Hydrosilylation of Alkynes catalysed by *trans*-Di-μ-hydrido-bis(tertiary phosphine)bis(silyl)diplatinum Complexes

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But-1-yne, phenylacetylene, but-2-yne, and diphenylacetylene undergo hydrosilylation in 70—90% yield using diplatinum complexes $[\{Pt(SiR_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ [SiR_3 = $Si(CH_2Ph)Me_2$, $SiCl_3$, or $SiEtMe_2$] as catalysts. Many of the reactions proceed exothermically after initial warming of the reactants. The stereochemistry of the products from but-1-yne, phenylacetylene, and but-2-yne has been established by ^{1}H n.m.r. spectroscopy. Hydrosilylation of but-1-yne and phenylacetylene affords as the major product *trans*-$EtCH{=}CHSiR_3$ [SiR_3 = $SiMe_2Ph$, $SiEt_3$, $SiCl_3$, $SiCl_2Me$, $SiClMe_2$, and $Si(OEt)_3$] and *trans*-$PhCH{=}CHSiR_3$ respectively corresponding to *cis*-SiH addition. Products corresponding to non-terminal addition are formed in minor amounts, and not at all foı phenylacetylene and the chlorosilanes. But-2-yne gives vinylsilanes *cis*-$MeCH{=}C(Me)(SiR_3)$, as expected for *cis* addition, and the same stereochemistry is inferred for the products from diphenylacetylene.

WE have previously reported[1] that the diplatinum complexes $[\{Pt(SiR_3)(\mu\text{-}H)(R'_3P)\}_2]$ or their precursors $[Pt(olefin)_2(R'_3P)]$ are efficient catalysts for the hydrosilylation of mono-olefins and dienes. These platinum complexes also catalyse the addition of silanes to alkynes to give vinylsilanes and the results are described herein.

Our knowledge of the hydrosilylation of alkynes is much less extensive than that of alkenes, but the formation by this method of industrially important trichloro(vinyl)silane was patented as early as 1952.[2] Compounds of Group 8 metals, especially hexachloroplatinic(IV) acid or platinum metal on supports such as charcoal or alumina,[3-6] are the best catalysts. Enneacarbonyldi-iron[7] and chlorotris(triphenylphosphine)rhodium[8] have also been used as catalysts for the hydrosilylation of acetylenes.

RESULTS AND DISCUSSION

Results for the hydrosilylation of the mono- and disubstituted acetylenes EtC≡CH, PhC≡CH, MeC≡CMe, and PhC≡CPh are summarised in Table 1. All the reactions proceed in high yield using low catalyst : reactant ratios (10^{-4}—10^{-5}). The stereochemistry of the products from but-1-yne, phenylacetylene, and but-2-yne is assigned conclusively from their ^{1}H n.m.r. spectra (Table 2), discussed below. With the two monosubstituted acetylenes, the major product is the *trans*-vinylsilane, corresponding to *cis* addition, with relatively minor formation of the geminal addition product. But-2-yne affords exclusively *cis* adducts, as expected for stereospecific *cis* additions. Similar patterns have been observed previously with H_2PtCl_6 as catalyst, whereas with radical-induced hydrosilylations largely *trans* additions occur.[3,6] Products obtained from diphenylacetylene (Table 1) are assigned a *cis* stereochemistry on the basis of earlier work with this acetylene using H_2PtCl_6 as catalyst.[9,10] Hydrosilylation of but-1-yne does not seem to have been previously reported, and there is only one reference[11] to but-2-yne, involving a reaction with dichloromethylsilane.

When H_2PtCl_6 or platinum on charcoal are used as catalysts it is usually necessary to heat the reactants under reflux or at *ca.* 100—150 °C. With the diplatinum complexes employed in the present study milder conditions are required, several of the hydrosilylations (Table 1) proceeding exothermically after briefly warming the reactants. Thus with but-1-yne, although it is necessary to heat the reactants to initiate reaction, the addition of the silanes to the acetylene is so strongly exothermic that the process must be complete in less time than that given in the Table. With this acetylene, in all cases both terminal and non-terminal adducts are formed with the proportion of the latter increasing in the sequence: $HSiMe_2Ph < HSiEt_3 < HSiCl_3 < HSiCl_2Me < HSiClMe_2 < HSi(OEt)_3$.

