

^1H , ^{13}C and ^{29}Si NMR study of α - and β -silylstyrenes and their adducts with dichlorocarbene

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Abstract

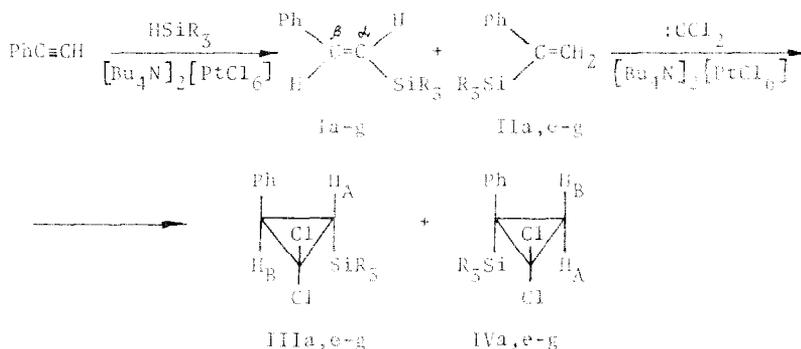
^1H , ^{13}C and ^{29}Si NMR spectra for the α - and β -silylstyrenes (*E*)- $\text{PhCH}=\text{CHSiR}_3$ (I) and $\text{PhC}(\text{SiR}_3)=\text{CH}_2$ (II) ($\text{R} = \text{Cl, Me, Ph}$), and those for some dichlorocarbene adducts of I and II ($\text{R} = \text{Me, Ph}$), were examined. From the ^{13}C NMR data, the phenyl substituent in the molecules I and II enhances the electronic effects of the organosilicon substituent at C_α , and weakens these effects on the C_β resonance. The degree to which polarization of the vinyl $\text{C}=\text{C}$ bond is polarized increases with increased electron-withdrawing properties of substituent R in the SiR_3 group in compounds I and II, and correlates with the reduced reactivity of the bond toward electrophilic dichlorocarbene. Several long-range coupling constants (CC) in the molecules I, II and in their adducts with $:\text{CCl}_2$ were measured. The estimated CC is a useful aid for the study of electronic effects in organosilicon compounds.

Introduction

^1H , ^{13}C and ^{29}Si NMR spectroscopy has been extensively applied to structural studies of organosilicon compounds including alkenylsilanes, and to the study of electronic effects due to the presence of a silicon atom [1–6]. To gain more detailed information on these subjects it is worthwhile to compare a wide range of structurally related compounds differing only in the nature of substituents at the silicon atom [2,4–6]. Here we describe the synthesis and multinuclear NMR spectroscopy of the silyl-styrenes (*E*)- $\text{PhCH}=\text{CHSiR}_3$ and $\text{PhC}(\text{SiR}_3)=\text{CH}_2$ ($\text{R} = \text{Cl, Me, Ph}$) and some of their dichlorocarbene adducts.

Results and discussion

Silylstyrenes (Ia–g and IIa,e–g) were prepared by the hydrosilylation, i.e. reaction of phenylacetylene with various silanes in the presence of bis(tetrabutylammonium)hexachloroplatinate at 80–140 °C during 1–3 h by a published procedure



a: R = Me, b: R₃ = Me₂Cl, c: R₃ = MeCl₂, d: R = Cl, e: R₃ = Me₂Ph, f: R₃ = MePh₂, g: R = Ph

Scheme 1

[7] (Scheme 1). The overall yield of the hydrosilylation products was nearly quantitative. The reaction of PhC≡CH with triorganosilanes in the presence of the same catalyst affords a mixture of *β-trans*- and *α*-silylstyrenes I and II, whereas chlorine-containing silanes add to phenylacetylene to give predominantly *β-trans* isomers (95–98%) [7].

