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Unusual mechanistic pathways. The novel chemistry of compounds with tris(trimethylsilyl)methyl or related ligands on silicon†

Colin Eaborn

School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ. E-mail: c.eaborn@sussex.ac.uk

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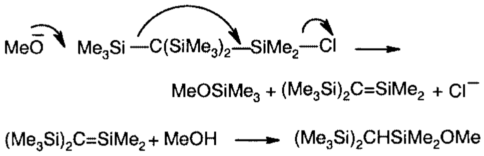
This review is concerned with compounds containing the very bulky tris(trimethylsilyl)methyl or closely related ligands in which three organosilyl substituents are attached to the central carbon atom. The prototype tris(trimethylsilyl)methyl ligand, $(Me_3Si)_3C$, is referred to as the 'trisyl' ligand and commonly denoted by Tsi. A *Dalton Perspective* dealing with compounds in which such groups are attached to metal or metalloid elements from all groups of the Periodic Table except 18 appeared recently,[1] but the chemistry of compounds in which such ligands are attached to functional silicon centres was considered to be too extensive for inclusion in that general survey, and so is reviewed here. It will become clear that much chemistry previously unobservable because of the great ease of nucleophilic attack at functional centres in 'normal' organosilicon compounds can be revealed by using the very bulky ligand to hinder that attack. Other unusual reactions appear to arise from the relief of the steric strain in the crowded compounds.

The compounds under consideration are usually made by reaction of appropriate silicon or organosilicon halides, *e.g.* $SiCl_4$ or Ph_2SiF_2,[2] with organolithium reagents of the types $(Me_3Si)_3CLi$, $(XMe_2Si)_3CLi$ (*e.g.* X = Ph), $(Me_3Si)(XMe_2Si)_2CLi$ (*e.g.* X = Ph), or $(Me_3Si)_2(XMe_2Si)CLi$ (*e.g.* X = OMe). The range of such ligands is described in ref. 1.

Since there is space available to summarize only a small part of the new chemistry developed during this programme a complete list (with titles) of the author's papers in the field is given as ESI.†

Steric hindrance to nucleophilic substitution

The exceptional degree of steric hindrance that could be provided by the trisyl ligand was first revealed by the observation that the silicon trichloride $TsiSiCl_3$ (obtained by reaction of $SiCl_4$ with TsiLi in a one molar proportion or excess) is stable towards boiling methanol or aqueous ethanol even in the presence of silver nitrate.[3] It does react slowly with 2 mol dm^{-3} NaOMe in boiling MeOH, but the main reaction is a fragmentation involving loss of an Me_3Si group rather than a simple substitution.[3,4] This type of reaction is better illustrated by the reaction of $TsiSiMe_2Cl$ to give $(Me_3Si)_2CHSiMe_2OMe$, formed by a novel β-elimination to give a silene followed by addition of MeOH (Scheme 1).[4] The initial process is analogous to an E2 elimination from organic halides but with attack at β-silicon rather than β-hydrogen. That the nucleophile attacks at an Me_3Si rather than the electronically favoured Me_2ClSi centre can be attributed to the fact that attack at the former results in relief of steric strain.



Scheme 1

This type of reaction was observed for all of the compounds $TsiSiMe_2X$ with X = Cl, Br, and I and $TsiSiPh_2X$ with X = F, Cl, Br and I. For the latter set the approximate relative rates for the various halides in MeONa/MeOH at the boiling point were (X =) F, 1; Cl, 2; Br, 3.5; I, 7, and for $TsiSiMe_2X$ they were Cl, 1; Br, 4; I, 20. These sequences are consistent with synchronous formation of the double bond and departure of X^-. The reaction of $TsiSiPh_2Cl$ was about five times as fast as that of $TsiSiMe_2Cl$, possibly because of greater relief of steric strain and perhaps some stabilization of the forming silene by the Ph groups. The reaction of $TsiSiMe_2H$ takes a different course, giving TsiH; apparently the small size of the hydride ligand allows attack of the MeO^- at the functional silicon centre but the Tsi^- anion leaves rather than the H^- because this relieves the great crowding in the pentacoordinate intermediate.

Direct replacement of the halogen X in $TsiSiMe_2X$, with X = F, Cl, Br or I, by the small hydride ligand can be brought about by treatment with $LiAlH_4$,[2] and direct nucleophilic substitution by small anions occurs for X = Cl, Br, or I upon treatment with CsF or pseudohalide salts, such as NaN_3 or KSCN in MeOH or MeCN, although the reactions in MeOH are accompanied by some formation of the elimination–addition product $(Me_3Si)_2CHSiMe_2OMe$.[5] (A little of this product may arise from the presence of methoxide ion in solutions of the salts of weak acids.) The much more reactive nitrate $TsiSiMe_2ONO_2$ gives solely the substitution product. Towards

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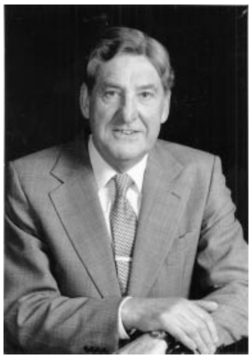
† Electronic supplementary information (ESI) available: a complete list of the author's publications, with titles, on compounds with trisyl or related ligands on silicon (and for comparison, on germanium or tin) or species containing trisyl-type groups not on a metal or metalloid. See http://www.rsc.org/suppdata/dt/b1/b106509m/

After studying at the (now) University of Wales, Bangor (PhD with E. D. Hughes 1947; Honorary Fellow 2000) Colin Eaborn was at the University of Leicester until 1962, when he moved to the University of Sussex as the founding Professor of Chemistry (Pro-Vice-Chancellor 1964–1973; Professor Emeritus 1988, Honorary DSc 1988). He was Honorary Secretary of the Chemical Society from 1968–1973. Honours include FRS (1970), Kipping Award for Organosilicon Chemistry of the American Chemical Society (1964), the Ingold Medal, Organometallic Award, and Main Group Award of the RSC.



Colin Eaborn

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NaN$_3$ the relative reactivities at 60 °C for the substitution of TsiSiMe$_2$X with X = ONO$_2$, I, Br and Cl are *ca.* 830 : 45 : 10 : 1.0. Towards KSCN in MeCN, in which exclusive substitution occurs, the corresponding values are approximately 3300 : 18 : 8 : 1.0. In the reactions of the bromide TsiSiMe$_2$Br in MeOH at 60 °C the relative reactivities of CsF, NaN$_3$ and KSCN are *ca.* 2.8 : 3.7 : 1. The iodide TsiSiMe$_2$I reacts with KSCN *ca.* 16 times as readily in MeCN as in MeOH, the difference being attributable to the weaker solvation of the SCN$^-$ in the former.

That elimination occurs almost exclusively in the reactions of the halides with NaOMe in MeOH but substitution greatly predominates for those with the other salts is tentatively attributed to the large bulk of the solvated methoxide ion, which inhibits attack at the functional centre.

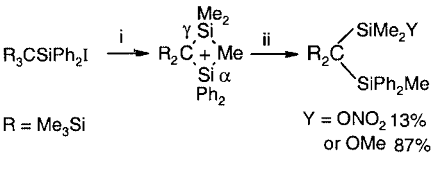
As implied above, the presence of even one H atom at the functional silicon centre greatly increases the reactivity towards nucleophilic attack. Thus TsiSiMeHI undergoes methanolysis rapidly at room temperature and TsiSiPhHI does so less readily.[6] Likewise, TsiSiBuHF reacts with PhLi to give TsiSiBuHPh, TsiSiH$_2$F with aryllithium compounds ArLi to give TsiSiH$_2$Ar, and TsiSiH$_3$ with BuLi to give TsiSiBu$_2$H.[7]

It is noteworthy that towards alkali metal salts TsiSiMe$_2$I is some 3–8 times more reactive than Bu$^{\mathrm{t}}_3$SiI.[8] (Remarkably the iodide Bu$^{\mathrm{t}}_3$SiI is some 5–7 times less reactive than the chloride Bu$^{\mathrm{t}}_3$SiCl, presumably because of the much greater crowding in a five-coordinate transition state for the iodide.) Towards KSCN in refluxing MeCN the diphenyl compound TsiSiPh$_2$I is at least 300 times less reactive than TsiSiMe$_2$I, and probably contains the most sterically hindered functional silicon centre so far observed.[9]

