Physical Organosilicon Chemistry. I. Nuclear Magnetic Resonance Studies of Ortho-, Meta-, and Para-Substituted Phenyltrimethylsilanes. Evidence Bearing on the Existence of $(p \rightarrow d)\pi$ "Back-Bonding" in Phenylsilanes

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Abstract: The chemical shift (δ) and ^{13}C–H coupling constant (J) of the methyl groups of 25 substituted phenyltrimethylsilanes were measured. The J values of the ortho, meta, and para compounds were individually correlated with the respective Hammett σ values, producing a slope, ρ, indicative of the ability of Si to transmit electronic effects. In comparison with the C, O, and N analogs, the Si is the most effective transmitter. The results can be explained in terms of $(p \rightarrow d)\pi$ "back-bonding" in the phenyltrimethylsilanes.

The possibility of interaction between the empty 3d orbitals of silicon and adjacent σ or π electrons has been the subject of much research and debate. This "back-bonding" has been invoked to explain the electronic characteristics of phenylsilanes, where the π system of the benzene ring is thought to donate electron density to the vacant 3d orbitals of silicon, forming a $(p \rightarrow d)\pi$ bond.

Because of the greater electronegativity of carbon relative to silicon, a silicon-containing group should be a better inductive electron donor than its carbon analog. Experiments to measure the donor properties of substituent groups directly bonded to a benzene ring indicate that the trimethylsilyl group is a net weak electron donor.[1] This result is generally rationalized as a near cancellation of the inductive electron donation by $(p \rightarrow d)\pi$ back-bonding electron withdrawal. This is derived from the fact that the trimethylsilyl group α to a benzene ring (for example, in $PhCH_2Si(CH_3)_3$) appears as a strong electron donor,[1e,g,l,p,2] despite the insulating, intervening methylene, yet when the silicon is bonded directly to the benzene ring (for example, in $PhSi(CH_3)_3$), it shows only weak electron donating properties.

The Hammett σ values have proven useful in correlating many molecular properties and reactivities of aromatic systems with the electronic demands of substituent groups.[3] In particular, the methyl group chemical shifts and ^{13}C–H coupling constants of substituted toluenes, anisoles, *tert*-butylbenzenes, and dimethylanilines,[4] the methyl group chemical shifts of substituted toluenes, acetophenones, and thioanisoles,[5] and the methyl group chemical shifts of substituted *tert*-butylbenzenes and phenyltrimethylsilanes[1m] have been correlated with the various σ values. The slopes, ρ, of the derived Hammett plots have been taken as a measure of the ability of the intervening moiety to transmit the electronic effects.

The object of this research was to determine the chemical shifts (δ) and ^{13}C–H coupling constants (J) of the methyl groups of an extensive series of ortho-, meta-, and para-substituted phenyltrimethylsilanes and to correlate these data with a set of Hammett σ values. The slope (ρ) of the lines may then be compared with those for the analogous carbon, oxygen, nitrogen, and sulfur compounds, and a measure of the relative ability of silicon to transmit electronic effects may be determined. Most of the evidence for $(p \rightarrow d)\pi$ bonding in phenylsilanes has been determined for the molecules in excited electronic states (esr,[1c,f,h,i] uv[1b,c,e,g,q]) or from reactivities (desilylation,[1l] acid strength,[1j,2] Birch reduction[1b]). Information concerning electronic ground-state interactions (nmr,[1a,m,n] photoelectron spectroscopy,[1o] charge-transfer complexes[1p]) is not as complete. This study provides additional information pertaining to the extent of $(p \rightarrow d)\pi$ bonding in the ground state of phenylsilanes.

Experimental Section

Preparation of Substituted Phenyltrimethylsilanes. All of the phenyltrimethylsilanes were prepared by either procedure A or procedure B (except for the nitro isomers). The compounds were distilled at reduced pressure and the center cut of the distillate was further purified by preparative gas chromatography (20 ft × $^3/_8$ in., 15% SE-30 on Chromosorb W, Varian Aerograph, Model 1868). Analytical information (Galbraith Laboratories, Knoxville, Tenn.), m/e of the parent ion (CEC-491 mass spectrometer), and the method of preparation are tabulated in Table I.

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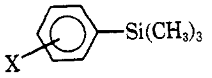
(2) C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 939 (1954).

