

## Interaction of *N*-Trimethylsilylimidazole with Electrophilic Trimethylsilyl Compounds. Part 1. Characterisation of Silylimidazolium Salts

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*N*-Trimethylsilylimidazole forms bistrimethylsilylimidazolium salts (5) in solution with Me<sub>3</sub>SiX (X = Br, I, OSO<sub>2</sub>CF<sub>3</sub>, or OClO<sub>3</sub>). The solutions are conducting, but evidence for ion pairing is presented. Chloro(trimethyl)silane does not produce a salt in solution at ambient temperature but does so at low temperature. N.m.r. evidence is presented for the structures, and used to obtain values of Δ*H*<sup>‡</sup> and Δ*S*<sup>‡</sup> for (5; X = Cl).

Reagents for organic synthesis based on electrophilic silicon compounds are becoming increasingly important and find wide use.<sup>1-4</sup> In particular the reagents trimethylsilyl trifluoromethanesulphonate<sup>5</sup> (TMST) and trimethylsilyl iodide<sup>6</sup> (TMSI) have opened up new areas of organic chemistry. Electrophilic silicon reagents are generally used in the presence of amines or other bases, and it is the question of the interaction, in solution, between these silicon compounds and amines that is addressed in this study.

It has been known for many years that *N*-trimethylsilylimidazole, and other amines, promote the silylation of alcohols, thiols, ketones, and other labile compounds.<sup>1,4</sup> Three different mechanisms are currently postulated for amine-assisted silylations. The first, and simplest, assigns the role of the amine as that of a proton acceptor, facilitating reaction by driving the equilibrium towards product formation.

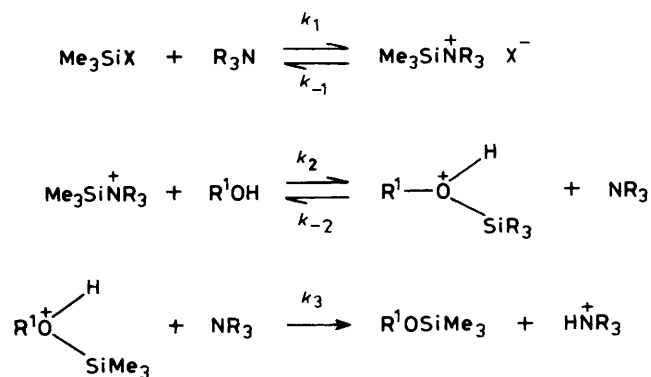
The second mechanism<sup>7</sup> involves a pre-equilibrium quaternisation of the amine by the electrophilic silane. The quaternised aminosilane is then the active silylation species, attacked by alcohol, or other nucleophile, in a rate-determining bimolecular displacement (Scheme).

The third mechanism<sup>8</sup> is kinetically equivalent to that shown in the Scheme, but the formation of a five-co-ordinate silyl species that is a molecular adduct between the silane and amine is postulated to be the initial step. The rate-determining step is attack by the alcohol on the five-co-ordinate silicon species.

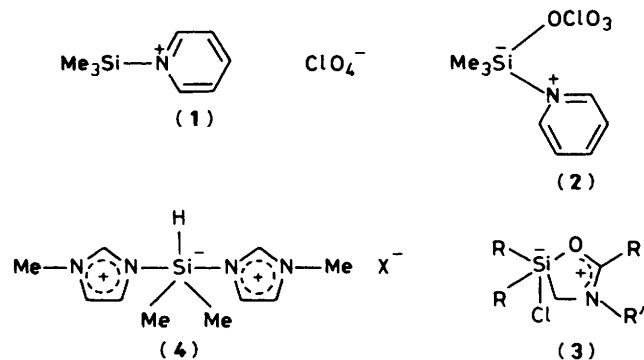
There is now a considerable body of evidence that the amine is intimately involved in the reaction and does not simply function as a proton acceptor. Chaudhary and Hernandez<sup>9</sup> showed that a mixture of triethylamine and 4-dimethylaminopyridine (DMAP) promoted silylations of alcohols by chloro(dimethyl)-*t*-butylsilane. The silylations were quantitative in the presence of catalytic amounts of DMAP, but did not proceed in its absence, despite the presence of stoichiometric amounts of triethylamine or pyridine. These observations were taken as evidence for the mechanism shown in the Scheme. The pre-equilibrium mechanism is also established for aminosilane solvolysis,<sup>10</sup> in which the initial step is protonation of the aminosilane.

