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Contributions to the chemistry of halosilane adducts

XVIII *. On the nature of compounds of trimethylhalosilanes with 1,1,3,3-tetramethylguanidine and 2-trimethylsilyl-1,1,3,3-tetramethylguanidine: preparation and characterization of mono- and bis-(2-trimethylsilyl)-1,1,3,3-tetramethylguanidinium halides

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Abstract

1,1,3,3-Tetramethylguanidine (TMG) and 2-(trimethylsilyl)-1,1,3,3-tetramethylguanidine (TMSTMG) react with trimethylhalosilanes Me_3SiHal in equimolar ratio with ionization of the Si–halogen bond to give the stable guanidinium salts $[(Me_2N)_2CNHSiMe_3]Hal$ (Hal = Cl (**1**), Br (**2**)) and $[(Me_2N)_2CN(SiMe_3)_2]Hal$ (Hal = Cl (**3**), Br (**4**), I (**5**)), respectively, involving tetracoordinate silicon. No reaction occurs with Me_3SiF. The same ionic species are present in $CHCl_3$ or CH_3CN solutions (IR, ^1H, ^{29}Si NMR), thus establishing for the first time, the formation of an ionic solid derivative of Me_3SiCl stable towards dissociation. Reaction with an excess of TMG gives an equilibrium mixture of TMSTMG and TMG · HHal. The bis(silyl)guanidinium salts are less stable towards dissociation than the mono(silyl) derivatives, the stability sequence being $Cl^- < Br^- < I^-$ within the series. The reactions of both types of compound have been investigated. The implications of the present and earlier results for the mechanisms of racemization and nucleophilic substitution at silicon are discussed.

Introduction

Reactions of trimethylhalosilanes with Lewis bases have been frequently investigated in order to gain information on donor–acceptor properties and on the

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correlation between composition and the structure of the products. Additional interest has recently been shown in investigation of the question of the role of added nucleophiles in the racemization of chiral organosilanes and in nucleophilic substitution at silicon [1–8]. Two mechanisms have been proposed, one of which involves an intermediate extra-coordinate silicon species [1,2] and the other an intermediate ionic species containing tetracoordinate silicon [3,5]. Both because of this and because mixtures of electrophilic trimethylsilyl compounds and nucleophiles such as amines and amides are frequently used as silylating agents in organic chemistry [7,9–11], there is much interest in the preparation and investigation of tetracoordinate ionic compounds, which have been postulated as active species in a series of silylating reactions [3–5,7,8], and of pentacoordinate molecular adducts of triorganohalosilanes. In the past, only a few compounds of the first type, derived from trimethylbromo- and trimethyliodo-silane, have been isolated and well characterised; examples are $[Me_3Si \cdot HMPT]Br(I)$, [3,12], $[Me_3Si \cdot py]Br(I)$ [13,14] or $[Me_3Si \cdot DMF]X$ (X = Br, I, OSO_2CF_3) [5]. Very recently, a series of further compounds of this type have been obtained by the reaction of Me_3SiX (X = Br, I, OSO_2CF_3, ClO_4) with various Lewis bases [7,15,16]; trimethylchlorosilane, however, was found not to react with these bases at room temperature, though reversible formation of a 1/1 adduct with trimethylsilylimidazole was observed in solution by NMR spectroscopy at −96 °C. At room temperature, this adduct was completely dissociated into its components. From the NMR spectral data for this compound it was judged to have the same structure as the corresponding ionic tetracoordinate compounds of Me_3SiX (X = I, Br), and this provided the first unambiguous evidence for the formation of such a compound from Me_3SiCl. No other ionic compound of Me_3SiCl has yet been unequivocally observed.

There is no well characterised example of a pentacoordinate molecular adduct between trimethylhalosilane and separate ligand. (Ligands bonded to silicon, which form chelates on coordination, are special cases and will not be considered here).

