Silicon-29 Nuclear Magnetic Resonance. Chemical Shift Substituent Effects[1]

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Abstract: Silicon-29 nmr chemical shifts ($\delta^{29}Si$) are reported for a number of aryltrifluoro- (**1-F**), aryltrichloro- (**1-Cl**), aryltriethoxy- (**1-OEt**), and aryltrihydrosilanes (**1-H**). $\delta^{29}Si$ for these series, with the exception of **1-Cl**, exhibited good linear correlations with Hammett's σ constants. In contrast to the chemical shift trends in **1-H** and in aryltrimethylsilanes (**1-CH₃**), silanes **1-F**, **1-Cl**, and **1-OEt** gave downfield shifts with increasing electron donation by meta and para substituents on phenyl. Semiempirical quantum chemical (CNDO/2) calculations of electron density at silicon for silanes **1-F**, **1-H**, and **1-CH₃** indicated no unusual reversal in the density trends to account for the observations. An additive although nonlinear relationship between $\delta^{29}Si$ and the summed electronegativities of the groups bonded to silicon was found, and its applicability was demonstrated for the estimation of $\delta^{29}Si$ for grossly different silanes.

Only recently have experimental and instrumental techniques become available that permit facile nmr studies on nuclei of low natural abundance. The advent of pulsed Fourier transform spectrometry (FT),[3] computer signal averaging, and relaxation reagents[4] has greatly reduced experimental difficulties, particularly in obtaining silicon-29 (^{29}Si) nmr spectra. For this nucleus, they have allowed spectral measurements despite preexisting problems of low natural abundance (4.7%),[5] relatively long relaxation times ($T_1 \geq 20$ sec),[6-9] low signal sensitivity (0.008 relative to $^1H = 1.0$),[5b] and the negative nuclear Overhauser effect ($\mu = -0.555$)[5a] that are characteristic of the magnetically active silicon isotope.

Previous studies on monotonic series of silanes, $(CH_3)_{4-n}SiX_n$, where X = F, Cl, OAc, OR, C_6H_5, C_2H_3,[6] and O_2CR,[10] $(CH_3)_{3-n}Si(X)_nOAc$ where X = OAc and OC_2H_5,[11] and $F_{4-n}SiY_n$, where Y = Cl, Br, and CH_3,[12] have established general trends of ^{29}Si chemical shifts. An investigation of the effect of structural, electronic, and solvent perturbations in various alkylsilanes provided a detailed description of the more subtle effects on the ^{29}Si resonance for this particular class of silanes.[13,14] Compilations of chemical shift data for additional silanes have also been given.[15-21] The potential of ^{29}Si nmr as a structural tool has been demonstrated by identification and differentiation of various siloxanes.[22,23] The relation of Si nuclear relaxation processes and the nuclear Overhauser phenomenon[7-9,24] to structural problems in silicon chemistry have likewise received attention.

A recent communication from this laboratory[25] reported the presence of totally different and unusual responses of ^{29}Si chemical shifts to changes in substitution of phenyl in the series of analogous phenyltrifluoro- and phenyltrimethylsilanes.[14] Although each series exhibited high degrees of linearity with Hammett constants, the slopes of the regression lines were of opposite sign. In view of these unexpected results, a systematic study of substituent effects on the ^{29}Si chemical shift has been conducted for silanes of the general formula, $XC_6H_4SiY_3$. In an effort to relate chemical shifts to electron charge densities, CNDO/2 calculations have been performed on representative series of phenylsilanes. The results of this investigation provide an explicit description of silicon chemical shifts and electronic perturbations thereon, for silanes of widely differing electronic environments. Generalized chemical shift trends established here provide a correlative unification of apparently unrelated literature data.

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(2) National Research Council Associate 1972–1973.

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Table I. Analytical Data[a] of Substituted Phenyltrifluorosilanes, $XC_6H_4SiF_3$

X	Bp,[b] °C (mm)	% found				% calcd			
		C	H	Si	F	C	H	Si	F
H	103–104	44.29	3.09	17.26	35.24	44.43	3.11	17.32	35.14
m-Cl	135–140	36.81	2.12	14.07	29.01	36.65	2.05	14.28	28.99
p-Cl	132–134	36.71	1.93	14.30	28.91	36.65	2.05	14.28	28.99
m-CH₃	123–125	47.49	4.19	15.72	32.26	47.71	4.00	15.94	32.34
p-CH₃	126–128	47.74	3.99	15.69	32.35	47.71	4.00	15.94	32.34
m-F	83–86	40.23	2.33	15.44	42.08	40.00	2.24	15.59	42.18
p-F	80–85	40.17	2.22	15.41	42.36	40.00	2.24	15.59	42.18
m-CF₃	95–100	36.61	1.75	12.03	49.72	36.53	1.75	12.20	49.52
p-CF₃	95–100	36.64	1.72	12.00	49.19	36.53	1.75	12.20	49.52
m-CH₃O	150–154	43.94	3.68	14.74	29.43	44.01	3.67	14.61	29.65
p-CH₃O	145–148	43.86	3.80	14.51	29.59	44.01	3.67	14.61	29.65
m-NO₂	60–62 (0.5)	35.01	2.07	13.75	27.33	34.78	1.95	13.56	27.51

[a] Elemental analysis performed by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] Unless otherwise stated, all boiling points are at 1 atm.

