New Platinum Hydrido Acetylides. Crystal and Molecular Structure of $[PtH\{C{\equiv}C-C(OH)MeEt\}(PPh_3)_2]$ †

Anita Furlani,* Silvia Licoccia, and Maria V. Russo
Istituto di Chimica Generale ed Inorganica, Università di Roma, Roma, Italy
Angiola Chiesi Villa and Carlo Guastini
Istituto di Strutturistica Chimica dell'Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, Parma, Italy

The complex *trans*-$[PtClH(PPh_3)_2]$ reacts with monosubstituted acetylenes $HC{\equiv}CR$ (R = CH_2OH, $CH(OH)Me$, $C(OH)Me_2$, $C(OH)MeEt$, $CH(OH)Ph$, $C_6H_{10}OH$, Ph, or $CMe{=}CH_2$) in the presence of NEt_2H to give *trans*-$[PtH(C{\equiv}CR)(PPh_3)_2]$, which have been characterized by i.r., u.v., and n.m.r. spectroscopy. An *X*-ray diffraction analysis was carried out on $[PtH\{C{\equiv}C-C(OH)MeEt\}(PPh_3)_2]$. Crystals are monoclinic, space group $P2_1/n$, with unit cell dimensions a = 15.560(3), b = 26.696(5), c = 9.038(2) Å, β = 98.51(2)°, Z = 4. A total of 3 855 observed reflections have been measured by single-crystal diffractometry and refined by blocked full-matrix least squares to R = 0.067. Co-ordination around platinum is distorted square planar and involves the acetylide ligand *trans* to hydrogen which was directly located. In some reaction conditions cationic intermediates have been demonstrated by conductivity measurements.

The reactions of *trans*-$[PtClH(PPh_3)_2]$ with phenylacetylene or isopropenylacetylene lead to the formation of styrene or isoprene complexes *via* insertion into the Pt–H bond.[1] Bonding to the metal occurs through the C^2 carbon atom of the alkenes.

Tertiary acetylenic alcohols, under similar reaction conditions, do not insert into the Pt–H bond but undergo easy dehydration.[2,3] When primary alkyl alcohols are used as precipitating agents mono-alkynyl complexes of the corresponding ethers are obtained, whilst intramolecular dehydration takes place if secondary or tertiary alcohols are used, and the reaction product is a related alkenylalkynyl complex.

This paper describes the influence of diethylamine on the reaction pathway.

Results and Discussion

When *trans*-$[PtClH(PPh_3)_2]$ reacts with monosubstituted acetylenes $HC{\equiv}CR$ [R = CH_2OH, $CH(OH)Me$, $C(OH)Me_2$, $C(OH)MeEt$, $CH(OH)Ph$, $C_6H_{10}OH$, Ph, or $CMe{=}CH_2$] in benzene or chloroform in the presence of NEt_2H (molar ratio 1 : 1 with acetylene), *trans*-$[PtH(C{\equiv}CR)(PPh_3)_2]$ complexes are formed (see Experimental section). The NEt_2H facilitates the elimination of hydrogen chloride between the chlorine atom of the complex and the acidic hydrogen of acetylene.

It is known that in similar reaction conditions, in the presence of hydrazine, an intramolecular elimination of hydrogen chloride on the starting complex takes place giving $[Pt(PPh_3)_2]$ and a subsequent formation of η-bonded platinum acetylene complexes $[Pt(HC{\equiv}CR)(PPh_3)_2]$ occurs.[1,4] The base exerts then an important role on the reaction mechanism.

The complex *trans*-$[PtH(C{\equiv}CPh)(PEt_3)_2]$ has been previously obtained by Glocking and Hooton [5] from *trans*-$[PtCl(SiMe_3)(PEt_3)_2]$ and $HC{\equiv}CPh$. The reaction requires one week and gives a mixture of various products from which the hydrido acetylide can be obtained in low yield. The same product has also be obtained by Tohda *et al.*[6] from $[PtClH(PEt_3)_2]$ and $NaC{\equiv}CPh$ in benzene. Our method is of wide applicability, gives good yields in very mild reaction conditions, and avoids the insertion and dehydration reactions previously observed.[2,3,7]

Elemental analysis and spectral data for the newly synthesized hydridoplatinum acetylides are reported in Table 1.