Although there have been frequent reports in the literature of the formation of ionic molecular adducts of Me_3SiCl, recent experimental evaluation and the critical appraisal of these earlier investigations have shown that in no case was unequivocal evidence in favour of their identification presented. Thus, it has been shown that, contrary to some reports [17–19], Me_3SiCl does not react with pyridine [20,21] and many other nitrogen bases or tri-t-butylphosphine [22]. In the case of the postulated molecular pentacoordinate 1/1 adducts of triorganohalosilanes, it has been demonstrated that the adduct, on the basis of conductivity measurements assumed to be $Me_3SiBr \cdot DMF$ [2], is ionic, containing tetracoordinate silicon [5]. The low conductivity of the compound in solution was attributed to ion pair formation [5]. This explanation does not take into account, however, the different experimental conditions used in the NMR experiments (2 *M* solutions) and conductivity measurements (0.1 *M* solution [2]), which would favour more extensive dissociation in the latter case. In our opinion, therefore, extensive dissociation of the compound in dilute solution is a more likely reason for the low conductivity in view of the high conductivity [2,3,5] of ionic compounds of this type. Similar considerations may be applied to the adduct $Ph_3SiCl \cdot OPPh_3$ [2,23] which was isolated as a solid. The low conductivity of the solution of this compound, which has been explained in terms of the presence of a molecular pentacoordinate compound, may equally well arise from extensive dissociation. An ionic structure, therefore, can not be excluded. Finally,

the formation of the adduct $Me_3SiCl \cdot OPPh_3$, which has been postulated [23] on the basis of ^{31}P NMR data for a solution of the components (but was not isolated) and for which a molecular structure was proposed on the basis of conductivity measurements [2], has not been substantiated [22]; the conductivities can also be interpreted in terms of unchanged starting compounds. In support of this interpretation, the formation of phosphine oxide adducts of triorganochlorosilanes in solution at ambient temperature can be practically excluded in the light of new investigations of similar systems [5].

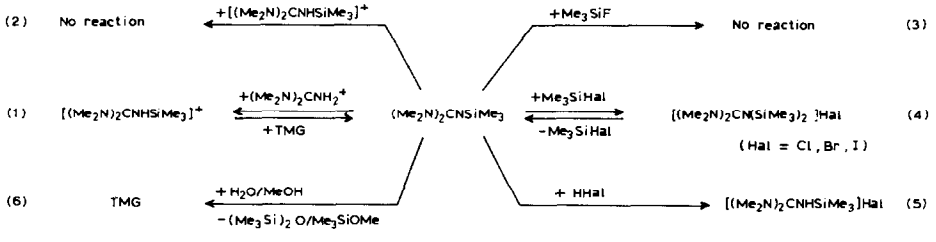
In our investigations on the ligand properties of guanidine derivatives and their reactions with chloromethylchlorosilanes, difficulties in the elucidation of the unexpectedly complicated reactions of these compounds [24] necessitated the investigation of the simpler reactions of the trimethylhalosilanes. The results enable us to throw light on the above mentioned problems. A series of new addition compounds of triorganohalosilanes and the first stable ionic 1/1 addition compounds of Me_3SiCl have been obtained.

Results

1,1,3,3-Tetramethylguanidine (TMG) reacts with the trimethylhalosilanes, Me_3SiHal (Hal = Cl, Br) to give the ionic addition compounds $[(Me_2N)_2CNHSiMe_3]Hal$ (Hal = Cl (**1**), Br (**2**)), according to eq. 1. The expected subsequent reaction

$$(Me_2N)_2CNH(TMG) + Me_3SiHal \rightarrow [(Me_2N)_2CNHSiMe_3]Hal \quad (1)$$

of the NH group involving proton abstraction by the base does not occur when stoichiometric amounts of the reagents or excess halosilane are used. This reaction can, however, be shown to occur as a reversible process in chloroform solution (see Scheme 1, reaction 1), when an excess of TMG is used. Measurable amounts of TMG · HHal are formed when more than two equivalents of TMG are added, and the equilibrium is ultimately complete towards TMG · HHal and 2-trimethylsilyl-1,1,3,3-tetramethylguanidine (TMSTMG). That the reaction is reversible is shown by the fact that addition of pentane or similar solvents to the equilibrium mixture results in precipitation of TMG · HHal and in a shift of the equilibrium to the right hand side (Scheme 1, reaction 1). Mixtures of TMG · HHal and TMSTMG (1/1), therefore, react in solution in a reversible fashion to give TMG and TMSTMG · HHal as the predominant species. The reaction is remarkable in view of the high basicity of TMG and is compatible with an even higher basicity of TMSTMG. Investigations of reactions of Me_3SiHal with excess of TMG gave no indication of the



Scheme 1

Table 1

NMR data [a] for 1/1 compounds of trimethylhalosilanes with 1,1,3,3-tetramethylguanidine and 2-trimethylsilyl-1,1,3,3-tetramethylguanidine in $CDCl_3$ (TMS as internal standard)

