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TRANSITION METAL—CARBON BONDS

XXXVII*. PLATINUM ACETYLIDE COMPLEXES FORMED FROM ETHYNYL ALCOHOLS OR ETHERS

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Summary

Several new platinum(II) acetylide complexes, *trans*-{Pt[C≡CCR$_1$R$_2$(OR$_3$)]$_2$-L$_2$} (R$_1$, R$_2$ = H, Me, Et; CR$_1$R$_2$ = cyclohexylidene; R$_3$ = H, Me or Ph), *trans*-[Pt(C=CCH$_2$CH$_2$OH)$_2$L$_2$], *trans*-[Pt(*p*-tolylacetylide)$_2$L$_2$] and *trans*-[PtX(*p*-tolylacetylide)L$_2$] (L = PMe$_2$Ph or in one case, AsMe$_2$Ph) have been prepared. Platinum(II) acetylide complexes with tertiary hydroxyl groups are easily dehydrated by acetic anhydride/pyridine to give platinum-enyne complexes. Analogous compounds with primary hydroxyl groups do not dehydrate but give acetates. ^{1}H and ^{13}C NMR data are given and the shift reagent Eu(fod)$_3$ was used to analyse the ^{1}H NMR spectrum of *trans*-[Pt(C≡CCH$_2$CH$_2$OH)$_2$(PMe$_2$Ph)$_2$].

Introduction

Several platinum(II) acetylides of the type *trans*-[Pt(C≡CH)$_2$L$_2$] (R = alkyl or aryl; L = tertiary phosphine) are known and have been prepared by methods such as treating PtCl$_2$L$_2$ with either an alkynyl magnesium halide in ether or with the sodio-derivative of the acetylene in liquid ammonia [2]. Other methods have been used; e.g., *trans*-[Pt(C≡CPh)$_2$(P-n-Pr$_3$)$_2$] is formed from *cis*-[PtCl$_2$-(P-n-Pr$_3$)$_2$] by treating it with phenylacetylene and hydrazine [3]. Monoacetylides of the type *trans*-[PtCl(C≡CR)L$_2$] have also been prepared [4,5].

In all the above-mentioned compounds the acetylide ligand is a purely hydrocarbon radical and very few platinum complexes containing a functionally substituted acetylide ligand have been prepared. However, 2-methyl-3-butyn-2-ol reacts with *cis*-[PtCl$_2$(PPh$_3$)$_2$] in the absence of base to give a monoacetylide, *trans*-{PtCl[C≡CCMe$_2$(OH)](PPh$_3$)$_2$}, whilst in the presence of ammonia the diacetylide *trans*-{Pt[C≡CCMe$_2$(OH)]$_2$(PPh$_3$)$_2$} forms [6]; in the presence

* For part XXXVI see ref. 1.

of sodium hydroxide the corresponding *cis*-diacetylide is formed. It was reported in the same paper [6] that attempts to prepare these mono- or di-acetylides by treating *cis*-$[PtCl_2(PPh_3)_2]$ with the sodio-derivative of the hydroxyacetylene in liquid ammonia were unsuccessful (but see our results below). A remarkable platinum(IV) acetylide hydride complex $\{PtH_2[C{\equiv}C(C_6H_{10})(OH)]_2(PPh_3)_2\}$ is formed when $[Pt(PPh_3)_4]$ is treated with ethynylcyclohexanol [7,8]. In other cases μ-bonded Pt^0 acetylene complexes $\{Pt[HC{\equiv}CC(OH)R_1R_2](PPh_3)_2\}$ are formed.

In this paper we describe the preparation and properties of a range of platinum(II) acetylide complexes $\{Pt[C{\equiv}CCR_1R_2(OR_3)]_2L_2\}$ (L = PMe_2Ph or, in one case, $AsMe_2Ph$); these are mainly alcohols (R_3 = H) but a few ethers with R_3 = Me, or Ph have also been prepared. Dimethylphenylphosphine was chosen as stabilizing ligand because its ^1H NMR resonance pattern is very useful in assigning stereochemistry.