In the u.v. spectra two bands are observed at 275 and 315—330 nm, which in some cases appear as shoulders on the continuously increasing absorption. Similar spectra have been observed for analogous monoacetylides [8] having a chlorine atom in a *trans* position to the $C{\equiv}CR$ group. The bands were identified as due to charge-transfer transitions which overlap the ligand-field bands. In the spectra of isopropenylacetylene and phenylacetylene complexes the conjugation of the unsaturated radicals with the π system of the complex shifts the band at 315 nm to *ca.* 330 nm.

All the complexes are characterized by two i.r. bands in the 2 000—2 120 cm^{-1} region. By analogy with the i.r. spectrum of *trans*-$[PtH(C{\equiv}CPh)(PEt_3)_2]$ [5] the band at *ca.* 2 100 cm^{-1} can be attributed to the $C{\equiv}C$ stretching vibration of the σ-bonded acetylene while the other at *ca.* 2 040 cm^{-1} is due to the Pt–H stretching vibration. In the spectra of *trans*-$[PtHX(PEt_3)_2]$ (X = NO_3, Cl, Br, I, NO_2, SCN, CN, or $C{\equiv}CPh$) the Pt–H stretching frequencies are observed in the range 2 020—2 242 cm^{-1}.[9] The position of these bands depends on the *trans*-influence of the ligand *trans* to the hydrogen atom.[5,9] The low values observed in the spectra of our complexes are consistent with the previously reported data for *trans*-$[PtH(C{\equiv}CPh)(PEt_3)_2]$ [5] and confirm a high *trans*-influence of the $C{\equiv}CR$ group. The i.r. spectra of the isopropenylacetylene complex exhibit several bands in the 2 000—2 100 cm^{-1} region, whose intensity, number and frequency are dependent on the crystallization procedure used in the purification of reaction product. Different i.r. spectra for various crystalline adducts of *trans*-$[PtClH(PPh_3)_2]$ [10] and *trans*-$[PtCl(C{\equiv}CMe{=}CH_2)(PPh_3)_2]$ have been previously observed.[11,12] *X*-Ray measurements revealed in such cases different crystal packing and the presence of different solvent molecules in the lattice. Solid state interactions between the solvent molecules and the ligands exert an influence on the bending and stretching vibrations and are responsible for the splitting and shifting of the bands in the spectra of such complexes.

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† Hydrido(3-hydroxy-3-methylpent-1-ynyl-(triphenylphosphine)-platinum(II).

Supplementary data available (No. SUP 23389, 28 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Elemental analyses and spectroscopic data

Complex	Analysis [a] (%) C	Analysis [a] (%) H	Yield (%)	M.p. (°C)	U.v. (nm) [b] max.	U.v. (nm) [b] shoulder	I.r. (cm^{-1}) [c] ν(Pt–H)	I.r. (cm^{-1}) [c] ν(C≡C)	N.m.r.[d] τ/p.p.m.	N.m.r.[d] $J(^{195}Pt-H)$	N.m.r.[d] $J(^{31}P-H)$
$[PtH(C\equiv C-CH_2OH)(PPh_3)_2]\cdot\frac{1}{2}CHCl_3$	54.25 (53.70)	4.10 (3.90)	52	100—103	275	315	2 047	2 109	16.35	648.2	15.0
$[PtH\{C\equiv C-CH(OH)Me\}(PPh_3)_2]\cdot CHCl_3$	58.05 (57.25)	4.30 (4.20)	54	107—110		275, 315	2 049	2 110	16.35	648.1	15.4
$[PtH\{C\equiv C-C(OH)Me_2\}(PPh_3)_2]$	60.85 (61.25)	4.80 (4.75)	56	145—147	275	315	2 043	2 110	16.34	651.9	15.3
$[PtH\{C\equiv C-C(OH)MeEt\}(PPh_3)_2]$	61.50 (61.70)	4.85 (4.95)	50	149—151		275, 315	2 045	2 111	16.35	657.0	15.3
$[PtH\{C\equiv C-CH(OH)Ph\}(PPh_3)_2]$	62.95 (63.45)	4.80 (4.50)	68	127—129	275	315	2 045	2 113	16.36	652.6	15.0
$[PtH(C\equiv C-C_6H_{10}OH)(PPh_3)_2]$	62.30 (62.65)	5.10 (5.00)	49	110—114		275, 320	2 035	2 118	16.41	659.9	15.4
$[PtH(C\equiv C-Ph)(PPh_3)_2]\cdot C_6H_6$	66.35 (66.75)	4.80 (4.70)	90	143—146	330	275	2 050 2 038	2 115 2 080	16.22	647.4	15.4
$[PtH(C\equiv C-CMe=CH_2)(PPh_3)_2]\cdot C_6H_6$	65.30 (63.35)	5.20 (4.90)	70	131—133	324	275	2 043	2 103,[e] 2 072	16.34	642.0	15.4
							2 042 2 035 2 015	2 103,[f] 2 078			

