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INVESTIGATION OF THE FACTORS CONTROLLING THE REGIOSELECTIVITY OF THE HYDROSILYLATION OF ALKYNES CATALYSED BY *trans*-DI-μ-HYDRIDOBIS(TRICYLCOHEXYLPHOSPHINE)-BIS(SILYL)DIPLATINUM COMPLEXES

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Summary

The hydrosilylation of terminal and internal alkynes and also of some hydroxy-alkynes catalysed by *trans*-di-μ-hydridobis(tricyclohexylphosphine)-bis(silyl)diplatinum complexes is described. These diplatinum complexes are very efficient catalysts for such hydrosilylations; high yields (80—98%) can be obtained under mild conditions with a catalysts/reactant ratio of 10^{-4}—10^{-5}/1. Addition of hydrosilanes X_3SiH to the alkynes RC≡CH, RC≡CR and RC≡CR′ proceeds in a stereospecific *cis* fashion yielding *trans*-RCH=CHSiX_3, *cis*-RC(SiX_3)=CHR and mixtures of the regioisomers *E*-RC(SiX_3)=CHR′ and *E*-RCH=C(SiX_3)R′ respectively. In the case of terminal alkynes, minor amounts of internal adducts corresponding to Markownikow addition of the hydrosilanes are also formed. The effects of variation of the reaction conditions (concentration of reactants or catalyst and temperature) upon the rate and regioselectivity of the addition were assessed. The regioselectivity increases as the asymmetry of the electron density of the acetylenic π-bonds increases; the regioselectivity is explained in terms of a qualitative molecular orbital treatment of the transition state formed in the insertion step of the alkyne into the Pt—H bond.

Introduction

In a previous paper [1] on the hydrosilylation of alkynes catalysed by *trans*-di-μ-hydridobis(tricyclohexylphosphine)bis(silyl)diplatinum complexes we reported that for the two terminal alkynes studied both terminal and non-terminal 1/1 adducts were formed. The proportion of the non-terminal adducts, which are the minor products, is only slightly dependent upon the nature of the silane even though the silyl groups have different *trans*-effects.

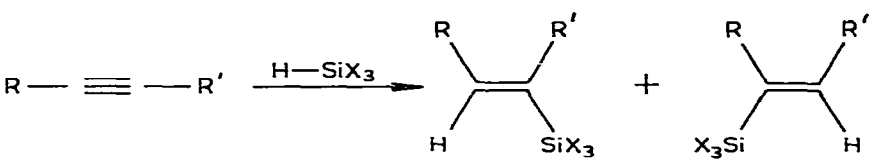
Since the silane does not seem to control the regioselectivity of the reaction, attempts were made to ascertain which of the other factors encountered in the hydrosilylation reactions control the orientation of the addition. Some of the factors studied were the nature of the alkyne and the reaction conditions, such as the relative ratio of the reactants, the concentration of catalyst, and the temperature, and the results are presented below, along with an interpretation.

Results and discussion

Results for the hydrosilylation of the terminal and internal alkynes studied are summarised in Tables 1 and 2, respectively.

Hydrosilylation of terminal alkynes affords as the major product *trans*-$RCH{=}CHSiX_3$ [R = n-C_3H_7(n-Pr), n-C_4H_9(n-Bu), n-C_5H_{11}(n-Pent), $(CH_2)_4CH$-(CyPent), $Me_2C(OH)$—, MeEtC(OH)—, PhCH(OH)—, and SiX_3 = $SiEt_3$, $SiMeCl_2$ and $SiCl_3$], corresponding to *cis*-antiMarkownikow addition of the hydrosilane. Non-terminal addition products are formed in minor amounts, corresponding to *cis*-Markownikow addition of the hydrosilane. For the sake of simplicity we will call the former *trans*-products and the latter *gem*-products.

Hydrosilylation of symmetrically substituted internal alkynes affords only *cis*-$RCH{=}C(R)(SiX_3)$ {R = Et, or $HOMe_2C$ and SiX_3 = $SiEt_3$ and/or $SiMeCl_2$, and $SiCl_3$ when R = Et} as expected for stereospecific *cis*-SiH addition. From the stereospecific *cis* addition of the hydrosilanes to non-symmetrically substituted internal alkynes mixtures of regioisomers of *E*-silylalkenes are formed according to the following general equation:



where R = Me, R′ = Et and R = Me, R′ = n-C_3H_7

and SiX_3 = $SiEt_3$, $SiMeCl_2$ and $SiCl_3$

All the reactions studied proceed under mild conditions ($t \simeq 65°C$), in high yield (~80—98%), at a low catalyst/reactant ratio (10^{-4}—10^{-5}). The reactions also take place slowly at room temperature under these conditions, but increasing the catalyst concentration can give reaction times at room temperature comparable to those given in Tables 1 and 2. After a brief warming of the reactants, all the reactions, except for those of the hydroxy-alkynes, proceed exothermically and are very fast; in most cases the mixture boils and the reaction is over in a few minutes. For these reactions the times given in Tables 1 and 2 are the times at which 90—98% of the reactants are consumed. For the slower reactions the times were estimated on the basis of plots of the yield(%) of the products against time.

The reactions under consideration were all also carried out in the presence of an excess of silane, but there was no formation of detectable amounts of 1/2 adducts. It is noteworthy that bis(silyl)alkanes are formed in considerable

TABLE 1

HYDROSILYLATION OF TERMINAL ALKYNES [a] IN THE PRESENCE OF THE CATALYST $[(Cy_3P)(BzMe_2Si)(\mu\text{-}H)Pt]_2$

Alkyne (amount (mmol))	Silane (amount (mmol))	Time (h)	Product (Yield (%))	Yield (%) [b]
n-PrC≡CH (10)	Et_3SiH (10)	5	*trans*-n-PrCH=CHSiEt_3 (96) H_2C=C(n-Pr)(SiEt_3) (4)	92
n-PrC≡CH (10)	Cl_2MeSiH (10)	1.5	*trans*-n-PrCH=CHSiMeCl_2 (95) H_2C=C(n-Pr)(SiMeCl_2) (5)	86
n-PrC≡CH (20)	Cl_3SiH (30)	1.25	*trans*-n-PrCH=CHSiCl_3 (96) H_2C=C(n-Pr)(SiCl_3) (4)	88
n-BuC≡CH (10)	Et_3SiH (10)	3.75	*trans*-n-BuCH=CHSiEt_3 (96) H_2C=C(n-Bu)(SiEt_3) (4)	93
n-BuC≡CH (10)	Cl_2MeSiH (15)	1.5	*trans*-n-BuCH=CHSiMeCl_2 (94) H_2C=C(n-Bu)(SiMeCl_2) (6)	97
n-BuC≡CH (20)	Cl_3SiH (30)	1.5	*trans*-n-BuCH=CHSiCl_3 (950) H_2C=C(n-Bu)(SiCl_3) (5)	94
n-PentC≡CH (10)	Et_3SiH (10)	2.5	*trans*-n-PentCH=CHSiEt_3 (95) H_2C=C(n-Pent)(SiEt_3) (5)	97
n-PentC≡CH (10)	Cl_2MeSiH (20)	1.5	*trans*-n-PentCH=CHSiMeCl_2 (96) H_2C=C(n-Pent)(SiMeCl_2) (4)	95
n-PentC≡CH (20)	Cl_3SiH (40)	1.5	*trans*-n-PentCH=CHSiCl_3 (96) H_2C=C(n-Pent)(SiCl_3) (4)	93
CyPentC≡CH (10)	Et_3SiH (20)	1.5	*trans*-CyPentCH=CHSiEt_3 (100)	97
CyPentC≡CH (10)	Cl_2MeSiH (25)	1.5	*trans*-CyPentCH=CHSiMeCl_2 (100)	92
CyPentC≡CH (10)	Cl_3SiH (25)	1.5	*trans*-CyPentCH=CHSiCl_3 (100)	90
$Me_2C(OH)C{\equiv}CH$ [c] (10)	Et_3SiH (10)	20	*trans*-$Me_2C(OH)CH$=CHSiEt_3 (93) H_2C=C(SiEt_3)C(OH)Me_2 (7)	88
MeEtC(OH)C≡CH [c] (10)	Et_3SiH (10)	18	*trans*-MeEtC(OH)CH=CHSiEt_3 (93) H_2C=C(SiEt_3)C(OH)MeEt (7)	90
PhCH(OH)C≡CH [c] (10)	Et_3SiH (10)	40	*trans*-PhCH(OH)CH=CHSiEt_3 (84) H_2C=C(SiEt_3)CH(OH)Ph (16)	81

[a] Reaction conditions : *t*, 65°C, Argon atmosphere, mmol catalyst/mmol alkyne = 7.4×10^{-5}/1, absence of solvent, except for the reaction of the alkyne PhCH(OH)C≡CH where 0.5 ml of toluene were used as solvent because the reactants are not mixed. [b] Hydrosilylation products weighed after distillation. [c] In these reactions the catalyst/alkyne ratio was 1.5×10^{-4}/1.