Reactions *via* bridged cations

Bridging by Me groups

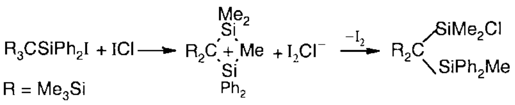
In the hope that blocking of nucleophilic attack at silicon might permit detection of the long-sought three-coordinate silylium ions ≡Si$^+$ as reaction intermediates we examined the reaction of the iodide TsiSiMe$_2$I with the electrophilic reagent AgNO$_3$ in MeOH. This gave mainly TsiSiMe$_2$OMe along with TsiSiMe$_2$ONO$_2$, consistent with reaction *via* a cation, but that this type of reaction was not a straightforward substitution became evident when the products from TsiSiPh$_2$I were found to be the rearranged species (Me$_3$Si)$_2$(Ph$_2$MeSi)CSiMe$_2$Y with Y = OMe or ONO$_2$ (Scheme 2).[10] (For organosilicon chemists the generation of organosilicon nitrates and similar salts in MeOH was an unexpected novelty.) Likewise treatment of TsiSiPh$_2$I with AgO$_2$CMe or Hg(O$_2$CMe)$_2$ in MeCO$_2$H gave exclusively (Me$_3$Si)$_2$(Ph$_2$MeSi)CSiMe$_2$OCOMe, and that with silver salts AgY in aprotic media also gave exclusively rearranged products (Me$_3$Si)$_2$(Ph$_2$MeSi)CSiMe$_2$Y, *e.g.* Y = OClO$_3$.[11] We suggested that the initial reaction of the iodide TsiSiPh$_2$I with the silver salt involves formation of an Me-bridged cation, which is then attacked by a nucleophile at the less sterically hindered γ-Si atom with ring opening, to give rearranged (Me$_3$Si)$_2$(Ph$_2$MeSi)CSiMe$_2$Y (Scheme 2).[10]



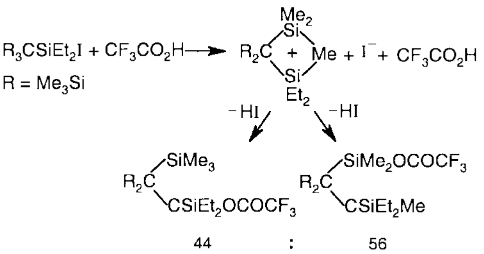
Scheme 2 Reagents: i, AgNO$_3$ −AgI; ii, NO$_3^-$ or MeOH.

Correspondingly, the rearranged chloride (Me$_3$Si)$_2$(Ph$_2$MeSi)CSiMe$_2$Cl was formed exclusively when TsiSiPh$_2$I was treated with ICl, the ionization in this case involving generation of I$_2$Cl$^-$, which then delivers Cl$^-$ to the γ-site (Scheme 3).[12]

The iodide TsiSiEt$_2$I also reacted with the strongly electrophilic solvent CF$_3$CO$_2$H to give an approximately 56 : 44 mixture of rearranged and unrearranged trifluoroacetates, showing that ionization to give the bridged ion also occurs under these conditions (Scheme 4).[10]

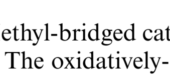


Scheme 3 Reaction of TsiSiPh$_2$I with ICl.



Scheme 4 Solvolysis of TsiSiEt$_2$I in CF$_3$CO$_2$H.

In general, these reactions of the iodides TsiSiRR′I with electrophilic reagents appear to involve initial formation of a methyl-bridged cation **I**, which can then be attacked at either the α- or γ-Si centre. When R and R′ are organic groups such as alkyl, aryl or vinyl, the proportion of reaction at these two positions seems usually to be determined mainly by the relative degrees of steric hindrance there. For example, in reaction with AgO$_2$CMe in MeCO$_2$H the iodide TsiSiPhMeI gave a 78 : 22 mixture of rearranged and unrearranged acetate, and TsiSiEt$_2$I gave approximately equal amounts of rearranged and unrearranged acetate.[10] However, when R and or R′ are H or halogen atoms or groups such as OMe, electronic effects seem to predominate. Thus, reactions of the iodide TsiSiMeFI (like those of the chloride TsiSiMeClI) with silver salts or ICl gave exclusively rearranged products (Me$_3$Si)$_2$(FMe$_2$Si)CSiMe$_2$X even though the F atom is smaller than Me.[13] In contrast, similar reactions of TsiSi(OMe)$_2$I and TsiSiMe(OMe)I unexpectedly gave only unrearranged products.[14] Again, in the reaction of TsiSiMeHI with AgBF$_4$ in CH$_2$Cl$_2$, the presence of the H on the functional silicon centre was expected to favour attack of the nucleophile at that centre but in fact the predominant products were the rearranged (Me$_3$Si)$_2$(HMe$_2$Si)CSiMe$_2$F and (Me$_3$Si)$_2$C(SiMe$_2$F)$_2$ formed from it, although in Et$_2$O only unrearranged TsiSiMeHF was formed.[13] There are not sufficient data to allow speculation about the way in which electronic effects of R and R′ influence the proportion of attack at the α-site of cation **I**.



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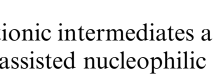

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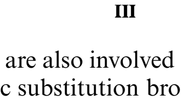


III

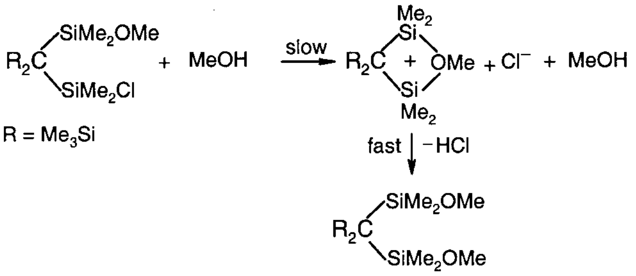
Methyl-bridged cationic intermediates are also involved in:

a) The oxidatively-assisted nucleophilic substitution brought about by *m*-chloroperoxybenzoic acid (containing some water) in MeOH.[15] Thus TsiSiMe$_2$I and TsiSiPh$_2$I give TsiSiMe$_2$OH and (Me$_3$Si)$_2$(Ph$_2$MeSi)CSiMe$_2$OH, respectively. (For the corresponding reactions of alkyl iodides see ref. 16.)

b) The UV-catalysed methanolysis of TsiSiPh$_2$I,[17] as described later.

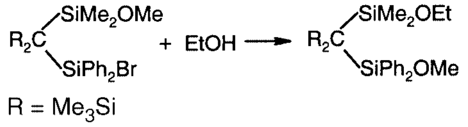
Bridging by other groups: migration and anchimeric assistance

From the early days of the programme we tentatively assumed that in reactions of the iodides with silver salts or of the hydrides with ICl the migration of the Me group to form the bridged cation of type **I** was synchronous with the electrophilically-assisted separation of the iodide ion and thus provided anchimeric assistance.[10] There was soon no doubt that anchimeric assistance was provided, and much more strongly, by other groups.[18] The most striking examples are that the chloride $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Cl$ undergoes methanolysis at least 10^6 times as readily as $TsiSiMe_2Cl$ (Scheme 5)[19] and $(Me_3Si)_2(MeOMe_2Si)CSiPh_2Cl$ > 10^8 times as readily as $TsiSiPh_2Cl$.[20]



Scheme 5 Methanolysis of $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Cl$.

The chloride $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Cl$ also reacts readily with silver salts AgY in inert solvents to give the expected $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Y$ species under conditions in which $TsiSiMe_2Cl$ is inert, and even the hydride $(Me_3Si)_2(MeOMe_2Si)CSiMe_2H$ undergoes such reactions.[21] Migration of the OMe group was observed when (i) treatment of $(Me_3Si)_2(MeOMe_2Si)CSiPh_2Br$ with $AgBF_4$ in Et_2O gave a 4 : 1 mixture of the rearranged $(Me_3Si)_2C(MeOPh_2Si)CSiMe_2F$ and unrearranged $(Me_3Si)_2(MeOMe_2Si)CSiPh_2F$,[22] and (ii) ethanolysis of $(Me_3Si)_2(MeOMe_2Si)CSiPh_2Br$ gave exclusively the rearranged product $(Me_3Si)_2(EtOMe_2Si)CSiPh_2OMe$ (Scheme 6).[20]

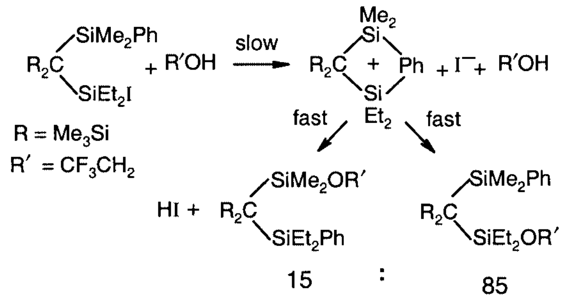


Scheme 6 Migration of an OMe group.

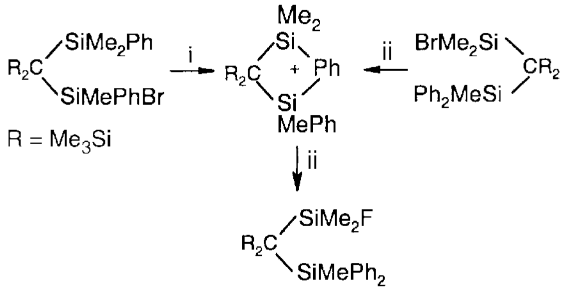
In the anchimerically-assisted solvolysis of the compounds $(Me_3Si)_2(MeOMe_2Si)CSiMe_2X$ in MeOH or MeOH–dioxane mixtures (*cf.* Scheme 5) the order of reactivity is $X = Br > NO_3 > O_3SC_6H_4Me\text{-}p > Cl, SCN > O_2CCF_3 > NCS > O_2CPh, O_2CMe \gg F, N_3, H$.[23a] Autocatalysis by the formed HX was observed for X = Br, O_2CPh and O_2CMe, and catalysis by added HBr in several cases, and this was particularly effective for $X = N_3$. As expected, since only one OMe group can bridge, there are only relatively small rate increases, involving successive factors of 9 and 18, on going from $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ to $(Me_3Si)(MeOMe_2Si)_2CSiMe_2Cl$ and $(MeOMe_2Si)_3CSiMe_2Cl$.[23b] A diagnostic feature of unimolecular, anchimerically-assisted, solvolyses is that they are faster in the more acidic CF_3CH_2OH (which provides more electrophilic assistance to the leaving of X) than in MeOH.

