

Silicon-29 NMR access to stereochemistry of molecules. 2. (Trimethylsilyl)cyclopropyl compounds

Micheline Grignon-Dubois, Michel Laguerre, Bernard Barbe, and Michel Petraud

Organometallics, 1984, 3 (7), 1060-1063 • DOI: 10.1021/om00085a016 • Publication Date (Web): 01 May 2002

Downloaded from <http://pubs.acs.org> on April 26, 2009

More About This Article

The permalink <http://dx.doi.org/10.1021/om00085a016> provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article



ACS Publications
High quality. High impact.

2.3-2.6 (br m, 1.6, SiCH₂), 0.33-0.46 (d, 2.6, FSiCH₃). A higher boiling fraction contained XIXb (0.49 g).

X-ray Structure Analysis of VI. A crystal of 2,8-dibromo-5,10-dimethyl-10-fluoro-10,11-dihydro-5H-dibenz[*b,f*]-[1,4]azasilepine with well-developed faces was attached to a glass fiber. Pertinent crystal and intensity data are given in Table IV. Systematic absences of *h*0*l*, *l* odd, and 0*k*0, *k* odd, uniquely determine the space group *P*2₁/*c*. Thirteen reflections with $2\theta > 15^\circ$ were centered with a programmed centering routine; cell parameters were obtained by least-squares refinement of these angles. The intensities of three standard reflections were measured every 97 reflections and decreased in intensity approximately 22% during the data collection. A linear correction for loss of intensity was applied during the data reduction. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those described previously.²⁹ Standard deviations were assigned as follows: $\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0.05I)^2]^{1/2}$, where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, *I* = net intensity, *B* = total background count, and *K* = ratio of scan time to background time.

The structure was solved by an iterative application of the Σ_2 relationship with 129 normalized structure factors of magnitude 1.3 or greater. An *E* map based on the set of phases for the solution with the largest consistency index (0.98) gave the positions of the non-hydrogen atoms of the structure. Least-squares refinement of the non-hydrogen atoms with isotropic thermal parameters gave a discrepancy factors *R* = 0.052 and *R*_w = 0.066; all hydrogen atoms were located in an electron density difference map (*R* = 0.060) and included in the final refinement with thermal parameters fixed at 5.0 Å². Final positional parameters with estimated standard deviations are given in Table V. Atomic scattering factors and real and imaginary anomalous dispersion

corrections for Br and Si were taken from ref 30. The highest residual electron density in the final difference map was 0.60 e Å⁻³ near the region of Br(1).

Acknowledgment. M.A.L. and T.E.R. acknowledge support through the National Science Foundation Undergraduate Research Participation Program (1979). A portion of this work was supported by the Graduate School of the University of Missouri—St. Louis through the Summer Fellowship Program (J.Y.C.) and the Weldon Spring Fund (E.R.C.). The generous use of the facilities of the University of Wisconsin—Madison (J.Y.C.) and of the Miles Laboratories, Inc. (V.H.T.C.) for a part of the investigation is gratefully acknowledged.

Registry No. IIa, 75482-82-5; IIb, 89889-26-9; IIIa, 71445-82-4; IIIb, 89889-27-0; IIIc, 89889-28-1; IIId, 89889-29-2; VI, 75499-01-3; VII, 71445-86-8; IX, 3991-61-5; Xa, 89889-30-5; Xb, 89889-31-6; XIa, 89889-32-7; XIb, 89908-12-3; XIIa, 89921-98-2; XIIb, 89889-33-8; XIII, 89889-34-9; XIV, 89889-35-0; XVa, 89889-36-1; XVb, 89889-37-2; XVI, 89889-38-3; XVIII, 89889-39-4; XIXa, 18407-40-4; XIXb, 18407-42-6; XX, 27977-42-0; XXI, 89889-40-7; KCN, 151-50-8; KF, 7789-23-3; KOH, 1310-58-3; Cl₃SiCHClCH₃, 7787-82-8; Me(ClCH₂CH₂)SiCl₂, 7787-85-1; Bu₄N⁺F⁻, 429-41-4; Me(ClCH₂)SiCl₂, 1558-33-4; 2-methylphenyl phenyl ether, 3991-61-5; 2-chloro-1,1,2-trifluoroethylamine, 40062-89-3; 2,2',4,4'-tetrabromomethylidiphenylamine, 3666-95-3; (3-chloropropyl)methylidichlorosilane, 7787-93-1; diphenyl ether, 101-84-8.