TABLE 2

HYDROSILYLATION OF INTERNAL ALKYNES [a] IN THE PRESENCE OF THE CATALYST [(Cy_3P)($BzMe_2Si$)(μ-H)Pt]$_2$

Alkyne (amount (mmol))	Silane (amount (mmol))	Time (h)	Product (Yield (%))	Yield (%) [b]
$CH_3C{\equiv}CCH_2CH_3$ (10)	Et_3SiH (10)	0.75	*E*-$(CH_3)(Et_3Si)C{=}CHCH_2CH_3$ (65) *E*-$CH_3CH{=}C(SiEt_3)(CH_2CH_3)$ (35)	97
$CH_3C{\equiv}CCH_2CH_3$ (10)	Cl_2MeSiH (15)	1	*E*-$(CH_3)(Cl_2MeSi)C{=}CHCH_2CH_3$ (65) *E*-$CH_3CH{=}C(SiMeCl_2)(CH_2CH_3)$ (35)	96
$CH_3C{\equiv}CCH_2CH_3$ (10)	Cl_3SiH (20)	3	*E*-$(CH_3)(Cl_3Si)C{=}CHCH_2CH_3$ (70) *E*-$CH_3CH{=}C(SiCl_3)(CH_2CH_3)$ (30)	94
$CH_3C{\equiv}CCH_2CH_2CH_3$ (10)	Et_3SiH (10)	1	*E*-$(CH_3)(Et_3Si)C{=}CHCH_2CH_2CH_3$ (60) *E*-$CH_3CH{=}C(SiEt_3)(CH_2CH_2CH_3)$ (40)	96
$CH_3C{\equiv}CCH_2CH_2CH_3$ (10)	Cl_2MeSiH (15)	1	*E*-$(CH_3)(Cl_2MeSi)C{=}CHCH_2CH_2CH_3$ (72) *E*-$CH_3CH{=}C(SiMeCl_2)(CH_2CH_2CH_3)$ (28)	95
$CH_3C{\equiv}CCH_2CH_2CH_3$ (10)	Cl_3SiH (20)	3.5	*E*-$(CH_3)(Cl_3Si)C{=}CHCH_2CH_2CH_3$ (68) *E*-$CH_3CH{=}C(SiCl_3)(CH_2CH_2CH_3)$ (32)	92
$CH_3CH_2C{\equiv}CCH_2CH_3$ (10)	Et_3SiH (10)	0.5	*cis*-$(CH_3CH_2)(Et_3Si)C{=}CHCH_2CH_3$	98
$CH_3CH_2C{\equiv}CCH_2CH_3$ (10)	Cl_2MeSiH (15)	0.5	*cis*-$(CH_3CH_2)(Cl_2MeSi)C{=}CHCH_2CH_3$	95
$CH_3CH_2C{\equiv}CCH_2CH_3$ (10)	Cl_3SiH (15)	1.5	*cis*-$(CH_3CH_2)(Cl_3Si)C{=}CHCH_2CH_3$	93
$(HOMe_2C{:})_2$ [c] (10)	Et_3SiH (15)	17	*cis*-$HOMe_2CC(SiEt_3){=}CHCMe_2OH$	85
$(HOMe_2C{:})_2$ (10)	Me_2PhSiH (10)	15	*cis*-$HOMe_2CC(SiMe_2Ph){=}CHCMe_2OH$	83

[a] Reaction conditions : *t*, 65°C, Argon atmosphere, mmol catalyst/mmol alkyne 1.5×10^{-4}/1, absence of solvent. [b] Hydrosilylation products weighed after distillation. [c] In these reactions were also used 2.0 ml of toluene as solvent.

amounts in the hydrosilylation of alkynes catalysed by platinum on charcoal, H_2PtCl_6 or nitrogeneous bases [2—5]. The fact that bis(silyl)alkanes are not formed with diplatinum complexes as catalysts can be related to the ability of these catalysts to promote the hydrosilylation of terminal but not internal and cyclic alkenes [6]. Thus, the *trans*-products as well as the regioisomer *E*-silylalkenes do not undergo further hydrosilylation since they are internal alkenes. However the *gem*-products, which are terminal alkenes, would be expected to undergo further hydrosilylation. The failure of the *gem*-products to react further might have been due either to loss of the catalytic activity of the catalytic species after the addition of 1 mol of the hydrosilane per mol of alkyne or to steric factors. We found that the catalytic species do, in fact, retain their cata-

lytic activity at the end of the reaction, since they promote the reaction of further freshly-added alkyne and hydrosilane. Furthermore, the *gem*-products do not undergo hydrosilylation on adding further hydrosilane and a new sample of the catalyst. Thus, the failure of the *gem*-products to undergo hydrosilylation must be attributed to steric factors. This is also supported by the fact that diisobutelene(2,3,3-trimethylbut-1-ene), which has a similar structure to the *gem*-products, undergoes no hydrosilylation under the same conditions, even though it is a terminal alkene.

Hydrosilylation of the hydroxyalkynes was carried out only with trialkylsilanes, because chlorosilanes very readily undergo alcoholysis. The Si—H bond can also undergo alcoholysis, especially on treatment with saturated or olefinic alcohols in the presence of group VIII metals or their salts [7,8], and products resulting from the alcoholysis of the Si—H bond are formed in considerable amounts during the hydrosilylation of acetylenic alcohols using the Speier catalyst (H_2PtCl_6) [9]. In contrast, with the diplatinum complexes as catalysts, no such products were formed. This fact may be due to the milder conditions required for the hydrosilylation of acetylenic alcohols using the diplatinum complexes, since with H_2PtCl_6 it is necessary to heat the reactants at ~180—200°C for more than 12 h [10—12]. It is relevant to note at this point that the regioselectivity of the hydrosilylation of acetylenic alcohols varies considerably on going from diplatinum complexes to Pt/C and H_2PtCl_6 as catalysts. Hydrosilylation of $Me_2C(OH)C{\equiv}CH$ with Et_3SiH in the presence of Pt/C affords only the *gem*-product in low yield (~52%), while in the presence of H_2PtCl_6 a mixture of the *trans*- and *gem*-products is formed, with the latter predominating.

The results in Tables 1 and 2 show that the nature of the silane has only a very small influence on the regioselectivity of the additions, as we have previously noted [1]. The other factors which might control the regioselectivity were investigated, and the results are discussed below.

(i) Effect of the concentration of silane and alkyne on the rate and regioselectivity of the addition

The effect of the concentration of the silane and alkyne on the rate and regioselectivity was examined for four representative systems. The yield (%) of the products formed in a specified time was used as a measure of the rate.

The first system (Table 3) examined was a 1-heptyne/Et_3SiH/$\{(Cy_3P)(Me_3Ge)(\mu\text{-H})Pt\}_2$. This system, which belongs to the group giving strongly exothermic reactions, was selected on the basis of the boiling points (b.p.) of its constituents. The b.p. of 1-heptyne (99.74°C/760 Torr) and Et_3SiH (107.7°C/760 Torr) are sufficiently close that the ratio of the two reactants in the liquid phase will not change significantly during the strongly exothermic reaction.

The second system (Table 4) $Me_2C(OH)C{\equiv}CH/Et_3SiH/\{(Cy_3P)(Me_2BzSi)(\mu\text{-H})Pt\}_2$, chosen as representative for the hydrosilylations of the hydroxyalkynes, which proceed smoothly and are not strongly exothermic.

The other two systems (Table 5), 2-Pentyne/Et_3SiH/$\{(Cy_3P)(Me_3Ge)(\mu\text{-H})Pt\}_2$ and 2-Hexyne/Et_3SiH/$\{(Cy_3P)(Me_3Ge)(\mu\text{-H})Pt\}_2$, are representative of the reactions which proceed smoothly at room temperature, but after the initial brief warming are strongly exothermic. Thus, in order to avoid any

TABLE 3

EFFECT OF THE CONCENTRATIONS OF SILANE AND ALKYNE ON THE RATE AND REGIOSELECTIVITY OF THE SYSTEM 1-HEPTYNE/Et_3SiH/$[(Cy_3P)(Me_3Ge)(\mu\text{-}H)Pt]_2$ [a]

mmol of Alkyne	mmol of Silane	Time (h)	Yield (%)	Isomer distribution (%)	
				trans	*gem*
15	5	1	20	97	3
		7.5	80	97	3
10	5	1	26	98	2
		3.5	78	98	2
5	5	1	69	95	5
		2.5	100	95	5
5	10	0.25	100	92	8
5	15	1	100	92	8

[a] Reaction conditions : *t*, 65°C; Argon atmosphere; catalyst/silane or catalyst/alkyne = 7.4×10^{-5}/1 whichever is not in excess.