Migration of a γ-Ph group was observed in the reaction of $(Me_3Si)_2(PhMe_2Si)CSiEt_2I$ with $AgBF_4$ in Et_2O to give the rearranged and unrearranged fluorides $(Me_3Si)_2(PhEt_2Si)CSiMe_2F$ and $(Me_3Si)_2(PhMe_2Si)CSiEt_2F$ in *ca.* 60 : 40 ratio,[24] and in the solvolysis in CF_3CH_2OH to give the corresponding trifluoroethoxides in 85 : 15 ratio (Scheme 7).[25] Reaction of either $(Me_3Si)_2(PhMe_2Si)CSiMePhBr$ or $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Br$ with $AgBF_4$ in CH_2Cl_2 or Et_2O (which usually tends to disfavour rearrangement) gave >95% of $(Me_3Si)_2(Ph_2MeSi)CSiMe_2F$ (Scheme 8).[26]

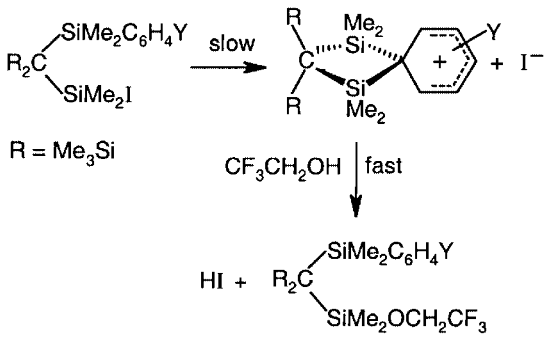
That Ph and other aryl groups also provide substantial anchimeric assistance to the ionization was very effectively confirmed by the very large effects of the substituents Y in solvolysis of the iodides $(Me_3Si)_2(YC_6H_4Me_2Si)CSiMe_2I$ in $(CF_3)_2CHOH$ and in CF_3CH_2OH (Scheme 9), which leaves no doubt that the aryl groups are participating directly in the rate-determining step. Thus in $(CF_3)_2CHOH$ the compound with Y = *p*-OMe is 2×10^5 times as reactive as that with Y = *m*-CF_3 (Table 1).[27] Values of log *k*, where *k* is the observed rate constant, against σ-constants are impressively linear in both cases, with unusually high ρ-values of −7.6 and −6.6, respectively. (An explanation is offered in ref. 27 of why the correlation does not require use of σ^+-constants, as was expected since the bridged cation closely resembles a Wheland intermediate in classical electrophilic aromatic substitutions.) The data for the reactions in MeOH and H_2O–dioxane, also shown in Table 1, are considered later.



Scheme 7 Trifluoroethanolysis of $(Me_3Si)_2(PhMe_2Si)CSiEt_2I$.



Scheme 8 Reagents: i, $AgBF_4$, −AgBr; ii, BF_4^-, $-BF_3$.



Scheme 9 Solvolysis of $(Me_3Si)_2(PhMe_2Si)CSiMe_2I$ in CF_3CH_2OH.

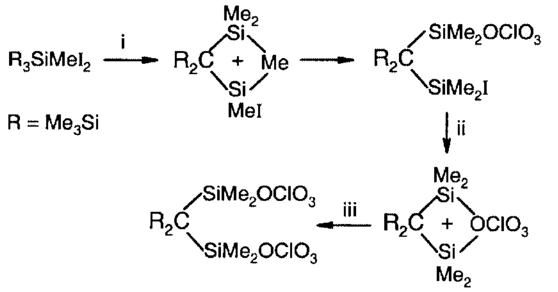
Studies of the assistance by a vinyl group were revealing.[28,29] The iodide $(Me_3Si)_2(CH_2{=}CHMe_2Si)CSiEt_2I$ was found to be very similar in reactivity to $TsiSiEt_2I$ towards salts in MeOH or MeCN or towards MeOH alone, but towards CF_3CH_2OH, which promotes ionization, the former iodide is *ca.* 500 times the more reactive, and *ca.* 1500 times towards the even more electrophilic CF_3CO_2H. Towards silver salts in Et_2O or CH_2Cl_2 the vinyl-containing iodide is some 200–400 times the more reactive, and a significant feature is that the ratio of rearranged to unrearranged product is *ca.* 2 : 1 for the vinyl-containing iodide compared with 1 : 1 for $TsiSiEt_2I$, consistent with the much stronger bridging by $CH_2{=}CH$ than by Me, which allows attack at the γ-Si to compete more effectively with that at the α-Si in the intermediate cation.

Table 1 First order rate constants $k/10^{-8}$ s^{-1} for reactions of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)SiMe_2I$ with alcohols or water

Y	$k((CF_3)_2CHOH)$[a]	$k(CF_3CH_2OH)$[a]	k(MeOH)[b]	$k(H_2O)$[b,c]
p-OMe	3.05×10^3	1.40×10^3	13200	8050
p-Me	6.3×10^2	1.65×10^2	1550	2300
H	2.02×10	1.75×10	510	2120
p-Cl	3.7×10^{-1}	8.5×10^{-1}	340	2870
m-CF_3	1.60×10^{-2}	2.15×10^{-2}	300	3050

[a] At 35 °C. [b] At 61 °C. [c] 5 vol% in dioxane.

That F, $OClO_3$, OSO_2CF_3 and $OSO_2C_6H_4Me$-*p* can also bridge and supply anchimeric assistance was first shown by the observation that treatment of $TsiSiMeI_2$ with one molar proportion of $AgBF_4$ or the relevant AgX gave solely the compounds $(Me_3Si)_2C(SiMe_2F)_2$ or $(Me_3Si)_2C(SiMe_2X)_2$ along with unchanged $TsiSiMeI_2$.[19] Evidently, after initial formation of rearranged $(Me_3Si)_2(XMe_2Si)CSiMe_2I$ anchimeric assistance by X results in rapid replacement of the remaining iodine atom (Scheme 10).



Scheme 10 Reagents: i and ii, $AgClO_4$, −AgI, $-ClO_4^-$; iii, ClO_4^-.

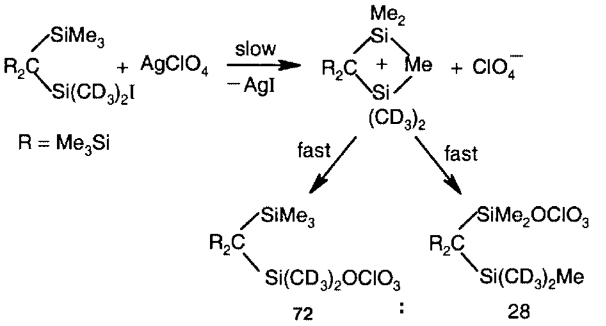
Some γ-Z groups that have been observed to undergo migration and/or to provide anchimeric assistance, in the approximate order shown, in one or more of the types of reaction known to involve intermediate cations are: OCOMe[18,30] > OMe[20–23] > $OCOCF_3$[18] > MeS[31] > PhS, PhO[31] > $OClO_3$,[19] OSO_2CF_3,[19] N_3[32,33] > F[19] > Cl[32–34] > NCS[33] > Ph[24–27] > CH=CH_2[28] > Me. (The assistance by the acetoxy group probably involves bridging *via* the carbonyl group in a six-membered ring, as in **II**.[30]) In addition, as we have seen, the anchimeric assistance by aryl groups YC_6H_4 varies over a wide range, in solvolysis of the iodides $(Me_3Si)_2(YC_6H_4Me_2Si)CSiMe_2I$ in $(CF_3)_2CHOH$.[27] The strongest assistance is provided by an NMe_2 group, but the reactivity of even the chloride $(Me_3Si)_2(Me_2NMe_2Si)CSiMe_2Cl$ is so great that quantitative assessment has not yet been possible.[35] Hydrogen has been shown to bridge (see the section on crystallographic evidence) and can be expected to provide anchimeric assistance, but there is no conclusive evidence that it does so.[33]

MNDO calculations by A. J. Kos of the decrease in energy on going from the model acyclic ion $H_2C(SiH_2Z)(SiH_2^+)$ to the corresponding Z-bridged ion gave the following values: (Z =) OH, 263; F, 237; Cl, 139; Me, −3 kJ mol^{-1}.[19] (For some *ab initio* calculations see ref. 36.)

It is remarkable that the weak internal 'solvation' by coordination by a γ-Me group to the forming positively-charged silicon centre prevails over solvation of the unbridged cation by the solvent in reactions in MeOH. Presumably it is because the external solvation is sterically inhibited.

Is the bridged cation ever free?