[a] Calculated values in parentheses. [b] In $CHCl_3$. [c] Nujol mulls. [d] In $CDCl_3$, with $SiMe_4$ as internal standard; *J* values in Hz. [e,f] Modifications by different crystallization solvents: [e] from $CHCl_3EtOH$; [f] from C_6H_6–EtOH.

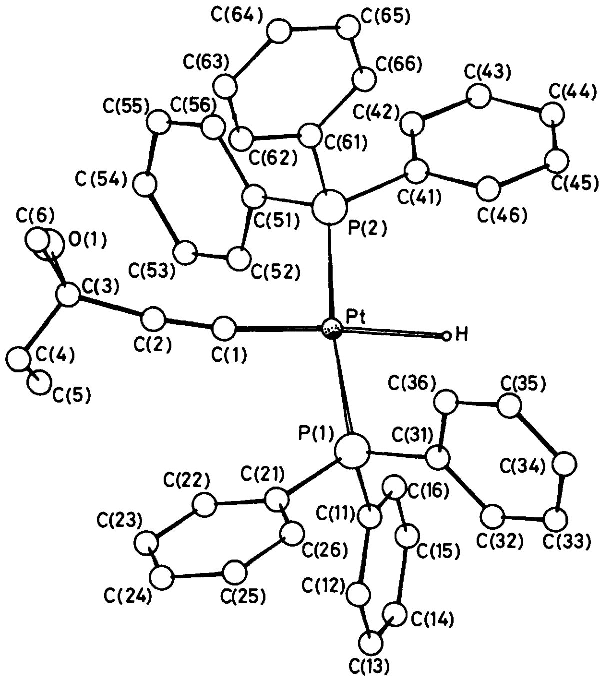

Figure. Projection of $[PtH\{C\equiv C-C(OH)MeEt\}(PPh_3)_2]$ showing the adopted numbering scheme

The n.m.r. spectra are characterized by a triplet of triplets in the high-field region where the Pt–H resonances are usually observed. The characteristic pattern is due to the natural abundance of ^{195}Pt (33.7%). The Pt–H signals have been observed in the spectra of *trans*-$[PtHX(PEt_3)_2]$ complexes in the range τ 33.6 (X = NO_3) to 16.12 (X = C≡CPh).[9] These τ values have been correlated with a low *trans*-influence for the NO_3 group and a high one for the C≡CR group. The *J*(Pt–H) coupling constants are also correlated with the *trans*-influence of the ligands *trans* to hydrogen [*J*(Pt–H) = 1 322 Hz for X = NO_3, *J*(Pt–H) = 778 Hz for X = CN].[9] The *J*(Pt–H) values given in Table 1, which are consistent with those of similar complexes, confirm a high *trans*-influence of the acetylide groups. An increase in the electron density at the platinum will reduce the effective nuclear charge and thus reduce the *J*(Pt–H) values, as observed in the n.m.r. spectra of hydrido acetylides.

Some authors have predicted an increase in the Pt–H bond distance in the Pt complexes in which the ligand in the *trans* position to hydrogen exerts a high *trans*-influence. Buckingham and Stephens [13] predicted that in the square planar platinum hydrides $[PtHX(PEt_3)_2]$ (X = NO_3, Cl, Br, I, NO_2, NCS, or CN) a proton situated above the co-ordination plane should exert low-field shifting of the Pt–H signal. On the basis of such predictions a long Pt–H bond distance, with the hydrogen atom out of the co-ordination plane, should be expected in this series of complexes. The structural data for *trans*-$[PtH\{C\equiv C-C(OH)MeEt\}(PPh_3)_2]$ are given below.

Discussion of the Structure.—The structure consists of monomeric units where the acetylide ligand, *trans* to hydrogen, is σ-bonded to platinum (Figure). Co-ordination is completed to distorted square planar by two phosphorus atoms from the triphenylphosphines. The Pt–C bond length [1.90(1) Å] falls in the lower part of the range of values quoted in Table 2 and in the literature [1.921(12)—2.024(6)] [1,14,15] for acetylide complexes. For reasons discussed below the geometry of the acetylide ligand has been established with only moderate accuracy and this limits the use of the Pt–C bond length as a guide to discussion.