Frye *et al.*<sup>11</sup> recently showed that alcoholysis of chlorosilanes is accelerated according to the nucleophilicity of the added amine and is unrelated to its p*K*<sub>a</sub>. In a detailed discussion, the mechanistic evidence was reviewed and the mechanism in the Scheme strongly supported.

The mechanism involving five- and six-co-ordinate silicon intermediates was proposed by Corriu<sup>12</sup> and is supported by conductivity measurements and kinetic data. However, as mechanisms two and three are kinetically indistinguishable it is of great importance to establish the nature of the species present in silylation mixtures. In view of the very large number of known organosilicon compounds it is perhaps surprising that

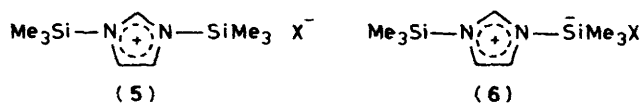


Scheme. A mechanism for silylation involving pre-equilibrium quaternisation of amines



relatively little is known about silyl salts of bases and nucleophiles. Hensen *et al.*<sup>13</sup> recently determined the X-ray crystal structure of a four-co-ordinate, ionic 1:1 adduct of pyridine and iodo(trimethyl)silane, but the integrity of the salt species in solution was not established. Barton and Tully<sup>14</sup> in a study of silyl perchlorates observed a high frequency proton n.m.r. shift in a 1:1 mixture of pyridine and trimethylsilyl perchlorate (TMSP) in acetonitrile. This was attributed to the formation of either (1) or (2). The ionic complex (1) was preferred but not positively identified. The five-co-ordinate complex (2) is possible, but by analogy with other systems is unlikely. Only one stable trialkyl-substituted five-co-ordinated silicon series (3)<sup>15</sup> is known, and only one open-chain five-co-ordinate organosilyl series (4)<sup>16</sup> has been characterised.

There are some reports of halogenosilanes forming ionic silicon(IV) adducts with nucleophiles in solution. Ebsworth<sup>17</sup>

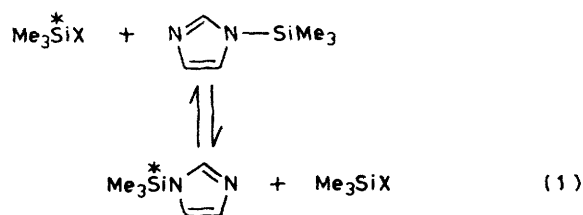


concluded that a 1:1 ionic adduct and a 1:2 adduct were formed on addition of  $\text{H}_3\text{SiI}$  to triethylamine. With other amines and halogenosilanes, non-conducting adducts with five- or six-coordination at silicon were formed. Beattie and Parrett<sup>18</sup> measured the i.r. spectra and conductivity of some adducts of TMSI and TMSP with hexamethylphosphoramide or trimethylamine and postulated that the adducts were ionic, with  $\text{I}^-$  or  $\text{ClO}_4^-$  having been displaced from silicon.

Chojnowski *et al.*<sup>7</sup> used  $^{31}\text{P}$  n.m.r. and conductivity measurements to demonstrate the ionic nature of the adduct between bromotrimethylsilane (TMSBr) and hexamethylphosphoramide, and isolated the salt as an analytically pure compound. Recently we<sup>19</sup> have used  $^{29}\text{Si}$  n.m.r. to establish that various halogenosilanes, and TMST, form ionic four-coordinate silicon complexes with dimethylformamide, in solution.

All the forgoing studies, while demonstrating that under appropriate conditions silicon can form ionic adducts, have not related to common silylation conditions. For example, whereas TMSI forms an ionic adduct with trimethylamine,<sup>18</sup> it does not do so, to any observable extent, in solution, with the more accessible triethylamine.<sup>20</sup>

There are numerous suggestions<sup>5-7,9,11</sup> that the first step in many silylations is the formation of an ionic adduct, but most of these claims are unsubstantiated by clear spectroscopic evidence. The aim of this first part of a study on silylations was to examine the nature of the interaction of  $\text{Me}_3\text{SiX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OCIO}_3$ , or  $\text{OSO}_2\text{CF}_3$ ) with *N*-trimethylsilylimidazole (NTMSIm) by a combination of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  n.m.r. spectroscopy, and conductivity measurements. Careful analysis of such data allows the distinction to be made between the formation of adducts (5) and (6), and the further possibility of a degenerate silyl-exchange reaction (1).