In accounting for the proportion of rearranged products in reactions of a range of iodides of the type TsiSiRR′I we had assumed that in the case of $TsiSiMe_2I$ there would be essentially equal amounts of rearranged and unrearranged products from the symmetrical Me-bridged cation **III**, only to find that in reactions of the deuterium-labelled iodide $(Me_3Si)_3CSi(CD_3)_2I$ this was far from the case.[37,38] Thus, in reactions of the labelled iodide with AgY in aprotic solvents (see, for example, Scheme 11) the percentage P_R of rearranged product $(Me_3Si)_2C\{Si(CD_3)_2Me\}SiMe_2Y$ was usually found to be significantly below the expected value of 50, in some cases <10, and to vary markedly with the solvent. This was tentatively attributed to rapid preferential attack at the α-site of the cation **III** by the anion Y^- liberated near that site from an ion pair $[Ag^+ \cdots Y^-]$ upon formation of AgI.



Scheme 11 Reaction of $(Me_3Si)_3CSi(CD_3)_2I$ with $AgClO_4$ in CH_2Cl_2.

Subsequently, reactions of the labelled iodide with ICl were found to give chlorides with P_R values between 15 and 42 depending on the solvent, and this was correspondingly attributed to rapid transfer of Cl^- from I_2Cl^- formed near the α-site.[38] Thus it is clear that in these reactions the bridged cation is never fully free before it is captured. It should be noted, however, that it does not take much additional steric hindrance at the α-site to overcome the preference for attack at that site; thus TsiSiPhMeI with $Hg(O_2CCH_3)_2$ in $MeCO_2H$ gives the rearranged and unrearranged acetates in *ca.* 78 : 22 ratio, and $TsiSiEt_2I$ under similar conditions gives the isomeric acetates in *ca.* 50 : 50 ratio.[10] (However, the latter iodide with ICl in CCl_4 gives the rearranged and unrearranged chlorides in only 35 : 65 ratio.[11]) The reaction of $TsiSi(CH=CH_2)_2Cl$ with AgO_2CCF_3 in CF_3CO_2H likewise gives the rearranged and unrearranged trifluoroacetates in *ca.* 50 : 50 ratio.[39]

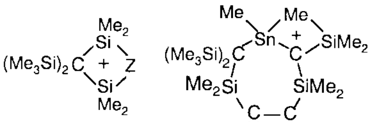
When we turned to reactions of the labelled iodide in alcohols we encountered further surprises. We had expected that in reactions with silver salts AgY in alcohols ROH, the alkoxide products would have P_R values in the region of 50 since the ROH molecules should be equally available at the α- and γ-sites, but in fact for R = Me apparent values of between *ca.* 29 ± 8 and 38 ± 8 were observed, depending on R and Y.[40] The large uncertainty in the values implies that we cannot be certain that there is any real variation between them, but it does seem that the expectation of P_R values of 50% is not realized and that even under these conditions the cation is never fully free. Mean P_R values were apparently somewhat higher for reactions in EtOH, Pr^iOH or Bu^tOH but still significantly below 50. We tentatively suggest that attack at the α-site may be an ROH molecule preassociated with the I atom of $TsiSiMe_2I$ or one associated with the separating Y^- before the cation is fully formed.

As expected, the proportion of $TsiSiMe_2Y$ (irrespective of the position of the labelled groups) in the $TsiSiMe_2Y$–$TsiSiMe_2OR$ mixture formed from various silver salts increased markedly as the bulk of the alcohol was increased and so its ability to compete with Y^- lowered. Thus, in the extreme case, the reaction with $AgBF_4$ gave 11% of fluoride product in MeOH, 52% in EtOH, 81% in $Pr^{i}OH$, and 83% in $Bu^{t}OH$. The highest P_R value observed for the $TsiSiMe_2Y$ products was 17, and most were well below that. (Readers consulting the relevant paper[40] should note that in the footnote to Table 1 it was wrongly stated that Otf denoted O_2CCF_3 and Otfa denoted O_3SCF_3, whereas the reverse was the case.)

Another way in which to find out whether the intermediate bridged-cation is fully formed and separated before attack by the incoming nucleophile is to generate the ion from both directions to see whether the ratio of isomeric products is the same in both cases. This was initially done with the iodides $(Me_3Si)_2(ClMe_2Si)CSiEt_2I$ and $(Me_3Si)_2(ClEt_2Si)CSiMe_2I$.[32] In the reaction with $AgBF_4$ in CH_2Cl_2 the first iodide gave $(Me_3Si)_2(ClEt_2Si)CSiMe_2F$ and $(Me_3Si)_2(FEt_2Si)CSiMe_2Cl$ in *ca.* 2 : 1 ratio and the second in *ca.* 3 : 1 ratio, and although these ratios are only approximate it does seem that even when there is powerful bridging by Cl there is some bias towards attack at the α-site, and thus that the intermediate cation may not be fully free before capture. However, a similar study involving the good bridging group Ph revealed no such bias. Thus, as mentioned previously, when the isomeric bromides and $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Br$ and $(Me_3Si)_2(PhMe_2Si)CSiMePhBr$ were treated with $AgBF_4$ in either CH_2Cl_2 or Et_2O both gave >95% of the fluoride $(Me_3Si)_2(Ph_2MeSi)CSiMe_2F$ (Scheme 8).[26]

Crystallographic evidence for the existence of bridged cations

Although results of MNDO[19] and *ab initio* calculations[36] were consistent with the existence of the bridged cations suggested by the mechanistic studies there was no direct experimental evidence for them. Very recently, however, Lickiss and his coworkers have determined the crystal structures of the tetra(pentafluorophenyl)borate salts of the phenyl- and hydride-bridged cations **IVA** and **IVB**.[41]



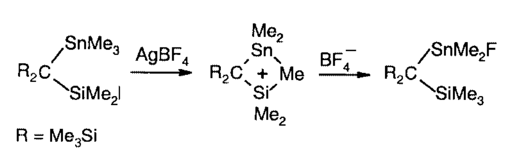
IVA Z = Ph
IVB Z = H

V

Migration of a Me group to silicon from germanium and to or from tin

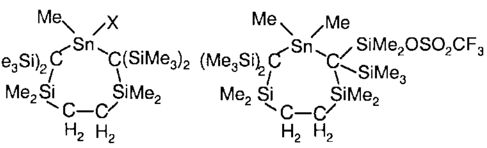
Migration of a methyl group from Ge to Si was observed in the reaction of the silicon bromide $(Me_3Si)_2(Me_3Ge)CSiMe_2Br$ with silver salts AgY.[42] With AgO_2CCF_3 in CF_3CO_2H the ratio of rearranged product $(Me_3Si)_3CGeMe_2OCOCF_3$ to unrearranged $(Me_3Si)_2(Me_3Ge)CSiMe_2OCOCF_3$ was 65 : 35, with $AgBF_4$ in CH_2Cl_2 the ratio of rearranged to unrearranged species was 30 : 70, and with AgO_3SCF_3 the rearranged $(Me_3Si)_3CGeMe_2OSO_2CF_3$ was the sole product. The $(Me_3Si)_2(Me_3Ge)CSiMe_2Br$ is much more reactive than $TsiSiMe_2Br$ under these conditions, indicating that an Me group attached to germanium is much more effective than one attached to Si in providing anchimeric assistance.

Similar migration from tin was observed when $(Me_3Si)_2(Me_3Sn)CSiMe_2I$ was treated with silver salts, the products being wholly the rearranged $(Me_3Si)_3CSnMe_2Y$ (Scheme 12).[43] The predominance of rearranged product in most cases is consistent with attack of the nucleophile at the larger, and thus less hindered, metal centre in the intermediate, *i.e.* Ge or Sn.



Scheme 12 Migration of Me from tin to silicon.

More recently, Me migration in the opposite direction, from silicon to tin, has been observed.[44] When the highly crowded organotin iodide **1a**, which in effect has two trisyl groups on tin, was treated with AgO_2CCF_3 or $AgBF_4$ the product isolated was that of direct replacement of I^- by $CF_3CO_2^-$, *i.e.* compound **1b** or **1c**. However, when AgO_3SCF_3 was used, the product, obtained in 68% yield after recrystallisation, was the rearranged silicon triflate **2**. There is evidence that the initial product is the tin triflate **1d**, which then ionizes, probably with anchimeric assistance by an Me group on silicon, to give the bridged cation **V** and triflate anion. The tin atom in **V** is extremely crowded, and so, sometimes at least, there is irreversible attachment of the triflate ion to the silicon atom of the bridge.

