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during, and after elution of the peak due to **8**, and the sum of the intensities of the ion of m/z 179 was related to that of the ion of m/z 177. The $I_{137/135}$ ratio was similarly obtained.

Calculations of Oxygen-18 Content. Unless otherwise noted, all intensity ratios reported are corrected for natural abundance contributions and are thus representative of isotopic enrichment of a particular isotope. These corrections were made in the case of **6** by subtracting from the experimentally observed $I_{179/177}$ the $I_{179/177}$ calculated for an ion of formula $C_{10}H_{11}NO_2$ from natural abundance levels of isotopes ($I_{179/177,\text{calcd}} = 0.010$, from mass spectral tables). Although corrections to $I_{179/177}$ and $I_{137/135}$ could be made similarly in the case of **8**, the values subtracted from these observed ratios were experimentally obtained by analysis of standard unlabeled **8** analyzed immediately before analysis of labeled samples of **8**. Analysis of standard **8** was done in order to ensure that the MS technique was accurate from day to day.

For a compound containing two atoms of a particular element (in this case, oxygen), the isotopes of which are randomly distributed between the two positions and in which a = relative amount of the oxygen that is ^{16}O and b = relative amount that is ^{18}O, then eq 12 gives the relative

$$(a + b)^2 = 1 = a^2 + 2ab + b^2 \qquad (12)$$

distribution of the various isotopic species.[31] Thus, for **6** and **8**, whose molecular weights are both 177, $2ab/a^2 = I_{179/177}$. Since $b = 1 - a$, then both a and b can be obtained from the $I_{179/177}$ ratio. In the particular preparation of **6**-^{18}O used for most of the work reported, the values of a and b were 0.843 and 0.157, respectively. Therefore, the relative intensities of the various labeled species were as follows: **6**-$^{18}O,^{18}O = b^2 = 0.025$, **6**-$^{16}O,^{18}O = 2ab = 0.265$, and **6**-$^{16}O,^{16}O = a^2 = 0.710$.

o-Acetamidoacetophenone (**8**) contains two chemically different oxygens, a nonexchangeable amide oxygen and a readily exchangeable ketone oxygen. As indicated in the Results section, the ion of m/z 135 results from loss of ketene from the amide portion of **8**. Measurement of the labeling extent in this fragment ion, which now contains only one oxygen, the ketone oxygen, may be used to obtain not only the amount of labeling at this position but, by difference, the amount of labeling of the amide oxygen.

The fraction of the ketone oxygen that has undergone exchange (KE) with solvent oxygen may be obtained from eq 13, where $I_{137/135,\text{calcd}}$ is the

$$\text{KE} = 1 - (I_{137/135}/I_{137/135,\text{calcd}}) \qquad (13)$$

expected ratio for an ion of formula C_8H_9NO containing relative amounts of ^{18}O to ^{16}O of 0.157:0.843. Knowledge of the fraction of the ketone oxygen of **8** that has undergone exchange allows calculation of a theoretical $I_{179/177}$ ratio (eq 14), which represents the expected result if all

$$I_{179/177,\text{theor}} = \frac{[(0.265/2) + (0.265/2)(1 - \text{KE}) + 0.025(\text{KE})]}{0.710 + (0.265/2)(\text{KE})} \qquad (14)$$

of the amide oxygen originated from a peroxide oxygen of **6**. The percent of amide oxygen that actually becomes labeled with ^{18}O during the reaction may then be calculated by eq 15. Equation 14 includes terms

$$\%\ \text{amide oxygen labeled} = \frac{(100)(I_{179/177} - I_{137/135})}{(I_{179/177,\text{theor}} - I_{137/135})} \qquad (15)$$

that deal with complications leading to changes in the theoretical $I_{179/177}$ ratio arising from exchange of the ketone oxygen. Of the **6** initially used, 2.5% is labeled with ^{18}O in both oxygens and, since its molecular weight is 181, should not contribute to the theoretically predicted $I_{179/177}$. Exchange of the ketone oxygen leads, however, to an ion with a molecular weight of 179 and therefore directly affects the observed and theoretically predicted $I_{179/177}$ values. Following similar reasoning further, it can be seen that **6** contains 26.5% of $^{16}O^{18}O$ material. Since the peroxide oxygens are considered to be randomly labeled with ^{18}O, 26.5/2% of this material is labeled in a peroxide oxygen theoretically destined to be the ketone oxygen of **8** (and, therefore, exchangeable), and 26.5/2% is destined for the nonexchangeable amide oxygen of **8**. Exchange does not affect the latter oxygen but does lead to a lowering of the predicted I_{179} and a corresponding increase in the predicted I_{177} value due to exchange of the ketone oxygen.