Hydrosilylations of phenylacetylene occurred at room

[1] M. Green, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Dalton*, preceding paper.
[2] C. A. Mackenzie, L. Spialter, and M. Schoffman, B.P. 684,597/1952 (*Chem. Abs.*, 1954, **48**, 2761).
[3] R. A. Benkeser and R. A. Hickner, *J. Amer. Chem. Soc.*, 1958, **80**, 5298.
[4] V. A. Ponomarenko, V. G. Cherkaev, A. D. Petrov, and N. A. Zadorokhnŷi, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1958, 247.
[5] V. A. Ponomarenko, V. G. Cherkaev, and N. A. Zadorokhnŷi, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1960, 1610.
[6] R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Amer. Chem. Soc.*, 1961, **83**, 4385.
[7] N. A. Kuz'mina, E. Ts. Chukovskaya, and R. Kh. Freidlina, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1967, 1272.
[8] I. Ojima, M. Kumagai, and Y. Nagai, *J. Organometallic Chem.*, 1974, **66**, C14.
[9] J. W. Ryan and J. L. Speier, *J. Amer. Chem. Soc.*, 1964, **86**, 895.
[10] A. G. Brook, K. H. Pannell, and D. G. Anderson, *J. Amer. Chem. Soc.*, 1968, **90**, 4374.
[11] J. W. Ryan and J. L. Speier, *J. Org. Chem.*, 1966, **31**, 2698.

TABLE 1

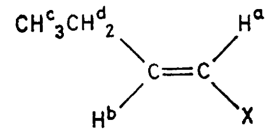
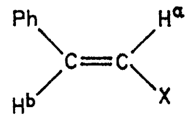
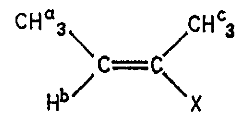
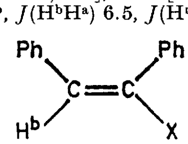
Hydrosilylation of acetylenes

Acetylene (amount/mmol)	Silane (amount/mmol)	Catalyst [a]	θ_c/°C (t/h)	Product (yield/%)	Yield (%) [b]
EtC≡CH (15)	$HSiMe_2Ph$ (10)	A 1 mg [7.4×10^{-5}]	40 (0.1) [c]	*trans*-EtCH=CH$SiMe_2Ph$ (95) CH_2=C(Et)($SiMe_2Ph$) (5)	74
(15)	$HSiEt_3$ (10)	A 1 mg [7.4×10^{-5}]	50 (0.5) [c]	*trans*-EtCH=CH$SiEt_3$ (92) CH_2=C(Et)($SiEt_3$) (8)	88
(35)	$HSiCl_3$ (25)	B 2 mg [6.0×10^{-5}]	65 (3) [c]	*trans*-EtCH=CH$SiCl_3$ (90) CH_2=C(Et)($SiCl_3$) (10)	88
(30)	$HSiCl_2Me$ (20)	A 2 mg [7.4×10^{-5}]	75 (0.5) [c]	*trans*-EtCH=CH$SiCl_2Me$ (86) CH_2=C(Et)($SiCl_2Me$) (14)	80
(15)	$HSiClMe_2$ (10)	A 1 mg [7.4×10^{-5}]	60 (0.2) [c]	*trans*-EtCH=CH$SiClMe_2$ (85) CH_2=C(Et)($SiClMe_2$) (15)	85