TABLE 4

EFFECT OF THE CONCENTRATIONS OF SILANE AND ALKYNE ON THE RATE AND REGIOSELECTIVITY OF THE SYSTEM $Me_2C(OH)C{\equiv}CH$/Et_3SiH/$[(Cy_3P)(Me_2BzSi)(\mu\text{-}H)Pt]_2$ [a]

mmol of Alkyne	mmol of Silane	Time (h)	Yield (%)	Isomer distribution (%)	
				trans	*gem*
20	10	2.75	17	92	8
		24	39	92	8
		99.5	74	90	10
10	10	2.75	27	93	7
		24	53	93	7
10	20	1	41	98	2
		2.75	68	98	2

[a] Reaction conditions : *t*, 50°C; Argon atmosphere; catalyst/silane or catalyst/alkyne = 1.5×10^{-4}/1, whichever is not in excess.

TABLE 5

EFFECT OF THE CONCENTRATIONS OF SILANE AND ALKYNE ON THE RATE AND REGIOSELECTIVITY OF THE SYSTEMS 2-PENTYNE/ET_3SiH/$[(Cy_3P)(Me_3Ge)(\mu\text{-}H)Pt]_2$ AND 2-HEXYNE/Et_3SiH/$[(Cy_3P)(Me_3Ge)(\mu\text{-}H)Pt]_2$ [a]

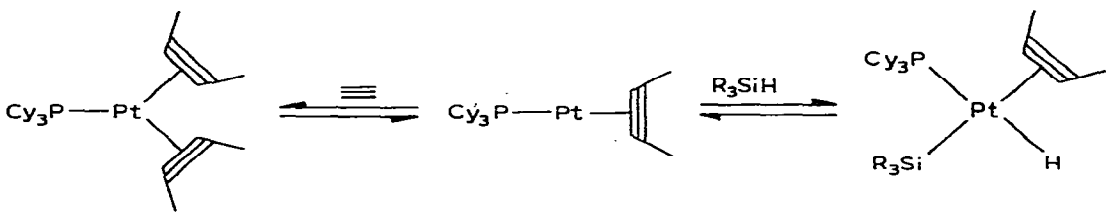
Alkyne	mmol of Alkyne	mmol of Silane	Time (h)	Yield (%)	Isomer distribution (%)	
					C(2)-$SiEt_3$	C(3)-$SiEt_3$
EtC≡CMe						
	10	5 [b]	2.25	44	73	27
			4	69	74	26
	5	5	1	75	75	25
			2.25	90	74	26
	5	10	1	83	76	24
			2	100	75	25
n-PrC≡CMe						
	10	5 [b]	2.25	40	70	30
			4	62	70	30
	5	5	1	66	73	27
			2.25	82	72	28
	5	10	1	75	72	28
			2	100	72	28

[a] Reaction conditions : Room temperature; Argon atmosphere; catalyst/silane or catalyst/alkyne = 3.0×10^{-4}/1, whichever is not in excess. [b] In these reactions after 1 h the yields were lower than 10%.

change in the ratio of the two constituents in the liquid phase due to their different boiling points the reactions were carried out at room temperature.

As is evident from the data shown in Tables 3—5 the concentration of the silane and alkyne markedly influences the rate. Increasing the silane concentration relative to the alkyne concentration causes a considerable increase in rate, while increasing the alkyne concentration cause a considerable decrease.

These observations can be explained in terms of the catalytic cycle proposed for the hydrosilylation of alkynes [1]. This cycle involves the following equilibrium:



(I) (II)

It is evident that increase in the silane concentration will increase the concentration of the catalytically active species (II), and so the rate of the hydrosilylation. On the other hand, increase of the alkyne concentration will increase the concentration of I and lower the concentration of II and so the reaction rate.

The results in Tables 3—5 also demonstrate that the concentration of silane and alkyne does not control the regioselectivity of the addition, only very small variations in the isomer distribution being observed.

(ii) Effect of the catalyst concentration on the rate and regioselectivity of the addition

The results in Table 6 show that the catalyst concentration has a significant effect on the rate, but does not affect the regioselectivity. Increasing the catalyst concentration increases the rate, as expected for a homogeneous catalytic process [13].

The rate and the regioselectivity are independent of the nature of the silyl substituent involved the diplatinum complex, indicating that in a given hydrosilylation the catalytically active intermediate species have the same composition whichever diplatinum complex is initially used.

(iii) Effect of the temperature on the rate and regioselectivity of the addition

Table 7 shows the effects of temperature for the system $Me_2C(OH)C{\equiv}CH$/ Et_3SiH/$\{(Cy_3P)(Me_2BzSi)(\mu\text{-}H)Pt\}_2$, which is suitable for such a study since it is still relatively slow at higher temperatures, and so can be studied in a broad temperature range. (This is also true for other systems containing hydroxyalkynes.) It will be seen that raising the temperature increases the rate, but does not affect the regioselectivity.

It is clear that the main factor controlling the regioselectivity is the nature of the alkyne. If we assume that the ratio of the two regioisomers formed (major

TABLE 6

EFFECT OF THE CONCENTRATION OF CATALYST ON THE RATE AND REGIOSELECTIVITY OF THE HYDROSILYLATION SYSTEM PhCH(OH)C≡CH/Et_3SiH/[$(Cy_3P)(Me_2BzSi)(\mu\text{-}H)Pt]_2$ [a]

[Catalyst] / [alkyne]	Time (h)	Yield (%)	Isomer distribution (%)	
			trans	*gem*
$7.4\ 10^{-5}$	2	traces	—	—
	14	14	82	18
	62	48	80	20
$1.5\ 10^{-4}$	2	8	85	15
	14	28	84	16
	36	80	83	17
$3.0\ 10^{-4}$	1	12	83	17
	2	16	85	15
	14	55	85	15
$6.0\ 10^{-4}$	1	24	85	15
	2	33	84	16
$7.4\ 10^{-4}$	1	31	84	16
	2	39	85	15

[a] Reaction conditions : *t*, 60°C; Argon atmosphere: [alkyne] = [silane] = 5.0 mmol; 0.5 ml of toluene were used as solvent.

product/minor product) is a measure of the regioselectivity, the observed regioselectivity falls in the sequence:

$$RC{\equiv}CH \simeq MeEtC(OH)C{\equiv}CH \simeq Me_2C(OH)C{\equiv}CH > PhCH(OH)C{\equiv}CH >> RC{\equiv}CR'$$

This sequence can be interpreted in terms of the nature of the interaction of

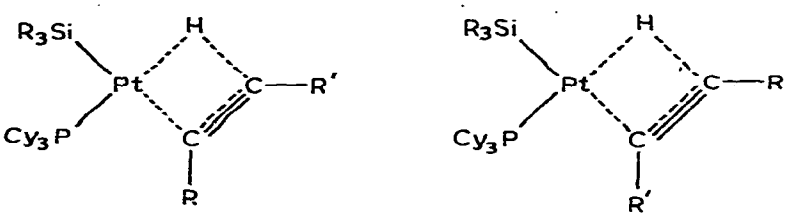
TABLE 7

EFFECT OF THE TEMPERATURE ON THE RATE AND THE REGIOSELECTIVITY OF THE HYDROSILYLATION SYSTEM $Me_2C(OH)C{\equiv}CH/Et_3SiH/[(Cy_3P)(Me_2BzSi)(\mu\text{-}H)Pt]_2$ [a]

Temperature (°C)	Time (h)	Yield (%)	Isomer distribution (%)	
			trans	*gem*
40	1	<10	—	—
	24	33	93	7
	70	81	92	8
50	1	18	93	7
	24	53	94	6
60	1	26	93	7
	7	60	93	7
80	1	33	92	8
	2	56	92	8
100	1	47	91	9
	2	69	91	9

[a] Reactions conditions : Argon atmosphere, [$Me_2C(OH)C{\equiv}CH$] = 5.0 mmol [Et_3SiH] = 5.0 mmol; [catalyst]/[silane] = 1.5×10^{-4}/1; In the absence of soivent.

the catalyst with the frontier orbitals of the alkyne in the transition state for the migration of the hydrogen from platinum to an acetylenic carbon atom. The stereospecificity of the reactions studied, corresponding to *cis*-SiH addition, suggests that a four centred-six electron (4*c*—6*e*) transition state is possibly formed in the nucleophilic attack on the coordinated alkyne by the hydride. Depending on the orientation of the alkyne relative to the Pt—H bond, two possible regioisomer transition states can be formulated, as follows.



(a) (b)

In the transition state a the hydride is migrating to the C—R′ acetylenic carbon atom and in the transition state b to the C—R one.

A qualitative molecular orbital treatment of the transition state reveals that the orientation of the alkyne relative to the Pt—H bond is determined by the nature of the interaction between frontier orbitals of the catalyst and the alkyne. Since the frontier orbitals are combined according to the principle of the maximum overlap [14], and qualitatively, the preferred regioisomer transition state will be that in which the atoms with the larger terminal coefficients of the interacting frontier orbitals interact [15].

The electron density distribution in the catalyst frontier orbitals will depend on the nature of the ligands attached to the central atom (e.g. Cy_3P, R_3Si and H^-). This is because the electronic effects of the ligands affect the energy and the coefficients of the combined atomic orbitals. In our studies the only ligand affecting the electron density distribution in the catalyst frontier orbitals is the silyl group, since the other two ligands are the same in all the reactions studied.

