Silicon-29 NMR access to stereochemistry of organosilicon compounds. 3. Vinylic silanes

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constants were obtained: $a = 22.42$ Å, $b = 22.43$ Å, $c = 22.44$ Å, $\alpha = 99.03$; $\beta = 98.96°$, $\gamma = 99.05°$, and $V = 10818$ Å^3. With the assumption of approximately the same monomer volume as found for the hexamer, an estimate of 90 monomers per unit cell is derived from the unit cell volume. For the possible Z values of 18 or 36, $Z = 18$ indicates pentamers, or possibly decamers, of 1.

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Registry No. 1 (hexamer), 113725-88-5; 1 (homopolymer), 73589-65-8.

Supplementary Material Available: Tables of complete structural parameters (bond lengths, bond angles, torsion angles, and least-squares planes), positional parameters, general displacement parameter expressions, and intensity data (14 pages); a listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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^{29}Si NMR Access to Stereochemistry of Organosilicon Compounds. 3. Vinylic Silanes

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^{29}Si NMR data are reported for a series of vinylic and acetylenic silanes. Chemical shifts were measured and ^{29}Si,^{1}H coupling constants were determined by using the selective polarization transfer (SPT) technique. It was found in particular that there is a relationship between ^3J and the stereochemistry of the molecules.

In a previous paper,[1] we described the first stereochemical study using ^{29}Si NMR spectroscopy and showed that this technique is capable of determining with precision the geometry of silylcyclopropyl compounds. It was found in particular that there is a Karplus-type relationship for $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ coupling constants.

We now focus on the vinylsilanes, a class of compounds that is useful in organic synthesis.[2] Because vinylsilanes can undergo regiospecific functionalization, it appears important to be able to determine their geometric configuration.

Results and Discussion

Vinylsilanes have been the subject of intensive studies for a number of years. Publications reporting ^{29}Si NMR chemical shifts are numerous but rarely contain ^{29}Si,^{1}H coupling constant values; if present, the latter are generally incomplete.[3a]

Recently, Jakobsen[3b] determined the ^{29}Si,^{1}H coupling constants of vinyltrimethylsilane by double-resonance Hamiltonian analysis of a spectrum in which the SiMe$_3$ protons are selectively decoupled and concluded that it would be impossible to make such a determination without such an analysis because of the complexity of the ^{29}Si spectrum, especially when it is obtained by the SPT (selective polarization transfer) technique. Concurrently, we were studying this compound by using the SPT technique. We found the same coupling constant values and obtained a perfect simulation as shown in Figure 1.

To the best of our knowledge, a systematic study of ^{29}Si,^{1}H coupling constants in substituted vinylsilanes as a function of stereochemistry and the substitution on silicon and carbon has not been reported. We have recorded ^{29}Si NMR spectra of 11 vinylic silanes of known stereochemistry. Complete analysis of the SPT spectra with polarization transfer from the trimethylsilyl protons, which are very easy to obtain, is possible by using a computer simulation program such as the one we have described.[1,4] It allows the determination of all of the coupling constants (even the smallest ones) with a precision better than 0.3 Hz (cf. Figure 2). Stereochemical assignment then becomes possible from examination of ^3J values. Results are given in Table I which also contains data on vinyltrimethylsilane itself and on two alkynylsilanes.

1. Chemical Shifts. Although the ^{29}Si chemical shifts of some vinylsilanes have been investigated previously,[3,5] we have redetermined these values in order to have a uniform set of results. Because of differences in the solvents used and the operating conditions, some discrepancies between our data and literature values were observed; chemical shifts may vary within a 2 ppm range.[3a,5,6]

We observed negative chemical shift values for all silicon atoms linked to a double bond. In compound **9**, Si$_b$ res-

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[2] (a) Dunoguès, J. *Actual. Chim.* **1986**, 11. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1983. (c) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.

[3] (a) Marsmann, H. *NMR: Basic Princ. Prog.* **1981**, *17*, 65. (b) Jakobsen, H. J.; Kanyha, P. J.; Brey, W. S. *J. Magn. Reson.* **1983**, *54*, 134.

[4] (a) Grignon-Dubois, M.; Laguerre, M. *Actual. Chim.* **1983**, 21. (b) Grignon-Dubois, M.; Laguerre, M. *Comput. Chem.* **1985**, *9*(4), 279. (c) This program is commercially available from Interchim, 33, rue des Cordeliers, F-75013 Paris, France.