Experimental Section

Preparation of the Silanes. All silanes used in this study were prepared by standard reactions and are known compounds with the exception of the substituted phenyltrifluorosilanes. The phenyltrichlorosilanes were prepared by the addition of the appropriate Grignard reagent, XC_6H_4MgBr, to an ethereal solution containing excess silicon tetrachloride. The phenyltriethoxysilanes were obtained upon treatment of the corresponding phenyltrichlorosilanes with ethanol. The phenylsilanes were synthesized by reduction of the appropriate phenyltrichlorosilane with sodium bis(2-methoxyethoxy)aluminum hydride. The phenyltrifluorosilanes, with the exception of the *m*-nitro derivative, were prepared by heating the corresponding phenyltrichlorosilanes with excess sodium hexafluorosilicate[26,27] in the absence of solvent and distilling over the fluorosilane. *m*-Nitrophenyltrifluorosilane[26] was made by direct nitration of phenyltrifluorosilane with nitric and sulfuric acid. The position of the nitro group in the nitrophenyltrifluorosilane was established by conversion of this material, by reported procedures,[28] into the *m*-nitrophenyltriethanolnitrilosilane (*m*-nitrophenylsilatrane), whose structure had been determined by X-ray analysis.[29] Melting point and ir data for the silatrane prepared from the nitrophenyltrifluorosilane were identical with those for an authentic sample. Elemental analyses and boiling points of the phenyltrifluorosilanes are summarized in Table I.

Spectra. All nmr measurements were obtained on a Varian XL-100-15 spectrometer operating in the pulsed FT mode under control of a Varian 620/L 16K computer. The ²⁹Si spectra were obtained at a spectrometer frequency of 19.9 MHz using an internal deuterium field/frequency lock system with 12-mm spinning sample tubes. The ²⁹Si chemical shifts were directly outputted from the computer. Free induction decay data were accumulated over approximately 1000 transients and subsequently transformed into frequency nmr spectra. Solution composition and spectral width varied among the arylsilanes and are given in Table II. All ²⁹Si spectra were obtained for solution containing a relaxation

Table II. Solution Composition and Nmr Instrumental Conditions Employed for the Spectra of the Arylsilanes, $XC_6H_4SiY_3$[a]

——Arylsilane——			Spectral	
Y	Concn (M)	Internal ref (0.1 M)	width (Hz)	Precision (ppm)
F	0.5	TMS	2500	±0.11
OEt	0.5	TMS	2500	±0.07
Cl	0.5	TMS	1000	±0.02
H	0.2	TMOS	500	±0.01

[a] Common component: 0.1 M $Cr(AcAc)_3$ with $CDCl_3$ solvent.

(26) D. L. Bailey and R. M. Pike, U. S. Patent 3,020,302 (1962); *Chem. Abstr.*, **56**, 15548 (1962).
(27) Union Carbide Corp. Fr. Patent 1,303,018 (1962); *Chem. Abstr.*, **58**, 9138b (1963).
(28) M. G. Voronkov, *Rev. Pure Appl. Chem.*, **13**, 35 (1966).
(29) J. W. Turley and F. P. Boer, *J. Amer. Chem. Soc.*, **90**, 5102 (1968).

agent, chromium(III) acetylacetonate [$Cr(AcAc)_3$]. The $Cr(AcAc)_3$ permitted sufficient relaxation of the nucleus, yet introduced no observable shift, so that zero pulse delay could be used and satisfactory spectra obtained within 35 min of pulsing. The silicon chemical shifts were measured from an internal reference of TMS or TMOS and are reported with respect to TMOS. In those cases that TMOS could not be used directly (due to chemical reactivity), the chemical shifts were obtained relative to TMS and then adjusted numerically for the shift of TMOS relative to TMS under conditions identical with those employed in the comparative study.

Calculations. CNDO/2 calculations of the silanes were performed using the QCPE 91 program[30] unmodified and were based upon tetrahedral bond angles at silicon. The following bond lengths were employed for various Si linkages:[31] Si–F, 1.55; Si–H, 1.48; Si–C(methyl), 1.88; Si–C(phenyl) 1.87 Å. Normal $-C_6H_4X$ geometry was used directly as given in standard sources.[31] Where necessary, chemically reasonable dihedral angles were adopted. In the calculations for members of a given series bond distances were assumed to remain constant for all bonds to silicon.

Results

Silicon-29 chemical shifts ($\delta^{29}Si$)[32] for a number of meta- and para-substituted phenyltrifluoro- (**1-F**), phenyltrichloro- (**1-Cl**), phenyltriethoxy- (**1-OEt**), and phenyltrihydrosilanes (**1-H**) are reported in Table III.
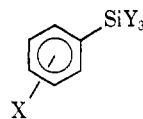
Y = F (**1-F**)
Y = Cl (**1-Cl**)
Y = OEt (**1-OEt**)
Y = H (**1-H**)
X = H, F, Cl, CF₃, OCH₃, NO₂ (*m*- or *p*-)

The parent phenylsilanes (X = H) exhibited the following order of increasing $\delta^{29}Si$: **1-F** < **1-H** < **1-OEt** < **1-Cl**. Resonances for silanes **1-F**, **1-Cl**, and **1-OEt** shifted to higher fields upon substitution of the phenyl ring with electron withdrawing groups and to lower fields with electron donating groups. An opposite trend was observed for the silanes **1-H**. Correlations of $\delta^{29}Si$ with Hammett constants are given in Figure 1 for the phenylsilanes presented here along with a previously reported series of phenyltrimethylsilanes, $XC_6H_4Si(CH_3)_3$ (**1-CH₃**).[14] Correlation coefficients (*r*) of 0.97 or greater were observed for all phenylsilanes with the exception of the series **1-Cl** where it was found to be 0.874.