In view of the variation in the magnitude of the *trans*-effects of the silyl ligands used, a marked dependence of the electron density distribution in the catalyst frontier orbitals upon the nature of the silyl ligand would be expected, and this will lead to a considerable dependence of the regioselectivity upon the nature of the silane. However, the presence of the strongly electron releasing tricyclohexylphosphine ligand increases the electron density on platinum, and this prevents large changes in the electron density distribution in the catalyst's frontier orbitals arising from differing *trans*-effects of the silyl ligands. This may account for the smallness of the effect of the silane on the regioselectivity of the addition, but experiments with less basic phosphines would be needed to confirm this.

The electron density distribution in the alkyne's frontier orbitals (π-HOMO and π^*-LUMO) depends upon the substituents attached to the *sp* carbon atoms [15,16]. In general, as the difference between the relative magnitudes of the two *sp* carbon *p* coefficients of the π-HOMO and π^*—LUMO increases, the asymmetry of the electron density of the acetylenic π-bonds also increases. We have used as the measure of the electron density distribution in the frontier

orbitals of the alkyne the chemical shifts of the ^{13}C resonances of the *sp* carbon atoms, since it is well known that the ^{13}C NMR chemical shifts reflect the electron density distribution on the carbon atoms [17]. The differences between the ^{13}C chemical shifts of the *sp* carbon atoms can be used as an approximation of the differences between the relative magnitudes of the two *sp* carbon atom *p* coefficients of the π-HOMO and π^*-LUMO.

For the alkynes RC≡CH (n-PrC≡CH, n-BuC≡CH, n-PentC≡CH, CyPentC≡CH, MeEtC(OH)C≡CH and $Me_2C(OH)C{\equiv}CH$), where the differences between the chemical shifts of the C(2) and C(1) carbon atoms ($\delta_{C(2)} - \delta_{C(1)}$) are 15—20 ppm [18,19] the differences between the relative magnitudes of the C(2) and C(1) *p* coefficients of the π-HOMO and π^*-LUMO will be large. In these alkynes the largest coefficient is on the C(1) in the π-HOMO and on the C(2) in the π^*-LUMO. For the alkyne PhCH(OH)C≡CH the difference between the relative magnitudes of the coefficients will be smaller, since the difference between the ^{13}C chemical shifts of the *sp* carbon atoms is 8.8 ppm.

For the alkynes RC≡CR′ (n-PrC≡CMe, EtC≡CMe), where the differences between the chemical shifts of the *sp* carbon atoms ($\delta_{C(3)} - \delta_{C(2)}$) are only 3—5 ppm, the differences between the relative magnitudes of the coefficients will be very small. In these alkynes the largest coefficient is on the C(2) in the π-HOMO and on the C(3) in the π^*-LUMO. For the symmetrically disubstituted acetylenes, RC≡CR, (EtC≡CEt and $HOMe_2CC{\equiv}CCMe_2OH$) the differences between the chemical shifts of the *sp* carbon atoms are zero and the electron density of the acetylenic π-bonds is absolutely symmetrical. In these alkynes the relative magnitudes of the C(3) and C(4) coefficients are similar for both π-HOMO and π^*-LUMO.

In Fig. 1 is depicted qualitatively the interaction of the frontier orbitals of the catalyst and the alkyne in the four-centred transition state; the π-HOMO of the alkyne interacts with the catalyst unoccupied d^2p^2 hybrid orbital of the catalyst and the π^*-LUMO of the alkyne with the bonding σ-MO ($d^2p_\sigma^2 - s_\sigma$) of the catalyst. (We note that the alkynes actually possess four frontier orbitals, two π-HOMO perpendicular to each other and two π^*-LUMO also perpendicular to each other, but, for simplicity, only the two frontier orbitals (π-HOMO and π^*-LUMO) are shown in Fig. 1.)

In terms of the interaction of the frontier orbitals shown in Fig. 1, it is easy to interpret the observed regioselectivity in the hydrosilylation of alkynes. Thus, in the case of the alkynes RC≡CH the centre for the nucleophilic attack by the hydride will be the C(2) carbon atom, since the largest coefficient in the π^*-LUMO is on this carbon atom. The probability of migration of the hydride to the C(1) carbon atom in these alkynes will be very small since on this carbon atom is the largest coefficient of the π-HOMO and the smallest coefficient of the π^*-LUMO. In the case of the alkynes, PhCH(OH)C≡CH, RC≡CR′ and RC≡CR as the differences between the relative magnitudes of the *p* coefficients in the π-HOMO and in the π^*-LUMO decrease the probability for migration of the hydride to the carbon atom with the smaller coefficient of the π^*-LUMO on it will increase. In the extreme case of the alkynes RC≡CR, the hydride has an equal chance of migration to either of the acetylenic carbon atoms, since the relative magnitudes of the two *sp* carbon coefficients are similar for both π-HOMO and π^*-LUMO.

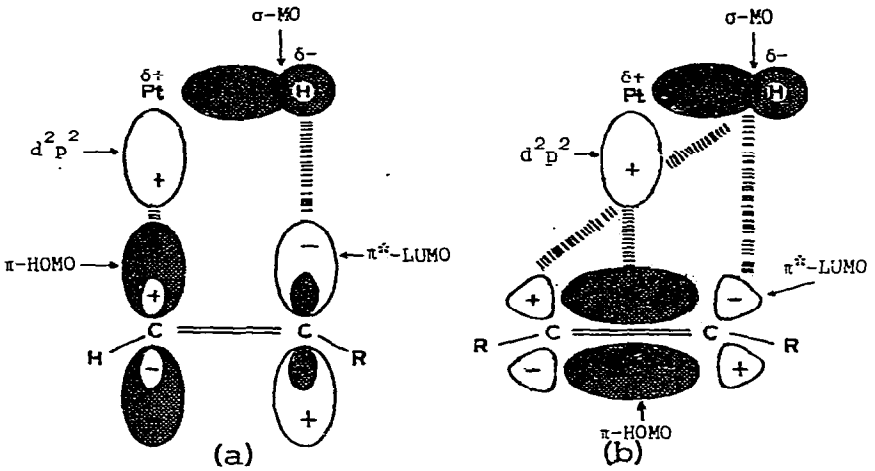


Fig. 1. Interaction mode of the frontier orbitals of the catalyst and alkyne in the four-centred transition state (a) terminal alkynes and (b) symmetrically disubstituted acetylenes.

It should be noted that steric factors also play an important role in determining the orientation of the alkyne relative to the Pt—H bond. However in the present study, the steric factors favor the same orientation of the alkynes relative to the Pt—H bond, as this is determined by the mode of interaction of the frontier orbitals in the transition state.

Experimental

Measurements

The boiling points were obtained using a Büchi apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a Varian A-60A (60 MHz) spectrometer using TMS as internal standard. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer operating in the Fourier transform mode at 20 MHz, as described elsewhere [19]. Analytical gas chromatography (GLC) was carried out on a Hewlett-Packard 7620A instrument fitted with a flame-ionisation detector, using 3ft × 0.25 in glass columns packed with 3% w/w OV-101 on Gas Chrom Q. Infrared spectra in the range 4000—250 cm^{-1} were measured as neat liquids with a Perkin-Elmer 467 spectrophotometer. Elemental analyses of carbon and hydrogen were determined on a Perkin-Elmer 240 Elemental analyser. The chlorine content of chlorinated products was determined volumetrically [20].

Materials

All the unsaturated organic compounds and the hydrosilanes used were commercial products. The liquid reagents were distilled in an inert atmosphere before use.

The *trans*-di-μ-hydridobis(tricyclohexylphosphine)bis(silyl or germyl) diplatinum complexes were prepared by the published method [21].

Product analysis

Products were identified by their spectra (IR, ^{1}H NMR, ^{13}C NMR and Mass Spectra) and elemental analyses.

