

## SHORT COMMUNICATIONS

Electronic effects on ligand redistribution between  $RR'R''SiCl$  and  $Me_3SiNMe_2$ 

Redistribution reactions in organometallic chemistry have received considerable attention during the past several years. Extensive reviews have been written on this subject<sup>1-3</sup>. Frequently significant deviations from random redistributions occur<sup>2-3</sup>, but the direction and magnitude of these deviations have been difficult to predict.

The extent of the deviations from random redistributions for a series of mercury halides have been accounted for in terms of electrostatic stabilization of the bonds<sup>4</sup>. Similarly the redistributions of a series of compounds, OPXYZ, with a series SPXYZ were found to deviate from statistical values in a direction to favor molecules with the more electronegative atom, oxygen, on the phosphorus bearing the more electronegative substituents<sup>5</sup>. In contrast, the redistribution of alkoxy or dimethylamino groups with chlorine on the central atom of boron<sup>6,7</sup>, silicon<sup>8</sup>, phosphorus<sup>9</sup>, or arsenic<sup>10</sup> were found to deviate to favor combinations in which the most electronegative ligand was on the central atom with the least numbers of electronegative substituents.

It has been suggested that the deviations arise largely from an enthalpy effect. Some direct thermochemical measurements support this suggestion<sup>8</sup>, other measurements, however, indicate that entropy factors must also play an important role<sup>10,11</sup>.

We have now found that equilibrium constants for the following reaction can be correlated by a Taft linear free energy relationship:



From this correlation one can make a quantitative estimate of the equilibrium constants for other related reactions.

Equilibrium constants were determined for twelve different triorganochlorosilanes reacting with trimethyl(dimethylamino)silane. The equilibrium constants were determined on approximately ten mole per cent solutions of the reactants in carbon tetrachloride employing the NMR method of Van Wazer and associates<sup>8</sup>. The NMR tubes were filled by vacuum-line distillation and transfer of the volatile components. The reactants in the sealed NMR tubes were then allowed to equilibrate about a week at room temperature. They were then placed in the cavity of a Varian A-60 spectrometer at 37° for about 30 min. Each tube contained a trace of precipitate dimethylamine hydrochloride which served as catalyst for the exchange\*. The equilibrium constants determined at different lapsed times were in agreement, within experimental error, indicating that equilibrium was attained rapidly. This would support the findings of Van Wazer and Moedritzer<sup>8</sup> who found that dimethyldichlorosilane equilibrated with the corresponding dimethylaminosilane within three minutes.

The chlorosilanes were either prepared by conventional organometallic techniques, or were already available from Dow Corning Corporation Laboratories. They

\* A similar catalyst,  $R_4NCl$ , has been reported to promote exchange<sup>12</sup>.

were distilled through a Nester Faust 18" spinning band apparatus and checked for purity by gas-liquid chromatography before they were employed for the redistribution studies.

Table I contains the list of equilibrium constants, the Taft substituent constants<sup>13</sup> for the substituents on the chlorosilanes, and the deviations in free energy changes from those expected for random redistributions. Fig. 1 is a plot of the logarithm of the equilibrium constant *versus* the sum of the Taft substituent constants

TABLE I

REDISTRIBUTION OF CHLORINE WITH DIMETHYLAMINE GROUPS ON TRIORGANOSILICON COMPOUNDS

Chlorosilane	$K_e^a$	$\Delta F_{dev.}$ (kcal/mole)	$\Sigma\sigma^*RR'R''^b$
n-Pr <sub>3</sub> SiCl	0.5	+0.4	-0.35
iso-Pr <sub>3</sub> SiCl	0.6	+0.4	-0.57
Me <sub>3</sub> SiCl <sup>c</sup>	1.0	0	0
Me <sub>2</sub> ViSiCl	1.7	-0.3	0.40 <sup>d</sup>
CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Me <sub>2</sub> SiCl	1.9	-0.4	0.32
HMe <sub>2</sub> SiCl	2.6	-0.6	0.49
(Me <sub>3</sub> SiO) <sub>2</sub> SiCl	3.1	-0.7	0.54 <sup>e</sup>
PhMe <sub>2</sub> SiCl	3.5	-0.8	0.60
ClCH <sub>2</sub> Me <sub>2</sub> SiCl	7.9	-1.3	1.05
MePhViSiCl	9.4	-1.4	1.00
MePh <sub>2</sub> SiCl	16.0	-1.7	1.20
HPh <sub>2</sub> SiCl	27.6	-2.1	1.69
Cl <sub>2</sub> CHMe <sub>2</sub> SiCl	38.2	-2.2	1.94

<sup>a</sup> Determined on approximately 10 mole per cent solutions of reactants in CCl<sub>4</sub> at 37° by Van Wazer<sup>8</sup> NMR technique. <sup>b</sup> From Taft<sup>13</sup>, except where noted. <sup>c</sup> By definition. <sup>d</sup>  $\sigma^*$  Value for Vi from Pal'm<sup>15</sup>. <sup>e</sup> Estimated from linear relationship  $\text{Log } K_e = 0.89 \Sigma\sigma^*$ .

