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HYDROGENOSILANES: PENTACOORDINATION AND PSEUDOROTATION

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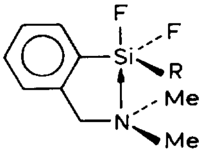
Summary

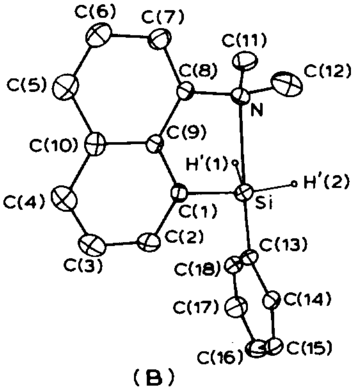
A ^1H NMR study of pentacoordinated trihydrogenosilanes shows that there is only a very low energy barrier to isomerisation by pseudorotation at silicon.

In contrast, this process is not detected over a large range of temperature for dihydrogeno silanes. The Si–H bond has a high equatorial preference which stabilises the geometry of the trigonal bipyramidal structures.

Pseudorotation at silicon has been established by Martin et al. [1] in pentacoordinate siliconate compounds and by us [2] in the case of compounds **A**, which are good models for the intermediates involved in nucleophilic substitution.



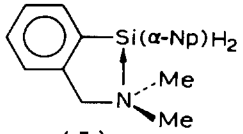
(A: R = F, Me)



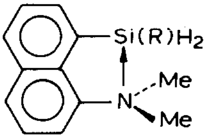
(B)

In the case of hydrogenosilanes, such as **B**, the coordination of the nitrogen atom takes place at the apical position with the Si–H bond in the equatorial position [3], in good agreement with retention of configuration observed in nucleophilic displacements at Si–H bonds [4].

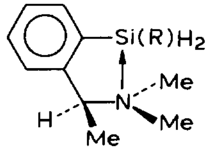
This paper is devoted to the study of the geometry and pseudorotation of the dihydrogeno- and trihydrogenosilanes I–IV.



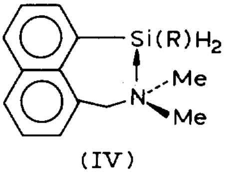
(I)



(IIIa: R = Ph;
IIIb: R = H)



(IIa: R = α-Np;
IIb: R = H)



(IV)

Dihydrogenosilanes, I, IIa, IIIa and IVa

For compound I, the formation of an intramolecular N → Si bond (as revealed by ^{29}Si NMR data) does not induce diastereotopy in the NMe_2 group even down to −100°C in the ^1H NMR spectra (Table 1). Similarly for IIIa, no diastereotopy can be detected in the NMe_2 group by ^1H NMR at low temperature, but the existence of N → Si coordination has been confirmed by X-ray investigation [3]; the X-ray study shows the trigonal bipyramidal complex to have a plane of symmetry, which accounts for the observed equivalence of the NMe_2 protons. However, it was conceivable that in solution a fast equilibration process, e.g. pseudorotation, is responsible for this equivalence, and thus it was necessary to verify whether such a process does occur.

A study of compounds IIa and IVa has enabled us to resolve this problem. For IIa, the chirality at the benzylic position can induce diastereotopy in the *N*-methyl group independently of possible isomerisation at silicon. This diastereotopy is detectable by ^1H NMR and can be used as a probe for N → Si coordination.

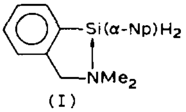
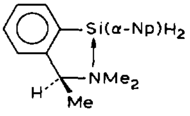
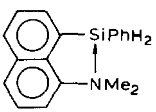
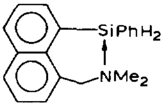
The dihydrogenosilane IIa shows interesting ^1H NMR behaviour at low temperature. The prochilarity of the two hydrogen atoms attached to silicon is observable below −20°C, and the *N*-methyl groups become diastereotopic below −72°C. Over the temperature range −20°C to −100°C, the AB spectrum for the SiH_2 group is slightly displaced but not modified (Table 1).

For IVa the ^1H NMR spectra show diastereotopism of the NMe_2 group, the benzylic protons and two Si–H signals. The $\Delta G^\star$ values, calculated at the coalescence temperature for SiH_2, benzylic CH_2 and $N(CH_3)_2$ signals are the same ($\Delta G^\star$ 10.2 kcal mol^{-1}). In accord with the X-ray results [3], we can assume that IVa has a structure in which the two hydrogen atoms occupy equatorial positions and the phenyl group the apical position.