## Results and Discussion

When equimolar quantities of  $\text{Me}_3\text{SiX}$  ( $\text{X} = \text{Br}, \text{I}, \text{OSO}_2\text{CF}_3$ , or  $\text{OCIO}_3$ ) and NTMSIm were mixed in dry hexane, creamy-white precipitates of 1:1 adducts were formed quantitatively in all cases. Proton n.m.r. analysis of the hexane solutions, after the moisture-sensitive precipitates had been filtered off, showed no signals attributable to trimethylsilyl groups, or the imidazole ring, confirming that the reaction is stoichiometric and quantitative. The solids produced are moderately soluble in  $\text{CDCl}_3$ , and very soluble in  $\text{CD}_2\text{Cl}_2$  and  $\text{CD}_3\text{CN}$ . As demonstrated later, the n.m.r. spectra and conductivity measurements are consistent with the ionic salt structure (5) for each of these examples.

The addition of (trimethyl)chlorosilane (TMSCl) to NTMSIm in hexane at ambient temperature did not afford a precipitated salt. At low temperatures the formation of (5;  $\text{X} = \text{Cl}$ ) did occur, and this is discussed in detail later.

The n.m.r. spectroscopic data for the imidazolium salts (5)

Table 1.  $^{29}\text{Si}$  n.m.r. chemical shifts of  $\text{Me}_3\text{SiX}$  and NTMSIm

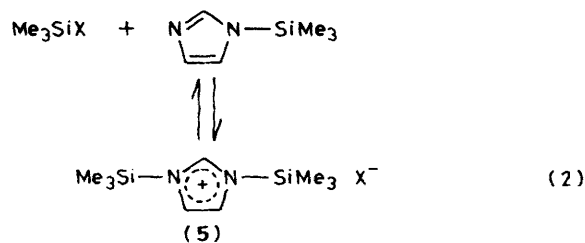
	$\delta(^{29}\text{Si})^a$		
	$\text{CDCl}_3$	$\text{CD}_2\text{Cl}_2$	$\text{CD}_3\text{CN}$
$\text{Me}_3\text{SiCl}$	31.0	31.1	32.0
$\text{Me}_3\text{SiBr}$	26.4	27.6	28.7
$\text{Me}_3\text{SiI}$	9.6	10.2	12.1
$\text{Me}_3\text{SiOSO}_2\text{CF}_3$	43.4	43.9	46.1
$\text{Me}_3\text{SiOCIO}_3$		45.1	<i>b</i>
$\text{Me}_3\text{SiIm}$	13.3	13.5	14.2

<sup>a</sup> Relative to internal  $\text{Me}_4\text{Si}$ , and measured at 17.76 MHz. All chemical shift values in all Tables refer to sharp, single lines, unless stated otherwise. <sup>b</sup>  $\text{Me}_3\text{SiOCIO}_3$  reacts with acetonitrile over 1–2 h.

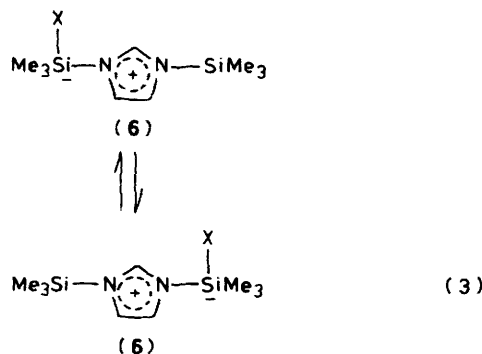
Table 2.  $^{29}\text{Si}$  n.m.r. chemical shifts of bis-silylimidazolium ions (5).

X	$\delta(^{29}\text{Si})$		
	$\text{CDCl}_3$	$\text{CD}_2\text{Cl}_2$	$\text{CD}_3\text{CN}$
Br	26.5	26.3	26.3
I	26.5	26.9	26.4
$\text{CF}_3\text{SO}_3$	26.7	26.9	26.7
$\text{ClO}_4$	26.1	26.1	26.1

and the reagents used are presented in Tables 1–6 and their analysis is now given. It can be demonstrated that the equilibrium shown in equation (2) lies substantially to the right



for  $\text{X} = \text{Br}, \text{I}, \text{OSO}_2\text{CF}_3$ , or  $\text{OCIO}_3$  in solution in  $\text{CDCl}_3$ ,  $\text{CD}_3\text{CN}$ , or  $\text{CD}_2\text{Cl}_2$ . Table 1 gives the  $^{29}\text{Si}$  n.m.r. chemical shifts of the TMSX compounds in the three solvents used in this study. Table 2 shows that equimolar mixtures of TMSX ( $\text{X} \neq \text{Cl}$ ) in solution have sharp, single  $^{29}\text{Si}$  resonances all appearing within about  $\pm 0.4$  p.p.m. of  $\delta$  26.4. The position of these resonances is significantly different from the mean value for TMSX and NTMSIm, ruling out the exchange reaction shown in equation (1). As the silicon atoms are in identical magnetic environments, regardless of counterion, the structure (5) could be inferred from the  $^{29}\text{Si}$  n.m.r. data alone. The equilibrium shown in equation (3) can be discounted. First, if the moiety X were involved in