The high value of the Pt–H distance (1.98 *versus* 1.78 Å in $[\{PtH(\mu-SiMe_2)[P(C_6H_{11})_3]\}_2]$,[16] and 1.66 Å in $[PtH(SB_9H_{10})(PEt_3)_2]$ [17]) and the out-of-plane displacement of hydride (0.34 Å) from the mean co-ordination plane [Pt,C(1),P(1),P(2): $0.1579X' - 0.5163Y' - 0.8418Z' = -2.5875$; Pt 0.010(2), C(1) – 0.044(12), P(1) – 0.030(4), P(2) – 0.040(5) Å] are in agreement with the high *trans*-influence of the acetylide ligand deduced from the i.r. and n.m.r. data and with the hypothesis of Buckingham and Stephens [13] (already quoted) on these kinds of complexes. However, the *trans*-influence of a C≡CR group can be more surely tested in complexes where the

Table 2. Selected bond lengths (Å) and angles (°) in *trans*-chloroplatinum(II) acetylide complexes

Complex	Pt–Cl	Pt–C	C≡C	Pt–C≡C	C≡C–	Ref.
trans-$[PtCl(C\equiv C{-}CMe{=}CH_2)(PPh_3)_2]\cdot\frac{1}{2}C_6H_6$	2.296(5)	2.14(3)	1.09(4)	151(3)	170(2)	11
trans-$[PtCl\{C\equiv C{-}C_6H_{10}(OEt)\}(PPh_3)_2]$	2.345(5)	1.94(2)	1.22(2)	172(1)	178(2)	2
trans-$[PtCl(C\equiv C{-}CMe{=}CH_2)(PPh_3)_2]\cdot\frac{3}{2}CHCl_3$	2.45(1) 2.363(6)	1.88(6) 1.84(2)	1.07(8) 1.22(3)	169(5) 175(1)	173(6) 178(2)	12
trans-$[PtCl(C\equiv CPh)(PEt_2Ph)_2]$	2.407(5)	1.98(2)	1.18(3)	163(2)	174(2)	*

* C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organomet. Chem.*, 1973, **60**, C70; and ref. 15.

trans-ligand is chlorine, the Pt–Cl distances being more accurately determined than either Pt–H or Pt–C. As it can be seen from the data quoted in Table 2, the values of the Pt–Cl distances fall in a rather large range indicating that there is not a simple correlation between the nature of the ligand and its *trans*-influence, but other factors may be important. One of them could be that pointed out by Manojlović-Muir and Muir [18] who suggested that the *trans*-influence of the carbon-donor ligands depends mainly on the extent of metal-to-ligand π-back donation. Unfortunately, most of the data quoted in Table 2, in particular those involving carbons, are of a low accuracy and firm conclusions on this argument are difficult to make.

The Pt–P bond lengths [Pt–P(1) 2.279(4), Pt–P(2) 2.267(5) Å] fall in the range usually observed (2.27—2.33 Å) for *trans*-$[Pt(PPh_3)_2]$ complexes.[1,2,11,12,14] The angles P(1)–Pt–C(1) and P(2)–Pt–C(1) open to 96.4(4) and 91.5(3)° with respect to a regular square planar arrangement, apparently in order to relieve steric interactions between the ligands [C(1) ··· C(21), 3.44(2); C(1) ··· C(22), 3.21(2); C(1) ··· C(51), 3.32(2); C(1) ··· C(52), 3.39(2) Å are the shortest intramolecular contacts between acetylide and phosphines]. The PPh_3 ligands have the usual geometry. It is worth noting that the largest inter-bond angles at P(1) and P(2) involve the C(21) and C(41) atoms [Pt–P(1)–C(21), 118.9(4); Pt–P(2)–C(41), 117.8(5)°] which are closer to the metal co-ordination plane [15] as indicated by the torsion angles: C(1)–Pt–P(1)–C(21), −18.7(6); C(1)–Pt–P(2)–C(41), −166.6(6); C(1)–Pt–P(1)–C(11), 102.9(5); C(1)–Pt–P(1)–C(31), −138.4(5); C(1)–Pt–P(2)–C(51), −46.7(6); and C(1)–Pt–P(2)–C(61), 73.1(6)°.