(15)	$HSi(OEt)_3$ (10)	A 1 mg [7.4×10^{-5}]	65 (1)	*trans*-EtCH=CH$Si(OEt)_3$ (72) CH_2=C(Et)[$Si(OEt)_3$] (16)	83 [d]
PhC≡CH (5)	$HSiMe_2Ph$ (10)	C 1.5 cm^3, 4.1×10^{-4} mol dm^{-3} in hexane [1.2×10^{-4}]	25 (19)	*trans*-PhCH=CH$SiMe_2Ph$ (68) CH_2=C(Ph)($SiMe_2Ph$) (32)	84
(5)	$HSiEt_3$ (10)	C 1 mg [1.6×10^{-4}]	25 (45)	*trans*-PhCH=CH$SiEt_3$ (89) CH_2=C(Ph)($SiEt_3$) (11)	90
(10)	$HSiCl_3$ (20)	B 2 cm^3, 3.4×10^{-4} mol dm^{-3} in toluene [6.8×10^{-5}]	25 (23)	*trans*-PhCH=CH$SiCl_3$ (100)	80
(10)	$HSiCl_2Me$ (20)	A 2 mg [1.5×10^{-4}]	25 (20)	*trans*-PhCH=CH$SiCl_2Me$ (100)	81
(10)	$HSiClMe_2$ (20)	A 2 mg [1.5×10^{-4}]	25 (20)	*trans*-PhCH=CH$SiClMe_2$ (100)	92
(10)	$HSi(OEt)_3$ (16)	A 2 mg [1.5×10^{-4}]	65 (24)	*trans*-PhCH=CH$Si(OEt)_3$ (76) CH_2=C(Ph)[$Si(OEt)_3$] (24)	80
(10)	$HSiMe_3$ (20)	A 1 mg [7.4×10^{-5}]	25 (70)	*trans*-PhCH=CH$SiMe_3$ (82) CH_2=C(Ph)($SiMe_3$) (18)	80
MeC≡CMe (15)	$HSiMe_2Ph$ (10)	A 2 mg [1.5×10^{-4}]	40 (0.25) [c]	*cis*-MeCH=C(Me)($SiMe_2Ph$)	97
(15)	$HSiEt_3$ (10)	A 2 mg [1.5×10^{-4}]	65 (0.2) [c]	*cis*-MeCH=C(Me)($SiEt_3$)	92
(15)	$HSiCl_3$ (10)	B 2 mg [1.5×10^{-4}]	100 (0.25) [c]	*cis*-MeCH=C(Me)($SiCl_3$)	87
(35)	$HSiCl_2Me$ (30)	A 1 mg [2.5×10^{-5}]	65 (0.5) [c]	*cis*-MeCH=C(Me)($SiCl_2Me$)	87
(30)	$HSiClMe_2$ (23)	A 2.5 mg [8.1×10^{-5}]	55 (0.2) [c]	*cis*-MeCH=C(Me)($SiClMe_2$)	94
(20)	$HSi(OEt)_3$ (10)	A 2 mg [1.5×10^{-4}]	65 (2)	*cis*-MeCH=C(Me)[$Si(OEt)_3$]	87
(10)	H_2SiPh_2 (5)	A 2.5 mg [3.7×10^{-4}]	70 (1)	*cis*-MeCH=C(Me)($SiPh_2H$)	92
PhC≡CPh [e] (5)	$HSiMe_2Ph$ (6.7)	A 1 mg [1.5×10^{-4}]	40 (0.5) [c]	*cis*-PhCH=C(Ph)($SiMe_2Ph$)	86
(5)	$HSiEt_3$ (6.25)	A 2 mg [3.0×10^{-4}]	50 (0.75) [c]	*cis*-PhCH=C(Ph)($SiEt_3$)	95
(5)	$HSiCl_3$ (12.5)	A 1 mg [1.5×10^{-4})	65 (8)	*cis*-PhCH=C(Ph)($SiCl_3$)	76
(5)	$HSiCl_2Me$ (10)	A 1 mg [1.5×10^{-4}]	60 (3)	*cis*-PhCH=C(Ph)($SiCl_2Me$)	82
(5)	$HSiClMe_2$ (12)	A 1 mg [1.5×10^{-4}]	50 (3) [c]	*cis*-PhCH=C(Ph)($SiClMe_2$)	84
(5)	$HSi(OEt)_3$ (6.3)	A 2 mg [3.0×10^{-4}]	65 (2)	*cis*-PhCH=C(Ph)[$Si(OEt)_3$]	82