1,1-Dichloro-2-triorganosilylcyclopropanes (IIIa,e-g,IVa,e-g) were obtained from mixtures of Ia,e-g and IIa,e-g by a published procedure [8], viz. the addition of dichlorocarbene generated in the two-phase system CHCl₃/50% aq. NaOH in the presence of the same catalyst as that used for hydrosilylation (Scheme 1). The process occurs quantitatively at room temperature during 1–4 h depending on the silyl group R substituent in compounds I and II. Dichlorocarbene generated in this way is a singlet [9], hence the reaction of alkenylsilanes I, II with :CCl₂ proceeds *cis*-stereospecifically and results in a mixture of the appropriate adducts III and IV, the ratio of *α*- and *β*-isomers being retained. Products III have the *trans*-configuration, ³J(H_A–H_B) 10.5–11.0 Hz. The cyclopropanes IIIa,f,g, IVa,f,g are novel.

The ¹H NMR spectral parameters for the synthesized silylstyrenes Ia–g, IIa,e–g (Table 1) closely resemble those reported in the literature [7,10,11]. The ¹H NMR spectra of compounds IIIe and IVe (Table 1) are identical with those reported previously [8]. NMR spectra for compounds I–IV on other nuclei had not been studied systematically earlier.

The ¹H, ¹³C, ²⁹Si NMR spectral parameters for the entire set of compounds, prepared according to Scheme 1 are listed in Tables 1–3. Qualitatively, the shielding behaviour of nuclei in the molecules I–IV tends to coincide and so can be exemplified by compound I. To clarify the effect of the phenyl group at the double bond in silylstyrene molecules we compared vinylic ¹³C chemical shifts (CS) in compounds I (Table 2) with known values [4] for the vinylsilanes ^HCH₂=^αCHSiR₃ (Va–f). The two values appear to be linearly correlated:

$$(1) \delta(^{13}\text{C}_\alpha)^{\text{I}} = -45.96 + 1.26\delta(^{13}\text{C}_\alpha)^{\text{V}} \quad r = 0.998, s = 1.2, n = 6$$

$$(2) \delta(^{13}\text{C}_\beta)^{\text{I}} = +28.29 + 0.89\delta(^{13}\text{C}_\beta)^{\text{V}} \quad r = 0.998, s = 0.9, n = 6$$

Table 1

¹H and ²⁹Si chemical shifts (ppm) and ¹H-¹H CC (Hz) for silylstyrenes and silyldichlorocyclopropanes

(I) PhC=C(SiR3)H_A (H_B on the other carbon)

(II) PhC=C(SiR3)H_B (H_A on the other carbon)

(III) PhC1C(SiR3)C1H_A (H_B on the other carbon)

(IV) PhC1C(SiR3)C1H_B (H_A on the other carbon)

Compound	SiR ₃	δ(²⁹ Si)	δ(¹ H _A)	δ(¹ H _B)	δ(¹ H-CH ₃)	J(H _A -H _B)
Ia	Si(CH ₃) ₃	-6.33 ^a	6.49	6.88	0.17	19.16
Ib	Si(CH ₃) ₂ Cl	+19.01	6.44	7.06	0.57	19.12
Ic	Si(CH ₃)Cl ₂	+17.72	6.41	7.22	0.90	18.90
Id	SiCl ₃	-2.16	6.38	7.34	-	18.76
Ie	SiPh(CH ₃) ₂	-10.41	6.60	6.99	0.44	19.25
If	SiPh ₂ CH ₃	-13.72	6.78	7.00	0.73	19.14
Ig	SiPh ₃	-16.61	7.00	7.03	-	19.05
IIa	Si(CH ₃) ₃	-4.31	5.61	5.83	0.18	3.14
IIe	SiPh(CH ₃) ₂	-8.36	5.67	5.99	0.42	2.93
IIf	SiPh ₂ CH ₃	-10.97	5.62	6.16	0.68	2.83
IIg	SiPh ₃	-14.60	5.72	6.30	-	2.90
IIIa	Si(CH ₃) ₃	+2.36	1.32	2.77	0.24	11.00
IIIe	SiPh(CH ₃) ₂	-2.69	1.43	2.84	0.53 and 0.46	10.55
IIIf	SiPh ₂ CH ₃	-7.40	1.75	2.92	0.76	10.48
IIIg	SiPh ₃	-11.84	2.08	2.90	-	10.61
IVa	Si(CH ₃) ₃	+6.60	1.95	1.79	0.08	6.20
IVe	SiPh(CH ₃) ₂	+0.65	1.93	1.75	0.42 and 0.36	6.10
IVf	SiPh ₂ CH ₃	-4.43	2.07	1.90	0.56	5.86
IVg	SiPh ₃	-9.98	2.13	2.02	-	5.78