(3) (a) H. H. Jaffé, *Chem. Rev.*, **53**, 91 (1953); (b) R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, **81**, 5343 (1959); (c) R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959); (d) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 709 (1963); (e) *ibid.*, **85**, 3146 (1963); (f) R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *ibid.*, **88**, 1413 (1966); (g) *ibid.*, **87**, 3260 (1965); (h) R. T. C. Brownlee and R. W. Taft, *ibid.*, **90**, 6537 (1968); (i) R. W. Taft and J. W. Rakshys, Jr., *ibid.*, **87**, 4387 (1965).

(4) C. H. Yoder, R. H. Tuck, and R. E. Hess, *ibid.*, **91**, 539 (1969).

(5) S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966).

Table I. Analytical Data of Substituted Phenyltrimethylsilanes



X	Ref	Procedure	Yield, %	% found C	% found H	% found Si	% calcd C	% calcd H	% calcd Si	m/e parent ion	Mol wt
o-F–	6	A	21	63.98	7.82	16.61	64.23	7.82	16.68	168	168.27
m-F–		A	31	64.47	7.76	16.92	64.23	7.82	16.68	168	168.27
p-F–	*a*	A	38	64.35	7.89	16.48	64.23	7.82	16.68	168	168.27
o-CH_3–	7	B	29	73.13	9.85	17.20	73.09	9.85	17.20	164	164.30
m-CH_3–	7	B	47	72.97	9.72	17.20	73.09	9.85	17.20	164	164.30
p-CH_3–	7	B	32	72.95	9.69	17.19	73.09	9.85	17.20	164	164.30
o-CH_3O–		A	23	66.84	8.84	15.34	66.61	8.94	15.57	180	180.30
m-CH_3O–	*b*	A	30	66.85	8.80	15.48	66.61	8.94	15.57	180	180.30
p-CH_3O–	*c*	A	43	66.50	8.87	15.31	66.61	8.94	15.57	180	180.30
o-Ph–	7	B	27	79.80	8.09	12.61	79.58	8.01	12.40	226	226.37
m-Ph–	7	B	31	79.65	8.15	12.23	79.58	8.01	12.40	226	226.37
p-Ph–	7	B	25	79.80	7.95	12.26	79.58	8.01	12.40	226	226.37
o-CF_3–		A	38	55.27	5.93	13.01	55.02	6.00	12.86	218	218.25
m-CF_3–		A	25	54.84	5.87	12.60	55.02	6.00	12.86	218	218.25
p-CF_3–		A	22	55.31	5.90	12.95	55.02	6.00	12.86	218	218.25
o-Cl–	6	A	21	58.71	6.90	14.95	58.51	7.09	15.20	184[d]	184.27[d]
m-Cl–	7	A	37	58.77	6.93	14.93	58.51	7.09	15.20	184[d]	184.27[d]
p-Cl–	7	A	37	58.42	7.04	15.35	58.51	7.09	15.20	184[d]	184.27[d]
m-$Si(CH_3)_3$	7	A	20	64.88	9.94	25.08	64.78	9.96	25.24	222	222.43
p-$Si(CH_3)_3$	7	A	38	64.77	9.94	25.41	64.78	9.96	25.24	222	222.43
o-NO_2–	*i*	*e*	60[f]	55.45	6.89	14.17	55.35	6.70	14.38	195	195.27
m-NO_2–	*i*	*e*	60[f]	55.55[g]	6.95[g]	14.01[g]	55.35	6.70	14.38	195	195.27
p-NO_2–	*i*	*e*	60[f]	55.55[g]	6.95[g]	14.01[g]	55.35	6.70	14.38	195	195.27
p-PhO–		A	4	74.16	7.30	11.79	74.32	7.48	11.58	*h*	*h*
Unsubstituted		*j*								150	150.24

[a] J. D. Roberts, E. A. McElhill, and R. Armstrong, *J. Amer. Chem. Soc.*, **71**, 2923 (1949). [b] R. A. Benkeser, R. H. Hickner, D. I. Hoke, and O. H. Thomas, *ibid.*, **80**, 5289 (1958). [c] R. A. Benkeser and H. R. Kripiak, *ibid.*, **75**, 4528 (1953). [d] Mass of ^{35}Cl isotope. [e] See Experimental Section for procedure. [f] Combined yield of ortho, meta, and para isomers, ratio *ca.* 1:1:1. [g] Analyzed as mixture of meta and para isomers. [h] Not determined. [i] J. L. Speier, *J. Amer. Chem. Soc.*, **75**, 2930 (1953). [j] Purchased from Pierce Chemical Co.

