

Preliminary communication

A ^{29}Si , ^{13}C AND ^1H NMR STUDY OF THE INTERACTION OF VARIOUS HALOTRIMETHYLSILANES AND TRIMETHYLSILYL TRIFLATE WITH DIMETHYL FORMAMIDE AND ACETONITRILE. A COMMENT ON THE NUCLEOPHILE INDUCED RACEMISATION OF HALOSILANES.

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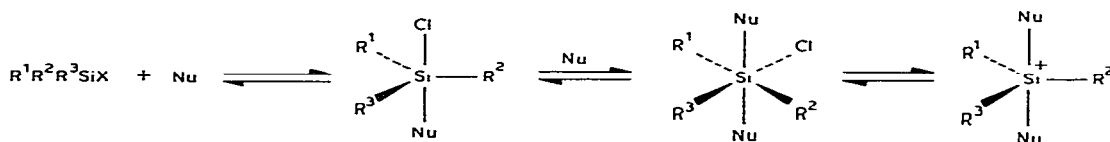
(Received August 19th, 1982)

Summary

The ^{29}Si , ^{13}C and ^1H NMR spectra of 1/1 mixtures of Me_3SiI and $\text{Me}_3\text{SiOSO}_2\text{CF}_3$ with DMF in CD_2Cl_2 show signals that are consistent with the formation of $\text{Me}_3\text{SiO}=\overset{\ominus}{\text{C}}\text{H}(\text{NMe}_2)\text{X}^-$ but not with penta- or hexa-coordinate silicon species. The spectra of a 1/1 mixture of Me_3SiBr and DMF show a rapidly exchanging, equilibrium mixture of $\text{Me}_3\text{SiO}=\overset{\ominus}{\text{C}}\text{H}(\text{NMe}_2)\text{Br}^-$ and starting materials. No strong evidence for salt formation between DMF and Me_3SiCl was obtained. The spectra of Me_3SiX ($\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{OSO}_2\text{CF}_3$) in CD_3CN indicate that neither adduct formation nor extra coordination at silicon is significant.

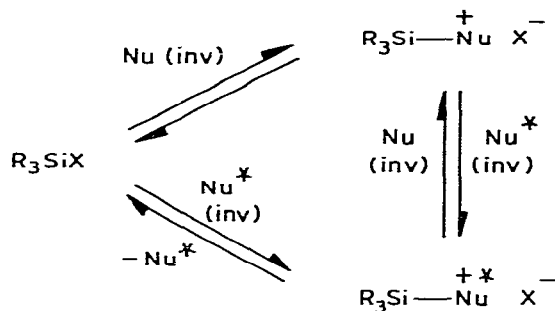
There is currently considerable debate concerning the role of added nucleophiles, such as HMPT, DMF, DMSO, R_3PO and CH_3CN , in the racemisation of chiral organosilanes [1—5] and in the nucleophilic substitution at silicon [6].

Two basic mechanisms have been postulated. The most widely accepted racemisation mechanism, deduced from kinetic and conductimetric studies is that proposed by Corriu [1]. This mechanism involves extension of coordination at silicon and is shown in Scheme 1.



SCHEME 1

An alternative racemisation mechanism, involving displacement of halide by the nucleophile has been proposed by Chojnowski [2] and is shown by Scheme 2. This mechanism is also compatible with the kinetic results and is based on the isolation of ionic adducts of Me_3SiBr and HMPT [2].



SCHEME 2

Corriu [1] has reported that the mechanism in Scheme 2 is a special case for labile SiBr bonds with good nucleophiles. In a detailed conductimetric study [1] he showed that 1/1 mixtures of DMF and Me_3SiBr in CD_2Cl_2 were non-conducting and concluded that this was *prima facie* evidence for the formation of molecular adducts with five (or six) coordinate silicon.

We undertook a preliminary study of the interaction of Me_3SiX ($\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{OSO}_2\text{CF}_3$) with DMF, and the weaker nucleophile CD_3CN , in CD_2Cl_2 , by NMR spectroscopy. ^{29}Si NMR spectroscopy is a particularly useful probe for coordination at silicon since the chemical shift range is large and highly indicative of coordination number [7].