Conductivity Measurements.—Clark and co-workers [19-23] have extensively studied the cationic intermediates involved in many reactions of $[PtHXL_2]$ or $[PtMeXL_2]$ (X = halide, L = phosphine or arsine) leading to the formation of acetylide, acyl, alkoxycarbene, vinyl, and vinyl ether complexes. They identified these cationic compounds by n.m.r. measurements and sometimes isolated them as PF_6^- or BPh_4^- salts.

Table 3. Conductivity measurements. Influence of the reaction components

Reagents	κ/μS cm^{-1}	Products
(*i*) *trans*-$[PtClH(PPh_3)_2]$ (100 mg) in $CHCl_3$ (50 cm^3)	0.1	
$HC\equiv C{-}CMe_2OH$ (0.5 cm^3)	0.1	
$C(OH)Me_3$ (10 cm^3)	0.1	
NEt_2H (0.5 cm^3)	0.3	$[PtH(C\equiv CR)(PPh_3)_2]$ [a]
(*ii*) *trans*-$[PtClH(PPh_3)_2]$ (100 mg) in $CHCl_3$ (50 cm^3)	0.1	
MeOH (25 cm^3)	2.5	
NEt_2H (0.5 cm^3)	25.0	
After 1 h	35.0	
$HC\equiv C{-}CH(OH)Ph$ (0.5 cm^3)	42.0	
After 24 h	58.3	$[PtH(C\equiv CR')(PPh_3)_2]$ [b]
(*iii*) NEt_2H (0.5 cm^3) in $CHCl_3$ (50 cm^3)	0.1	
MeOH (25 cm^3)	5.8	
trans-$[PtClH(PPh_3)_2]$ (100 mg)	27.1	
$HC\equiv C{-}CH(OH)Ph$ (0.5 cm^3)	45.0	$[PtH(C\equiv CR')(PPh_3)_2]$ [b]
(*iv*) NEt_2H (0.5 cm^3) in $CHCl_3$ (50 cm^3)	0.1	
MeOH (25 cm^3)	5.4	
$HC\equiv C{-}CH(OH)Me$ (0.5 cm^3)	10.3	
trans-$[PtClH(PPh_3)_2]$ (100 mg)	46.0	$[PtH(C\equiv CR'')(PPh_3)_2]$ [c]

[a] R = CMe_2OH. [b] R′ = CH(OH)Ph. [c] R″ = CH(OH)Me.

We have carried out conductivity measurements on our reaction mixtures in order to state the existence of ionic species in solution. Results are given in Tables 3 and 4. Experiments described in Table 3 show the influence of the different components on the conductivity values. We have found that *trans*-$[PtClH(PPh_3)_2]$ dissolved in $CHCl_3$ exhibits a very low conductivity which does not increase by adding primary or tertiary alkyl alcohols [examples (*i*) and (*ii*)]. However, the conductivity of the solution increases drastically by adding NEt_2H [example (*ii*)]. From examples (*iii*) and (*iv*) we can see that this high conductivity value is not due to an acid–base type reaction between amine and alcohol or acetyl-

Table 4. Conductivity measurements. Influence of the dielectric constant ε of various alcohols R–OH on the specific conductivity κ of the reaction mixtures

		κ/μS						
				(C) [c]		(D) [d]		
R	ε_{R-OH}	(A) [a]	(B) [b]	$t = 0$	$t = 24$ h	$t = 0$	$t = 24$ h	$t = 48$ h
Me	32.63	98.4	76.5	22.9	88.3	7.3	45.7	43.2 [e]
CH_2Me	24.30	29.9	21.4	2.9	16.2	0.7	3.4	4.7 [e]
$(CH_2)_2Me$	20.10	9.8	6.2	0.8	3.5	0.3	0.8	1.0
$(CH_2)_2CHMe_2$	14.70	1.1	0.2	0.2	0.3	0.1	0.1	0.2
CMe_3	10.90	0.6	0.1	0.2	0.2	0.1	0.1	0.1 [f]

