Nucleophile-assisted racemisation of halosilanes; an alternative pathway involving halide exchange *

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Abstract

An NMR method using diastereotopic halosilanes, $PhCH(Me)SiMe_2X$ (X = Cl or Br) has been developed for studying nucleophile-assisted racemisations of halosilanes. A mechanism for racemisation involving halide exchange is proposed to account for the observation that, at low temperatures, the halosilane is undergoing inversion of configuration while the four-coordinate nucleophile-halosilane adduct is stereochemically rigid.
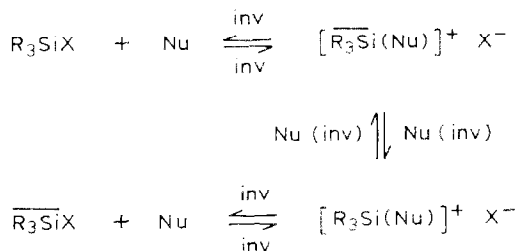
Introduction

The mechanism of nucleophilic substitution at silicon has been studied on numerous occasions, but remains the subject of active controversy. The most contentious aspect is the rôle of extracoordinated silicon intermediates in such reactions. The nucleophile-assisted racemisation of chiral silanes has been used by many workers as a probe for the mechanism of nucleophilic substitution at silicon [1–5]. Corriu [1,2] has advanced powerful arguments for a mechanism involving extracoordinated intermediates, as shown in Scheme 1.
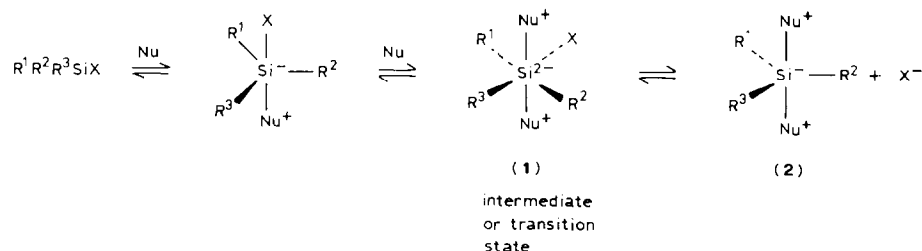
Scheme 1. The Corriu scheme [1,2].

Chojnowski [4] has proposed an alternative mechanism for racemisation that proceeds by a double displacement mechanism, as shown in Scheme 2.

$$R_3SiX \quad + \quad Nu \quad \overset{inv}{\underset{inv}{\rightleftharpoons}} \quad \left[\overline{R_3Si(Nu)}\right]^+ \ X^-$$

$$Nu \ (inv) \ \Big\Uparrow \Big\Downarrow \ Nu \ (inv)$$

$$\overline{R_3SiX} \quad + \quad Nu \quad \overset{inv}{\underset{inv}{\rightleftharpoons}} \quad \left[R_3Si(Nu)\right]^+ \ X^-$$

Scheme 2. The Chojnowski scheme [4].

This second mechanism has found support from Frye [5], and from our own previous studies [6].

Both mechanisms are compatible with a reaction that is second order in nucleophile, has a small $\Delta H^{\ddagger}$ and a large negative $\Delta S^{\ddagger}$ [7,8]. Cartledge [3] used halosilacyclo-butanes and -pentanes in an attempt to distinguish between the two symmetrical intermediates, 1 and 2, involved in Scheme 1. Rapid nucleophile-promoted halide exchange was observed between two different halosilanes, and it was proposed that ionic intermediates were involved, as shown in eq. 1.

$$\left[R_3Si(Nu)_2\right]^+ X^- + R^1_3SiY \rightleftharpoons \left[R_3Si(Nu)_2\right]^+ Y^- + R^1_3SiX \tag{1}$$
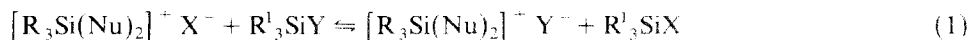
As halide exchange and racemisation are both occurring in the same reaction, some support is gained for 2 being the key intermediate in racemisations, rather than 1. Halide exchange through ionic intermediates is also compatible with the double displacement mechanism shown in Scheme 2.

We have recently shown that a wide range of nucleophiles form four-coordinate complexes with Me_3SiX (X = I, OSO_2CF_3, Br (and Cl at low temperature with N-(trimethylsilyl)imidazole)) [6,9–11] and, as expected, these salts are highly susceptible to nucleophilic attack [10]. Our current studies are aimed at a detailed kinetic and thermodynamic investigation of nucleophile-induced racemisations, in order to evaluate the rôle of four- or five-coordinate intermediates. This first report describes an NMR method using achiral silanes for the study of these reactions.

