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Synthesis of *cis*-$[\mathrm{Pt(C{\equiv}CR)_2(PPh_3)_2}]$ and *trans*-$[\mathrm{PtCl(C{\equiv}CR)(PPh_3)_2}]$ Complexes. Crystal and Molecular Structures of *cis*-$[\mathrm{Pt\{C{\equiv}CC(OH)Me_2\}_2(PPh_3)_2}]\cdot\mathrm{H_2O}$, *trans*-$[\mathrm{PtCl\{C{\equiv}CC(OH)Me_2\}(PPh_3)_2}]\cdot0.5\mathrm{PhMe}$, and *trans*-$[\mathrm{PtCl\{C{\equiv}CC(OH)MeEt\}(PPh_3)_2}]\cdot\mathrm{Me_2CO}$.† Influence of Bases and their Concentration on the Reactivity of *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$

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Complexes *cis*-$[\mathrm{Pt(C{\equiv}CR)_2(PPh_3)_2}]$ [R = C(OH)Me$_2$, C(OH)MeEt, CH(OH)Ph, or Ph] can be obtained from *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ and HC≡CR in 30% aqueous ammonia as solvent. Complexes *trans*-$[\mathrm{PtCl(C{\equiv}CR)(PPh_3)_2}]$ [R = CH$_2$OH, CH(OH)Me, C(OH)Me$_2$, C(OH)MeEt, $\mathrm{C_6H_{10}OH}$, or CH$_2$NEt$_2$] are obtained by using chloroform (or dichloromethane)–diethylamine as solvent. No dehydration reactions of the acetylenic alcohols are observed. *X*-Ray analyses on *cis*-$[\mathrm{Pt\{C{\equiv}CC(OH)Me_2\}_2(PPh_3)_2}]\cdot\mathrm{H_2O}$, *trans*-$[\mathrm{PtCl\{C{\equiv}CC(OH)Me_2\}(PPh_3)_2}]\cdot0.5\mathrm{PhMe}$, and *trans*-$[\mathrm{PtCl\{C{\equiv}CC(OH)MeEt\}(PPh_3)_2}]\cdot\mathrm{Me_2CO}$ revealed in the *cis* complex the presence of a water molecule forming two strong hydrogen bonds with the two *cis*-oriented hydroxy-groups of the acetylide ligands. In all the complexes the co-ordination around platinum is distorted square planar with the acetylide ligands σ-bonded to platinum. Crystallographic details: *cis*-$[\mathrm{Pt\{C{\equiv}CC(OH)Me_2\}_2(PPh_3)_2}]\cdot\mathrm{H_2O}$, monoclinic, space group $P2_1/c$, with a = 15.473(5), b = 21.725(6), c = 13.439(4) Å, β = 113.95(3)°, and Z = 4; R 0.052 for 3 110 observed reflections; *trans*-$[\mathrm{PtCl\{C{\equiv}CC(OH)Me_2\}(PPh_3)_2}]\cdot0.5\mathrm{PhMe}$, triclinic, space group $P\bar{1}$, with a = 11.695(3), b = 19.690(6), c = 9.214(2) Å, α = 101.88(3), β = 104.26(3), γ = 85.55(3)°, and Z = 2; R = 0.053 for 3 961 observed reflections; $[\mathrm{PtCl\{C{\equiv}CC(OH)MeEt\}(PPh_3)_2}]\cdot\mathrm{Me_2CO}$, triclinic, space group $P\bar{1}$, with a = 15.544(6), b = 12.567(4), c = 11.719(3) Å, α = 91.12(3), β = 105.36(3), γ = 111.39(3)°, and Z = 2; R = 0.046 for 4 704 observed reflections. The influence of NH$_3$, NHEt$_2$, and H$_2$NNH$_2$ on the reactivity of *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ with monosubstituted acetylenes is discussed.

We have previously found that *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ is an active catalyst for the linear polymerization of phenylacetylene and 2-methylbut-3-yn-2-ol.[1,2] Complexes with Pt–C σ bonds could be active intermediates. In an attempt to confirm this hypothesis we tried to prepare $[\mathrm{PtCl(C{\equiv}CR)(PPh_3)_2}]$ and $[\mathrm{Pt(C{\equiv}CR)_2(PPh_3)_2}]$ complexes following the procedure reported by Chatt and Shaw.[3] We obtained *trans*-$[\mathrm{PtCl(C{\equiv}CPh)(PPh_3)_2}]$ and *cis*- and *trans*-$[\mathrm{Pt(C{\equiv}CPh)_2(PPh_3)_2}]$ from phenylacetylene,[4] but failed to obtain analogous complexes from 2-methylbut-3-yn-2-ol.

With the aim of establishing general synthetic methods for platinum acetylides we studied the reactivity of *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ with monosubstituted acetylenes in the presence of bases. In this paper we report the reaction conditions under which *cis*-$[\mathrm{Pt(C{\equiv}CR)_2(PPh_3)_2}]$ and *trans*-$[\mathrm{PtCl(C{\equiv}CR)(PPh_3)_2}]$ complexes can be prepared, avoiding dehydration of any hydroxy-substituents of the acetylene. We also discuss the reactivity of *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ with monosubstituted acetylenes in the presence of NH$_3$, NHEt$_2$, and H$_2$NNH$_2$.

Results and Discussion

cis-$[\mathrm{Pt(C{\equiv}CR)_2(PPh_3)_2}]$ *Complexes*.—The complex *cis*-$[\mathrm{Pt(C{\equiv}CPh)_2(PPh_3)_2}]$ was the first example of a bis(triphenylphosphine)platinum bis(acetylide)[4] of *cis* configuration; its structure was confirmed by *X*-ray analysis.[5] Cullen and Hou[6] prepared *cis*-$[\mathrm{Pt(C{\equiv}CCF_3)_2(PPh_3)_2}]$ in 9% yield by treating tetrakis(triphenylphosphine)platinum(0) in benzene with 3,3,3-trifluoropropyne for 5 months at room temperature. Its structure was assigned on the basis of ^{19}F n.m.r. spectroscopy. Earlier, Harbourne and Stone[7] had reported that 3,3,3-trifluoropropyne reacts under similar conditions to yield the η-bonded complex $[\mathrm{Pt(HC{\equiv}CCF_3)(PPh_3)_2}]$ after 2 weeks.

From the reaction between *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ and HC≡CR [R = Ph, C(OH)Me$_2$, C(OH)MeEt, or CH(OH)Ph] in 30% aqueous ammonia under reflux for a few minutes (see Experimental section) we have now obtained *cis*-bis(acetylides), although in mixtures with their *trans* isomers. The *cis* complexes can be isolated by fractional crystallization from benzene–ethanol at room temperature (Table 1).

The *cis* structure was confirmed by *X*-ray analysis of the complex *cis*-$[\mathrm{Pt\{C{\equiv}CC(OH)Me_2\}_2(PPh_3)_2}]$ (see below), which revealed the presence of a water molecule in 1 : 1 stoicheiometry.

The i.r. spectrum of *cis*-$[\mathrm{Pt\{C{\equiv}CC(OH)Me_2\}_2(PPh_3)_2}]\cdot\mathrm{H_2O}$ exhibits a band at 3 540 cm^{-1} (free OH), and a broad band between 3 450 and 3 150 cm^{-1}, with two unresolved maxima at *ca.* 3 320 and 3 280 cm^{-1}, indicating hydrogen bonding, as confirmed by the *X*-ray analysis (see below). A doublet at 2 165—2 145 cm^{-1} can be attributed to the C≡C stretching

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† *cis*-Bis(3-hydroxy-3-methylbut-1-ynyl)bis(triphenylphosphine)platinum–water (1/1), *trans*-chloro(3-hydroxy-3-methylbut-1-ynyl)bis(triphenylphosphine)platinum–toluene (2/1), and *trans*-chloro(3-hydroxy-3-methylpent-1-ynyl)bis(triphenylphosphine)platinum–acetone (1/1).

Supplementary data available (No. SUP 23953, 58 pp.): structure factors, thermal parameters, H-atom co-ordinates for the three complexes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.

Table 1. Analytical and spectral data for the *cis*-$[Pt(C\equiv CR)_2(PPh_3)_2]$ complexes

R	Yield (%)	M.p. (θ/°C)	Analyses (%)[a]		I.r.[b] (cm^{-1})		U.v.
			C	H	ν(OH)	ν(C≡C)	$\lambda_{max.}$/nm[c]
$C(OH)Me_2$	60	180—183	61.4 (61.1)	5.35 (5.5)	3 540 3 320br 3 280br	2 165 2 145	286 275
C(OH)MeEt	40	184—187	62.3 (61.85)	5.5 (5.4)	3 510 3 320br 3 280br	2 130	285 275 (sh)
CH(OH)Ph	35	161—164	65.3 (64.85)	4.9 (4.65)	3 420br	2 125 2 100	285 275 (sh)
Ph	30	206—208	67.8 (67.75)	4.35 (4.35)[d]		2 125	314

[a] Calculated values in parentheses, for $[Pt(C\equiv CR)_2(PPh_3)_2]\cdot H_2O$ unless otherwise indicated. [b] Nujol mull. [c] $CHCl_3$ solution. [d] For $[Pt(C\equiv CR)_2(PPh_3)_2]$.