Procedure A.[6] To a mixture of 2.4 g (0.10 g-atom) of magnesium metal and 10.8 g (0.10 mol) of chlorotrimethylsilane in 75 ml of tetrahydrofuran (THF) was added 17.5 g (0.10 mol) of *m*-bromofluorobenzene at a rate which maintained the THF at its reflux temperature. After addition was complete and the magnesium had reacted completely, stirring was continued at room temperature for 2 hr. Following the addition of 50 ml of saturated aqueous ammonium chloride solution, the organic layer was separated, dried with magnesium sulfate, and distilled. After vpc of the distillate, 5.4 g (32%) of pure *m*-fluorophenyltrimethylsilane was obtained.

Procedure B.[7] A mixture of 4.6 g (0.20 g-atom) of sodium metal and 100 ml of toluene was heated to its reflux temperature and a solution of 21.8 g (0.10 mol) of *o*-iodotoluene, 10.8 g (0.10 mol) of chlorotrimethylsilane, and 50 ml of toluene was carefully added. The reaction was maintained at its reflux temperature for 4 hr, the solution was cooled, the sodium salts were removed by filtration, and the mixture was distilled. The distillate, purified by vpc, yielded 4.8 g (29%) of *o*-methylphenyltrimethylsilane.

***o*-, *m*-, and *p*-Nitrophenyltrimethylsilane.** Phenyltrimethylsilane was nitrated in acetic anhydride-fuming nitric acid,[8] affording an approximately 1:1:1 mixture of the ortho, meta, and para isomers. The pure ortho isomer was separated from the meta and para isomers by vpc, the latter two being obtained as a mixture of 36% meta and 64% para. The combined yield of the three isomers was 60%.

Nuclear Magnetic Resonance Data. A. Chemical Shifts (δ). The methyl group chemical shifts were determined on a Varian Associates HA-100 nmr spectrometer. Individual δ's were measured at concentrations of 3, 6, and 9 wt % in methylene chloride and extrapolated to infinite dilution. Chemical shifts were measured relative to the methylene chloride lock signal and have been converted to cycles per second downfield of tetramethylsilane (TMS) by subtraction from the resonance signal of TMS at infinite dilution in the same solvent (529.70 cps). The reported values are extrapolated from the average of three sweeps (50 cps) per point (measured on a frequency counter). The extrapolation was linear within the concentration range and the probable error of δ is ±0.05 cps.

B. ^{13}C–H Coupling Constants (J). The coupling constants were determined on a Varian Associates HR-60 nmr spectrometer equipped with a frequency counter. Solutions were 50 vol % (or saturated solutions of the solid samples) in methylene chloride, which served as the internal lock. The J values reported are the average of three sweeps at 250 cps. These values were compared to those obtained for neat solutions on a Varian Associates A-60 nmr spectrometer equipped with a phase lock and precalibrated against known compounds. The values of the neat and 50% solutions were identical within experimental error (±0.15 cps). The values reported are those from the HR-60 measurements.

Results

The chemical shifts (δ) and ^{13}C–H coupling constants (J) were found to correlate best with the "normal" Hammett σ values,[3a] rather than with σ^0,[3g] σ_R^0,[3e,h] or σ_I.[3c] The plots of the δ and J values *vs.* σ appear in Figures 1–5, the experimental values of J and δ are given in Table II, and the slopes (ρ) and linear correlation coefficients of the plots are presented in Table III. It is apparent that, contrary to the results of J *vs.* σ plots for *tert*-butylbenzenes, dimethylanilines, and anisoles,[4] the results for the ortho, meta, and para isomers here cannot be accommodated by a single line. (It must be pointed out that other workers have investigated mainly para isomers and the accommodation of para and meta by a single line may be fortuitous.) However, good correlations were obtained when the ortho, meta, and para compounds were treated separately.

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(6) C. Eaborn, K. L. Jaura, and D. R. M. Walton, *J. Chem. Soc.*, 1198 (1964).

(7) H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *J. Amer. Chem. Soc.*, **73**, 3798 (1951).

(8) J. L. Speier, *ibid.*, **75**, 2930 (1953).