Rather than using chiral silanes involving lengthy preparations and resolutions, we have chosen to study compounds of type 3 in which the methyl groups are diastereotopic, giving rise to separate signals in the ^1H and ^{13}C NMR spectra.
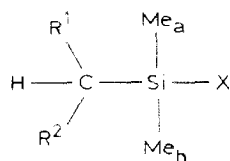
(3)

Compounds of type 3 also have the advantage of being more similar to the commonly-used Me_3SiX derivatives than the rather cumbersome NpPhMeSiX compounds (Np = 1-naphthyl). These compounds 3 are also ideal for studying rapid inversions of configuration (half-life, 10^{-1}–10^{-5} s).

Furthermore, unlike other techniques, NMR spectroscopy provides direct information on the chemical environment of the nuclei under study. Thus, structural changes induced in both silanes and nucleophiles during a reaction can be examined in detail in a non-intrusive fashion.

When R^1 and R^2 are different groups, (and not hydrogen) in **3**, the diastereotopic methyl groups a and b are not exchangeable by any symmetry operation, but may be exchanged by inversion of configuration at silicon; a process akin to racemisation. Under conditions where such an inversion is fast on the NMR time-scale, the two separate signals of Me^a and Me^b collapse to a frequency-averaged singlet. Such dynamic processes can be readily modelled by a suitable computer program, such as DNMR-4 [12] and pseudo-first-order rate constants k_{obs} can be easily determined (eq. 2).

$$\frac{\text{Rate of reaction}}{[R_3SiX]} = \frac{d[R_3SiX]}{dt} / [R_3SiX] = k_{obs} \qquad (2)$$

In the study of nucleophile-induced racemisations, the order with respect to added nucleophile can be obtained by measuring k_{obs} at a variety of nucleophile concentrations and applying standard kinetic methods.

To our knowledge, this method has not been hitherto successfully applied to silicon compounds to determine kinetic orders, although a preliminary report [13] did appear on chloride exchange at silicon prior to the ready availability of NMR analysis programs.

Results and discussion

The compounds used in this study were of type **4**, but we also synthesised derivatives of type **5**, the compounds **4** were ideal for study by NMR spectroscopy,
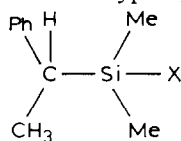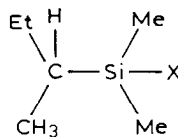
(**4** ; X = Cl , Br , OSO_2CF_3)   (**5** ; X = Cl , OSO_2CF_3)

giving well-separated singlets for the two Si–Me groups in both the ^{1}H and ^{13}C NMR spectra. Compounds **5** were not useful, as the small electronic difference between Me and Et did not induce an observable diastereotopicity in the SiMe groups.

Before attempting dynamic NMR studies on **4** with added nucleophiles, we examined the compounds produced on addition of nucleophiles to **4** as a comparison with our studies on Me_3SiX [6,9–11]. Here, we concentrate on the nucleophiles hexamethylphosphoramide (($Me_2N)_3PO$; HMPA) and N-methylimidazole (MeIm). On mixing the halosilane and nucleophile in pentane, solid 1/1 adducts were obtained for $MeIm/PhCH(Me)SiMe_2Br$, $HMPA/PhCH(Me)SiMe_2Br$ and, interestingly, MeIm also formed a solid, well-characterised adduct with $PhCH(Me)SiMe_2Cl$. Although solid bromosilane adducts are well known from previous work [6,9–11], chlorosilanes do not usually form such derivatives readily.

The ^{1}H, ^{13}C and ^{29}Si NMR spectra of solutions of the bromosilane adducts were quite different from the spectra of the individual components and clearly showed

Table 1

Kinetic study on the HMPA induced inversion of PhCHMeSiMe$_2$Br in CD$_2$Cl$_2$

[PhCHMeSiMe$_2$Br] (mol dm^{-3})	[HMPA] (mol dm^{-3})	Silane/HMPA	Observed rate constant, (k_{obs}/s^{-1})
0.9197	0.0	1.0/0.0	0.0
0.9196	0.0053	1.0/0.006	11.2
0.9188	0.0105	1.0/0.011	34.1
0.9179	0.016	1.0/0.017	56.0

that, in solution, the only observable species were the salts [PhCH(Me)SiMe$_2$(Nu)]$^+$ Br$^-$ (**6**; Nu = MeIm or HMPA). The solid chlorosilane adduct, PhCH(Me)SiMe$_2$Cl · MeIm, on dissolution in CDCl$_3$ or CD$_2$Cl$_2$, gave NMR resonances very similar to those of uncomplexed **4** (X = Cl) and MeIm. Thus, the equilibrium shown in eq. 3 in solution lies far to the right for X = Br and far to the left for X = Cl for Nu = MeIm or HMPA.

$$PhCH(Me)SiMe_2X + Nu \rightleftharpoons \left[PhCH(Me)SiMe_2(Nu) \right]^+ X^- \tag{3}$$
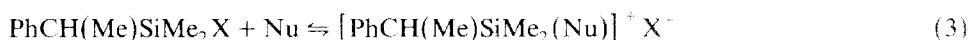
Not surprisingly, the spectra of equimolar solutions of silane and nucleophile, added together in CD$_2$Cl$_2$ or CDCl$_3$, were identical to those of the dissolved solid adducts. From these, and other, experiments, it is clear that the solution behaviour of PhCH(Me)SiMe$_2$X–Nu derivatives is closely similar to that of the Me$_3$SiX derivatives.