Table 2. Reaction conditions,[a] and analytical and spectral data for the *trans*-$[PtCl(C\equiv CR)(PPh_3)_2]$ complexes

R	Amount/mmol		Solvent[b]	*t*/min	Yield (%)	M.p. (θ/°C)	Analyses (%)[c]			I.r.[d] (cm^{-1})			U.v.
	HC≡CR	$NHEt_2$					C	H	Cl	ν(OH)	νC≡C)	ν(Pt–Cl)	$\lambda_{max.}$/nm[e]
CH_2OH	9	3	CH_2Cl_2	15	47.5	238—241	58.0 (57.8)	4.15 (4.1)	4.8 (4.4)	3 580	2 150	300	295 (sh)
CH(OH)Me	7	8	$CHCl_3$	15	51.0	190—193	58.1 (58.3)	4.4 (4.3)	4.0 (4.3)	3 480br	2 140	320	295 (sh)
$C(OH)Me_2$	10	8	$CHCl_3$	120	60.0	201—203	60.4 (60.5)	4.8 (4.7)	4.0 (3.9)[f]	3 590	2 120	320	295 (sh)
C(OH)MeEt	8	8	$CHCl_3$	120	62.0	172—174	60.85 (60.1)	5.0 (4.6)	4.15 (3.95)[g]	3 600 3 580 (sh)	2 130	315	295 (sh)
$C_6H_{10}OH$[h]	7	8	$CHCl_3$	120	45.0	228—229	63.5 (63.05)	5.2 (5.2)	2.60 (3.65)[i]	3 580 3 550 (sh)	2 130	330	295 (sh)
CH(OH)Ph	8	8	$CHCl_3$	15	10.0	205—208	61.4 (61.0)	4.0 (4.0)	4.1 (4.0)	3 585	2 120 2 100	320	295 (sh)
CH_2NEt_2	3.5	3	CH_2Cl_2	60	20.0	204—206	59.85 (59.7)	4.8 (4.9)	4.55 (4.1)		2 140	320	256[j]

[a] In all reactions 0.63 mmol of *cis*-$[PtCl_2(PPh_3)_2]$ was used. [b] 40 cm^3. [c] Calculated values in parentheses. [d] Nujol mull. [e] In $CHCl_3$ solution unless otherwise indicated. [f] Calc. for $[PtCl(C\equiv CR)(PPh_3)_2]\cdot 0.5PhMe$. [g] Calc. for $[PtCl(C\equiv CR)(PPh_3)_2]\cdot Me_2CO$. [h] 1-Hydroxycyclohexyl. [i] Calc. for $[PtCl(C\equiv CR)(PPh_3)_2]\cdot PhMe$. [j] In EtOH solution.

vibration and a strong band is observed at 1 660 cm^{-1}. The i.r. spectra of the other *cis* complexes of the acetylenic alcohols are similar (see Table 1).

A single band at *ca.* 2 125 cm^{-1} is present in the spectra of *cis*-$[Pt(C\equiv CR)_2(PPh_3)_2]$ [R = C(OH)MeEt and Ph] however. It is noteworthy that some *trans* complexes exhibit split bands at *ca.* 2 100 cm^{-1}.[8] A splitting of the C≡C stretching absorption into a doublet cannot thus be taken as an indication of the *cis* structure of bis(triphenylphosphine)platinum bis(acetylides). The presence of an intense absorption at 540 cm^{-1} in the i.r. spectra of all the complexes listed in Table 1, as previously reported,[9,10] may instead be considered to be proof of the presence of two triphenylphosphine molecules in a *cis* orientation.

From the reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and phenylacetylene in 30% aqueous ammonia the *cis*-bis(acetylide) complex can be separated by chromatography on a silica column. 1,4-Diphenylbutadiyne and $[Pt(\eta\text{-}HC\equiv CPh)(PPh_3)_2]$ were also formed (see Experimental section).

The side reactions probably take place through a mechanism involving reductive elimination of *cis*-$[PtCl_2(PPh_3)_2]$ to form $[Pt(PPh_3)_2]$, favoured by the presence of the base, and oxidative dimerization of HC≡CPh to form PhC≡C–C≡CPh. The active species $[Pt(PPh_3)_2]$ would then react with phenylacetylene in excess to give $[Pt(\eta\text{-}HC\equiv CPh)(PPh_3)_2]$. The overall process can be formulated as in reaction (i).

$$\textit{cis}\text{-}[PtCl_2(PPh_3)_2] + 2\,NH_3 + 3\,HC\equiv CPh \longrightarrow [Pt(\eta\text{-}HC\equiv CPh)(PPh_3)_2] + PhC\equiv C\text{–}C\equiv CPh + 2\,NH_4Cl \quad \text{(i)}$$

Evidence for the formation of dimerization products of the acetylenic radicals was obtained only in the reaction with phenylacetylene.

Attempts were made to prepare *cis* complexes from *cis*-$[PtCl_2(PPh_3)_2]$ and $HC\equiv CCH_2OH$, $HC\equiv CC_6H_{10}OH$, HC≡CCH(OH)Me and $HC\equiv CC(Me)=CH_2$ under similar conditions. The compound $HC\equiv CCH_2OH$ gave a crude mixture from which *trans*-$[Pt(C\equiv CCH_2OH)_2(PPh_3)_2]$ and $[Pt(\eta\text{-}CH\equiv CCH_2OH)(PPh_3)_2]$ could be separated in low yield, but no *cis*-bis(acetylide) could be obtained. The reactions with the other acetylenes gave complex mixtures of products. Attempted purification by fractional crystallization or column chromatography led only to the more stable *trans* isomers.

trans-$[PtCl(C\equiv CR)(PPh_3)_2]$ *Complexes*.—The complex *cis*-$[PtCl_2(PPh_3)_2]$ reacts with acetylenes in $CHCl_3$, in the presence of $NHEt_2$ ($NHEt_2$: HC≡CR molar ratio *ca.* 1 : 1), giving *trans*-$[PtCl(C\equiv CR)(PPh_3)_2]$ complexes (Table 2). Intramolecular dehydration of the hydroxy-groups of acetylenic alcohols, previously observed under similar conditions,[10] does not take place. T.l.c. shows the presence of *trans*-bis(acetylide) complexes as side products, however.

Monochloroacetylides were purified by fractional crystallization from various solvents. Chromatography on silica gel columns is unsatisfactory because of the occurrence of intra- or inter-molecular dehydration involving the hydroxy groups of the acetylene ligand.

X-Ray analyses of *trans*-[PtCl{C≡CC(OH)Me$_2$}(PPh$_3$)$_2$] and *trans*-[PtCl{C≡CC(OH)MeEt}(PPh$_3$)$_2$] reveal the presence of solvent molecules (see below).

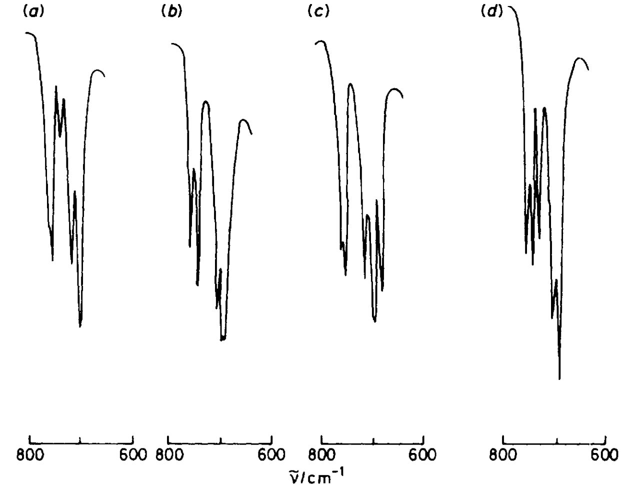

Figure 1. I.r. spectra of *trans*-[PtCl{C≡CC(OH)Me$_2$}(PPh$_3$)$_2$] crystallized from: (*a*) toluene; (*b*) benzene—acetone; (*c*) benzene-t-butyl alcohol; (*d*) dichloromethane–diethyl ether

The i.r. spectra of the *trans*-[PtCl(C≡CR)(PPh$_3$)$_2$] complexes show a band at *ca.* 320 cm^{-1}, due to the Pt–Cl stretching vibration. A band at 540 cm^{-1} is of low intensity, as in the spectra of other *trans*-bis(triphenylphosphine)platinum complexes.[9] The OH stretching band occurs at *ca.* 3 600 cm^{-1}.