[a] A = [{Pt[Si(CH_2Ph)Me_2](μ-H)[$(C_6H_{11})_3P$]}$_2$], B = [{Pt($SiCl_3$)(μ-H)[$(C_6H_{11})_3P$]}$_2$], C = [{Pt($SiEtMe_2$)(μ-H)[$(C_6H_{11})_3P$]}$_2$]. The concentration in square brackets is the catalyst : silane or catalyst : acetylene ratio, whichever is not in excess. [b] Hydrosilylation products weighed after distillation. [c] After heating reactants to temperature indicated, hydrosilylation proceeded exothermically. [d] Additional 12% was unidentified product. [e] Hexane solvent (2 cm^3) was used in experiments with this acetylene.

TABLE 2

Spectroscopic data for hydrosilylation products

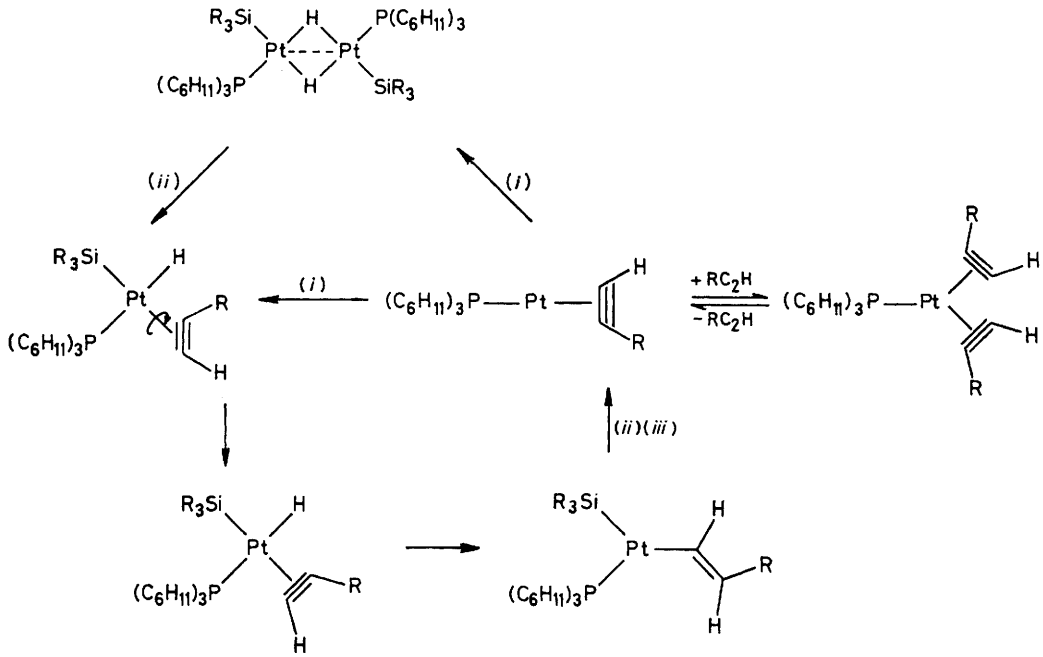
Compound	$\tilde{\nu}_{max.}$(C=C) [a] /cm^{-1}	^{1}H N.m.r. (τ) [b]
		
X = SiMe$_2$Ph	1 615s	9.68 (s, 6 H, CH$_3$Si), 8.99 [t, 3 H^c, $J(H^cH^d)$ 7.5], 7.84 [m, 2 H^d, $J(H^dH^c)$ 7.5, $J(H^dH^a)$ 1.4, J (H^{d}H^b) 5.4], 4.23 [d of t, 1 H^a, $J(H^aH^b)$ 18.5, $J(H^aH^d)$ 1.4], 3.81 [d of t, 1 H^b, $J(H^bH^a)$ 18.5, $J(H^bH^d)$ 5.4], 2.67—2.50 (m, C$_6$H$_5$)
SiEt$_3$	1 616s	9.41 (m, 6 H, CH$_2$Si), 9.06 (t, 9 H, CH_3CH$_2$Si), 8.98 [t, 3 H^c, $J(H^cH^d)$ 6], 7.86 [m, 2 H^d, $J(H^dH^c)$ 6, $J(H^dH^a)$ 1.4, $J(H^dH^b)$ 5.5], 4.46 [d of t, 1 H^a, $J(H^aH^b)$ 18.5, $J(H^aH^d)$ 1.4], 3.88 [d of t, 1 H^b, $J(H^bH^a)$ 18.5, $J(H^bH^d)$ 5.5]
SiCl$_3$	1 605s, br	8.91 [t, 3 H^c, $J(H^cH^d)$ 7], 7.69 [m, 2 H^d, $J(H^dH^c)$ 7, $J(H^dH^a)$ 1.6, $J(H^dH^b)$ 5.6], 4.18 [d of t, 1 H^a, $J(H^aH^b)$ 18, $J(H^aH^d)$ 1.6], 3.23 [d of t, 1 H^b, $J(H^bH^a)$ 18, $J(H^bH^d)$ 5.6]
SiCl$_2$Me	1 619s	9.17 (s, 3 H, CH$_3$Si), 8.93 [t, 3 H^c, $J(H^cH^d)$ 7], 7.74 [m, 2 H^d, J (H^{d}H^c) 7, $J(H^dH^a)$ 1.6, $J(H^dH^b)$ 5.5], 4.22 [d of t, 1 H^a, $J(H^aH^b)$ 18.5, $J(H^aH^d)$ 1.6], 3.42 [d of t, 1 H^b, $J(H^bH^a)$ 18.5, $J(H^bH^d)$ 5.5]
SiClMe$_2$	1 636	9.55 (s, 6 H, CH$_3$Si), 8.97 [t, 3 H^c, $J(H^cH^d)$ 7], 7.81 [m, 2 H^d, $J(H^dH^c)$ 7, $J(H^dH^a)$ 1.6, $J(H^dH^b)$ 5.5], 4.30 [d of t, 1 H^a, $J(H^aH^b)$ 18.5, $J(H^aH^d)$ 1.6], 3.66 [d of t, 1 H^b, $J(H^bH^a)$ 18.5, $J(H^bH^d)$ 5.5]
Si(OEt)$_3$	1 618s	8.98 (t, 3 H^c,), 8.76 (t, 9 H, SiOCH$_2$$CH_3$), 7.81 [m, 2, H^d, $J(H^dH^c)$ 7, $J(H^dH^a)$ 1.6, $J(H^dH^b)$ 5.6], 6.15 (q, 6 H, SiOCH$_2$), 4.57 [d of t, 1 H^a, $J(H^aH^b)$ 19, $J(H^aH^d)$ 1.6], 3.49 [d of t, 1 H^b, $J(H^bH^a)$ 19, $J(H^bH^d)$ 5.6]
		
