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Nuclear Magnetic Resonance Studies of Hydrosilanes. III.[1] A Correlation of Hammett σ Constants with ^{29}Si-H Coupling Constants for Substituted Phenoxy- and (Phenylthio)dimethylsilanes

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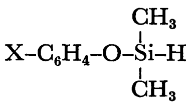
The ^{29}Si–H coupling constants and Si–H chemical shifts have been determined for a series of substituted phenoxy- and (phenylthio)dimethylsilanes. The $J(^{29}\text{Si–H})$ values are shown to be correlated well with the Hammett σ constants for the substituent on benzene ring in compounds Ar–Y–SiMe$_2$H, where Y=O and S. In comparison with the data for the analogs of the other types of organodimethylsilanes, such as aryldimethylsilanes, substituted benzyldimethylsilanes, and aryltetramethyldisilanes, the present results are discussed on the basis of the substituent effects through the intervening oxygen and sulfur. The transmission efficiency of Y was in the order, $\text{S} > \text{CH}_2 \approx \text{SiMe}_2 > \text{O}$. For the series of (phenylthio)dimethylsilanes, the $J(^{29}\text{Si–H})$ values observed were larger than those for the predicted ones. This deviation was interpreted in terms of the sulfur d-orbital participation *via* the electron-acceptor, "σ-π" conjugation.

There have been many reports on Hammett treatment NMR data, proton chemical shifts and ^{13}C–H coupling constants, for a variety of substituted aromatics, such as toluenes, *t*-butylbenzene, *N,N*-dimethylanilines, anisoles, methylthiobenzenes, phenyltrimethylsilanes, *etc.*[2–10] We have recently determined the ^{29}Si–H and ^{13}C–H coupling constants and SiH chemical shifts for a series of substituted phenylsilanes, phenylmethylsilanes and phenyldimethylsilanes and found that there exist excellent correlations between the coupling constants and the Hammett σ constants of the ring substituents for these series.[11,12] Cartledge and Riedel have also shown that the ^{29}Si–H and ^{13}C–H coupling constants for a series of substituted benzyldimethylsilanes and phenyltetramethyldisilanes are directly proportional to the Hammett σ constant for the *meta* and *para* substituents and that the ρ values for the relationships can be interpreted in terms of transmission of electronic substituent effects through C–Si and Si–Si bonds.[13]

The transmission of substituent effects is quite an interesting subject in silicon chemistry and one of the problems in this fields concerns the role of d-orbitals in transmitting the electronic effects of substituents. In view of our continuing interest in the chemistry of organosilicon hydrides[11,14] we have prepared two series of compounds, phenoxy- (**1**) and (phenylthio)dimethylsilanes (**2**) and have determined the ^{29}Si–H coupling constants and Si–H chemical shifts. In the present paper, we will describe the Hammett dependence of the ^{29}Si–H coupling constants for the two series of compounds. The transmission efficiency of substituent effects of oxygen and sulfur was compared with those for the structurally related compounds in which Y=CH$_2$ and SiMe$_2$, and the electronic structure of Y which affects the magnitude of the $J(^{29}\text{Si–H})$ values is also discussed.



$\text{X–C}_6\text{H}_4\text{–O–}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}\text{–H}$

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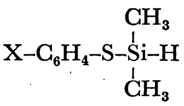


$\text{X–C}_6\text{H}_4\text{–S–}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}\text{–H}$

2

Results and Discussion

Transmission Efficiency of Y. Table 1 summarized all the NMR parameters determined for the two series, phenoxy- and (phenylthio)dimethylsilanes, and lists the Hammett σ constants for the substituent on benzene ring of these compounds. The Si–H coupling constants (J) for the two series of compounds are plotted against the Hammett σ constants in Fig. 1, giving the respective straight-line relationships. The slope (ρ), intercept (C) and correlation coefficient (γ) were determined by the method of least-squares and are given in Table 2, in

Table 1. NMR data for substituted phenoxy- and (phenylthio)dimethylsilanes (XC$_6$H$_4$–Y–SiMe$_2$H)

