The Preparation and Observation by ^{29}Si N.M.R. Spectroscopy of Simple, Acyclic, Five-co-ordinate Silicon Salts.

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Five-co-ordinate complexes $[Nu_2SiMe_2H]^+X^-$; Nu = 3-methyl-1-imidazolio, *N,N*-dimethylaminopyridinio, or pyridinio; X = Cl, I, or OSO_2CF_3, have been identified in solution by ^{29}Si n.m.r. spectroscopy, and in some cases isolated as analytically pure compounds.

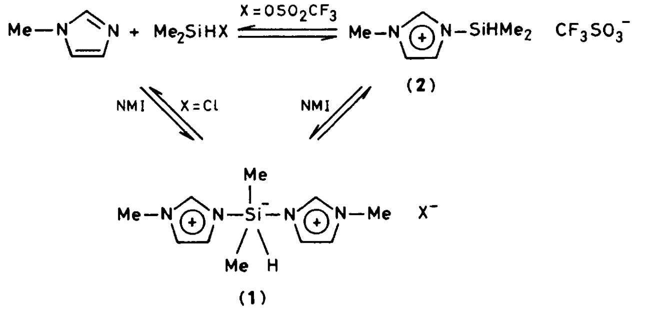
Five-co-ordinate silicon species are well established as intermediates in nucleophilic substitutions at silicon[1] but their direct observation for acyclic 'organic' silicon compounds has proved elusive. Numerous stable five- and six-co-ordinate derivatives of silicon are known, and in some cases *X*-ray structural determinations are available.[2] However, the majority of such compounds contain both chelating ligands and strongly electron-withdrawing substituents on silicon, and as such are poor models for the intermediates involved in organosilicon substitution reactions.

We have prepared and characterised, for the first time, some simple, non-chelated five-co-ordinate silicon salts (**1**) that will serve as excellent models for possible intermediates in nucleophilic substitution at silicon.

For example, hydridodimethylbis-(3-methyl-1-imidazolio)silicon(IV) chloride (**1**, X = Cl) was readily prepared by the addition of a deficiency of *N*-methylimidazole (NMI) to neat chlorodimethylsilane (DMCS) at ambient temperature. The salt (**1**) precipitated as a pure, air-stable, but highly moisture-sensitive compound [m.p. 90 °C (decomp.), satisfactory C, H, and N analyses] (Scheme 1).

By contrast, the addition of deficiency of NMI to dimethylsilyl triflate ($Me_2HSiOSO_2CF_3$) (DMST) in hexane resulted in the formation of the four-co-ordinate complex, hydridodimethyl(3-methyl-1-imidazolio)]silicon(IV) triflate (**2**) (m.p. 51—54 °C, satisfactory C, H, and N analyses) (Scheme 1).

The five-co-ordinate silicon complex (**1**, X = OSO_2CF_3) can be prepared by the addition of two equivalents of NMI to one equivalent of DMST in hexane–chloroform, from which it separated as an analytically pure oil (Scheme 1). Attempts to crystallise the oil have, so far, been unsuccessful.



Scheme 1. X = Cl, I, or OSO_2CF_3.

Silicon-29 n.m.r. spectroscopy was the principal method by which the five-co-ordination at silicon in (**1**) was confirmed. Figure 1 shows the variation in ^{29}Si chemical shift in $CDCl_3$, as aliquots of NMI were added to a known concentration of DMCS or DMST. The chemical shift of DMCS is 12 p.p.m. relative to internal $SiMe_4$ and is characteristic of a four-co-ordinate compound;[3] as NMI was added to the solution the ^{29}Si n.m.r. resonance moved steadily to low frequency. The limiting value for (**1**) is −81 p.p.m., characteristic of five-, rather than six-co-ordination at silicon.[4,5] The ^{29}Si n.m.r. peak at all DMCS/NMI ratios was sharp (linewidth <10 Hz), confirming that the equilibrium shown in Scheme 1 is fast on the n.m.r. timescale.

The behaviour of DMST with NMI is rather different from that of DMCS at low NMI concentrations. At NMI/DMST ratios less than one, two separate resonances were observed in the ^{29}Si n.m.r. spectra: one at +24 p.p.m., corresponding to DMST, and one at +10 p.p.m., assigned to (**2**) [confirmed by comparison of the ^{29}Si n.m.r. shift with that of a solution of (**2**) in $CDCl_3$.] When equimolar quantities of NMI and DMST were present only (**2**) was observed, and as more NMI was added, a single peak moved to low frequency with a limiting value of −82 p.p.m., as for DMCS. Thus, the equilibrium between DMST and (**2**) (Scheme 1) is slow on the n.m.r. timescale, whereas the equilibrium between (**2**) and (**1**) is fast. The reaction of iododimethylsilane with NMI has only been