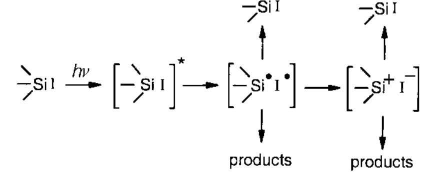


1a X = I
1b X = O_2CCF_3
1c X = F
1d X = OSO_2CF_3

2

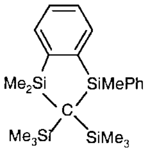
Reactions catalysed by UV radiation

Ultra-violet irradiation of $TsiSiPh_2I$ in inert solvents gives products derived from the initial free radical $TsiSiPh_2^{\bullet}$ (see below) but in MeOH the unrearranged methoxide $TsiSiPh_2OMe$ and rearranged $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OMe$ are formed in 1 : 2 ratio.[17] Some of the rearranged nitrate $(Me_3Si)_2(Ph_2MeSi)CSiMe_2ONO_2$ was also formed when the reaction was carried out in the presence of $LiNO_3$. Irradiation of the iodide in aniline gave very predominantly the rearranged anilide $(Me_3Si)_2(Ph_2MeSi)CSiMe_2NHPh$. Furthermore, irradiation of $TsiSi(CD_3)_2I$ in MeOH gave the rearranged and unrearranged methoxides in 40 : 60 ratio. It seems that initial generation of a radical pair $[\equiv Si^{\bullet}I^{\bullet}]$ can be followed by electron transfer to give an ion pair $[\equiv Si^+ I^-]$ (Scheme 13). This behaviour is very similar to that observed by Kropp and his colleagues for irradiation of alkyl iodides in similar media.[45]

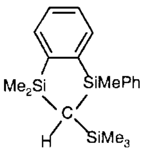


Scheme 13 Course of photoylsis of compounds $TsiSiR_2I$.

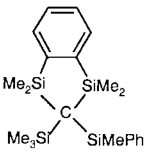
Irradiation of $TsiSiPh_2I$ in hexane or diethyl ether initially gave mainly the rearranged iodide $(Me_3Si)_2(Ph_2MeSi)CSiMe_2I$ along with some unidentified products;[17] it is likely that the methyl migration occurs in the initial radical rather than in an ion since such migrations occur also during the thermolysis of the iodide (see below).[46] The rearranged iodide was also the initial product in anisole as solvent, but on prolonged irradiation the major product was the disilaindane derivative **VI**, which was one of the products formed in a free radical process in the thermolyis of $TsiSiPh_2I$.[46] Formation of the rearranged bromide $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Br$ when the iodide $(Me_3Si)_3CSiPh_2I$ is subjected to UV irradiation in 1-bromohexane[9] may also involve migration of a methyl group within an ion pair formed *via* an initial radical pair, but migration within the free radical cannot be ruled out.



VI



VII



VIII

The observed formation of the unrearranged chloride $TsiSiPh_2Cl$ (along with I_2) when the irradiation of the iodide was carried out in CCl_4 is what would be expected for generation of the free radical $TsiSiPh_2^{\bullet}$. (Similar irradiation of Bu^t_3SiI gave Bu^t_3SiCl along with some Cl_3CCCl_3.[9]) The reaction of $TsiSiMe_2I$ with methanol to give the methoxide $TsiSiMe_2OMe$ is also catalysed by UV light, but the reaction is much slower than that of the diphenyl analogue. (The methanolysis of Bu^t_3SiI is similarly catalysed.) Photocatalysed methanolysis of the azide $TsiSiMe_2N_3$ occurs more readily.[9]

Migration of Me and Ph groups within silenes and silyl radicals

An important observation was that thermolysis of the fluoride $TsiSiPh_2F$ generates the silene $(Me_3Si)_2C{=}SiPh_2$ within which Me and Ph groups rapidly migrate to give mixtures of this species with its isomers $(Me_3Si)(Ph_2MeSi)C{=}SiMe_2$, and $(Me_3Si)(PhMe_2Si)C{=}SiPhMe$. In the absence of trapping agents these cyclise to give the disilaindane derivative **VII** and its isomers.[47] Such rapid isomerization of silenes was later found to be a general phenomenon, and in particular was shown by Wiberg and his colleagues to occur with silenes generated under much milder conditions, and even to take place rapidly on the NMR time scale in solutions of compounds of the type $(Me_3Si)_2(XSiMe_2)CLi$ by transient separation of LiX within a solvent cage[48] (see also ref. 49). The ready elimination of Me_3SiX from various compounds containing a $(Me_3Si)_3C$–MX linkage was subsequently used by others to generate, for example, the first stable phospha-, arsa- and bora-alkenes as mentioned in our earlier review.[1]

The ready migration of Me and Ph groups observed for the silene $(Me_3Si)_2C{=}SiPh_2$ and for an Me group in the silylium ion $(Me_3Si)_3CSiPh_2^+$ also appears to take place in the corresponding silyl radicals $(Me_3Si)_3CSiPh_2^{\bullet}$ generated by thermolysis of $(Me_3Si)_3CSiPh_2I$.[46] The main products include the disilaindanes **VI** and **VIII** and species derived from them. It seems that 1,3-migrations of Me and Ph groups take place within the initially formed radical $(Me_3Si)_3CSiPh_2^{\bullet}$ to give the rearranged radicals $(Me_3Si)_2(Ph_2MeSi)CSiMe_2^{\bullet}$ and $(Me_3Si)_2(PhMe_2Si)CSiMePh^{\bullet}$ and then cyclisations occur by intermolecular free radical aromatic substitutions to give **VI** and **VIII**, respectively. Corresponding reactions occur with $(Me_3Si)_3CSiPhMeI$. Formation of the rearranged bromide $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Br$ when the iodide $(Me_3Si)_3CSiPh_2I$ is subjected to UV irradiation in 1-bromohexane may also involve migration of a methyl group within a free radical.[9]

Methanolysis of $TsiSiMe_2X$ with X = I, OSO_2CF_3, OCN or $OClO_3$. A mechanistic enigma

An intriguing mechanistic problem is presented by the methanolysis of the compounds $TsiSiMe_2X$, where X is one of the very good leaving groups I,[6,50] OSO_2CF_3,[51] OCN,[51] or $OClO_3$,[6,50,51] and also that of TsiSiRHI where R = Ph,[6] Me[6] or F.[51] The most striking feature of the reactions is that they are only very slightly accelerated by the presence of NaOMe, and this initially led us to suggest, by analogy with the classical observations on alkyl halides, that the reactions must be unimolecular and so involve rate-determining ionization.[6,50] This suggestion had to be withdrawn, however, when $TsiSiEt_2I$ was found to give exclusively the unrearranged methoxide $TsiSiEt_2OMe$, indicating that a cation was not, in fact, involved,[52] and later it was shown that there is no rearrangement during methanolysis or hydrolysis of $TsSi(CD_3)_2I$,[53a] $TsiSiEt_2I$ or $TsiSiPh_2I$.[52] (Rearrangement does occur when a solution of $TsSi(CD_3)_2I$ is irradiated with UV light,[53b] as discussed later.) Furthermore, the rates of methanolysis of the iodides $TsiSi(C_6H_4Y)HI$ are increased by electron withdrawal by Y, as expected for rate-determining nucleophilic attack but not for ionization.[54]

Another remarkable feature of the methanolysis of the highly reactive species $TsiSiMe_2X$ with X = OSO_2CF_3, OCN, or $OClO_3$ is that although addition of 1% of water increases the rate by only about 5–6 times, depending on X, the product is wholly the hydroxide (for X = OCN the hydroxide is exclusively formed even with only 0.07% of water present, indicating that, molecule for molecule, the selectivity towards water involves a factor of >5000).[51] For want of a better explanation we tentatively suggest that there is preferential preassociation of one or more water molecules at the reaction site of the substrate. This still leaves the question of why the solvolysis in MeOH or $MeOH/H_2O$ is not significantly accelerated by the presence of methoxide or hydroxide ions, especially since the compounds $TsiSiMe_2X$ with X = Cl, Br, I, or ONO_2 do react with the ions N_3^-, F^- and SCN^- in MeOH,[5] and we suggest that the bulk of the solvated MeO^- and HO^- ions inhibits reaction at the highly sterically-hindered centres.

We noted above that in the methanolysis of the compounds TsiSiPhHX the reaction of the iodide is not accelerated by base whereas those of the compounds with X = ONO_2, Br, Cl, F, *etc.* are.[6,55] In neutral MeOH at 35 °C the fluoride is unreactive and the relative rates of reaction of the chloride, nitrate, bromide and iodide are *ca.* 1 : 5 : 90 : 1200, but even with as little as 0.02 mol dm^{-3} NaOMe present the fluoride is substantially more reactive than the other halides![55] It seems likely that formation of a five-coordinate intermediate is rate-determining, the intermediate being more readily formed from the fluoride because of the smaller size and higher electronegativity of the F atom.