CNDO/2 calculations were performed on silanes **1-F**, **1-H**, and **1-CH₃**. For these silanes, Figures 2–4

(30) Quantum Chemistry Program Exchange No. 91, University of Indiana, Bloomington, Ind.
(31) "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. 11 (1958).
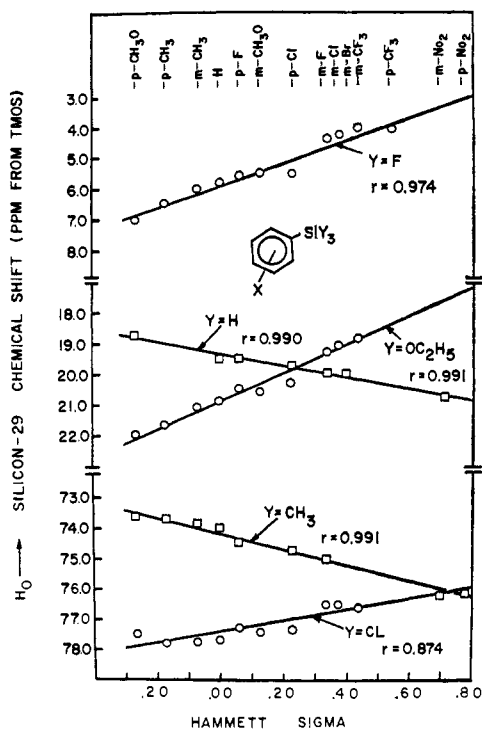(32) Positive δ values indicate low field side of reference.

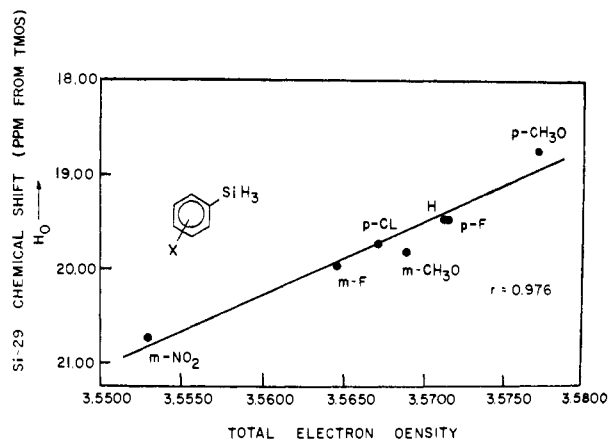**Figure 1.** Hammett plots of silicon-29 nmr chemical shifts of arylsilanes, 1-F, 1-OEt, 1-Cl, 1-H, and 1-CH₃.

Figure 2. Plot of silicon-29 nmr chemical shifts of aryltrihydrosilanes vs. CNDO-computed electron density at silicon.

Figure 3. Plot of silicon-29 nmr chemical shifts of aryltrifluorosilanes vs. CNDO-computed electron density at silicon.

Figure 4. Plot of silicon-29 nmr chemical shifts of aryltrimethylsilanes vs. CNDO-computed electron density at silicon.

Table III. ²⁹Si Chemical Shifts of Arylsilanes, XC₆H₄SiY₃ (ppm from Tetramethoxysilane)[a]

| | Chemical shift of silane for | | | |
| | | | Y = | |
X	Y = H[b,c]	Y = Cl[d]	OC₂H₅[d]	Y = F[d]
H–	19.44	77.60	20.88	5.77
m-CH₃O–	19.81	77.39	20.53	5.45
p-CH₃O–	18.74	77.47	21.97	6.99
m-CH₃–		77.72	21.22	5.91
p-CH₃–		77.78	21.65	6.46
m-F–	19.95	76.48	19.16	4.40
p-F–	19.46	77.12	20.46	5.61
m-Cl–		76.46	19.04	4.29
p-Cl–	19.72	77.23	20.12	5.51
m-Br–	19.73			
m-CF₃–		76.62	18.80	4.17
p-CF₃–				4.16
m-NO₂–	20.74			

[a] Spectra obtained on Varian XL-100-15 spectrometer for solutions containing 0.5 M arylsilane, 0.1 M tetramethoxy- (TMOS) or tetramethylsilane (TMS), and 0.1 M chromium(III) acetylacetonate in CDCl₃ using the pulsed FT mode. Chemical shift of TMOS was −78.48 ppm from TMS. Positive chemical shift values indicate low field side of TMOS. [b] TMOS internal reference. [c] Arylsilane concentration 0.2 M. [d] TMS internal reference.

present the relationship between the CNDO-computed total electron densities at silicon and the corresponding experimental δ²⁹Si values. Electron density values incorporating only σ or π contributions failed to yield satisfactory correlations. In each series, an increase in the electron withdrawing ability of the substituents is reflected by a decrease in calculated electron density around the silicon atom.