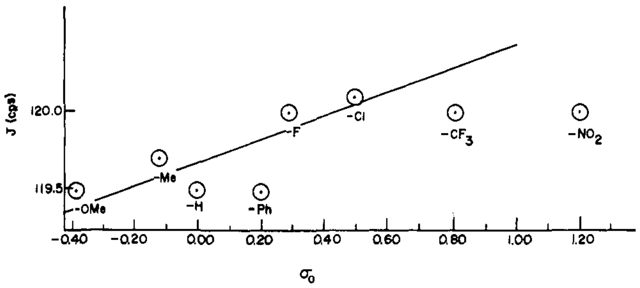


Figure 1. Plot of ^{13}C–H coupling constant (J) *vs.* σ_o.

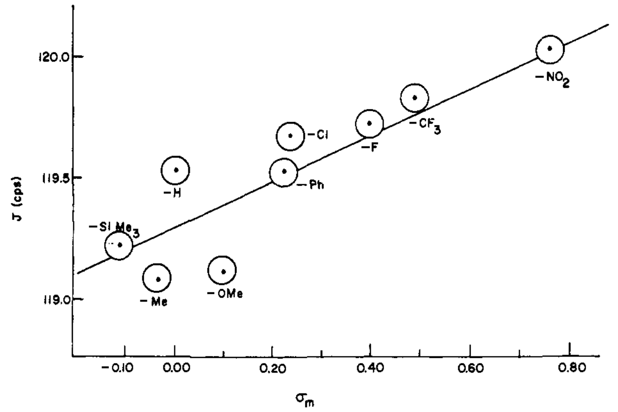


Figure 2. Plot of ^{13}C–H coupling constant (J) *vs.* σ_m.

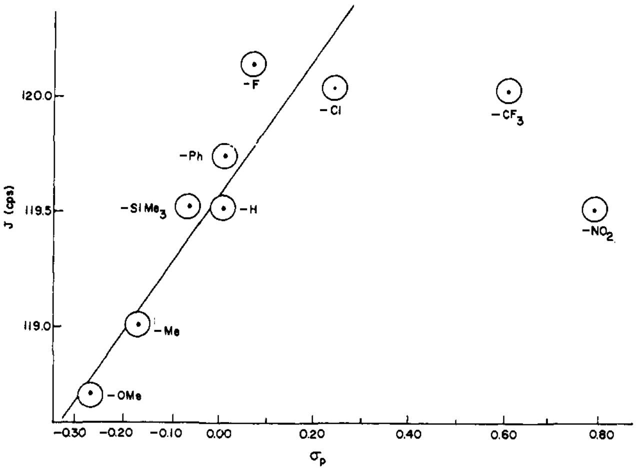


Figure 3. Plot of ^{13}C–H coupling constant (J) *vs.* σ_p.

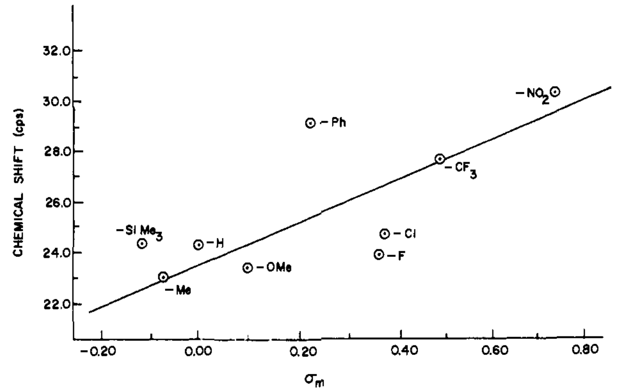


Figure 4. Plot of chemical shift (δ) *vs.* σ_m.

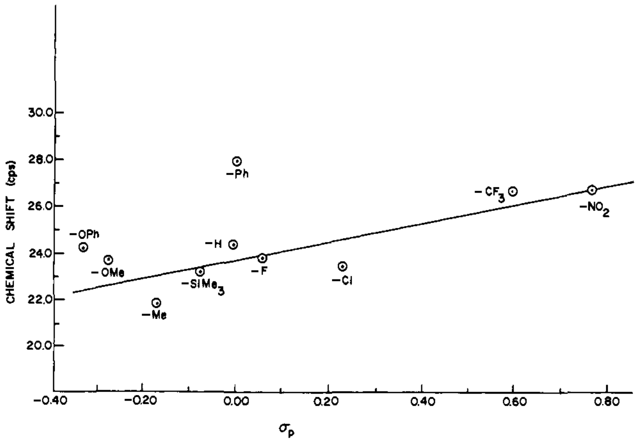


Figure 5. Plot of chemical shift (δ) *vs.* σ_p.