Supplementary Material Available: Tables of anisotropic thermal parameters for the bromine atoms and isotropic thermal parameters for non-hydrogen atoms, bond distances and angles, and structure factor amplitudes and a stereoscopic packing diagram (11 pages). Ordering information is given on any current masthead.

(27) The synthesis of PhSi(Me)CH₂C₆H₅F has been reported but the boiling point was given without the pressure.²⁸

(28) Drozdov, V. A.; Kreshkov, A. P.; Romanova, A. D. *Zh. Obshch. Khim.* 1970, 40, 104.

(29) See program references in: Corey, E. R.; Paton, W. F.; Corey, J. Y. *J. Organomet. Chem.* 1979, 179, 241. Bellavance, P. L.; Corey, E. R.; Corey, J. Y.; Hey, G. W. *Inorg. Chem.* 1977, 16, 462.

(30) "International Tables of X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974.

²⁹Si NMR Access to Stereochemistry of Molecules. 2. (Trimethylsilyl)cyclopropyl Compounds

Micheline Grignon-Dubois*

Laboratoire de Chimie du Silicium et de l'Étain associé au CNRS (LA 35), Université de Bordeaux I,
33405 Talence Cédex, France

Michel Laguerre

ERA 890, Université de Bordeaux II, Faculté de Pharmacie, 33000 Bordeaux, France

Bernard Barbe and Michel Pétraud

CESAMO, Université de Bordeaux I, 33405 Talence Cédex, France

Received November 22, 1983

²⁹Si NMR spectra of cyclopropylsilanes were recorded by using the SPI technique. The variation of ²⁹Si-¹H coupling constants with stereochemistry was studied. Our results confirm the dependence of ³*J* on the relative position of the Me₃Si group and also the unexpected zero value for ²*J'* (H_α to the silicon). As far as chemical shifts are concerned, the additivity rule seems to exist.

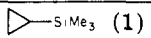
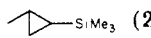
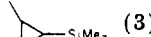

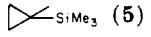
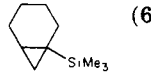
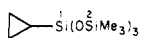
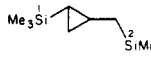

In a previous paper¹ we were able to show for the first time that ²⁹Si-¹H long-range coupling constants can be used to determine the stereochemistry of organosilicon

synthons of the bicyclo[*n*.1.0]alkane type A. In particular we have shown that the magnitude of the coupling constants ³*J*(²⁹Si...¹H) across the cyclopropane ring is a function of the dihedral angle between the C-H and the C-Si bonds. This suggests a Karplus type relationship.

In order to verify the generality of this relationship, we

(1) Grignon-Dubois, M.; Laguerre, M.; Barbe, B.; Pétraud, M. *Organometallics* 1984, 3, 359.

Table I. NMR Data for Compounds 1-9

	$\delta_{29\text{Si}}$	spin systems ^a	² J	² J' and ² J''	³ J _c	³ J _t	³ J'
 (1)	2.6	Si(H ₉)2 ³ J _c 2 ³ J _t	6.3	0	6.3	3.4	
 (2)	1.4	Si(H ₉)2 ³ J _c ³ J _t	6.3	0	6	3.9	
trans							
 (3)	1.4	Si(H ₉) ³ J _c ³ J _t ³ J _t	6.3		5.8	3.2	3.5
cis							
 (4)	0.7	Si(H ₉) ³ J _c ³ J _t	6.3	0	5.8	2.8	
 (5)	4.3	unresolved					
 (6)	4.17	Si(H ₉)2 ³ J _c ³ J _t	6.3	0	5.2	4	
 (7)	Si ₁ , -67.3 Si ₂ , 7.2	Si2 ³ J _c 2 ³ J _t Si(H ₉)		0	8	5.4	
 (8)	Si ₁ , 1.05 Si ₂ , 1.3	Si(H ₉)2 ³ J _c ³ J _t Si(H ₉)2 ² J'' ³ J'	6.3 6.3	0 5.8	6	3.5	1
trans							
 (6)	1.5	Si(H ₉)2 ² J'' ³ J'	6.3	5.8			1