TABLE 8

^{1}H NMR DATA [a] FOR THE HYDROSILYLATION PRODUCTS FROM TERMINAL ALKYNES

Compound	^{1}H NMR data (τ, ppm) [b]
trans-$CH_3CH_2CH_2^XC(H^B)$ = $C(H^A)SiCl_3$	9.03(t, 3H, CH_3, ^3J(HH) = 7.0); 8.46 (sextet; 2H, CH_2, ^3J(HH) = 7.0); 7.73 (q, 2H, H^X, ^3J(HH) = 7.0); 4.18 (unsym. d of t, 1H, H^A, J(AB) = 19.0, J(AX) = 1.0); 3.30 (unsym. d of t, 1H, H^B, J(AB) = 19.0, J(BX) = 6.0).
trans-$CH_3CH_2CH_2^XC(H^B)$ = $C(H^A)Si(CH_3)Cl_2$	9.17 (s, 3H, $SiCH_3$); 9.07 (t, 3H, CH_3, ^3J(HH) = 6.2); 8.54 (m, 2H, CH_2); 7.82(m, 2H, H^X); 4.23 (unsym. d of t, 1H, H^A, J(AB) = 19.0, J(AX) = 1.1); 3.48 (unsym. d of t, 1H, H^B, J(AB) = 19.0, J(BX) = 5.9).
trans-$CH_3CH_2CH_2^XC(H^B)$ = $C(H^A)Si(CH_2CH_3)_3$	9.70—8.87 (m, 18H, $SiCH_2CH_3$, CH_3); 8.87—8.24 (m, 2H, CH_2); 7.94 (m, 2H, H^X); 4.42 (unsym. d of t, 1H, H^A, J(AB) = 19.0, J(AX) = 1.0); 3.92 (unsym. d of t, 1H, H^B, J(AB) = 19.0, J(BX) = 5.7).
trans-$CH_3(CH_2)_2CH_2^XC(H^B)$ = $C(H^A)SiCl_3$	9.05 (t, 3H, CH_3, ^3J(HH) = 5.5); 8.57 (m, 4H, $(CH_2)_2$); 7.73 (m, 2H, H^X); 4.20 (unsym. d of t, 1H, H^A, J(AB) = 19.0, J(AX) = 1.0); 3.30 (unsym. d of t, 1H, H^B, J(AB) = 19.0, J(BX) = 6.0).
trans-$CH_3(CH_2)_2CH_2^XC(H^B)$ = $C(H^A)$ $Si(CH_3)Cl_2$	9.35 (s, 3H, $SiCH_3$); 9.06 (t, 3H, CH_3, ^3J(HH) = 5.0); 8.58 (m, 4H, $(CH_2)_2$); 7.78 (m, 2H, H^X); 4.25 (unsym. d of t, 1H, H^A, J(AB) = 18.5, J(AX) = 1.1); 3.50 (unsym. d of t, 1H, H^B, J(AB) = 18.5, J(BX) = 5.9).
trans-$CH_3(CH_2)_2CH_2^XC(H^B)$ = $C(H^A)Si(CH_2CH_3)_3$	9.70—8.85 (m, 18H, $SiCH_2CH_3$, CH_3); 8.83—8.43 (m, 4H, $(CH_2)_2$); 7.92 (m, 2H, H^X); 4.45 (unsym. d of t, 1H, H^A, J(AB) = 19.0, J(AX) = 1.0); 3.96 (unsym. d of t, 1H, H^B, J(AB) = 19.0, J(BX) = 5.5).
trans-$CH_3(CH_2)_3CH_2^XC(H^B)$ = $C(H^A)SiCl_3$	9.07 (t, 3H, CH_3, ^3J(HH) = 6.0); 8.62 (m, 6H, $(CH_2)_3$); 7.72 (q, 2H, H^X, ^3J(HH) = 7.0); 4.19 (unsym. d of t, 1H, H^A, J(AB) = 18.5, J(AX) = 1.5); 3.30 (unsym. d of t, 1H, H^B, J(AB) = 18.5, J(BX) = 6.0).
trans-$CH_3(CH_2)_3CH_2^XC(H^B)$ = $C(H^A)$ $Si(CH_3)Cl_2$	9.19 (s, 3H, $SiCH_3$); 9.09 (t, 3H, CH_3, ^3J(HH) = 5.0); 8.63 (m, 6H, $(CH_2)_3$); 7.82 (m, 2H, H^X); 4.26 (unsym. d of t, 1H, H^A, J(AB) = 18.5, J(AX) = 1.1); 3.51 (unsym. d of t, 1H, H^B, J(AB) = 18.5, J(BX) = 6.0).
trans-$CH_3(CH_2)_3CH_2^XC(H^B)$ = $C(H^A)Si(CH_2CH_3)_3$	9.50—8.84 (m, 18H, $SiCH_2CH_3$, CH_3); 8.84—8.42 (m, 6H, $(CH_2)_3$); 7.92 (m, 2H, H^X); 4.43 (unsym. d of t, 1H, H^A, J(AB) = 19.0, J(AX) = 1.0); 3.93 (unsym. d of t, 1H, H^B, J(AB) = 19.0, J(BX) = 5.5).
trans-$(CH_2)_4CH^XC(H^B)$ = $C(H^A)SiCl_3$	8.35 (m, 8H, $(CH_2)_4$); 7.41 (m, 1H, H^X); 4.22 (unsym. d of d, 1H, H^A, J(AB) = 18.5, J(AX) = 1.0); 3.31 (unsym. d of d, 1H, H^B, J(AB) = 18.5, J(BX) = 6.0).
trans-$(CH_2)_4CH^XC(H^B)$ = $C(H^A)Si(CH_3)Cl_2$	9.19 (s, 3H, $SiCH_3$); 8.36 (m, 8H, $(CH_2)_4$); 7.48 (m, 1H, H^X); 4.30 (unsym. d of d, 1H, H^A, J(AB) = 19.0, J(AX) = 1.0); 3.55 (unsym. d of d, 1H, H^B, J(AB) = 19.0, J(BX) = 6.0).
trans-$(CH_2)_4CH^XC(H^B)$ = $C(H^A)Si(CH_2CH_3)_3$	9.72—8.80 (m, 15H, $SiCH_2CH_3$); 8.40 (m, 8H, $(CH_2)_4$); 7.57 (m, 1H, H^X); 4.46 (unsym. d of d, 1H, H^A, J(AB) = 19.0, J(AX) = 1.0); 3.94 (unsym. d of d, 1H, H^B, J(AB) = 19.0, J(BX) = 6.0).
trans-$(CH_3)_2C(OH)C(H^B)$ = $C(H^A)Si(CH_2CH_3)_3$	9.55—8.83 (m, 15H, $SiCH_2CH_3$); 8.76 (s, 6H, CH_3); 4.33 (unsym. d, 1H, H^A, J(AB) = 19.2); 3.88 (unsym. d, 1H, H^B, J(AB) = 19.2).
trans-$(CH_3CH_2)(CH_3)C(OH)C(H)^B$ = $C(H^A)Si(CH_2CH_3)_3$	9.65—8.88 (m, 18H, CH_2CH_3, $SiCH_2CH_3$); 8.80 (s, 3H, CH_3); 8.72—8.37 (m, 2H, CH_2CH_3); 4.31 (unsym. d, 1H, H^A, J(AB) = 19.0); 3.97 (unsym. d, 1H, H^B, J(AB) = 19.0).
trans-$(C_6H_5)CH^X(OH)C(H^B)$ = $C(H^A)Si(CH_2CH_3)_3^c$	9.60—8.80 (m, 15H, $SiCH_2CH_3$); 7.76 (s, br, 1H, —OH); 4.97 (d, 1H, H^X, J(BX) = 5.0, J(AX) = 1.0); 4.15 (unsym. d of d, 1H, H^A, J(AB) = 18.5, J(AX) 1.0); 3.85 (unsym. d of d, 1H, H^B, J(AB) = 18.5, J(BX) = 5.0); 2.74 (s, 5H, C_6H_5).

TABLE 8 (continued)

[a] The ^{1}H NMR spectra were obtained in $CDCl_3$ or CCl_4 solutions using TMS as an internal standard. [b] t = triplet, q = quartet, unsym. d of t = unsymmetrical doublet of triplets, s = singlet, m = multiplet, unsym. d. of d = unsymmetrical doublet of doublets, unsym. d = unsymmetrical doublet. Coupling constants (J) in Hz. [c] In the ^{1}H NMR spectrum of this compound which is formed together with its regio-isomer $(C_6H_5)C(OH)(H^X)C(SiEt_3) = C(H^A)(H^M)$ there are also peaks corresponding to this regio-isomer at 4.82 (t, 1H, H^X), 4.54 (d of d, 1H, H^M, J(AM) = 2.0 Hz) and 4.15 (d of d, 1H, H^A, J(AM) = 2.0 Hz).

The stereochemistry of the products was established from the proton-proton coupling constants observed in their ^{1}H NMR spectra. The olefinic protons of the hydrosilylation products from terminal alkynes (Table 8) give second order spectra which show a characteristic *trans*-$CH^A{=}CH^B$-coupling constant $J_{AB} \simeq$ 19 Hz [3,22,23]. In reactions where relatively small amounts of the adducts $R(X_3Si)C{=}CH_2$ were formed, these isomers were also identified from their ^{1}H NMR spectra. Thus, in the ^{1}H NMR spectrum of the mixture of the regio-isomers formed from $Me_2C(OH)C{\equiv}CH$, in addition to the peaks due to the protons of the major product (*trans*-product), there are also two doublets at 4.66 and 4.21 τ due to the geminal protons (H^AH^M) of the *gem*-product, with J_{AM} 2.0 Hz. For the product $MeEtC(OH)C(SiX_3){=}CH_2$ the two doublets appear at 4.60 and 4.28 τ (J_{AM} 2.0 Hz). The *gem*-products from the terminal alkyl acetylenes and the chlorosilanes show only one multiplet at 4.0 and 4.25 τ for the $SiCl_3$ and $SiMeCl_2$ groups, respectively. However, for the $SiEt_3$ group the *gem*-products give two multiplets at 4.65 and 4.35 τ in accordance with the ^{1}H NMR spectra of analogous vinylsilanes [24]. The relative ratio of the two regioisomers formed from the terminal alkynes was determined by comparison of the intergrated intensities of the peaks due to the olefinic protons of the two regioisomers. In the case of the regioisomers from $Me_2C(OH)C{\equiv}CH$, very good results were also obtained by comparing the integrated intensities of the peaks due to the methyl protons of the two regioisomers.