^a -6.49 in [20].

It can be seen from the NMR data that the SiR₃ group exhibits electron-withdrawing properties with respect to the π-bond [2,4-6]. By comparing the slopes of the correlation equations (1) and (2) it can be deduced that the effect of the phenyl substituent in compounds Ia-g manifests itself by the enhancement of SiR₃ group electronic effects on C_α, and by weakening those on the C_β-resonance. This is consistent with the direction of C=C bond polarization in the styrenes, i.e. the CH₂-carbon is shielded to a greater extent than CH- [12]. Additionally, the presence of a SiR₃ group at the C=C bond in styrene molecules (as in the case of vinylsilanes) substantially reduces the net charge over this bond as revealed by the sum of vinylic ¹³C CS (Table 4). This is an indication of the acceptor properties of the organosilicon substituent. The extent of vinylic C=C bond polarization in these molecules rises with growing electron-withdrawing properties of substituents R in the SiR₃ group of compounds I, II. As judged by the difference in ¹³C_α and ¹³C_β CS (Table 2), charge partition increases * in the following sequence: SiMe₃ < SiMe₂Ph < SiMe₂Cl ≈ SiPh₂Me < SiPh₃ < SiMeCl₂ < SiCl₃. These findings are consistent

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* This approach does not take into account differences introduced by the β- and γ-effects of substituent SiR₃ into C_α and C_β shielding.

Table 2

¹³C Chemical shifts (ppm) for silylstyrenes and silyldichlorocyclopropanes

Compound	(I)		(II)		(III)		(IV)		C ₆ H ₅		
	C _α	C _β	C _α	C _β	CCl ₂	C _R	C _i	C _o	C _m	C _p	
Ia	130.05	144.17					138.95	126.87	129.00	128.61	
Ib	125.17	147.14				-0.76	137.76	127.35	129.13	129.40	
Ic	121.77	149.70				2.56	136.71	127.76	129.24	130.21	
Id	119.32	151.99				6.09	135.82	128.13	129.35	130.97	
Ie	127.54	145.97					138.98	128.37	129.00	127.04	
If	125.41	141.79					138.57	128.40	129.02	127.14	
Ig	123.52	149.46					138.57	128.44	129.08	127.30	

IIa	145.32	126.72	-	-0.43(CH ₃)	144.17	127.22	128.43	127.61
IIe	149.34	127.35	-	-1.81(CH ₃), 138.71(C _i), 134.53(C _o), 128.37(C _m), 129.57(C _p)	144.67	128.85	128.37	126.93
IIIf	149.41	127.56	-	-2.96(CH ₃), 136.55(C _i), 135.68(C _o), 128.40(C _m), 129.86(C _p)	144.34	128.84	128.34	127.14
IIIf	149.46	128.00	-	134.77(C _i), 136.92(C _o), 128.46(C _m), 130.05(C _p), -0.87	144.47	128.65	128.35	127.30
IIIa ^a	26.99	39.10	66.78	-2.26(CH ₃), 137.33(C _i)	136.39			
IIIe ^a	26.42	39.30	66.42	-3.40(CH ₃), 135.42(C _i)	135.98			
IIIIf ^a	25.63	39.44	66.72	133.50(C _i)	135.82			
IIIg ^a	24.91	39.63	65.89	-0.71	135.67			
IVa ^a	32.46	30.87	67.51	-1.78(CH ₃), 136.30(C _i)	140.94			
IVe ^a	35.26	31.16	66.69	-1.76(CH ₃), 135.40(C _i)	140.67			
IVf ^a	35.96	31.18	66.13	133.23(C _i)	140.32			
IVg ^a	30.22	31.83	66.15		139.85			

