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COMPLEXES OF PLATINUM(II) WITH α-HYDROXYACETYLENES AND THEIR DEHYDRATION PRODUCTS

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Summary

μ-Platinum acetylene complexes $(Ph_3P)_2Pt(H—C≡C—R)$ (R = $C(CH_3)_2OH$, $C(CH_3)(CH_2CH_3)OH$, $\overline{C(OH)CH_2CH_2CH_2CH_2CH_2}$ react with the corresponding α-hydroxyacetylenes to give *trans*-$(Ph_3P)_2Pt(C≡C—R)_2$. In contrast, α-hydroxyacetylenes and *cis*-$(Ph_3P)_2PtCl_2$ react with elimination of HCl and water to give platinum—enyne complexes, *trans*-$(Ph_3P)_2PtCl(C≡CR')$ or *trans*-$(Ph_3P)_2$-$Pt(C≡C—R')_2$ (R' = $C(CH_3)=CH_2$, $C(CH_3)=CHCH_3$, $\overline{C=CHCH_2CH_2CH_2CH_2}$).

Introduction

For several years we have been interested in the polymerisation and aromatisation reactions of acetylenic hydrocarbons in the presence of nickel and platinum complexes [1—5]. We found that bis(triphenylphosphine)platinum complexes are active catalysts for the linear polymerisation of acetylenes and from the polymerisation several platinum acetylides which are probably active intermediates, were isolated [2,3]. With the aim of preparing new complexes of catalytic interest we have now made some platinum complexes of α-hydroxyacetylenes.

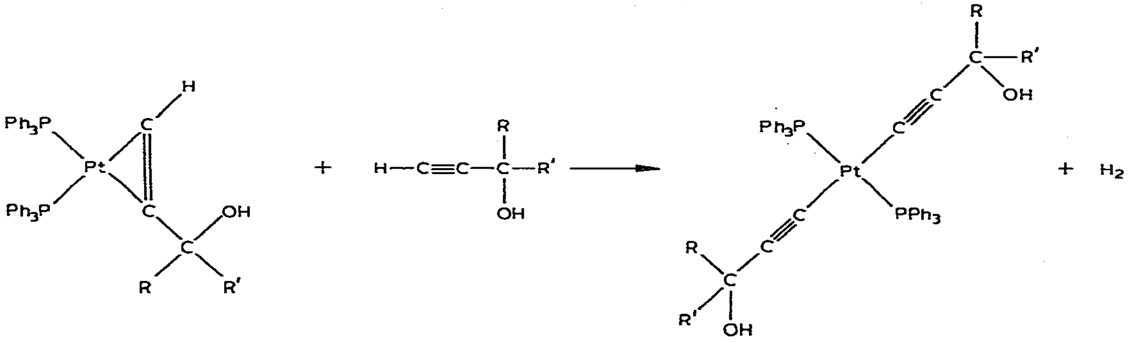
Nelson et al. recently described the synthesis and properties of μ-bonded platinum acetylene complexes $(Ph_3P)_2Pt(R—C≡C—R')$ where the acetylene group is a monosubstituted (R = H) or disubstituted (R = R') α-hydroxyacetylene [6—9]. They also obtained a *trans*-dihydridobis(triphenylphosphine) bisacetylide of platinum(IV) from 1-ethynylcyclohexanol [7], but failed to obtain similar hydrides of platinum and palladium from treatment of 1-ethynylcycloheptanol or 1-ethynylcyclopentanol with $(Ph_3P)_nPd$ or $(Ph_3P)_nPt$; instead *trans*-bis(triphenylphosphine) bisacetylides of palladium(II) or platinum(II) were isolated [10].

We have obtained no evidence for the formation of platinum(IV) hydrides and bis(triphenylphosphine)platinum(II) acetylides were readily obtained. However, we find that under mild conditions dehydration of the coordinated α-hydroxyacetylene can occur. IR and NMR spectra and dipole moments indicate a *trans* structure for all the products.

Partial dehydration reactions were also observed by Shaw et al. [11] in the preparation of analogous complexes from *cis*-$[P(CH_3)_2Ph]_2PtCl_2$ and some tertiary ethynyl alcohols in the presence of hydrazine hydrate. They report that platinum(II) acetylide complexes containing tertiary hydroxyl groups undergo complete dehydration by acetic anhydride pyridine to give platinum—enyne complexes, but we find that the presence of a dehydrating agent is unnecessary for dehydration of the tertiary alcohol.