Results and discussion

We have prepared the complexes *trans*-$[Pt(C{\equiv}CR)_2(PMe_2Ph)_2]$ [R = $CR_1R_2(OR_3)$] by three methods (see Experimental for details):

(1). By treating *cis*-$[PtCl_2(PMe_2Ph)_2]$ with the sodio-derivative of the acetylene in liquid ammonia [formed in situ from the acetylene and sodamide (1 mol)]. Previously it had been reported that this method was unsuccessful for the preparation of $\{Pt[C{\equiv}CC(OH)Me_2]_2(PPh_3)_2\}$ [6].

(2). By refluxing the acetylene and *cis*-$[PtCl_2(PMe_2Ph)_2]$ in ethanol in the presence of hydrazine hydrate.

(3). By refluxing the acetylene and *cis*-$[PtCl_2(PMe_2Ph)_2]$ in ethanol in the presence of 880 ammonia.

Method 1 was suitable for several tertiary ethynyl alcohols, for but-3-yn-1-ol and for $HC{\equiv}CCH_2OMe$ and $HC{\equiv}CCH_2OPh$ but it gave an oil for $HC{\equiv}CCH_2OH$. Methods 2 and 3 were suitable for $HC{\equiv}CCH_2OH$ and its methyl or phenyl ethers but gave mixtures with tertiary ethynyl alcohols. Possibly tertiary alcohols underwent partial dehydration whilst being refluxed in the presence of base to give 'enynes'. Secondary ethynyl alcohols, $HC{\equiv}CCH(Me)(OH)$ or $HC{\equiv}CCH(Ph)(OH)$, did not give solid products, probably because they contain asymmetric centres. We have also prepared *trans*-[Pt(*p*-tolylacetylide)$_2$(PMe_2Ph)$_2$] by all three methods and the monoacetylide, *trans*-[PtCl(*p*-tolylacetylide)(PMe_2Ph)$_2$] in 70% yield by refluxing *cis*-$[PtCl_2(PMe_2Ph)_2]$ with an excess of *p*-tolylacetylene in ethanol containing hydrazine hydrate (one mol per platinum atom). The dimethylphenylarsine complex $[Pt(C{\equiv}CCMe_2OH)_2(AsMe_2Ph)_2]$ was also prepared by method 1 but it was rather unstable and its solutions tended to smell of free dimethylphenylarsine.

The new complexes are shown in Table 1 together with microanalytical and other data. They were characterized by IR and ^1H NMR spectroscopy (Table 2) and in two cases by ^{13}C NMR spectroscopy (Table 3).

Our acetylide complexes prepared from hydroxyacetylenes showed two absorption bands due to O—H stretch: a sharp band 3590-3600 cm^{-1} due to ν(OH) (free) and a weaker broader band 3410-3490 cm^{-1} assigned to ν(OH) where the OH is interacting either with the platinum or with another OH group

