver and hydrolyses in aqueous methanol to give Ph_3SiOH, $Ba(OH)_2$, and H_2 but little else seems to be known about this interesting compound or its calcium and strontium analogues [288].

7.3. *R_3SiMgR' species*

The reagent $PhMe_2SiMgMe$ acts as a $PhMe_2Si$ transfer reagent and undergoes a variety of reactions such as palladium-catalysed coupling with enol phosphates [111], regioselective additions to allenes catalysed by copper [289], and silylation of acetylenes which may occur with intramolecular cyclization [290], or regioselectivity to give (*E*)-1-silyl-1-alkenes [231], (Eqs. (35)–(39)). Although R_3SiMgR'' species have found some utility in organic synthesis they do not yet seem to have found use in inorganic chemistry.



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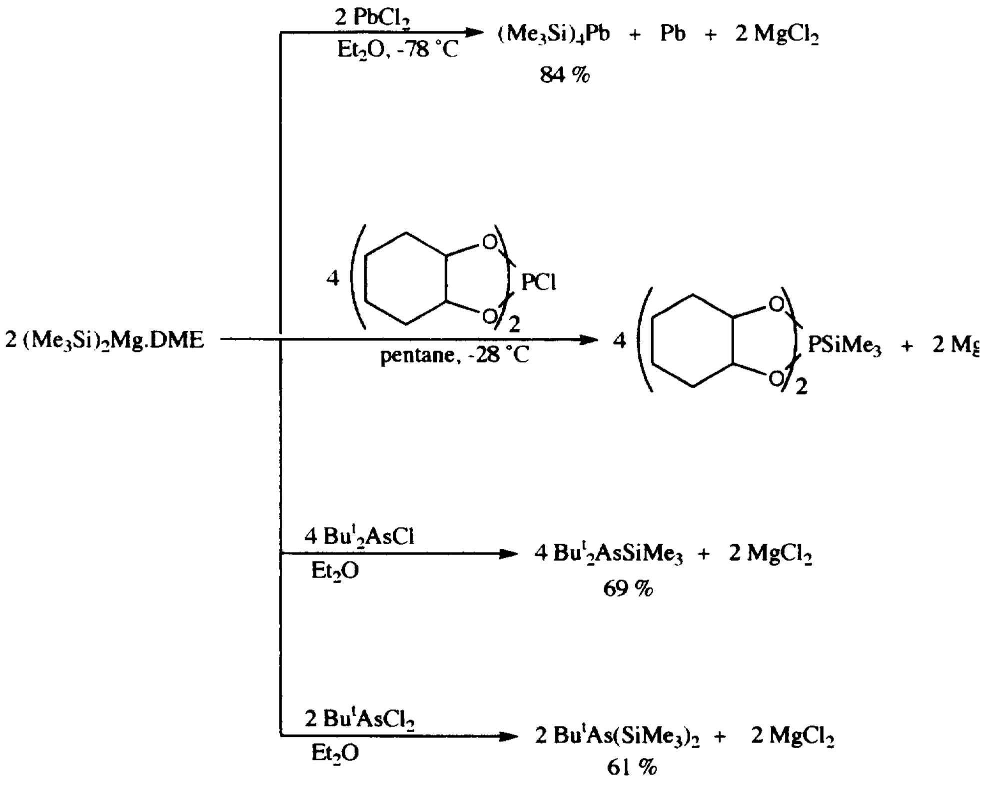
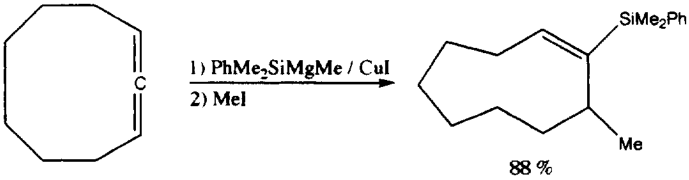


Scheme 11. Reactions of $(Me_3Si)_2Mg.DME$.



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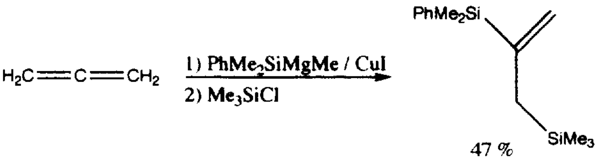
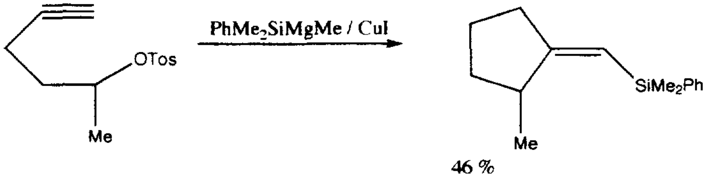
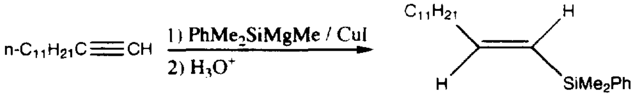


(37)



(38)



(39)

The reaction of three equivalents of $PhMe_2SiMgMe$ with $ZnBr_2$ affords a reagent formulated as $(PhMe_2Si)_3ZnMgMe$ which undergoes regioselective transition metal catalysed addition to alkenes [232,233]. The reaction between three equivalents of $PhMe_2SiLi$, MeMgI, and $MnCl_2$ affords a similar reagent formulated as $(PhMe_2Si)_3MnMgMe$ which reacts with terminal acetylenes to give 1,2-disilyated 1-alkenes, with mono- and bis(trimethylsilylated) acetylenes to give tri- and tetrasilylated alkenes (including the bulky $(Me_3Si)_2C{=}C(SiMe_3)_2$), and with alkenyl halides, alkenyl sulphides and enol phosphates to give vinyl silanes in good yields [234].

8. Conclusions

Although the chemistry of the silicon derivatives of the elements of groups 1 and 2 has developed rather slowly in comparison with their organic counterparts the uses of such compounds in inorganic and organic synthesis is now growing rapidly. The growth in the synthetic application of such compounds has not, however, been matched by structural studies and much needs to be done to determine whether such compounds have the rich structural diversity found for their organic analogues. Recent work in the field of organic synthesis suggests that silylmagnesium reagents and their derivatives have great potential but this has yet to be realized in organometallic or inorganic synthesis.

Note added in proof

Since this article was originally written two important papers on silyllithium reagents have been published. The 1,2-dilithiodisilane derivative 1,2-dilithio-1,2-diisopropyl-1,2-disilaacenaphthendiide can be prepared by treatment of the corresponding 1,2-dichlorodisilane with excess lithium. NMR spectroscopy and theoretical calculations suggest that each lithium interacts with only one silicon atom and that there is some degree of covalency in the Si—Li bond [295]. The reaction of the cyclotrisilane $\{[2\text{-}(Me_2NCH_2)C_6H_4]_2Si\}_3$ with lithium in dioxane or in THF gives the 1,3- or 1,2,-dilithio species $Li\{[2\text{-}(Me_2NCH_2)C_6H_4]_2Si\}_3Li$ and

Li{[2-(Me_2NCH_2)C_6H_4]$_2$Si}$_2$Li respectively. The 1,3-dilithiotrisilane has a solid state structure in which the lithium atoms are coordinated by both NMe_2 groups on the adjacent silicon and by a dioxane solvent molecule. In contrast the 1,2-dilithiodisilane is unsymmetrical with one lithium being coordinated by two adjacent NMe_2 groups and are THF molecule and the second lithium coordinated by one NMe_2 group and by two THF molecules. Again NMR spectroscopy indicates that there is some covalent character in the Si—Li interaction [296].

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