Bis-halo *N,N*-Bisdimethylsilylmethylacetamides as Dynamic Probes for the Effect of Coordination on Reactivity at Silicon

Alan R. Bassindale* and Moheswar Borbaruah

Chemistry Department, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

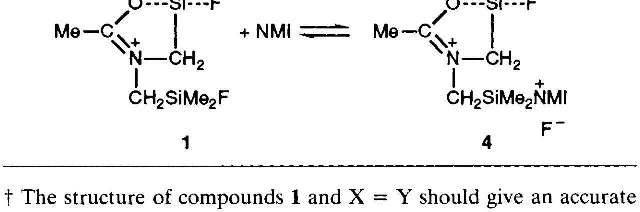
A series of bis-halo *N,N*-bisdimethylsilylmethylacetamides **1** has been designed and used to investigate the effect of coordination on reactivity at silicon; pentacoordinated SiCl and SiBr bonds are thermodynamically activated towards nucleophilic substitution by *N*-methylimidazole (NMI) and hexamethylphosphoramide (HMPA), by contrast coordination of R_3SiF renders the SiF bond less prone to substitution by nucleophiles than that in the tetracoordinated R_3SiF.

It has been widely reported that a pentacoordinate silicon centre can be activated towards nucleophilic substitution relative to its tetracoordinate parent.[1] The detailed nature of this activation is not entirely certain and its origin in kinetic or thermodynamic (or both) factors is unresolved.

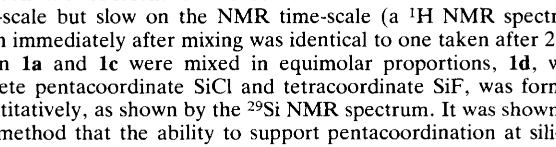
This bis-halo *N,N*-bisdimethylsilylmethylacetamide[2] system was chosen for study because there are two silicon centres in the molecule that for X = Y differ only in the coordination at silicon. Investigations can therefore be carried out on the two centres at the same time and under identical conditions. The pentacoordinate nature of one silicon centre in X = Y = Cl has been demonstrated by X-ray crystallography[2b] and the two environments are discrete on the NMR time-scale even at 120°.[2b] The relative reactivity of the two silicon centres to substitution was measured by examining the effect on the NMR spectra of adding increasing aliquots of nucleophiles, NMI and HMPA, to **1**. In previous studies[3,4] we have shown that for Me_3SiX the tendency to undergo substitution to form Me_3SiNu^+, as determined by NMR measurements of the equilibrium constants, decreased in the expected order $Me_3SiBr > Me_3SiCl > Me_3SiF$.[5] For the series **1** the ^{29}Si NMR chemical shifts and coupling constants can be used to give unequivocal information about the site of substitution. Tetracoordinate CH_2SiMe_2Z nuclei resonate in the ^{29}Si NMR at δ 25 ± 5 and pentacoordinate silicon nuclei are shielded by between δ 40 and 100, appearing between about δ −15 and −80.[6] Silicon nuclei bonded to fluorine are recognized by SiF coupling to give a doublet with J_{SiF} *ca.* 270 ± 20 Hz. In each example studied the two different silicon nuclei give two separate sets of signals, with one in each of the ranges described. When NMI (0.5 equiv.) was added to a solution of **1a** (X = Cl) in $CDCl_3$ the ^{29}Si NMR signal from pentacoordinate silicon at δ −39 broadened so much that it almost disappeared into the base-line, while that from the tetracoordinate SiCl, at δ 26.8 remained unchanged. The ^1H NMR spectrum of the imidazole ring protons showed that the NMI was coordinated.[7] At a molar ratio of 1 : 1 for NMI: **1a** there were again two ^{29}Si resonances, one unchanged at δ 26.8 and the other, a less broad singal ($\Delta\nu_{1/2}$ 25 Hz) at δ −54. At a ratio of 2 : 1 for NMI: **1a** the ^{29}Si NMR resonance at δ −54 had sharpened to a normal line width ($\Delta\nu_{1/2}$ 2 Hz) while the resonance from the tetracoordinate silicon appeared at δ 18.4. These observations are unambiguously interpreted as attack by the nucleophile at the pentacoordinate silicon with sequential displacement of chloride by NMI as shown in Scheme 1.

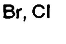
The prior coordination of the chlorosilane to the amido oxygen atom therefore thermodynamically activates the silicon to substitution. In a competition between the two silicon environments in **1a** for 1 equiv. of NMI or HMPA it is the pentacoordiante silicon that is essentially exclusively substituted. The same result was found for the dibromo compound **1b** with NMI and HMPA, and for the mixed fluorochloro and fluorobromo compounds **1d** and **e**,† where the chloride or bromide ions were displaced from the pentacoordinated silicon centres while the SiF coupling was maintained throughout.