TABLE 1

PERCENTAGE YIELD, COLOUR, MELTING POINT, AND ANALYTICAL DATA FOR SOME PLATINUM ACETYLIDES

Complex[a]	Colour	M.p. (°C)	Analytical data found (calcd.) (%)	
			C	H
$Pt(C{\equiv}CCH_2OH)_2L_2$	White	172-174	45.45 (45.45)	4.85 (4.75)
$Pt(C{\equiv}CCH_2OMe)_2L_2$	White	103-106	47.6 (47.3)	5.4 (5.30)
$Pt(C{\equiv}CCH_2OPh)_2L_2$	White	148-149	55.8 (55.65)	5.1 (4.95)
$Pt(C{\equiv}CCH_2CH_2OH)_2L_2$	White	132-134	47.3 (47.3)	5.5 (5.30)
$Pt[C{\equiv}CCMe_2(OH)]_2L_2$	White	158-161	48.7 (49.0)	5.65 (5.70)
$Pt[C{\equiv}CCMe_2(OH)]_2L'_2$	White	158-160	43.4 (43.05)	5.05 (5.00)
$Pd[C{\equiv}CCMe_2(OH)]_2L_2$	White	109-110	56.7 (56.9)	6.6 (6.60)
$Pt[C{\equiv}CC(Et)(Me)(OH)]_2L_2$	White	147-149	50.7 (50.5)	6.1 (6.05)
$Pt[C{\equiv}CC_6H_{10}(OH)]_2L_2$	White	184-187	53.8 (53.55)	6.1 (6.20)
$Pt[C{\equiv}CC(CH_3){=}CH_2]_2L_2$	Yellow	138-140	51.4 (51.9)	5.05 (5.35)
$Pt[C{\equiv}CC(Et){=}CH_2]_2L_2$	Yellow	95-99	53.45 (53.4)	5.9 (5.75)
$Pt[C{\equiv}CC(CH_3){=}CHCH_3]_2L_2$				
$Pt(C{\equiv}CCH_2CH_2OCOCH_3]_2L_2$	White	159-162	48.45 (48.5)	5.25 (5.25)
$Pt(C{\equiv}CCH_2OCOCH_3)_2L_2$	White	131-136	47.15 (46.9)	4.95 (4.85)

[a] L = PMe_2Ph, L' = $AsMe_2Ph$.

(hydrogen bonding). To distinguish between these possibilities the IR absorption spectra were measured in chloroform solution at one concentration and then again at half the concentration and twice the pathlength: the sharp peak 3590-3600 cm^{-1} increased in intensity and the broader peak 3410-3490 cm^{-1} decreased. This concentration dependence strongly suggests that the OH interaction assuming the peak at lower frequency is intermolecular i.e. it is very probably caused by hydrogen bonding with another OH group. The complex $Pt[C{\equiv}CCMe_2(OH)]_2(AsMe_2Ph)_2$ showed both a broad IR absorption band due to ν(OH) (hydrogen bonded) and a sharp band due to ν(OH) (free) as a Nujol mull but only the band due to ν(OH) (free) in chloroform solution.

All the PMe_2Ph complexes showed one ^1H NMR triplet pattern due to the phosphorus methyls, indicating *trans*-phosphines. The ranges of values are τ7.98-8.14, $|^2J(P{-}H) + {}^4J(P{-}H)| = 7.2\text{-}7.5$ and $^3J(Pt{-}H) = 23.4\text{-}33$ Hz. The hydroxyl resonance for the complexed acetylide is found at higher field in the ^1H NMR spectrum than the free acetylene, i.e. in the range τ8.1-8.8, seemingly indicating less association of the hydroxyl groups in the complex than in the free

TABLE 2

IR (cm^{-1}) AND ^1H NMR DATA[a] FOR THE HYDROXYACETYLIDE AND ETHER ACETYLIDE COMPLEXES

	IR absorption ($CHCl_3$) (cm^{-1})			τ (ppm)	J (Hz)	Assignment
	ν(C≡C)	Free ν(OH)	H-bonded ν(OH)			
$Pt(C{\equiv}CCH_2OH)_2L_2$	2120	3600	3450	5.84s	^4J(Pt—H) = 11.5	CH_2
					^5J(Pt—H) = 1.6	OH
				8.80s[b]		OH
$Pt(C{\equiv}CCH_2CH_2OH)_2L_2$	2110		3520	7.6tt	^3J(H—H) = 5.9	$CH_2C{\equiv}C$
					^4J(Pt—H) = 13.5	
				6.6dt	^3J(H—H) = 5.9	CH_2OH
					$^3J(CH_2—OH)$ = 5.3	
$Pt[(C{\equiv}CCMe_2(OH)]_2L_2$	2120	3590	3440	8.10t	$^3J(HO—CH_2)$ = 5.3	OH
				8.64s		CH_3
$Pt[C{\equiv}CCMe_2(OH)]_2L'_2$	2110	3590	[c]	8.38s		OH
				8.66s		CH_3
$Pt[C{\equiv}C(Me)(Et)(OH)]_2L_2$	2120	3590	3410	8.66s		CH_3
				8.6m		CH_2CH_3
				8.48s		OH
$Pt[C{\equiv}CC_6H_{10}(OH)]_2L_2$	2110	3590	3450vw	8.40s		OH
				8.42m		CH_2
$Pt(C{\equiv}CCH_2OMe)_2L_2$	2110			5.92s	^4J(Pt—H) = 12.4	CH_2
				6.82s		OMe
$Pt(C{\equiv}CCH_2OPh)_2L_2$	2115			2.96m		OPh
				5.82s	^4J(Pt—H) = 11.7	CH_2