Compound		$\delta(^{29}Si)$ (ppm)	$\delta(^1H)$ (ppm)	
			SiMe	NMe_2
$(Me_2N)_2CNH$ (TMG)		–	–	2.72
$[(Me_2N)_2CNH_2]Cl$ (TMG·HCl)		–	–	3.09
Me_3SiCl		30.23 [b]	0.41	–
$[(Me_2N)_2CNHSiMe_3]Cl$ (**1**)		13.20	0.38	3.09
	−50 °C	–	0.42	3.33, 3.10, 3.07 [d]
Me_3SiBr		26.60 [c]	0.55	–
$[(Me_2N)_2CNHSiMe_3]Br$ (**2**)		13.76	0.40	3.14
	−60 °C	–	0.38	3.32, 3.08, 3.06 [d]
$(Me_2N)_2CNSiMe_3$ (TMSTMG)		−19.46 [b]	0.09	2.71
$[(Me_2N)_2CN(SiMe_3)_2]Cl$ (**3**)		–	0.36	3.38, 3.25 [e]
$[(Me_2N)_2CN(SiMe_3)_2]Br$ (**4**)		14.84	0.35	3.41, 3.25 [e]
Me_3SiI		10.60 [c]	0.80	–
$[(Me_2N)_2CN(SiMe_3)_2]I$ (**5**)		14.83	0.36	3.39, 3.27 [e]
$(Me_2N)_2C{=}O$ (TMU)		–	–	2.80
TMU/Me_3SiCl (1/1)		30.78	0.43	2.79
	+90 °C	–	0.43	2.79
	−60 °C	31.4	–	–

[a] All spectra recorded at room temperature unless otherwise indicated. [b] Pure liquid. [c] In CD_2Cl_2. [d] Intensity ratio 1/1/2. [e] No collapse of doublet at 100 °C.

formation of 1/2 (Me_3SiHal/base) adducts; e.g. unchanged TMSTMG · HBr (**2**) is observed in a 1/1 mixture of TMSTMG · HBr and TMG in chloroform even at −70 °C (^1H NMR, Table 1).

The IR spectra (Table 2) of the solid compounds **1** and **2** are essentially identical, thus ruling out the possibility that weak bands in the 500–200 cm^{-1} region can be assigned to Si-halogen vibrations. Moreover, the bands in this region are less intense than expected for Si-halogen vibrations.

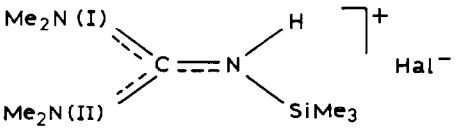
The ^1H NMR spectra of the dissolved compounds **1** and **2** are identical except for small deviations in the δ-values that are possibly due to the presence of different anions (Table 1). The relative signal intensities confirm their 1/1 composition. The chemical shifts of the NMe_2 group are similar and close to that for TMG · HCl, confirming the ionic structure of these compounds in solution. No dissociation of **1** and **2** into their components or into TMSTMG and HHal is observed in chloroform solutions up to 100 °C. The ^{29}Si resonances (Table 1) are also essentially similar. They are shifted to lower field relative to those for TMSTMG, and are different from the averaged values of the starting compounds, thus ruling out mixtures of the components. The results give further support to the cationic structure of the compounds.

Dynamic behaviour of **1**, **2** (and also of **3**, **4** and **5**), similar to that of TMG is observed, owing to restricted rotation of the NR_2 groups about the CN bonds (variable temperature ^1H NMR). The rate of rotation decreases in the order $C{-}NMe_2(I) > C{-}NMe_2(II) > CNHSiMe_3$. The rate of rotation for the latter two groups are only slightly different (by a factor of ca. 2). This sequence may be mainly due to steric factors.