^a Si(H₉) represents the silicon coupled with the nine equivalent protons of the SiMe₃ group, the constant being ²J.

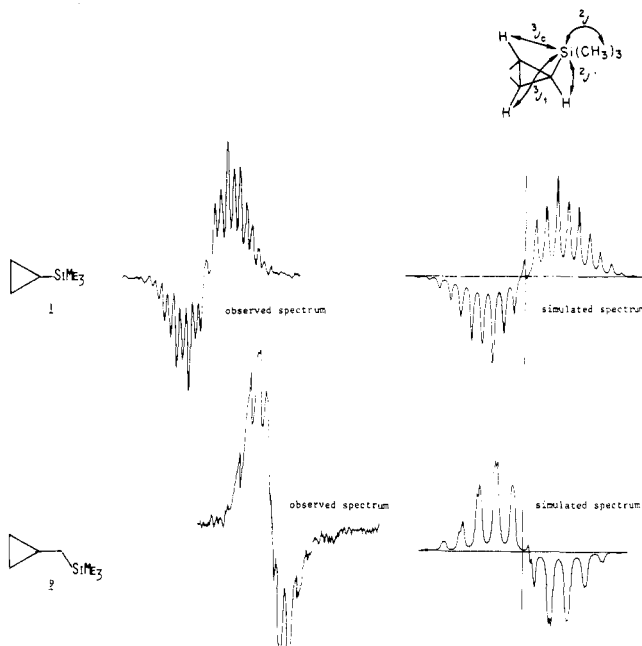


Figure 1. Observed and simulated spectra for compounds 1 and 9.

have studied other models of known stereochemistry. The results obtained with the cyclopropane derivatives 1-9 are presented in Table I.

Results and Discussion

The coupling constant studies were realized by employing the technique of selective population inversion (SPI)¹ in selectively irradiating one of the proton transitions of the SiMe₃ group. In the case of 7, because the silicon bound to the ring bears no methyl groups, a classical sweep without decoupling was performed. SPI is a pulse sequence for the improvement of sensitivity of an NMR experiment for nuclei with low magnetogyric ratio (²⁹Si, -0.531 10⁻⁴ rads s⁻¹). A weak irradiating H₂ field is selectively applied to one of the ¹H transition in the ²⁹Si-¹H satellite spectrum for 0.1 s in order to assume complete population inversion. Then excitation of the ²⁹Si resonance

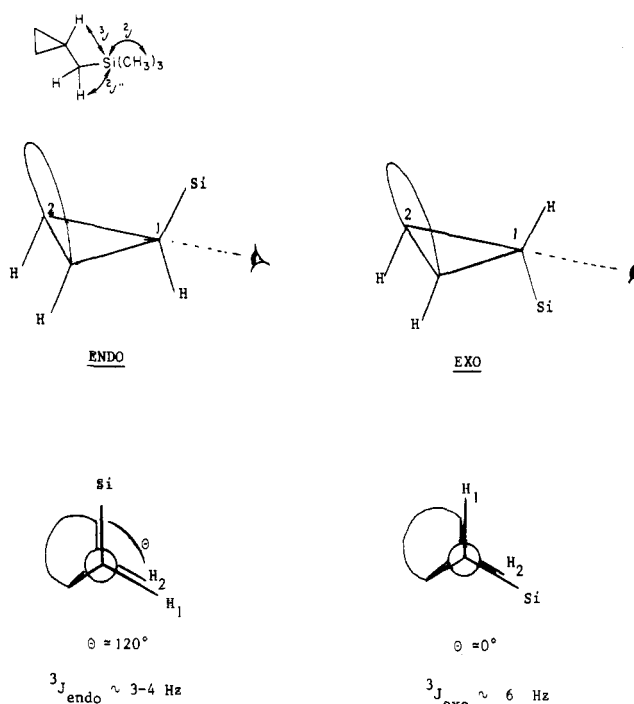


Figure 2. Variation of the ³J(²⁹Si-¹H) coupling constant according to the dihedral angle value.