[a] In $CDCl_3$ at 60 MHz unless stated otherwise, τ-values ± 0.02, J values ±0.1 Hz, s = singlet, d = doublet, t = triplet. [b] At 90 MHz τ-values ± 0.01, J values ± 0.1 Hz, tt = triplet of triplets, dt = doublet of triplets. [c] In Nujol mull peaks at 3460 and 3590 cm^{-1}.

TABLE 3

^{13}C NMR DATA[a] FOR $HC{\equiv}CCMe_2(OH)$ AND *trans*-$Pt[C{\equiv}CCMe_2(OH)]_2(EMe_2Ph)_2$ (E = P, or As)

	E = P	E = As	$HC{\equiv}CCMe_2(OH)$
$^1J(^{195}Pt—^{13}C)$	892	915	
$\delta(Pt—^{13}C)$	97.2	90.9	70.3
$^2J(^{31}P—Pt—^{13}C)$	14.9		
$^2J(^{195}Pt—C{\equiv}^{13}C)$	255	252	
$\delta(Pt—C{\equiv}^{13}C)$	113.9	116.2	89.0
$^3J(^{195}Pt—C{\equiv}C—^{13}C)$	20.6	20.6	
$\delta(Pt—C{\equiv}C—^{13}C)$	66.6	66.6	64.8
$\delta[Pt—C{\equiv}CC(^{13}CH_3)_2OH]$	32.4	32.6	31.2
$\lvert^1J(^{31}P—^{13}C) + {}^3J(^{31}P—^{13}C)\rvert$	41.2		
$\delta[E—CH_3]$	14.6	10.7	
$\delta(P—^{13}C)$[b]	132		
$\lvert^2J(^{31}P—o-^{13}C) + {}^4J(^{31}P—o-^{13}C)\rvert$	10.3		
$\delta(o—^{13}C)$	131.8	132.1	
$\lvert^3J(^{31}P—m-^{13}C) + {}^5J(^{31}P—m-^{13}C)\rvert$	10.4		
$\delta(m—^{13}C)$	128.2	129.0	
$\lvert^4J(^{31}P—p-^{13}C) + {}^6J(^{31}P—p-^{13}C)\rvert$	≃0		
$\delta(p—^{13}C)$	130.1	130.3	

[a] In deuteriochloroform, at 22.62 MHz. Shifts with respect to $SiMe_4$. J values ± 1.5 Hz, δ values ± 0.1 ppm. [b] Resonance obscured by $o—^{13}C$ resonance, therefore ^1J(P—C) could not be measured.

ligand. This is a similar result to that reported for platinum(0) hydroxyacetylene complexes [7], in which the OH resonance is also shifted upfield relative to the free ligand.