[5] Lippmaa, E.; Magi, M.; Chvalovsky, V. S.; Schraml, J. *Collect. Czech. Chem. Commun.* **1977**, *42*, 318.

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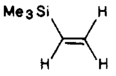
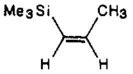
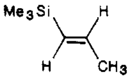
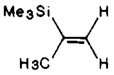
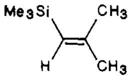
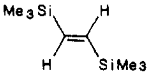
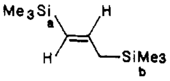
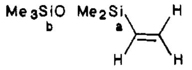
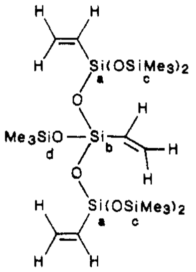
Table I. ^{29}Si NMR Data for Compounds 1-11

products	δ (TMS)	$^{2}J^{a}$	$^{2}J'$ or $^{2}J''^{a}$	$^{3}J_{c}^{a}$	$^{3}J_{t}^{a}$	^{4}J or other^{a}
 **1**	−6.9	6.6 (9 H)	6.4 (1 H)	8.5 (1 H)	15.2 (1 H)	
 **2**	−10.6	6.7 (9 H)	8.6 (1 H)		12.6 (1 H)	1.4 (3 H)
 **3**	−8.3	6.7 (9 H)	6.5 (1 H)	7.5 (1 H)		1 (3 H)
 **4**	−4.8	6.65 (9 H)		7.3 (1 H)	13.9 (1 H)	4. 6 (3 H)
 **5**	−11.5	6.7 (9 H)	4. 6 (1 H)			1 (3 H)^{b}
 **6**	−7.75	6.6 (9 H)	9.6 (1 H)	9.6 (1 H)		
 **7**	Si$_a$ −8.65 Si$_b$ +0.15	6.5 (9 H) 6.5 (9 H)	6.9 (1 H) 8.5 (2 H)	6.2 (1 H)		 2 (2 H)
 **8**	Si$_a$ −3.9 Si$_b$ +8.2	6.75 (6 H) 6.7 (9 H)	7.1 (1 H)	9.4 (1 H)	16.15 (1 H)	
 **9**	Si$_a$ −78.1 Si$_b$ −79.9 Si$_c$ +8.4 Si$_d$ +8.7	 6.8 (9 H) 6.8 (9 H)	9.9 (1 H) 9.8 (1 H)	12 (1 H) 13.2 (1 H)	17.2 (1 H) 16.3 (1 H)	
$Me_3SiC\equiv CCH_3$ (**10**)	−19.44	6.9 (9 H)				1.6 (3 H)
$(Me_3SiC\equiv CCH_2-)_2$ (**11**)	−19.0	7.1 (9 H)				0.65 (2 H)

^{a} $J(^{29}Si, ^{1}H)$ coupling constants are given at ±0.2 Hz (absolute values). ^{b} Only one CH_3 is coupled.

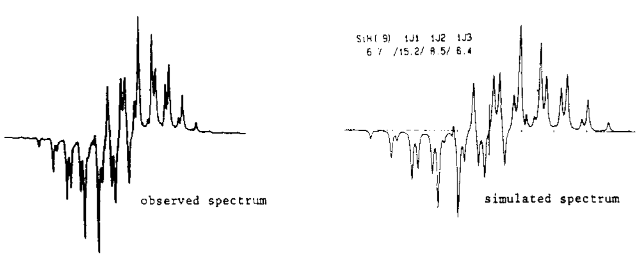
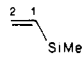


Figure 1. ^{29}Si SPT spectra of vinyltrimethylsilane (polarization transfer from the trimethylsilyl protons).

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

entry		β-effect, ppm	γ-effect, ppm
a	one CH_3 on C_1	+2.8	
b	one CH_3 on C_2 (cis)		−3.0
c	one CH_3 on C_2 (trans)		−0.8
d	two CH_3 on C_2		−3.9
e	$SiCH_2$ on C_2 (trans)		−1.75
f	Me_3Si on C_2 (trans)		−0.85

onates at about −80 ppm which is a normal value for a silicon atom linked to three oxygen atoms.[3a]

It may be noticed that the silicon chemical shifts decrease in compounds **1**–**5** according to the sequence **4** < **1** < **3** < **2** < **5**. It seems that the introduction of the methyl group in position 2 (γ-effect) of the double bond has a shielding effect whereas it has a deshielding effect when it is in position 1 (β-effect) (cf. Table II). Values in entries a–c of Table II are in good agreement with the results of Mitchell and Marsmann.[14] As we mentioned earlier, these effects are comparable to those we observed with cyclopropylsilanes but are greater in magnitude.[1b]