X	Y=O $J(^{29}\text{Si–H})$ (Hz)	Y=O δ(Si–H) (ppm)	Y=S $J(^{29}\text{Si–H})$ (Hz)	Y=S δ(Si–H) (ppm)	σ
p-MeO	−207.6	294.6	−207.8	277.8	−0.268
m-Me$_2$N	−207.8	296.4			−0.211
p-Me	−207.8	294.0	−208.3	280.2	−0.170
m-Me			−209.0	280.2	−0.069
H	−208.0	298.8	−209.7	283.2	−0.000
p-Cl	−209.4	295.8	−210.1	280.2	+0.227
m-Cl	−209.6	298.2			+0.373

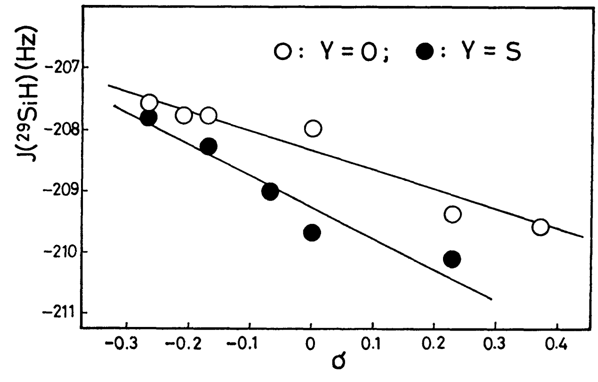


Fig. 1. Hammett plot of the $J(^{29}\text{Si–H})$ in Ar–Y–SiMe$_2$H *vs.* σ constant for the substituent on the benzene ring.

which the data for aryldimethylsilanes obtained by our previous work[11] and those for substituted benzyldimethylsilanes and aryltetramethyldisilanes by Cartledge and co-worker[13] were listed together.

The Si–H coupling constants presented in the Table 1 exhibited the expected trend in the two series. The presence of an electron-donating substituent (X) leads to a decrease in absolute magnitude of the coupling constant, whereas the presence of an electron-attracting substituent increases it. For example, the ^{29}Si–H coupling constants for *p*-methoxyphenoxy-, phenoxy-, and *m*-chlorophenoxysilane are −207.6, −208.0, and −209.6 Hz, respectively.

TABLE 2. THE ρ VALUES AND INTERCEPTS FOR Ar–Y–SiMe$_2$H OBSERVED FOR $J(^{29}\text{Si–H})$

Y	$-\rho$ (Hz/σ)	$-C$ (Hz)	γ[a]	Ref.
S	4.9	209.3	0.956	this work
O	3.3	208.4	0.989	this work
CH$_2$	4.4	186.7	0.978	13
SiMe$_2$	4.0	174.8	0.967	13
none	6.7	188.5	0.990	11

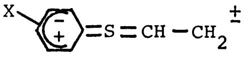
a) Correlation coefficient.

As seen from Fig. 1, the $J(^{29}\text{Si–H})$ values of phenoxy- and phenylthiosilanes correlate well with Hammett σ constant. The ρ values obtained from phenoxy- and phenylthiosilanes were −3.3 and −4.9 Hz/σ with $\gamma=$ 0.989 and 0.956, respectively, and can be compared with those of the other related silanes listed in Table 2. It is seen from the ρ values that the transmitting efficiency of the intervening Y (atom or group) in Ar–Y–SiMe$_2$H decreases in the order:

$$S > CH_2 \approx SiMe_2 > O.$$

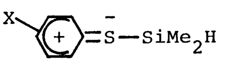
With respect to the transmission of substituent effect through Y in the type of compounds, XC$_6$H$_4$–Y–H, Marcus *et al.* have paid particular attention to oxygen and sulfur when they form part of Y.[2] Thus, by comparing the ρ values for anisoles (Y=OCH$_2$) with that for methylthiobenzene (Y=SCH$_2$) in the Hammett dependence of the methyl proton chemical shifts, they found that the efficiency of oxygen in transmitting the substituent effects is greater than that of sulfur. This observation was explained in terms of the balance of various factors, such as nonconjugative and conjugative effects of Y, medium effect, *etc.* They also discussed the transmission efficiency of these atoms by citing several experimental results other than chemical shifts and commented that the sulfur atom must show greater efficiency when it acts as an electron acceptor in conjugated systems ("conjugative-acceptor case").