In the ^{1}H NMR spectra of complexes of the type *trans*-[Pt(C≡CCH$_2$OR)$_2$-(PMe$_2$Ph)$_2$] (where R = H, Me or Ph), platinum(195) coupling to the methylene group of from 11.5 to 12.4 Hz is found. The phosphorus coupling with the methylene group in *trans*-[Pt(C≡CCH$_2$OH)$_2$(PMe$_2$Ph)$_2$] cannot be seen due to broadening of the resonance by coupling to the OH. However, on addition of CF_3CO_2H (0.02 mol per Pt atom) the resonance sharpens up considerably allowing the phosphorus coupling to be measured. The resonance appears as a triplet indicating equal coupling to both phosphorus atoms, J(P—H) = 1.6 Hz. The corresponding coupling for the complexes *trans*-[Pt(C≡CCH$_2$OMe)$_2$(PMe$_2$Ph)$_2$] and *trans*-[Pt(C≡CCH$_2$OPh)$_2$(PMe$_2$Ph)$_2$] was not observed. In the tertiary alcohol complexes of the type *trans*-{Pt[C≡CCR$_1$R$_2$(OH)]$_2$(PMe$_2$Ph)$_2$} (where R = alkyl), platinum coupling to the R groups was not observed. For the complex *trans*-[Pt(C≡CCH$_2$CH$_2$OH)$_2$(PMe$_2$Ph)$_2$] the methylene group resonance adjacent to the triple bond, and the hydroxyl resonance were both obscured by the P—Me resonances. The effect of the addition of Eu(fod)$_3$ on the 60 MHz ^{1}H NMR spectrum of *trans*-[Pt(C≡CCH$_2$CH$_2$OH)$_2$(PMe$_2$Ph)$_2$] was therefore studied. The chemical shift of the methylene and hydroxyl protons decreased linearly with the amount of Eu(fod)$_3$ added, in the range R = 0 to 0.1, where R = moles Eu(fod)$_3$/moles Pt complex. The changes in shift are OH > CH$_2$OH > C≡CCH$_2$. With R = 0.01 and 0.1 M platinum complex the shifts are 58, 13.2 and 8.4 Hz respectively. The free alcohol HC≡CCH$_2$CH$_2$OH showed virtually the same shifts at this concentration i.e. 0.1 M, R = 0.01. The position of the OH resonance in the free complex is calculated to be τ8.10 by extrapolation. Changes in the chemical shift values for the PMe$_2$Ph ligands were less than for the acetylide ligand. With R = 0.2 and a complex concentration of 0.2 M the PMe shifts downfield 60 Hz the *o*-hydrogens downfield 62 Hz and the *m*- or *p*-hydrogens downfield by 17 Hz.

We have also compared ^{13}C NMR data for the two complexes *trans*-{Pt-[C≡CCMe$_2$(OH)$_2$]L$_2$} (L = PMe$_2$Ph or AsMe$_2$Ph). The data are shown in Table 3 together with those for H≡CCMe$_2$OH.

The $^1J(^{195}\text{Pt—C})$ value of 892 Hz for *trans*-{Pt[C≡CCMe$_2$(OH)]$_2$(PMe$_2$Ph)$_2$} is considerably higher than the corresponding value for *trans*-[PtPh$_2$(PEt$_3$)$_2$] which is 594 Hz [8]. The increase is probably mainly due to a change from sp^2 to *sp* hybridized carbon. The ^1J(Pt—C) value increases on replacing phosphorus by arsenic from 892 to 915 Hz. This reflects a greater Pt—C bond strength for the arsine complex [9]. J(Pt—C) decreases greatly on moving along the carbon chain in the acetylide i.e. ^1J(Pt—C) = 892, ^2J(Pt—C) = 255 and ^3J(Pt—C) = 20.6 Hz (see Table 3).

The complex *trans*-{Pt[C≡CCMe$_2$(OH)$_2$]$_2$(PMe$_2$Ph)$_2$} is dehydrated easily to the yellow complex *trans*-{Pt[C≡CC(Me)=CH$_2$]$_2$(PMe$_2$Ph)$_2$} by refluxing it for 5 min in acetic anhydride containing a small amount of pyridine. The IR spectrum of the complex shows two peaks attributable to the triple bond at 2110 and 2080 cm^{-1}, both in a Nujol mull and in benzene solution (Table 4). This is similar to the IR spectrum reported for the complex *trans*-[Pt(C≡CCH=CH$_2$)$_2$(PEt$_3$)$_2$] [10] which shows peaks at 2100 and 1985 cm^{-1} due to the triple

