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^{29}Si NMR OF PENTACOORDINATE SILICON DERIVATIVES

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Summary

^{29}Si NMR is useful as a direct probe for intramolecular pentacoordination in the compounds o-(Me_2NCH_2)C_6H_4SiXYZ. The temperature dependence of chemical shifts indicates the existence of an equilibrium between tetra- and penta-coordinate forms. α-Np[o-Me_2NCH_2)]$C_6H_4SiH_2$ proves to be the first silicon derivative without halogen or chalcogen to show intramolecular pentacoordination. This coordination may account for the reactivity of the Si–H bond in this compound.

Stable pentacoordinate silicon compounds serve as models for the study of nucleophilic attack and of isomerization at silicon [1,2]. In compounds of the type o-(Me_2NCH_2)C_6H_4SiXYZ, the aminoaryl substituent can provide intramolecular pentacoordination, while allowing for a range of substituents at silicon. These compounds are believed to exhibit trigonal bipyramidal geometry similar to that in related germanium and tin compounds [3,4].

The presence of $N \rightarrow Si$ coordination in the series of compounds has been detected from their ^{1}H NMR spectra in which the N–Me_2 groups become diastereotopic at low temperature [5]. The tendency towards pentacoordination was found to be dependent on substitution at silicon, with X = Br, Cl, OAc > SR, F; no coordination was observed for X = H or OR. This ordering of substituents is the same as that observed for the amount of inversion of configuration upon substitution, and for the rate of racemization, of Si–X compounds [5].

^{1}H NMR is effective in proving the existence of complexes which exchange slowly enough to be observed on the NMR time scale. However if freezing out of diastereotopic signals does not occur, the method does not distinguish between rapid exchange and the absence of pentacoordination. It is therefore desirable to find out if a rapid equilibrium exists between closed and open forms of the complex (eq. 1).

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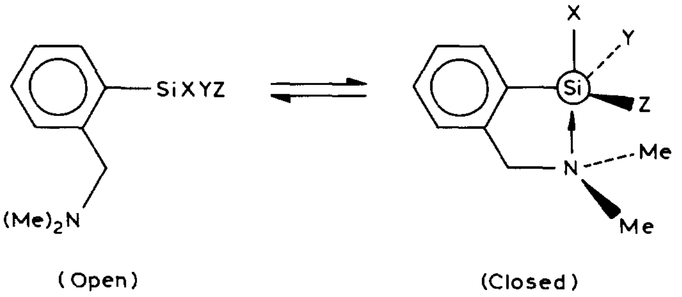
^{29}Si NMR provides a method to determine both the presence of pentacoordination and the position of such an equilibrium.



(1)

We have studied this system using variable temperature ^{29}Si NMR. Tetra- and penta-coordinate silicon centers are known to differ significantly in their ^{29}Si resonance frequencies [6,7]. The chemical shift of the open form of ArSiXYX (Ar = *o*-(Me_2NCH_2)C_6H_4) should be closely approximated by that of PhSiXYZ. As the temperature is lowered the equilibrium should shift towards the coordinated form with a concomitant upfield shift of the ^{29}Si resonance. The temperature dependent ^{29}Si NMR chemical shifts for the aryl- and phenyl-silanes studied are recorded in Table 1.

For compounds **7a–10a**, which have X = Y = Z = Me or OR, the ^{29}Si chemical shifts are essentially unchanged from those of the reference compounds **7b–10b**. We conclude that no N → Si coordination takes place in these compounds. The surpris-

TABLE 1

^{29}Si NMR CHEMICAL SHIFTS OF Ar vs. Ph SUBSTITUTED SILANES (ppm) [a]

		60°C	30°C	0°C	−30°C	−60°C	Δ_0	K_{30}
$ArMeSiF_2$	**(1a)**	−38.60	−40.82	−43.04	−46.22	−49.23	47.2	1.6
$PhMeSiF_2$	**(1b)**	−12.27	−12.07	−11.90	−11.70	−11.40		
ArMeSiHF	**(2a)**	−33.98	−36.13	−38.30	−41.29	−43.96	62.6	2.5
PhMeSiHF	**(2b)**	–	8.58	–	8.97	–		
Ar_2SiF_2	**(3a)**	−51.48	−52.95	−54.65	−57.02	−59.62	46.7	1.0
Ph_2SiF_2	**(3b)**	−29.65	−29.57	−29.46	−29.33	−29.23		
$ArSiF_3$	**(4a)**	−101.47	−102.27	−103.21	−103.96	−104.86	32.1	8.1
$PhSiF_3$	**(4b)**	−72.83	−72.86	−72.92	−72.97	−73.14		
ArNpSiHCl	**(5a)**	−55.01	−57.59	−60.61	−63.63	−66.29	67.5	3.4
PhNpSiHCl	**(5b**	−5.65	−5.56	−5.47	−5.38	−5.29		
$ArNpSiH_2$	**(6a)**	−46.39	−47.25	−48.18	−49.45	−50.77	20.2	1.4
$PhNpSiH_2$	**(6b)**	−35.74	−35.63	−35.52	−35.40	−35.28		
$ArSi(OMe)_3$	**(7a)**	−54.28	−53.99	−53.79	−53.60	−53.45		
$PhSi(OMe)_3$	**(7b)**	–	−54.56	–	−53.85	–		
$ArSi(OEt)_3$	**(8a)**	−57.60	−57.17	−56.73	−56.30	−55.84		
$PhSi(OEt)_3$	**(8b)**	–	−57.76	–	−56.69	–		
$ArMeSi(OEt)_2$	**(9a)**	−18.40	−18.19	−18.00	−17.93	−17.86		
$PhMeSi(OEt)_2$	**(9b)**	–	−17.94	–	−17.20	–		
$ArSiMe_3$	**(10a)**	−4.85	−4.89	−4.92	−4.94	−4.96		
$PhSiMe_3$	**(10b)**	–	−4.11	–	−4.06	–		