The least-squares plots of J *vs.* σ show reasonably good correlation coefficients. The values for the *o*- and *p*-nitro and trifluoromethyl compounds were omitted from the computation (see Discussion). In addition, the *o*-phenyl compound has been excluded from the mathematical treatment of Figure 1 (if included, ρ = 0.63 cps/σ, correlation coefficient = 0.730). The justification for this latter exclusion rests upon the severe steric requirements upon placing a phenyl ring adjacent to a trimethylsilyl group. Indeed, the large upfield shift of the resonance of the methyl groups in *o*-phenylphenyltrimethylsilane (δ −2.99 cps) indicates that the *o*-phenyl is tilted out of the molecular plane, placing the methyls in the shielding region (**1**); this lack

Table II. Methyl Group Chemical Shifts and ^{13}C–H Coupling Constants of Substituted Phenyltrimethylsilanes

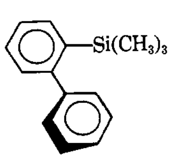
Substituent	Chemical shift, cps[a] Ortho	Meta	Para	Coupling constants, cps Ortho	Meta	Para
-Cl	34.40	24.60	23.30	120.1	119.7	120.0
$-OCH_3$	23.40	23.60	23.70	119.5	119.1	118.7
$-CH_3$	29.90	23.10	21.90	119.7	119.1	119.0
-F	29.20	24.10	23.60	120.0	119.7	120.1
-Ph	−3.00	29.10	27.90	119.5	119.5	119.7
$-CF_3$	34.00	27.70	26.30	120.3	119.8	120.0
$-Si(CH_3)_3$	*b*	24.40	23.10	*b*	119.2	119.5
-OPh	*b*	*b*	23.70	*b*	*b*	*b*
Unsubstituted		24.20			119.5	

[a] Positive values are downfield of TMS at 100 MHz. [b] Not determined.

Table III. Least-Squares Analyses of Plots of Methyl Group Chemical Shifts and ^{13}C–H Coupling Constants *vs.* σ

Plot	ρ, cps/σ	Linear correlation coefficient
(δ *vs.* σ)$_m$	6.86	0.828
(δ *vs.* σ)$_p$	3.99	0.864
(J *vs.* σ)$_o$[a]	0.73	0.896
(J *vs.* σ)$_m$	1.12	0.869
(J *vs.* σ)$_p$	2.89	0.921

[a] Values of σ_o are from example 31 in M. Charton, *J. Amer. Chem. Soc.*, **91**, 6649 (1969).



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of coplanarity also minimizes any resonance interaction between the phenyl rings.

The correlations of δ with σ were not as good as those of J, an observation paralleling other reported cases.[4] No correlation could be made for the ortho-substituted compounds, undoubtedly owing to anisotropy effects. For the para- and meta-substituted compounds, the phenyl substituents have also been excluded from the least-squares computation. (Both exhibit marked downfield shifts.)

Discussion

Theory predicts that the more electronegative the group (or atom) adjacent to a C–H bond, the greater the ^{13}C–H coupling constant, J.[4] Silicon is less electronegative than carbon (0.7 unit on the Pauling scale), and in comparing the J's of unsubstituted phenyltrimethylsilane (**2**), *tert*-butylbenzene (**3**), dimethylaniline (**4**), and anisole (**5**), the expected trend is observed (Table IV).

Table IV. ^{13}C–H Coupling Constants of C_6H_5–$M(CH_3)_i$

M	i	J, cps
Si	3	119.5
C	3	125.5
N	2	134.45
O	1	143.0

Although a complete study has been reported on the relationship of J and σ with varying substitution of the phenyl ring on the above latter three classes of compounds,[4] no data were heretofore available for the analogous silicon derivatives. The silanes represent a particularly interesting case for study because of the possibility of (p → d)π back-bonding making a contribution to the transmission of electronic effects.[9] Regardless of the mechanism of the (p → d)π donation, the net result should be a decrease in the "effective electronegativity" of the silicon and a concurrent decrease in the J. The chemical shifts (δ) are similarly affected, with decreased electronegativity resulting in an upfield shift.