Table 2

Principal IR spectral bands (cm^{-1}) of compounds **1**, **2**, **4** and **5** in the range 2000–1500 and 500–200 cm^{-1}

Compound	Bands (cm^{-1})	
	2000–1500	500–200
TMG	1605s, 1488s, 1405m	420vw, 365vw
1	1650sh,m, 1594vs, 1559s, 1544s	464m, 364m, 292m
2	1650sh,m, 1605vs, 1562s, 1547s	462m, 370m, 298m
4	1645w, 1608vs, 1578w, 1525m	442w, 405w, 380vw, 300w
5	1650sh,w, 1600s, 1572sh,w, 1518m	435w, 400w, 372vw, 290w
TMSTMG	1676vs,br, 1650m	465w, 360w, 340w, 318w

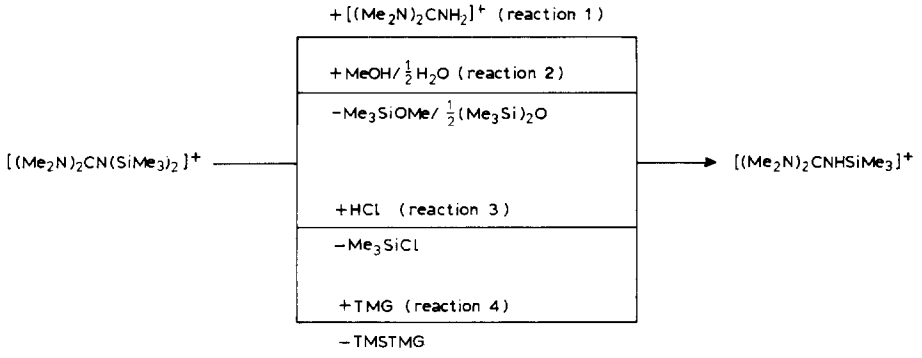


The simple and smooth addition of halosilanes to TMG without subsequent HHal abstraction by the strong base TMG prompted an investigation of the corresponding reactions of TMSTMG. This compound can be obtained only with difficulty by direct reaction of Me_3SiCl with excess of TMG (as discussed above and in the experimental part). It was, therefore, prepared by the lithiation of TMG and subsequent reaction with Me_3SiCl. The new compound readily reacts with Me_3SiHal (Hal = Cl, Br, I) to give 1/1 addition compounds (isolated as white solids) as shown in Scheme 1, reaction 4. No reaction takes place with Me_3SiF. The new compounds $[(Me_2N)_2CN(SiMe_3)_2]Hal$ (Hal = Cl (**3**), Br (**4**), I (**5**)) are ionic both in the solid and in solution, like the mono(silyl)guanidinium compounds (identical IR spectra of the solids, Table 2; absence of Si-halogen vibrational bands; identical ^1H NMR and ^{29}Si NMR spectra of their $CDCl_3$ solutions, Table 1; δ-values of NMe_2 proton signals in the guanidinium range with typical low field shifts relative to TMG; ^{29}Si NMR signals in the δ-range of mono(silyl)guanidinium compounds).

These reactions demonstrate the great ease of formation of the guanidinium cation, which enables the addition of a second $SiMe_3$ group to an already silylated amino group with ionization of the Si–halogen bond, including the Si–Cl bond of Me_3SiCl. *trans*-Silylation, which is the expected reaction for a silylamine, does not occur. The stability of these compounds towards dissociation into their components is, however, lower than that of the corresponding mono(silyl)guanidinium compounds. It increases from the chloride (**3**) to the iodide (**5**). Compound **3** is already partially dissociated at 25 °C (but separates as a solid upon interaction of the pure components); the bromide **4** starts to dissociate above 50 °C, while the iodide **5** shows no sign of dissociation even at +100 °C (all in chloroform solution). ^1H NMR measurements of the reversible dissociation equilibria of **3** and **4** in $CHCl_3$ solutions allowed the estimation of the enthalpy of formation of **3** and **4**, and this confirmed the qualitative results (ΔH_f(**3**) 23 ± 4 kcal/mol; ΔH_f(**4**) 30 ± 2 kcal/mol).

Reactivity

All new compounds isolated in the present study are extremely sensitive to hydrolysis leading to $(Me_3Si)_2O$ and TMG · HHal. Corresponding reactions occur



Scheme 2

with MeOH or HCl to give TMG · HHal and Me_3SiOMe or Me_3SiCl. For the bis(silyl) compounds, these reactions proceed via the mono(silyl) compounds, which can be obtained in quantitative yield when equimolar amounts of the reactants are used (Scheme 2, reactions 2 and 3). The latter reactions may proceed via intermediates, as shown in eq. 2, owing to a temporary local excess of the reagent.

$$x[(Me_2N)_2CN(SiMe_3)_2]Hal + xHX \rightarrow (x-y)[(Me_2N)_2CNHSiMe_3]Hal + xMe_3SiX + y/2[(Me_2N)_2CNH_2]Hal + y/2[(Me_2N)_2CN(SiMe_3)_2]Hal \rightarrow x[(Me_2N)_2CNHSiMe_3]Hal + xMe_3SiX \; (X = O_{1/2}, Hal, OMe) \qquad (2)$$