^a Analysis of aromatic carbon signals was not complete due to their overlapping.

Table 3

 ^{29}Si - ^1H , ^{29}Si - ^{13}C , ^{13}C - ^1H CC (Hz) for silylstyrenes and silyldichlorocyclopropanes

Compound	^{29}Si - H_A	^{29}Si - H_B	^{29}Si - C_α	^{29}Si - C_R	^{13}C - H_A	^{13}C - H_B	^{29}Si - H_R	^{13}C - H_R
(I)								
Ia	4.86	7.70	65.4	54.0	135.5	150.7	6.67	118.8
Ib	7.05	9.19	76.5	59.8	138.2	151.7	7.03	121.6
Ic	9.75	11.21	93.1	71.3	143.8	153.8	7.75	123.7
Id	12.96	13.99	118.1	-	148.5	155.2	-	-
Ie	4.69	7.42	67.6	54.2(CH ₃) 67.7(C ₁)	135.1	152.0	6.59	119.0
If	4.98	7.55	69.8	55.5(CH ₃) 69.4(C ₁)	137.6	152.9	6.64	120.8
Ig	5.00	7.58	72.2	71.2(C ₁)	^a	^a	-	-
IIa	7.23	13.42	^a	^a	160.1	152.0	6.67	119.6
IIe	7.55	13.70	^a	^a	158.3	154.4	6.59	120.2
IIf	7.52	14.26	^a	^a	159.3	153.8	6.64	120.6
IIg	7.55	14.80	^a	^a	^a	^a	-	-
IIIa	2.12	5.27	58.3	53.3	^a	^a	^a	^a
IIIe	2.05	5.80	59.9	55.2(CH ₃) 69.1(C ₁)	^a	^a	6.67	^a
IIIf	1.91	6.23	62.4	56.9(CH ₃) 70.7(C ₁)	^a	^a	6.67	^a
IIIg	2.41	6.44	64.4	73.1(C ₁)	^a	^a	6.59	^a
IVa	6.04	4.13	59.4	53.8	^a	^a	-	^a
IVe	6.52	4.03	58.8	55.2(CH ₃) 69.2(C ₁)	^a	^a	6.54	^a
IVf	6.67	3.88	63.2	57.6(CH ₃) 70.9(C ₁)	^a	^a	6.59	^a

^a Not determined.

Table 4
The sum of vinylic ^{13}C chemical shifts in alkenylsilanes

Compound	$\Sigma\delta(^{13}\text{C})$	Ref.
$\text{CH}_2=\text{CH}_2$	246.6	12
$\text{Me}_3\text{SiCH}=\text{CH}_2$	268.9 ^a	2
(<i>E</i>)- $\text{Me}_3\text{SiCH}=\text{CHSiMe}_3$	300.0	3
$(\text{Me}_3\text{Si})_2\text{C}=\text{CH}_2$	279.0	3
$\text{PhCH}=\text{CH}_2$	249.9	12
(<i>E</i>)- $\text{PhCH}=\text{CHSiMe}_3$	274.2	this work
$\text{Ph}(\text{SiMe}_3)\text{CH}=\text{CH}_2$	272.0	this work

^a 270.03 [4], 270.1 [5], 268.27 [6a].

with the reactivity data obtained for the styrylsilanes Ia,e–g and IIa,e–g by treating them with dichlorocarbene having electrophilic properties. Upon substitution of the methyl groups for phenyl ones in the radical SiR_3 the rate at which I and II convert to the dichlorocyclopropane adducts III, IV declines. When $\text{R}_3 = \text{Me}_3$ complete conversion occurs within 1 h, with $\text{R}_3 = \text{Ph}_3$ within 4 h, and with $\text{R}_3 = \text{Me}_2\text{Ph}$ and MePh_2 at 3 and 3.5 h, respectively.