The reactivity of the bisfluoro compound **1c** was quite different from that of the other bishalogeno derivatives. When NMI (0.5 equiv.) was added to a solution of **1c**, the doublet in the ^{29}Si NMR spectrum at δ 29 (J_{SiF}, 287 Hz), assigned to the tetracoordinate fluorosilane, disappeared while the doublet at δ −23.5 (J_{SiF}, 257 Hz) from the pentacoordinate silicon was unchanged. On addition of NMI (1.5 equiv.) a broad resonance ($\Delta\nu_{1/2}$ 100 Hz) centred at δ 29 appeared, while the doublet at δ −23.5 remained. These observations are only consistent with attack at the four-coordinate silicon with displacement of the fluoride ion, while the five-coordinate fluorosilane was inert. The equilibrium constant for the reaction **1** = **4** is very small as the ^{29}Si chemical shift in the tetracoordinate region is very close to that of the initial



Scheme 1





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a; X = Y = Cl
b; X = Y = Br
c; X = Y = F (made from **1a** or **1b** by treatment with SbF_3)
d; X = Cl, Y = F
e; X = Br, Y = F
f; X, Y = Br, Cl

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† The structure of compounds **1** and X = Y should give an accurate indication of the relative tendency of X and Y to stabilize pentacoordination at silicon. The tendency to undergo expansion of coordination was measured by mixing equivalent quantities of two of the homohalogeno compounds **1a**, **b** or **c** in $CDCl_3$. Exchange of halogens between the different environments was fast on the laboratory time-scale but slow on the NMR time-scale (a ^1H NMR spectrum taken immediately after mixing was identical to one taken after 2 h). When **1a** and **1c** were mixed in equimolar proportions, **1d**, with discrete pentacoordinate SiCl and tetracoordinate SiF, was formed quantitatively, as shown by the ^{29}Si NMR spectrum. It was shown by this method that the ability to support pentacoordination at silicon decreases in the order Br > Cl > F which is consistent with Corriu *et al.*s' previous results.[8]

tetracoordinate fluorosilane and the ^{1}H NMR spectra show that the NMI is not measurably coordinated. By contrast, Corriu and coworkers have found, in a different system, that anionic pentacoordinate fluorosilanes are activated to nucleophilic substitution relative to the neutral tetracoordinate fluorosilanes.[9]

The behaviour of **1c** with fluoride ion, although it is more complex, again confirmed that the four-coordinate fluorosilane centre is more reactive than the five-coordinate fluorosilane centre. The addition of a trace of fluoride ion, (one drop of 1 mol dm^{-3} tetrabutylammonium fluoride in tetrahydrofuran (THF), *ca.* 5% water) caused the doublet in the ^{29}Si NMR from the four-coordinate fluorosilane to collapse to a singlet ($\Delta\nu_{1/2}$ 20 Hz) leaving the five-coordinate silicon doublet unchanged, consistent with a fast exchange of fluoride between the four-coordinate SiF and F$^-$ (although it could be due to traces of HF rather than simply fluoride ion[10]). As more fluoride was added to **1c** the fluoride ion added to the four-coordinate silicon as shown by the monotonic low frequency shift in the ^{29}Si NMR from δ 29 for pure **1c** to a singlet at δ −74 at 1 equiv. of added fluoride. The position of the ^{29}Si NMR resonance of the five-coordinate silicon remained unchanged (at δ −23.5) throughout but it collapsed from the initial doublet to a singlet at 0.5 equiv. of fluoride ion. Thus, although fluoride exchange does take place at the five-coordinate silicon it is much slower than at the four-coordinate silicon, where extension of coordination by addition of fluoride also takes place.

The experiments described above are uninformative concerning the relative rates at which the silicon nuclei are undergoing substitution but do show clearly that in **1**, silicon–bromide and silicon–chloride are thermodynamically activated to substitution by coordination of an oxygen nucleophile, whereas silicon–fluoride is deactivated by coordination. One elegant explanation of this behaviour is derived mainly from the calculations of Gordon and coworkers.[11] The two axial ligands in a five-coordinate silicon complex share the electron density and the complexes with the strongest hypervalent bonds are those in which both ligands are from the same period (such as F and O). In complexes where the ligands are from different periods the more strongly bound ligand (from the lower period) tends to repel the other ligand so that the complex resembles an ion–dipole complex. This effect will activate bromide and chloride to attack by first period nucleophiles, such as NMI, HMPA and fluoride. Further experiments are in progress using related systems to probe the relationship between coordination and reactivity at silicon.

We thank the Dow Corning Corporation for generous financial support and Professor Mark Gordon for useful discussion.

Received, 17th November 1992; Com. 2/06126K

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