Discussion

Chemical shifts for the ¹⁹F, ³¹P, and ¹³C nuclei[33–35] have previously been shown to be dominated by changes in the paramagnetic term (σ_p) in the total shielding expression (σ_t), with diamagnetic (σ_d) and nonlocalized

effects (σ') remaining relatively constant (eq 1). Although this formulation has been extended to all nonzero spin nuclei other than hydrogen, direct calculation of this has not yet been made for silicon. The para-

$$\sigma_t = \sigma_d + \sigma_p + \sigma' \qquad (1)$$

(33) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).
(34) J. R. Van Wazer in "Determination of Organic Structures by Physical Methods," Vol. 4, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., 1971, p 335.
(35) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).
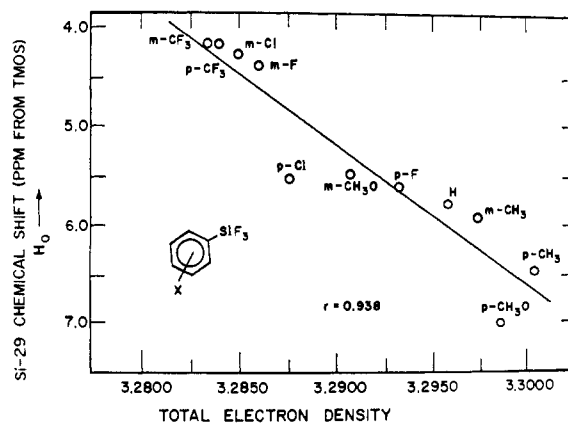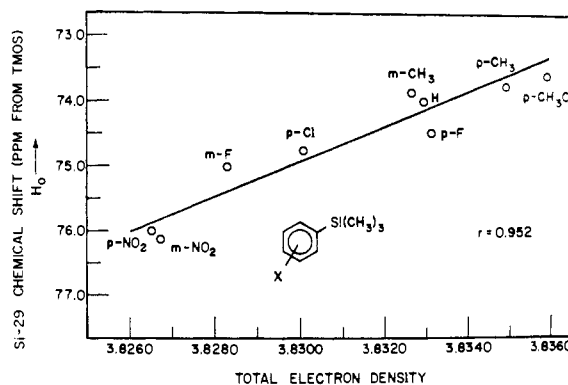
magnetic expression (eq 2) represents those parameters

$$\sigma_{\mathrm{p}} = -(2e^2\hbar^2/3\Delta m^2 c^2)(\langle r^{-3}\rangle_{\mathrm{p}} P_{\mathrm{u}} + \langle r^{-3}\rangle_{\mathrm{d}} D_{\mathrm{u}}) \quad (2)$$

affecting the chemical shift, assuming both p and d electron contributions. For closely related compounds of the type under consideration here, changes in σ_{p} will arise largely from changes in the expectation values of the inverse cube of p and d electron distances from the nucleus, $\langle r^{-3}\rangle_{\mathrm{p}}$ and $\langle r^{-3}\rangle_{\mathrm{d}}$, respectively, and changes in the p and d electron "unbalance," P_{u} and D_{u}, respectively.[33] For similar compounds, the average excitation energy, Δ, is generally assumed to remain constant. Although $\langle r^{-3}\rangle$ has been shown to be at least two or three orders of magnitude greater for p electrons than for d electrons within the same shell, this can be counterbalanced by the fact that the D_{u} term has been estimated to range between 0 and 12 compared to the P_{u} term with values between 0 and 2.[36] For a nucleus such as silicon, which has available low energy vacant orbitals, the relative magnitudes of the p- and d-orbital terms in eq 2 are not clear. Since the P_{u} and D_{u} terms represent elements of the charge density–bond order matrix in the LCAO–MO framework and involve bonding parameters of hybridization, coordination number, and ionicity, their complexity precludes, at present, even an estimate of the direction of chemical shift to be expected from substitution at silicon. In the absence of reliable bonding parameters for the subject silanes, we have chosen to treat the chemical shift data in an empirical manner.

The Hammett plots, presented in Figure 1, for the chemical shifts of the five series of substituted phenylsilanes, $XC_6H_4SiY_3$, illustrate the response of the silicon chemical shift upon systematic substitution in the phenyl group. The silicon nucleus of the silanes ranges from those with electron-rich environments, as in $1\text{-}CH_3$, to those which are electron deficient ($1\text{-}F$). Since substitution occurs at sites well removed from silicon, steric and anisotropic effects are expected to remain essentially constant throughout a given series. These plots indicate the inconsistent response of the $^{29}\mathrm{Si}$ resonance to a given set of substituents and errors which may arise from extrapolating generalizations of substituent shifts based on insufficient data. The equally good linear Hammett correlations for all series, with the exception of $1\text{-}Cl$, demonstrates the regularity of the change in $\delta^{29}\mathrm{Si}$ with substitution in any one system. However, the magnitudes and sign of the slopes for these series differ inconsistently among themselves.

Although the relationship between electron density at a nucleus and its chemical shift appears reasonably linear for proton nmr (excluding steric and other nonelectronic effects), such associations for heavier nuclei seem less reliable.[37] The CNDO-computed electron densities for silanes $1\text{-}H$, $1\text{-}CH_3$, and $1\text{-}F$ (Figures 2–4) indeed suggest this to be the situation for silicon also. In each case, the computed total electron density was found to decrease consistently with the increased electron withdrawing ability of the substituent. Since attempted correlations involving only σ- or π-contributions did not show any reversal from that based on total density in the series $1\text{-}F$, electron density consid-

erations alone cannot adequately account for the sign changes in slopes in the Hammett plots. The possibility does exist, however, that these semiempirical calculations based on assumed and possibly incorrect geometries may fail to provide those electronic descriptions necessary for nmr correlations.