When **6**-^{18}O was reacted in D_2O, there was a small amount of exchange of deuterium into the methyl ketone group. Therefore, in these cases before the percents of ^{18}O labeling were calculated by the methods described above, small corrections were made[21] on the observed $I_{179/177}$ and $I_{137/135}$ ratios. The magnitude of these corrections was determined from the relative intensities of the 178 and 136 peaks.

Registry No. 6, 13177-23-6; **7**, 67152-54-9; **8**, 5234-26-4.

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Transmission of Substituent Effects through the Silicon-Silicon Bond

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Abstract: The transmission of substituent effects through the Si-Si bond was measured by monitoring $^{13}C-^{1}H$ coupling constants and ^{1}H, ^{13}C, and ^{29}Si chemical shifts in substituted disilanes of the type $XSi(CH_3)_2Si(CH_3)_3$ (X = F, Cl, Br, CN, OC_2H_5, $N(CH_3)_2$, CH_3) and through the NCH_3 $^{13}C-^{1}H$ coupling constants and basicities of the series $XSi(CH_3)_2Si(CH_3)_2N(CH_3)_2$ (X = Cl, OC_2H_5, $N(CH_3)_2$, CH_3). Coupling constants and ^{1}H and ^{13}C chemical shifts correlated well with a variety of inductive parameters. Comparisons with the carbon analogues indicated that the C-C linkage transmits substituent effects about twice as effectively as the Si-Si bond. Indeed, the silicon-silicon bond in some systems behaves virtually as an insulator rather than conductor of substituent effects. This difference can be attributed to electrostatic field effects without recourse to $(p-d)\pi$, $(d-d)\pi$, or dative interactions.

Explorations of the ability of the carbon-carbon linkage to transmit the effect of substituents have served as keystones for our present understanding of electrical and spatial effects in organic chemistry. The unsurpassed ability of carbon to catenate and thereby provide the greatest number of systems amenable to such studies has led, however, to a dearth of information about the transmission of substituent effects through other catenated linkages. Because of its ability to catenate and the fact that it is isoelectronic in valence electrons with carbon, silicon provides an excellent opportunity to study the effects of increased size (and consequently longer substituent-reaction site distance), greater polarizability, and the presence of d orbitals which allow for $(p-d)\pi$, $(p-d-d)\pi$, etc. interactions. The present study is an attempt to evaluate the transmission of electrical effects through the Si-Si bond in disilanes through the monitoring of $^{13}C-^{1}H$ coupling constants and ^{13}C, ^{1}H, and ^{29}Si chemical shifts in the

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Table I. Chemical Shifts and $^{13}C-^{1}H$ Coupling Constants for $(CH_3)_3M^2M^1(CH_3)_2X^a$

X	prep^b	$\delta(^1H)$		$\delta(^{13}C)$		$\delta(^{13}C)/\delta(^{29}Si)$		$J(^{13}C-^1H)$	
		$M^1(CH_3)$	$M^2(CH_3)$	$M^1(CH_3)$	$M^2(CH_3)$	M^1	M^2	$M^1(CH_3)$	$M^2(CH_3)$
				M = C					
CH_3	comm	0.90	0.90	25.79	25.79	35.05	35.05	124.1	124.1
NH_2	1	1.20	0.87						124.6
OH	2	1.16	0.96	25.22	25.07	74.78	37.21	125.2	124.7
Cl	3	1.58	1.07	28.60	26.07	79.19	39.15	127.9	125.7
Br	3	1.83	1.14	30.51	26.70	79.72	39.87	127.9	125.9
				M = Si					
CH_3	comm	0.02	0.02	−2.39	−2.39	−19.34	−19.34	119.5	119.5
$N(CH_3)_2$	4	0.09	0.04	−1.35	−2.54	0.71	−21.76	119.0	119.45
OCH_2CH_3	dh	0.13	0.04	−0.76	−2.01	14.90	−22.90	118.8	119.8
F	5	0.24	0.05	0.40	−2.62	35.31	−22.73	119.8	119.7
Cl	6	0.42	0.13	2.12	−2.92	23.50	−18.39	121.4	120.4
Br	7	0.58	0.15	1.93	−2.98	18.94	−17.87	121.9	120.5
CN	8	0.38	0.25					122.8	120.7