From the J's of the unsubstituted compounds (Table IV), silicon still appears to be the least electronegative of the series Si, C, N, O, but the relationship between J and electronegativity is far from linear (Table V). Although the $\Delta\chi$ for Si to C is almost 75% greater than the resulting $\Delta\chi$ for C to N and N to O, the corresponding ΔJ is 33% less. This admittedly crude comparison (comparing elements from the second and third row of the periodic table may not be valid) is consistent with a contribution from the phenyl system to the effective electronegativity of the silicon of a magnitude greater than that for the analogous carbon, nitrogen, and oxygen systems.

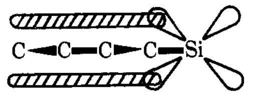
Table V. Comparison of Differences in Pauling Electronegativity ($\Delta\chi$) with Shift of ^{13}C–H Coupling Constant (ΔJ) in Compounds **2**, **3**, **4**, and **5**

	$\Delta\chi$	ΔJ, cps
(Si to C)$_{2\rightarrow3}$	0.70	6.0
(C to N)$_{3\rightarrow4}$	0.45	9.0
(N to O)$_{4\rightarrow5}$	0.45	8.5

From the plots of J *vs.* σ (Figures 1–3), the ρ values can be compared with those cited above for the corresponding carbon, nitrogen, and oxygen compounds. The values for *tert*-butylbenzenes, dimethylanilines, and anisoles are 0.568, 2.68, and 1.08 cps/σ, respectively. It is seen from Table III that in the para position, silicon is a more effective transmitter of electronic effects than is carbon, oxygen, or nitrogen; in the meta position, silicon is more effective than carbon, comparable to oxygen, and poorer than nitrogen. The ρ of the J *vs.* σ_o plot is surprisingly small. This could be due to the choice of σ_o values or/and steric factors. It has been suggested that steric factors are important in ortho substitution only when one group is large, *e.g.*, *tert*-butyl.[10] Unfortunately, trimethylsilyl meets this criterion. However, the ortho plot is qualitatively similar to the para plot. The fact that silicon is a better transmitter of electronic effects when it is in the para position than in the meta position is suggestive of an interaction of the substituent and the silicon *via* the π framework of the aromatic system. In comparison to the C, O, and N analogs, it appears that this mode of interaction is more effective for silicon than for the second-row elements. The fact that silicon is a better transmitter of electronic effects in the meta position than is carbon probably reflects the greater polarizability of silicon relative to carbon. The effectiveness of silicon para is best interpreted in terms of (p → d)π back-bonding.

The mode of interaction of the phenyl π system with the vacant 3d orbitals of silicon can be crudely depicted by overlap of a vacant silicon 3d orbital of appropriate symmetry with the occupied π orbital of the phenyl ring (**6**) which, in the extreme case, could place a formal negative charge on a doubly bonded silicon (**7**). The small range of J's suggests that the extreme **7** is not approached to any extent.

Referring to Figures 1 and 3, over the range of electron donors and weak electron acceptors, one observes the change of J to be linear with σ. However, for strong electron acceptors (–CF_3, –NO_2) a discontinuity occurs. This may be explained by the electron density of the π system (and at the carbon attached to silicon in particular) being so depleted that back-bonding becomes ineffective. Since the degree of back-bonding is almost certainly small to begin with, a disappearance of the effect with a decrease in π-electron density is not unexpected.



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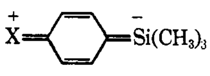

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The comparison of the plots of δ *vs.* σ (Figures 4–5) does not afford much information. With the excep-

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(9) A referee has suggested that the enhanced transmission of electronic effects may be explained in terms of the greater polarizability of silicon and that d orbitals need not be invoked. The possibility of polarization contributing to the observed effects cannot be excluded, but the evidence for some (p → d)π bonding in phenylsilanes is well documented (see ref 3p and articles cited therein). Molecular orbital calculations (CNDO with inclusion of 3d orbitals) of $PhSiMe_3$ and $PhSiH_3$ indicate a small degree of π bonding between the phenyl ring and the silicon. Work on the MO calculations of substituted phenylsilanes is continuing in this laboratory and will be the subject of a subsequent paper.

(10) M. Charton, *J. Amer. Chem. Soc.*, **91**, 6649 (1969).

tion of the phenyl substituent, a linear relationship exists for the para and meta series. The ortho series suffers from (a) anisotropic effects of the substituents on the δ and (b) uncertainty in the values of σ_o[10] chosen. The δ values were found to be quite solvent dependent (in methylene chloride), with the compounds having the more polar substituents generally being the most affected.