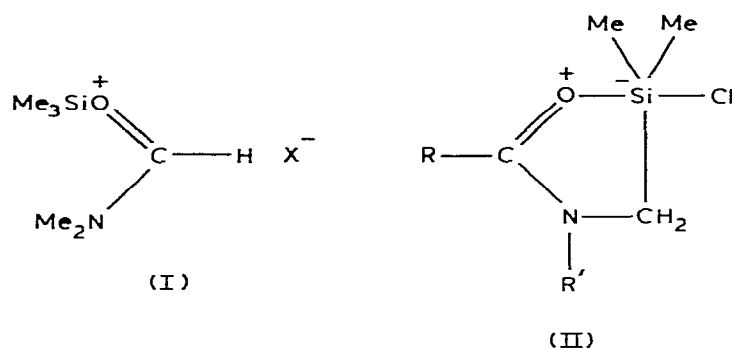
TABLE 1

NMR DATA FOR 1/1 MIXTURES OF Me_3SiX ($\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{OSO}_2\text{CF}_3$) AND DMF IN CD_2Cl_2

Compound(s) ^a	δ (^{29}Si) (ppm)	δ (^{13}C) (ppm)		δ (^1H) (ppm)	
		C=O	NMe	H-C=O	N-Me
HCONMe ₂	—	162.4	31.3, 36.4	8.01	2.87, 2.94
Me ₃ SiCl	30.5	—	—	—	—
Me ₃ SiCl/HCONMe ₂	31.05	162.3	31.2, 36.3	8.52	3.0, 3.25
Me ₃ SiCl/10 HCONMe ₂	31.37	162.4	31.3, 36.3	8.11	2.89, 2.92
Me ₃ SiBr	26.6	—	—	—	—
Me ₃ SiBr/HCONMe ₂	33.62	163.2	33.4, 38.5	8.85	3.0, 3.26
Me ₃ SiBr/10 HCONMe ₂	42.11	162.4	31.2, 36.4	8.18	2.87, 2.871, 3.05
Me ₃ SiI	10.6	—	—	—	—
Me ₃ SiI/HCONMe ₂	43.94	163.0	37.1, 42.0	9.35	3.3, 3.69
Me ₃ SiOSO ₂ CF ₃	44.27	—	—	—	—
Me ₃ SiOSO ₂ CF ₃ /HCONMe ₂	43.99	164.5	36.8, 42.2	9.45	3.2, 3.46
		-29.4(CD ₂ Cl ₂)			
		-33.0(CD ₃ CN)			

^a All spectra run on Jeol FX90Q at ambient temperatures with ca 2 M solutions and with internal TMS.

The ^{29}Si , ^{13}C and ^1H chemical shifts for 1/1 mixtures of Me_3SiX with DMF in CD_2Cl_2 solution are given in Table 1. We believe that the data in Table 1 are consistent with formation of I to a greater or lesser extent depending on X. As the ^{29}Si NMR signal for Me_3SiX ($\text{X} = \text{I}, \text{OSO}_2\text{CF}_3$) moves to high frequency an addition of equimolar quantities of DMF, reaction is taking place to give a four-coordinate Me_3SiY species bonded to a strongly electron-withdrawing group [7]. No stable five or six coordinate Me_3SiY_n ($n = 2$ or 3) complexes have been isolated or characterised but Yoder [8] has reported several five coordinate species (II). These serve as more than adequate models for the coordination of DMF with halosilanes. We prepared a complex II where $\text{R} = \text{R}' = \text{Me}$ [8] and its substantial low-frequency shifts in two solvents are reported in Table 1. Thus the high frequency shifts observed for DMF adducts are strongly indicative of four coordination at silicon. Further evidence for species I is gained from the observation that the ^{29}Si chemical shifts for $\text{Me}_3\text{SiX/DMF}$ approach the same value of ca. δ 44 ppm, independent of the counterion for $\text{X} = \text{I}, \text{Br}, \text{OSO}_2\text{CF}_3$. With bromide as counterion the equilibrium lies between I and reactants but is moved towards I by addition of excess DMF.