[a] Ppm downfield (+) from Me_4Si for shifts; Hz ± 0.2 for coupling constants. [b] comm = commercially available; dh = described here.

series of compounds $XSi(CH_3)_2Si(CH_3)_3$ (X = F, Cl, Br, CN, OC_2H_5, $N(CH_3)_2$, CH_3) and measurement of NCH_3 $^{13}C-^{1}H$ coupling constants and basicities (toward $CDCl_3$) in the series $XSi(CH_3)_2Si(CH_3)_2N(CH_3)_2$ (X = Cl, OC_2H_5, $N(CH_3)_2$, CH_3).

Experimental Section

Hexamethyldisilane, 2,2,3,3 tetramethylbutane, *N,N,N',N'*-tetramethylethylenediamine, and 2-(dimethylamino)ethanol were available commercially. (*β*-Chloroethyl)dimethylamine was available as the hydrochloride. Prior to use, the hydrogen chloride was neutralized with sodium carbonate solution at 0 °C, and the amine was extracted with cold methylene chloride.

References for compounds prepared according to published methods are listed in Table I.

Ethoxypentamethyldisilane. A mixture of ethanol (0.91 g, 0.020 mol) and triethylamine (1.99 g, 0.020 mol) in 75 mL of petroleum ether was added to pentamethylchlorodisilane (3.28 g, 0.020 mol) in 100 mL of petroleum ether, and the solution was stirred for 3 h at 0 °C. Filtration of the solid triethylamine hydrochloride and fractional distillation through a 30-cm column packed with glass helices yielded the product: bp 140 °C (lit.[9] bp 141 °C); yield 2.5 g (71%).

1-(Dimethylamino)-2-ethoxytetramethyldisilane. 1-Chloro-2-ethoxytetramethyldisilane (15.7 g, 0.08 mol) in 100 mL of petroleum ether was stirred in a dry ice bath as anhydrous dimethylamine (10.8 g, 0.24 mol) in petroleum ether was added dropwise. After 1 h the solid dimethylamine hydrochloride was filtered under a nitrogen atmosphere, and the solvent was removed by a simple distillation. Fractional distillation through a spinning band column resulted in the product: bp 85–87 °C (18 torr); yield 12.4 g (75%). Anal. Calcd for $C_8H_{23}Si_2ON$: C, 46.77; H, 11.28. Found: C, 46.00; H, 11.03.

1-(Dimethylamino)-2-chlorotetramethyldisilane. To 1,2-dichlorotetramethyldisilane (20.5 g, 0.11 mol) and triethylamine (11.1 g, 0.11 mol) in 100 mL of petroleum ether was added anhydrous dimethylamine (5.0 g, 0.11 mol) in petroleum ether slowly with stirring. The reaction mixture was stirred for 1 h in the dry ice bath, brought to room temperature, and stirred for an additional 3 h. After removal of the solid triethylamine hydrochloride and simple distillation to remove the solvent, the product was isolated by fractional distillation using a spinning band column: bp 48–55 °C (15 torr); yield 7.5 g (35%).

(*β*-Ethoxyethyl)dimethylamine. Finely divided sodium metal (10.32 g, 0.45 mol) was added to 2-(dimethylamino)ethanol (50.0 g, 0.56 mol) in 100 mL of diethyl ether at 0 °C. When hydrogen gas evolution ceased, ethyl bromide (49 g, 0.45 mol) was added dropwise and the mixture was stirred for 3 h. Fractional distillation through a 30-cm column packed with glass helices resulted in the product: bp 116 °C (lit.[10] bp 116 °C); yield 35 g (66%).

Dimethylpropylamine. Excess dimethylamine was refluxed with *n*-propyl chloride in 200 mL of dioxane for 4 h. Distillation through a 30-cm column filled with glass helices yielded the product: bp 64–66 °C (lit.[11] bp 65.5 °C); yield 3 g (14%).