The *E*-regioisomers formed from the unsymmetrically substituted internal alkynes were analysed and identified from the analysis of the ^{1}H and ^{13}C NMR spectra of their mixtures without isolation of each isomer. The full ^{13}C NMR data will be published elsewhere [25].

The ^{1}H NMR spectra of the mixtures of the regioisomeric *E*-silylalkenes (Table 9) in CCl_4 or $CDCl_3$ solutions are very complex because there is insufficient separation of the peaks from the isomers. However, in C_6D_6 solutions some of the peaks are well separated, particularly those due to the methyl protons (H^aprotons) of the two regioisomers. This is shown in Fig. 2 where the ^{1}H NMR spectra of a representative mixture, obtained in CCl_4 and C_6D_6 solutions are presented. The changes observed in the ^{1}H NMR spectra of the mixtures of the regioisomeric *E*-silylalkenes using C_6D_6 as solvent are due to well known Aromatic Solvent Induced Shift (ASIS) [25]. Since the ASIS is due to the formation of weak collision complexes between the solute and the aromatic solvent it is easy to explain the observed changes, since the orientation mode of the benzene molecule will depend on the structure of the solute molecule. In the molecules of the two regioisomers the solvation centers will be at different positions depending on the position of the silyl substituent and thus the corre-

TABLE 9

^{1}H NMR DATA FOR THE HYDROSILYLATION PRODUCTS FROM INTERNAL ALKYNES

Compound	Solvent	^{1}H NMR data (τ, ppm) [a]
		E-$CH_3^aC(X) = CH^bCH_2^cCH_3^d$(1), *E*-$CH_3^aCH^b = C(X)CH_2^cCH_3^d$(2)
X = $SiCl_3$	CCl_4	8.91 {unsym. t, 3H, H^d(1)(2), ^3J(HH) = 7.0}; 8.12 {m, unres., 3H, H^a(1)}; 8.14 {d, 3H, H^a(2), ^3J(HH) = 7.0}; 8.03—7.36 {m, 2H, H^c(1)(2)}; 3.76—3.21 {m, 1H, H^b(2)}.
	C_6D_6	9.25 {unsym. t, 3H, H^d(1), ^3J(HH) = 7.0}; 9.14 {umsym. t, 3H, H^d(2), ^3J(HH) = 7.0}; 8.61 {d, 3H, H^a(2), ^3J(HH) = 7.0}; 8.36 {m, unres., 3H, H^a(1)}; 8.44—7.59 {m, 2H, H^c(1)(2)}; 3.86—3.42 {m, 1H, H^b(1)(2)}.
$Si(CH_3)Cl_2$	CCl_4	9.18 {s, 3H, $SiCH_3$}; 8.95 {unsym. t, 3H, H^d(1)(2), ^3J(HH) = 7.0}; 8.19 {m, unres., 3H, H^a(1)(2)}; 8.09—7.48 {m, 2H, H^c(1)(2)}; 4.08—3.51 {m, 2H, H^c (1)(2)}; 4.08—3.51 {m, 1H, H^b(1)(2)}.
	C_6D_6	9.42 {s, 3H, $SiCH_3$}; 9.21 {unsym. t, 3H, H^b(1), ^3J(HH) = 7.0}; 9.05 {unsym. t, 3H, H^d(2), ^3J(HH) = 7.0}; 8.56 {d, 3H, H^a(2), ^3J(HH) = 7.0}; 8.34 {m, unres. 3H, H^a(1)}; 8.29—7.60 {m, 2H, H^c(1)(2)}; 4.12—3.70 {m, 1H, H^b(1)(2)}.
$Si(CH_2CH_3)_3$	CCl_4	9.71—8.79 {m, 18H, $Si(CH_2CH_3)_3$(1)(2), H^d(1)(2)}; 8.36 {m, unres., 3H, H^a(1)}; 8.31 {d, 3H, H^a(2), ^3J(HH) = 7.0}; 8.13—7.63 {m, 2H, H^c(1)(2)}; 4.53—4.13 {m, 1H, H^b(1)(2)}.
	C_6D_6	9.70—8.77 {m, 18H, $Si(CH_2CH_3)_3$(1)(2), H^d(1)(2)}; 8.38 {d, 3H, H^a(2), ^3J(HH) = 7.0}; 8.34 {m, unres., 3H, H^a(1)}; 8.20—7.60 {m, 2H, H^c(1)(2)}; 4.40—3.99 {m, 1H, H^b(1)(2)}.
		E-$CH_3^aC(X) = CH^bCH_2^cCH_2^dCH_3^e$(1), *E*-$CH_3^aCH^b = C(X)CH_2^cCH_2^dCH_3^e$(2)
X = $SiCl_3$	CCl_4	9.03 {unsym. t, 3H, H^e(1)(2), ^3J(HH) = 7.0}; 8.82—8.23 {m, 2H, H^d(1)(2)}; 8.12 {m, unres., 3H, H^a(1)(2)}; 8.00—7.50 {m, 2H, H^c(1)(2)}; 3.75—3.18 {m, 1H, H^b(1)(2)}.
	C_6D_6	9.25 {unsym. t, 3H, H^e(1)(2), ^3J(HH) = 7.0}; 9.13—8.63 {m, 2H, H^d(1)(2)}; 8.53 {d, 2H, H^a(2), ^3J(HH) = 7.0}; 8.31 {m, unres., 3H, H^a(1)}; 8.25—7.60 {m, 2H, H^c(1)(2)}; 3.81—3.36 {m, 1H, H^b(1)(2)}.
$Si(CH_3)Cl_2$	CCl_4	9.19 {s, 3H, $SiCH_3$}; 9.06 {unsym. t, 3H, H^e(1)(2), ^3J(HH) = 7.0}; 8.86—8.31 {m, 2H, H^d(1)(2)}; 8.19 {d, 3H, H^a(2), ^3J(HH) = 7.0}; 8.19 {m, unres., 3H, H^a(1)}; 8.56—8.06 {m, 2H, H^c(1)(2)}; 4.46—4.01 {m, 1H, H^b(1)(2)}.
	C_6D_6	9.42 {s, 3H, $SiCH_3$}; 9.23 {unsym. t, 3H, H^e(1), ^3J(HH) = 6.5}; 9.47 {unsym. t, 3H, H^e(2), ^3J(HH) = 6.5}; 8.99—8.42 {m, 2H, H^d(1)(2)}; 8.53 {d, 3H, H^a(2), ^3J(HH) = 7.0}; 8.31 {m, unres., 3H, H^a(1)}; 8.21—7.64 {m, 2H, H^c(1)(2)}; 4.09—3.64 {m, 1H, H^b(1)(2)}.
$Si(CH_2CH_3)_3$	$CDCl_3$	9.70—8.90 {m, 18H, $Si(CH_2CH_3)_3$, H^e(1)(2)}; 8.90—8.40 {m, 2H, H^d(1)(2)}; 8.36 {m, unres., 3H, H^a(1)}; 8.33 {d, 3H, H^a(2), ^3J(HH) = 7.0}; 8.13—7.68 {m, 2H, H^c(1)(2)}; 4.47—3.97 {m, 1H, H^b(1)(2)}.
	C_6D_6	9.65—8.46 {m, 20H, $Si(CH_2CH_3)_3$, H^e, H^d(1)(2)}; 8.36 {d, 3H, H^a(2), ^3J(HH) = 7.0}; 8.31 {m, unres., 3H, H^a(1)}; 8.13—7.66 {m, 2H, H^c(1)(2)}; 4.35—3.90 {m, 1H, H^b(1)(2)}.
		cis-$CH_3^aCH_2^bC(X) = CH^cCH_2^dCH_3^e$
X = $SiCl_3$	CCl_4	8.90 {t, 6H, H^a, H^e, ^3J(HH) = 7.0}; 8.02—7.40 {m, 4H, H^b, H^d}; 3.58 {t, 1H, H^c, ^3J(HH) = 7.0}.
	C_6D_6	9.18 {t, 3H, H^a, ^3J(HH) = 7.0}; 9.02 {t, 3H, H^e, ^3J(HH) = 7.0}; 8.37—7.50 {m, 4H, H^b, H^d}; 3.63 {t, 1H, H^c, ^3J(HH) = 7.0};
$Si(CH_3)Cl_2$	CCl_4	9.17 {s, 3H, $SiCH_3$}; 8.94 {t,6H, H^a, H^e, ^3J(HH) = 7.0}; 8.05—7.47 {m, 4H, H^b, H^d}; 3.87 {t, 1H, H^c, ^3J(HH) = 6.7}.
$Si(CH_2CH_3)3$	$CDCl_3$	9.70—8.83 {m, 21H, $Si(CH_2CH_3)_3$, H^a, H^e}; 8.18—7.58 {m, 4H, H^b, H^d}; 4.32 {t, 1H, H^c, ^3J(HH) = 6.7}.
		cis-$(CH_3^a)_2C(OH)C(X) = CH^bC(OH)(CH_3^a)_2$

TABLE 9 (continued)

Compound	Solvent	^{1}H NMR data (τ, ppm) [a]
X = $Si(CH_2CH_3)_3$	$CDCl_3$	9.32 {m, 6H, $SiCH_2$}; 9.06 {m, 9H, Si—C—CH_3}; 8.60 {s,6H, H^a}; 8.54 {s, 6H, H^c}; 5.75 {s, 2H, —OH}; 4.33 (s, 1H, H^b}.
$Si(CH_3)_2(C_6H_5)$	$CDCl_3$	9.65 {s, 6H, $SiCH_3$}; 8.72 {s, 6H, H^a}; 8.66 {s, 6H, H^c}; 5.32 {s, br, 2H, —OH}; 4.22 {s, 1H, H^b}; 2.55, 3H, m, p-C_6H_5}; 2.38 {m, 2H, o-C_6H_5}.