[a] All samples were approx, 10% in $CDCl_3$, with shifts reported relative to internal TMS.

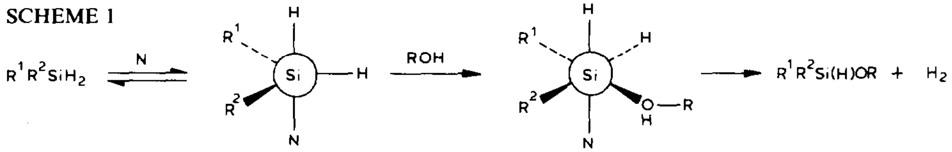
ing lack of coordination in the alkoxy compounds **7a–9a** is consistent with the results of ^{1}H NMR studies of **9a**, and has been ascribed to the inability of the Si–OR bond to undergo stretching [5]. The results for these compounds could also be rationalized as due to competitive back-bonding by lone pairs on oxygen. Data for these pairs of compounds (**7a,b–10a,b**) also show that the presence of an *o*-CH_2NMe_2 group has little effect on the ^{29}Si chemical shift when coordination does not occur; that is, there are no significant steric or electronic effects of the *ortho* group on the ^{29}Si resonance which might mask the effects of coordination.

In those compounds which contain halogen bonded to silicon (**1–5**), significant differences are found between the ^{29}Si chemical shifts for each pair of compounds, with the compounds containing the *o*-CH_2NMe group showing upfield shifts of 23 to 52 ppm. This finding indicates N → Si coordination in these compounds as concluded from earlier studies of ^{1}H and ^{19}F NMR for the same substances [4,5].

The dihydrogen compound $ArNpSiH_2$ (**6a**) shows a significant upfield shift compared to its reference compound **6b** of 14 ppm at 30°C. The ^{29}Si NMR experiment therefore provides evidence for N → Si coordination in this compound, which was not detected in earlier ^{1}H NMR measurements. Compound **6a** is the first organosilane without halogen or chalcogen substitution to show intramolecular pentacoordination. This may be due to minimized steric and electronic repulsion between the hydrogens and the approaching nucleophile.

The intramolecular coordination found for **6a** is accompanied by enhanced reactivity for this compound compared to **6b**. For example, alcohols and organic acids react under moderate conditions with **6a**, but not **6b**, to give mono- or di-substitution products. This high reactivity associated with intramolecular coordination supports the earlier hypothesis that the Si–H bond is activated toward substitution by coordinative expansion of the silicon atom [8], as shown in Scheme 1.

SCHEME 1



The temperature dependence of the chemical shifts in Table 1 provides evidence for equilibrium between the open and closed forms in solution (eq. 1). All of the compounds in which N → Si coordination occurs (**1a–6a**) show upfield shifts of the ^{29}Si resonance as the temperature is decreased, consistent with the shifting of equilibrium toward the coordinated form. A single resonance was observed at all temperatures, indicative of rapid equilibrium on the NMR time scale ($k > 4000$ sec^{-1}). The noncoordinating compounds **1b–10b** and **7a–10a** show only very small downfield shifts (< 1 ppm) upon cooling from +60 to −60°C.

From an analysis of the temperature dependence of the ^{29}Si NMR data, a value was calculated for Δ_0, the chemical shift difference between the open and closed forms [9]. This difference has been correlated with N–Si bond length in compounds of the type $Ar_2Si(OCH_2CH_2)_2NR$ [10]. The relationship of Δ_0 to complexing ability is also indicated in the current study, since the sequence $ArNpSiHCl > ArMeSiHF > ArMeSiF_2 \gg ArNpSiH_2$ is the same for Δ_0 and for $\Delta G^{\ddagger}$ from ^{1}H-NMR. Values for the equilibrium constants, K_{30} = [closed]/[open], were also calculated in Table 1; these values indicate that substantial amounts of both closed and open forms are present at this temperature.

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