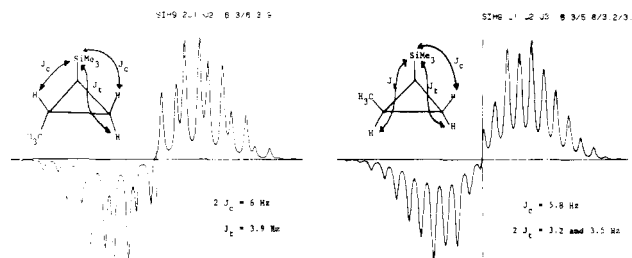


Figure 3. The influence of stereochemistry on differences in spectrum appearance: compounds 2 and 3.

by a strong H₁ pulse is performed, and the free induction decay is sampled so the spectra display an enhancement of $\gamma(\text{H})/\gamma(\text{Si}) \approx 5$.

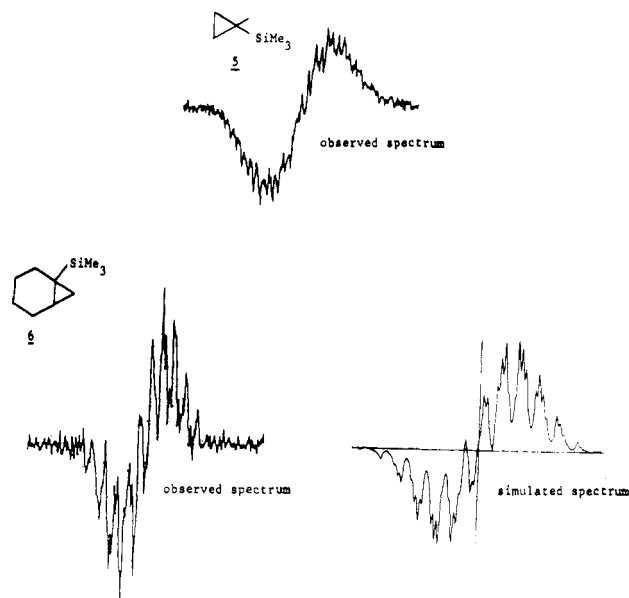


Figure 4. Comparison of the spectra of compounds 5 and 6.

Table II. β and γ Effects of Methyl Substituents on $\delta(^{29}\text{Si})$ in Cyclopropyl- and Vinylsilanes

	$\beta,^a$ ppm	$\gamma,^a$ ppm		$\beta,^a$ ppm	$\gamma,^a$ ppm
CH ₃ on 1	+1.7		CH ₃ on 1	+2.8	-
CH ₃ on 2 cis		-1.2	CH ₃ on 2 cis		-3.0
CH ₃ on 2 trans		-1.2	CH ₃ on 2 trans		-0.8
2CH ₃ on 2		-1.9	2CH ₃ on 2		-3.9

^a β or $\gamma = \delta(\text{Si})(\text{methyl compound}) - \delta(\text{Si})(\text{unsubstituted compound})$.

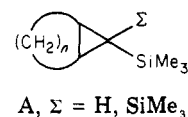
Spectra generally were very complex (90–360 theoretical peaks); their analysis could only be performed by building up a computer simulation program without which this work could not be achieved as emphasized by a recent paper of Jakobsen et al.⁴ Our spectra simulation program³ allowed us to determine the value of the coupling constants with a precision greater than 0.3 Hz in all cases (Table I and Figures 1, 3, and 4).