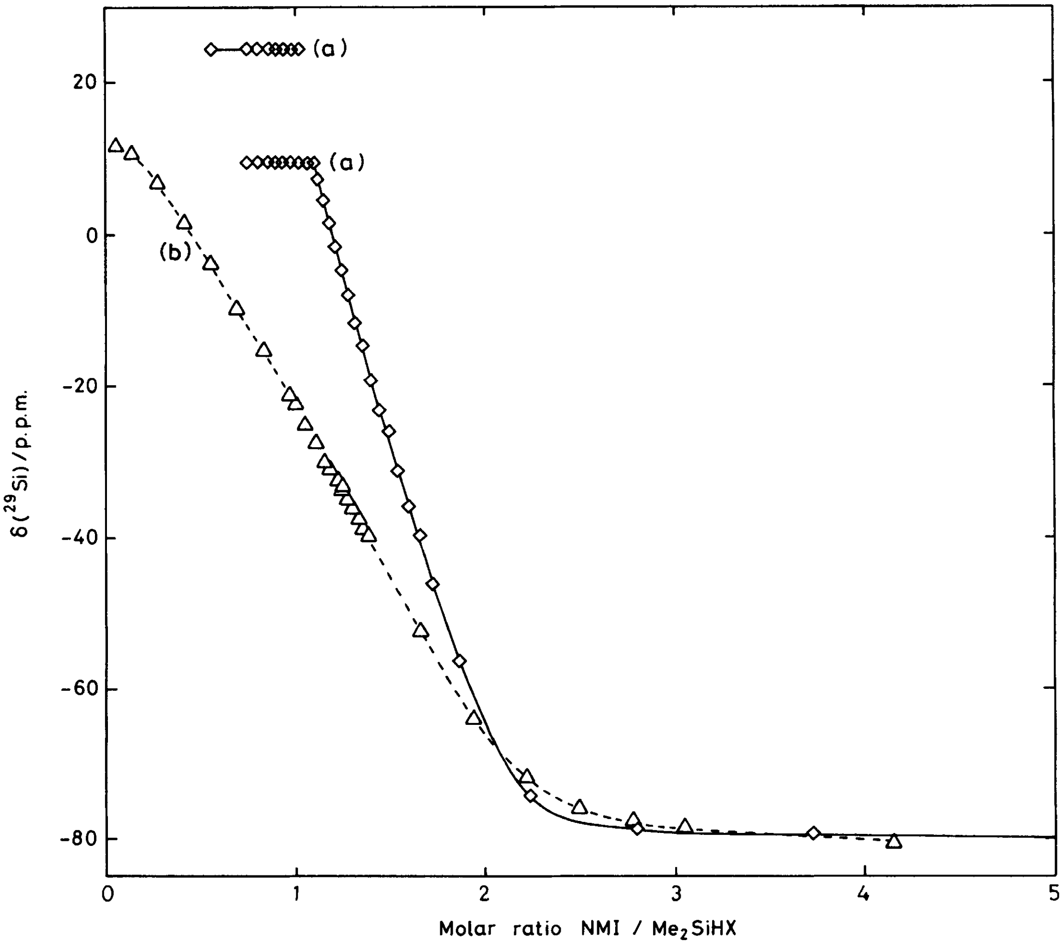


Figure 1. ^{29}Si Chemical shift titration of NMI against (a) DMST and (b) DMCS.

studied at high NMI concentrations where the same limiting chemical shift of −82 p.p.m. was observed, confirming that the same silicon species (**1**) is present for all three counterions. The ^{1}H and ^{13}C n.m.r. spectra are consistent with the structures postulated for (**1**) and (**2**).

When the solid (**1**, X = Cl) or the oil (**1**, $X = OSO_2CF_3$) was dissolved in $CDCl_3$, a single peak was observed in the ^{29}Si n.m.r. spectrum. The chemical shift of a solution of (**1**, X = Cl) in $CDCl_3$ was concentration dependent. A single peak was observed at −59.5 p.p.m. (0.83 M), which moved to high frequency (−23.0 p.p.m. at 0.29 M) on dilution. Similar behaviour was observed for (**1**, $X = OSO_2CF_3$). As expected from the stoicheiometry, there is more five-co-ordinated species present at high concentrations.

The ionic nature of (**1**) and (**2**) was confirmed by conductivity measurements. The four-co-ordinate salt (**2**) has a higher molar conductivity (in CH_2Cl_2) than (**1**, $X = OSO_2CF_3$). The five-co-ordinate salt (**1**, X = Cl) has a lower molar conductivity than (**1**, $X = OSO_2CF_3$), possibly owing to ion pairing of the former in the relatively non-polar dichloromethane solvent. More detailed conductivity studies will be reported in further papers.

Other nitrogen-centred nucleophiles behave similarly to NMI in forming five-co-ordinated species. Pyridine forms an analogue of (**1**) with DMST ($\delta^{29}Si$ −44 p.p.m.) but does not react at all with DMCS at ambient temperature. 4-Dimethylaminopyridine forms five-co-ordinate species with both DMCS and DMST ($\delta^{29}Si$ −52 p.p.m.).

Five-co-ordination at silicon in this series has, so far, only been directly observed for dimethylsilyl species. Trimethyl-, triethyl-, t-butyldimethyl-, and diphenylmethyl-silyl derivatives can form four-co-ordinate salts analogous to (**2**) but there is no evidence for extra co-ordination with open-chain nucleophiles in these examples.

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