**Table 3.**  $^{13}\text{C}$  N.m.r. chemical shifts of  $\text{Me}_3\text{SiX}$  and  $\text{NTMSIm}$ 

	$\delta(^{13}\text{C})^a$								
	$\text{CDCl}_3$			$\text{CD}_2\text{Cl}_2$			$\text{CD}_3\text{CN}$		
	C-2	C-4, -5	$\text{SiCH}_3$	C-2	C-4, -5	$\text{SiCH}_3$	C-2	C-4, -5	$\text{SiCH}_3$
$\text{Me}_3\text{SiCl}$			3.3			3.3			3.2
$\text{Me}_3\text{SiBr}$			4.1			4.2			4.1
$\text{Me}_3\text{SiI}$			5.6			5.6			5.6
$\text{Me}_3\text{SiOSO}_2\text{CF}_3$			0.34			0.29			0.29
$\text{Me}_3\text{SiOClO}_3$			0.7			0.8			
$\text{Me}_3\text{SiIm}$	140.2	125.5	-0.46	140.2	125.5	-0.46	139.9	125.2	-0.57

<sup>a</sup> Relative to internal  $\text{Me}_4\text{Si}$  and measured at 22.5 MHz.**Table 4.**  $^{13}\text{C}$  N.m.r. chemical shifts of bis-silylimidazolium ions (5)

X	$\delta(^{13}\text{C})$								
	$\text{CDCl}_3$			$\text{CD}_2\text{Cl}_2$			$\text{CD}_3\text{CN}$		
	C-2	C-4, -5	$\text{SiCH}_3$	C-2	C-4, -5	$\text{SiCH}_3$	C-2	C-4, -5	$\text{SiCH}_3$
Br	142.7	125.2	-1.3	144.1	124.5	0.0	143.4	125.3	-0.57
I				143.0	124.5	0.0	143.6	125.6	-0.57
$\text{CF}_3\text{SO}_3$				141.0	124.1	-0.8	142.2	125.0	-0.97
$\text{ClO}_4$				143.3	124.9	-0.69	142.3	125.2	-0.52

**Table 5.**  $^1\text{H}$  N.m.r. chemical shifts of  $\text{Me}_3\text{SiX}$  and  $\text{NTMSIm}$ 

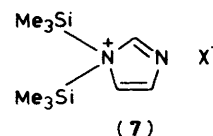
	$\delta(^1\text{H})^a$								
	$\text{CDCl}_3$			$\text{CD}_2\text{Cl}_2$			$\text{CD}_3\text{CN}$		
	H-2	H-4, -5	$\text{SiCH}_3$	H-2	H-4, -5	$\text{SiCH}_3$	H-2	H-4, -5	$\text{SiCH}_3$
$\text{Me}_3\text{SiCl}$			0.43			0.42			0.42
$\text{Me}_3\text{SiBr}$			0.58			0.57			0.57
$\text{Me}_3\text{SiI}$			0.80			0.79			0.79
$\text{Me}_3\text{SiOSO}_2\text{CF}_3$			0.50			0.49			0.48
$\text{Me}_3\text{SiOClO}_3$						0.35			—
$\text{Me}_3\text{SiIm}$	7.60	7.08	0.46	7.60	7.07	0.45	7.60	7.06	0.43

<sup>a</sup> Relative to internal  $\text{Me}_4\text{Si}$  and measured at 89.56 MHz.**Table 6.**  $^1\text{H}$  N.m.r. chemical shifts of bis-silylimidazolium ions (5)