In the region 800—600 cm^{-1} (Figure 1) different features are observed in the i.r. spectra of *trans*-[PtCl{C≡CC(OH)Me$_2$}(PPh$_3$)$_2$] recrystallized from various solvent mixtures. Similar modifications of i.r. spectra have been observed previously for different crystalline adducts of [PtCl{C≡CC(Me)=CH$_2$}(PPh$_3$)$_2$] [11,12] and for [PtH(Cl)(PPh$_3$)$_2$].[13]

Structural Features.—*cis*-[Pt{C≡CC(OH)Me$_2$}$_2$(PPh$_3$)$_2$]·H$_2$O *Complex* (1). The structure consists of monomeric units (Figure 2) where platinum is co-ordinated *via* σ bonds to two acetylide ligands and two triphenylphosphine molecules in a nearly square-planar *cis* arrangement (Tables 3 and 4). The water molecule, which was detected by the *X*-ray analysis, is not simply a crystallization molecule, but plays an important role in stabilizing the *cis* complex. The water oxygen atom forms two strong hydrogen bonds with the two *cis*-oriented hydroxy-groups acting as a donor atom (Table 3 and Figure 2). As a consequence of the presence of the hydrogen bonds and of steric interactions between the ligands, the bond angles around Pt differ from the 90° for a regular square-planar arrangement, ranging from 84.4(5) to 98.7(2)°, the largest value involving the bulky *cis*-triphenylphosphines (Table 3). The Pt–C distances [Pt–C(1) 2.02(2) and Pt–C(6) 1.99(2) Å]

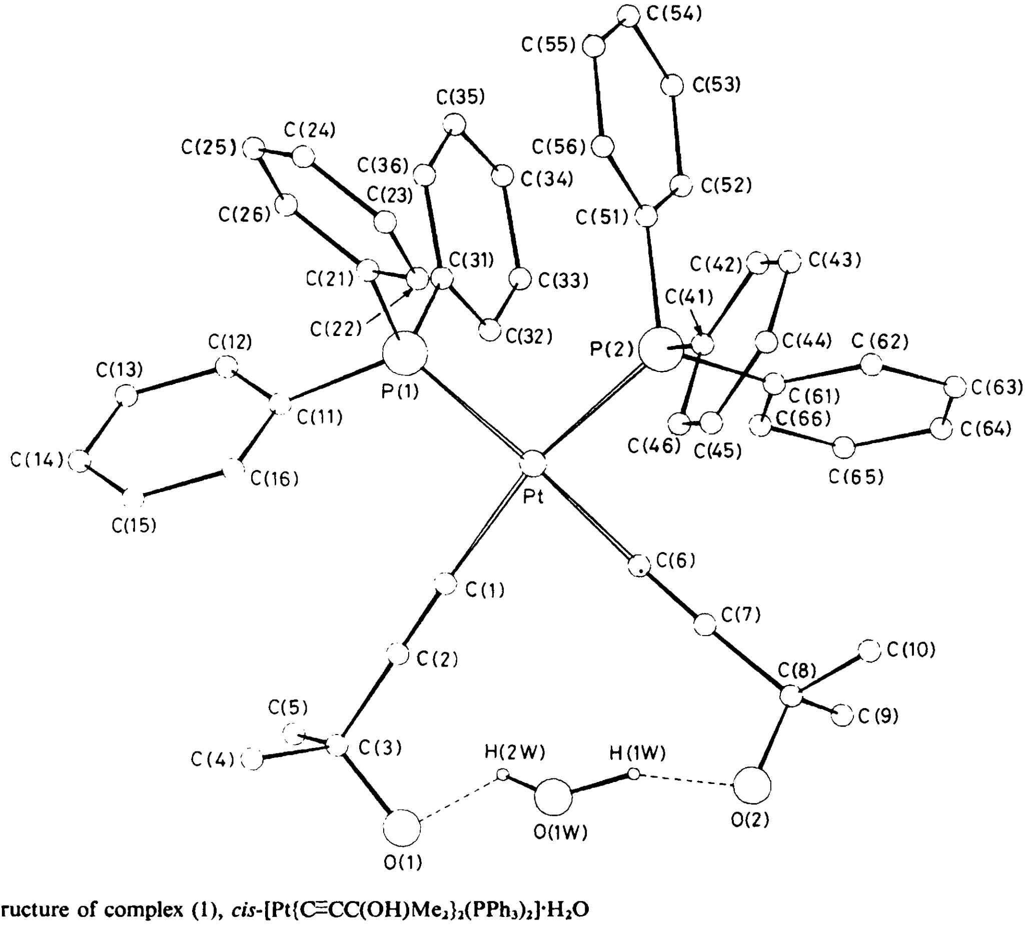

Figure 2. The structure of complex (1), *cis*-[Pt{C≡CC(OH)Me$_2$}$_2$(PPh$_3$)$_2$]·H$_2$O

Table 3. Selected interatomic distances (Å) and angles (°) for *cis*-$[Pt\{C\equiv CC(OH)Me_2\}_2(PPh_3)_2]\cdot H_2O$ (1)

Pt–C(1)	2.02(2)	C(2)–C(3)	1.51(2)	C(7)–C(8)	1.51(2)	P(1)–C(21)	1.83(1)
Pt–C(6)	1.99(2)	C(3)–O(1)	1.41(2)	C(8)–O(2)	1.45(2)	P(1)–C(31)	1.83(1)
Pt–P(1)	2.307(5)	C(3)–C(4)	1.52(2)	C(8)–C(9)	1.49(3)	P(2)–C(41)	1.82(1)
Pt–P(2)	2.331(5)	C(3)–C(5)	1.49(3)	C(8)–C(10)	1.56(3)	P(2)–C(51)	1.85(1)
C(1)–C(2)	1.17(2)	C(6)–C(7)	1.19(2)	P(1)–C(11)	1.84(1)	P(2)–C(61)	1.83(1)
O(1W)–H(2W)	1.05	O(1W) · · · O(1)	2.73(2)	O(1) · · · O(2^{i}) *	2.81(2)	H(1W) · · · O(2)	1.60
O(1W)–H(1W)	1.14	O(1W) · · · O(2)	2.69(2)	H(2W) · · · O(1)	1.85	H(1) · · · O(2^{i}) *	1.98
O(1)–H(1)	0.93						
C(1)–Pt–C(6)	84.5(6)	C(2)–C(3)–C(5)	109(1)	C(7)–C(8)–C(9)	110(2)	C(11)–P(1)–C(31)	105.0(5)
P(2)–Pt–C(6)	84.4(5)	C(2)–C(3)–C(4)	110(1)	O(2)–C(8)–C(10)	107(2)	C(21)–P(1)–C(31)	109.3(5)
P(2)–Pt–C(1)	168.1(5)	O(1)–C(3)–C(5)	113(1)	O(2)–C(8)–C(9)	113(2)	Pt–P(2)–C(41)	115.0(4)
P(1)–Pt–C(6)	176.3(5)	O(1)–C(3)–C(4)	107(1)	C(9)–C(8)–C(10)	109(2)	Pt–P(2)–C(51)	120.5(4)
P(1)–Pt–C(1)	92.3(5)	C(4)–C(3)–C(5)	110(2)	Pt–P(1)–C(11)	118.2(4)	Pt–P(2)–C(61)	109.4(4)
P(1)–Pt–P(2)	98.7(2)	Pt–C(6)–C(7)	178(1)	Pt–P(1)–C(21)	115.1(4)	C(41)–P(2)–C(51)	103.9(5)
Pt–C(1)–C(2)	177(2)	C(6)–C(7)–C(8)	177(2)	Pt–P(1)–C(31)	109.2(4)	C(41)–P(2)–C(61)	104.9(5)
C(1)–C(2)–C(3)	178(2)	C(7)–C(8)–O(2)	108(1)	C(11)–P(1)–C(21)	99.1(5)	C(51)–P(2)–C(61)	101.3(5)
C(2)–C(3)–O(1)	107(1)	C(7)–C(8)–C(10)	110(1)				
H(1W)–O(1W)–H(2W)	133	O(1W)–H(2W)–O(1)	139	O(1)–H(1)–O(2^{i}) *	148	O(1W)–H(1W)–O(2)	158

* i $x, \bar{y} - \frac{1}{2}, z + \frac{1}{2}$.