TABLE 4

IR (± 2 cm^{-1}) AND ^1H NMR DATA[a] FOR THE ENYNE AND ACETYLIDE ACETATE COMPLEXES

	IR absorption (cm^{-1})			τ (ppm)	J (Hz)	Assignment
	ν(C≡C)	ν(C=C)	ν(C=O)			
$Pt[C{\equiv}CC(Me){=}CH_2]_2L_2$	2110	1600		5.05s		CH_2
	2080			8.13s		CH_3
$Pt[C{\equiv}CC(Me){=}CHCH_3]_2L_2$[b]	2092	1598		4.69	J(H—H) = 6.4	$CHCH_3$
				5.17s		CH_2
$Pt[C{\equiv}CC(Et){=}CH_2]_2L_2$[b]				8.39m		Me and Et
$Pt(C{\equiv}CCH_2OAc)_2L_2$	2130		1740	5.40t	J(P—H) = 3.4	CH_2
					J(Pt—H) = 13	
				8.06s		Ac
$Pt(C{\equiv}CCH_2CH_2OAc)_2L_2$	2115		1730	6.08t	J(H—H) = 7.1	CH_2OAc
				7.55	J(P—H) = 3	$CH_2C{\equiv}C$
					J(H—H) = 7	
					J(Pt—H) = 13.5	
				8.08s		Ac

[a] In deuteriochloroform at 60 MHz (see Table 2). [b] In deuteriochloroform at 90 MHz (see Table 2).

bond. The spectrum also contains a strong absorption at 1600 cm^{-1} due to the double bond.

In the ^1H NMR spectrum the 'enyne' methyl resonance appears as a singlet at τ8.13 (Table 4). A broad singlet due to the vinyl protons is seen at τ5.05. This broadness is probably due to a small coupling with the methyl group, and possibly due to coupling to platinum(195). In the case of *trans*-{$Pt[C{\equiv}CC(Et)(Me)(OH)]_2(PMe_2Ph)_2$} dehydration gives a mixture of complexes with a ca. 1/1 proportion of the two groups C(Me) = CHMe and C(Et) = CH_2. The ^1H NMR patterns of these two groups show a quartet at τ4.69, integrating for one proton, and a broad singlet integrating for two protons at τ5.17. These resonances are assigned to the respective vinylic protons.

The complex *trans*-{$Pt[C{\equiv}CC(CH_3){=}CH_2]_2(PMe_2Ph)_2$} was further characterised by its UV absorption spectrum in ethanol with λ_{max} ($\log_{10}\epsilon$) of 222(4.61), 238(4.56), 282(4.18), 321(4.30) nm. The absorptions at 222 and 238 nm are attributed mainly to the organic ligand (cf. $HC{\equiv}CC(CH_3){=}CH_2$ where λ_{max} = 222 and 236 nm in ethanol).

The complex *trans*-{$Pt[C{\equiv}CC(CH_3){=}CH_2]_2(PMe_2Ph)_2$} was also prepared by treating *cis*-$[PtCl_2(PMe_2Ph)_2]$ with 2-methyl-3-butenyne, in alcoholic solution in the presence of 880 ammonia (see Experimental for details).

The acetylides containing primary hydroxyl groups, *trans*-$[Pt(C{\equiv}CCH_2OH)_2(PMe_2Ph)_2]$ and *trans*-$Pt(C{\equiv}CCH_2CH_2OH)_2(PMe_2Ph)_2]$ react with acetic anhydride under the same conditions as tertiary alcohols to give the corresponding acetate. The ^1H NMR and IR data for the complexes are recorded in Table 4.

Experimental

Meltings points were determined on a Kofler hot-stage microscope apparatus and are corrected. ^1H NMR spectra were recorded on a Perkin—Elmer R12

60 MHz spectrometer or Bruker HFX 90 MHz spectrometer and ^{13}C spectra at 22.62 MHz also on the Bruker HFX spectrometer. Infrared spectra were recorded on a Perkin—Elmer Model 457 spectrometer (4000-250 cm^{-1}) or Grubb—Parsons D.B.3/D.N.2 spectrometer (500-200 cm^{-1}).