The electronic effects of the SiR_3 groups are transmitted over considerable distances as indicated by substantial changes in phenyl carbon CS at the C=C bond (Table 2).

In order to assess the character of electronic effects exerted by the silyl groups using the known correlations [13], we estimated the reactivity constants, σ_{R}^0 and σ_1 , for bulky organosilicon substituents in the molecules I and II, the latter being viewed as monosubstituted benzenes (Table 5). It follows from the σ estimates that substitution of the chlorine atom at silicon for a phenyl group affects the resonance component of the electronic effect of the group. At the same time, according to the inductive mechanism, the substituent $-\text{CH}=\text{CHSiR}_3$ acts as acceptor with respect to the benzene ring regardless of the nature of substituent R at the silicon atom. The SiR_3 group, being closer to the benzene cycle in the *gem*-isomers II, affects the inductive constant σ_1 more appreciably, i.e. the entire substituent serves as a σ -donor with respect to the benzene cycle. The substituent attached directly to the silicon atom, as in other cases [13], displays σ -donor and π -acceptor properties (Table 5).

Variation in electronic properties of SiR_3 substituents also affects ^1H and ^{29}Si CS (Table 1). Enhanced acceptor properties of the SiR_3 group in the molecules I–IV bring about a downfield shift of ^1H resonances for the vicinal protons and SiCH_3 group. The influence of substituents at silicon on the geminal to silicon proton CS in compounds I–IV is more complex: an increase in the number of chlorine atoms at silicon causes a slight upfield shift of resonance signals, while the presence of phenyl groups leads to a downfield resonance displacement for these protons.

^{29}Si CS bear a U-shaped relationship to the charge on the silicon atom [1] and hence are difficult to interpret. An additive upfield displacement of ^{29}Si resonances with increasing number of phenyl groups in substituent SiR_3 (Table 1) may be attributable to the paramagnetic component of shielding and is due to the increased positive charge on the silicon atom. An increase in the number of chlorine atoms at Si is accompanied by a gain in CC values $^1J(^{29}\text{Si}-^{13}\text{C})$ (Table 3). According to

Table 5
 Reactivity constants for bulky silicon-containing substituents

<i>n</i>	$-\text{CH}=\text{CHSiMe}_{3-n}\text{Cl}_n$		$-\text{CH}=\text{CHSiMe}_{3-n}\text{Ph}_n$		$\text{CH}_2=\text{C}(\text{SiMe}_{3-n}\text{Ph}_n)$		$\text{PhCH}=\text{CH}(\text{SiMe}_{2-n}\text{Ph}_n)$		$\text{CH}_2=\text{C}(\text{SiMe}_{2-n}\text{Ph}_n)$	
	σ_R°	σ_I°	σ_R°	σ_I°	σ_R°	σ_I°	σ_R°	σ_I°	σ_R°	σ_I°
0	-0.02	0.12	-0.02	0.12	-0.04	-0.14	0.06	-0.11	0.06	-0.11
1	0.01	0.20	-0.10	0.07	-0.07	-0.20	0.07	-0.09	0.07	-0.09
2	0.05	0.28	-0.09	0.09	-0.06	-0.20	0.08	-0.06	0.08	-0.06
3	0.08	0.35	-0.09	0.12	-0.05	-0.19	-	-	-	-