Proton NMR spectra were recorded on a Perkin-Elmer R-32 spectrophotometer. Pentamethyldisilanyl derivatives were run neat with a small trace of benzene to produce a lock signal from which to measure the $^{13}C-^{1}H$ satellites. The 2,3,3-trimethylbutyl derivatives were dissolved in dichloromethane to concentrations between 1.3 and 1.4 M, solvent providing the lock signal.

The proton NMR spectra of (dimethylamino)tetramethyldisilanyl derivatives and their carbon analogues were run on a Varian A-60D spectrophotometer. *N*-methyl coupling constants were measured by using a Hewlett-Packard 200 CD wide-range audiooscillator and a 522B electronic counter.

IR spectra were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer using tenfold expansion in the 2400–2100-cm^{-1} range. Standard sodium chloride solution cells containing a 1:5 molar ratio of $CDCl_3$ to sample were used.

Carbon-13 and silicon-29 chemical shifts were recorded on a Brüker WM 240 NMR spectrometer as 30% solution in $CDCl_3$.

Results and Discussion

Although there have been a variety of studies of the electronic effect of the disilanyl group,[12-17] only a few reports of substituent effects in the disilane linkage have appeared. Van Dyke and MacDiarmid recorded proton chemical shifts and $^{29}Si-^{1}H$ coupling constants for a series of substituted disilanes. The similar shifts for the substituents H, N, O, and F, as well as the substituent-dependent difference in $J(^{29}Si-^{1}H)$ for the SiH_2 and SiH_3 groups were attributed to an interaction between the substituent and the SiH_3 group across the Si–Si bond or through space.[18] Cartledge and Riedel established a reasonably good Hammett plot of J_1-

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Table II. Correlations (r)

	independent variable[a]						
dependent variable	F	σ_I	σ^*	σ_P	ν	X_P	no.[b]
$J(^{13}C-^1H)$,[c] Si^2CH_3	0.82	0.77	0.80	0.86	0.35	0.33	7
excl X = F	0.96	0.95	0.97	0.91	0.22	0.90	6
$\delta(^1H)$, Si^2CH_3	0.77	0.75	0.77	0.82	0.14	0.36	7
excl X = F	0.91	0.93	0.93	0.86	0	0.93	6
$J(^{13}C-^1H)$,[c] C^2CH_3	0.92	0.98	0.97	0.75	0.57	0.26	5
$\delta(^1H)$, C^2CH_3	0.92	0.93	0.94	0.89	0.65	0.22	5

[a] Variables taken from ref 23 and 22. [b] Number of compounds in series. [c] In hertz.

($^{29}Si-^1H$) in $XC_6H_4Si(CH_3)_2Si(CH_3)_2H$ with about the same sensitivity (slope) to substituents as the series of $SC_6H_4CH_2Si(CH_3)_2H$. The correlation of sigma constants with the $^{13}C-^1H$ coupling constants of the silyl methyl groups was mediocre (r = 0.84).[19]

Proton, carbon-13, and silicon-29 chemical shifts and $^{13}C-^1H$ coupling constants for the series $(CH_3)_3Si-Si(CH_3)_2X$ (X = CH_3, F, Cl, Br, CN, $N(CH_3)_2$, OCH_2CH_3) and the carbon analogs $(CH_3)_3CC(CH_3)_2X$ (X = CH_3, Cl, Br, NH_2, OH) are recorded in Table I. The ^{29}Si shifts of the chloro and fluoro derivatives are in good agreement with the values for these compounds reported previously.[20] Because of the focus on the transmission of substituent effects through the M–M bond, it will be appropriate to examine the shifts of the atoms, and the attached methyl groups, β to the substituent. Comparisons of these shifts of the X = CH_3 and X = Cl derivatives for the carbon series reveals that the ^1H and ^{13}C shifts of the chloro derivative appear at lower field as expected. Moreover, the $^{13}C-^1H$ coupling constant of the β-methyl group is also significantly higher. The dependence of $^{13}C-^1H$ coupling constant on the overall electron-withdrawing effect of the substituent has been amply demonstrated.[21] Comparisons of the same two derivatives in the silicon series reveal the same general trends except for the ^{13}C shift of the β-methyl group which appears at higher field in the chloro derivative.