Concurrent mechanisms of solvolysis

Fortuitously, the data obtained for solvolysis of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)SiMe_2I$ in $(CF_3)_2CHOH$, CF_3CH_2OH, MeOH and 5 vol% H_2O in dioxane (Table 1) reveal that the ionization mechanism involving intermediate formation of a bridged cation, which for convenience we denote as S_N1, and the mechanism involving direct nucleophilic attack by the solvent, which we denote as S_N2, can operate alongside one another.[27] The rate constants in the fluorinated alcohols, which promote ionization, decrease in a normal pattern from the *p*-OMe to the *m*-CF_3 compound, with plots of log k against Hammett σ-constants being linear in both cases. For the reactions with MeOH, after an initial sharp fall on going from Y = *p*-OMe to *p*-Me to H there is much smaller fall to Y = *p*-Cl and *m*-CF_3, and for the reaction with water the rate falls from Y = *p*-OMe to *p*-Me, then only slightly to Y = H and then rises to *p*-Cl and *m*-CF_3. The data for the reactions with MeOH and water can be nicely interpreted in terms of concurrent operation of the S_N2 and S_N1 processes, and a breakdown of the overall rate constants into the two components, based on plausible assumptions, is shown in Table 2. It will be seen for the parent compound with Y = H, the S_N2 process makes a substantial contribution even in MeOH and is the greatly dominant process in H_2O–dioxane. For Y = *m*-CF_3 the reaction with

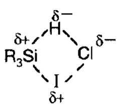
Table 2 Approximate breakdown of the observed rate constants $k/10^{-8}$ s^{-1} into S_N2 and S_N1 components for reactions of the iodides $(Me_3Si)_2C(SiMe_2C_6H_4Y)SiMe_2I$ with MeOH or H_2O (5 vol% in dioxane) at 61 °C

	MeOH		H_2O	
Y	$k(S_N2)$	$k(S_N1)$	$k(S_N2)$	$k(S_N1)$
p-OMe	122	13080	1600	6450
p-Me	134	1416	1750	550
H	145	365	2120	180
p-Cl	218	122	2790	80
m-CF_3	280	20	3035	15

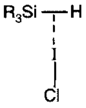
MeOH is almost wholly of the S_N2 type, and for the reactions of the *p*-Cl and *m*-CF_3 compounds in H_2O–dioxane the contribution of the S_N1 process is negligible. The relatively small spread of rates in the S_N2 reactions with MeOH and H_2O is consistent with that in the reactions of the iodides with KSCN in MeCN–CCl_4 at 35 °C, for which the relative rates are (Y =) *p*-OMe, 1.0; *p*-Me, 1.1; H, 1.2; *p*-Cl, 1.7; *m*-CF_3, 2.3.

Reactions of TsiSiRR′X (X = H or I) with halogens or interhalogens

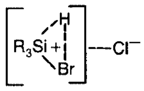
Our observation that treatment of $TsiSiMe_2H$ with a 1 molar proportion of ICl in CCl_4 gave the iodide $TsiSiMe_2I$, which was converted into the chloride by a further molar proportion of ICl, suggested that the previously observed reaction of Et_3SiH with one equivalent of ICl to give the chloride also proceeds *via* initial formation of the iodide.[3] A four-centre mechanism **IX** for the formation of the iodide is unlikely because of the unfavourable bond polarities. The reaction essentially involves interaction of the electrophile with the electrons of the Si–H bond, and so attack by the positive end of the I–Cl dipole, as in **X**. This concept was formalised by Sommer for reactions with BrCl in terms of rate-determining formation of an intermediate ionic intermediate **XI**, which then rapidly breaks down by separation of HCl.[56] To provide a basis for future mechanistic discussions we provide a brief summary of our observations on the reactions of both trisyl-silicon hydrides and iodides with halogens or interhalogens.



IX



X



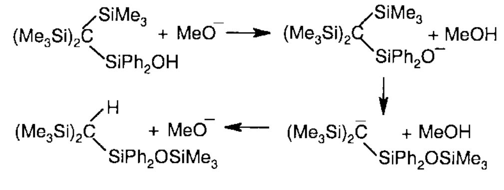
XI

As already mentioned, when $TsiSiPh_2H$ was taken along with a 1 molar proportion of ICl the unrearranged iodide $TsiSiPh_2I$ was formed, but when this was treated with a molar proportion of ICl the product was exclusively the rearranged chloride $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Cl$, and this result was interpreted in terms of Scheme 3.[12] The iodide $TsiSiPh_2I$ also reacted readily with IBr in CCl_4 to give exclusively the rearranged bromide $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Br$. When $TsiSiEt_2I$ was used with ICl the rearranged $(Me_3Si)_2(Et_2MeSi)CSiMe_2Cl$ and unrearranged $TsiSiEt_2Cl$ were formed in 35 : 65 ratio, and when TsiSiMeEtI was used the rearranged and unrearranged chlorides were formed in 25 : 75 ratio. However, the iodides $TsiSi(OMe)_2I$, TsiSi(OMe)MeI and TsiSiMe(OH)I gave the corresponding chlorides without rearrangement.[14] The labelled iodide $TsiSi(CD_3)_2I$ reacted with ICl in MeOH to give the rearranged and unrearranged methoxides, $(Me_3Si)_2[(CD_3)_2MeSi]CSiMe_2OMe$ and $TsiSiMe_2OMe$ in *ca.* 1 : 3 ratio in a combined yield of 84% and the unrearranged chloride in 16% yield.[38]

When $TsiSiMe_2H$ was treated with a 1 molar proportion of ICl in MeOH, CH_3CO_2H or CF_3CO_2H the iodide $TsiSiMe_2I$ was obtained.[53c] (The reaction was very fast in CF_3CO_2H, but in MeOH was only as fast as in CCl_4.) The hydride also reacted with Br_2 or I_2 in MeOH to give the corresponding bromide or iodide. In MeOH the iodide reacted readily with ICl to give a mixture of $TsiSiMe_2Cl$ and $TsiSiMe_2OMe$, in keeping with the view that the reaction involved the intermediate bridged cation **I** (R = R′ = Me), which is captured by either ICl_2^- or MeOH, but the reaction was much slower than that in CCl_4, in which $TsiSiMe_2Cl$ is exclusively formed. A few hydrides of the type under consideration give the chloride rather than the iodide even when treated with only a 1 molar proportion of ICl; for example, $(Me_3Si)_2(PhMe_2Si)CSiMe_2H$ gave $(Me_3Si)_2(PhMe_2Si)CSiMe_2Cl$.[57]

1,3-Migration of a silyl group from carbon to oxygen in a silanolate ion

The silanols $(Me_3Si)_3CSiMe_2OH$, $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OH$, $(PhMe_2Si)_3CSiMe_2OH$ and $(Me_3Si)_3CSiPh_2OH$ were found to undergo rearrangement in MeOH–NaOMe to give $(Me_3Si)_2CHSiMe_2OSiMe_3$, $(Me_3Si)_2CHSiMe_2OSiMePh_2$, $(PhMe_2Si)_2CSiMe_2OSiMe_2Ph$ and, $(Me_3Si)_2CHSiPh_2OSiMe_3$, respectively, by migration of a silyl group from carbon to oxygen within a silanolate ion, the first examples of such migration (Scheme 14).[58,59] The reactions are probably facilitated by (a) the release of steric strain, (b) the formation of a strong Si–O bond, and (c) stabilization of the formed carbanion by the three attached silyl groups. Remarkably the reactions of the Ph-containing silanols were complete within 2 min at room temperature in 0.1 mol dm^{-3} MeONa–MeOH whereas that of $(Me_3Si)_3CSiMe_2OH$ in 0.5 mol dm^{-3} MeONa–MeOH was only 90% complete in 6 h under reflux. This very large rate difference, observed irrespective of whether the Ph groups are in the migrating group or on the silicon atom receiving it, is puzzling, though greater relief of crowding in the Ph-containing silanols may play a part.

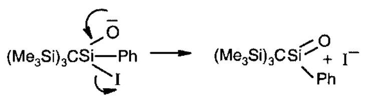


Scheme 14 Migration of a Me_3Si group within a silanolate ion.

Analogous rearrangement occurred when the silanol $(Me_3Si)_3CSiPh_2OH$ was treated with MeLi in Et_2O/THF to give $(Me_3Si)_2CLiSiPh_2OSiMe_3$, which upon treatment with Me_2HSiCl gave $(Me_3Si)_2C(SiMe_2H)(SiPh_2OSiMe_3)$.[59]

Internal nucleophilic displacements within silanolate ions. Generation of silanones and silanone radical anions

The hydroxy-iodide TsiSiPh(OH)I was the first compound to be isolated that had a halogen atom and a hydroxy group on the same silicon atom.[60] The fact that in MeOH containing NaOMe this compound is rapidly converted into TsiSiPh(OH)(OMe) whereas TsiSiPh(OMe)I is inert provided the first experimental indication of the generation of a silanone in the condensed phase. It is apparently produced by internal displacement of halogen as shown in Scheme 15.[59] Kinetic evidence

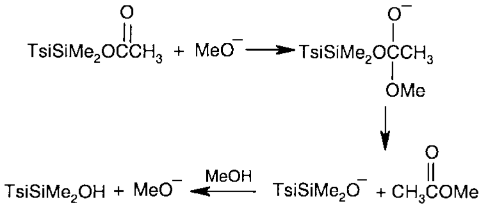


Scheme 15 Formation of a silanone.

for such a mechanism was subsequently obtained.[61] A range of hydroxysilyl radicals TsiSi(R)OH$^•$ was generated by abstraction of a hydrogen atom from the silanols TsiSiR(H)OH by Bu^{t}O$^•$ radicals, and in the presence of KOBu^t these were converted into the silanone radical anions TsiSi(R)=O$^•$, the EPR spectra of which were recorded.[62]

Reactions of carboxylates

Normally, organosilicon carboxylates ≡SiOCOR react with alcohols R′OH by nucleophilic displacement of RCO_2^- to give the alkoxide ≡SiOR′, but when such attack at silicon is sterically inhibited, as in TsiSiMe$_2$OCOR with R = Me, CF_3 or Ph, in MeOH containing NaOMe, the nucleophilic attack is at the carbonyl carbon to give the silanol TsiSiMe$_2$OH,[63] the mechanism corresponding with that of base-catalysed hydrolysis of organic esters (Scheme 16).