(1) **Chemical Shifts (δ).** It may be noted that the silicon chemical shifts decrease in the compounds 1–4 according to the $1 > 2 \approx 3 > 4$ sequence. Although many factors must be taken into consideration in arriving at the value of δ , it seems that the introduction of the methyl substituent in the 2-position (β effect) of the cyclopropane ring plays an important role in determining the shift. Moreover, the introduction of substituents β to silicon (γ effect) (in the case of 5 and 6) seems to have the opposite effect; in fact, a deshielding of silicon is observed ($5 \approx 6 > 1$). It should be noted that in the case of 2 and 3 the position of the methyl substituent has no influence on the chemical shift.

The comparison of our results (Table II) with those mentioned elsewhere about ethylenic series, propenylsilanes in particular,^{5,7} allows us to ascertain that a methyl group in the β position has a deshielding effect on δ_{Si} whereas it has a shielding effect when it is in the γ position ($\text{Si}-\text{C}_\alpha-\text{C}_\beta-\text{C}_\gamma$ or $\text{Si}-\text{C}(-\text{C}_\beta)-\text{C}$).

It is worth noting that the magnitude of these effects was greater for the ethylenic compounds than for the cyclopropanes. Moreover, our results were comparable to those reported by Maciel et al.⁶ in the series of derivatives $\text{Si}-(\text{CH}_2)_n\Sigma$.

(For a correct comparison, it is necessary to reverse the sign of β and γ effects given by these authors because the chemical shifts are reported with respect to the resonance of tetramethoxysilane with more positive numbers corresponding to greater shielding.) They also mentioned that effects observed in the ^{29}Si spectra were comparable in sign and magnitude to those observed in ^{13}C , ^{31}P , ^{14}N , and ^{11}B NMR spectra.



Comparison between 2 and 8 would indicate that the substituents CH₃ and CH₂SiMe₃ give rise to similar electronic effects. This is in accordance with literature observations.¹⁶

The study of compounds 8 and 9 yielded values that exclude the possibility of any interaction between the two SiMe₃ groups of 8.

(2) **Coupling Constants. (a) 2J .** Apart from compound 7, the value of 2J remains constant within this entire series. Keeping in mind that the same phenomenon is observed in mono- and disilylated bicyclo[*n*.1.0]alkanes¹ for which the values found were identically 6.3 Hz, it is not surprising that the examination of other series shows 2J of the SiMe₃ group to have a value characteristic of the particular class within which the envisaged derivatives fall.

R-SiMe ₃	2J (Hz) \pm 0.1 Hz
R = alkyl	6.3
R = vinyl	6.6
R = ethynyl	7.0

The higher value (7.7 Hz) of 2J observed in the case of compound 7 is explained by the presence of the $-\text{OSiMe}_3$ group whose electronegativity effect is compatible with literature reports.⁷

(b) $^2J'$. Examination of Table I indicates that the coupling constant $^2J'$ is zero when silicon is directly bonded to the ring. The absence of methyl groups on the silicon attached to the ring in derivative 7 results in a much simpler spectrum than in the previous examples; this confirms the value of zero for $^2J'$.

$^2J'$ was likely to be connected with the magnitude of the H-C-Si angle. With derivatives 1–8 where there is no steric hindrance, this angle has more or less the same value of about 114° (measured for 1¹⁰). In contrast, we had observed in a bicyclic series¹ that $^2J'$ was dependent on steric hindrance: equal to zero in “exo” isomers, $^2J'$ is no longer zero when silicon is in the “endo” position, which could be explained by a variation of the H-C-Si angle.

In the specific cases of 8 and 9, the silicon bonded directly to the CH₂ group is coupled with the protons of the latter, this constant having a value of 5.8 Hz. Again this is not unusual in that the CH₂Si group can rotate freely

(6) Scholl, R. L.; Maciel, G. E.; Musker, W. K. *J. Am. Chem. Soc.* **1972**, *94*, 6376.