Bonding Interpretations. In a previous $^{29}\mathrm{Si}$ nmr investigation[6] of several monotonic series of methylsilanes $(CH_3)_{4-n}SiX_n$, the reversal of shift direction observed when traversing those series of silanes containing electronegative groups was attributed to (p → d)π bonding. The authors assumed that "an increase in π bonding manifests itself as a shielding effect whereas increasing the polarity of the sp^3 orbitals causes deshielding." It is to be noted that those phenylsilanes which exhibited slopes in the Hammett plots (Figure 1) opposite to that observed for the aryltrimethyl- and aryltrihydrosilanes all contain Y groups (**2a**) capable of π bonding. Consequently, arguments similar to those given above[6] could be used to rationalize the reversed trend in chemical shifts observed for the series $1\text{-}F$, $1\text{-}Cl$, and $1\text{-}OEt$. Resonance contributing structure **2b** would be stabilized by electron
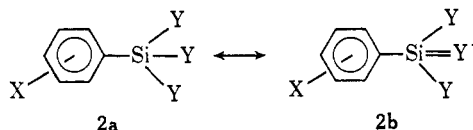
withdrawal from X, leading to an increase in π bonding, thereby affording a shielding of the Si nucleus. This shielding overcompensates for the deshielding effect produced by an increase in the polarization of the Si–Y bond from electron withdrawal by X in **2a**. For silanes $1\text{-}H$ and $1\text{-}CH_3$, **2b** would not be expected to contribute significantly to the ground state description of the phenylsilane, and consequently "normal" electronic effects should be observed. Indeed such a simplistic explanation appears attractive but it is not, however, supported by electron density estimates from CNDO calculations presented here. An alternate approach is suggested by the parallelism exhibited by the π-bonding ability of the groups attached to silicon and their electronegativities.

The Letcher–Van Wazer Treatment. In the studies of Letcher and Van Wazer[38] a theoretical treatment of $^{31}\mathrm{P}$ chemical shifts was derived in terms of electronegativity and π bonding. The contributions of p electrons to the chemical shift (ζ_{p}) formulated by Letcher and Van Wazer as a function of appropriate electronegativities, EN, in the molecule MRZ_3, is given as[38]

$$\zeta_{\mathrm{p}} = 3.0[\tfrac{1}{2}H_Z{}^2 + H_M H_Z + H_M] +$$
$$1.5/\sin^2(\theta/2)[H_Z - H_Z{}^2 + H_Z H_M - H_M] \quad (3)$$

where $H_Z = 1.0 + 1.6(EN_R - EN_M) + 0.035(EN_R - EN_M)^2$, $H_M = 1.0 + 1.6(EN_R - EN_Z) + 0.035(EN_R - EN_Z)^2$, and $\theta = $ M–R–Z bond angle. With these equations, curves were here obtained for silanes $MSiZ_3$, analogous to those generated for phosphorus.[38] The ζ_{p} calculated for various M's at $\theta = 109.5°$ and constant EN_Z values of 1.5, 2.5, and 3.7 are shown in Figure 5. In these curves a smaller ζ_{p} corresponds to resonance at higher magnetic fields. Analogous to the

(36) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **40**, 1714 (1964).

(37) Reference 5a, p 170.

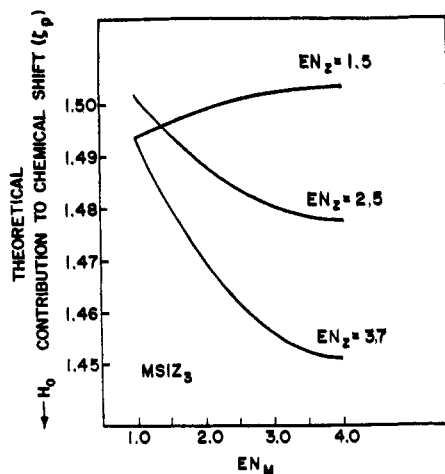(38) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1965); **45**, 2916, 2926 (1966).

Figure 5. Plots of the theoretical contribution of p electrons to the silicon chemical shift (ζ_p) for silanes MSiZ$_3$ as a function of EN_M with EN_Z at constant values of 1.5, 2.5, and 3.7.
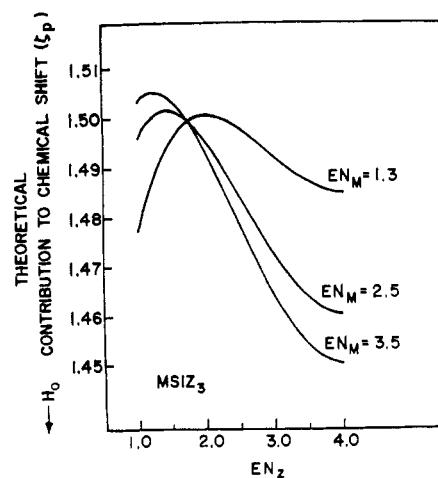

Figure 6. Plots of the theoretical contribution by p electrons to the silicon chemical shift (ζ_p) for silanes MSiZ$_3$ as a function of EN_Z with EN_M at constant values of 1.3, 2.5, and 3.5.