X = SiMe$_2$Ph	1 602s	9.41 (s, 6 H, CH$_3$Si), 3.25 [unsym. d, 1 H^a, $J(H^aH^b)$ 19], 2.91 [unsym. d, 1 H^b, $J(H^bH^a)$ 19], 2.75—2.21 (m, 10 H, C$_6$H$_5$)
SiEt$_3$	1 606s	9.30 (m, 6 H, CH_2Si), 9.00 (t, 9 H, CH_3CH$_2$Si), 3.55 [unsym. d, 1 H^a, $J(H^aH^b)$ 19], 3.10 [unsym. d, 1 H^b, $J(H^bH^a)$ 19], 2.84—2.48 (m, 5 H, C$_6$H$_5$)
SiCl$_3$	1 603s	3.56 [unsym. d, 1 H^a, $J(H^aH^b)$ 19], 2.61 [unsym. d, 1 H^b, $J(H^bH^a)$ 19], 2.58 (m, 5 H, C$_6$H$_5$)
SiCl$_2$Me	1 608vs	9.10 (s, 3 H, CH$_3$Si), 3.61 [unsym. d, 1 H^a, $J(H^aH^b)$ 19], 2.79 [unsym. d, $J(H^bH^a)$ 19], 2.63 (m, 5 H, C$_6$H$_5$)
SiClMe$_2$	1 605vs	9.33 (s, 6 H, CH$_3$Si), 3.45 [unsym. d, 1 H^a, $J(H^aH^b)$ 19], 2.85 [unsym. d, 1 H^b, $J(H^bH^a)$ 19], 2.65—2.39 (m, 5 H, C$_6$H$_5$)
Si(OEt)$_3$	1 601s	8.73 (t, 9 H, CH$_3$), 6.10 (q, 6 H, CH$_2$), 3.81 [unsym. d, 1 H^a, $J(H^aH^b)$ 19], 2.77 [unsym. d, 1 H^b, $J(H^bH^a)$ 19], 2.69—2.57 (m, C$_6$H$_5$)
SiMe$_3$	1 610s	9.70 (s, 9 H, CH$_3$Si), 3.53 [unsym. d, 1 H^a, $J(H^aH^b)$ 19], 3.13 [unsym. d, 1 H^b, $J(H^bH^a)$ 19], 2.90—2.48 (m, 5 H, C$_6$H$_5$)
		
X = SiMe$_2$Ph	1 620s	[c] 9.63 (s, 6 H, CH$_3$Si), 8.35 [d of q, 3 H^a, $J(H^aH^b)$ 6.3, $J(H^aH^c)$ 0.9], 8.32 [d of q, 3 H^c, $J(H^cH^b)$ 1.6, $J(H^cH^a)$ 0.9], 4.0 [q of q, H^b, $J(H^bH^a)$ 6.3, $J(H^bH^c)$ 1.6], 2.60 (m, 5 H, C$_6$H$_5$)
SiEt$_3$	1 621s	[c] 9.36 (m, 6 H, CH$_2$Si), 9.02 (t, 9 H, CH_3CH$_2$Si), 8.37 [d of q, H^a, $J(H^aH^b)$ 7, $J(H^aH^c)$ 0.9], 8.34 (m, 3 H^c,) 4.14 (m, 1 H^b)
SiCl$_3$	1 623vs	[c] 8.70 [d of q, 3 H^a, $J(H^aH^b)$ 6.8, $J(H^aH^c)$ 0.9], 8.44 [d of q, 3 H^c, $J(H^cH^b)$ 1.7, $J(H^cH^a)$ 0.9], 3.70 [q of q, 1 H^b, $J(H^bH^a)$ 6.8, $J(H^bH^c)$ 1.7]
SiCl$_2$Me	1 625vs	[c] 9.44 (s, 3 H, CH$_3$Si), 8.57 [d of q, 3 H^a, $J(H^aH^b)$ 6.6, $J(H^aH^c)$ 0.9], 8.33 [d of q, 3 H^c, $J(H^cH^b)$ 1.7, $J(H^cH^a)$ 0.9], 3.93 [q of q, 1 H^b, $J(H^bH^a)$ 6.6, $J(H^bH^c)$ 1.7]
SiClMe$_2$	1 622s	[c] 9.75 (s, 6 H, CH$_3$Si), 8.49 [d of q, 3 H^a, $J(H^aH^b)$ 6.5, $J(H^aH^c)$ 0.9], 8.34 [d of q, 3 H^c, $J(H^cH^b)$ 1.7, $J(H^cH^a)$ 0.9], 4.07 [q of q, 1 H^b, $J(H^bH^a)$ 6.5, $J(H^bH^c)$ 1.7]
Si(OEt)$_3$	1 622s	[c] 8.80 (t, 9 H, CH_3CH$_2$), 8.39 [d of q, 3 H^a, $J(H^aH^b)$ 6.8, $J(H^aH^c)$ 1.0], 8.20 [d of q, 3 H^c, $J(H^cH^b)$ 1.7, $J(H^cH^a)$ 1.0], 3.63 [q of q, 1 H^b, $J(H^bH^a)$ 6.8, $J(H^bH^c)$ 1.7]
SiPh$_2$H	1 621s	[c] 8.42 [d of q, 3 H^a, $J(H^aH^b)$ 6.5, $J(H^aH^c)$ 0.9], 8.24 [d of q, 3 H^c, $J(H^cH^b)$ 1.7, $J(H^cH^a)$ 0.9], 4.68 (s, 1 H, HSi), 3.86 [q of q, 1 H^b, $J(H^bH^a)$ 6.5, $J(H^bH^c)$ 1.7], 2.60 (m, br, 10 H, C$_6$H$_5$]
		