X	$\delta(^1\text{H})$								
	$\text{CDCl}_3$			$\text{CD}_2\text{Cl}_2$			$\text{CD}_3\text{CN}$		
	H-2	H-4, -5	$\text{SiCH}_3$	H-2	H-4, -5	$\text{SiCH}_3$	H-2	H-4, -5	$\text{SiCH}_3$
Br	9.93t ( <i>J</i> 1.8 Hz)	7.78d ( <i>J</i> 1.8 Hz)	0.79	9.79t ( <i>J</i> 1.5 Hz)	7.48d ( <i>J</i> 1.5 Hz)	0.72	8.91br	7.59d ( <i>J</i> 1.5 Hz)	0.63
I				9.34br	7.52d ( <i>J</i> 1.2 Hz)	0.75	8.74br	7.62d ( <i>J</i> 1.2 Hz)	0.65
$\text{CF}_3\text{SO}_3$	8.77t ( <i>J</i> 1.4 Hz)	7.40d ( <i>J</i> 1.4 Hz)	0.62	8.63br	7.42d ( <i>J</i> 1.2 Hz)	0.64	8.46	7.54	0.57
$\text{ClO}_4$				8.52br	7.39d ( <i>J</i> 1.0 Hz)	0.64	8.33	7.49d ( <i>J</i> 1.2 Hz)	0.59

bonding to silicon the differing shielding properties of different X would result in non-identical chemical shifts for (6) as X varied. Secondly, in  $^{29}\text{Si}$  n.m.r. spectra, five-co-ordination at silicon is manifested by significant, low-frequency chemical shifts, as compared with four-co-ordination.<sup>16,21</sup> The resonance at  $\delta$  ca. 26 is consistent with trimethylsilyl groups attached to a single, moderately electron-withdrawing group.<sup>22</sup> Thirdly, the solutions are conducting (see later). The  $^{29}\text{Si}$  n.m.r. spectra do

not allow the exclusion of (7) but that structure appears unlikely on both steric and electronic grounds.



The  $^{13}\text{C}$  n.m.r. data (Tables 3 and 4) are again consistent with the structure (5) in solution. The  $^{13}\text{C}$  n.m.r. spectra of (5) are slightly more dependent on the counterion than the  $^{29}\text{Si}$  n.m.r. spectra, and we attribute this to variations in ion-pairing in solution (see later). The imidazole ring carbon atoms in (5) give rise to two resonances, corresponding to C-2 and the equivalent C-4 and C-5. The high frequency shifts of 1–3 p.p.m. of the C-2 resonance and the low frequency shifts of ca. 1 p.p.m. of the C-4 and -5 resonance of (5), relative to those in NTMSIm, are very similar to those observed by Pugmire and Grant<sup>23</sup> for the related protonation of imidazole. The similarity of the  $^{13}\text{C}$  chemical shifts to those on protonation of imidazole, and the equivalence of C-4 and C-5, are inconsistent with (7), unless an unlikely, complex, degenerate bis-silyl migration is postulated.

The proton n.m.r. spectra of (5) (Tables 5 and 6) are particularly interesting in the light of the  $^{13}\text{C}$  and  $^{29}\text{Si}$  n.m.r. spectra. The imidazole H-2 resonance in (5) shows a highly variable high-frequency shift, relative to NTMSIm, that depends on both solvent and counterion. In  $\text{CD}_2\text{Cl}_2$ ,  $\delta(\text{H-2})$  varies between 9.79 for (5; X = Br) and 8.52 for (5; X =  $\text{ClO}_4$ ); cf. 7.6 in NTMSIm. We attribute this variation to differing extents of ion-pair formation. There is some evidence that related salts are non-conducting, and hence tight-ion-paired in relatively non-polar solutions.<sup>5</sup> In more polar solvents, such as  $\text{CD}_3\text{CN}$  where the counterion is more solvated, the salts (5) would be expected to be less ion-paired. This is reflected in the smaller variation of the chemical shifts of H-2 of (5) in  $\text{CD}_3\text{CN}$ , as compared with  $\text{CD}_2\text{Cl}_2$ . In each solvent the  $^1\text{H}$  chemical shift trends for H-2 are similar and the high-frequency shift decreases in the order X = Br > I >  $\text{CF}_3\text{SO}_3$  >  $\text{ClO}_4$ . This order is consistent with increasing solvation of the anions in highly polar media, and appropriate to the expected order for ion-pairing with the charged, bis-silylimidazolium cation. The variations in  $^{13}\text{C}$  n.m.r. chemical shifts and other  $^1\text{H}$  chemical shifts are rather small and irregular, and no firm correlations can be made. It is to be expected that the counterion would reside in the region of lowest electron density, close to C-2 and H-2. The variation of proton chemical shifts with electron density is more predictable than that for carbon nuclei,<sup>24</sup> accounting for the better correlation of H-2 chemical shifts with counterion solvation.