The large solvent effect makes any comparison of the ρ values for phenylsilanes with those of *tert*-butylbenzenes, dimethylanilines, and anisoles questionable. However, the ρ values for **2** are similar to those for **3** ($(Si(CH_3)_3)_m$, 6.86 cps/σ; $(Si(CH_3)_3)_p$, 3.99 cps/σ; $C(CH_3)_3$, 4.56 cps/σ), while those for **4** (9.59 cps/σ) and **5** (16.2 cps/σ) are greater, owing probably to the presence of lone electron pairs in the latter two.[4] Such correlations of δ and σ for protons are common,[5] but the magnitude of the effect is generally small and the system is not sensitive to small changes in the electron distribution. The similarity between the ρ values of *tert*-butylbenzenes and phenyltrimethylsilanes has been reported (5.38 *vs.* 5.86 cps/σ, measured at 60 MHz).[1m]

In conclusion, the correlation of J *vs.* σ in substituted phenyltrimethylsilanes indicates that silicon's effective electronegativity is more affected by the nature of the substituent than that for the analogous atom in comparable carbon, nitrogen, and oxygen compounds. This is particularly pronounced when the silicon is para, permitting the maximum effect of $(p \rightarrow d)\pi$ back-bonding between the phenyl π system and the silicon 3d orbitals. When the π-electron density of the phenyl is significantly reduced, as with the strong electron-acceptor substituents $-CF_3$ and $-NO_2$, the J values do not correlate with σ for the ortho and para isomers. The correlation of J *vs.* σ over the entire range of meta substituents suggests that the degree of $(p \rightarrow d)\pi$ back-bonding here is smaller than that in the directly conjugated ortho and para cases. The same trend of para substitution being more effective than meta substitution for transmission of the electronic effects is observed in the correlation of δ *vs.* σ.

The magnitude of the shifts are quite small, suggesting either that $(p \rightarrow d)\pi$ back-bonding in the ground state is not a large effect or that the $^{13}C-H$ coupling constants are not a sensitive test of this effect. Work is currently in progress to determine the $^{29}Si-^{1}H$ coupling constants of the series $X-C_6H_4-SiH_3$ to resolve this point. Additionally, because of the reduced number of basis sets required for $-SiH_3$ (relative to $-SiMe_3$), MO calculations will allow a differentiation between polarization effects and $(p \rightarrow d)\pi$ back-bonding. These problems will be dealt with in a later paper.

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The Phosphorus–Phosphorus Bond. I. Complexes Containing Highly Connected Phosphorus Atoms, $H_nMe_{3-n}PPF_5$. The Directly Bonded Phosphorus–Phosphorus Coupling Constant

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Abstract: The reaction of alkylphosphines with PF_5 has produced the Lewis adducts $Me_3P \rightarrow PF_5$, $HMe_2P \rightarrow PF_5$, and $H_2MeP \rightarrow PF_5$, which have been characterized by nmr spectroscopy and reaction stoichiometry. These molecules ostensibly contain both octahedral and tetrahedral P-atom environments. The trimethylphosphine complex is a white solid which is stable at 25° *in vacuo*, but there is a marked decrease in stability as the number of hydrogen atoms in the molecule is increased. Equilibrium studies showed that the complexes have a stronger P–P coordinate bond than the similar P–N bond and that PF_5 is a stronger acid than BF_3 toward PMe_3. Although $^2J_{PF_{eq}}$ approximates +200 Hz for all three adducts, $^2J_{PF_{ax}}$ is zero. The P–P coupling in these molecules (+720 Hz) is the largest ever observed for a direct P–P bond. Evidence is presented which favors the dominance of the orbital and/or dipolar contributions to $^1J_{PP}$ when at least one phosphorus has a lone pair of electrons.

The facility of complex formation between PF_5 and donor molecules such as amines and ethers[1,2] and a brief report of Me_3PPF_5[3] led us to treat phosphorus pentafluoride with alkylphosphines in order to test the viability of a P–P bond constituted by P atoms of high connectivity. The envisaged $H_nR_{3-n}P_P \rightarrow PF_5$ coordinate link affords a "model" single bond since neither of the P atoms possesses a lone pair of electrons which might enter into p_π–d_π multiple bonding.[4] The sign and magnitude of $^1J_{PP}$ for a model single bond is of particular interest since only one other such sign de-

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