Preparation of platinum acetylides using the sodio-derivatives of the acetylenes in liquid ammonia

trans-{*Pt*[*C*≡*CCMe*$_2$*(OH)*]$_2$*(PMe*$_2$*Ph)*$_2$}. Sodamide in liquid ammonia was prepared from sodium (0.30 g, 13.1 mmol) and liquid ammonia (20 ml) in the presence of hydrated ferric nitrate (ca. 10 mg). 2-Methyl-3-butyn-2-ol (1.32 g, 15.66 mmol) was added followed by *cis*-dichlorobis(dimethylphenylphosphine)-platinum(II) and dry ether (5 ml). Stirring was continued for 30 min, ammonium chloride (ca. 1 g) was added and the solution was allowed to warm to room temperature. Extraction with benzene and addition of n-hexane gave white needles of *trans*-{Pt[C≡CCMe$_2$(OH)]$_2$(PMe$_2$Ph)$_2$} (0.83 g, 1.34 mmol, 81%). The following compounds were prepared in a similar manner: *trans*-[Pt(C≡CC$_6$H$_5$)$_2$(PMe$_2$Ph)$_2$] (81%), *trans*-[Pt(C≡CCH$_2$OMe)$_2$(PMe$_2$Ph)$_2$] (64%), *trans*-[Pt(C≡CCH$_2$OPh)$_2$(PMe$_2$Ph)$_2$] (67%), *trans*-{Pt[C≡CC(Me)(Et)(OH)]$_2$-(PMe$_2$Ph)$_2$} (60%), *trans*-{Pt[C≡CC$_6$H$_{10}$(OH)]$_2$(PMe$_2$Ph)$_2$} (72%), *trans*-{Pt[C≡CC-Me$_2$(OH)]$_2$(AsMe$_2$Ph)$_2$} (48%).

Preparation of platinum acetylides using hydrazine hydrate as a base

Preparation of trans-[Pt(C≡*CC*$_6$*H*$_5$*)*$_2$*(PMe*$_2$*Ph)*$_2$*]*. *cis*-Dichlorobis(dimethylphenylphosphine)platinum(II) (0.66 g, 1.18 mmol) was refluxed in ethanol (5 ml) with hydrazine hydrate (0.24 g, 4.72 mmol). After 2 min a yellow solution resulted. Phenylacetylene (0.94 g, 9.44 mmol) was added and refluxing was continued for 30 min. The solution was cooled to —8°C. The yellow needles that precipitated were filtered off, giving *trans*-[Pt(C≡CC$_6$H$_5$)$_2$(PMe$_2$Ph)$_2$] (0.65 g, 0.96 mmol, 81%). The following complexes were prepared in a similar manner: *trans*-[Pt(*p*-tolylacetylide)$_2$(PMe$_2$Ph)$_2$] (46%), *trans*-[Pt(C≡CCH$_2$OH)$_2$(PMe$_2$Ph)$_2$] (63%), *trans*-[Pt(C≡CCH$_2$OMe)$_2$(PMe$_2$Ph)$_2$] (64%). All the above crystallise from benzene/hexane.

Preparation of trans-[PtCl(p-tolylacetylide)(PMe$_2$*Ph)*$_2$*]*. *cis*-Dichlorobis-(dimethylphenylphosphine)platinum(II) (0.50 g, 0.83 mmol) was refluxed in ethanol (5 ml), with hydrazine hydrate (0.042 g, 0.83 mmol). After 2 min a yellow solution resulted. *p*-Tolylacetylene (0.10 g, 0.83 mmol) was added, and refluxing was continued for 30 min. The solution was cooled to —8°C. The white prisms that precipitated were filtered off, giving *trans*-[PtCl(*p*-tolylacetylide)-(PMe$_2$Ph)$_2$] (0.36 g, 0.58 mmol, 70%). It formed white prisms from benzene/hexane.