Table 4. Equations of least-squares planes and, in square brackets, distances (Å) of atoms from these planes *

Complex (1), *cis*-$[Pt\{C\equiv CC(OH)Me_2\}_2(PPh_3)_2]\cdot H_2O$
Co-ordination plane: Pt, P(1), P(2), C(1), C(6)
$-0.9632X + 0.0047Y - 0.2687Z = -3.7002$
[Pt −0.006(2), P(1) 0.006(5), P(2) 0.010(5), C(1) 0.140(18), C(6) 0.056(20)]

Complex (2), *trans*-$[PtCl\{C\equiv CC(OH)Me_2\}(PPh_3)_2]\cdot 0.5PhMe$
Co-ordination plane: Pt, P(1), P(2), Cl, C(1)
$0.0415X - 0.3765Y - 0.9255Z = -2.9609$
[Pt −0.005(1), P(1) 0.021(4), P(2) 0.021(4), Cl −0.003(4), C(1) −0.057(16)]

Complex (3), *trans*-$[PtCl\{C\equiv CC(OH)MeEt\}(PPh_3)_2]\cdot Me_2CO$
Co-ordination plane: Pt, P(1), P(2), Cl, C(1)
$0.1995X + 0.9582Y + 0.2053Z = 3.2516$
[Pt −0.028(2), P(1) 0.043(3), P(2) 0.043(3), Cl −0.027(4), C(1) −0.142(9)]

* *X*, *Y*, and *Z* are co-ordinates (Å) referred to an orthogonal system of axes. The transformation matrix used was:

$$\begin{array}{ccc} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\sin\beta\cos\alpha \\ 0 & 0 & c\sin\beta\sin\alpha \end{array}$$

are in the range of values quoted in the literature [14] for acetylide *trans* complexes. Bond distances and angles in the two independent acetylide ligands are normal and the Pt–C≡C–C systems do not deviate significantly from linearity (Table 3).

The two Pt–P distances [Pt–P(1) 2.307(5) and Pt–P(2) 2.331(5) Å], which fall in the upper part of the range of values observed for *trans* complexes,[14] are significantly different, Pt–P(2) being longer apparently in order to relieve steric interactions between the ligands. The distances C(6) · · · C(61) 3.14(2), C(6) · · · C(66) 3.25(2), C(6) · · · C(46) 3.32(2), C(1) · · · C(11) 3.28(2), and C(1) · · · C(16) 3.22(2) Å are the shortest intramolecular contacts between the co-ordinating ligands. As observed for *trans*-$[Pt(PPh_3)_2]$ complexes [15] the largest Pt–P–C angles [Pt–P(1)–C(11) 118.2(4) and Pt–P(2)–C(51) 120.5(4)°] involve the carbon atoms which are close to the co-ordination plane as indicated by the torsion angles C(1)–Pt–P(1)–C(11) −5.1(6) and P(1)–Pt–P(2)–C(51) −13.3(5)°.

Packing is mainly determined by an intermolecular O(1)–H(1) · · · O(2^{i}) hydrogen bond (Table 3) involving the hydroxy-groups of adjacent molecules. No other contact is less than the sum of the van der Waals radii. Thus it can be concluded that the O(2)–H hydroxy-group, whose hydrogen atom could be not located, is not engaged as a donor in any hydrogen bond, in agreement with the presence in the i.r. spectrum of a band at 3 540 cm^{-1} due to free OH groups.

trans-$[PtCl\{C\equiv CC(OH)Me_2\}(PPh_3)_2]\cdot 0.5PhMe$, *Complex* (2), *and trans*-$[PtCl\{C\equiv CC(OH)MeEt\}(PPh_3)_2]\cdot Me_2CO$, (3). In both complexes the structure consists of monomeric units where the organic ligand, *trans* to chlorine, is σ bonded to platinum (Figures 3 and 4). The co-ordination geometry is similar in the two complexes apart from some differences in bond angles which are probably due to the substitution of a methyl group by ethyl. The co-ordination around the platinum atom is square planar, with a small tetrahedral displacement (Table 4). The Pt–Cl and the Pt–C bond distances are compared with values for other complexes in Table 5. It is well known that the *trans* influence in platinum(II) square-planar complexes has two main components: the electrostatic component and the metal-to-ligand multiple-bond characteristic. The role of both effects can be evaluated from the data in Table 5, when the ligand at Pt is the –C≡C–R group, and the *trans*-Pt–Cl bond distance is affected. The change in the electron-donating ability of the R substituents should allow the electrostatic effect to be evaluated. A comparison of the Pt–Cl bond distances in complexes (2), (3), (5), and (6) (Table 5) suggests that the electrostatic influence has a small effect, all the Pt–Cl distances being similar. The phenyl substituent [complex (4)] has a major influence however. This could be due either to an electrostatic effect or to the influence of conjugation, *i.e.* metal–carbon multiple-bond formation, which is excluded by the value of the Pt–C distance however. The C≡C unit is a very difficult group to polarize (the differences in the C≡C bond distance are not significant), and, further, its influence is high *per se*. Moreover the Pt–C bond distances are very similar in the four complexes (2)—(5). The isopropenyl substituent [complex (6)] should provide an example of a complex with Pt–C multiple bond which is expected to have a

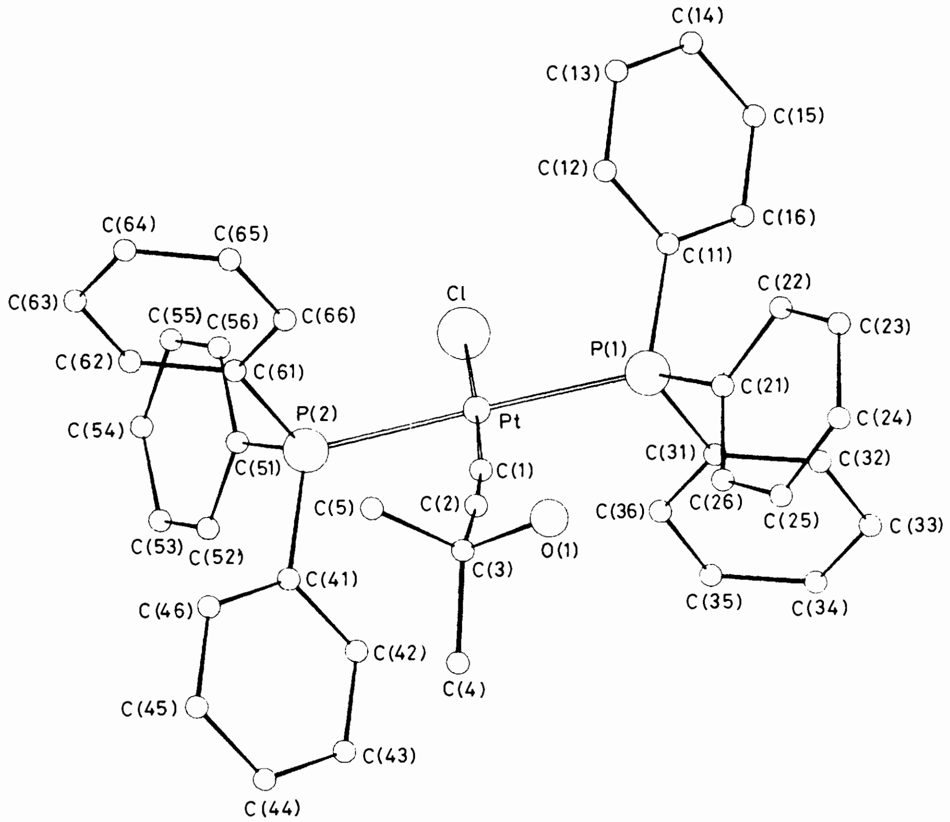

Figure 3. The structure of complex (2), *trans*-$[PtCl\{C{\equiv}CC(OH)Me_2\}(PPh_3)_2]\cdot 0.5PhMe$

