Journal of Organometallic Chemistry, 446 (1993) C3–C5

JOM 23173PC

Preliminary Communication

The effect of pentacoordination on silicon-29 NMR chemical shifts and silicon–hydrogen coupling constants *

Alan R. Bassindale and Jianxiong Jiang

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

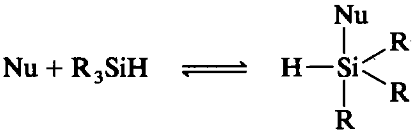
(Received August 21, 1992)

Abstract

The coordination of R_3SiH compounds with a nucleophile, Nu, to give the adduct $R_3SiH \cdot Nu$ produces changes in the ^{29}Si NMR chemical shift and ^1J(SiH) that follow similar trends. Coordination of highly electronegative, 'soft', ligands is accompanied by the strongest low frequency shifts and the greatest increase in ^1J(SiH). Formal coordination of 'hard' electropositive ligands such as methyl can result in high frequency shifts and a decrease in ^1J(SiH). The ^{29}Si NMR chemical shift range for the pentacoordinate neutral, anionic and cationic adducts is about δ −110 to −47 ppm, whereas the range for the related four-coordinate silanes is greater at δ +24 to −76 ppm.

The silicon–hydrogen bond in pentacoordinate complexes has an enhanced reactivity compared with the equivalent bond in the related tetracoordinate compounds, as has been convincingly demonstrated by Corriu and others [1–6]. The active hydrogen is normally expected to be in an equatorial position in trigonal bipyramidal complexes [7]. We are interested in pentacoordinate silicon hydrides as intermediates, or models for intermediates, in nucleophilic substitutions at silicon, and, with varying ligands around silicon, as potentially 'tunable' reducing agents. Most of the species in which we have an interest are only available in solution and are not therefore susceptible to definitive structure determination by X-ray crystallography. Alternative methods must be used, of which ^{29}Si NMR is by far the most useful [8], but there are rather few examples of pentacoordinate silicon hydrides for which ^1J(SiH) and $\delta(^{29}\mathrm{Si})$ have been reported.

In this preliminary study, the effect of coordination on ^1J(SiH) and $\delta(^{29}\mathrm{Si})$ has been established for some reactions of the type shown in eqn. (1).



$$\mathrm{Nu} + \mathrm{R_3SiH} \rightleftharpoons \mathrm{H{-}Si(Nu)(R)_3} \qquad (1)$$

Eight new complexes have been formed in solution by the addition of an equimolar amount of nucleophile to an electrophilic silane. In the examples reported here (Table 1) there is overwhelming evidence for a simple extension of coordination by complexation with one molar equivalent of nucleophile. The observations leading to the conclusion that eqn. (1), with the equilibrium far to the right, is an accurate description of the reactions are:

- The solutions of neutral nucleophiles with neutral silanes at 1 : 1 stoichiometry do not conduct electricity, but in most cases the conductivity rises sharply as the ratio of nucleophile to silane increases beyond 1 : 1;
- The ^{29}Si NMR spectra of the 1 : 1 mixtures are concentration independent and have the same coupling constants and chemical shifts at 25°C and −60°C;
- As the amount of nucleophile is increased in a series of aliquots, *either* the ^{29}Si NMR chemical shift of the mixture changes monotonically up to a 1 : 1 ratio followed by a discontinuity as further species are produced, *or* the starting silyl hydride and the new species can both be observed up to a 1 : 1 ratio, where only the signal from the new species is observed;
- With HMPA the direct coordination of one molecule to the silane is proven by the observation of a doublet in the ^{29}Si NMR spectrum resulting from P–Si coupling;
- The ^{29}Si NMR signals of the new species are shifted to low frequency in accordance with previous observations [8,9].

Other reactions, including substitution reactions and equilibrium with hexacoordinate complexes would not exhibit the kind of behaviour described above. In this communication only reactions that satisfy all of the appropriate observations are included.

Table 1 gives the ^{29}Si NMR chemical shifts and ^1J(SiH) for the new complexes. (The coupling constants have a negative sign but are reported as measured, which is as a difference between two resonances.) There is no direct relationship between $\delta(^{29}\mathrm{Si})$ and

---

Correspondence to: Dr. A.R. Bassindale.

* Dedicated to Professor M.G. Voronkov in recognition of his distinguished contributions to organosilicon chemistry.