[a] $[NEt_3Ph]Cl$ (2.65 × 10^{-3} mol dm^{-3}) in $CHCl_3$ (κ = 0.40 μS cm^{-1}), diluted 1 : 1 with ROH; final concentration of solution = 1.325 × 10^{-3} mol dm^{-3}. [b] $[NEt_3Ph]Cl$ (1.325 × 10^{-3} mol dm^{-3}) in mixtures C_6H_6–ROH (1 : 1). [c] $[PtClH(PPh_3)_2]$ (2.65 × 10^{-3} mol dm^{-3}) in C_6H_6 (κ = 0.1 μS cm^{-1}) + NEt_2H (0.5 cm^3) and $HC\equiv C{-}CMe_2OH$ (0.5 cm^3) (κ = 0.1 μS cm^{-1}), diluted 1 : 1 with ROH. All the mixtures have given the mono-hydrido acetylides. [d] $[PtClH(PPh_3)_2]$ (2.65 × 10^{-3} mol dm^{-3}) in C_6H_6 + $HC\equiv C{-}CMe_2OH$ (0.5 cm^3) (κ = 0.1 μS) cm^{-1}, diluted 1 : 1 with ROH. [e] Reaction products $[PtCl\{C\equiv C{-}CMe_2(OR)\}(PPh_3)_2]$. [f] Reaction product $[PtCl\{C\equiv C{-}CMe{=}CH_2\}(PPh_3)_2]$.

Table 5. Fractional atomic co-ordinates ($\times 10^4$) for $[PtH\{C{\equiv}C{-}C(OH)MeEt\}(PPh_3)_2]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt	1 832(0)	979(0)	2 170(1)	C(44)	−1 812(6)	431(5)	3 078(14)
P(1)	3 115(2)	635(2)	3 242(4)	C(45)	−1 090(6)	163(5)	2 764(14)
P(2)	465(3)	1 247(2)	1 322(5)	C(46)	−405(6)	415(5)	2 249(14)
C(11)	3 320(7)	731(4)	5 278(9)	C(51)	328(9)	1 913(4)	1 767(14)
C(12)	4 161(7)	705(4)	6 065(9)	C(52)	775(9)	2 090(4)	3 119(14)
C(13)	4 303(7)	783(4)	7 608(9)	C(53)	673(9)	2 587(4)	3 545(14)
C(14)	3 604(7)	887(4)	8 365(9)	C(54)	125(9)	2 907(4)	2 619(14)
C(15)	2 764(7)	913(4)	7 578(9)	C(55)	−322(9)	2 730(4)	1 267(14)
C(16)	2 622(7)	835(4)	6 034(9)	C(56)	−220(9)	2 234(4)	841(14)
C(21)	4 134(6)	844(4)	2 604(12)	C(61)	170(9)	1 190(6)	−689(11)
C(22)	4 326(6)	1 355(4)	2 688(12)	C(62)	656(9)	1 458(6)	−1 601(11)
C(23)	5 104(6)	1 530(4)	2 288(12)	C(63)	475(9)	1 410(6)	−3 153(11)
C(24)	5 690(6)	1 194(4)	1 803(12)	C(64)	−191(9)	1 093(6)	−3 794(11)
C(25)	5 498(6)	683(4)	1 719(12)	C(65)	−677(9)	825(6)	−2 882(11)
C(26)	4 720(6)	508(4)	2 119(12)	C(66)	−497(9)	874(6)	−1 330(11)
C(31)	3 116(7)	−46(3)	2 949(13)	O(1)	1 955(20)	2 802(12)	95(33)
C(32)	3 445(7)	−381(3)	4 079(12)	C(1)	2 321(9)	1 553(3)	1 372(15)
C(33)	3 459(7)	−893(3)	3 779(13)	C(2)	2 510(13)	1 960(4)	814(22)
C(34)	3 144(7)	−1 071(3)	2 349(13)	C(3)	2 674(38)	2 425(10)	−194(38)
C(35)	2 816(7)	−736(3)	1 220(13)	C(4)	3 448(42)	2 682(24)	447(54)
C(36)	2 802(7)	−224(3)	1 520(13)	C(5)	3 224(25)	2 795(15)	2 006(48)
C(41)	−443(6)	933(5)	2 048(14)	C(6)	2 564(23)	2 436(13)	−1 985(38)
C(42)	−1 165(6)	1 200(5)	2 362(14)	H	1 491	308	2 831
C(43)	−1 850(6)	949(5)	2 876(14)				

ene. Thus it seems that a strongly co-ordinating ligand like NEt_2H is necessary to displace the chlorine atom from the co-ordination sphere giving an ionic species, $[PtH(NEt_2H)(PPh_3)_2]^+Cl^-$, which leads then to the formation of the hydrido acetylide complex.