Hammett plots of Figure 1, these graphs also show both positive and negative slopes with changes in M. There is a discrepancy between the EN_M values at which theoretically computed (*ca.* 1.5–2.5) and the experimentally found (*ca.* 2.3–3.0) reversal in slope occur. Similarly, ζ_p values were calculated for MSiZ$_3$ as a function of Z at constant EN_M values of 1.3, 2.5, and 3.5 (Figure 6). An experimental counterpart of Figure 6 for EN_M at 2.5 is given in Figure 7. Although the EN_Z at minimum chemical shift of Figures 6 and 7 do not agree, these graphs certainly contain common features of nonlinearity over wide changes in electronegativity.

Electronegativity Sum Parameter. In work reported on the reactivity of hydrosilanes,[39] complex experimental results were found correlatable with the sum of substituent parameters of all substituents around silicon. It appeared that a similar summation parameter might be useful in the present case. To test this hypothesis, the δ^{29}Si values for more than 40 silanes (Table IV) of general structure **3** obtained from the litera-

$$R_4\text{—Si—}R_2$$

with R_1 above and R_3 below the Si.

3
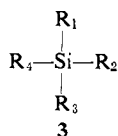
ture[6,12,14] and from in-house experiments were plotted against the summation of electronegativities (ΣEN_i) over all *i* substituents, R_1, R_2, R_3, and R_4 (Figure 8). The resultant relation is best defined as a higher order function of ΣEN_i. The group electronegativity values (EN) of R_i, with the exception of phenyl and vinyl groups, were taken from standard sources.[40] To better fit the observed resonances of phenyl and vinyl silanes to the plot, their EN values were taken as 2.5 rather than the literature's 3.0. Others have submitted that phenyl and vinyl groups on silicon require special values.[41]

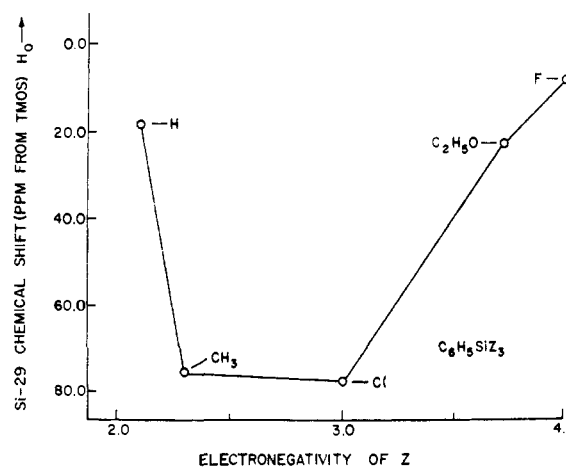Although the δ^{29}Si values found in the literature were obtained under various experimental conditions and,

(39) L. Spialter, L. Pazdernik, S. Bernstein, W. A. Swansiger, G. R. Buell, and M. E. Freeburger, *Advan. Chem. Ser.*, No. 112, 65 (1972).
(40) P. R. Wells, *Progr. Phys. Org. Chem.*, 6, 111 (1968).
(41) C. J. Attridge, *J. Organometal. Chem.*, 13, 259 (1958).

Figure 7. Plot of silicon-29 nmr chemical shifts of phenylsilanes, $C_6H_5SiY_3$, *vs.* the electronegativity of Z.

hence, are not strictly comparable, the plot (Figure 8) shows a surprisingly consistent pattern. This suggests the presence of an additivity principle for silicon chemical shifts in which an important parameter is closely related to group electronegativity values. Least-squares fitting of the data in Figure 8 to a generalized fourth-power polynomial gave the following relation for δ^{29}Si in ppm relative to TMOS.

$$\delta^{29}\text{Si} = 6.14 \times 10^3 - 1.82 \times 10^3(\Sigma EN_i) + 1.95 \times$$
$$10^2(\Sigma EN_i)^2 - 9.17(\Sigma EN_i)^3 + 0.161(\Sigma EN_i)^4 \quad (4)$$

This expression for an *a priori* prediction of silicon chemical shifts appears to agree within about ±10 ppm of that found experimentally.

Although such a treatment of chemical shifts is not adequate for quantitative work, the overall observed general trend is consistent with the data presented here and with the theoretical electronegativity dependence proposed by Letcher and Van Wazer. Silanes **1-H** and **1-CH₃** possess ΣEN_i values which lie to the left of the minimum in Figure 8, and, consequently, any small increase in the electronegativity of the phenyl group would be predicted to produce a downfield shift; con-
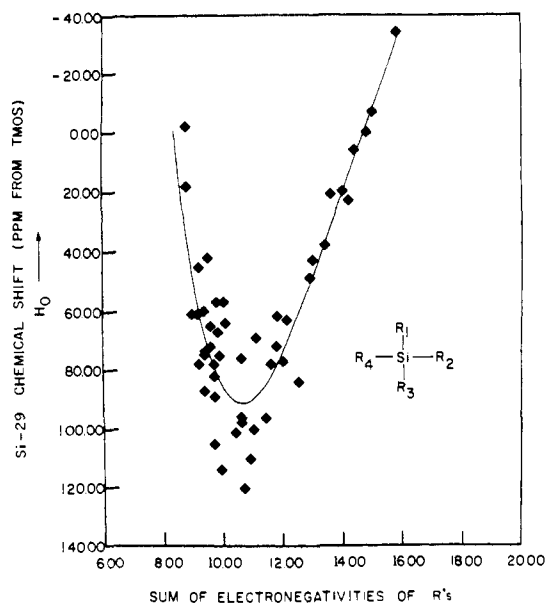
Figure 8. Plot of silicon-29 nmr chemical shifts of silanes R_1R_2Si-R_3R_4 as a function of the sum of electronegativities of R_i.