X = SiMe$_2$Ph	1 601vs	9.41 (s, 6 H, CH$_3$Si), 2.99—2.17 (m, br, 16 H)
SiEt$_3$	1 601vs	9.19 (m, 6 H, CH$_2$Si), 8.91 (t, 9 H, CH$_3$), 3.10 (s, 1 H^b), 2.70 (m, br, 10 H, C$_6$H$_5$)
SiCl$_3$	1 603vs [d]	3.04—2.40 (m, br)
SiCl$_2$Me	1 604vs [d]	9.03 (s, 3 H, CH$_3$Si), 2.90—2.45 (m, 11 H)
SiClMe$_2$	1 601s [d]	9.34 (s, 6 H, CH$_3$Si), 2.92—2.50 (m, 11 H)
Si(OEt)$_3$	1 601m	8.80 (t, 9 H, CH_3CH$_2$), 6.15 (q, 6 H, OCH$_2$), 2.87 (m, br, 11 H)

[a] For neat liquids. [b] In CDCl$_3$ solutions unless otherwise indicated, coupling constants (J) in Hz. [c] In C$_6$D$_6$. [d] Nujol mull.

temperature, but reaction with triethoxysilane was very slow under these conditions. Heating phenylacetylene with the silanes to 65 °C initiates a fast exothermic *reaction*. Terminal addition took place exclusively with the chlorosilanes, but non-terminal products were observed with $HSiMe_2Ph$, $HSiEt_3$, $HSiMe_3$, and $HSi(OEt)_3$. But-2-yne was not hydrosilylated at room temperature but, except for $HSi(OEt)_3$ and H_2SiPh_2, it was observed that warming the reactants led to fast exothermic reactions. At 70 °C, diphenylsilane afforded only the 1 : 1 adduct even in the presence of excess of but-2-yne. For the hydrosilylation of diphenylacetylene, hexane was used as solvent, and after warming the reactants for a few minutes addition proceeded rapidly. At room temperatures reaction appeared not to occur, or proceeded only very slowly.

$R'_3Si = Me_2PhSi$, Et_3Si, $(EtO)_3Si$, or Me_3Si] were formed these isomers were also identified by analysis of their ^1H n.m.r. spectra. Thus these spectra all show geminal proton–proton couplings of 3—6 Hz [11,13] and, for example, that of $Ph(Me_2PhSi)C=CH_2$ may be assigned: τ 9.44 (s, 6 H, Me_3Si), 4.17 (d, 1 H, J 3.0), 3.86 (d, 1 H, J 3.0 Hz), and 2.75—2.21 (complex m, 10 H, C_6H_5).

In discussing possible mechanisms for the hydrosilylation of acetylenes reported here there are two aspects which require comment. These are the frequently observed induction period, and also the dependence of the regioselectivity on the nature of the substituents on the reacting silane. Extending the ideas previously proposed concerning the hydrosilylation of olefins with the same catalysts,[1] it is reasonable to suggest that the induction period relates to the cleavage of the bridged