2. Coupling Constants $^{n}J(^{29}Si,^{1}H)$. (a) ^{1}J. The coupling to the nine equivalent protons of the SiMe$_3$ group, as we observed in other series,[1] remains constant and close

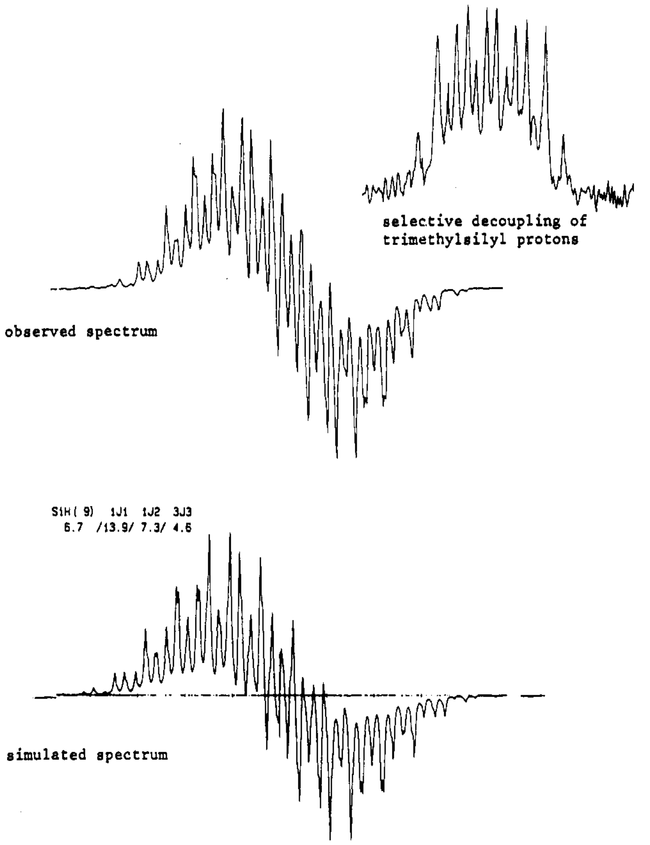
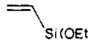
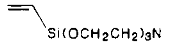
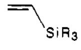
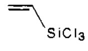
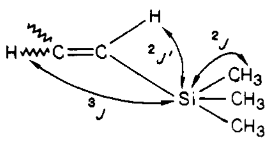


Figure 2. ^{29}Si SPT spectra of compound 4 (polarization transfer from the trimethylsilyl protons).

Table III. Influence of Silicon Substituents upon $^2J'$ Coupling Constants

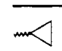
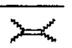
compds	$^2J'$, Hz	ref
 Si(OEt)$_3$	8.1	7
 Si(OCH$_2$CH$_2$)$_3$N	5.8	7
 SiR$_3$	4.6–8.6	2
 SiCl$_3$	26.1	6

to 6.7 Hz, a value that seems to be characteristic of trimethylvinylsilanes. The values observed for Si$_b$ in 8 and for Si$_c$ and Si$_d$ in 9 are compatible with those in the literature reports.[2] For the two alkyne derivatives we also found typical values: i.e., 7.0 ± 0.1 Hz.[3a,12]



(b) $^2J'$. The coupling to the vinylic proton in α-position varies from 4.6 (5) to 9.9 (9) Hz. It seems to be sensitive to the substituents borne by the silicon and becomes greater with increasing oxygen substitution (from 6.4 to 9.9 Hz). Some other examples found in the literature are given in Table III, but in the case of CH$_2$=CHSiCl$_3$ the data are doubtful and for all these compounds no other coupling constants have been given. [The authors refered to ^4J value (although there is no corresponding proton) but did not mention the ^3J coupling constants.] In the specific case of 7 the coupling constant between Si$_b$ and the two adjacent protons is equal to 8.5 Hz. For allylsilane, $^2J'$ was found to be 8.8 Hz.[8] Keeping in mind that in the 1-(trimethylsilyl)-2-((trimethylsilyl)methyl)cyclopropane this coupling was smaller (5.8 Hz), it seems that the presence of a double bond increases all the coupling constants (Table IV).