A third remarkable synthesis of **1** and **2** was observed in the reaction of TMSTMG with HCl(Br) (Scheme 1, reaction 5) which was also found to proceed quantitatively. Finally, these compounds and TMSTMG · HI are also obtained from reactions of **3**, **4** and **5** with TMG, according to Scheme 2, reaction 4. The quantitative nature of these reactions underlines the lower stability of bis(silyl)guanidinium compounds compared to mono(silyl)guanidinium compounds. Steric reasons may play an important role in the higher donor strength of TMG towards Me_3SiHal compared to TMSTMG, which is the reverse of the ease of proton donation.

Of particular interest are the interactions of **1** and **2** with TMG or TMSTMG between -80 and $+80\,^{\circ}C$. At ambient temperature, fast exchange of the NMe_2 and of the $SiMe_3$ groups of these compounds in the ^1H NMR time scale (80 MHz) is observed. At lower temperature the averaged NMe_2 signals split into the signals of the respective compounds. Fast exchange of TMG and TMSTMG with **2** or **4** does not occur up to $+100\,^{\circ}C$, and Me_3SiCl or Me_3SiBr do not exchange rapidly with TMSTMG and **1** or **2** below $+90\,^{\circ}C$. These results correspond to observations in related systems, namely [Me_3Si · HMPT]Br/HMPT [3], bis (*N*-trimethylsilylimidazolium) halides ([TMSimiTMS]Hal)/*N*-trimethylsilylimidazol (TMSimi) and [TMSimiTMS]Hal/Me_3SiHal [16]. In the last two systems, it was shown that the exchange TMSimiTMS/TMSimi does not occur via dissociation/reassociation as it does in the case of [TMSimiTMS]Hal/Me_3SiHal but by nucleophilic attack of TMSimi on $[TMSimi]^+$. This mechanism could operate in the exchanges in the present systems **1**, **2**/TMG (eq. 3). It would also explain the slower exchange of **3** or **4** with TMG or TMSTMG relative to **1** and **2**. Nucleophilic attack may be hindered

by the steric interactions of the two $SiMe_3$ groups, which are also responsible for the more hindered rotation about the CN bonds in these compounds compared to the monosilyl derivatives. Another possible explanation for the exchange is proton transfer (NH...N), which possibly occurs in the system TMSTMG · HBr (**2**)/TMSTMG (eq. 4) and may operate in the system TMSTMG · HBr (**2**)/TMG.

$$[(Me_2N)_2CNHSiMe_3]^+ + (Me_2N)_2CN^*H \rightarrow (Me_2N)_2CNH + [(Me_2N)_2CN^*HSiMe_3]^+ \quad (3)$$

$$[(Me_2N)_2CNHSiMe_3]^+ + (Me_2N)_2CN^*SiMe_3 \rightarrow (Me_2N)_2CNSiMe_3 + [(Me_2N)_2CN^*HSiMe_3]^+ \quad (4)$$

Further investigations are necessary to throw more light on these aspects.

Discussion

The ease of formation and isolation of stable ionic addition compounds of trimethylchlorosilane is the result of the high propensity for formation of the guanidinium cation. It is to be expected that stable ionic compounds of trimethylchlorosilane will also be obtained from other ligands which give cations with a similarly high mesomeric stabilization. It is of interest in this context that tetramethylurea (TMU), although isoelectronic with TMG, does not react or even interact with trimethylchlorosilane (pure compounds or chloroform solution, ^1H and ^{29}Si NMR, Table 1).