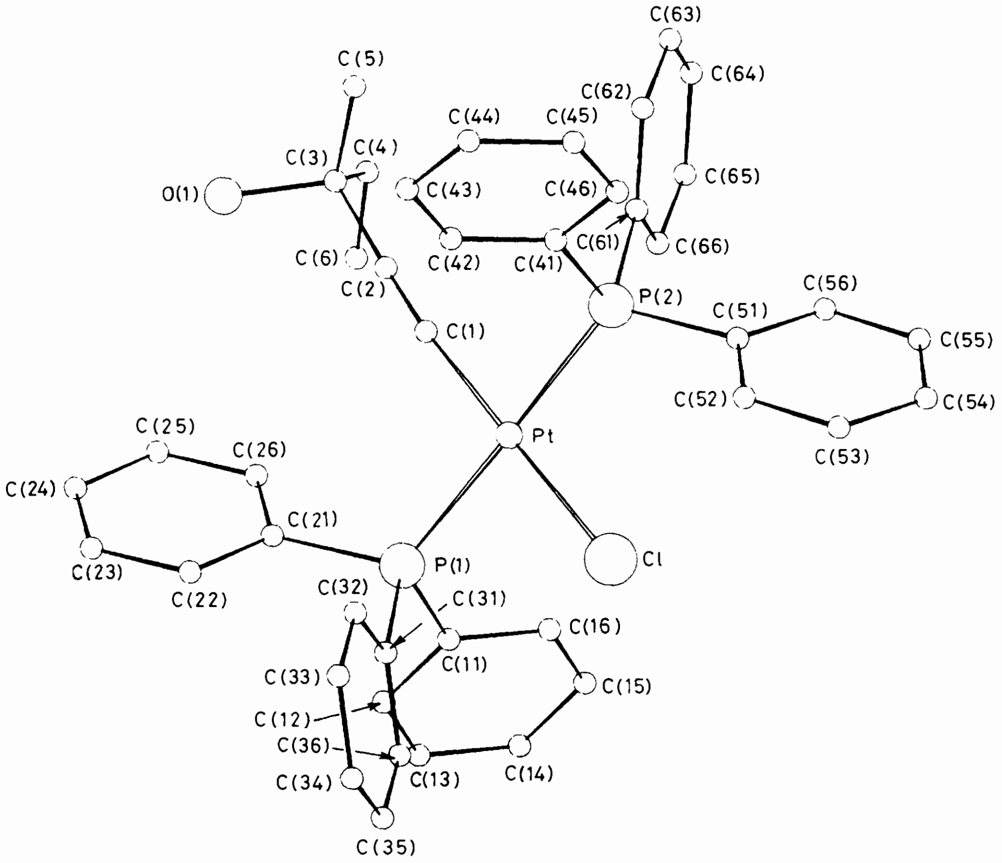

Figure 4. The structure of complex (3), *trans*-$[PtCl\{C{\equiv}CC(OH)MeEt\}(PPh_3)_2]\cdot Me_2CO$

Table 5. Selected bond lengths (Å) for *trans*-$[PtCl(C\equiv CR)(PPh_3)_2]$ complexes

Complex	(4)	(6)	(2)	(5)	(3)
R	Ph	$C(Me)=CH_2$	$C(OH)Me_2$	$C_6H_{10}(OEt)$	C(OH)MeEt
Pt–Cl	2.407(5)	2.363(6)	2.356(5)	2.345(5)	2.336(4)
Pt–C	1.98(2)	1.84(2)	1.95(2)	1.94(2)	1.988(9)
Pt–P	2.284(5)	2.296(5)	2.311(4)	2.307(4)	2.321(4)
Pt–P	2.325(5)	2.300(5)	2.320(4)	2.310(4)	2.320(4)
C≡C	1.18(3)	1.22(3)	1.18(2)	1.22(2)	1.15(2)
Ref.	20 *	12	Present work	19	Present work

* The data are for molecule 2, molecule 1 being affected by disorder.

large *trans* influence, but the Pt–Cl distance is unexpectedly little affected. The P–C distance in complex (6) may be unusually short owing to a conjugation effect. Unfortunately this effect cannot be demonstrated unequivocally by the sequence of C–C bond distances in the organic residues, which have high standard deviations. However, the main conclusion is that even in the presence of a structurally proven M–C multiple bond, the Pt–Cl distance is only slightly affected.

It is worth noting that in the complexes in Table 5 the Pt–P distances [mean 2.308(5) Å] are significantly longer than those in *trans*-$[PtH\{C\equiv CC(OH)Me_2\}(PPh_3)_2]$ [mean 2.273(5) Å [16]] which contains the same organic residue as complex (2), but hydrogen instead of chlorine *trans* to it. This is probably a consequence of the small size of hydrogen with respect to chlorine which allows the phosphine ligands to approach closer to the metal.

The geometry of the triphenylphosphine ligands is as expected with the Pt–P–C angles equal to or greater than tetrahedral values and the C–P–C angles smaller. As usual the largest Pt–P–C angles involve the carbon atoms closer to the co-ordination plane. Complex (2): Pt–P(1)–C(21) 119.9(3), Pt–P(2)–C(51) 116.5(4), C(1)–Pt–P(1)–C(21) −10.5(6), Cl–Pt–P(2)–C(51) 14.4(4)°; complex (3): Pt–P(1)–C(21) 118.4(2), Pt–P(2)–C(51) 117.1(2); C(1)–Pt–P(1)–C(21) −19.3(4), Cl–Pt–P(2)–C(51) 14.4(3)°.

All the other bond distances and angles are normal except for those involving the ethyl and methyl groups of compound (3) which are affected by high thermal motion. No contact less than the sum of the van der Waals radii is present, so in both structures the hydroxy-groups are free.

Reactivity of cis-$[PtCl_2(PPh_3)_2]$ *with Acetylenes in the Presence of Bases.—Ammonia.* (*i*) Chatt and Shaw [3] reported that *trans*-$[Pt(C\equiv CR)_2L_2]$ complexes can be prepared by the reaction of a sodium acetylide, $NaC\equiv CR$ (R = H, Me, or Ph), with $[PtCl_2L_2]$ (L = PEt_3 or $AsEt_3$) in liquid ammonia. Empsall *et al.*[17] prepared several acetylide complexes by using the sodium derivatives of acetylenic alcohols (formed *in situ* in liquid ammonia) and *cis*-$[PtCl_2L_2]$ (L = PMe_2Ph or $AsMe_2Ph$). By an analogous procedure we have obtained *cis*- and *trans*-$[Pt(C\equiv CPh)_2(PPh_3)_2]$ and *trans*-$[PtCl(C\equiv CPh)(PPh_3)_2]$,[4] but the same method did not give good results with 2-methylbut-3-yn-2-ol, because side reactions involving the hydroxy-group take place and complex mixtures of products are formed.

(*ii*) If the reactions between *cis*-$[PtCl_2(PPh_3)_2]$ and $HC\equiv CR$ (see above) are carried out by using 30% aqueous ammonia as solvent, *cis*-$[Pt(C\equiv CR)_2(PPh_3)_2]$ complexes can be obtained even when R contains a hydroxy-group. The stability of the *cis* complexes depends on the formation of hydrogen bonds between the hydroxy-group of the alcohol ligand and a water molecule, which is trapped between the two ligands in *cis* positions. When steric requirements inhibit the formation of hydrogen bonds, the stability of the *cis*-bis(acetylides) is low and the *trans* isomers are formed during crystallization.

(*iii*) When the acetylenic alcohols $HC\equiv CR$ [R = $C(OH)Me_2$, C(OH)MeEt, or $C_6H_{10}OH$] are refluxed with *cis*-$[PtCl_2(PPh_3)_2]$ in the presence of a few drops of 30% aqueous ammonia for 10—15 min, the *trans*-bis(acetylides) $[Pt(C\equiv CR')_2(PPh_3)_2]$ are obtained.[10] Intramolecular dehydration of the tertiary hydroxy-groups takes place, however, and complexes of alkenylalkynes are formed (*i.e.* R′ is an alkenyl rather than a hydroxyalkyl group).

A similar dehydration was observed when the tertiary acetylenic alcohols were refluxed for *ca.* 12 h with *cis*-$[PtCl_2(PPh_3)_2]$ in chloroform, without addition of a base; *trans*-$[PtCl(C\equiv CR')(PPh_3)_2]$ complexes were formed. Substitution of both chloro-substituents by acetylenic radicals is difficult in the absence of a base but the intramolecular dehydration still occurs.[10]

Diethylamine. (*i*) In a previous investigation we found that if $NHEt_2$ is used as solvent, the reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and the acetylenes $HC\equiv CR$ {R = Ph, $C(Me)=CH_2$, $[CH_2]_6C\equiv CH$, CH_2OH, CH(OH)Me, CH(OH)Ph, $CH_2CH(OH)Me$, $C(OH)Me_2$, C(OH)MeEt, $C_6H_{10}OH$, CH_2NHMe, CH_2NMe_2, CH_2NHCH_2Ph, or CH_2NEt_2}, under reflux for a few minutes (in the presence of CuI as a catalyst) gives *trans*-$[Pt(C\equiv CR)_2(PPh_3)_2]$ complexes in high yields.[8] Diethylamine facilitates the elimination of HCl and the formation of Pt–C σ bonds, and inhibits dehydration reactions.

(*ii*) Complexes *trans*-$[PtCl(C\equiv CR)(PPh_3)_2]$ can be obtained from acetylenic alcohols when *cis*-$[PtCl_2(PPh_3)_2]$ reacts with $HC\equiv CR$ (R includes a hydroxy-substituent) in chloroform in the presence of diethylamine (ratio of $NHEt_2$ to $HC\equiv CR$ *ca.* 1 : 1). No dehydration of the tertiary hydroxy-groups takes place under these conditions.