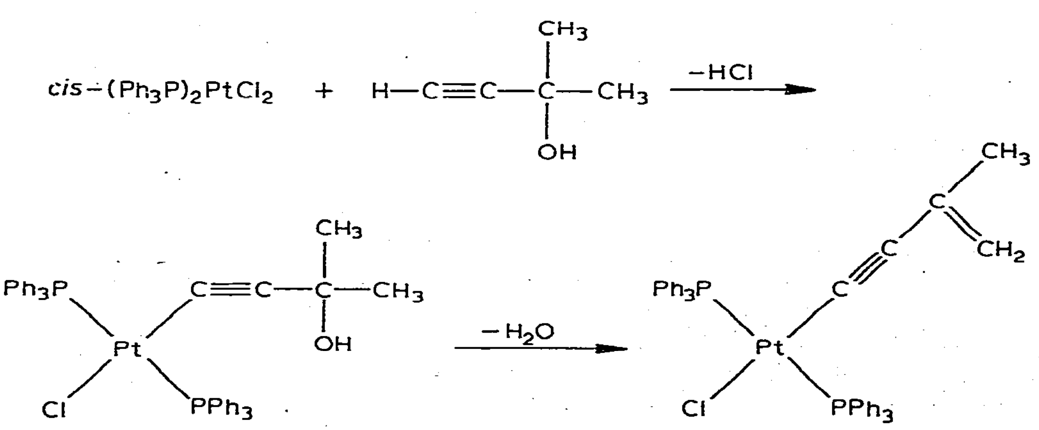
Results

(a) μ-Bonded platinum complexes of α-hydroxyacetylenes undergo the following reaction when warmed with the corresponding α-hydroxyacetylenes:

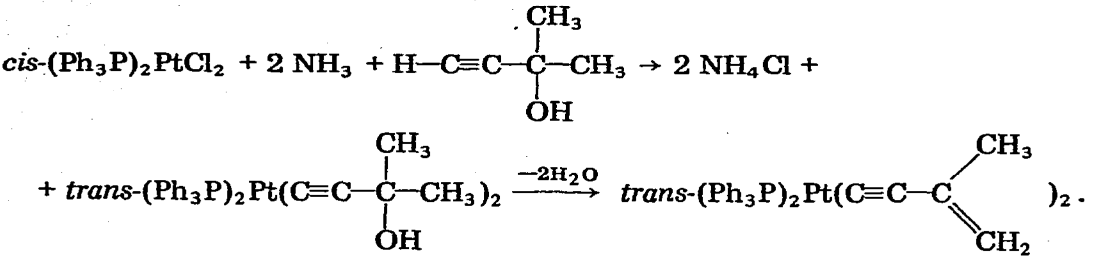


This reaction is consistent with the mechanism proposed by Nelson et al. [10] for the synthesis of bis(triphenylphosphine) bisacetylides of palladium and platinum, starting from $(Ph_3P)_4M$ (M = Pd or Pt); they reported that the intermediates in the reaction are μ-bonded complexes.

(b) When *cis*-$(Ph_3P)_2PtCl_2$ is refluxed in $CHCl_3$ with an α-hydroxyacetylene (for about 12 h) one of the two chlorine atoms is replaced by an acetylene group. Dehydration of the hydroxyacetylene occurs and a *trans*-bis(triphenylphosphine)-chloroenyneplatinum complex is formed. The reaction with 2-methylbut-3-yn-2-ol is represented below:



(c) Heating *cis*-$(Ph_3P)_2PtCl_2$ under reflux with neat α-hydroxyacetylene and a few drops of NH_4OH (32%) gives the *trans*-bis(triphenylphosphine)bisenyne complex. The reaction with 2-methylbut-3-yn-2-ol is:



$$cis\text{-}(Ph_3P)_2PtCl_2 + 2\,NH_3 + H{-}C{\equiv}C{-}\underset{OH}{\overset{CH_3}{C}}{-}CH_3 \rightarrow 2\,NH_4Cl +$$

$$+\ trans\text{-}(Ph_3P)_2Pt(C{\equiv}C{-}\underset{OH}{\overset{CH_3}{C}}{-}CH_3)_2 \xrightarrow{-2H_2O} trans\text{-}(Ph_3P)_2Pt(C{\equiv}C{-}C(CH_3){=}CH_2)_2.$$

Some physical properties of the products isolated are listed in Table 1.