The *general* dependence of these parameters on the electron-withdrawing effect of substituent is demonstrated in Table II by the generally good correlations between the "inductive" parameters (F, σ_I,and σ^*) and $^{13}C-^1H$ coupling constants and ^1H chemical shifts at the β atom. The ^{29}Si chemical shifts of the β atom do not correlate well with any of the substituent parameters. Correlations with para Hammett constants, group electronegativities.[22] σ_R, and Charton's υ values[23] were generally not as successful. Multiple correlations (for example, with F and R, σ_I and σ_R and σ_I and v) were not significantly better than the bivariate correlations. The correlation of both β $^{13}C-^1H$ coupling constants and methyl proton shifts for the silicon series are considerably improved by elimination of the fluoro derivative. The β-methyl group $^{13}C-^1H$ coupling constants for both series also exhibit a strong correlation with the ^1H β-methyl chemical shifts (r = 0.94 for both the carbon and silicon series).

Because the $^{13}C-^1H$ coupling constants are the least sensitive to nonelectronic effects such as solvent effects, anisotropy, etc., these afford the best comparison of the relative transmitting abilities of the two linkages. The difference in β-methyl constants between the methyl and chloro derivatives is 1.6 and 0.9 Hz for the carbon and silicon series, respectively. The slopes of the $^{13}C-^1H$ coupling constant–σ^* least-squares correlations are 0.64 and 0.30, respectively (elimination of the fluoro derivative results in a slope of 0.37). Both comparisons indicate a considerably more effective transmission of substituent effects through the C–C linkage.

Table III. NCH_3 $^{13}C-^1H$ Coupling Constants (±0.2 Hz) and Relative Basicities (±3 cm^{-1}) toward $CDCl_3$ of $XM(CH_3)_2M(CH_3)_2N(CH_3)_2$

X	prep[c]	NMe $J(^{13}C-^1H)$,[b] Hz	$\Delta\upsilon$,[c] cm^{-1}
	M = C		
CH_3	1	132.1	76
$N(CH_3)_2$	1	133.9	46
CH_3[a]	dh	131.2	81
$N(CH_3)_2$[a]	comm	132.2	71
OCH_2CH_3[a]	dh	132.5	65
OH[a]	comm	132.9	33
Cl[a]	comm	133.2[d]	
	M = Si		
CH_3	4	132.4	58
$N(CH_3)_2$	4	132.4	58
OCH_2CH_3	dh	132.6	60
Cl	dh	133.1	55

[a] Actual structure: $XCH_2CH_2N(CH_3)_2$. [b] Neat liquids. [c] Relative to reported value for (C–D): 2264 cm^{-1}. [d] Measured at 0 °C in CH_2Cl_2. [e] comm = commercially available; dh = described here.

In Table III are presented the NCH_3 $^{13}C-^1H$ coupling constants of the series $XM(CH_3)_2M(CH_3)_2N(CH_3)_2$ and their relative basicities toward $CDCl_3$ as measured by the difference ($\Delta\nu$) in C–D stretching vibration of $CDCl_3$ in the gaseous state and in mixture with the bases. Because of structural similarities within a given series $\Delta\nu$ can be assumed to be proportional to the strength of the hydrogen bond to the base.[24] As in previous work the magnitude of the NCH_3 coupling constant will be assumed to reflect the degree to which the remainder of the molecule removes electron density from the nitrogen.[25] Included in the table are a series of carbon compounds of the type $XCH_2CH_2N(CH_3)_2$ that are not strictly analogous to the silicon compounds but nevertheless can be used for comparisons of substituent effects. That the effects in the two carbon series—$XC(CH_3)_2C(CH_3)_2N(CH_3)_2$ and $XCH_2CH_2N(CH_3)_2$—run parallel can be judged from a comparison of the X = CH_3 and X = $N(CH_3)_2$ derivatives. In each series the $N(CH_3)_2$ derivative has the higher coupling constant and lower $\Delta\nu$, although the differences are larger in the $XC(CH_3)_2C(CH_3)_2N(CH_3)_2$ series.