0022-328X/93/$6.00

TABLE 1. ^{29}Si Chemical shift and coupling constant data for some pentacoordinate complexes

R_3SiH	Nucleophile	$R_3SiH \cdot Nu$	δ/ppm [a]	J(SiH)/Hz	$\Delta\delta$/ppm [b]	ΔJ/Hz [c]	Ref.
$MeHSi(OTf)_2$	–		−9	306			
	TfO^-	$MeHSi(OTf)_3^-$	−67	351	−58	+44	[d]
	NMI [e]	$MeHSi(OTf)_2 \cdot NMI$	−52	331	−47	+25	[d]
	HMPA [e]	$MeHSi(OTf)_2 \cdot HMPA$	−61 [f]	346	−52	+46	[d]
	DMPU [e]	$MeHSi(OTf)_2 \cdot DMPU$	−68	354	−59	+48	[d]
$HSi(OTf)_3$	–		−76	416			
	Me^-	$MeHSi(OTf)_3^-$	−67	351	+9	−65	[d]
$MeHSi(HMPA)_2^{2+}$			−23 [g]	300			
	HMPA	$MeHSi(HMPA)_3^{2+}$	−72	327	−49	+27	[d]
$PhHSi(OTf)_2$	–		−28	323			
	NMI	$PhHSi(OTf)_2 \cdot NMI$	−89	372	−61	+49	[d]
	DMPU	$PhHSi(OTf)_2 \cdot DMPU$	−93	338	−65	+15	[d]
	HMPA	$PhHSi(OTf)_2 \cdot HMPA$	−83	345	−55	+22	[d]
H_3SiOTf	–		−23	254			
	Et_3N	$H_3SiOTf \cdot NEt_3$	−74	267	−51	+13	13
$HSiOEt_3$	–		−59	285			
	EtO^-	$HSi(OEt)_4^-$	−88	223	−29	−62	14
	H^-	$H_2Si(OEt)_3^-$	−81	218	−22	−67	5
$HSiOPh_3$	–		−71	320			
	PhO^-	$HSi(OPh)_4^-$	−112	296	−41	−24	14
$HSiO^iPr_3$	–		−63	285			
	$^iPrO^-$	$HSi(O^iPr)_4^-$	−91	214	−28	−71	14
	H^-	$H_2Si(O^iPr)_3^-$	−87	210	−24	−75	5

[a] Solvent $CD_3CN/CDCl_3$. [b] $\Delta\delta = \delta$(pentacoordinate) − δ(tetracoordinate). [c] $\Delta J = J$(pentacoordinate) − J(tetracoordinate). [d] This work. [e] NMI, 1-methylimidazole; HMPA, hexamethylphosphoramide; DMPU, dimethylpropyleneurea. [f] Doublet, J(SiP) = 4.4 Hz. [g] Triplet, J(SiP) = 4.5 Hz.

^1J(SiH); a plot of $\delta(^{29}Si)$ *versus* ^1J(SiH) consists of an essentially random distribution of points. The only discernable trend is that complexes with the greatest number of electron-withdrawing ligands, such as triflate and coordinated HMPA and NMI, have the largest ^1J(SiH) coupling constants. This observation is directly comparable with that for the four-coordinate silanes for which various theoretical and semi-empirical correlations have been attempted, and where the best correlations are with electronegativities or related parameters such as Taft polar constants [10–12]. The Si–H coupling constant for four-coordinate compounds has been related successfully to indices of reactivity such as Hammett constants, but much more data and a sophisticated data treatment will be required before chemically useful information can be extracted from J(SiH) for pentacoordinate complexes.

Table 1 also lists the change in ^{29}Si NMR chemical shift, $\Delta\delta$, and ^1J(SiH), ΔJ, on coordination. These latter values are either the actual values as measured for eqn. (1), or extrapolated values for hypothetical reactions. For example, $MeHSi(OTf)_3^-$ was made by coordination of the triflate anion with $MeHSi(OTf)_2$, giving rise to the $\Delta\delta$ and ΔJ values shown in Table 1. The same complex could conceivably be made from Me^- and $HSi(OTf)_3$, with different values of $\Delta\delta$ and ΔJ. These new values are valid for examining the effects of coordination on chemical shifts and coupling constants as they simply represent a different route to the same product. The changes in chemical shift and