Table IV. Comparison of the Magnitude of the ^{29}Si,^{1}H Coupling Constants in Cyclopropyl- and Vinylsilanes

	Σ	
⩾Si–Σ		
^2J	6.3	6.7
$^2J'$	0	4–9
^3J	3–6	6–16
^4J	0	1–1.15

(c) ^3J. A perusal of Table I shows that in all cases $^3J_{trans}$ is greater than $^3J_{cis}$ as $^3J(^1H,^1H)$ coupling constants. Therefore, there would seem to be a direct relationship between $^3J(^{29}Si,^1H)$ and the stereochemistry of the molecules as we found previously for cyclopropyl compounds.[1] Mitchell and co-workers[13,14] have reported similar results for $^3J(^{119}Sn,^{13}C)$ in vinyltin compounds. The absolute magnitude of ^3J increases with progressive oxygen substitution on silicon as shown with 8 and 9 (effects are weaker for $^3J_{trans}$) while it seems to decrease with electropositive substitution on carbon by CH$_3$ or CH$_2$SiMe$_3$. On other hand, Me$_3$Si substitution increases ^3J. These observations fit well with other reports in the literature,[3a] especially those of Danyluk for chloro compounds.[9]

(d) ^4J. Long-range coupling constants, ^4J, between vinylic silicon and alkyl groups in the β-position of the double bond are always weak. In the case of 5 we observed ^4J for only one methyl group (the other one may have $^4J \leqslant 0.5$ Hz). Comparison of the values with those of cyclopropylsilanes (Table IV) for which ^4J had not been observed[1] and acetylenic compounds 10 and 11 for which we found values of 1.6 and 0.65 Hz shows that long-range coupling constants are only observed when π-electrons permit transmission of the interaction. Similar values have been observed for aromatic and polyaromatic derivatives.[10,11]

3. Use of ^{29}Si NMR in the Assignment of SiMe$_3$ Peaks in ^{1}H NMR. The basic idea of these experiments was to take advantage of the polarization transfer selectivity in frequency for correlating ^{1}H and ^{29}Si chemical shifts. By examining the ^{29}Si spectra and knowing which of the satellites is being irradiated, we can achieve the attribution of proton signals of the SiMe$_3$ group of polysilylated derivatives and isomer mixtures, as reported in previous work.[1] In the case of 7, the use of SPT allows the SiMe$_3$ group of the ring to be assigned as a singlet at δ 0.12 and the CH$_2$SiMe$_3$ group as a singlet at δ 0.07 (C$_6$D$_6$).

Experimental Section

Materials. Vinyltrimethylsilane (1) is commercially available. Methylpropenylsilanes 2–4 were prepared as described by Seyferth and Vaughan;[15] 6 and 7 were prepared by silylation of vinyl- or allyltrimethylsilane[16] and 10 and 11 from propargyl bromide. 8 and 9 were obtained by cohydrolysis of vinylchlorosilanes and a large excess of Me$_3$SiCl.

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(12) Bennetau, B.; Birot, M.; Déléris, G.; Dunoguès, J.; Pillot, J.-P.; Barbe, B.; Pétraud, M. *Rev. Silicon, Germanium, Tin and Lead Compds.* **1985**, *8*, 327.

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(15) Seyferth, D.; Vaughan, L. G. *J. Organomet. Chem.* **1963**, *1*, 138.

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Spectroscopy Measurements. Spectra were recorded on a Bruker WH 90 (17.87 MHz for ^{29}Si) and a Bruker WM 500 (99.27 MHz for ^{29}Si). All samples were 50% solutions in C_6D_6 (10-mm tube). Chemical shifts are given downfield (δ) from Me_4Si as internal standard.

For the SPT spectra, the experiments were performed by using the technique previously describe in the literature.[17] The following parameters were used: time for SPT π pulse = 0.1 s, time for ^{29}Si pulse = 11 μs ($\alpha = 90°$), and recycle delay = 5 s. The theoretical spectra were calculated on a Leanord Sil Z16 PC and were drawn on a Hewlett-Packard 7475 A digital plotter.

Acknowledgment. We thank MM. B. Barbe and M. Pêtraud (Cesamo, University of Bordeaux I) for carrying out the 90-MHz measurements and D. Davoust (University of Paris VI) for the 500-MHz measurements. Special thanks are also due to Dr. T. N. Mitchell of Dortmund University for helpful and valuable discussions.