Having established that four-coordinate salts are formed in solution for the bromide derivatives of HMPA and MeIm, but are not observable in high concentration for the chloride, we may now discuss the nucleophile-induced racemisations in solution. It was found that addition of about 10^{-2} molar equivalents of HMPA or MeIm to **4** (X = Br) was sufficient to induce coalescence of the diastereotopic methyl groups in **4**, but up to 10^{-1} molar equivalents of HMPA or MeIm were required for coalescence of the methyl groups in **4**. (X = Cl).

Brief kinetic studies, by adding progressive amounts of HMPA to **4** in CD$_2$Cl$_2$, are summarised in Tables 1 and 2. For the bromide, the order with respect to HMPA, obtained from a plot of log$_{10}$([HMPA]) vs. log$_{10}$(k_{obs}), is 1.5, and that for the chloride is 1.2. A full discussion of these orders, and those for many other nucleophiles, will appear in forthcoming publications. However, this established that the method gives reproducible kinetic orders.

Table 2

Kinetic study on the HMPA induced inversion of PhCHMeSiMe$_2$Cl in CD$_2$Cl$_2$

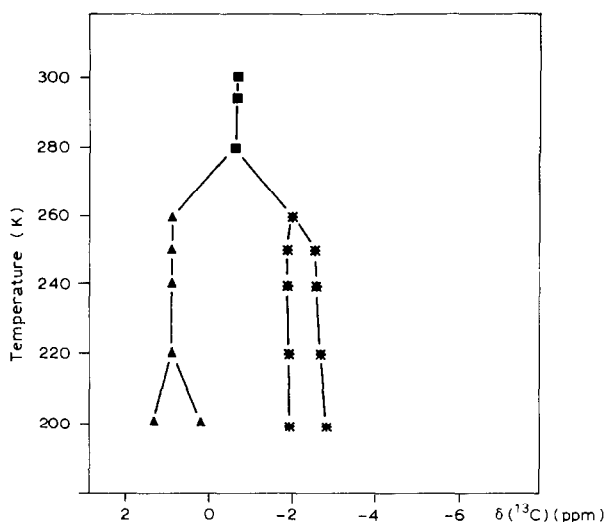| [PhCHMeSiMe$_2$Cl] (mol dm^{-3})	[HMPA] (mol dm^{-3})	Silane/HMPA	Observed rate constant (k_{obs}/s^{-1})
0.925	0.0	1.0/0.0	0.0
0.916	0.052	1.0/0.056	27.5
0.9154	0.057	1.0/0.062	32.6
0.9138	0.067	1.0/0.073	36.0
0.9130	0.072	1.0/0.079	40.0
0.912	0.077	1.0/0.085	42.0

Fig. 1. Variable temperature NMR study of a 2/1 mixture of PhCH(Me)SiMe$_2$Br and HMPA. The ^{13}C NMR signal of the SiMe group is represented. ■: averaged signal from bromosilane and four-coordinate HMPA adduct; ★: HMPA-bromosilane adduct; ▲: bromosilane.

A variable temperature NMR experiment revealed some quite unexpected results, and proved invaluable in interpreting the mechanism of nucleophile-induced racemisation of halosilanes. A mixture of **4** (X = Br) (2 molar equivalents) and HMPA (1 molar equivalent) in CD$_2$Cl$_2$ was examined by ^{13}C and ^{29}Si NMR spectroscopy. The ^{13}C NMR resonances of the SiMe groups at different temperatures are represented in Fig. 1, and full NMR data are given in Table 3. As previously discussed, the bromosilane readily undergoes complexation with HMPA, and it is predicted that, under the conditions of this experiment, the mixture consists essentially of equivalent quantities of **4** (X = Br) and **6** (Nu = HMPA). Accordingly, the ^{13}C NMR spectrum of the SiMe groups at 300 K is a sharp singlet, with the resonance intermediate in frequency between those of **6** (Nu = HMPA) and **4** (X = Br). Thus, at this temperature, the salt and bromosilane are undergoing rapid exchange, with inversion of configuration. As the temperature was reduced to 280 K, the singlet disappeared to give two new, broad singlets. The singlet at about δ 1 ppm corresponds to the bromosilane, undergoing rapid inversion of configuration, and the singlet at δ −2 ppm represents the HMPA salt **6**, similarly undergoing rapid inversion. On further reduction of the temperature to 250 K, the bromosilane signal remained a singlet but the HMPA adduct showed two peaks, corresponding to slow exchange. The bromosilane resonance eventually splits into two peaks at 200 K. This is a highly significant result, as it is clear that the bromosilane at 250 K is undergoing inversion of configuration under conditions where the HMPA adduct is stereochemically rigid. In Scheme 2, inversion of the adduct is rate-limiting, so it follows that in this case the bromosilane is undergoing inversion by an alternative mechanism. Similar results were obtained for the reaction of PhCH(Me)SiMe$_2$Br with MeIm, as shown in Fig. 2 and Table 4.