Fueno *et al.* have also determined the proton chemical shifts for a series of aryl vinyl ethers and aryl vinyl sulfides and found a good carrelation between the chemical shifts for β-proton and Hammett σ constants.[9] It has been shown that the ρ-value of the sulfide series is greater than that of the ethers, and that the result supports the above Marcus' conjecture regarding an enhanced transmission efficiency of sulfur relative to oxygen. In the sulfur compounds, various electronic contributions, such as electron-donating, electron-accepting Pπ-dπ, and through-conjugative interaction[15,16] were taken into consideration to explain the transmission efficiency. They have concluded that the transmission through sulfur is enhanced by the contribution of the canonical structure involving "through-conjugative" interaction which was defined as Pπ-dπ-Pπ conjugation:

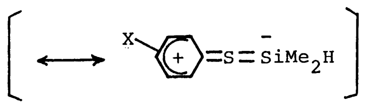


Subsequently, by comparing the Hammett dependence of the ^{13}C chemical shifts in the two series of compounds, they have obtained a similar results which supports the "through-conjugative" participation of sulfur d-orbitals in π-conjugation.[17]

In our system, the transmission efficiency of subsituent effect of sulfur was shown to be greater than that of oxygen. This fact would be attributed to the presence of sulfur atom attached to the silicon. Considering that sulfur has electron-accepting d-orbitals and lone-pair electrons available for electron donation and that silicon also electron-accepting d-orbitals,[18] the contribution of a canonical structure containing the electron-accepting conjugation is possible. This is the structure A. In addition, this conjugation could be reached to the silicon, forming a new type of "through-conjugative" interaction, or Pπ-dπ-dπ conjugation (B), as the resonance structure of A, which is similar to that of aryl vinyl sulfides as shown by Fueno and coworkers.[9,17] However, it is not clear at the present time whether the contribution of such conjugation (B) is necessary or not to explain the enhanced transmission of substituent effect.

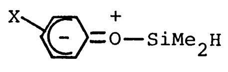


Pπ-dπ conjugation (A)

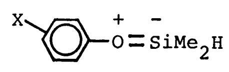


Pπ-dπ-dπ conjugation (B)
(or "through-conjugative"
interaction)

Similarly, oxygen in the phenoxide series serves as an electron donor to form Pπ-Pπ (C) and Pπ-dπ (D) conjugations. However, there can be no contribution by such a "through-conjugative" interaction as above mentioned.



Pπ-Pπ conjugation (C)



Pπ-dπ conjugation (D)

The ρ values of −4.4 and −4.0 Hz/σ for the two series of Y=CH$_2$ and SiMe$_2$, respectively, suggest roughly equal transmitting abilities for carbon and silicon.[13] This result is consistent with that obtained from the ^{13}C chemical shifts for the type of compounds, XC$_6$H$_4$–Y–(CH$_3$)$_3$ where Y=C and Si.[19] It is interesting, however, that the transmission efficiency of the two systems falls between those for the systems of Y=S and O.

It is worthwhile to note that the ρ value (-6.7 Hz/σ) for phenyldimethylsilanes is to be the greatest one (Table 2). The transmitting ability of the system is easily rationalized by the structure and the SiH group is one atom closer to the benzene ring than it is in the other series.

In contrast, the plots of the Si–H chemical shifts, listed in Table 1, *vs.* Hammett σ constants in the two series of oxygen and sulfur exhibited essentially no good correlation. In these cases, the correlations of the δ(SiH) with Hammett σ constants were too poor.

Electronic Behavior of Y. Although factors governing the magnitude of Si–H coupling constants cannot be said to be fully understood, the effective electronegativity of the substituent attached to silicon affects it,[11,14,20,21] as has been shown by Jensen's equation.[22] In the present system, Ar–Y–SiMe$_2$H, the magnitude of the Si–H coupling constants can be definitely related to the effective electronegativity of Y because of only change of Y. Thus, the greater this electronegativity, the greater the coupling constant. This is readily seen from an examination of the Si–H coupling constants in Table 3. The J values for (phenylthio)dimethylsilane, phenoxydimethylsilane, phenyldimethylsilane, benzyldimethylsilane, and phenyltetramethyldisilane are -209.7, -208.0, -188.3, -186.9, and -175.0 (Hz), respectively.