Table IV. Chemical Shift and Sum of Electronegativity Values for Silanes Used in Figure 8

Silane[a]	Chemical shift[b] (ppm from TMOS)	ΣEN_i[c]
Me_2SiH_2	38.0[d]	8.8
$PhSiH_3$	18.0[d]	8.8
Me_3SiH	61.0[d]	9.0
$PhMeSiH_2$	41.6[d]	9.0
Me_4Si	78.5[e]	9.2
$PhMe_2SiH$	60.9[d]	9.2
Ph_2SiH_2	44.6[d]	9.2
$PhSiMe_3$	74.0,[e] 75[d]	9.4
Ph_2SiMe_2	72.0[d]	9.6
Vi_2SiMe_2	64.8[e]	9.6
Me_3SiCH_2OH	78.2[f]	9.7
Me_3SiCH_2Cl	81.6[g]	9.7
$Me_3SiCHCl_2$	89.0[e]	9.7
Vi_3SiMe	57.9[e]	9.8
Ph_3SiMe	67.0[d]	9.8
$MeSiCl_3$	115.0[d]	9.9
$PhMe_2SiCH_2Cl$	75.2[e]	9.9
Vi_4Si	57.0[d]	10.0
$Vi_2MeSiCH_2Cl$	64.5[e]	10.1
$Me_2ClSiCHCl_2$	101.1[f]	10.4
Ph_2MeSiH	60.0[d]	10.4
Et_3SiOH	97.8[f]	10.6
Me_3SiOMe	96.5[d]	10.6
$PhSiHCl_2$	76.3[f]	10.6
Me_2SiCl_2	120.0[d]	10.7
Me_3SiF	110.4[g]	10.9
$MeCl_2SiCH_2Cl$	100.1[f]	11.0
Cl_3SiH	69.2[f]	11.1
$MeSiCl_3$	96.0[d]	11.4
$PhSiCl_3$	77.7[f]	11.6
$Cl_3SiCHCl_2$	72.0[f]	11.8
$(EtO)_2MeSiH$	62.4[f]	11.8
$Me_2Si(OMe)_2$	77.0[d]	12.0
$SiCl_4$	63.0[d]	12.1
Me_2SiF_2	83.8[g]	12.5
Ph_2SiF_2	49.0[d]	12.9
Cl_3SiF	42.9[g]	13.0
$MeSi(OMe)_3$	38.0[d]	13.4
$PhSi(OMe)_3$	21.0[f]	13.6
Cl_2SiF_2	20.0[g]	14.0
CH_3SiF_3	23.2[g]	14.2
$PhSiF_3$	6.0[f]	14.4
$(MeO)_4Si$	0.0[d]	14.8
$ClSiF_3$	-6.7[g]	15.0
SiF_4	-34.0[g]	15.8

[a] Abbreviations: Et = ethyl, Me = methyl, Ph = phenyl, Vi = vinyl. [b] Positive chemical shift values indicate low field side of reference. [c] Reference 40. [d] Reference 6. [e] Reference 14 original data converted using $\delta^{Si(CH_3)_4}$ 78.5 ppm. [f] Data taken from this laboratory. [g] Reference 12; original data converted using δ^{SiF_4} -34.0 ppm.

versely silanes 1-F, 1-Cl, and 1-OEt would be expected to exhibit an opposite upfield shift for a corresponding change in electronegativity. Concomitantly, those silanes which lie in the vicinity of the minimum in Figure 8 should display irregular chemical shifts with changes in the effective electronegativity of the groups. This could account for the substantially poorer correlation of $\delta^{29}Si$ with Hammett constants found for 1-Cl.

This U-shaped dependence on electronegativity also predicts similar shifts for silicon in grossly different electronic environments. For example, a chemical shift of about 20 ppm downfield from TMOS is correctly estimated for both phenyltrihydrosilane and phenyltriethoxysilane although the electronic properties of the -OEt and -H differ considerably.

Although the above description appears to relate many of the chemical shift studies presently available, its limitations must be realized. For example, the ^{29}Si chemical shifts of various methyl silylcarboxylates, $(CH_3)_nSi(O_2CR)_{4-n}$, have been reported[10] for $n = 1, 2$, and 3 with R's of varying electronic character. The chemical shifts of the members of a given monotonic series (R remaining constant) gave the expected minimum with increasing n. These values agreed with that predicted from Figure 8. However, within each series, the effect of varying R from electron-donating to electron-withdrawing types produced downfield shifts. The electronegativity sum parameter offered here predicts, for $n = 1$ and 2, a chemical shift trend opposite to that observed. For $n = 3$, however, the ΣEN_i value lies close to the minimum and either direction of change may be anticipated.

In addition, silanes containing bromine or iodine were omitted because of significant deviations from the general trend illustrated in Figure 8. The "heavy atom effect," analogous to that observed for the iodo- and bromomethanes,[42] has been invoked to explain the abnormal high-field chemical shifts for such halosilanes.