Hydrazine. (*i*) Complexes $[Pt(\eta\text{-}HC\equiv CR)(PPh_3)_2]$ are obtained in the reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and acetylenes in the presence of hydrazine or other reducing agents.[18–20] Keubler *et al.*[21] studied in detail the reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and hydrazine and found that $[Pt(N_2H)_2(PPh_3)_2]X$, $[PtH(Cl)(PPh_3)_2]$, and $[Pt(PPh_3)_2]$ were formed depending on the relative amounts of hydrazine and platinum complex. During our investigation of the reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and $HC\equiv CC(Me)=CH_2$ in the presence of hydrazine, we found that $[Pt\{\eta\text{-}HC\equiv CC(Me)=CH_2\}(PPh_3)_2]$, *trans*-$[PtCl\{C(=CH_2)C(Me)=CH_2\}(PPh_3)_2]$, and *trans*-$[Pt\{C\equiv CC(Me)=CH_2\}\{C(=CH_2)C(Me)=CH_2\}(PPh_3)_2]$ could be obtained depending on the exact conditions (see Experimental section and ref. 22 for details). The reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and phenylacetylene in ethanol in the presence of hydrazine hydrate gives a mixture of *trans*-$[Pt(C\equiv CPh)\{C(Ph)=CH_2\}(PPh_3)_2]$ and $[Pt(\eta\text{-}HC\equiv CPh)(PPh_3)_2]$. The complexes $[PtCl\{C(R)=CH_2\}(PPh_3)_2]$ and $[Pt(C\equiv CR)\{C(R)=CH_2\}(PPh_3)_2]$ [R = $C(Me)=CH_2$ or Ph] are products of insertion of the acetylenes $HC\equiv CR$ into the Pt–H bond of [PtH(Cl)-

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for *cis*-$[Pt\{C\equiv CC(OH)Me_2\}_2(PPh_3)_2]\cdot H_2O$ (1)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Pt(1)	2 550(1)	126(1)	478(1)	C(25)	4 861(6)	1 960(4)	3 689(8)
P(1)	2 737(3)	760(2)	1 928(4)	C(26)	4 019(6)	1 625(4)	3 304(8)
P(2)	2 374(3)	880(2)	−825(3)	C(31)	1 680(6)	1 235(4)	1 581(9)
O(1)	2 326(10)	−2 164(5)	1 640(10)	C(32)	818(6)	936(4)	1 031(9)
O(2)	2 508(10)	−1 772(5)	−2 100(10)	C(33)	−28(6)	1 261(4)	739(9)
C(1)	2 560(11)	−641(7)	1 339(12)	C(34)	−11(6)	1 884(4)	998(9)
C(2)	2 524(11)	−1 089(7)	1 802(14)	C(35)	851(6)	2 182(4)	1 548(9)
C(3)	2 510(12)	−1 678(7)	2 396(12)	C(36)	1 697(6)	1 858(4)	1 840(9)
C(4)	3 478(15)	−1 794(8)	3 297(15)	C(41)	3 340(6)	926(5)	−1 267(8)
C(5)	1 786(20)	−1 624(9)	2 863(23)	C(42)	3 465(6)	1 445(5)	−1 806(8)
C(6)	2 346(12)	−459(7)	−734(13)	C(43)	4 203(6)	1 464(5)	−2 149(8)
C(7)	2 211(11)	−797(7)	−1 481(14)	C(44)	4 816(6)	965(5)	−1 953(8)
C(8)	1 985(13)	−1 204(8)	−2 462(14)	C(45)	4 691(6)	446(5)	−1 414(8)
C(9)	946(15)	−1 304(10)	−3 022(17)	C(46)	3 953(6)	427(5)	−1 071(8)
C(10)	2 338(15)	−895(9)	−3 273(14)	C(51)	2 156(7)	1 691(4)	−576(9)
O(1W)	2 925(12)	−1 917(5)	31(10)	C(52)	1 222(7)	1 890(4)	−930(9)
C(11)	2 921(7)	401(4)	3 236(7)	C(53)	1 028(7)	2 500(4)	−768(9)
C(12)	2 424(7)	609(4)	3 835(7)	C(54)	1 769(7)	2 911(4)	−252(9)
C(13)	2 662(7)	394(4)	4 892(7)	C(55)	2 704(7)	2 712(4)	101(9)
C(14)	3 397(7)	−28(4)	5 350(7)	C(56)	2 897(7)	2 102(4)	−60(9)
C(15)	3 894(7)	−236(4)	4 751(7)	C(61)	1 324(6)	711(5)	−2 064(7)
C(16)	3 656(7)	−22(4)	3 694(7)	C(62)	1 263(6)	865(5)	−3 098(7)
C(21)	3 781(6)	1 256(4)	2 381(8)	C(63)	427(6)	758(5)	−4 011(7)
C(22)	4 384(6)	1 222(4)	1 843(8)	C(64)	−348(6)	496(5)	−3 890(7)
C(23)	5 225(6)	1 557(4)	2 228(8)	C(65)	−287(6)	342(5)	−2 856(7)
C(24)	5 464(6)	1 926(4)	3 151(8)	C(66)	549(6)	449(5)	−1 943(7)

$(PPh_3)_2]$, which is formed as an intermediate in the reaction between $[PtCl_2(PPh_3)_2]$ and hydrazine, and are also obtained if $[PtH(Cl)(PPh_3)_2]$ is used as starting material.[22]

From the reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and acetylenic alcohols in the presence of hydrazine we obtained only the complexes $[Pt(\eta\text{-}HC\equiv CR)(PPh_3)_2]$ [R = CH_2OH, $CH(OH)Me$, $C(OH)Me_2$, $C(OH)MeEt$, or $C_6H_{10}OH$] in good yields.[20] Therefore the reaction mechanisms depend largely on the substituent R of the acetylenes.

Experimental

All chemicals were reagent grade and were used without further purification. The complex *cis*-$[PtCl_2(PPh_3)_2]$ was prepared according to the literature method.[23]

I.r. spectra were recorded on a Perkin-Elmer model 580-B spectrometer for Nujol mulls, u.v. spectra on a Beckman DK-2A spectrophotometer for solutions in $CHCl_3$. Elemental analyses were carried out by the Laboratorio di Microanalisi, Istituto di Chimica Farmaceutica, Pisa, Italy. Analytical and physical data are in Tables 1 and 2.

Syntheses.—*cis*-$[Pt(C\equiv CR)_2(PPh_3)_2]$ [R = $C(OH)Me_2$, $C(OH)MeEt$, *and* $CH(OH)Ph$]. A suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.5 g, 0.63 mmol), in 30% aqueous ammonia (30 cm^3) with the acetylenic alcohol $HC\equiv CR$ (*ca.* 5 mmol) was refluxed for 15 min. The products were obtained by addition of absolute ethanol (30 cm^3) and purified by recrystallization from benzene–ethanol.

cis-$[Pt(C\equiv CPh)_2(PPh_3)_2]$. A suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.5 g, 0.63 mmol) in 30% aqueous ammonia (30 cm^3) with $HC\equiv CPh$ (*ca.* 5 mmol) was stirred at room temperature for 5 min. The crude product, obtained by addition of absolute ethanol (*ca.* 30 cm^3), was chromatographed on a silica gel column. Elution with $CHCl_3$ gave four fractions, containing (in order) 1,4-diphenylbutadiyne, *trans*-$[Pt(C\equiv CPh)_2(PPh_3)_2]$, *trans*-$[PtCl(C\equiv CPh)(PPh_3)_2]$, and *cis*-$[Pt(C\equiv CPh)_2(PPh_3)_2]$.[4] Crystallization of the crude reaction mixture from $CHCl_3$–EtOH sometimes led to the complex $[Pt(\eta\text{-}HC\equiv CPh)(PPh_3)_2]$, which decomposes on attempted chromatography.

trans-$[PtCl(C\equiv CR)(PPh_3)_2]$. The preparation of *trans*-$[PtCl\{C\equiv CC(OH)Me_2\}(PPh_3)_2]$ is typical. The complex *cis*-$[PtCl_2(PPh_3)_2]$ (0.5 g, 0.63 mmol), $HC\equiv CC(OH)Me_2$ (1 cm^3, 10 mmol), and diethylamine (0.8 cm^3, 8 mmol) were added to $CHCl_3$ (40 cm^3) and the mixture was refluxed for 2 h. On addition of acetone (50 cm^3) the product separated as a white microcrystalline powder which was recrystallized from toluene (or benzene)–acetone (1 : 2).