The corresponding mechanism, but involving a five-coordinate species, is shown in Scheme 3. If k_2 is rate-limiting, as expected, rates of racemisation of halosilane

Table 3

Variable temperature NMR study of a 2/1 mixture of PhCHMeSiMe$_2$Br and HMPA in CD$_2$Cl$_2$ [a]

Assignments δ(ppm)	HMPA	Silane	Temperature (K)							
			300	295	280	260	250	240	220	200
^{13}C										
ipso-C	–	143.1	142.5	142.5	142.5	142.5br	142.9 142.2	142.6 142.2	142.6 142.1	142.5 142.1
meta-C		128.9	128.8	128.8	128.8	128.8	129.0 128.6	129.0 128.6	129.0 128.6	129.0 128.6
ortho-C	–	128.0	127.8	127.8	127.8	127.8	127.8	127.8	127.9 127.7	127.9 127.7
para-C	–	125.9	125.9	125.9	125.9	125.9	125.9sbr	126.0 125.7	126.0 125.7	126.0 125.7
CH	–	32.3	30.9sbr	30.9sbr	30.8sbr	31.5vbr 29.9vbr	31.6sbr 29.8sbr	31.6 29.8,29.7	31.5 29.7,29.6	31.4 29.6, 29.5
Me	–	15.3	14.7	14.7	14.7	14.6br	14.9br 14.2sbr	14.9 14.2	14.9 14.1	14.8 14.0
SiMe	–	1.7,0.6	–0.6br	–0.5br	–0.5vbr	0.9vbr –1.9vbr	1.0sbr –1.8, –2.5	0.9 –1.8, –2.5	1.0vbr –1.9, –2.6	1.4,0.3sbr –1.9, –2.8
PN(CH$_3$)	36.9d		37.2d	37.2d	37.1d	37.1d	37.0d	37.0d	36.9d	36.8d
^2J(PC)	3.9		5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
^{29}Si										
SiMe	–	29.2	26.6br	26.4br	30.3vbr 23.9vbr	29.8,23.8d [b]	nr	30.0,23.9d	30.2,23.8d	30.4,23.7d
^2J(PSi)(Hz)			13.7			13.7		12.7	11.7	11.7

[a] Quantities used: PhCHMeSiMe$_2$Br 1.0 cm^3, 5.011 mmol; HMPA, 0.44 cm^3, 2.507 mmol; solvent 1.2 cm^3, CD$_2$Cl$_2$. [b] Slightly broadened.

Table 4

Variable temperature NMR study of a 2/1 mixture of PhCHMeSiMe$_2$Br and MeIm in CD$_2$Cl$_2$ [a]

Assignments δ(ppm)	MeIm	Silane	Temperature (K)							
			300	295	280	260	240	220	200	185
^{13}C										
ipso-C	–	143.1	142.5sbr	142.2sbr	142.2vbr	142.8 141.5	142.8 141.5	142.7 141.4	142.5	141.8
meta-C	–	128.9	128.9	128.9	128.9	129.1 128.7	129.1 128.7	129.1 128.7	128.6	128.0
ortho-C	–	128.0	127.8	127.8	127.8	127.9 127.7	127.9 127.7	128.0 127.8	127.9	127.2
para-C	–	125.9	126.0	126.0	126.0	126.2 125.8	126.3 125.8	126.2 125.9	125.8	125.1
CH	–	32.3	30.3vbr	31.5vbr	31.8vbr 28.6vbr	31.9 28.5	31.8 28.4	31.7 28.4sbr	31.4 28.1br	30.6br
Me	–	15.3	14.7sbr	14.7sbr	14.7vbr	15.1 14.2	15.1 14.1	14.9 14.1	14.8 13.8sbr	14.0sbr 12.4vbr
SiMe	–	1.7,0.6	−1.4vbr	−1.4vbr	0.9vbr −3.8vbr	1.0vbr −3.4, −4.5	1.5,0.4br −3.4, −4.7	1.5,0.3 −3.4, −4.7	1.3,0.1 −3.5, −5.2	0.6, −0.6 −4.2, −6.0
C(2)	137.8	–	141.7	141.7	141.7	141.7	141.5	141.4	141.3	140.6br
C(4)	129.4	–	125.3	125.3	125.3	125.3	125.3sbr	124.8sbr	obscured	obscured
C(5)	120.1	–	124.1	124.1	124.1	124.2	124.3sbr	124.3sbr	124.3vbr	obscured
N–CH$_3$	33.2	–	36.6	36.6	36.6	36.6	36.5	36.5	36.4sbr	35.7br
^{29}Si										
SiMe	–	29.2	26.2vbr	28.4vbr 23.9vbr	29.6vbr 23.3vbr	29.8 23.2	30.0 23.1	30.2 23.0	30.3 23.8	30.2 22.5