(42) W. M. Litchman and D. M. Grant, J. Amer. Chem. Soc., 90, 1400 (1968).

Conclusions

It is clear from this study that substituent effects on the silicon resonance are not uniform and that chemical shift assignments based upon analogies even to closely related silanes can lead to error. Until reliable bonding parameters for silicon compounds incorporating d orbitals become available, interpretation of silicon chemical shift data based upon a $(p \rightarrow d)\pi$ mechanism should be made with caution. The present state of theory is not sufficiently advanced to permit an analysis of bonding and electronic implications nor to account for the highly inconsistent relationships observed. The empirical U-shaped curve, at present, appears best to describe the silicon-29 chemical shifts except for those silanes containing bromine or iodine and does so without invoking any explicit π-bonding contributions.

Complexation of Phenylboronic Acid with Lactic Acid. Stability Constant and Reaction Kinetics

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Abstract: Phenylboronic acid, $PhB(OH)_2$, forms a 1:1 complex with lactic acid in which the hydroxyl proton of the ligand is displaced by boron. The stability constant for the reaction was determined by pH titration methods and found to be 3.7×10^{-3} ($\pm 10\%$). The kinetics were studied by the temperature-jump relaxation technique. The rate constant for the reaction of fully protonated lactic acid with $PhB(OH)_2$ is 140 M^{-1} sec^{-1} ($\pm 10\%$); the rate constant for the reaction of the acid anion is 1500 M^{-1} sec^{-1} ($\pm 10\%$). This is discussed in terms of a mechanism in which the interaction of the electron-rich carboxylate anion with the phenyl ring on $PhB(OH)_2$ is reflected in the relatively greater rate constant for the reaction of the acid anion.

Boric acid forms complexes with α-hydroxy carboxylic acids in which the hydroxyl proton of the ligand is displaced by boron.[1] On this process boron undergoes a change in coordination number from three to four, the ligands being bidentate and forming five-membered chelate rings. The overall reaction is then
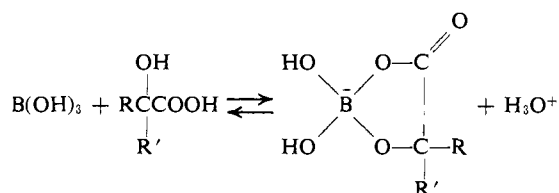
The existence of the proposed five-membered chelate rings in solution has recently been demonstrated by vibrational spectroscopy for both α-hydroxy carboxylic acid complexes[2] and polyol complexes.[3]

There are a few studies in the literature on fast boric acid reactions. Eyring[4] has shown that polyborate formation is quite rapid. In his interpretation of the kinetics, it was assumed that the reaction of $B(OH)_3$ with OH^- to produce the tetrahedral $B(OH)_4^-$ is diffusion controlled. The assumption has been questioned recently.[5] In either case, this process is faster by several orders of magnitude than the overall complexation of boric acid with tartaric acid[6] and is clearly not responsible for the differences in rate observed among various ligands.

The results of the study of the tartaric acid complexation suggest that at least two factors are important in accounting for differences in reaction rate among ligands. One is the acidity of the ligand and the other

is the notion that any interaction of ligand with boric acid which stabilizes a four-coordinate species would be reflected in an increased rate.

The present study, the reaction of phenylboronic acid, $PhB(OH)_2$, with lactic acid, was undertaken to examine further the effect of ligand donor atom protonation on the reaction rates. Secondly, a first study of the effect on reaction of substitution on boron can be carried out.

Experimental Section

Phenylboronic acid (Alfa) and lactic acid (minimum 85%, Mallinkrodt Analytical Reagent) were used without further purification. Stock solutions of lactic acid were prepared by dilution. They were refluxed for at least 12 hr to effect complete hydrolysis of the anhydride present in the 85% solution.[7] Stock solutions were standardized by pH titrations using a Corning Model 12 research pH meter. pH was accurate to ± 0.01 pH unit. Titrations were carried out in a nitrogen atmosphere in a double-walled beaker which was maintained at 25° by a circulating water bath. All solutions were made up to an ionic strength of 0.1 M by addition of KNO_3.

Stability constants were also determined by pH titration methods. The activity coefficient of H^+ ion was calculated using the Davies equation.[8]

$$\log \gamma_{\pm} = -0.5|z_+z_-| \left\{ \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right\}$$

All kinetic experiments were carried out on a temperature-jump instrument which utilizes the method of Joule heating. The temperature jump is produced by the discharge through the solution of a 0.1 μf high voltage capacitor charged to 30 kV. The ionic strength of the solution is maintained at a minimum of 0.1 M. Under these conditions the resistance of the cell is about 100 Ω. The rise time is of the order of a few microseconds. About 1 ml of solution is heated, the temperature rise being 10°. Reactions are monitored spectrophotometrically and recorded on a storage oscilloscope. Relaxation times are measured from photographs of the reaction traces.

The experimental reaction traces were plotted semilogarithmically. In all cases simple exponentials were observed. The relaxation

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(5) E. Yeager, F. H. Fisher, J. Miceli, and R. Bressel, *J. Acoust. Soc. Amer.*, **53**, 1705 (1973).

(6) K. Kustin and R. Pizer, *J. Amer. Chem. Soc.*, **91**, 317 (1969).

(7) W. D. Bancroft and H. L. Davis, *J. Phys. Chem.*, **35**, 2508 (1931).

(8) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).