[a] Coupling constants (J) in Hz; unsym. t = unsymmetrical triplet, m. unres = multiplet unresolved, br = broad.

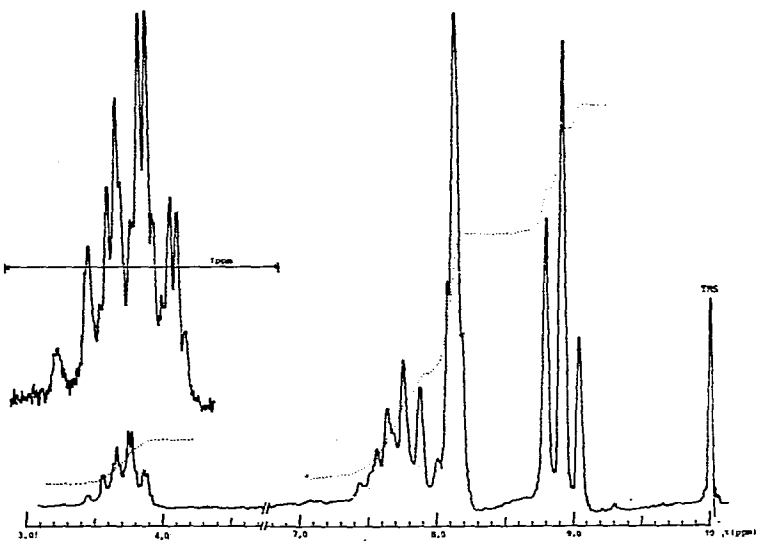


Fig. 2. ^{1}H NMR spectra of the mixture of the two regioisomers E-$CH_3C(SiCl_3)$=$CHCH_2CH_3$ and E-CH_3CH=$C(SiCl_3)(CH_2CH_3)$ a) in CCl_4 solution and b) in C_6D_6 solution.

sponding protons in the two isomers will be shielded or deshielded to different extents. By making use of the ASIS we can ascertain the presence of the two regioisomers in the mixture and calculate their ratio. The multiplet due to the olefinic protons of the regioisomers (Fig. 2) is a composite band resulting from the partial superposition of two multiplets. One of them is a triplet of quartets and the other one a quartet of triplets. The first multiplet is due to the olefinic proton of the regioisomer *E*-$CH_3CH{=}C(R)(SiX_3)$ and the second to the olefinic proton of the regioisomer *E*-$CH_3C(SiX_3){=}CHR$. By analysis of the partially obscured multiplets we can calculate their chemical shifts and proton-proton coupling constants. The results are listed in Table 10. In C_6D_6 solution the multiplet due to the olefinic protons of the regioisomers changes its shape and width relative to those observed in an inert solvent (CCl_4 or $CDCl_3$) which indicates the presence of the two isomers in the mixture, and this is supported by the changes in the rest of the spectrum. Thus, the peaks due to the methyl protons in C_6D_6 solution are well separated and their multiplicities are as expected on the basis of the structures of the two regioisomers. For the triethylsilyl derivatives the separation of the peaks due to the methyl protons is insufficient to be used either in CCl_4 of C_6D_6 solutions. Further support for the presence of the two regioisomers comes from the study of the ^{13}C NMR spectra of the mixtures. The integrated intensities of the well separated peaks due to the methyl protons of the two regioisomers gives the ratio of the latter, and the results agree well with those obtained from analysis of the ^{13}C NMR spectra [25].

The stereochemistry of the two regioisomeric *E*-silylalkenes formed from the unsymmetrically substituted internal alkynes was established by comparison of the observed proton-proton coupling constants (Table 10) with those of analogous compounds which have *E*-structures [1,23,26]. The *cis*-structure of the products from the symmetrically substituted acetylenes is assumed on the basis of the stereospecific *cis*-SiH addition which is characteristic for the diplatinum catalysts. In the case of the adducts formed from hex-3-yne the *cis*-structure is confirmed by the fact that the half-band-width of each peak of the triplet due to the olefinic proton is about 2.0 Hz. This shows that the coupling constant $J(H^bH^c)$ is less than 2.0 Hz, in agreement with those for analogous compounds having *cis*-structures [1]. The *cis*-structure of the adducts from 2,5-dimethyl-2,5-dihydroxyhex-3-yne was confirmed by a chemical method; on heating these adducts at 100°C in the presence of $KHSO_4$ and an antioxidant (hydroquinone) they were converted quantitatively into 2,2,5,5-tetramethyl-3-silyldihydrofuran derivatives, as expected from their *cis*-structure.

Hydrosilylation reactions

All reactions were carried out under pure argon in tubes (capacity ca. 100 cm^3) fitted with Westef stopcocks and a standard joint, so that the vessel could be attached to a vacuum system. For non-volatile reagents the reactions can also be carried out into Schlenk tubes (capacity ca. 80 cm^3). The results summarised in Tables 1 to 7 were obtained using procedures illustrated by the following examples.

(a) 2-methyl-but-3-ynol-2 and triethylsilane. A Schlenk tube was charged with Et_3SiH (1.6 ml, 10.0 mmol) $Me_2C(OH)C{\equiv}CH$ (1.0 ml, 10.0 mmol) and 2.0

TABLE 10

CHEMICAL SHIFTS (τ, ppm) [a] AND COUPLING CONSTANTS (J in Hz) OF THE MULTIPLETS DUE TO THE OLEFINIC PROTONS OF THE REGIO-ISOMER *E*-SILYLALKENES

Product	^{1}H NMR data
E-$CH_3^aC(SiCl_3)=CH^bCH_2^cCH_3^d$	3.58(3.67) {t of q, H^b, $J(H^bH^c)$ = 7.0, $J(H^bH^a) \simeq 1.7$}
E-$CH_3^aCH^b=C(SiCl_3)CH_2^cCH_3^d$	3.43(3.63) {q of t, H^b, $J(H^bH^a)$ = 7.0, $J(H^bH^c) \simeq 1.5$}
E-$CH_3C(SiMeCl_2)=CHCH_2CH_3$	3.85(3.94) {t of q, H^b, $J(H^bH^c)$ = 7.0, $J(H^bH^a) \simeq 1.5$}
E-$CH_3CH=C(SiMeCl_2)CH_2CH_3$	3.71(3.90) {q of t, H^b, $J(H^bH^a)$ = 7.0, $J(H^bH^c) \simeq 1.5$}
E-$CH_3C(SiEt_3)=CHCH_2CH_3$	4.32(4.20) {t of q, H^b, $J(H^bH^c)$ = 7.0, $J(H^bH^a) \simeq 1.7$}
E-$CH_3CH=C(SiEt_3)CH_2CH_3$	—(4.13) {q of t, H^b, $J(H^bH^a)$ = 7.0, $J(H^bH^c) \simeq 1.5$}
E-$CH_3^aC(SiCl_3)=CH^bCH_2^cCH_2^dCH_3^e$	3.57(3.63) {t of q, H^b, $J(H^bH^c)$ = 7.0, $J(H^bH^a) \simeq 1.5$}
E-$CH_3^aCH^b=C(SiCl_3)CH_2^cCH_2^dCH_3^e$	3.40(3.58) {q of t, H^b, $J(H^bH^a)$ = 7.0, $J(H^bH^c) \simeq 1.5$}
E-$CH_3C(SiMeCl_2)=CHCH_2CH_2CH_3$	3.84(3.91) {t of q, H^b, $J(H^bH^c)$ = 7.0, $J(H^bH^a) \simeq 1.5$}
E-$CH_3CH=C(SiMeCl_2)CH_2CH_2CH_3$	3.68(3.86) {q of t, H^b, $J(H^bH^a)$ = 7.0, $J(H^bH^c) \simeq 1.5$}
E-$CH_3C(SiEt_3)=CHCH_2CH_2CH_3$	4.29(4.16) {t of q, H^b, $J(H^bH^c)$ = 6.7, $J(H^bH^a) \simeq 1.7$}
E-$CH_3CH=C(SiEt_3)CH_2CH_2CH_3$	4.17(4.10) {q of t, H^b, $J(H^bH^a)$ = 7.0, $J(H^bH^c) \simeq 1.5$}

[a] ^{1}H NMR spectra were obtained in CCl_4 and C_6D_6 (figures in parentheses) solution using TMS as an internal standard.