The *relative* effect of substituents on the NCH_3 $^{13}C-^1H$ coupling constants can be appreciated most readily by comparing the CH_3 and Cl derivatives of the $XCH_2CH_2N(CH_3)_2$ series with those of the disilane series: the difference in the carbon family is 2.0 Hz, wheras in the silicon family the difference is 0.7 Hz. Indeed, the range of constants for all four members of the silicon family is only 0.7 Hz compared to 2.0 Hz for the carbon series.

The similarity of basicities of the members of the silicon series is also evident—the values of $\Delta\nu$ are all within experimental error. The values of $\Delta\nu$ for the $XCH_2CH_2N(CH_3)_2$ series, on the other hand, vary from 81 for the methyl derivative to 64 for the ethoxy derivative (the low value for the OH derivative is probably a result of intra- or intermolecular hydrogen bonding of OH to the $N(CH_3)_2$ group). Hence, both the NCH_3 coupling constants and basicities[26] are indicative of a sizeable attenuation of substituent effects through the Si–Si bond in these derivatives.

The greater transmission of substituent effects through the C–C bond relative to the Si–Si bond could be attributed to the following: (a) the shorter distance between substituent and "reaction site" in the carbon derivatives which would result in greater electrostatic field effects, (b) a decrease in the effective electronegativity of those substituents with lone pairs of electrons when attached to silicon due to (p–d)π interactions between these substituents and the attached silicon [the diffusion of electron density back to silicon

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Table IV. Charge-Dipole and Dipole-Dipole Interaction Energies (kcal/mol) for the Chloro Derivatives[a]

	charge-dipole $XMMNH(CH_3)_2^+$	dipole-dipole $XMMN(CH_3)_2$	ratio of M = C to M = Si	
			eclipsed	trans
		M = C		
eclipsed	1.0	1.2	1.4[b]	1.7[b]
trans	4.2	0.6	4[c]	6[c]
		M = Si		
eclipsed	0.7	0.3		
trans	2.4	0.1		

[a] Using the classical equations for these interactions,[29] approximate interatomic distances and angles,[30] assumed bond moments of 2.1, 2.1, 1.0, and 0.7, for the C–Cl, Si–Cl, C–N, and Si–N bond, respectively, and a dielectric constant of 1. [b] Charge-dipole. [c] Dipole-Dipole.

could then be transmitted to the β-silicon by the inductive effect, the electrostatic field effect, or by (d–d)π interaction between the two silicons]; (c) intramolecular interaction directly between electron-rich substituents and the beta silicon by n(p)→d σ (HOMO–LUMO) interactions of the type previously postulated to account for the "α" effect observed in various β-halo, -amino, or -alkoxy silanes;[27] (d) a difference in conformational preference between the carbon and silicon systems which could effect the relative magnitudes of electrostatic or intramolecular interactions.

The good correlation of NMR parameters for the silicon series (with the exclusion of the fluoro derivative) with σ_I and σ^* values suggests that (p–d)π and intramolecular interactions are absent, constant, or proportional to these "inductive" parameters. Because of the diversity of electronic effects within the set of substituents (e.g., OC_2H_5 and Cl with lone pairs that can release electron density through (p–d)π or intramolecular interaction, CH_3 that can interact only by hyperconjugation, and CN that can accept electron density by (d–p)π interaction), it is unlikely that these interactions are constant or proportional to the inductive parameters. Therefore, these interactions can be assumed to be small and negligible.[28]

The electrostatic field calculations shown in Table IV indicate a similar ratio of charge–dipole effects, as would be found in the conjugate acids of the bases, regardless of the conformation of the species (assuming that both carbon and silicon series have the same preferred conformation). The ratio of the calculated classical dipole–dipole interactions produces even higher ratios although the absolute magnitudes of the interactions are less. For the reaction

$$XMMN(CH_3)_2 + H^+ \rightarrow XMMN(CH_3)_2H^+$$

the difference in potential energy due to these interactions for the chloro derivative of each series relative to the methyl derivative (where the $M-CH_3$ bond moment can be assumed to be close to zero) would be 1.3 kcal/mol[31] more favorable for the silicon series assuming the compounds exist in the more stable trans conformation.[32] The *lower* basicity of the chloro (and other) silicon compounds can of course be explained on the basis of N–Si (p–d)π interactions. But the *change* in electrostatic interaction from one substituent, X, to another can be assumed to be at least 1.5–2 times greater for the carbon series in reactions like proton transfers or hydrogen bonding where the charge–dipole interaction is significant. Through its effect on the effective nuclear charge,[33] the electrostatic field effect also contributes to changes in NMR parameters such as coupling constants and chemical shifts.