The DMF ^{13}C and ^1H resonances also shift to high frequency on the addition of Me_3SiX ($\text{X} = \text{I}, \text{Br}, \text{OSO}_2\text{CF}_3$) and are consistent with O-silylation, comparing closely with those obtained by Reynolds and McClelland [9] for O-protonation of DMF in aqueous solutions. From the spectroscopic data it is not possible to be unequivocal about the nature of the interaction between Me_3SiCl and DMF but the ^1H shifts to high frequency are indicative of a small equilibrium concentration of I ($\text{X} = \text{Cl}$).

We conclude that the ionic species I are formed for DMF and Me_3SiX ($\text{X} = \text{I}, \text{Br}, \text{OSO}_2\text{CF}_3$) and that the non-conductance of I ($\text{X} = \text{Br}$) observed by Corriu [1] is due to tight ion pairing in the relatively non polar CD_2Cl_2 .

As a probe for the possible intermediacy of species I in the racemisation of organohalosilanes, we briefly investigated the dynamic behaviour of I ($\text{X} = \text{I}$) with DMF and Me_3SiI . The NMR spectra of 0.5/1, 1.5/1 and 2/1 mixtures of Me_3SiI and DMF were measured, and the results given in Table 2.

When DMF is in a two-fold excess over Me_3SiI a very sharp signal is observed at δ 44 ppm, in the same position as the somewhat broadened signal for the 1/1 mixture. This confirms that the observed species cannot be $\text{Me}_3\text{Si}(\text{DMF})_2$.

TABLE 2

NMR SPECTRA OF MIXTURES OF Me₃SiI AND DMF IN CD₂Cl₂ WITH VARIOUS STOICHIOMETRIES

Ratio of Me ₃ SiI/DMF	δ (²⁹ Si) (ppm)	δ (¹³ C) (ppm)		δ (¹ H) (ppm)	
		C=O	NMe	H-C=O	NMe
0.5/1	44.0	163.1	35.7, 40.6	9.05	3.2, 3.5
1/1	44.0	163.0	37.1, 42.0	9.35	3.3, 3.69
1.5/1	no signal observed	163.0	37.1, 42.0	9.38	3.3(d), 3.68(d)
2.0/1	10.8	163.0	37.1, 42.0	9.38	3.3, 3.68

Additionally only one sharp set of ¹H and ¹³C NMR signals are observed showing that DMF exchange with I (X = I) is fast on the NMR time scale. Me₃SiI also exchanges with I (X = I) as shown by the broadening, disappearance and reappearance of the Me₃Si signal at δ 10.8 ppm as the ratio of Me₃SiI/DMF is increased from 1/1 to 2/1. These observations are consistent with the kinetic data [1,2] and with the observation of halide/halide exchange catalysed by nucleophiles [3].

Finally, we examined the ²⁹Si NMR spectra of Me₃SiX solutions in CD₃CN to look for evidence of salt formation or increased coordination at silicon. The results are given in Table 3.

TABLE 3

²⁹Si NMR CHEMICAL SHIFTS OF Me₃SiX IN CD₃CN ^a

Me ₃ SiX	δ (²⁹ Si) (ppm)	
Me ₃ SiCl	31.0	(30.05)
Me ₃ SiBr	28.7	(26.6)
Me ₃ SiI	12.1	(10.3)
Me ₃ SiOSO ₂ CF ₃	46.1	(44.3)

^a Values in CD₂Cl₂ in parentheses, ca. 0.5 M solutions, with internal TMS.

Although small high frequency shifts are observed in CD₃CN relative to CD₂Cl₂ these are not necessarily due to salt formation, and may be accounted for by increased Si-X bond polarisation (for example the ²⁹Si chemical shift of Me₃SiI is 8.29 ppm in the less polar CDCl₃). The only safe conclusion is that the major species in CD₃CN are the molecular Me₃SiX species, rather than salts, or species involving extended coordination at silicon.

In conclusion, we suggest that our data show that the Chojnowski mechanism [2] merits serious consideration, although the present results are uninformative about the role of weak nucleophiles such as CD₃CN.

We are continuing these studies with different silanes and nucleophiles, and also R₃SnX compounds where extracoordination is a serious possibility, even with labile stannanes.

Acknowledgments. We thank the Open University for support of T. Stout, and Gordon Howell for assistance with some of the NMR spectra.

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