TABLE 11

ANALYTICAL AND IR DATA FOR HYDROSILYLATION PRODUCTS FROM ALKYNES AND Et_3SiH

Compound	b.p. (°C/760 Torr)	C Found (Calcd)(%)	H Found (Calcd)(%)	ν(C=C)
trans-n-$C_3H_7CH=CHSiEt_3$ [a]	207	71.62 (71.65)	13.16 (13.12)	1618s (13.12)
trans-n-$C_4H_9CH=CHSiEt_3$ [a]	226	72.62 (72.64)	13.25 (13.21)	1620vs
trans-n-$C_5H_{11}CH=CHSiEt_3$ [a]	247	73.45 (73.49)	13.30 (13.28)	1618s
trans-n-$(CH_2)_4CHCH=CHSiEt_3$ [a]	236	74.17 (74.20)	12.61 (12.65)	1615vs
trans-$Me_2C(OH)CH=CHSiEt_3$	216	65.90 (65.93)	12.06 (12.07)	1615m [b]
trans-MeEtC(OH)CH=CHSiEt$_3$	240	67.23 (67.21)	12.20 (12.22)	1615m
trans-PhCH(OH)CH=CHSiEt$_3$ [c]	270—274	72.54 (72.52)	9.71 (9.74)	1615m
cis-$CH_3CH_2C(SiEt_3)=CHCH_2CH_3$ [a]	215	72.58 (72.64)	13.25 (13.21)	1610vs
E-$CH_3C(SiEt_3)=CHCH_2CH_3$	208—210	71.68 (71.65)	13.18 (13.12)	1612vs
E-$CH_3CH=C(SiEt_3)CH_2CH_3$				
E-$CH_3C(SiEt_3)=CHCH_2CH_2CH_3$	218—220	72.67 (72.64)	13.18 (13.21)	1616s
E-$CH_3CH=C(SiEt_3)CH_2CH_2CH_3$				

[a] Molecular weights were obtained from mass spectra, M^+ 184, 198, 212, 210 and 198 respectively. [b] In the IR spectra of the hydroxy derivatives there exist also the characteristic strong broad bands in the region of ca. 3360 cm^{-1} due to the hydroxyl group. [c] Isomeric mixture: *trans*-PhCH(OH)=CHSiEt$_3$ (84%) and PhCH(OH)C(SiEt$_3$)=CH_2 (16%).

mg of the catalyst $[(Cy_3P)(Me_2BzSi)(\mu\text{-H})\,Pt]_2$. After 20 h at 65°C the ^{1}H NMR spectrum revealed complete consumption of the acetylene and the silane. The distilled product 1.7 g (8.8 mmol, 88%) was shown by ^{1}H NMR spectroscopy to consist of 93% *trans*-$Me_2C(OH)CH{=}CHSiEt_3$ and 7% $Me_2C(OH)C(SiEt_3){=}CH_2$.

The other hydrosilylation reactions of the alkynes with Et_3SiH were carried out analogously. The analytical and IR data and the boiling points of the triethylsilyl derivatives are listed in Table 11.

(b) Pent-2-yne and trichlorosilane. The reaction vessel was charged with 2.0 mg of the catalyst $[(Cy_3P)(Me_2BzSi)(\mu\text{-H})Pt]_2$ and attached to the vacuum line. Pent-2-yne (10.0 mmol) and trichlorosilane (20.0 mmol) were distilled in, and the mixture was allowed to warm to room temperature. After 3 h at 65°C the ^{1}H NMR spectrum indicated complete consumption of the alkyne. Fractional distillation afforded 1.9 g (9.4 mmol, 94%) of the mixture of the two regioisomers. ^{1}H and ^{13}C NMR studies showed that this consisted of 70% $CH_3C(SiCl_3){=}CHCH_2CH_3$ and 30% $CH_3CH{=}C(SiCl_3)(CH_2CH_3)$.

The other reactions of the alkynes with Cl_3SiH and $MeCl_2SiH$ were carried

TABLE 12

ANALYTICAL AND IR DATA FOR HYDROSILYLATION PRODUCTS FROM ALKYNES AND Cl_3SiH OR Cl_2MeSiH

Compound	b.p. (°C/760 Torr)	Cl Found (Calcd)(%)	ν(C=C)	ν(Si—Cl)
trans-n-$C_3H_7CH{=}CHSiCl_3$	180(81—84/45) [a]	51.90 (52.25)	1610s,br	578vs,br
trans-n-$C_3H_7CH{=}CHSiMeCl_2$	177	38.50 (38.71)	1616s	535vs,br
trans-n-$C_4H_9CH{=}CHSiCl_3$	206(79—80/16)	48.27 (48.88)	1605s,br	580vs,br
trans-n-$C_4H_9CH{=}CHSiMeCl_2$	203.5(82.5/17)	35.68 (35.96)	1615s	535vs,br
trans-n-$C_5H_{11}CH{=}CHSiCl_3$	220(100/69)	45.68 (45.92)	1616vs,br	570vs,br
trans-n-$C_5H_{11}CH{=}CHSiMeCl_2$	218	33.08 (33.57)	1616vs	535vs,br
trans-$(CH_2)_4CHCH{=}CHSiCl_3$	228	46.15 (46.32)	1610vs,br	570vs,br
trans-$(CH_2)_4CHCH{=}CHSiMeCl_2$	226	33.81 (33.90)	1610vs	535vs,br
cis-$CH_3CH_2C(SiCl_3){=}CHCH_2CH_3$	192	48.53 (48.58)	1610vs	573vs,br
cis-$CH_3CH_2C(SiMeCl_2){=}CHCH_2CH_3$	188	35.67 (35.96)	1610vs	649vs,br
E-$CH_3C(SiCl_3){=}CHCH_2CH_3$ *E*-$CH_3CH{=}C(SiCl_3)CH_2CH_3$	174—175	51.88 (52.25)	1608s	585vs,br
E-$CH_3C(SiMeCl_2){=}CHCH_2CH_3$ *E*-$CH_3CH{=}C(SiMeCl_2)CH_2CH_3$	169—170	38.40 (38.71)	1608s	545vs,br
E-$CH_3C(SiCl_3){=}CHCH_2CH_2CH_3$ *E*-$CH_3CH{=}C(SiCl_3)CH_2CH_2CH_3$	183—185	48.38 (48.88)	1608s	580vs,br
E-$CH_3C(SiMeCl_2){=}CHCH_2CH_2CH_3$ *E*-$CH_3CH{=}C(SiMeCl_2)CH_2CH_2CH_3$	178—180	35.74 (35.96)	1615s	545vs,br

[a] Figures in parentheses are the boiling points given in the literature [27—30].

out in this way. The analytical and IR data and the boiling points of the chlorinated products are listed in Table 12.

(c) 2,5-dimethyl-2,5-dihydroxyhex-3-yne and dimethylphenylsilane. A Schlenk tube was charged with 2,5-dimethyl-2,5-dihydroxyhex-3-yne (1.18 g, 10.0 mmol) dimethylphenylsilane (1.6 ml, 10.0 mmol) 2.0 mg of the catalyst $[(Cy_3P)(Me_2BzSi)(\mu\text{-}H)Pt]_2$ and 2.0 ml of toluene as solvent. After 15 h at 65°C the ^1H NMR spectrum revealed complete consumption of the silane. After distillation of the volatiles, recrystallisation of the residual white solid from toluene or petroleum ether afforded 2.31 g (8.3 mmol, 83%) of the white crystalline *cis*-$HOMe_2CC(SiMe_2Ph)=CHCMe_2OH$. m.p. 138—140°C; Anal. Found: C, 69.12; H, 9.76. $C_{16}H_{26}O_2Ci$ calcd.: C, 69.00; H, 9.41%. IR (Nujol mull): ν_{max} 3150vs(br), 1594m, 1245s, 1185vs, 1162vs, 1110s, 980m, 970m, 948s, 914m, 830vs, 810vs, 770s, 730vs, 700vs, 650s, 500m, 470s,

Hydrosilylation of the 2,5-dimethyl-2,5-dihydroxyhex-3-yne with triethylsilane similarly gave 2.2 g (8.5 mmol, 85%) of the white crystalline *cis*-$HOMe_2CC(SiEt_3)=CHCMe_2OH$. m.p. 84—85°C (lit. [27] 84.5—86.5°C); Anal. Found C, 65.16; H, 11.92. $C_{14}H_{30}O_2Si$ calcd.: C, 65.05; H, 11.70%. IR (Nujol mulls): ν_{max} 3260—3130vs(br) 1585m, 1245s, 1228vs, 1198vs, 1175vs, 1145vs, 1015vs, 1000vs, 960vs, 908s, 828s, 778s, 730s, 700vs, 612s, 510s, 436s.

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