^{29}Si NMR OF FIVE- AND SIX-COORDINATE ORGANOSILICON COMPLEXES

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Summary

Silicon-29 NMR is shown to be powerful tool for characterizing five- and six-coordinate organosilicon complexes. Chemical shifts for twenty seven compounds are given, and the general trends with structural changes are discussed.

The possibility of valence shell expansion is one reason for the often marked differences in chemical behavior between silicon and carbon. The valence expansion for silicon leads to compounds (and proposed reaction intermediates) in which the coordination number of silicon rises above four. Stable five- and six-coordinate silicon compounds result only when the silicon atom is bonded to highly electronegative atoms like fluorine, chlorine, oxygen or nitrogen. A well-known example of this is the fluorosilicate anion SiF_6^{2-} in which the fluorines are located in octahedral array about silicon. Other negatively charged hexacoordinate and pentacoordinate complexes are known including the catecholates [1] and diolates [2]. Cationic and neutral complexes are also known in which silicon is penta- and hexa-coordinate. For example, tris(acetylacetonato)silicon (IV) chloride hydrochloride was first prepared by Dilthey [3] in 1903. Since that time a number of structurally related cationic hexacoordinate tris(1,3-dicarbonyl) and tropolonato chelates have been prepared and characterized [4,5]. Several pentacoordinate cationic silicon chelates have recently been described [6] as well as some neutral bis(1,3-dicarbonyl)diacyloxy complexes [7].

Earlier characterization of these five- and six-coordinate compounds had centered largely around crystalline forms. Other characterization work depended extensively on elemental analysis, and differences in IR and UV spectra compared to typical tetravalent silicon compounds [8]. ^{29}Si NMR offers a unique method for characterizing these complexes since their chemical shifts generally appear at much higher field than the normal range (+45 to —135 ppm, positive

values downfield from Me$_4$Si) found for most tetravalent silicon compounds [9]. For example, a shielding effect of ca. 20 ppm of the ^{29}Si resonance in silatranes relative to the corresponding triethoxysilanes has been attributed to pentacoordination in the silatranes [10]. Several known and a number of new [11] five- and six-coordinate silicon complexes have been prepared and characterized and their ^{29}Si NMR chemical shifts determined. The chemical shift data are presented in Table 1. All ^{29}Si spectra were obtained on a Varian XL-100-15 NMR spectrometer operating in the Fourier transform (FT) mode at 19.9 MHz for ^{29}Si. Samples were run under complete proton decoupling conditions using deuterated solvents for field/frequency control. Spectral windows of 5000 Hz (8192 data points) and pulse widths of 75 μs (45° flip angle) were used. The samples were doped with ca. 0.1 M tris(acetylacetonato)chromium [Cr(acac)$_3$] to shorten the ^{29}Si T$_1$'s and enable pulse repetition times of 0.8 s to be used. Samples were prepared as concentrated as possible. No effect of solvent, Cr(acac)$_3$ or concentration on the ^{29}Si chemical shift was noted.

Although there are too many gaps in structural types to enable any predictable correlation between structure and chemical shift to be made, a number of trends are apparent, particularly among the cationic complexes. For example, hexacoordinate cationic and neutral complexes in which the chelate ring is derived from a 1,3-diketone and all ligands are attached through oxygen, display nearly identical chemical shifts regardless of charge type of the 1,3-dicarbonyl compound (1—12, 15, 16). The chelate derived from a ketoester (13), however, is shifted downfield slightly (approximately 4 ppm).