Neutral or ionic pentacoordinate species of Me_3SiHal or $[(Me_2N)_2CNRSiMe_3]^+$ (R = H, $SiMe_3$) could not be identified in any of the investigated reactions with unidentate ligands (IR, NMR). The coordination of the nitrogen donor ligand appears to be dependent upon the ionization of the Si–Cl or Si–N bond respectively, leading formally to the stronger acceptor $SiMe_3^+$. A similar suggestion has been put forward to rationalise the formation of ionic $[SiMe_3 \cdot py]Br(I)$ from $Me_3SiBr(I)$ and pyridine [14]. Different behaviour may be found for unidentate ligands bonded to the coordinating silicon atom, thus forming chelates on coordination [25*,26*], as mentioned earlier, and such ligands are not considered in the present context. It remains to be seen whether pentacoordinate molecular 1/1 adducts of trimethylhalosilanes with free unidentate ligands can be obtained at all, since even the cationic compounds described here do not add further TMG, to form (cationic) pentacoordinated adducts, in spite of their better acceptor properties relative to R_3SiHal. In accord with these findings, no reaction is observed with Me_3SiF, neither formation of a molecular pentacoordinate complex nor formation of an ionic compound requiring the ionization of the Si–F bond (as shown by the ^1H NMR spectra of mixtures of pure compounds or chloroform solutions between −80 to +80 °C). As pointed out in the Introduction, no pentacoordinate molecular 1/1 adducts of other triorganohalosilanes are known. These results are significant for the question of the mechanism of nucleophilically assisted substitution and induced racemization of organohalosilanes.

Following the identification of an ionic 1/1 adduct of trimethylchlorosilane and trimethylsilylimidazole (TMSimi) formed at low temperature [15], we have now

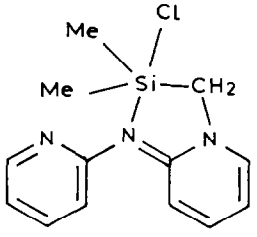
* Only the literature describing such compounds for the first time is given.

shown for the first time the possibility of the simple and easy ionization of the Si–Cl bond in a triorganohalosilane with formation of addition compounds stable at ambient and higher temperatures in the solid state as well as in solution. The ionization does not require the more readily ionized Si–Br or Si–I bonds or formation of Si–O bonds as suggested earlier [1,2].

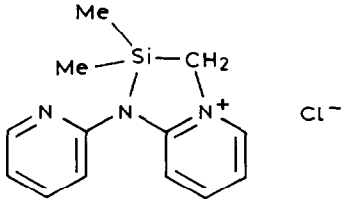
The present compounds may, however, be regarded as special cases, since their formation is favoured by the high mesomeric stabilization of the guanidinium cation, and so it is of interest that Lewis bases with less favourable mesomeric stabilization were also recently shown to react with trimethylhalosilanes (Hal = I, Br, Cl) to form (more or less stable) ionic tetracoordinate compounds. Thus the present new data supply further evidence of the ionic mechanism of reactions of triorganohalosilanes (with the exception of fluorosilanes) and thereby substantiate earlier suggestions mentioned above. On steric grounds, also, this mechanism appears to be more plausible. Triorganohalosilanes with sterically demanding substituents have been used in the mechanistic investigations and formation of hexacoordinated species from such silanes might not be an easy process. Formation of hexa- or penta-coordinate silicon compounds containing three organic ligands and unidentate non-chelating ligands, which would support the mechanism, involving expanded coordination at silicon has not yet been established. The compounds $Et_3SiI(Br) \cdot$ 2-vinylimidazole [27] may belong to this type, but no structural data are available.

Although the present results are in favour of the ionic mechanism for reactions of triorganohalosilanes, we agree with Corriu [1] that the coordination expansion mechanism is feasible, but suggest that it may be more likely with species other than triorganohalosilanes.

The two mechanisms are closely related, especially if the second step of the mechanism postulated by Corriu [2] involves the ionic pentacoordinate species he suggests as an alternative intermediate. The pentacoordinate species corresponds to the frozen transition state of the ionic mechanism. The two mechanisms can be regarded as extremes between which gradations may be possible depending upon the experimental conditions. This assumption is supported by the isolation of compound **6** in our laboratory [28]. This compound exhibits a temperature dependent equilibrium between an ionic tetracoordinate structure (**6b**) at low temperature (with ionization of the Si–Cl bond) and a molecular pentacoordinate structure (**6a**) at ambient temperature. These structures respectively correspond to the first stage of the mechanism with expanded coordination at silicon (**6a**) and to the ionic form (**6b**), though in a system involving an intramolecularly chelating ligand.