From these results we can draw the following conclusions for the structures of the dihydrogenosilanes: (i) Intramolecular N → Si coordination occurs, confirming previous ^{29}Si NMR results [5] and in line with X-ray structures [3]. (ii) Pseudorotation does not take place in the case of compounds IIa and IVa since a doublet ^1H NMR

TABLE 1

^{1}H NMR DATA FOR DIHYDROGENOSILANES [a]

Compounds	T (°C)	$\delta(SiH_2)$ (ppm)	$\delta(NMe_2)$ (ppm)
 (I)	+20	5.14(s)	2.10(s)
	−100	5.18(s)	2.00(s)
 (IIa)	+20	5.15(s)	2.15(s)
	−100	5.12, 5.02(d)	2.00, 2.40(d)
		$\Delta G^\star$ 9.7 kcal mol^{-1}	
 (IIIa)	+20	5.30(s)	2.24(s)
	−100	5.38(s)	2.10(s)
 (IVa)	+20	4.95(s)	1.98(s)
	−100	4.86, 4.76(d)	1.70, 2.20(d)
		$\Delta G^\star$ 10.2 kcal mol^{-1} [b]	

[a] Chemical shifts were measured on a Varian EM 390 apparatus (^{1}H) in $CDCl_3$ or CD_2Cl_2 using TMS as internal reference. [b] The $\Delta G^\star$ values calculated at the coalescence temperature from SiH_2, benzylic CH_2 and NMe_2 signals are the same.

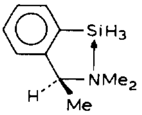
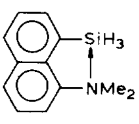
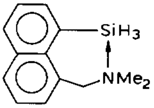
signal is observed for the SiH_2 protons at low temperature. In this case, the pseudorotation process has a higher $\Delta G^\star$ value than the N → Si bond breaking process ($\Delta G^\star > 10$ kcal mol^{-1}). (iii) The Si–H bond in trigonal bipyramidal complexes always occupies an equatorial position both in solution and in the solid.

Trihydrogenosilanes IIb, IIIb and IVb

Intramolecular N → Si coordination is geometrically very favourable in the trihydrogenosilane IIIb. For the silanes IIb and IVb, similar N → Si coordination occurs at low temperature. For the closed forms of each silane (IIb, IIIb and IVb) it is not possible to distinguish the chemical shifts of the potentially non-equivalent SiH_3 hydrogen atoms. The ^{1}H NMR signal of the SiH_3 group remains a singlet down to −100°C in each case (Table 2). We attribute this equivalence to a rapid pseudorotation at silicon via a Berry or turnstile process in accord with our previous studies on analogous fluorosilyl compounds [2].

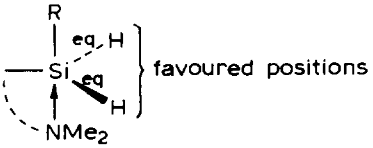
TABLE 2

^{1}H NMR DATA FOR TRIHYDROGENOSILANES [a]

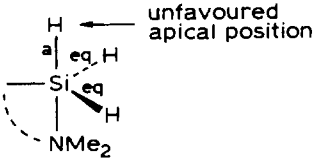
Compounds	T (°C)	$\delta(SiH_3)$ (ppm)	$\delta(NMe_2)$ (ppm)
 (IIb)	+20	4.14(s)	2.07(s)
	−100	4.14(s)	1.35, 2.24(d)
		$\Delta G^\star$ 10 kcal mol^{-1}	
 (IIIb)	+20	4.44(s)	2.58(s)
	−100	4.40(s)	2.50(s)
 (IVb)	+20	4.44(s)	2.03(s)
	−100	4.44(s)	1.76, 2.25(d)
		$\Delta G^\star$ 10.5 kcal mol^{-1} [b]	

[a] Chemical shifts were measured on a VARIAN EM 390 apparatus (^{1}H) in $CDCl_3$ or CD_2Cl_2 using TMS as internal reference. [b] The $\Delta G^\star$ values calculated at the coalescence temperature from benzylic CH_2 and NMe_2 signals are respectively 10.5 and 10.8 kcal mol^{-1}.

The marked difference in behaviour between the dihydro- and trihydrogeno-silanes occurs because of the high affinity of SiH bond for equatorial position. In the dihydrogeno species both hydrogen atoms occupy the preferred equatorial position which confers additional stability on the trigonal bipyramidal structure. In consequence the pseudorotation process has a relatively high $\Delta G^\star$ value (> 10 kcal mol^{-1}).



In contrast, the trihydrogenosilanes always have one hydrogen atom in the apical position and two hydrogen atoms in the favoured equatorial positions. Exchange between these three positions explains why pseudorotation with a low energy barrier ($\ll 7$ kcal mol^{-1}) is observed in these systems.



The results reported in this paper confirm the very high equatorial preference of the Si–H bond in trigonal bipyramidal complexes [2].

Acknowledgement

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