The decreasing trend in the absolute magnitude follows the order of decreasing electrogegativity of Y, except the case of Y=S. The ^{29}Si–H coupling constant of phenylthiosilane is greater than what would be predicted on the basis of the electronegativity of Y. Table 3 shows the correlation of the J values for the five hydrosilanes with the electronegativity of respective Y's on the Pauling scale. The plots of J(^{29}Si–H) for the compounds of Y=SiMe$_2$, none, CH$_2$, and O *vs.* the electronegativity (En) of the respective key atoms in Y show approximately a linear relationship, while the plot for the sulfur compound anormally deviates from the relationship. This deviation is attributable to sulfur attached to silicon. Within the framework of the "through-conjugation," it is possible to assume that the contribution of the structure *via* the interaction between d-orbital of sulfur and Si–H bond electrons, "σ-π" interaction, appears to play an important role affecting the silicon hybrid orbitals bonded to the hydrogen. The direction of the electron shifts *via* the conjugation is opposite to those of the conjugation A and B, and the following canonical structures can be illustrated as E and F. Thus, the charge-separated contributors would tend to increase the s character of the Si–H bond due to the structure change around the silicon (sp^3→sp^2), producing the enhancement of the absolute magnitude of the Si–H coupling constant.

TABLE 3. COMPARISONS OF THE J(^{29}Si–H) FOR THE RELATED COMPOUNDS

Compound	J(^{29}Si–H) (Hz)	En[a)]	Ref.
Ph–S–SiMe$_2$H	-209.7	2.5	this work
Ph–O–SiMe$_2$H	-208.0	3.5	this work
Ph–CH$_2$–SiMe$_2$H	-186.9	2.5	13
Ph–SiMe$_2$–SiMe$_2$H	-175.0	1.8	13
Ph–SiMe$_2$H	-188.3	2.5	11

a) Electronegativity (Pauling scale) of the key atom in the intervening Y atom or group.

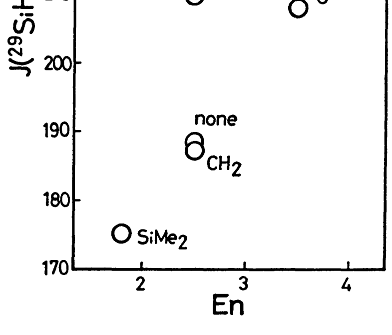
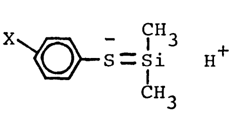
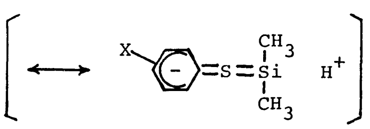


Fig. 2. Plot of the J(^{29}Si–H) *vs.* the electronegativity (En) of the key atom in Y.



"σ-π" conjugation (E)



"through-conjugative" interaction (F)

Recently, Ojima, Nihonyanagi, and Nagai have determined the J(^{29}Si–H) for two series of sulfur compounds, RR′(PhS)SiH and RR′(EtS)SiH, and showed that these compounds have considerably large J values compared to that for triethylsilane.[23,24] They have stated that the large absolute values may reflect the large fraction of s character employed by silicon in the Si–H bond. This explanation is consistent with the idea of the "σ-π" interaction and provides supporting evidence for our present results.

On the other hand, the electron-accepting "σ-π" conjugation cannot occur in the series of phenoxysilanes, but oxygen serves as an electron donor, forming the Pπ-Pπ (C) and Pπ-dπ (D) conjugations. Although the two conjugations actually seem possible as has been shown by many workers in a variety of oxygen-bonded silicon compounds, the Pπ-dπ conjugation (D) in the present system should contribute to decrease the magnitude of the Si–H coupling constant. However, as the plot of the J(^{29}Si–H) for phenoxydimethylsilane *vs.* the electronegativity of oxygen appears to be in line of the correlation as shown in Fig. 2, the contribution of the conjugative interaction (D) might not be so important.

Experimental

All boilling points are uncorrected. IR spectra were recorded using neat liquid films with a Hitachi EPI-G3 spectrometer. Mass spectra were obtained with a Hitachi RMU-6L spectrometer. GLC analyses were conducted using Ohkura Model 807 and 1700 gas chromatographs.