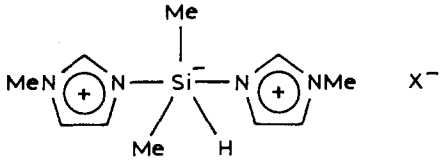


(6a)



(6b)

Small changes of the substituents at silicon in **6** may lead to drastic changes in coordination behaviour. Substitution of $ClMe_2SiCH_2$ by $BrMe_2SiCH_2$ leads to the exclusive formation of the ionic structure **6b** (with Br^- instead of Cl^-) within the accessible temperature range (−80 to +140 °C), while the $Cl_2MeSiCH_2$ derivative is exclusively present as structure **6a**. It cannot be converted into the ionic form **6b**. (We shall report on these compounds in more detail soon). It therefore seems feasible that the change of the substituents at silicon may also induce changes in the mechanism discussed above in which, however, the change is from ionic tetracoordinate to ionic pentacoordinate (or molecular hexacoordinate) (while in **6a** and **6b** it is from ionic tetracoordinate to molecular pentacoordinate). Some evidence for this assumption may be found in the formation of a series of isolated ionic pentacoordinate 1/2 adducts of monobromo- and monoiodo-silanes (not however, of triorgano derivatives) [13,29] and the recently reported formation of the chlorosilane adduct **7** [6].



(**7**)

(X = Cl, I, OSO_2CF_3)

While these compounds are formed easily, no corresponding structurally well characterised ionic pentacoordinate adduct of a triorganohalosilane is known, demonstrating a strong substituent effect on the composition and structure of the adducts. Adduct **7** corresponds to the postulated intermediate or transition state of the second stage of the coordinative mechanism (in the ionic alternative) or to the frozen transition state of the ionic mechanism. In view of these findings, it is to be expected that further examples of compounds of this type will be found.

The clear preference for formation of ionic tetracoordinate adducts in the reactions of the triorganohalosilanes must be due to the inductive effect of the organic groups, which facilitates the ionization of the Si–halogen bond and at the same time makes coordination of the second ligand molecule more difficult. Apparently, substitution of only one organic group by a more electronegative substituent counteracts this effect to such an extent that a second ligand can be coordinated.

It is to be expected from the present results that mixtures of TMG and TMSTMG in combination with triorganohalosilanes will afford very good silylating agents. Systematic investigations along this line have still to be made. In one case, the alcoholysis of Ph_2SiCl_2 with a sterically demanding alcohol, comparative data are available [8], but the effect is less pronounced than expected. In the first step of the alcoholysis, TMG displays the second strongest effect (i.e. next to DMAP), but in the substitution of the second Si–Cl group, it is much less effective relative to other nucleophiles. The result is surprising in the light of the present investigations, but may reflect steric factors. The steric requirements in the interaction of TMG with the silane are more demanding than for any of the other investigated nucleophiles [8]. Further investigations are therefore desirable.

Experimental

All manipulations were carried on a standard vacuum line. Rigorous precautions were taken to exclude moisture. Trimethylchloro-, -bromo- and -iodo-silane were purified by distillation and stored in a vessel on the vacuum line. Before use, a considerable quantity of the silane was condensed off to ensure complete removal of traces of hydrogen halide. 1,1,3,3-Tetramethylguanidine (Merck) was stored over 4 Å molecular sieves (Merck). Elemental analyses (Table 3) were carried out by Mikroanalytisches Labor Pascher, Remagen. ^{1}H and ^{29}Si NMR spectra were recorded on a Bruker WH-300 (300 MHz) (^{1}H and ^{29}Si) or a Bruker WP-80 (80 MHz) spectrometer. Infrared spectra were recorded with a Perkin–Elmer IR spectrophotometer 283, using Nujol mulls on CsI optics.

Preparation of 2-trimethylsilyl-1,1,3,3-tetramethylguanidine (TMSTMG, $(NMe_2)_2CN\text{-}SiMe_3$)

40 ml of a 1.69 *M* solution of n-butyllithium (n-BuLi) in hexane (Ventron) was added dropwise with stirring to 7.49 g (0.065 *M*) TMG in 140 ml of benzene cooled in an ice bath. The mixture was then refluxed for 2 h and the solvent was then evaporated off until $LiNC(NMe_2)_2$ separated as a while solid. It was filtered off and dried in vacuo. To a stirred suspension of this solid in 150 ml of n-pentane, a solution of 7.5 g (0.069 *M*) trimethylchlorosilane in 50 ml of n-pentane was added dropwise, and the mixture was refluxed for 4–5 h. LiCl was filtered off, and, since it was observed to retain a considerable amount of TMSTMG, washed carefully 3 times with 50 ml portions of pentane. Fractional distillation of the combined filtrates yielded TMSTMG as the main fraction (colourless liquid b.p. 191–192 °C). The purity of the sample was checked by ^{1}H NMR (Table 1).