Reaction of trans-{Pt[C≡*CCMe*$_2$*(OH)]*$_2$*(PMe*$_2$*Ph)*$_2$*} with acetic anhydride*

trans-{Pt[C≡CCMe$_2$(OH)]$_2$(PMe$_2$Ph)$_2$} (0.10 g, 0.16 mmol) was refluxed in acetic anhydride (5 ml), with one drop of pyridine, for 5 min. The resulting yellow solution was allowed to cool to room temperature, and water (4 ml) was added. The yellow solid *trans*-{Pt[C≡CC(CH$_3$)CH$_2$]$_2$(PMe$_2$Ph)$_2$} (0.036 g, 0.060 mmol, 38%) was filtered off and washed three times with water. The complex crystallises as yellow plates from hot hexane.

The mixture of complexes *trans*-{Pt[C≡CC(C_2H_5)=CH_2]$_2$(PMe_2Ph)$_2$} and *trans*-{Pt[C≡CC(CH_3)=$CHCH_3$]$_2$(PMe_2Ph)$_2$} was prepared in the same manner.

Acetylation of trans-[Pt(C≡CCH_2OH)$_2$(PMe_2Ph)$_2$]

trans-[Pt(C≡CCH_2OH)$_2$(PMe_2Ph)$_2$] (0.19 g, 0.32 mmol) was refluxed in acetic anhydride (2 ml) and pyridine (1 drop) for 2 min. The resultant colourless solution was allowed to cool to room temperature and water (4 ml) was added. White solid precipitated, and was filtered off and washed three times with water to give *trans*-{Pt[C≡CCH_2O(CO)CH_3]$_2$(PMe_2Ph)$_2$} (0.16 g, 0.25 mmol, 77%). It formed white prisms from ethanol.

trans-{Pt[C≡CCH_2CH_2O(CO)CH_3]$_2$(PMe_2Ph)$_2$} was prepared in a similar manner.

Preparation of trans-{Pt[C≡CC(CH_3)=CH_2]$_2$(PMe_2Ph)$_2$}

cis-Dichlorobis(dimethylphenylphosphine)platinum(II) (0.30 g, 0.48 mmol) was refluxed in ethanol (3 ml). 880 ammonia (1.5 ml) was added and the mixture was refluxed for a further 5 min. A yellow solution resulted. HC≡CC(CH_3)=CH_2 (0.32 g, 4.80 mmol) was added, and refluxing was continued for 1 h. The yellow solution was allowed to cool to room temperature. Yellow plates of *trans*-{Pt[C≡CC(CH_3)=CH_2]$_2$(PMe_2Ph)$_2$} (0.24 g, 0.40 mmol, 83%) were filtered off. It formed yellow plates from n-hexane.

The following complexes were prepared in a similar manner: *trans*-[PtC≡CC_6H_5)$_2$(PMe_2Ph)$_2$ (81%), *trans*-[Pt(*p*-tolylacetylide)$_2$(PMe_2Ph)$_2$] (75%).

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References

1 J.M. Duff, B.E. Mann, B.L. Shaw and B. Turtle, J. Chem. Soc. Dalton, (1974) 139.
2 J. Chatt and B.L. Shaw, J. Chem. Soc., (1959) 4020.
3 J. Chatt and G.A. Rowe, International Conference on Coordination Chemistry, (1959) 117.
4 I. Collamati and A. Furlani, J. Organometal. Chem., 17 (1969) 457.
5 C.D. Cook and G.S. Jauhal, Can. J. Chem., 45 (1967) 301.
6 A. Furlani, P. Bicev, M.V. Russo and P. Carusi, J. Organometal. Chem., 29 (1971) 321.
7 J.H. Nelson, H.B. Jonassen and D.M. Roundhill, Inorg. Chem., 8 (1969) 2591.
8 D.M. Roundhill and H.B. Jonassen, Chem. Commun., (1968) 1233.
9 M.H. Chisholm, H.C. Clark, L.E. Manzer and J.B. Stothers, J. Amer. Chem. Soc., 94 (1972) 5087.
10 H. Masai, K. Sonogashira and N. Hagihara, J. Organometal. Chem., 26 (1971) 271.