Scheme 16 Base-catalysed methanolysis of TsiSiMe$_2$OCOCH$_3$.

A study of the reactions of the related carboxylate VsiSiMe$_2$OCOCF$_3$, where Vsi denotes the vinyl-containing ligand (Me$_3$Si)$_2$(CH$_2$=CHMe$_2$Si)C, with nucleophiles in MeOH showed that some salts, *e.g.* CaF$_2$ and KSCN, gave solely products formed by nucleophilic attack at Si (*i.e.* VsiSiMe$_2$F and VsiSiMe$_2$NCS), that KOCN gave exclusively the silanol VsiSiMe$_2$OH, and that NaN$_3$ gave mainly the latter along with some VsiSiMe$_2$N$_3$.[64] Amines, *e.g.* MeNH$_2$ and H$_2$NNH$_2$, are very effective in promoting formation of the silanol, as is the peroxide ion HO_2^-. Except for the unexpected effectiveness of KOCN the sequence of ability of various species to facilitate the cleavage of the acyl–oxygen bond is fairly similar to that for reaction of aryl acetates in water.

The first silicon cyanates and thiocyanate

Only isocyanates, $R_xSi(NCO)_{4-x}$, were known previously. The first cyanates isolated were TsiSiMe$_2$OCN, TsiSiMe(OMe)(OCN), (Me$_3$Si)$_2$(Ph$_2$MeSi)CSiMe$_2$OCN and TsiSiMe(NCO)(OCN), obtained by reaction of TsiSiMe$_2$I, TsiSiMe(OMe)I, TsiSiPh$_2$I and TsiSiMe(NCO)I, respectively, with AgOCN in CH$_2$Cl$_2$.[65,66] Isomerization of TsiSiMe$_2$OCN to the isocyanate occurs in the molten state or in solution upon heating, and is very rapid in MeOH containing NaOMe or in MeCN containing KOCN.[67] The thermal isomerizations appear to involve rate-determining ionization to the methyl-bridged cation.[67] Determination of the crystal structure of (Me$_3$Si)$_2$(Ph$_2$MeSi)CSiMe$_2$OCN gave the first structural data for a silicon cyanate; the OCN and SiOC angles are 175(1)° and 124 ± 5°, respectively.[68]

The cyanate TsiSiMe$_2$SiOCN proved to be as reactive as the triflate TsiSiMe$_2$SiOSO$_2$CF$_3$ towards MeOH, and even more reactive than the latter when water was present.[51]

The only known silicon thiocyanate, (Me$_3$Si)$_2$(MeOMe$_2$Si)CSiMe$_2$SCN, was made by treatment of the reactive chloride (Me$_3$Si)$_2$(MeOMe$_2$Si)CSiMe$_2$Cl with AgSCN in MeCN.[69] [However, (Me$_3$Si)$_2$(CH$_2$=CHMe$_2$Si)CSiMe$_2$SCN appeared to be formed initially when (Me$_3$Si)$_2$C(SiMe$_2$CH=CH$_2$)I was treated with AgSCN to give finally (Me$_3$Si)$_2$(CH$_2$=CHMe$_2$)CSiMe$_2$NCS.[28]]

Unusual hydrogen-bonded structures

Silanols bearing trisyl-type groups have shown a range of unusual hydrogen-bonded structures.[70–77] Most notable is that of the first silanetriol stable at room temperature, TsiSi(OH)$_3$.[76,77] [The structure of *cyclo*-C$_6$H$_{11}$Si(OH)$_3$, consisting of infinite sheets, had been previously determined at −90 °C.[78] Other stable triols have been obtained more recently.[79]] This triol decomposes only at its melting point of 285–290 °C, and the crystal structure consists of discrete trigonal cages formed from six molecules maximally hydrogen-bonded. The cage, which can be regarded as a distorted sphere, has a sizeable cavity, 5.1 Å across at the narrowest point.

The structures of the compounds (PhMe$_2$Si)$_3$CSiMe$_2$OH,[76] TsiSiPh(OH)I,[77] and TsiSiPh(OMe)I[77] showed clear hydrogen bonding between OH groups and the π-electrons of the aryl groups, establishing the common occurrence of such interaction, which had been previously observed only for the diol HO(SiPh$_2$)$_7$OH.[80] In the hydrogen bonds the H atoms of the OH groups lie over peripheral π-electrons of the ring, not the centroid. (Examination in the light of these findings of reported structures of two other silanols containing aryl groups revealed the hitherto unrecognised presence of this type of bonding.[77] Other examples have since been reported.)

Concluding remarks

The study of compounds with the very bulky trisyl and related ligands on silicon has revealed new types of reaction at silicon centres. In particular they have shown that alkyl and a wide range of other groups can readily undergo intramolecular 1,3-migration from one silicon centre to another within cations, free radicals and silenes. Mechanistic studies have shown that some organosilicon iodides and related compounds can, like alkyl halides, undergo solvolysis in protic species by two distinct routes, one involving ionization in the rate-determining step and the other involving direct nucleophilic attack by the solvent, and that under appropriate conditions these two processes can occur alongside one another. A novel elimination, somewhat analogous to an E2 reaction of alkyl halides, involving generation of a silene by attack by base at a β-silicon centre has also been observed, as has the previously unknown intramolecular migration of organosilyl groups from carbon to oxygen attached to a γ-silicon centre. Ejection of I$^-$ from the silanolate ion TsiSiPh(I)O$^-$ has been shown to generate TsiPhSi=O, providing the first example of generation of a silanone in solution. Steric inhibition of nucleophilic attack at highly sterically hindered silicon centres in organosilyl acetates has allowed detailed study of the consequences of attack at the carbonyl centre, and revealed close analogies with reactions of organic carboxylates. The first silicon cyanates have been obtained, and the mechanism of their ready isomerization to isocyanates investigated. The first silicon thiocyanate has also been made.

There are still several questions left unanswered in respect of details of the new mechanisms. There is no reason to doubt that additional new species and new modes of reaction will be observed by further studies of compounds bearing trisyl-type ligands. For example, a field awaiting exploration is that of reactions at pseudohalide groups in compounds such as TsiSiMe$_2$X, X = CN, NCO, OCN, NCS, SCN, N$_3$, *etc.* in which steric inhibition of nucleophilic displacement of X can be expected to allow reactions of the kind shown by their alkyl analogues.

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References

1 C. Eaborn and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2001, 1541.

2 C. Eaborn, D. A. R. Happer, K. D. Safa and D. R. M. Walton, *J. Organomet. Chem.*, 1978, **157**, C50.

3 S. S. Dua, C. Eaborn, D. A. R. Happer, S. P. Hopper, K. D. Safa and D. R. M. Walton, *J. Organomet. Chem.*, 1980, **191**, 355.

4 C. Eaborn, D. A. R. Happer and K. D. Safa, *J. Organomet. Chem.*, 1980, **191**, 355.

5 Y. Y. El-Kaddar, C. Eaborn and P. D. Lickiss, *J. Organomet. Chem.*, 1993, **460**, 7.

6 C. Eaborn and F. M. S. Mahmoud, *J. Chem. Soc., Chem. Commun.*, 1981, 63; C. Eaborn and F. M. S. Mahmoud, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1309.

7 D. B. Azarian, C. Eaborn and P. D. Lickiss, *J. Organomet. Chem.*, 1987, **330**, 1.

8 C. Eaborn and A. K. Saxena, *J. Organomet. Chem.*, 1984, **271**, 33.

9 C. Eaborn and F. A. Fattah, *J. Organomet. Chem.*, 1990, **396**, 1.

10 C. Eaborn, D. A. R. Happer, S. P. Hopper and K. D. Safa, *J. Organomet. Chem.*, 1979, **170**, C9; C. Eaborn, D. A. R. Happer, S. P. Hopper and K. D. Safa, *J. Organomet. Chem.*, 1980, **188**, 179.

11 S. S. Dua and C. Eaborn, *J. Organomet. Chem.*, 1981, **204**, 21.

12 C. Eaborn and S. P. Hopper, *J. Organomet. Chem.*, 1980, **192**, 27.

13 C. Eaborn and D. E. Reed, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1687.

14 C. Eaborn and D. E. Reed, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1695.

15 A. I. Al-Wassil, C. Eaborn and A. K. Saxena, *J. Chem. Soc., Chem. Commun.*, 1983, 974.

16 R. I. Davidson and P. J. Kropp, *J. Org. Chem.*, 1982, **47**, 1904 and references therein.

17 C. Eaborn, K. D. Safa, A. Ritter and W. Binder, *J. Chem. Soc., Chem. Commun.*, 1981, 175; C. Eaborn, K. D. Safa, A. Ritter and W. Binder, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1397.

18 C. Eaborn and S. P. Hopper, *J. Organomet. Chem.*, 1979, **170**, C51.

19 C. Eaborn and D. E. Reed, *J. Chem. Soc., Chem. Commun.*, 1983, 495.

20 N. H. Buttrus, C. Eaborn, P. B. Hitchcock, P. D. Lickiss and S. T. Najim, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1753.

21 A. I. Al-Wassil, C. Eaborn and M. N. Romanelli, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1753.

22 N. H. Buttrus, C. Eaborn, P. B. Hitchcock, P. D. Lickiss and S. T. Najim, *J. Chem. Soc., Perkin Trans. 2*, 1987, 891.