TABLE 4. SUBSTITUTED PHENOXYDIMETHYLSILANES, XC_6H_4–O–$SiMe_2H$, AND THEIR ANALYTICAL RESULTS

Substituent X	Bp (°C/mmHg)	Formula	Found (Calcd) % C	Found (Calcd) % H	Mol wt[a] Found (Calcd)	n_D^{20}
P-MeO	87/13	$C_9H_{14}O_2Si$	59.34 (59.30	7.64 7.74)	182 (182.3)	1.5042
m-Me_2N	93/5	$C_{10}H_{17}NOSi$	61.53 (61.49	8.65 8.77)	195 (195.3)	1.5253
p-Me	—[b]	$C_9H_{14}OSi$	65.12 (64.99	8.45 8.50)	—[c]	1.4847
H	72—74/32	$C_8H_{12}OSi$	62.87 (63.10	7.72 7.94)	—[c]	1.4859
m-Cl	80/14	$C_8H_{11}OSiCl$	51.47 (51.46	5.76 5.94)	186 (186.7)	—
p-Cl	—[b]	$C_8H_{11}OSiCl$	51.58 (51.46	6.00 5.94)	—[c]	1.5018

a) By mass spectrum. b) Isolated by preparative GLC. c) No molecular peak was observed, but the peak corresponding to M^+-15.

TABLE 5. SUBSTITUTED PHENOXYDIMETHYLSILANES, XC_6H_4–O–$SiMe_2H$, AND THEIR SPECTRAL DATA

Substituent X	NMR (CCl_4, TMS) (δ ppm)			IR (neat) (cm^{-1})	
	$Si\underline{H}_3$[a]	$Si\underline{H}$[b]	X–$C_6\underline{H}_4$–	Others	νSiH
p-MeO	0.30	4.91	6.71(s, 4H)	3.72 (s, 3H)	2118
m-Me_2N	0.33	4.94	6.95—7.15 (m, 4H)	2.91 (s, 6H)	2115
p-Me	0.29	4.90	6.63; 6.74 (quart, 4H)	2.24 (s, 4H)	2118
H	0.33	4.98	6.50—7.40 (m, 5H)		2120
p-Cl	0.32	4.93	6.74; 7.16 (quart, 4H)		2115
m-Cl	0.35	4.97	6.45—7.30 (m, 4H)		2120

a) (d, 6H). b) (m, 1H).

TABLE 6. SUBSTITUTED (PHENYLTHIO)DIMETHYLSILANES, XC_6H_5–S–$SiMe_2H$, AND THEIR SPECTRAL DATA

Subst. X	NMR (CCl_4, TMS) (δ, ppm)	IR (neat, sandwich) (cm^{-1})	MS (100 °C, 70 eV) *m/e* (intensity)
p-MeO[a]	0.28,[b] 3.75 (s, 3H, $\underline{Me}O$), 4.63,[c] 7.00 (q, 4H, $Ph\underline{H}$)	3060, 2956, 2131,[d] 1599, 1497, 1464, 1289, 1250,[e] 1176, 1036, 896, 866, 826, 768.	59(83), 67(32), 73(22), 97(31), 108(78), 119(49), 125(72), 133(45), 139(29), 140 (M^+-SiMe_2)(100), 167(24), 168(46), 183(22), 198[f](85).
p-Me	0.30,[b] 2.30 (s, 3H, *p*-$\underline{Me}$), 4.67,[c] 7.13 (q, 4H, $Ph\underline{H}$)	3020, 2960, 2135,[d] 1493, 1253,[e] 1092, 898, 868, 808, 767, 663.	45(24), 59(14), 61(27), 73(16), 75(21), 91(100), 119(48), 123(23), 124(87) (M^+-SiMe_2), 133(38), 182[f](weak).
m-Me[g]	0.32,[b] 2.30 (s, 3H, *m*-$\underline{Me}$), 4.67,[c] 7.04 (m, 4H, $Ph\underline{H}$)	3055, 2960, 2135,[d] 1595, 1478, 1255,[e] 1080, 900, 870, 840, 780, 690.	45(28), 59(13), 61(44), 71(35), 91(100), 119(38), 124(M^+-SiMe_2)(93), 133 (32),182[f](weak).
H	0.32[b], 4.72[c], 7.30 (m, 5H, $Ph\underline{H}$).	3063, 2956, 2131,[d] 1582, 1472, 1439, 1251,[e] 1022, 897, 863, 836, 767, 757, 731, 680, 660.	45(16), 59 (15), 61(18), 75(15), 77(14), 84(16), 109(26), 110(M^+-SiMe_2) (100), 119(52), 133(41), 168[f](weak).
p-Cl[h]	0.32,[b] 4.67,[c] 7.25 (q, 4H, $Ph\underline{H}$).	3022, 2952, 2127,[d] 1472, 1384, 1249,[e] 1091, 1008, 890, 860, 832, 817, 760.	45(23), 59(19), 61(19), 73(26), 75(35), 108(33), 109(56), 119(65), 133(52), 144 (M^+-SiMe_2) (100), 146(37), 202[f] (weak).