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Registry No. $(CH_3)_3SiSi(CH_3)_3$, 1450-14-2; $(CH_3)_3SiSi(CH_3)_2Cl$, 1560-28-7; $(CH_3)_3SiSi(CH_3)_2Br$, 18139-94-1; $(CH_3)_3SiSi(CH_3)_2N(CH_3)_2$, 26798-98-1; $(CH_3)_3SiSi(CH_3)_2OCH_2CH_3$, 18297-47-7; $(CH_3)_3SiSi(CH_3)_2F$, 812-20-4; $(CH_3)_3SiSi(CH_3)_2CN$, 1560-29-8; $(CH_3)_3CC(CH_3)_3$, 594-82-1; $(CH_3)_3CC(CH_3)_2NH_2$, 29772-54-1; $(CH_3)_3CC(CH_3)_2OH$, 594-83-2; $(CH_3)_3CC(CH_3)_2Cl$, 918-07-0; $(CH_3)_3CC(CH_3)_2Br$, 16468-75-0; $(CH_3)_3CC(CH_3)_2N(CH_3)_2$, 3733-36-6; $(CH_3)_2NC(CH_3)_2C(CH_3)_2N(CH_3)_2$, 82045-29-2; $CH_3CH_2CH_2N(CH_3)_2$, 926-63-6; $(CH_3)_2NCH_2CH_2N(CH_3)_2$, 110-18-9; $CH_3CH_2OCH_2CH_2N(CH_3)_2$, 26311-17-1; $HOCH_2CH_2N(CH_3)_2$, 108-01-0; $ClCH_2CH_2N(CH_3)_2$, 107-99-3; $(CH_3)_3SiSi(CH_3)_2N(CH_3)_2$, 26798-98-1; $(CH_3)_2NSi(CH_3)_2Si(CH_3)_2N(CH_3)_2$, 26798-99-2; $CH_3CH_2OSi(CH_3)_2Si(CH_3)_2N(CH_3)_2$, 82045-30-5; $ClSi(CH_3)_2Si(CH_3)_2N(CH_3)_2$, 82045-31-6; $ClC(CH_3)_2C(CH_3)_2NH(CH_3)_2^+$, 82045-32-7; $ClSi(CH_3)_2Si(CH_3)_2NH(CH_3)_2^+$, 82045-33-8; ethanol, 64-17-5; 1-chloro-2-ethoxytetramethyldisilane, 82045-34-9; dimethylamine, 124-40-3; 1,2-dichlorotetramethyldisilane, 4342-61-4; ethyl bromide, 74-96-4; propyl chloride, 540-54-5.

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(27) See, for example: West, R.; Whatley, L. S.; Lake, K. J. *J. Am. Chem. Soc.* **1960**, *83*, 761. Bellama, J. M.; MacDiarmid, A. G. *J. Organomet. Chem.* **1970**, *24*, 91. Pola, J.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1977**, *42*, 3581; **1978**, *43*, 3192. Sevast'yanova, E. I.; Khorshev, S. Ya.; Egorochkim, A. N.; Kuz'min, O. V. *Zh. Obshch. Khim.* **1979**, *49*, 795.

(28) Except perhaps for the fluoro derivative.

(29) Maelwyn-Hughes, E. A. "Physical Chemistry"; Pergamon Press: New York, 1957; Chapter 7.

(30) Sutton, L. E., Ed. *Spec. Publ.—Chem. Soc.*, **1958**, No. 11.

(31) Note that a positive dipole–dipole interaction in the free base increases the basicity of the compound, whereas a positive charge–dipole interaction in the conjugate acid decreases the basicity.

(32) Nagy, J.; Zsombok, G.; Hengge, E. *J. Organomet. Chem.* **1979**, *182*, 165. Nagy, J.; Ferenczi-Gresz, S.; Hengge, E.; Waldhor, S. *Ibid.* **1975**, *96*, 199.

(33) See, for example: Grant, D. M.; Litchman, W. M. *J. Am. Chem. Soc.* **1965**, *87*, 3994. Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: New York, 1965.