SCHEME (*i*) R_3SiH; (*ii*) RC_2H; (*iii*) $-RCH=CHSiR_3$

The stereochemistry of the products from MeC≡CH, PhC≡CH, and MeC≡CMe is established from the proton–proton coupling constants observed (Table 2). The vinylsilanes obtained from the two monoacetylenes show a characteristic *trans*-$CH^a=CH^b$ coupling constant $J(H^aH^b) \simeq 19$ Hz.[12-14] The products from but-2-yne show spectra characteristic of the group *cis*-$CH^a_3CH^b=C(CH^c_3)X$, with $J(H^aH^b) \simeq 6.5$, $J(H^bH^c) \simeq 1.7$, and $J(H^aH^c) \simeq 1$ Hz.[11,13] In those reactions (Table 1) where relatively small amounts of the adducts $R(R'_3Si)C=CH_2$ [R = Et and $R'_3Si = Me_2PhSi$, Et_3Si, Cl_3Si, Cl_2MeSi, $ClMe_2Si$, or $(EtO)_3Si$; R = Ph and

binuclear species by the reacting acetylenes, this process leading to the formation of a mononuclear platinum(II)–acetylene π-complex. The observed high *trans* effect of silyl ligands [15] suggests that in this intermediate the acetylene would occupy a position *trans* to the silyl group. The regioselectivity of the addition would be expected to be controlled by the next step involving rotation of the acetylene into the co-ordination plane, followed by migration of the hydrogen from platinum on to an acetylenic carbon with formation of a platinum(II) vinyl complex (see Scheme). Reductive migration of the silyl group from the metal on to carbon would

[12] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 242.
[13] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, p. 278.
[14] R. A. Benkeser, R. F. Cunico, S. Dunny, P. R. Jones, and P. G. Nerlekar, *J. Org. Chem.*, 1967, **32**, 2634.
[15] J. Chatt, C. Eaborn, and S. D. Ibekwe, *Chem. Comm.*, 1966, 700; J. Chatt, C. Eaborn, S. D. Ibekwe, and P. N. Kapoor, *J. Chem. Soc.* (*A*), 1970, 1343.

then regenerate the platinum(0) catalyst.* Support for this suggestion derives from the previously observed migration of hydrogen,[19] methyl,[20] allyl,[21] and halogen [22] from transition metals on to σ-bonded vinyl groups.

The magnitude of the *trans* effect of the silyl ligand is known [15] to be dependent on the substituents attached to the silicon. It is interesting, therefore, that there is little difference in the regioselectivity of the reaction of, for example, EtC≡CH with $HSiEt_3$ or $HSiCl_3$, where $SiEt_3 \gg SiCl_3$ in *trans* effect, indicating that this is not a controlling factor. Since in these reactions a sterically demanding tricyclohexylphosphine ligand is assumed to be present, it is possible that steric factors control the orientation of the addition reactions.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded using a Varian HA100 spectrometer, i.r. spectra were measured with a Perkin-Elmer 457 spectrophotometer, and g.l.c. separations were carried out [23] using 3 ft × 0.25 in glass columns packed with 3% w/w OV-101 on Gas Chrom Q with a Pye 104 instrument fitted with a flame-ionisation detector. Analytical data are summarised in Table 3. In those reactions which afforded products corresponding to both terminal and non-terminal addition the relative proportions of the isomers formed (Table 1) were established both by ^{1}H n.m.r. and g.l.c. studies.

Hydrosilylation of Acetylenes.—Experimental data are summarised in Table 1; only two representative experiments will be described.

(a) *Phenylacetylene and dimethylphenylsilane*. A glass tube (*ca*. 100 cm^3) fitted with a Westef high-vacuum greaseless stopcock and standard tapered joint was charged with phenylacetylene (1.1 cm^3, 10 mmol), dimethylphenylsilane (3 cm^3, 20 mmol), and $[\{Pt[Si(CH_2Ph)Me_2](\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ (1 mg). After 0.75 h at 65 °C a ^{1}H n.m.r. spectrum revealed complete consumption of the acetylene. N.m.r. and g.l.c. studies showed that the distilled product (2.3 g, 96%) consisted of 84% *trans*-PhCH=CHSiMe$_2$Ph and 16% Ph(Me$_2$PhSi)C=CH$_2$. The corresponding room-temperature experiment (Table 1) afforded a higher proportion of the non-terminal isomer.

(b) *But-2-yne and trichlorosilane*. The reaction vessel was charged with but-2-yne (15 mmol), trichlorosilane (10 mmol), and $[\{Pt(SiCl_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ (2 mg) and the mixture was heated briefly (15 min) initiating an exothermic reaction. After 30 min a ^{1}H n.m.r. of a sample showed quantitative consumption of the silane. G.l.c. studies revealed that the *product* (1.66 g, 87%) after distillation was pure and it was characterised by analysis (Table 3), n.m.r. (Table 2), and i.r.: $\nu_{max.}$ (liquid film) at 3 026m (sh), 2 986m (sh), 2 926s, 2 866m, 1 623vs, 1 443s,br, 1 383s, 1 170s, 1 006s, 936s, 836s, 708vs, 593vs,br, and 527vs cm^{-1}.