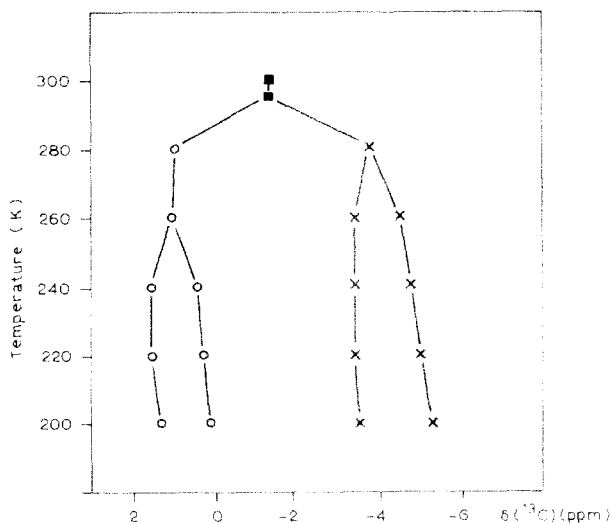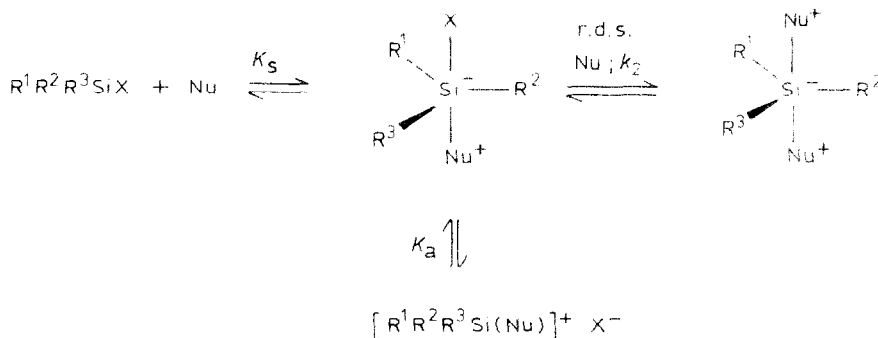[a] Quantities used: PhCHMeSiMe$_2$Br: 1.0 cm^3, 5.056 mmol; MeIm: 0.2 cm^3, 2.542 mmol; solvent: 1.2 cm^3 CD$_2$Cl$_2$.

220

Fig. 2. Variable temperature NMR study of a 2/1 mixture of PhCH(Me)SiMe$_2$Br and MeIm. The ^{13}C NMR signal of the SiMe group is represented. ■: averaged signal from bromosilane and MeIm adduct; ○: bromosilane; ×: MeIm-bromosilane adduct.

and adduct can be shown to be equal since they go through the same intermediate. One mechanism which does account for these observations involves halosilane inversion via halide exchange (eq. 4). Sommer [14] and Prince [15,16] have observed
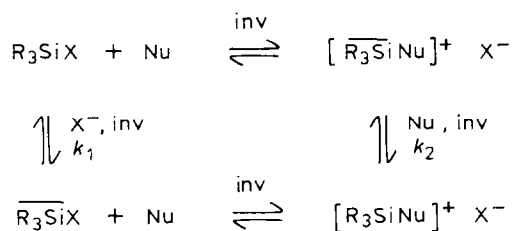
$$Br^- + R_3SnBr \underset{inv}{\overset{inv}{\rightleftharpoons}} R_3SiBr + Br^- \tag{4}$$

this type of halide exchange. It is rapid, and involves inversion of configuration [13]. We also found that the addition of trace amounts of $[NBu_4]^+ Br^-$ to PhCH(Me)Si-Me$_2$Br resulted in the ready collapse of the SiMe signals to a singlet. We therefore propose an extension to the double displacement mechanism, as shown in Scheme 4.

Halide exchange may not be the only mechanism involved in nucleophile-assisted racemisation of halosilanes, but we believe it to be predominant for good leaving groups, such as Br^-, I^- and $[OSO_2CF_3]^-$, with good nucleophiles such as HMPA

Scheme 3

$$R_3SiX \quad + \quad Nu \quad \overset{inv}{\rightleftharpoons} \quad [\overline{R_3Si\,Nu}]^+ \quad X^-$$

$$\uparrow\downarrow \; \begin{array}{l} X^-, inv \\ k_1 \end{array} \qquad\qquad\qquad \uparrow\downarrow \; \begin{array}{l} Nu, inv \\ k_2 \end{array}$$

$$\overline{R_3SiX} \quad + \quad Nu \quad \overset{inv}{\rightleftharpoons} \quad [R_3Si\,Nu]^+ \quad X^-$$

Scheme 4. A novel extended double displacement mechanism for the nucleophile-assisted racemisation of halosilanes.