Different chemical shifts are also observed for those complexes in which the chelate ring is 5-membered (14, 19—22, 24—27). For those samples in which the analogous diketone and tropolone complexes are available, the tropolonato derivatives appear at much lower field (compare 1 with 14, and 18 with 20). It is interesting to note that the cationic and anionic hexacoordinate complexes 14, 24 and 25 have essentially the same chemical shift regardless of which ligand, catechol or tropolone, is attached. The analogous pentacoordinate complexes, 20 and 27, differ by 50 ppm, however, with the catechol derivative at lower field. Confirmation that 27 remained intact in solution (1,1,2,2-tetrachloroethane-d_2) was obtained from the ^{13}C spectrum which showed only resonances arising from the chelated catechol ring (149.4, 118.9, 110.6 ppm relative to Me$_4$Si), the phenyl ring (139.8, 134.6, 128.7, 127.2 ppm) and the triethylammonium group (46.3, 8.2 ppm). It has been suggested [13] that similarities in chemical shift among the hexacoordinate complexes is due to the symmetry of distribution of the ligands in these compounds which effectively cancels any charge on the central atom. These symmetry effects disappear in the pentacoordinate complexes which should have a definite dipole moment. This concept is supported by the substantial chemical shift differences observed between the anionic catechol and cationic tropolone pentacoordinate derivatives (19—22 and 27).
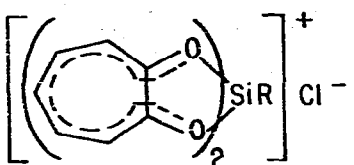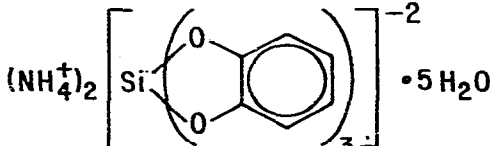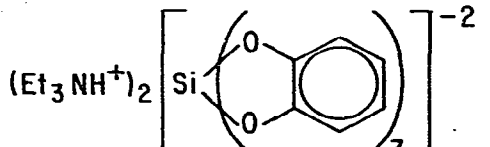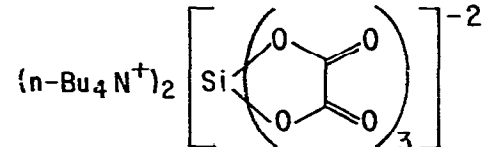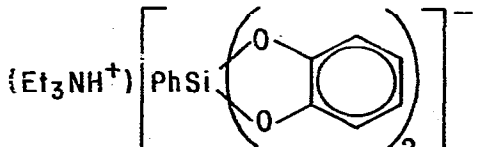
The chemical shift of the cationic pentacoordinate tropolonates is clearly affected by the nature of the non-chelating group. Those tropolone complexes in which the silicon atom is bonded to sp^2 hybridized carbon in R (19 and 20) are shielded by ca. 13 ppm relative to the alkyl derivatives (21 and 23). This trend is identical to that observed for the tetravalent series, (Me$_3$SiO)$_3$Si$^+$R

TABLE 1

SILICON-29 CHEMICAL SHIFTS OF PENTA- AND HEXACOORDINATE SILICON COMPLEXES

Compound				δ Si[a]	Solvent

Cationic Hexacoordinate

	R^1	R^2	R^3	X^-		
1	Me	H	Me	HCl_2^-	−194.4	$CDCl_3$
2	Me	H	Me	$ZnCl_3^-$	−193.7	DMSO-d_6
3	Ph	H	Ph	SbF_6^-	−191.4	Acetone-d_6
4	Ph	H	Me	HCl_2^-	−192.4	DMSO-d_6
5	Me	Me	Me	HCl_2^-	−195.7	Acetone-d_6
6	Me	Ph	Me	HCl_2^-	−195.3	Acetone-d_6
7	Me	Cl	Me	HCl_2^-	−196.4	Acetone-d_6
8	$-CH_2(CH_2)_2CH_2-$		Me	HCl_2^-	−195.0	DMSO-d_6
9	$-CH_2CH_2CH_2-$		Me	HCl_2^-	−191.2	Acetone-d_6
10	t-Bu	H	t-Bu	HCl_2^-	−193.8	$CDCl_3$
11	Me	2,4-dinitrophenyl	Me	SbF_6^-	−195.9	DMSO-d_6
12	Me	$\overset{O}{\underset{\parallel}{C}}CH_3$	Me	HCl_2^-	−197.2	$CDCl_3$
13	EtO	H	Ph	HCl_2^-	−187.9	Acetone-d_6

14		−139.4 CD_3OD

Neutral Hexacoordinate

	R^1	R^2	X	Y		
15	Me	Me	OAc	OAc	−196.8	DMSO-d_6
16	Ph	Ph	OAc	OAc	−195.4	DMSO-d_6
17	Me	Me	Me	Cl	−149.5	$CDCl_3$