Preparation of compounds 1–5

All the guanidinium salts were prepared by the following procedure. At least an equimolar amount of the halosilane was condensed onto a weighed amount of TMG or TMSTMG at liquid nitrogen temperature. The mixture was then slowly warmed to room temperature with continuous stirring. Solids were formed in all cases. After another 3 h stirring the excess of silane was removed by condensation and the remaining solid dried in vacuo. Yields were practically quantitative. The compounds decompose before melting, exact melting points cannot be obtained.

Use of an excess of halosilane is important for obtaining pure compounds. As mentioned earlier proton abstraction takes place in the presence of an excess of

Table 3

Microanalytical data for compounds **1**, **2**, **4** and **5**

Compound	Analysis (Found (Calcd.) (%))	
	Nitrogen	Halogen
1	18.8 (18.91)	16.0 (15.95)
2	15.6 (15.67)	30.8 (29.56)
4	12.4 (12.34)	24.1 (23.47)
5	10.8 (10.92)	33.2 (33.09)

TMG. The reactions are best carried out in the absence of a solvent which may cause complications. Thus, hydrocarbon solvents cause precipitation of TMG · HHal, thereby shifting the equilibrium towards this compound and the formation of TMSTMG as byproduct.

Reaction of Me_3SiCl with excess TMG

Me_3SiCl was first condensed onto a large excess of TMG (molar ratio 1/30) at liquid nitrogen temperature. A white precipitate was immediately formed on warming to room temperature. After 3 h stirring, dry n-pentane (5 times the volume of the reaction mixture) was added and after stirring the mixture was filtered. The precipitate was washed 3 times by condensing some of the washing pentane back to the precipitate and stirring and filtering the mixture. Finally the white solid was dried in vacuo. Analysis and ^1H NMR data showed it to be TMG · HCl containing about 2% of **1**. The filtrate contained unreacted TMG and TMSTMG, but essentially no **1**, indicating that practically complete reaction had occurred.

Separation of TMSTMG from this mixture by fractional distillation is possible, but difficulties arise when TMG is present in considerable excess. These difficulties are avoided in the alternative method of preparation of TMSTMG given above.

*Reaction of **1** and **2** with TMG*

When a concentrated solution of **1** and TMG (1/10) in $CHCl_3$ was prepared a crystalline precipitate of pure TMG · HCl (^1H NMR) formed after some hours standing. The solution contained TMSTMG (δ 0.09 ppm), TMG, and additional TMG · HCl, but essentially no starting material **1**. TMG · HCl is rather soluble in $CDCl_3$, and crystallizes only partially from the solution. More $CDCl_3$ was added to the mixture until the precipitate redissolved. The solution now contained a considerable amount of **1** (^1H NMR: Si–Me signals δ 0.16 ppm, averaged signals for **1** and TMSTMG throughout). The shift of the NMe_2 signal remained practically constant because of essentially equal chemical shifts of TMG and TMSTMG and of TMG · HCl and **1**; changes in the concentrations of TMG and **1** are compensated by equivalent changes of TMSTMG and TMG · HCl concentrations. Finally, $CDCl_3$ solutions of TMG and **1** in increasing molar ratios were prepared. Typical SiMe δ values for **1**/TMG mixtures (molar ratio) are 0.27 ppm for 1/1.8; 0.14 ppm for 1/5.3; and 0.10 ppm for 1/11. Similar results are obtained for mixtures of **2** and TMG.

Reactions of guanidines and guanidinium compounds with H_2O, MeOH and HHal

A weighed amount of **4** contained in an evacuated tube fitted with break seals was allowed to react with an equimolar amount of gaseous MeOH at room temperature for 18 h. The NMR spectrum of the solid obtained after condensing off the volatile Me_3SiOMe indicated the formation of compound **2** and TMG · HBr (compare eq. 2). The solid was then heated for about 30 min at 90 °C in a sealed tube with break seals to complete the reaction. No further volatile components were formed. The white solid **2** was identified by ^1H NMR spectroscopy.

Similar results were obtained from reactions involving equimolar amounts of water and HBr under similar conditions. Addition of one equivalent of HCl to a known amount of TMSTMG in chloroform resulted in the formation of **1** (^1H NMR). Dissociation equilibria of **3** and **4** were investigated by variable temperature

^{1}H NMR. The relative molar ratios of the compounds and their dissociation products were estimated, and ΔH values were then calculated by standard methods.

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