and MeIm, where the concentration of free nucleophile is negligible. However for chlorosilanes, at ambient temperature, the concentration of both adduct and chloride ion is very small. The ^{29}Si NMR spectrum of $PhCH(Me)SiMe_2Cl$ (1 molar equivalent) with HMPA (1.5 molar equivalent) showed only chlorosilane down to 240 K. At 200 K, adduct formation appeared to be almost complete. The ^{13}C NMR spectrum at ambient temperature showed rapid inversion of configuration at silicon. Under these conditions, the concentration of nucleophile is high, as is the concentration of chlorosilane. The equilibrium demands that the concentration of adduct and chloride ion is equal. In this case the dominant mechanistic pathway will depend largely on the relative rate constants for halide exchange and attack of free nucleophile on the adduct, which have not been evaluated.

A simple experiment was designed to illustrate halide exchange with different halogens and possibly throw light on the question of halide exchange versus double displacement. $PhCH(Me)SiMe_2Cl$, $PhCH(Me)SiMe_2Br$ and HMPA were mixed in
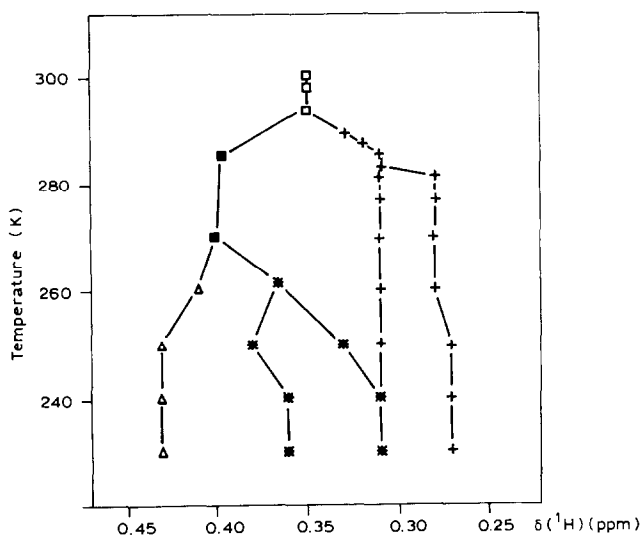
Fig. 3. Variable temperature NMR study of a 1/1/0.45 molar mixture of $PhCH(Me)SiMe_2Br$, $PhCH(Me)SiMe_2Cl$ and HMPA. The ^1H NMR signal of the SiMe group is represented. □: all species exchanging; ■: HMPA-bromosilane adduct and bromosilane exchanging; △: bromosilane; +: chlorosilane; ★: bromosilane - HMPA adduct.

CD_2Cl_2 in molar proportions of $1/1/0.45$. Under these conditions, the HMPA should be almost all consumed as **6** (Nu = HMPA), and the concentrations of free nucleophile will be correspondingly very low. Figure 3 represents the variable temperature ^1H NMR spectra of the SiMe groups within this mixture. At 300 K, a single SiMe resonance was observed, corresponding to rapid exchange with inversion of configuration of all species within the system. Thus, bromosilane and chlorosilane are both undergoing halide exchange, most probably through eq. 5. The

$$R_3SiCl \overset{Br}{\underset{inv}{\rightleftharpoons}} \overline{R_3SiBr} \overset{Br}{\underset{inv}{\rightleftharpoons}} R_3SiBr \overset{Cl}{\underset{inv}{\rightleftharpoons}} \overline{R_3SiCl} \tag{5}$$

equilibrium between bromide ion and chlorosilane lies significantly towards the chlorosilane. As the temperature was lowered to 290 K, two broad single resonances were observed. The one at high frequency corresponds to bromosilane undergoing rapid exchange with its HMPA adduct, and the low frequency resonance is attributed to chlorosilane and bromide ion undergoing exchange. At about 285 K, the chlorosilane resonances appeared as two separate signals, indicating that no exchange is taking place. Below 280 K, the bromosilane/HMPA mixture behaved as previously described, when no chlorosilane was present. In this one experiment, the following exchanges have been demonstrated: degenerate bromide–bromide exchange; bromide–chloride exchange, and presumably nucleophile–nucleophile exchange (double displacement mechanism). No conclusions can yet be drawn concerning the relative importance of halide exchange and double displacement for chlorosilanes. However, examination of Scheme 4 shows that the rate of racemisation via halide exchange is equal to $k_1[R_3SiX][X^-]$, and the rate for double displacement equals $k_2[\{R_3Si(Nu)\}^+][Nu]$, hence eq. 6. From the stoichiometry of

$$\frac{\text{rate of inversion via halide exchange}}{\text{rate of inversion via double displacement}} = \frac{k_1[R_3SiX][X^-]}{k_2[\{R_3Si(Nu)\}^+][Nu]} \tag{6}$$

the adduct formation, $[\{R_3Si(Nu)\}^+] = [X^-]$, and hence eq. 7. We have shown that at higher concentrations of nucleophile, inversion via halide exchange can dominate. Equation 7 shows that at lower concentrations of nucleophile, such as those used in

$$\frac{\text{rate of inversion via halide exchange}}{\text{rate of inversion via double displacement}} = \frac{k_1[R_3SiX]}{k_2[Nu]} \tag{7}$$

Tables 1 and 2, inversion via halide exchange will be even more important. We are at present continuing these studies with different silanes and nucleophiles, in order to examine the general applicability of this halide exchange mechanism.