Complexes IV and VII were prepared from isopropenylacetylene by similar methods (see Experimental). We describe here only two complexes of isopropenylacetylene which are identical to those obtained from 2-methylbut-3-yn-2-ol, and the others will be the subject of a future paper.

Mass spectra

Molecular weights were determinaed by mass spectrometry and osmometric measurements. In the mass spectra the molecular ions (M) were clearly evident except for complex V. The spectra of complexes I, II and III show ions of (M—18) and (M—36), which were absent in the breakdown patterns of the other complexes, for which peaks corresponding to the loss of the dehydrated acetylene were identified. This confirms that dehydration of α-hydroxyacetylenes occurs during the synthesis.

IR spectra

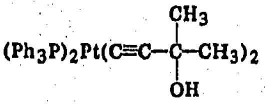
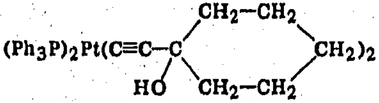
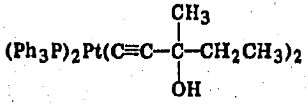
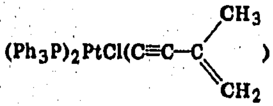
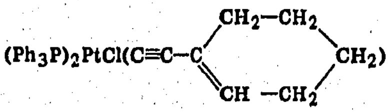
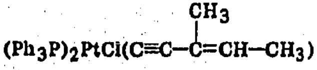
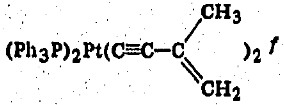
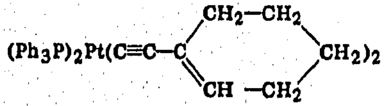
The IR spectra of complexes I, II and III exhibit an OH band at about 3600 cm^{-1}. This band is absent in the spectra of the other complexes. The C≡C band is always at 2110 ± 5 cm^{-1}, but in the spectra of the complexes IV and VII the band is split into a doublet at 2100—2125 cm^{-1} (IV) and 2080—2105 cm^{-1} (VII). Isopropenylacetylene exhibits the C≡C band at 2120 cm^{-1} with a shoulder at 2140 cm^{-1}. On coordination the position of this band shifts to lower frequencies and the splitting increases.

Complexes IV and VII exhibit an intense band at 878 cm^{-1} assignable to the out-of-plane deformation vibrations of the $=CH_2$ groups. Complexes V and VIII show a band of medium intensity at 835 cm^{-1} assignable to the trisubstituted $R^1R^2{-}C{=}CHR^3$ group. Complex VI exhibits a band of low intensity at 850 cm^{-1}; the position and intensity of this band suggests the presence of a trisubstituted alkene group in the molecule. Thus the elimination of water involves the CH_2 rather than the CH_3 group.

In Fig. 1 we show some low-frequency IR spectra in order to correlate features of the spectra with the stereochemistry of the bis(triphenylphosphine)platinum complexes. In the spectra of *cis* complexes the band of triphenylphosphine at 540 cm^{-1} increases in intensity and its frequency remains almost unchanged (Fig. 1, spectra b, c, d). In the spectra of complexes I—VIII this band is absent or is very weak (see some examples in Fig. 1 spectra e, f, g, h).

TABLE 1

ELEMENTAL ANALYSES AND PHYSICAL PROPERTIES OF COMPLEXES

No.	Complex	Analysis found (calcd.) (%)		M.p. (°C)	Molecular weight			UV$_{max}$ λ(nm) [c]	log ε
		C	H		A [a]	B [b]	calcd.		
I	 $(Ph_3P)_2Pt(C{\equiv}C{-}C(CH_3)(OH){-}CH_3)_2$	62.6 (62.5)	5.04 (5.0)	247–250	875	885	885.1	322	3.76
II		64.93 (64.64)	5.31 (5.39)	238–241	970	965	965.1	322	3.83
III	 $(Ph_3P)_2Pt(C{\equiv}C{-}C(CH_3)(OH){-}CH_2CH_3)_2$	63.02 (63.07)	5.56 (5.26)	207–209	909	913	913.1	321	3.81
IV	 $(Ph_3P)_2PtCl(C{\equiv}C{-}C(CH_3){=}CH_2)$	60.53 59.56 (60.04)	4.56 [d] 4.25 [e] (4.27)	200–203	813	819	819.6	309	3.89
V		61.0 (61.43)	4.84 (4.54)	216–219	851		859.6	316	3.86
VI	 $(Ph_3P)_2PtCl(C{\equiv}C{-}C(CH_3){=}CH{-}CH_3)$	60.45 (60.5)	4.78 (4.44)	177–180		834	833.6	313	3.78
VII	 $(Ph_3P)_2Pt(C{\equiv}C{-}C(CH_3){=}CH_2)_2$ [f]	64.9 64.75 (65.40)	4.80 [d] 4.65 [e] (4.71)	227–230	851	849	849.1	341	4.05
VIII		67.13 (67.17)	5.25 (5.17)	239–242		929	929.1	352	4.05