To confirm that the species (5) were ionic in solution, conductivity titrations were carried out with neat  $\text{Me}_3\text{SiX}$  (X = Cl, Br, I, or  $\text{OSO}_2\text{CF}_3$ ) added to NTMSIm in dry  $\text{CH}_2\text{Cl}_2$ . The results are shown in the Figure. For X = I or  $\text{OSO}_2\text{CF}_3$  the conductivity increased rapidly until the reagents were equimolar, and then, as more  $\text{Me}_3\text{SiX}$  was added there was a slight, but consistent fall in conductivity. These data suggest that for X = I and  $\text{OSO}_2\text{CF}_3$  the equilibrium of equation (2) lies substantially to the right. The shape of the conductivity curves also strongly resemble those obtained by Chojnowski<sup>7</sup> for reaction of  $\text{Me}_3\text{SiX}$  with hexamethylphosphoramide. The concentration of TMSP was not known sufficiently accurately for quantitative, conductivity measurements (we were reluctant to effect purification by distillation), but approximate measurements showed very high conductivity and similar behaviour to TMSI and TMST.

The conductivity titration of TMSBr with NTMSIm in  $\text{CH}_2\text{Cl}_2$  did not show a sharp break at a 1:1 ratio of reagents, but increased until a ratio of ca. 1.3:1 was reached, and then fell slowly. The molar conductivity of (5; X = Br) is significantly smaller than that of (5; X = I or  $\text{OSO}_2\text{CF}_3$ ). Thus it appears that the equilibrium constant for formation of (5) is rather smaller for X = Br than for X = I,  $\text{OSO}_2\text{CF}_3$ , or  $\text{OCIO}_3$ , and to a first approximation the conductivity follows the order of the high-frequency  $^1\text{H}$  n.m.r. shift observed for H-2. Again, these observations are consistent with differing degrees of ion-pair formation.

The conductivity titration of TMSCl with NTMSIm differed

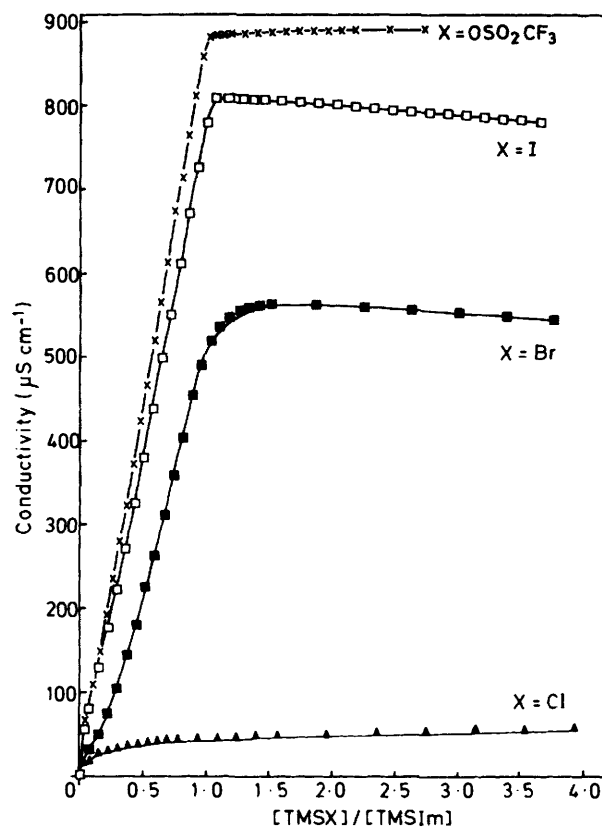


Figure. Conductivity titration: TMSX (X = Cl, Br, I, or  $\text{OSO}_2\text{CF}_3$ ) against TMSIm (solvent  $\text{CH}_2\text{Cl}_2$ ;  $[\text{TMSIm}]$  0.11M)

significantly from that of the other silanes in this study. There was no inflection in the conductivity, up to a four-fold molar excess of TMSCl, although the conductivity did increase steadily, if slightly. The fact that (5; X = Cl) was not precipitated from a hexane solution of NTMSIm at ambient temperature suggests that it is not very stable. However, as the conductivity did increase in the more polar  $\text{CD}_2\text{Cl}_2$ , a small equilibrium population of (5; X = Cl) seemed likely. We therefore carefully examined the n.m.r. spectra of NTMSIm-TMSCl mixtures over a range of temperatures. The results are given in Table 7 and indeed show that (5; X = Cl) is the major species at low temperatures. At ambient temperature the  $^{29}\text{Si}$  n.m.r. spectrum consists of a sharp, single resonance at the mean value of the chemical shifts of NTMSIm and TMSCl. This, together with the observation of single TMS resonances in the  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra, is strong evidence for the rapid, degenerate exchange shown in equation (1).