Different alcohols of different dielectric constants have a great influence on the κ values, as shown in Table 4. Measurements performed on solutions of $[NEt_3Ph]Cl$ in $CHCl_3$ (or C_6H_6) with ROH [(A) and (B) in Table 4] exhibit the same trend as the experiments on the reaction mixture [Table 4, (C)]. A primary alcohol of high dielectric constant is essential to demonstrate the presence of an ionic species, but the formation of hydrides takes place even when cationic intermediates are not detectable [Table 3, example (*i*)]. The polarity of the solvent then does not seem to have a determining role on the reaction pathway. The final values of κ in the mixtures containing diethylamine are probably due to the formation of $NEt_2H{\cdot}HCl$ as a side-product.

Similar conductivity measurements have been performed on analogous reaction mixtures in the absence of NEt_2H [Table 4, (D)], that is, on solutions from which the chloroalkynyl ether or the chloroalkenylalkynyl complexes have been previously obtained.[2,3] Even if, in lower concentration, cationic species seem to be present, their amount increases with time and can be demonstrated only in the mixtures containing MeOH or EtOH, the alcohols having higher dielectric constants. The cationic species in such conditions are probably formed through π co-ordination of acetylene to platinum with the consequent displacement of the chlorine atom from the co-ordination sphere giving $[PtH(HC{\equiv}CR)(PPh_3)_2]^+Cl^-$.[19,20] The acetylenic alcohol, π co-ordinated on the positively charged platinum atoms, undergoes the intramolecular or intermolecular dehydration reactions leading to the complexes of the alkynyl ethers or to the alkenylalkynyl compounds [Table 4, (D); R = Me, CH_2Me, or $(CH_2)_2CHMe_2$].

The final reaction products are then interpretable in terms of intramolecular rearrangements of the cationic intermediate and nucleophilic addition of the primary alcohol to the co-ordinated acetylene.

Further investigations on similar systems are in progress.

Experimental

Preparations.—All chemicals and solvents were reagent grade and were used without purification. The compound *trans*-$[PtClH(PPh_3)_2]$ was prepared according to standard literature methods.[24] The compounds *trans*-$[PtH(C{\equiv}CR)(PPh_3)_2]$ were prepared according to the following procedure: 500 mg of $[PtClH(PPh_3)_2]$ (6.6×10^{-4} mol) was refluxed in $CHCl_3$ (20 cm^3) with NEt_2H (0.5 cm^3) and $HC{\equiv}CR$ (0.5 cm^3). The reaction time was 10 min for R = CH_2OH, CH(OH)Me, CH(OH)Ph, $CMe{=}CH_2$, and Ph; 20 min for R = C(OH)MeEt; and 30 min for R = $C_6H_{10}OH$ and $C(OH)Me_2$. The products were obtained by addition of MeOH (30 cm^3) and purified by recrystallization from $CHCl_3$–MeOH (1 : 2).

Elemental analysis and physical properties are reported in Table 1.

Measurements.—Electronic spectra were recorded on a Beckman DK 2A spectrophotometer, i.r. spectra were run on a Perkin-Elmer model 580-B spectrometer as Nujol mulls, and n.m.r. spectra were recorded on a Bruker WH-90 in $CDCl_3$ solutions with $SiMe_4$ as internal standard.

Elemental analyses were carried out by the Laboratorio di Microanalisi, Istituto di Chimica Farmaceutica, Pisa.

Conductivity measurements were performed with a Digi-1 model conductivity meter with a cell of constant $k = 0.9626$.

Data Collection, Structure Determination, and Refinement of $[PtH\{C{\equiv}C{-}C(OH)MeEt\}(PPh_3)_2]$.—Preliminary photographs indicated the crystals to be monoclinic. Data were collected from a crystal of dimensions 0.08 × 0.42 × 0.69 mm on an 'on-line' Siemens AED single-crystal diffractometer using Mo-K_α radiation ($\lambda = 0.710\,69$ Å). The unit-cell parameters were obtained by a least-squares refinement of the 2θ values of 20 reflections having $2\theta > 30°$.