(7) Marsmann, H.; NMR: *Basic Princ. Prog.* **1981**, *17*, 65.

(8) Freeman, R.; Hill, H. D. W.; Kaptein, R. *J. Magn. Reson.* **1972**, *7*, 327.

(9) Clin, B.; De Bony, J.; Lalanne, P.; Biais, J.; Lemanceau, B. *J. Magn. Reson.* **1979**, *33*, 457.

(10) Kuznetsova, T. M.; Veniaminov, N. N.; Alekseev, N. V. *J. Struct. Chem. (Engl. Transl.)* **1979**, *20*, 454.

(2) Linde, S. A.; Jakobsen, H. J. *J. Am. Chem. Soc.* **1975**, *97*, 3219.

(3) Grignon-Dubois, M.; Laguerre, M. *Actual. Chim.* **1983**, *No. 10*, 21.

(4) Jakobsen, H. J.; Kanyha, P. J.; Brey, W. S. *Org. Magn. Reson.* **1983**, *54*, 134.

(5) Grignon-Dubois, M.; Laguerre, M.; Barbe, B.; Petraud, M., results to be published.

and thus it possesses a value similar to 2J .

(c) 3J . Taking into account previously obtained results, it would be reasonable to expect these models to have values differing according to their isomer differences: we have shown in the bicyclic series¹ that the 3J (${}^{29}\text{Si}\cdots{}^1\text{H}$) coupling constant was a function of the dihedral angle θ , with ${}^3J_{\text{exo}} > {}^3J_{\text{endo}}$, which suggests a Karplus type relationship (cf. Figure 2).

If the 3J (${}^{29}\text{Si}\cdots{}^1\text{H}$) coupling constant was really governed by such a relationship, we would expect here that ${}^3J_{\text{cis}} > {}^3J_{\text{trans}}$. The values reported in Table I reflect this. The comparison of **2** (for which two ${}^3J_{\text{cis}}$ and one ${}^3J_{\text{trans}}$ coupling constants are expected) and **3** (one ${}^3J_{\text{cis}}$ and two ${}^3J_{\text{trans}}$ coupling constants) shows particularly well J_{cis} to be greater than J_{trans} (cf. Figure 3). Thus, within this series, a relationship between geometry and coupling constants can be developed.

It is worth noting that the same phenomenon is well-known for 3J (${}^1\text{H}\cdots{}^1\text{H}$) in cyclopropyl compounds¹¹ and also is observed for cyclopropylsilanes.¹² Moreover, literature reports the same data for 3J (${}^{13}\text{C}\cdots{}^1\text{H}$) in a series of cyclopropyl derivatives¹³ and for 3J (${}^{119}\text{Sn}\cdots{}^1\text{H}$) in norbornylstannanes.¹⁴

The spectrum of **5** was not analyzed because of its extreme complexity (360 theoretical peaks), the coupling constants with the protons of the cyclopropyl methyl group being greater than 1 Hz. The spectrum of **6**, on the other hand, was analyzed (cf. Figure 4); the coupling constants with the protons of the large ring (CH_2) were found to be less than 0.5 Hz and thus have little effect on the resulting spectrum. In the case of **7**, the presence of three OSiMe_3 groups on the silicon bound to the ring increases considerably the values of the 3J coupling constants. This observation fits well with other reports in the literature.⁷

It is to be noted that the coupling constants ${}^3J_{\text{cis}}$ and ${}^3J_{\text{trans}}$ have the same value in both compounds **2** and **8**. This shows once again that the CH_2SiMe_3 group has an effect identical with that of the CH_3 group.

In none of the cases examined was a long-range coupling constant across the ring, in particular 4J , observed.