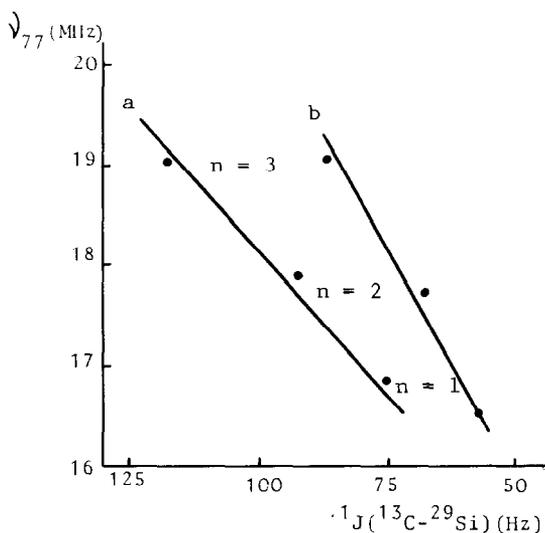


Fig. 1. ${}^1J({}^{29}\text{Si}-{}^{13}\text{C})$ CC in compounds Ib-d as a function of NQR frequency ν_{77} in the Si-Cl bond of chlorosilanes. a: $\text{Me}_{3-n}\text{Cl}_n{}^{29}\text{Si}-{}^{13}\text{CH}=\text{CH}_2$, b: $\text{Me}_{3-n}\text{Cl}_n{}^{29}\text{Si}-{}^{13}\text{CH}_3$.

Bent's hypothesis [14], this is consistent with enhanced Si-C bond *s*-character and decreased Si-Cl bond *s*-character. However, for the phenyl-containing compounds Ie-g, IIIe-g and IVe-g the ${}^1J({}^{29}\text{Si}-{}^{13}\text{C})$ value for all of the four Si-C bonds tends to increase relative to the corresponding trimethylsilyl derivatives Ia, IIIa and IVa (Table 3), which fails to comply with Bent's rule and is apparently due to the increased positive charge on the silicon atom. This is consistent both with the ${}^{29}\text{Si}$ resonance shift to higher fields in compounds I-IV (e-g) (Table 1), and with increased CC values ${}^1J({}^{13}\text{C}-{}^1\text{H})$ (Table 3).

The increase in positive charge on the silicon atom in compounds $\text{PhCH}=\text{CHSi}(\text{CH}_3)_{3-n}\text{Cl}_n$ with *n* varying from 1 to 3 also follows from the dependence of our values ${}^1J({}^{29}\text{Si}-{}^{13}\text{C})$ on the nuclear quadrupole resonance frequencies for the bond Si-Cl in the series $\text{CH}_2=\text{CHSi}(\text{CH}_3)_{3-n}\text{Cl}_n$ and $\text{CH}_3\text{Si}(\text{CH}_3)_{3-n}\text{Cl}_n$ [15] (Fig. 1). Symbatic variation of these values suggests that enhanced Si-C bond *s*-character for the value ${}^1J({}^{29}\text{Si}-{}^{13}\text{C})$ is accompanied by diminished ionic character of the bond Si-Cl (an increase in NQR frequencies).

The ${}^1J({}^{29}\text{Si}-{}^{13}\text{C})$ values for Ia-g and the sum of Pauling's electronegativity of substituents in SiR_3 are linearly correlated:

$${}^1J({}^{29}\text{Si}-{}^{13}\text{C}) = -149.6 + 28.4\sum\Delta E \quad r = 0.987, \quad s = 1.4, \quad n = 7$$