Optimum conditions for the preparation of the other $[PtCl(C\equiv CR)(PPh_3)_2]$ complexes are in Table 2.

trans-$[PtCl\{C(=CH_2)C(Me)=CH_2\}(PPh_3)_2]$. Hydrazine hydrate (7.2 mmol) was added dropwise to a suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.25 mmol) in absolute ethanol (10 cm^3). The compound $HC\equiv CC(Me)=CH_2$ (10.6 mmol) was added to the resultant clear solution, and the mixture refluxed for *ca.* 5 min. On cooling to 0 °C, the product was obtained in *ca.* 80% yield.

trans-$[Pt\{C\equiv CC(Me)=CH_2\}\{C(=CH_2)C(Me)=CH_2\}(PPh_3)]$. Hydrazine hydrate (10 mmol) was added dropwise to a suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.50 mmol) in absolute ethanol (40—50 cm^3). The compound $HC\equiv CC(Me)=CH_2$ (21.2 mmol) was added to the resultant clear solution, and the mixture refluxed for *ca.* 90 min. After 1—2 d at 0 °C, the product was obtained in *ca.* 50% yield.

$[Pt\{\eta\text{-}HC\equiv CC(Me)=CH_2\}(PPh_3)_2]$. The complex *cis*-$[PtCl_2(PPh_3)_2]$ (0.25 mmol) was suspended in a small volume of absolute ethanol (*ca.* 4 cm^3) and hydrazine hydrate (7.2 mmol) added dropwise. The compound $HC\equiv CC(Me)=CH_2$ (21.2 mmol) was added to the resultant clear solution and the mixture refluxed for *ca.* 20 min. On cooling the product was obtained in *ca.* 60% yield.

Crystal Structure Determinations.—*cis*-$[Pt\{C\equiv CC(OH)Me_2\}_2(PPh_3)_2]\cdot H_2O$ (1), *trans*-$[PtCl\{C\equiv CC(OH)Me_2\}(PPh_3)_2]\cdot 0.5PhMe$ (2), and *trans*-$[PtCl\{C\equiv CC(OH)MeEt\}(PPh_3)_2]\cdot Me_2CO$ (3) were mounted on a Philips PW 1100 diffractometer

Table 7. Fractional atomic co-ordinates (× 10^4) for *trans*-[PtCl{C≡CC(OH)Me_2}$(PPh_3)_2$]·0.5PhMe (2)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt	2 887(1)	2 033(1)	2 139(1)	C(26)	50(8)	3 073(4)	287(11)
Cl	2 999(3)	1 013(2)	3 134(5)	C(31)	130(8)	1 408(4)	387(10)
P(1)	876(3)	2 067(2)	1 943(4)	C(32)	−1 094(8)	1 438(4)	−153(10)
P(2)	4 896(3)	2 000(2)	2 266(4)	C(33)	−1 649(8)	932(4)	−1 365(10)
O(1)	2 099(16)	4 523(9)	638(26)	C(34)	−982(8)	396(4)	−2 036(10)
C(1)	2 866(12)	2 890(8)	1 376(18)	C(35)	241(8)	366(4)	−1 495(10)
C(2)	2 942(13)	3 409(8)	959(18)	C(36)	797(8)	872(4)	−283(10)
C(3)	3 120(18)	4 067(8)	467(23)	C(41)	5 161(8)	2 146(5)	501(9)
C(4)	3 236(29)	3 934(11)	−1 156(24)	C(42)	4 409(8)	1 849(5)	−873(9)
C(5)	4 158(24)	4 442(13)	1 512(32)	C(43)	4 602(8)	1 942(5)	−2 254(9)
C(71)	1 046(31)	4 613(21)	4 784(46)	C(44)	5 546(8)	2 332(5)	−2 260(9)
C(72)	625(49)	5 178(30)	4 005(50)	C(45)	6 298(8)	2 629(5)	−885(9)
C(73)	−439(44)	5 472(22)	4 046(45)	C(46)	6 105(8)	2 536(5)	496(9)
C(77)	2 029(50)	4 364(18)	4 587(69)	C(51)	5 689(9)	1 190(4)	2 552(12)
C(11)	569(9)	1 921(5)	3 705(9)	C(52)	6 077(9)	752(4)	1 362(12)
C(12)	1 263(9)	2 270(5)	5 074(9)	C(53)	6 630(9)	115(4)	1 580(12)
C(13)	1 072(9)	2 187(5)	6 463(9)	C(54)	6 795(9)	−84(4)	2 986(12)
C(14)	186(9)	1 755(5)	6 482(9)	C(55)	6 407(9)	354(4)	4 176(12)
C(15)	−508(9)	1 407(5)	5 113(9)	C(56)	5 854(9)	991(4)	3 959(12)
C(16)	−317(9)	1 490(5)	3 725(9)	C(61)	5 683(8)	2 662(4)	3 809(10)
C(21)	3(8)	2 844(4)	1 556(11)	C(62)	6 896(8)	2 580(4)	4 374(10)
C(22)	−715(8)	3 196(4)	2 488(11)	C(63)	7 503(8)	3 082(4)	5 552(10)
C(23)	−1 387(8)	3 778(4)	2 102(11)	C(64)	6 897(8)	3 665(4)	6 165(10)
C(24)	−1 340(8)	4 007(4)	783(11)	C(65)	5 683(8)	3 747(4)	5 600(10)
C(25)	−622(8)	3 655(4)	−149(11)	C(66)	5 076(8)	3 245(4)	4 422(10)

Table 8. Selected interatomic distances (Å) and angles (°) for *trans*-[PtCl{C≡CC(OH)Me_2}$(PPh_3)_2$]·0.5PhMe (2) and *trans*-[PtCl{C≡CC(OH)-MeEt}$(PPh_3)_2$]·Me_2CO (3)

	(2)	(3)		(2)	(3)		(2)	(3)
Pt–Cl	2.356(5)	2.336(4)	C(3)–O(1)	1.46(3)	1.49(2)	P(1)–C(21)	1.820(9)	1.829(6)
Pt–C(1)	1.95(2)	1.988(9)	C(3)–C(4)	1.50(3)	1.51(2)	P(1)–C(31)	1.815(8)	1.816(6)
Pt–P(1)	2.311(4)	2.321(4)	C(3)–C(5)	1.49(3)	1.47(2)	P(2)–C(41)	1.811(10)	1.828(5)
Pt–P(2)	2.320(4)	2.320(4)	C(4)–C(6)	—	1.39(3)	P(2)–C(51)	1.816(9)	1.832(7)
C(1)–C(2)	1.18(2)	1.15(2)	P(1)–C(11)	1.828(11)	1.830(5)	P(2)–C(61)	1.829(8)	1.819(6)
C(2)–C(3)	1.50(3)	1.52(2)						
	(2)	(3)		(2)	(3)		(2)	(3)
Cl–Pt–P(1)	87.8(2)	85.5(1)	C(2)–C(3)–C(5)	111(2)	110(1)	C(11)–P(1)–C(21)	104.4(5)	102.8(3)
Cl–Pt–P(2)	93.1(2)	94.0(1)	C(2)–C(3)–C(4)	112(1)	114(1)	C(11)–P(1)–C(31)	107.8(5)	106.4(3)
Cl–Pt–C(1)	177.3(5)	176.7(3)	O(1)–C(3)–C(5)	106(2)	106(1)	C(21)–P(1)–C(31)	101.6(5)	103.7(3)
P(1)–Pt–P(2)	178.5(1)	176.4(2)	O(1)–C(3)–C(4)	110(2)	108(1)	Pt–P(2)–C(41)	110.5(3)	112.0(3)
P(1)–Pt–C(1)	94.4(5)	94.2(3)	C(4)–C(3)–C(5)	111(2)	110(1)	Pt–P(2)–C(51)	116.5(4)	117.1(2)
P(2)–Pt–C(1)	84.7(5)	86.5(3)	C(3)–C(4)–C(6)	—	116(1)	Pt–P(2)–C(61)	112.4(3)	114.4(3)
Pt–C(1)–C(2)	175(1)	174(1)	Pt–P(1)–C(11)	110.4(3)	113.6(3)	C(41)–P(2)–C(51)	104.4(5)	103.0(3)
C(1)–C(2)–C(3)	176(2)	178(1)	Pt–P(1)–C(21)	119.9(3)	118.4(2)	C(41)–P(2)–C(61)	107.4(5)	106.3(3)
C(2)–C(3)–O(1)	107(2)	109(1)	Pt–P(1)–C(31)	111.8(3)	110.8(3)	C(51)–P(2)–C(61)	105.0(5)	102.9(3)

(graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,7$ Å) in a random orientation. The reduced cells were obtained using the program TRACER.[24] The unit-cell parameters were deduced from least-squares refinement of the 2θ values of 21 reflections having $2\theta > 26°$ for all complexes.