Cationic Pentacoordinate

18		−175.8 DMSO-d_6

TABLE 1 (*continued*)

Compound	δ Si [a]	Solvent

	R		
19	CH=CH$_2$	−141.3	DMSO-d_6
20	Ph	−141.8	DMSO-d_6
21	(CH$_2$)$_4$CH$_3$	−127.1	DMSO-d_6
22	CH$_3$	−128.6	DMSO-d_6

Anionic Hexacoordinate

23	ZnSiF$_6$	−185.3 [b]	D$_2$O

24	(NH$_4^+$)$_2$ [...] •5 H$_2$O	−135.3 [b]	DMSO-d_6

25	(Et$_3$NH$^+$)$_2$ [...]	−139.3	DMSO-d_6

26	(n-Bu$_4$N$^+$)$_2$ [...]	−173.3 [b]	C$_6$F$_6$

Anionic Pentacoordinate

27		−87.1	Acetone-d_6

	(Et$_3$NH$^+$) [PhSi ...]	−87.0	Cl$_2$DCCDCl$_2$

[a] Data in ppm relative to Me$_4$Si. Positive values are to lower field.
[b] Ref. 12.

where $\delta Si^* = -64.4$ (R = Me), -77.3 (R = Ph) and -79.4 (R = Vinyl) [14].

The value of ^{29}Si NMR in characterizing five- and six-coordinate silicon complexes should be evident from the data presented in Table 1. Additionally, this method can be used to establish whether a given ligand will form a hypervalent complex with silicon or remain tetravalent. For example, a reaction mixture of $SiCl_4$ and a bidentate ligand can be examined for resonances outside the normal Q region (-50 to -100 ppm) to detect the existence of a five- or six-coordinate complex.

^{29}Si NMR has facilitated the determination of an important side reaction occurring during preparation of pentacoordinate tropolonates, namely, that of carbon—silicon bond cleavage. Thus, in the reaction of tropolone with various substituted trichlorosilanes, two resonances were observed in the chelate region, one due to the desired pentacoordinate chelate, and the other arising from the hexacoordinate tris(tropolonato)silicon (IV) salt. The extent of cleavage depends on R and decreases in the order H ~ PhC≡C- > vinyl ~ phenyl > alkyl.

These applications demonstrate the potential of ^{29}Si NMR for studying this interesting class of silicon compounds.

References

1 C.L. Frye, J. Amer. Chem. Soc., 86 (1964) 3170.
2 C.L. Frye, J. Amer. Chem. Soc., 92 (1970) 1205.
3 W. Dilthey, Annalen, (1906) 344.
4 G. Shott, H.U. Kibbel and W. Hildebrandt, Z. Anorg. Allg. Chem., 371 (1969) 81.
5 E.L. Muetterties and C.M. Wright, J. Amer. Chem. Soc., 86 (1964) 5132.
6 G. Schott and K. Golz, Z. Anorg. Allg. Chem., 383 (1971) 314.
7 R.M. Pike and R.R. Luongo, J. Amer. Chem. Soc., 87 (1965) 1403.
8 L.H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill, New York, 1965, Chapter 1, Pages 4—24.
9 J. Schraml and J.M. Bellama, in F.D. Nachod, J.J. Zuckerman and E.W. Randall, (Eds.), Determination of Organic Structure by Physical Methods, Vol. 6, Academic Press, New York, 1976; Chapter 4; E.A. Williams and J.D. Cargioli, in G.A. Webb (Ed.), Annual Reports on NMR Spectroscopy, Vol. 9, Academic Press, New York, 1979.
10 R.K. Harris, J. Jones and S. Ng, J. Magn. Reson., 30 (1978) 521.
11 J.A. Cella, unpublished results, (1978).
12 H.C. Marsmann and R. Lower, Chem. Ztg., 97 (1973) 660.
13 R.K. Harris, private communication.
14 G. Engelhardt, H. Jancke, R. Radeglia, H. Kriegsmann, M.F. Larin, V.A. Pestunovich, E.I. Dubinskaja and M. Voronkov, Z. Chem., 17 (1977) 376.