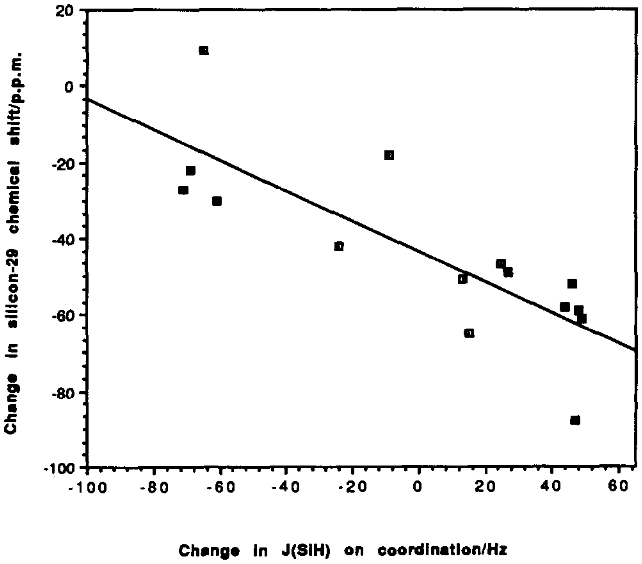


Fig. 1. A plot of the changes in chemical shift and one-bond silicon–hydrogen coupling constants of a four-coordinate silane on coordination of a nucleophile.

coupling constant were quantified to see whether there were any consistent trends that might help further in assigning coordination number changes in mixtures of silanes and nucleophiles in solution. Figure 1 shows the plot of $\Delta\delta$ against ΔJ for the fifteen reactions given in Table 1.

There is a convincing, if not close, correlation ($R^2 = 0.75$) between the change in ^{29}Si NMR chemical shift on coordination and the change in the one-bond silicon–hydrogen coupling constant. The change in electron density at the silicon nucleus is possibly a significant factor. The chemical shift for four-coordinate silicon bearing several strongly electron withdrawing groups is very closely related to the sum of the group electronegativities [11] and, as already mentioned, coupling constants are also affected by changes in electron demands at the nucleus. Quantum-chemical calculations by Voronkov and his coworkers [15] showed that the positive charge on the central silicon increases on coordination of nucleophiles and this serves to rationalize the changes shown in Fig. 1. Coordination of strongly electron withdrawing, soft nucleophiles causes large low frequency changes to the ^{29}Si NMR chemical shift and a significant increase in the magnitude of the Si–H coupling constant. On the other hand harder, less electron withdrawing nucleophiles, such as alkoxides and hydride cause low field shifts but the coupling constant magnitude decreases. There are not yet sufficient data to enable a detailed analysis to be made of the NMR parameters of pentacoordinate silanes but this initial study suggests that they are determined by factors as complex and elusive as those for the four-coordinate compounds.

References

1 J. Boyer, C. Breliere, R. J. P. Corriu, A. Kpoton, M. Poirier and G. Royo, *J. Organomet. Chem.*, *311* (1969) C39.
2 M. Kira, K. Sato and H. Sakurai, J. Org. Chem., 52 (1987) 949.
3 R. J. P. Corriu, G. F. Lanneau and M. Perrot, *Tetrahedron Lett.*, *29* (1988) 1271.
4 R. Corriu, G. Guerin, B. Henner and Q. Wang, *J. Organomet. Chem.*, *365* (1989) C7.
5 B. Becker, R. J. P. Corriu, C. Guerin, B. Henner and Q. Wang, *J. Organomet. Chem.*, *368* (1989) C25.
6 S. K. Chopra and J. C. Martin, *J. Am. Chem. Soc.*, *112* (1990) 5342.
7 C. Breliere, F. Care, R. J. P. Corriu, M. Poirier and G. Royo, *Organometallics*, *5* (1986) 388.
8 B. J. Helmer, R. West, R. J. P. Corriu, M. Poirier, G. Royo and A. De Saxe, *J. Organomet. Chem.*, *251* (1983) 295.
9 A. R. Bassindale and T. Stout, *J. Chem. Soc., Chem. Commun.*, (1984) 1387.
10 J. Schraml and J. M. Bellama, ^{29}Si-nuclear magnetic resonance, in *Determination of organic structures by physical methods*, Vol 6, Academic Press, New York, 1976.
11 H. Marsmann, ^{29}Si-NMR Spectroscopic Results, in *NMR* Vol. 17, Springer-Verlag, New York, 1981.
12 E. A. Williams, NMR Spectroscopy of organosilicon compounds, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, 1989.
13 A. R. Bassindale and T. Stout, *J. Organomet. Chem.*, *271* (1984) C1.
14 B. Becker, R. Corriu, C. Guerin, B. Henner and Q. Wang, *J. Organomet. Chem.*, *359* (1989) C33.
15 Yu. L. Frolov, S. G. Shevchenko and M. G. Voronkov, *J. Organomet. Chem.*, *292* (1985) 159.