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CONTRIBUTIONS TO GROUP IV ORGANOMETALLIC CHEMISTRY

VII *. THE EFFECT OF ELECTRONEGATIVITY ON SUBSTITUENT SHIFTS IN SILICON-29 NMR

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Summary

Silicon-29 NMR shifts for silanes of the type $Me_{2-n}Ph_nSiX_2$ (X = H, Me, Ph, F, Cl, NR_2 and OR) indicate that the shifts on replacement of a methyl by a phenyl group are largely determined by the electronegativity and donor ability of X.

A study of the silicon-29 NMR shift values for the series $Me_{4-n}SiPh_n$ indicated a fairly constant shift of about −4 ppm on replacement of a Me by a Ph group [2,3,4] although it was subsequently suggested that in general substituent parameters can only be used with caution [5,6,7].

In the course of our detailed investigation of 1,3-dioxa- and 1,3-diaza-2-silacycloalkanes and their precursors [8,9] we have obtained silicon-29 NMR shifts for a range of dialkoxy- and bis(dialkylamino)-silanes. The results show that the methyl → phenyl substituent shift is relatively constant for the same class of compound and a comparison with literature shift values for other compounds of the type $Me_{2-n}Ph_nSiX_2$ suggests that the magnitude of the effect is dependent on the electronegativity of X.

Results and discussion

Silicon-29 NMR shifts and methyl → phenyl substituent shifts ($\Delta\delta$) are given in Table 1, literature values being a mean of shifts taken from a review by Marsmann [6].

The general dependence of $\Delta\delta$ on the Pauling electronegativity of atoms X directly bonded to silicon is shown in Fig. 1, with OMe and NMe_2 representative of alkoxy and dialkylamino groups. The points appear to produce two sets of lines, of marginally different gradient for the first and second substituents, with the electro-

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* For part VI see Ref. 1.

TABLE 1

SILICON-29 NMR SHIFTS AND PHENYL SUBSTITUENT SHIFTS FOR SILANES OF THE TYPE $Me_{2-n}Ph_nSiX_2$ (ppm)

X	n			$\Delta\delta$	
	0	1	2	$Me_2 \rightarrow PhMe$	$MePh \rightarrow Ph_2$
H [a]	−39.60	−36.80	−33.79	+2.8	+3.01
Me [a]	0	−4.78	−8.62	−4.78	−3.84
Ph [a]	−8.62	−12.05	−13.98	−3.43	−1.93
Cl [a]	+31.93	+17.90	+6.25	−14.03	−11.65
NMe_2	−1.07	−9.06	−17.04	−7.99	−7.98
NEt_2	−5.52	−11 32	–	−5.80	–
OMe	−2.28 [a]	−14.89	−29.11	−12.61	−14.22
OEt	−6.25 [a]	−18.43	−32.36	−12.18	−13.93
OPr^i	−8.29	−21.96	−35.78	−13.67	−13.82
OPh	−6.10(2)	−21.19	−37.37	−15.09	−16.18
F	+4.45	−12.40	−29.8	−16.85	−17.4

[a] Ref. 5, mean values.

negative atoms N, O and F common to one set. Since these are the atoms which might be expected to back donate most strongly it is noteworthy that the $\Delta\delta$ values are less than would be obtained by extrapolation of the lines containing H, C and Cl.

One interpretation of these results is that the increased shielding at silicon which results from phenyl substitution is due to $(p \rightarrow d)\pi$ bonding from the phenyl group and that this would be enhanced by the presence of electronegative substituents X ($Ph \overset{\pi}{\rightarrow} Si \rightarrow X$). If however X were itself capable of $(p \rightarrow d)$ back donation this would partially offset the π-bonding between phenyl and silicon which would tend to

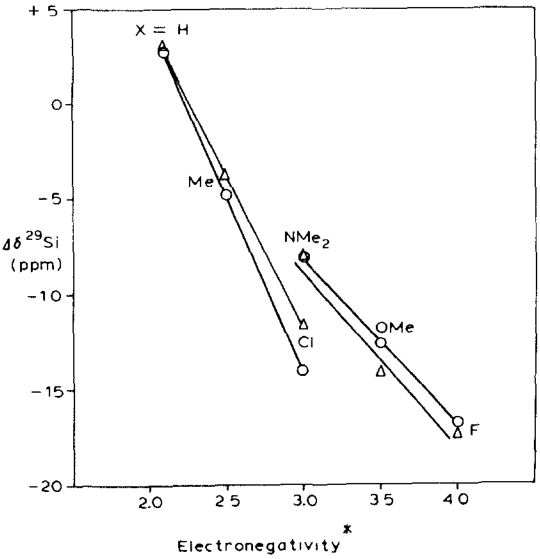

Fig. 1. $\Delta(Me \rightarrow Ph)\ \delta(^{29}Si)$ for compounds containing the $X_2Si\langle$ moiety. ○ $Me_2 \rightarrow MePh$, △ $MePh \rightarrow Ph_2$. * Electronegativity of atom in X bonded directly to silicon (after Pauling [11]).

reduce the increase in shielding ($\mathrm{Ph}\overset{\rightarrow}{-}\mathrm{Si}\overset{\leftarrow}{-}\mathrm{X}$). Also compatible with this explanation are the somewhat higher $\Delta\delta$ values when X is a phenoxy, rather than an alkoxy, group since some delocalisation of oxygen electrons into the oxygen–phenyl bond and away from silicon would be expected ($\mathrm{Ph}\overset{\rightarrow}{-}\mathrm{Si} \rightarrow \mathrm{O}\overset{\rightarrow}{-}\mathrm{Ph}$).

Substituent effects do not appear to have been connected with electronegativity in precisely this way before, although the linear relationship between absolute shift values and the electronegativity of X in compounds of the type Me_3SiX has been established [2]. The ligands N, O and F were found to be exceptional, and were observed to produce less deshielding of the silicon atom than might be expected, and the effect was attributed to $(p \rightarrow d)\pi$ bonding. It is of interest to note that, as reported by Wells [10], the π bonded phenyl groups and vinyl groups are found in the same category as N, O and F.

We associate the lower $\Delta\delta$ value, for $Me_2Si(NEt_2)_2$ (-5.80 ppm) as compared to $Me_2Si(NMe_2)_2$ -7.99 ppm) with steric crowding in $MePhSi(NEt_2)_2$, this view being supported by the fact that we were unable to prepare $Ph_2Si(NEt_2)_2$ from the interaction of dichlorodiphenylsilane and diethylamine.

Experimental

Dialkoxy- and bis(dialkylamino)-silanes were prepared from the appropriate dichlorosilanes by established methods.

Silicon-29 NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer in the Fourier transform mode using solutions of the sample in either $CDCl_3$ or CCl_4 with internal TMS as the standard. A trace of chromium acetylacetonate was used as a relaxation agent for some of the spectra.

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