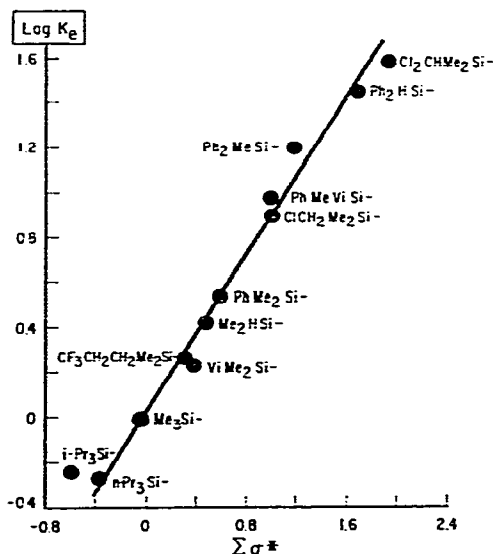


Fig. 1.  $\text{Log } K_e$  versus  $\Sigma\sigma^*(R, R', R'')$  for  $\text{Me}_3\text{SiNMe}_2 + \text{RR'R''SiCl} \rightleftharpoons \text{Me}_3\text{SiCl} + \text{RR'R''SiNMe}_2$ .

for substituents on the initial chlorosilane. The straight line has a slope of 0.89 with a correlation coefficient obtained by the method of least squares of 0.99\*. The most general equation would be:

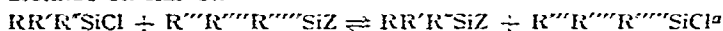
$$\log K_e = \rho^* \Delta \Sigma \sigma^*$$

where  $\rho^*$  is the slope of the line and  $\Delta \Sigma \sigma^*$  is the difference in the sum of the substituent constants attached to the chlorosilane and to the (dimethylamino)silane.

The deviations in free energy changes from that for random reorganization range from  $-0.4$  to  $+2.2$  kcal per mole. These large deviations if primarily due to enthalpy contributions represent significant changes in the bond energies of a silicon-nitrogen and a silicon-chlorine bond on only moderate changes in the rest of the molecule (*i.e.*, one still maintains three Si-C bonds). The deviation occurs in a direction so as to place the more polarizable nitrogen-containing ligand on the more electron deficient silicon atom. Deviations occur in a direction which results in maximum use of the vacant *d* orbitals on silicon. Similar explanations have been given to account for the results of equilibrium redistributions of nitrogen, oxygen and chlorine groups on boron<sup>15</sup> and fluorine, chlorine, oxygen and hydrogen groups on silicon<sup>16</sup>. Table 2 lists  $\rho^*$  values derived from literature values of redistribution equilibria, and calculated on the assumption that the Taft equation would hold for all of these redistribution reactions. Only qualitative comparisons of  $\rho^*$ , the measure of the sensitivity of the reaction to electronic effects, can be made because the data are obtained at different temperatures and no knowledge of the isoequilibrium temperatures is available. With the exception of hydrogen the less protonic the analogous H-Z compound, the greater is the sensitivity of the reaction to electronic effects of the other substituents. This would suggest that the more polarized the ligand-silicon bond, the less its strength is affected by the electronic nature of the other substituents, a concept easy to rationalize from valence bond considerations<sup>17</sup>. Electron-withdrawing substituents on silicon would enhance its *s* character in the silicon-ligand bond, thus strengthening the bond. More polarizable ligands would be greater affected than less polarizable ones resulting

TABLE 2

THE ELECTRONIC SENSITIVITY OF REDISTRIBUTION REACTIONS INVOLVING CHLORINE WITH OTHER LIGANDS ON SILICON



$$\log K_e = [\sigma^*(R) + \sigma^*(R') + \sigma^*(R'') - \sigma^*(R''') - \sigma^*(R''') - \sigma^*(R''''')] \rho^*$$

Z	Reactants	$K_e$	$\rho^*$	Temp.	Source
NMe <sub>2</sub>			-0.89	37°	This paper
H	MePhHSiCl	5.5	-0.35 <sup>b</sup>	37°	Ref. 10
	MePhClSiH				
OMe	Me <sub>2</sub> OMeSiCl	10 <sup>-2</sup>	-0.35	120°	Ref. 8
	Me <sub>2</sub> ClSiOMe				
CN	Me <sub>2</sub> SiCN	~ 2.3	~ -0.26	0°	Ref. 19
	H <sub>3</sub> SiCl				
Cl			0.00		By definition

<sup>a</sup> In this table the reverse reaction was employed to be consistent with other published data.

<sup>b</sup> A correlation coefficient of this value is considered excellent for this type of correlation<sup>14</sup>

in enhancement of their bond strengths to silicon. Similar explanations are obvious for other central atoms.

Deviations from the linear free energy relationship might be expected where strong non-constant mesomeric interactions take place between the substituent and silicon. This problem is currently being studied and will be treated in a subsequent paper. The effect of temperature and the exchange of other ligands with chlorine on silicon is also being investigated and will be presented at another time.

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## Organometal derivatives of 2-pyridone

2-Hydroxypyridine does not exhibit the expected phenolic properties, although etherification with diazomethane gives the *o*-ethyl ether. Methylation with methyl iodide, on the other hand, gives N-methyl-2-pyridone<sup>1,2</sup>. Here we describe reactions of 2-hydroxypyridine, under a variety of conditions<sup>3</sup>, with dibutyl dimethoxytin, dimethyldichlorosilane and aluminium ethylate.

The reaction products are prone to hydrolysis. Dibutyldi(2-pyridonato-1)tin and dimethyldi(2-pyridonato-1)silane, for example, hydrolyze quickly when exposed to humid air, to form 2-hydroxypyridine.

The infra-red spectra of dibutyldi(2-pyridonato-1)tin, dimethyldi(2-pyridonato-1)silane and tri(2-pyridonato-1)aluminium have pronounced carbonyl bands at 1670 cm<sup>-1</sup> and 1650 cm<sup>-1</sup>. The infra-red spectrum of N-methyl-2-pyridone has pro-

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