Long-range coupling constants involving vinylic ${}^{29}\text{Si}$ and ${}^1\text{H}$ nuclei have received only scant attention. The measurements of ${}^nJ({}^{29}\text{Si}-{}^1\text{H})$ in asymmetric multispin systems are limited by data reported previously [16-18]. Recently, we proposed a method for multiquantum coherence transfer which permits ${}^{29}\text{Si}$ -coupled ${}^1\text{H}$ spectra to be recorded with efficiently suppressed proton signals coupled to ${}^{28}\text{Si}$ [19]. This approach has been used by us for the measurement of several long-range ${}^{29}\text{Si}-{}^1\text{H}$ CC. It follows from the data given in Table 3 that the value ${}^3J({}^{29}\text{Si}-{}^1\text{H})$ is always greater for the *trans*-disposition of the interacting nuclei as compared to that for the

cis-orientation. The ^{29}Si - ^1H CC are substantially lower in the cyclopropane system of III and IV, than that for the vinyl moiety in I and II. It is likely that the double bond π -electrons play a crucial part in the transfer of spin information between the ^{29}Si and ^1H nuclei. Similarly, the $^nJ(^{29}\text{Si}-^1\text{H})$ values are dependent on the properties of substituents at the silicon atom: an increase in electron-withdrawing properties brings about a marked increase in the absolute value of the $^nJ(^{29}\text{Si}-^1\text{H})$ CC. This means that when sufficient experimental data has been accumulated, the values of long-range CC $^nJ(^{29}\text{Si}-^1\text{H})$ could be extended to the analysis of electronic effects in organosilicon compounds.

Experimental

^1H , ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker WM-360 spectrometer at 360, 90.5 and 71.5 MHz, respectively, using CDCl_3 as solvent. Chemical shifts are relative to tetramethylsilane used as internal standard. Measurements were accurate to within ± 0.01 ppm for $\delta(^1\text{H})$, ± 0.03 ppm for $\delta(^{13}\text{C})$ and $\delta(^{29}\text{Si})$, ± 0.03 Hz for $J(^{29}\text{Si}-^1\text{H})$, ± 0.1 Hz for $J(^{29}\text{Si}-^{13}\text{C})$ and $J(^{13}\text{C}-^1\text{H})$.

The silanes used in this study were purchased from Fluka products, except for HSiMe_3 , which was purchased from Petrarch. Phenylacetylene was purified by distillation under vacuum before use. Bis(tetrabutylammonium)hexachloroplatinate was prepared as described elsewhere [7].

Preparation of silylstyrenes (Ia-g + IIa-g). (General procedure)

5 mmol of the silane HSiR_3 , 0.005 mmol of the catalyst $[\text{Bu}_4\text{N}]_2[\text{PtCl}_6]$ and 5 mmol of $\text{PhC}\equiv\text{CH}$ in a Pierce reaction-vial (5 cc) was stirred at 80°C (HSiMe_3 and chlorosilanes), 120°C (Me_2PhSiH and MePh_2SiH) or 140°C (HSiPh_3) for 1-3 h. The course of the reaction was monitored by GLC on a Chrom-4 chromatograph in a $1.2\text{ m} \times 3\text{ mm}$ glass column, 5% OV-17/Chromosorb W-HP (80-100 mesh) as sorbent, helium as carrier gas (60 ml/min) at 120 - 200°C , depending on the mixture composition, and by GC/MS spectrometry (Cratos MS-25, 70 eV). Upon complete conversion of the starting compounds, the NMR spectra were recorded for the resulting silylstyrenes without prior treatment.

Dichlorocyclopropanation of silylstyrenes Ia,e-g and IIa,e-g. (General procedure)

To mixtures of α - and β -triorganosilylstyrenes (Ia,e-g + IIa,e-g) prepared as outlined above and containing the catalyst $[\text{Bu}_4\text{N}]_2[\text{PtCl}_6]$, was added chloroform (50 mmol). A 50% aqueous alkali solution (50 mmol NaOH) was added dropwise to the resulting solution and then stirred at room temperature until the starting silylstyrenes had disappeared completely (monitored by GLC and GC/MS analysis). The reaction mixture was diluted with water, the organic layer was removed, washed with water, and dried with anhydrous MgSO_4 . Chloroform was removed by distillation and the NMR spectra of the resultant adducts (III, IV) were recorded.

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