(3) Use of ${}^{29}\text{Si}$ NMR in the Assignment of SiMe Peaks in ${}^1\text{H}$ NMR. The basic idea of these experiments was to take advantage of the polarization transfer selectivity in frequency for correlating ${}^1\text{H}$ and ${}^{29}\text{Si}$ chemical shifts. By examining the ${}^{29}\text{Si}$ -H coupling constants in ${}^{29}\text{Si}$ spectra, by determining the relative position of each silicon, and in knowing which of the satellites is being irradiated, the attribution of proton signals of the SiMe_3 group of

polysilylated derivatives and isomers mixtures can be achieved as reported in previous works.^{1,15} In the case of **8**, use of SPI allows the SiMe_3 group of the ring to be assigned as a singlet at 0.16 ppm and the CH_2SiMe_3 group as a singlet at 0.25 ppm.

The ability of the SPI technique to allow peak assignments despite such a negligible difference in chemical shifts (i.e., $\Delta = 0.09$ ppm) is a visible demonstration of its superiority over INEPT and DEPT for such work. The information thus gleaned is also most valuable in that it aids in understanding the reactivity of such substrates while the reactions are monitored with proton NMR.

Conclusion

We have herein reported on a series of silylated cyclopropanes studied by ${}^{29}\text{Si}$ NMR. The chemical shifts observed in this series are all rationalizable as a function of the number and position of substituents on the ring. The measurement of the coupling constants furthermore shows (i) the absence of geminal coupling (2J) between the cyclopropane silicon and the proton in position α , (ii) that the value of 2J is constant within the entire series, and (iii) that a relationship exists between the values of 3J and the geometry of the molecule ($J_{\text{cis}} > J_{\text{trans}}$).

This final observation in itself favors the use of ${}^{29}\text{Si}$ NMR in stereochemical studies of organosilicon synthons. The high sensitivity of the SPI technique and the consequent possibilities of signal assignments in proton NMR of SiMe_3 groups can be foreseen to be very useful in studying the reactivity of polysilylated compounds.

Experimental Section

Spectra were recorded on a Bruker WH-90 spectrometer (17.87 MHz for ${}^{29}\text{Si}$) equipped with a Nicolet BNC 12 computer.

All samples were 80% solutions in C_6D_6 (10-mm tubes). Chemical shifts are given downfield (δ) from Me_4Si as internal standard.

For the decoupled ${}^{29}\text{Si}$ spectra, the experiments were performed by using the "gated decoupling pulse modulated interrupted proton band decoupling" technique⁶ in order to cancel the negative nuclear Overhauser effect. The following parameters were used: time pulse, 5.5 μs ($\alpha = 45^\circ$); recycle delay, 30 s.

For the SPI spectra, the experiments were performed by using the technique previously described in the literature.² The following parameters were used: time for SPI π pulse, 0.1 s; time ${}^{29}\text{Si}$ pulse, 11 μs ($\alpha = 90^\circ$); recycle delay, 5 s.

In all cases, a resolution enhancement was performed by using the RE technique.³

The theoretical spectra were calculated on a H.P. 85 microcomputer and were drawn on a 4662 Tektronix digital plotter.

Registry No. 1, 930-40-5; 2, 79237-33-5; 3, 79237-32-4; 4, 86994-17-4; 5, 79237-38-0; 6, 77508-36-2; 7, 90084-12-1; 8, 88410-28-0; 9, 931-82-8.

(15) Délérís, G.; Birot, M.; Dunogués, J.; Barbe, B.; Pétraud, M.; Lefort, M. *J. Organomet. Chem.*, in press.

(16) See for instance: Weidner, U.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 146.

(11) Patel, D. J.; Howden, M. E. H.; Roberts, J. D. *J. Am. Chem. Soc.* 1963, 85, 3218.

(12) Williamson, K. L.; Landford, C. A.; Nicholson, C. R. *J. Am. Chem. Soc.* 1964, 86, 762. Seyferth, D.; Dow, A. W.; Menzel, H.; Flood, T. C. *Ibid.* 1968, 90, 1081.

(13) Kingsbury, C. A.; Durham, D. L.; Hutton, R. *J. Org. Chem.* 1978, 43, 4696.

(14) Quintard, J. P.; Degueil-Castaing, M.; Barbe, B.; Pétraud, M. *J. Organomet. Chem.* 1982, 234, 41.