Crystal data. $C_{46}H_{44}O_2P_2Pt{\cdot}H_2O$ (1), $M = 903.9$, monoclinic, $a = 15.473(5)$, $b = 21.725(6)$, $c = 13.439(4)$ Å, $\beta = 113.95(3)°$, $U = 4\,129(2)$ Å^3, $Z = 4$, $D_c = 1.454$ g cm^{-3}, $F(000) = 1\,816$, μ(Mo-K_α) = 35.5 cm^{-1}, space group $P2_1/c$; crystal dimensions 0.32 × 0.34 × 0.32 mm.

$C_{41}H_{37}ClOP_2Pt{\cdot}0.5C_7H_8$ (2), $M = 884.3$, triclinic, $a = 11.695(3)$, $b = 19.690(6)$, $c = 9.214(2)$ Å, $\alpha = 101.88(3)$, $\beta = 104.26(3)$, $\gamma = 85.55(3)°$, $U = 2\,011(1)$ Å^3, $Z = 2$, $D_c = 1.460$ g cm^{-3}, $F(000) = 882$, μ(Mo-K_α) = 37.0 cm^{-1}, space group $P\bar{1}$; crystal dimensions 0.32 × 0.10 × 0.40 mm.

$C_{42}H_{39}ClOP_2Pt{\cdot}C_3H_6O$, $M = 910.3$, triclinic, $a = 15.544(6)$, $b = 12.567(4)$, $c = 11.719(3)$ Å, $\alpha = 91.12(3)$, $\beta = 105.36(3)$, $\gamma = 111.39(3)°$, $U = 2\,038(1)$ Å^3, $Z = 2$, $D_c = 1.483$ g cm^{-3}, $F(000) = 912$, μ(Mo-K_α) = 36.6 cm^{-1}, space group $P\bar{1}$; crystal dimensions 0.34 × 0.22 × 0.51 mm.

Intensities were recorded at room temperature by ω—2θ scans in the ranges 2θ 6—48° for complexes (1) and (2) and 6—49° for (3). No crystal decay or experimental instability was indicated by monitoring of standard reflections during the determinations. ψ Scans showed that crystal absorption effects could not be neglected, so the data for the three complexes were corrected for absorption by a semi-empirical method [25] with maximum and minimum corrections of 1.112—1.003 for complex (1), 1.356—1.003 for (2), and 1.133—1.003 for (3). 6 396 [for (1)], 6 276 [for (2)], and 6 629 [for (3)] unique reflections were collected; of these 3 110, 3 961, and 4 704, respectively, having $I > 3.0\sigma(I)$, were considered observed and used in the structure solutions and refinements.

Solution and refinement. The structures of the three complexes were solved by conventional heavy-atom methods (Patterson and Fourier) and refined by blocked full-matrix

Table 9. Fractional atomic co-ordinates (× 10^4) for *trans*-[PtCl{C≡CC(OH)MeEt}(PPh_3)$_2$]·Me_2CO (3)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Pt(1)	2 510(1)	2 374(1)	20(1)	C(26)	4 772(3)	1 446(5)	196(5)
Cl(1)	1 513(2)	2 722(3)	−1 681(3)	C(31)	3 583(4)	3 350(4)	−2 156(5)
P(1)	3 413(2)	2 205(2)	−1 214(2)	C(32)	3 959(4)	4 478(4)	−1 587(5)
P(2)	1 657(2)	2 666(2)	1 265(2)	C(33)	4 135(4)	5 401(4)	−2 254(5)
O(1)	5 256(6)	1 721(8)	3 531(8)	C(34)	3 935(4)	5 195(4)	−3 489(5)
C(1)	3 316(6)	1 982(7)	1 438(8)	C(35)	3 559(4)	4 068(4)	−4 057(5)
C(2)	3 706(8)	1 689(9)	2 273(9)	C(36)	3 383(4)	3 145(4)	−3 391(5)
C(3)	4 203(8)	1 307(10)	3 399(9)	C(41)	2 294(4)	4 063(4)	2 197(5)
C(4)	3 832(14)	13(13)	3 390(14)	C(42)	3 300(4)	4 563(4)	2 502(5)
C(5)	4 114(11)	1 846(15)	4 460(10)	C(43)	3 799(4)	5 629(4)	3 214(5)
C(6)	3 843(14)	−619(14)	2 413(19)	C(44)	3 292(4)	6 193(4)	3 622(5)
O(2)	−330(10)	4 048(16)	6 129(14)	C(45)	2 286(4)	5 692(4)	3 317(5)
C(7)	1 172(19)	5 334(15)	7 099(19)	C(46)	1 787(4)	4 627(4)	2 605(5)
C(8)	499(14)	4 391(18)	6 239(16)	C(51)	462(4)	2 681(5)	550(5)
C(9)	861(13)	3 754(17)	5 527(16)	C(52)	418(4)	3 565(5)	−136(5)
C(11)	2 853(4)	849(4)	−2 220(5)	C(53)	−476(4)	3 597(5)	−733(5)
C(12)	3 399(4)	484(4)	−2 787(5)	C(54)	−1 325(4)	2 744(5)	−644(5)
C(13)	2 975(4)	−568(4)	−3 524(5)	C(55)	−1 280(4)	1 861(5)	42(5)
C(14)	2 004(4)	−1 254(4)	−3 694(5)	C(56)	−387(4)	1 829(5)	639(5)
C(15)	1 457(4)	−889(4)	−3 127(5)	C(61)	1 410(5)	1 592(4)	2 279(5)
C(16)	1 882(4)	163(4)	−2 389(5)	C(62)	1 429(5)	1 862(4)	3 448(5)
C(21)	4 638(3)	2 277(5)	−524(5)	C(63)	1 160(5)	985(4)	4 150(5)
C(22)	5 434(3)	3 154(5)	−707(5)	C(64)	874(5)	−162(4)	3 683(5)
C(23)	6 364(3)	3 200(5)	−171(5)	C(65)	856(5)	−432(4)	2 514(5)
C(24)	6 498(3)	2 369(5)	549(5)	C(66)	1 124(5)	445(4)	1 812(5)
C(25)	5 703(3)	1 492(5)	732(5)				

least squares with anisotropic thermal parameters for all non-hydrogen atoms except for the phenyl rings which were treated as rigid regular hexagons. All hydrogen atoms for complexes (1)—(3) were introduced in the final refinement as fixed contributors ($U = 0.012$ Å^2).

For complex (1) the hydrogen atoms of the water molecule and one of the two hydroxy-groups were located on a difference electron-density map; other hydrogen atoms except for that of the other hydroxy-groups were introduced in calculated positions (C–H 1.08 Å). Final residual indices for (1) were $R = 0.052$, $R' = 0.048$, and $S = 2.5$ with weights $w = 1.1025/[\sigma^2(F_o) + 0.000\,238\ F_o^2]$; $R' = \Sigma w^{\frac{1}{2}}|\Delta F|/\Sigma w^{\frac{1}{2}}|F_o|$; $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$ (N_o = number of observed reflections, N_v = number of parameters to be determined). A final electron-density difference map showed no features >0.3 e Å^{-3}. Fractional atomic co-ordinates for the non-hydrogen atoms are in Table 6, and important bond lengths and angles are in Table 3.

For complex (2) the *X*-ray analysis revealed the presence of a toluene molecule of crystallization lying on a centre of symmetry, so its methyl carbon atom was assigned a site occupation factor of 0.5. None of the hydrogen atoms could be located from a difference map. They were introduced in calculated positions (C–H 1.08 Å) except for those of the hydroxy-group and toluene. The final *R* index was 0.053. Unit weights were used since these gave acceptable agreement analyses. A final difference map showed no features of chemical significance (all <0.4 e Å^{-3}). Fractional atomic co-ordinates are in Table 7 (excluding hydrogen atoms), and important bond lengths and angles are in Table 8.

For complex (3) the *X*-ray analysis revealed the presence of an acetone molecule of crystallization. All the hydrogen atoms except for those of the hydroxy group and the acetone molecule were located in a difference map. Those of the acetone molecule were introduced in calculated positions (C–H 1.08 Å). Final residual indices were $R = 0.046$, $R' = 0.046$, and $S = 1.75$ with weights $w = 1.064\,7/[\sigma^2(F_o) + 0.000\,329\ F_o^2]$. A final difference map showed no features >0.5 e Å^{-3}. Table 9 lists the final fractional atomic co-ordinates (excluding hydrogen atoms), and important bond lengths and angles are in Table 8.

Complex neutral-atom scattering factors for Pt, Cl, P, O, and C were taken from ref. 26, those for H from ref. 27. All calculations were carried out on the CDC 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale, using the SHELX 76 system of programs.[28]

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