Pentaco-ordinate Silicon Derivatives: ^{1}H N.M.R. Evidence

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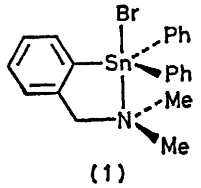
Summary The ^{1}H n m r spectra of o-$(Me_2NCH_2)C_6H_4SiX_2R$ and o-$(Me_2NCH_2)C_6H_4SiXR^1R^2$ indicate that the intramolecular Si–N co-ordination is controlled by the ability of the Si–X bond to be stretched and substituted with inversion of configuration

ALTHOUGH there are many examples of penta- and hexa-co-ordination at silicon,[1–4] mechanisms involving penta- and hexa-co-ordinate intermediates are not generally accepted [5] However, reaction pathways involving the extension of co-ordination at silicon, such as racemisation of halogenosilanes[6] and nucleophilic substitution with and without catalysis by Lewis bases,[7,8] have been considered. The recent synthesis of new pentaco-ordinated compounds[9,10] and the work of van Kolten and Noltes[11–13] with silicon surrounded by three carbon atoms led us to undertake a systematic study of silicon pentaco-ordination. Van Kolten and Noltes also reported the synthesis and molecular structure (trigonal bipyramidal) of a triorganotin halide (**1**) in which the o-$(Me_2NCH_2)C_6H_4$ group is intramolecularly bonded to the Sn atom.



(**1**)

In this paper we report the possibility of pentaco-ordination of a silicon atom bonded to several alkyl and aryl groups. We establish a correlation between the co-ordination ability and the nature of the functional groups bonded to the silicon atom.

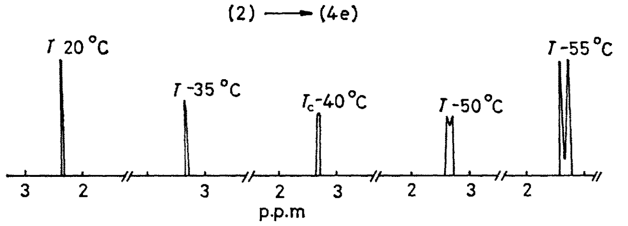


FIGURE. ^{1}H N.m.r. spectra of the NMe_2 group: T_c = temperature of coalescence; the solvent is CD_2Cl_2; internal reference is tetramethylsilane.

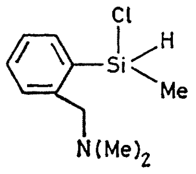
The o-$(Me_2NCH_2)C_6H_4$ ligand present in these structures allows the study of pentaco-ordination by ^{1}H n.m.r. spectroscopy. The formation of an intramolecular Si–N bond induces diastereotopy of the two Me groups (Figure). For each product the temperature of coalescence T_c is given in the Table.

These results show that extension of the co-ordination is possible with monofunctional silanes. They are in good agreement with the formation of a pentaco-ordinated complex as considered in a mechanism for the racemization of halogenosilanes[6] or for nucleophilic substitution catalysed by Lewis bases.[7,8] The results show that co-ordination is not a function of the electronegativity of X, but is controlled by the ability of the nitrogen atom to stretch the Si–X bond. Indeed, pentaco-ordination is difficult when the fluorine atom, which is the most electronegative, is present. With the OR group, even at −100 °C, the $N(Me)_2$ protons do not coalesce, whereas with the SR group an intramolecular co-ordination occurs at −65 °C. The results obtained in this study, when taken with our previous work,[6,7] suggest a close relationship between the rate of racemization of halogenosilanes, the substitution of R_3SiX with inversion of configuration, and the ease of pentaco-ordination at the silicon atom (Scheme).

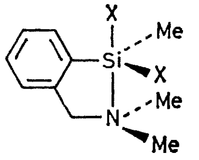
TABLE

Compd.	X	T_c/°C	$\Delta G^‡$ (T_c) /kcal mol^{-1} [a]
(**3a**)	H	—	—
(**3b**)	OEt	—	—
(**3c**)	F[b]	−105	8·3
(**3d**)	O_2CMe[d]	+20	15·8
(**3e**)	Cl[b]	+30	15·6
(**4a**)	OBu^t[c]	—	—
(**4b**)	SEt[c]	−65	10·8
(**4c**)	F[b]	−52	11·5
(**4d**)	O_2CMe[c]	−46	11·7
(**4e**)	Cl[b]	−40	12·3
(**4f**)	Br[d]	−10	13·8
(**5a**)	H[d]	—	—
(**5b**)	OMe[d]	—	—
(**5c**)	F[b]	−65	10·3
(**5d**)	Cl[c]	−35	12·3
(**5e**)	O_2CMe[d]	−35	12·0

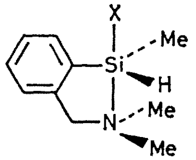
[a] 1 cal = 4·184 J. [b–d] The diastereotopism of the benzylic protons is difficult to observe We have found three cases: [b] the diastereotopism appears at T_c; [c] The benzyl protons are diastereotopic at all temperatures; [d] The diastereotopism does not appear.



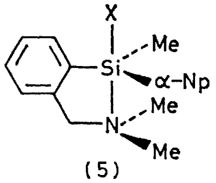
(**2**)



(**3**)



(**4**)



(**5**)

α-Np = α-Naphthyl.

Pentaco-ordination ability
H,OR < F,SR < OAc, Cl, Br
$\xrightarrow{\hspace{4cm}}$
Stereochemistry:
Retention $\xrightarrow{\hspace{2cm}}$ Inversion
Racemisation ability
$\xrightarrow{\hspace{4cm}}$

SCHEME.

The axial preference of electronegative groups in trigonal bipyramidal complexes is well known. The relationship between the pentaco-ordinate compounds presented here and the transition state for substitution of silicon with inversion of configuration is obvious. This can be taken as evidence that the ease of stretching of the Si–X bond is a significant factor in directing the stereochemistry of substitution towards inversion of configuration.

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