Experimental

Reactions and NMR spectra of halosilanes were carried out under dinitrogen, using rigorously dried solvents. NMR solvents were stored over activated 4A molecular sieves and under dinitrogen. NMR solutions were made up in a dry box in 10 mm stoppered tubes. NMR spectra were recorded on a JEOL FX90Q spectrometer.

Preparation of PhCH(Me)SiMe₂X

1-Methylbenzyldimethylsilane was prepared by an in situ Grignard reaction in THF. 1-chloroethylbenzene (79.7 g, 0.57 mol) was added dropwise over 1 h to a

stirred mixture of magnesium turnings (48.9 g, 2.01 mol) and chlorodimethylsilane (190 g, 2 mol) in THF (300 cm^3) containing a crystal of iodine. The mixture was maintained under an atmosphere of dinitrogen and heated under reflux for 4 h. Standard work-up procedures gave 1-methylbenzyldimethylsilane 78.1 g, 84%; b.p. 28°C, 0.3 mmHg. Found C, 73.45; H, 10.05. C$_{10}$H$_{16}$Si calcd.: C, 73.09; H, 9.81%. ^{1}H NMR: δ 7.35–7.11 (m, 5H, Ph); 3.93 (septet, J 3.3 Hz, 1H, SiH); 2.40 (q, J 7.3 Hz, 1H, CH) 1.48 (d, J 7.3 Hz, 3H, CH$_3$); 0.11 (d of d, J 3.3 Hz, $\Delta\delta$ 3.7 Hz, 6H, SiCH$_3$) ppm. ^{13}C NMR: δ 145.6 (ipso-C); 128.3 (m-C); 127.0 (o-C); 124.6 (p-C); 27.8 (CH); 15.5 (CH$_3$); -5.8 (SiCH$_3$); -5.9 (SiCH$_3$) ppm.

1-Methylbenzyldimethylchlorosilane was prepared by bubbling chlorine through a stirred solution of PhCH(Me)SiMe$_2$H (30.37 g, 0.19 mol) in tetrachloromethane (50 cm^3) at 0°C, under dinitrogen. The apparatus was illuminated with a 60 W light bulb, and the progress of the reaction monitored by ^{1}H NMR spectroscopy on aliquots. When the reaction was judged to be complete the mixture was distilled to give 1-methylbenzyldimethylchlorosilane, 30.33 g, 81.6%; b.p. 43–44°C, 0.1 mmHg. Found C, 59.78; H 8.22. C$_{10}$H$_{15}$ClSi calcd.: C, 60.43; H, 7.61%. ^{1}H NMR δ 7.44–7.17 (m, 5H, Ph); 2.52 (q, J 7.3 Hz, 1H, CH); 1.56 (d, J 7.3 Hz, 3H, CH$_3$); 0.42 (s, 3H, SiCH$_3$); 0.40 (s, 3H, SiCH$_3$) ppm. ^{13}C NMR: δ 143.2 (ipso-C); 128.7 (m-C); 127.9 (o-C); 125.8 (p-C); 32.1 (CH); 14.8 (CH$_3$); 0.7 (SiCH$_3$); -0.3 (SiCH$_3$) ppm. ^{29}Si NMR: δ 32.4 ppm.

1-Methylbenzyldimethylbromosilane was prepared by adding liquid bromine dropwise to a stirred solution of PhCH(Me)SiMe$_2$H (64.7 g, 0.39 mol) in CCl$_4$ (150 cm^3) at 0°C, under dinitrogen. The apparatus was illuminated by a 60 W light bulb. The reaction was monitored by NMR spectroscopy and was complete when the orange colour persisted. The mixture was distilled to give the extremely moisture sensitive 1-methylbenzyldimethylbromosilane, 77.21 g, 80.6%; b.p. 90–93°C, 0.3 mmHg. The liquid was > 99.5% pure by GLC, and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy showed no detectable impurities. Owing to handling problems with this particularly moisture sensitive material, a satisfactory microanalysis could not be obtained. Found C, 48.39; H, 6.70. C$_{10}$H$_{15}$BrSi calcd.: C, 49.38; H, 6.22%. NMR, ^{1}H NMR: δ 7.45–7.16 (m, 5H, Ph); 2.59 (q, J 7.7 Hz, 1H, CH); 1.58 (d, J 7.7 Hz, 1H, CH); 0.56 (s, 3H, SiCH$_3$); 0.54 (s, 3H, SiCH$_3$) ppm. ^{13}C NMR: δ 142.9 (ipso-C); 128.8 (m-C); 127.9 (o-C); 125.9 (p-C); 32.3 (CH); 15.3 (CH$_3$); 1.8 (SiMe); 0.5 (SiMe) ppm. ^{29}Si NMR: δ 30.8 ppm.