As the temperature was lowered the  $^{29}\text{Si}$  n.m.r. resonance moved 3 p.p.m. to high frequency, to  $\delta$  25.34 [close to the value for (5; X  $\neq$  Cl)]. Similarly the H-2 chemical shift at 188 K is  $\delta$  10.31, the highest value for any (5) [assuming that the effect of temperature on the chemical shifts of (5) is small]. This is also consistent with the ion-pairing hypothesis already presented, with chloride ion forming the tightest ion-pairs with (5). The complete order for ion-pairing in (5) is therefore X = Cl > Br > I >  $\text{OSO}_2\text{CF}_3$  >  $\text{OCIO}_3$ .

The variable-temperature spectra allow the calculation of values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the reaction shown in equation (2) when X = Cl. The values of K, the equilibrium constant, can be calculated from the chemical shifts. The resonance positions of the mixture, in the absence of salt formation, are known accurately, and the extrapolated limits for complete salt

**Table 7.** Variable-temperature n.m.r. data ( $^1\text{H}$  and  $^{29}\text{Si}$ ) for a 1:1 mixture of NTMSIm and TMSCl in  $\text{CD}_2\text{Cl}_2$ .

T/K	$\delta(^1\text{H})$			$\delta(^{29}\text{Si})$ SiCH <sub>3</sub>
	H-2	H-4, -5	SiCH <sub>3</sub>	
308	7.59	7.03	0.43	22.3 <sup>a</sup>
275	7.85	7.10	0.46	22.5
243	9.23	7.49	0.61	23.6
214	10.02	7.75	0.70	25.0
195	10.26	7.83	0.74	25.3
188	10.31	7.87	0.75	25.34

<sup>a</sup> This represents the measured and calculated mean of the  $\text{Me}_3\text{SiCl}$  and NTMSIm  $^{29}\text{Si}$  resonances.

formation were  $\delta$  25.5 for  $^{29}\text{Si}$ ; 10.45 for H-2; 7.96 for H-4 and -5; and 0.765 for SiCH<sub>3</sub>. The integrated form of the van't Hoff isochore was used:  $\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R$ . Plots of  $\ln K$  vs.  $1/T$  for all four nuclei gave good straight lines with very similar gradients and intercepts. Values of  $\Delta H^\circ$  ( $-42 \pm 5$  kJ mol<sup>-1</sup>) and  $\Delta S^\circ$  ( $-171 \pm 30$  J K<sup>-1</sup> mol<sup>-1</sup>) were obtained by taking the mean of the four data sets. Thus the formation of the salt (5) is exothermic, but the entropy of formation, as expected, is very large and negative. It appears that, at ambient temperature, TMSCl will not form salts readily for thermodynamic rather than kinetic reasons, as previously suggested by Beattie.<sup>18</sup>

It has thus been established that in mixtures of highly electrophilic trimethylsilanes and NTMSIm the predominant species in solution are the quaternised amine salts (5), which could well be the active silylation species. With chloro(trimethyl)silane, at ambient temperature, the concentration of (5; X = Cl) is likely to be very low; however this does not preclude it from being the active silylation species. The complete mechanism of silylation can only be elucidated by a thorough kinetic study, with a knowledge of all species in the solutions, and an understanding of their dynamic behaviour.

### Experimental

All solvents were dried, distilled under nitrogen, and stored under nitrogen, and over 4 Å molecular sieves. Chloroform was washed with water several times, dried with potassium carbonate, and distilled in the dark from calcium chloride. Hexane (h.p.l.c. grade), was distilled from sodium wire. Dichloro[ $^2\text{H}_2$ ]methane and [ $^2\text{H}_3$ ]acetonitrile (Aldrich, Gold Label) were distilled and stored over 4 Å molecular sieves. The silanes  $\text{Me}_3\text{SiX}$  (X = Cl, Br, imidazol-1-yl, or  $\text{OSO}_2\text{CF}_3$ ) were purchased from various suppliers, distilled, and stored under nitrogen in light-proof bottles. Most of these compounds react with molecular sieves to give hexamethyldisiloxane, so no drying agent was used. Iodo(trimethyl)silane (Aldrich) was distilled in the dark from copper powder, and stored in the dark over copper beads.

Trimethylsilyl perchlorate was prepared by the method of Beattie<sup>18</sup> and used, as prepared, in toluene solution.

N.m.r. spectra were run with a JEOL FX90Q spectrometer; all samples were made up in a nitrogen-filled dry-box, and the tubes were sealed with rubber septum caps.