Notes: [a] A osmometric. [b] B Mass spectrum. [c] Spectrum in $CHCl_3$. [d] Obtained from 2-methylbut-3-in-2-ol. [e] From isopropenylacetylene. [f] The identity of two compounds has been confirmed by X-ray diffraction [12].

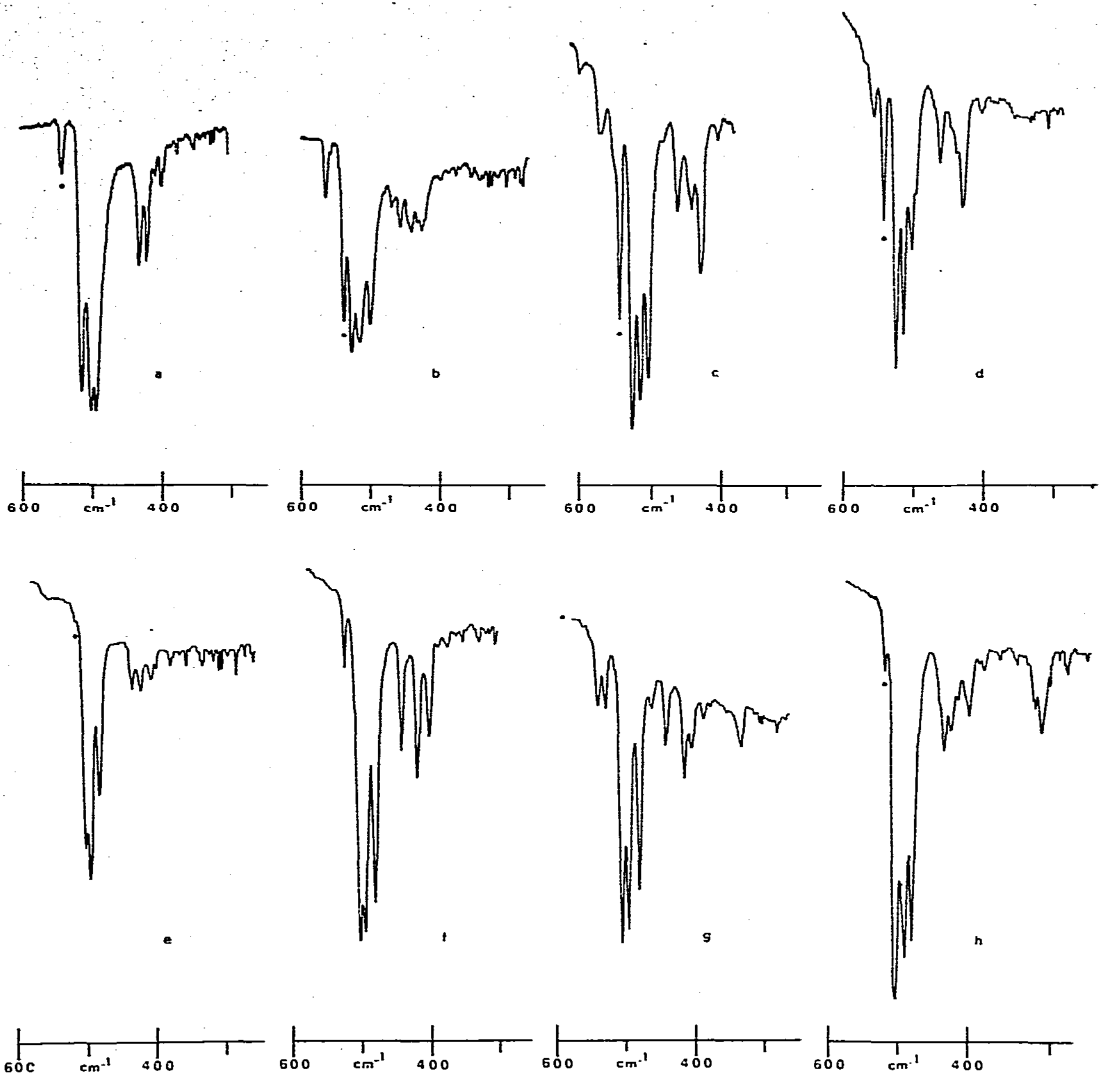


Fig. 1. IR spectra of: (a) $\mathrm{PPh_3}$; (b) *cis*-$\mathrm{(PPh_3)_2Pt(C{\equiv}C{-}C_6H_5)_2}$; (c) $\mathrm{(PPh_3)_2Pt(HC{\equiv}C{-}C(CH_3)_2OH)}$; (d) $\mathrm{(PPh_3)_2Pt(HC{\equiv}C{-}\underset{HO}{C}\left\langle{}^{CH_2-CH_2}_{CH_2-CH_2}\right\rangle CH_2)}$; (e) *trans*-$\mathrm{(PPh_3)_2Pt(C{\equiv}C{-}C\left\langle{}^{CH_2-CH_2}_{CH\,-CH_2}\right\rangle CH_2)_2}$; (f) *trans*-$\mathrm{(PPh_3)_2Pt(C{\equiv}C{-}C\left\langle{}^{CH_2}_{CH_3}\right.)_2}$; (g) *trans*-$\mathrm{(PPh_3)_2Pt(C{\equiv}C{-}C(CH_3)_2OH)_2}$; (h) *trans*-$\mathrm{(PPh_3)_2}$-$\mathrm{PtCl(C{\equiv}C{-}C\left\langle{}^{CH_2}_{CH_3}\right.)}$. * The starred band is at 540 ± 2 $\mathrm{cm^{-1}}$.

Mastin [13] and Tong Wai Lee et al. [14] made similar observations on the IR spectra of some *cis*- and *trans*-bis(triphenylphosphine)platinum complexes. In the spectra of complexes of *cis* structure the triphenylphosphine band at 540 $\mathrm{cm^{-1}}$ increases in intensity relative to the other bands, and it becomes weak or disappears in the spectra of complexes of *trans* structure. The low-frequency IR spectra thus indicate a *trans* structure for complexes I—VIII.

UV spectra