a) Found: C, 54.55; H, 6.88%. Calcd for $C_9H_{14}OSSi$: C, 54.49; H, 7.11%. b) (d, 6H, $Si\underline{Me}$). c) (m, 1H, $Si\underline{H}$). d) (νSiH). e) (SiMe). f) Molecular peak. g) Bp 85—86 °C/13 mmHg. h) Found: C, 48.00; H, 5.52%. Calcd for $C_8H_{11}ClSSi$: C, 47.39; H, 5.47%.

Materials. *sym*-Tetramethyldisilane was prepared *via* $LiAlH_4$-reduction of the corresponding dichlorosilane obtained by chlorination of hexamethyldisilane.[25] Hexamethyldisilane was obtained by MeMgBr-methylation of chlorodisilane fraction (bp 148—160 °C) in the "Direct Synthesis."[26] *p*-Methoxybenzenethiol (bp 85—88 °C/3 mmHg; lit,[27] bp 89 °C/5 mmHg) was prepared by the literature method from anisole *via* chlorosulfonation with chlorosulfuric acid and then Zn–H_2SO_4 reduction of the resulting *p*-methoxybenzenesulfonyl chloride.[28] *m*-Methylbenzenethiol (bp 80—84 °C/24 mmHg; n_D^{25} 1.5715; lit,[29] bp 90—93 °C/25 mmHg; n_D^{25} 1.568—1.571) was also prepared from toluidine *via* diazotization followed by treatment with potassium *O*-ethyl dithiocarbonate. All the other materials were commerically available.

Preparation of Substituted Phenoxydimethylsilanes. The method used for the reaction to give phenoxydimethyldisilane is representative.[30] Under argon, a mixture of phenol (10 mmol) and *sym*-tetramethyldisilane (10 mmol) was added with chlorotris(triphenylphosphine)rhodium, RhCl $(PPh_3)_3$, 0.5 mol% relative to the substrate used) and magnetically stirred at room temperature for 30 min at the stage of which gas evolution of dimethylsilane (Me_2SiH_2) ceased. GLC analysis for the resulting mixture thus obtained showed that almost of it was the reaction product, phenoxydimethylsilane, in a quantitative yield. The pure sample was obtained by distillation. Pertinent physical, spectral, and analytical data for all the compounds thus prepared are give in Tables 4 and 5.

Preparation of Substituted (Phenylthio)dimethylsilanes. Similarly, (phenylthio)dimethylsilanes were prepared by reacting substituted benzenethiols (4—15 mmol) with tetramethyldisilane (10—20 mmol) in the presence of RhCl$(PPh_3)_3$ catalyst (0.2—0.5 mol% relative) to the benzenethiols (r. t.; 10—60 min).[23,30] The yield of the products by GLC analyses were fairly high (40—70%), but the products, except *m*-methyl derivative which could be isolated by distillation (bp 85—86 °C/13 mmHg), were only isolable by preparative GLC in 90—98% purity and further purification could not be achieved because of their instabilities under the GLC conditions. Therefore, the pure samples for elemental analyses could not be obtained, but they are enough in purity for spectral determinations. Table 6 lists the physical and spectral data which were carefully determined.

NMR Measurements. NMR constants were determined from spectra obtained on a Varian A-60D spectrometer. Measurements of the coupling constants $J(^{29}Si\text{-}H)$ and Si–H chemical shifts were made in CCl_4 solution by the method described previously.[11]

References

1) References. 11 and 12 in the present paper are designated as "Nuclear Magnetic Resonance Studies of Hydrosilanes. I and II," respectively.

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