TABLE 3

Analytical data (%) [a]

Compound	C	H
trans-EtCH=CHSiMe$_2$Ph [b]	75.6 (75.7)	9.5 (9.5)
trans-EtCH=CHSiEt$_3$ [b]	69.9 (70.5)	13.5 (13.0)
trans-EtCH=CHSiCl$_2$Me [b]	35.2 (35.5)	6.0 (6.0)
trans-EtCH=CHSiClMe$_2$ [b]	48.9 (48.5)	8.9 (8.8)
trans-EtCH=CHSi(OEt)$_3$ [b]	54.8 (55.0)	10.1 (10.2)
trans-PhCH=CHSiMe$_2$Ph [b]	80.5 (80.6)	7.9 (7.6)
trans-PhCH=CHSiEt$_3$ [b]	77.2 (77.0)	10.5 (10.2)
trans-PhCH=CHSiCl$_3$	40.3 (40.4)	3.1 (3.0)
trans-PhCH=CHSiCl$_2$Me	50.0 (49.8)	4.9 (4.6)
trans-PhCH=CHSiClMe$_2$	61.2 (61.0)	7.0 (6.7)
trans-PhCH=CHSi(OEt)$_3$ [b]	62.9 (63.1)	8.4 (8.3)
trans-PhCH=CHSiMe$_3$ [b]	75.2 (74.9)	9.4 (9.2)
cis-MeCH=C(Me)(SiMe$_2$Ph)	76.2 (75.7)	9.4 (9.5)
cis-MeCH=C(Me)(SiEt$_3$)	70.2 (70.5)	13.0 (13.0)
cis-MeCH=C(Me)(SiCl$_3$)	25.4 (25.4)	4.0 (3.7)
cis-MeCH=C(Me)(SiClMe$_2$)	48.0 (48.5)	8.9 (8.8)
cis-MeCH=C(Me)[Si(OEt)$_3$]	54.7 (55.0)	9.9 (10.1)
cis-MeCH=C(Me)(SiPh$_2$H)	79.9 (80.6)	7.7 (7.6)
cis-PhCH=C(Ph)(SiMe$_2$Ph)	84.2 (84.0)	7.1 (7.1)
cis-PhCH=C(Ph)(SiEt$_3$)	82.1 (81.6)	8.9 (8.9)
cis-PhCH=C(Ph)(SiCl$_3$) [c]	53.7 (53.6)	3.6 (3.5)
cis-PhCH=C(Ph)(SiCl$_2$Me) [d]	61.5 (61.4)	4.7 (4.8)
cis-PhCH=C(Ph)(SiClMe$_2$) [e]	70.6 (70.4)	6.1 (6.3)
cis-PhCH=C(Ph)[Si(OEt)$_3$]	70.6 (70.1)	7.6 (7.7)

[a] Calculated values are given in parentheses. [b] Contains some of the CH$_2$=C isomer (see Table 1). [c] M.p. 44—46 °C. [d] M.p. 42—43 °C. [e] M.p. 31—32 °C.

We thank the Greek Government Scholarship Foundation for the award of a Fellowship (to C. A. T.), Dr. M. Murray for assistance in interpreting the n.m.r. data, and Mr. P. M. Stephens for separation of hydrosilylation products by g.l.c.

[6/2251 *Received, 9th December*, 1976]

* The synthesis of $[Pt(PhC_2Ph)_2]$ [16] and $[Pt(PPh_3)(PhC_2Ph)]$ [17] suggests that a 14-electron species $[Pt(RC_2H)\{(C_6H_{11})_3P\}]$ could be involved; however, the reported isolation of $[Ni\{(C_6H_{11})_3P\}(PhC_2Ph)_2]$ [18] suggests that a 16-electron three-co-ordinate complex might alternatively play a part in the catalytic cycle. Hence both species are depicted in the Scheme.

16 M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1976, 759.
17 J. Z. Nyathi, Ph.D. Thesis, Bristol University, 1976.
18 B. Büssemeier, Ph.D. Thesis, University of Bochum, 1973.
19 B. Çetinkaya, M. F. Lappert, and J. McMeeking, *Chem. Comm.*, 1971, 215; *J.C.S. Dalton*, 1973, 1975; A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 1972, **94**, 1886; J. W. Byrne, H. U. Blaser, and J. A. Osborn, *ibid.*, 1975, **97**, 3871.
20 J. Schwartz, D. W. Hart, and J. L. Holden, *J. Amer. Chem. Soc.*, 1972, **94**, 9269.
21 M. Bottrill, R. Davies, R. Goddard, M. Green, R. P. Hughes, B. Lewis, and P. Woodward, *J.C.S. Dalton*, 1977, 1252.
22 J. Forniés, M. Green, A. Laguna, M. Murray, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1515.
23 P. M. Stephens, M.Sc. Thesis, Bristol University, 1976.