Registry No. **1**, 754-05-2; **2**, 4964-02-7; **3**, 4964-03-8; **4**, 762-72-1; **5**, 18292-39-2; **6**, 18178-59-1; **7**, 52152-48-4; **8**, 1438-79-5; **9**, 113947-92-5; **10**, 6224-91-5; **11**, 1578-53-6; ^{29}Si, 14304-87-1.

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[17] Linde, S. A.; Jakobsen, H. J.; Kimber, B. J. *J. Am. Chem. Soc.* **1975**, *97*, 3219.

Synthesis and Structure of $[Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2]$. A Convenient Precursor to Pentamethylcyclopentadienyl Chemistry of Platinum

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Received September 2, 1987

Reaction of $[PtCl_3CO]^-$ with 2 equiv of $C_5Me_5MgCl\cdot THF$ affords $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (1) in >80% yield. Treatment of $[PtCl_3CO]^-$ with 1 equiv of $C_5Me_5MgCl\cdot THF$ yields a mixture of $[PtCl_3CO]^-$, 1, and $Pt(\eta^5\text{-}C_5Me_5)(CO)Cl$ (2), revealing the intermediacy of 2 in the reaction. A single-crystal X-ray structural determination of 1 was undertaken: formula $C_{22}H_{30}O_2Pt_2$; monoclinic, $P2_1/n$, $Z = 4$, $a = 10.428$ (2) Å, $b = 13.995$ (3) Å, $c = 15.143$ (4) Å, $\beta = 100.53$ (2)°; reflections with $I > 3\sigma(I) = 3452$; $R = 0.038$; $R_w = 0.043$. The dimeric structure consists of two staggered $Pt(\eta^5\text{-}C_5Me_5)(CO)$ units connected by a unbridged platinum–platinum bond of 2.636 (1) Å. Variable-temperature ^{13}C NMR spectroscopy was consistent with rapid CO exchange between the two platinum atoms.

Introduction

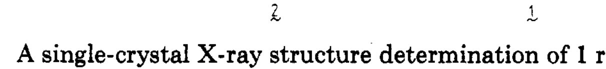
Due to a lack of suitable synthetic routes to the dimeric species $Pt_2(\eta^5\text{-}C_5R_5)_2(CO)_2$, whose analogues in other transition-metal groups provide ready access to an extensive chemistry, cyclopentadienyl chemistry of platinum has been slow to develop.[2]

We have previously described an improved synthesis of $Pt_2(\eta^5\text{-}C_5H_5)_2(CO)_2$ involving formate reduction of $[PtCl_3CO]^-$ to the platinum(I) complex $[Pt_2Cl_4(CO)_2]^{2-}$ followed by metathesis using $(C_5H_5)_2Mg$.[3,4] The modest overall yield from $[PtCl_3CO]^-$ (ca. 35%) and problems associated with elimination reactions of the cyclopentadienyl group on platinum through η^1 intermediates[5] led us to synthesize $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (1). In this paper we describe a new high-yield synthetic method to this important starting material.

Results and Discussion

We initially prepared the complex $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (1) in 65% overall yield by metathesis of the dianion $[Pt_2Cl_4(CO)_2]^{2-}$ with $C_5Me_5MgCl\cdot THF$. This method is, of course, analogous to that used for the synthesis of $Pt_2(\eta^5\text{-}C_5H_5)_2(CO)_2$.[4] However, we have now found that this same complex may be obtained *directly* from the reaction of THF solutions of $[PtCl_3(CO)]^-$ with 2 equiv of $C_5Me_5MgCl\cdot THF$ in >80% yields.

Treatment of $[PtCl_3(CO)]^-$ with 1 equiv of $C_5Me_5MgCl\cdot THF$ affords some insight into the course of this reduction. IR and NMR analysis of the reaction solution shows it to be a mixture of starting anion, the dimer 1, and $Pt(\eta^5\text{-}C_5Me_5)(CO)Cl$ (2) (see Table I). A second equivalent of the Grignard reagent converts this mixture primarily to $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$, clearly revealing the intermediacy of 2 in this reaction.[6] After crystallization of the dimer, the σ-coupled byproduct $C_5Me_5\text{–}C_5Me_5$ may be isolated from the residue by sublimation.[7]



(1)

A single-crystal X-ray structure determination of 1 revealed it to contain two $Pt(\eta^5\text{-}C_5Me_5)(CO)$ subunits, the two adjacent terminal carbonyl groups being orientated at approximately 105° to each other (Figure 1). The

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[1] This work was partially undertaken at Syracuse University, Syracuse, NY 13244-1200.

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