23 (*a*) C. Eaborn and M. N. Romanelli, *J. Chem. Soc., Perkin Trans. 2*, 1987, 657; (*b*) F. I. Aigbirhio, S. S. Al-Juiad, C. Eaborn, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1407.

24 C. Eaborn, P. D. Lickiss, S. T. Najim and W. A. Stańczyk, *J. Chem. Soc., Perkin Trans. 2*, 1993, 59.

25 C. Eaborn, K. L. Jones, P. D. Lickiss and W. A. Stańczyk, *J. Chem. Soc., Perkin Trans 2*, 1993, 395.

26 C. Eaborn, A. Kowalewska and W. A. Stańczyk, *J. Organomet. Chem.*, 1998, **560**, 41.

27 C. Eaborn, K. L. Jones and P. D. Lickiss, *J. Chem. Soc., Perkin Trans. 2*, 1992, 489.

28 G. A. Ayoko and C. Eaborn, *J. Chem. Soc., Chem. Commun.*, 1986, 630.

29 G. A. Ayoko and C. Eaborn, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1047.

30 C. Eaborn, P. D. Lickiss and A. D. Taylor, *J. Organomet. Chem.*, 1988, **338**, C27; C. Eaborn, P. D. Lickiss and A. D. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1809.

31 C. Eaborn, A. Kowalewska, J. D. Smith and W. A. Stańczyk, *J. Organomet. Chem.*, in the press.

32 C. Eaborn, P. D. Lickiss, S. T. Najim and M. N. Romanelli, *J. Organomet. Chem.*, 1986, **315**, C5.

33 C. Eaborn, P. D. Lickiss, S. T. Najim and M. N. Romanelli, *J. Organomet. Chem.*, 1993, **451**, 45.

34 C. Eaborn, P. D. Lickiss and S. T. Najim, *J. Chem. Soc., Perkin Trans. 2*, 1993, 391.

35 F. I. Aigbirhio, D.Phil. Thesis, University of Sussex, UK, 1988.

36 C. Maerker, J. Kapp and P. v. R. Schleyer, in *Organosilicon Chemistry II*, ed. N. Auner and J. Weiss, VCH, Weinheim, 1996, pp. 329–359.

37 A. I. Al-Mansour, J. R. Black, C. Eaborn, P. M. Garrity and D. A. R. Happer, *J. Chem. Soc., Chem. Commun.*, 1995, 705.

38 A. I. Almansour, H. A. Abubishait and C. Eaborn, *J. Organomet. Chem.*, 1997, **531**, 171.

39 G. A. Ayoko and C. Eaborn, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1289.

40 J. R. Black, C. Eaborn, P. M. Garrity and D. A. R. Happer, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1633.

41 P. D. Lickiss, personal communication, 2000.

42 C. Eaborn and A. K. Saxena, *J. Chem. Soc., Perkin Trans. 2*, 1987, 779.

43 S. M. Dhaher, C. Eaborn and J. D. Smith, *J. Chem. Soc., Chem. Commun.*, 1987, 1337.

44 A. Asadi, unpublished work.

45 P. J. Kropp, G. S. Poindexter, N. J. Pienta and D. C. Hamilton, *J. Am. Chem. Soc.*, 1976, **98**, 8135.

46 C. Eaborn and K. D. Safa, *J. Organomet. Chem.*, 1981, **204**, 169.

47 C. Eaborn, D. A. R. Happer, P. B. Hitchcock, S. P. Hopper, K. D. Safa, S. S. Washburne and D. R. M. Walton, *J. Organomet. Chem.*, 1980, **186**, 309.

48 N. Wiberg, M. Link and G. Fischer, *Chem Ber.*, 1989, **122**, 409 and references therein.

49 A. G. Avent, D. Bonafoux, C. Eaborn, M. S. Hill, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2000, 2183.

50 S. A. I. Al-Shali, C. Eaborn and F. M. S. Mahmoud, *J. Organomet. Chem.*, 1982, **232**, 215.

51 Y. Y. El-Kaddar, C. Eaborn, P. D. Lickiss and D. E. Reed, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1753.

52 S. A. I. Al-Shali, C. Eaborn, F. A. Fattah and S. T. Najim, *J. Chem. Soc., Chem. Commun.*, 1984, 318.

53 (*a*) A. I. Almansour, *J. Organomet. Chem.*, 1997, **543**, 83; (*b*) A. I. Almansour, personal communication, 2001; (*c*) C. Eaborn and A. I. Al-Mansour, *J. Organomet. Chem.*, 1983, **254**, 213.

54 D. B. Azarian, C. Eaborn and P. D. Lickiss, *J. Organomet. Chem.*, 1987, **328**, 256.

55 A. K. A. Al-Nasr, D.Phil. Thesis, University of Sussex, UK, 1992.

56 L. H. Sommer, *Stereochemistry Mechanism, and Silicon*, McGraw-Hill, New York, 1965, pp. 107–109.

57 C. Eaborn, K. L. Jones and P. D. Lickiss, *J. Organomet. Chem.*, 1994, **466**, 35.

58 R. Damrauer, C. Eaborn, D. A. R. Happer and A. I. Al-Mansour, *J. Chem. Soc., Chem. Commun.*, 1983, 348.

59 A. I. Al-Almansour, M. A. R. Al-Gurashi, C. Eaborn, F. A. Fattah and P. D. Lickiss, *J. Organomet. Chem.*, 1990, **393**, 27.

60 Z. Aiube, J. Chojnowski, C. Eaborn and W. A. Stańczyk, *J. Chem. Soc., Chem. Commun.*, 1983, 493.

61 J. Chmielecka, J. Chojnowski, C. Eaborn and W. A. Stańczyk, *J. Chem. Soc., Chem. Commun.*, 1987, 1337.

62 A. G. Davies, C. Eaborn, P. D. Lickiss and A. G. Neville, *J. Chem. Soc., Perkin Trans. 2*, 1996, 163.

63 R. I. Damja, C. Eaborn and A. K. Saxena, *J. Chem. Soc., Perkin Trans. 2*, 1985, 597.

64 G. A. Ayoko and C. Eaborn, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1357.

65 C. Eaborn, P. D. Lickiss, G. Marquina-Chidsey and E. Y. Thorli, *J. Chem. Soc., Chem. Commun.*, 1982, 1326.

66 C. Eaborn, Y. Y. El-Kaddar and P. D. Lickiss, *J. Chem. Soc., Chem. Commun.*, 1983, 1450.

67 C. Eaborn, Y. Y. El-Kaddar and P. D. Lickiss, *Inorg. Chim. Acta*, 1992, **200**, 337.

68 S. S. Al-Juaid, A. A. K. Al-Nasr, G. A. Ayoko, C. Eaborn and P. B. Hitchcock, *J. Organomet. Chem.*, 1995, **488**, 155.

69 C. Eaborn and M. N. Romanelli, *J. Chem. Soc., Chem. Commun.*, 1984, 1616.

70 N. H. Buttrus, R. I. Damja, C. Eaborn, P. B. Hitchcock and P. D. Lickiss, *J. Chem. Soc., Chem. Commun.*, 1985, 1385; S. S. Al-Juaid, N. H. Buttrus, Y. Derouiche, C. Eaborn, P. B.

Hitchcock and P. D. Lickiss, *J. Organomet. Chem.*, 1989, **371**, 287.
71 N. H. Buttrus, C. Eaborn, P. B. Hitchcock and P. D. Lickiss, *J. Organomet. Chem.*, 1986, **309**, 25.
72 S. S. Al-Juaid, C. Eaborn, P. B. Hitchcock and P. D. Lickiss, *J. Organomet. Chem.*, 1988, **349**, 29.
73 Z. H. Auibe, C. Eaborn, P. B. Hitchcock, P. D. Lickiss and J. L. Zora, *J. Organomet. Chem.*, 1985, **292**, 177.
74 N. H. Buttrus, C. Eaborn, P. B. Hitchcock, P. D. Lickiss and A. D. Taylor, *J. Organomet. Chem.*, 1986, **309**, 25.
75 S. S. Al-Juaid, C. Eaborn and P. B. Hitchcock, *J. Organomet. Chem.*, 1992, **423**, 5.
76 S. S. Al-Juaid, A. K. A. Al-Nasr, C. Eaborn and P. B. Hitchcock, *J. Chem. Soc., Chem. Commun.*, 1991, 1482.
77 S. S. Al-Juaid, A. K. A. Al-Nasr, C. Eaborn and P. B. Hitchcock, *J. Organomet. Chem.*, 1992, **429**, C9.
78 H. Ishida, J. L. Koenig and K. C. Gardner, *J. Chem. Phys.*, 1982, **77**, 5478.
79 See, for example, A. Klemp, H. Hatop, H. W. Roesky, H.-G. Schmidt and M. Noltemeyer, *Inorg. Chem.*, 1999, **38**, 5832.
80 Yu. E. Ovichinnikov, V. E. Shklover, Yu. T. Struchkov, V. V. Dement'ev, T. M. Frunze and B. A. Antipova, *J. Organomet. Chem.*, 1987, **335**, 157.