Crystal data. $C_{42}H_{40}OP_2Pt$, $M = 817.8$, Monoclinic, $a = 15.560(3)$, $b = 26.696(5)$, $c = 9.038(2)$ Å, $\beta = 98.51(2)°$, $U = 3\,713(1)$ Å^3, $D_m = 1.50$, $Z = 4$, $D_c = 1.463$ g cm^{-3}, $F(000) = 1\,632$, $\mu(\text{Mo-}K_\alpha) = 39.3$ cm^{-1}, space group $P2_1/n$ (from systematic absences), a non-standard setting of C^5_{2h}

Table 6. Selected bond distances (Å) and angles (°) for [PtH{C≡C-C(OH)MeEt}$(PPh_3)_2$]

Pt-C(1)	1.90(1)	C(1)-C(2)	1.25(2)	P(1)-C(11)	1.84(1)
Pt-P(1)	2.279(4)	C(2)-C(3)	1.58(4)	P(1)-C(21)	1.85(1)
Pt-P(2)	2.267(5)	C(3)-O(1)	1.55(6)	P(1)-C(31)	1.84(1)
Pt-H	1.98	C(3)-C(6)	1.60(5)	P(2)-C(41)	1.84(1)
		C(3)-C(4)	1.43(8)	P(2)-C(51)	1.84(1)
		C(4)-C(5)	1.53(7)	P(2)-C(61)	1.81(1)

C(1)-Pt-P(1)	96.4(4)	C(2)-C(3)-O(1)	103(3)
C(1)-Pt-P(2)	91.5(3)	C(2)-C(3)-C(6)	126(3)
P(1)-Pt-P(2)	171.8(2)	C(2)-C(3)-C(4)	110(3)
P(1)-Pt-H	76.4	O(1)-C(3)-C(6)	101(3)
P(2)-Pt-H	96.2	O(1)-C(3)-C(4)	102(3)
C(1)-Pt-H	169.1	C(4)-C(3)-C(6)	111(4)
Pt-C(1)-C(2)	170(1)	C(3)-C(4)-C(5)	100(4)
C(1)-C(2)-C(3)	169(2)		

Pt-P(1)-C(11)	112.4(4)	Pt-P(2)-C(41)	117.8(5)
Pt-P(1)-C(21)	118.9(4)	Pt-P(2)-C(51)	111.3(5)
Pt-P(1)-C(31)	110.9(4)	Pt-P(2)-C(61)	113.4(5)
C(11)-P(1)-C(21)	103.9(5)	C(41)-P(2)-C(51)	104.0(6)
C(11)-P(1)-C(31)	106.2(5)	C(41)-P(2)-C(61)	103.0(6)
C(21)-P(1)-C(31)	103.6(5)	C(51)-P(2)-C(61)	106.2(6)

(no. 14). Co-ordinates of equivalent positions are: x,y,z; $\bar{x},\bar{y},\bar{z}$); $\frac{1}{2} - x,\frac{1}{2} + y, \frac{1}{2} - z$; $\frac{1}{2} + x,\frac{1}{2} - y,\frac{1}{2} + z$.

Intensities were recorded at room temperature by the θ—2θ scan method in the range $5 < 2\theta < 50°$. No crystal decay was observed in the standard reflection monitored over the course of the experiment. Cor rection was made for Lorentz and polarization effects, but not for *X*-ray absorption. Refinement was carried out with 3 855 independent reflections for which $I > 2.0\sigma(I)$ (unique total data = 6 449).

The structure was solved by heavy-atom methods. The structure was refined by blocked full-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms except for those of the organic ligand which was found to be affected by disorder (or high thermal motion). This was the most satisfactory model obtained after several unsuccessful attempts to interpret the disorder in terms of ' partial ' atoms or to allow the disordered atoms to vary anisotropically. The accuracy of bond distances and angles involved is therefore rather low. Refinement converged at $R = 0.067$ ($R' = 0.070$). Phenyl rings were treated as rigid regular hexagons. Weights were applied according to the scheme $w = [\sigma^2(F_o) + 0.002(F_o)^2]^{-1}$ and this gave a satisfactory analysis of variance, $\Sigma w\Delta^2$ *versus* $|F|$, sin θ, and indices. A final electron-density difference synthesis showed no peaks >0.8 or < -0.6 e Å^{-3}, except in the immediate vicinity of the Pt atom. Excluding these peaks, the largest residual feature on the final difference map was a peak identifiable as the missing hydrido-ligand at a distance 1.98 Å from the Pt atom at the fourth co-ordination site of Pt. No other hydrogen atoms could be located. The hydrido-ligand was introduced in calculations with isotropic $U = 0.08$ Å^2 and not refined. Atomic scattering factors for hydrogen were taken from ref. 25 and complex neutral-atom scattering factors were used for all other atoms.[26]

Computations were carried out on the CYBER 7600 of the Consorzio Interuniversitario dell'Italia Nord-Orientale [Casalecchio with financial support from the University of Parma. SHELX system of programs was used.[27] The final atomic co-ordinates are given in Table 5 and selected bond distances and angles in Table 6.

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