Synthesis of 1 / 1 adducts of halosilanes with nucleophiles

Typically, the nucleophile and halosilane were added together in pentane under dinitrogen and the mixture cooled to -10°C until a solid precipitated. The solid was collected by filtration washed with dry pentane, and immediately stored under dinitrogen. All were solids that decomposed on heating.

PhCH(Me)SiMe$_2$Cl(MeIm) adduct; found C, 59.30; H, 7.87; N, 10.25. C$_{14}$H$_{21}$ClN$_2$Si calcd.: C, 59.87; H, 7.54; N, 9.97%. NMR spectra of dissolved solid adduct in CDCl$_3$, ^{1}H NMR: δ 7.67 (br s, 1H, im H(2)); 7.19–7.14 (m, 5H, Ph); 7.05 (br s, 1H, im H(4)); 6.90 (br s, 1H, im H(5)); 3.69 (s, 3H, NCH$_3$); 2.42 (q, J 7.7 Hz, 1H, CH); 1.45 (d, J 7.7 Hz, 3H, CH$_3$); 0.32 (s, 6H, SiCH$_3$) ppm; ^{13}C NMR: δ 142.6 (ipso-C), 137.8 (Im C(2)); 128.3 (m-C); 127.5 (o-C); 125.3 (p-C); 124.4 (Im C(4)); 120.4 (Im C(5)); 33.5 (NCH$_3$); 31.5 (CH); 14.4 (CH$_3$); -0.3 (SiCH$_3$) ppm; ^{29}Si NMR: δ 30.1 ppm.

PhCH(Me)SiMe$_2$Br (MeIm) adduct: found C, 52.54; H, 6.71; N, 8.48. C$_{14}$H$_{21}$BrN$_2$Si calcd.: C, 52.01; H, 6.55; N, 8.66%. NMR spectra of dissolved solid adduct in CDCl$_3$, ^{1}H NMR: δ 9.20 (br s, 1H, im H(2)); 7.5 (br s, 1H, im H(4)); 7.26–6.97 (m, 6H, Ph, im H(5)); 4.0 (s, 3H, NCH$_3$); 2.91 (q, J 7.7 Hz, 1H, CH); 1.39 (d, J 7.7 Hz, 3H, CH$_3$); 0.66 (s, 6H, SiCH$_3$) ppm; ^{13}C NMR: δ 140.7 (*ipso*-C); 139.8 (im C(2)); 128.8 (*m*-C); 127.2 (*o*-C); 126.0 (Im C(4)); 125.8 (*p*-C); 123.3 (Im C(5)); 35.3 (NCH$_3$); 28.4 (CH); 14.0 (CH$_3$); −4.1 (SiCH$_3$); ^{29}Si NMR: δ 23.5 ppm.

PhCH(Me)SiMe$_2$Br (HMPA) adduct; found C, 45.21; H, 8.19; N, 10.44. C$_{16}$H$_{33}$BrN$_3$OPSi calcd.: C, 45.49; H, 7.87; N, 9.95%. NMR spectra of dissolved solid adduct in CDCl$_3$, ^{1}H NMR: δ 7.31–7.08 (m, 5H, Ph); 2.71 (d, J 10.3 Hz, 18H, PNCH$_3$); 2.51 (q, J 7.7 Hz, 1H, CH); 1.44 (d, J 7.7 Hz, 3H, CH$_3$); 0.42 (s, 6H, SiCH$_3$) ppm; ^{13}C NMR: δ 141.5 (*ipso*-C); 128.7 (*m*-C); 127.4 (*o*-C); 125.9 (*p*-C); 37.0 (d, J(PC) 3.9 Hz, PNCH$_3$); 29.8 (CH); 14.1 (CH$_3$); −2.1 (SiCH$_3$) ppm. ^{29}Si NMR: δ 24.3 ppm.

NMR studies

Where kinetic orders were determined, the following method was adopted. The halosilane and solvent were mixed and added to the tube in a dinitrogen-filled dry-box, and a subaseal was fixed to the tube. The NMR spectra of the initial mixtures were obtained, and nucleophile added in aliquots using a microsyringe. The ^{13}C NMR spectra were recorded under standard proton-decoupled conditions. Matching of spectra with those calculated by DNMR-4 was carefully carried out. Each spectrum was separately simulated until an excellent fit was obtained. Other NMR studies required no special techniques other than care in exclusion of moisture.

The ^{29}Si NMR spectra were recorded at 17.76 MHz, using gated decoupling and a pulse width of 12 μs (40°) and a pulse delay of 10–50 s. Between 10 and 1000 transients were accumulated, depending on concentration.

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