Conductivity measurements were carried out using a PTI-10 digital conductivity meter. All experiments were performed under nitrogen in a specially constructed cell with a magnetic stirring facility. Successive samples of the silane were added through a septum using a microlitre syringe. The meter was

**Table 8.** Microanalytical data for bis-silylimidazolium salts (5)

X	Found (Required) (%)		
	C	H	N
Br	36.5(36.85)	7.2(7.2)	10.0(9.55)
I	31.7(31.8)	6.2(6.2)	8.65(8.2)
$\text{CF}_3\text{SO}_3$	33.15(33.1)	6.0(5.8)	7.9(7.7)
$\text{ClO}_4$	34.2(34.55)	6.3(6.8)	9.2(8.95)

calibrated, and frequently checked, with standard solutions of potassium chloride. The concentration of the nucleophile in the initial solution in dichloromethane was ca. 0.1M. The conductivity of  $\text{CH}_2\text{Cl}_2$  solutions of each of the silanes and NTMSIm, in isolation, was negligible ( $< 1 \mu\text{S cm}^{-1}$ ).

**General Procedure for the Preparation of Bis-silylimidazolium Salts (5).**—The trimethylsilyl compounds  $\text{Me}_3\text{SiX}$  (X = Br, I,  $\text{OSO}_2\text{CF}_3$ , or  $\text{OCIO}_3$ ) (2 mmol) was added dropwise to a stirred solution of NTMSIm (2 mmol) in dry hexane (5 cm<sup>3</sup>), under dry nitrogen. A precipitate formed immediately, and after being stirred for 5–10 min was filtered off under nitrogen and finally dried *in vacuo* to give an essentially quantitative yield of white, solid (5) (Table 8).

### References

- 1 E. Colvin, 'Silylation of Organic Compounds,' Butterworths, London, 1981.
- 2 W. P. Weber, 'Silicon Reagents for Organic Synthesis,' Springer-Verlag, Berlin, 1983.
- 3 I. Fleming, in 'Comprehensive Organic Chemistry,' vol. 3, part 13, Pergamon, Oxford, 1979.
- 4 C. A. Pierce, 'Silylation of Organic Compounds,' Pierce, Rockford, Illinois, 1968.
- 5 H. Emde, *Synthesis*, 1982, 1.
- 6 G. A. Olah and S. C. Narang, *Tetrahedron*, 1982, **38**, 2225.
- 7 J. Chojnowski, M. Cypryk, and J. Michalski, *J. Organomet. Chem.*, 1978, **161**, C31.
- 8 R. J. P. Corriu, G. Dabosi, and M. Martineau, *J. Organomet. Chem.*, 1978, **154**, 33.
- 9 S. K. Chaudhary and O. Hernandez, *Tetrahedron Lett.*, 1979, 99.
- 10 A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Organomet. Chem.*, 1970, **25**, 57.
- 11 H. K. Chu, M. D. Johnson, and C. L. Frye, *J. Organomet. Chem.*, 1984, **271**, 327.
- 12 R. J. P. Corriu and C. Guerin, *Adv. Organomet. Chem.*, 1982, **20**, 265, and references therein.
- 13 K. Hensen, T. Zengerly, P. Pickel, and G. Klebe, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 725.
- 14 T. J. Barton and C. R. Tully, *J. Org. Chem.*, 1978, **43**, 3649.
- 15 C. H. Yoder, C. M. Ryan, G. F. Martin, and P. S. Ho, *J. Organomet. Chem.*, 1980, **190**, 1.
- 16 A. R. Bassindale and T. Stout, *J. Chem. Soc., Chem. Commun.*, 1984, 1387.
- 17 H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc. A*, 1966, 1508; 1967, 705.
- 18 I. R. Beattie and F. W. Parrett, *J. Chem. Soc. A*, 1966, 1784.
- 19 A. R. Bassindale and T. Stout, *J. Organomet. Chem.*, 1982, **238**, C41.
- 20 A. R. Bassindale and T. Stout, unpublished observations.
- 21 E. A. Williams and J. D. Cargioli, *Annu. Rep. NMR Spectrosc.*, 1979, **9**, 221.
- 22 R. K. Harris and B. J. Kimber, *J. Magn. Reson.*, 1975, **17**, 174.
- 23 R. J. Pugmire and D. M. Grant, *J. Am. Chem. Soc.*, 1968, **90**, 4232.
- 24 J. B. Stothers 'Carbon-13 NMR Spectroscopy,' Academic Press, New York 1968.

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