We previously observed [15] that *trans*-$(Ph_3P)_2Pt(C{\equiv}C{-}C_6H_5)_2$ gave an UV spectrum with a maximum at 348 nm and the *cis* isomer (the structure of which has been confirmed by X-ray analysis [16]) absorbed at 314 nm. We erroneously assumed that the position of the UV maximum could be correlated with the stereochemistry of platinum acetylides [17].

We have now observed that complexes I, II and III (see Table 1), which on the basis of low-frequency IR spectra have a *trans* structure, exhibit a spectrum with a maximum at about 322 nm, and complexes VII and VIII show maxima at 341 and 352 nm, respectively. The position of the UV maximum thus seems to depend on the delocalisation of π electrons, which is greater in the bisenyne complexes and in the bis(phenyl acetylide) than in the analogous bisacetylides of hydroxy derivatives I, II and III.

Dipole moments and NMR spectra

In order to confirm the structural assignment suggested by the low-frequency IR spectra, we have measured dipole moments and examined the NMR spectra (Table 2). The possibility of decomposition (even slow) of the complexes in $CHCl_3$ led us to use C_6H_6 as solvent for the dipole moment determinations. Low dipole moments (1—2 Debyes) were found for complexes I—III, VII and VIII, confirming their *trans* structure. For comparison, measurements carried out on two complexes of *cis* structure gave 7.1 D for *cis*-$(Ph_3P)_2Pt(C{\equiv}C{-}C_6H_5)_2$ and 6.0 D for $(Ph_3P)_2Pt(H{-}C{\equiv}C{-}C(CH_3)(OH){-}CH_3)$.

In the NMR spectra because of the low solubility of our compelxes in C_6D_6, we observed only weak signals for the highly coupled hydrogens. However, the thirty hydrogens of the phenyl rings of the two triphenylphosphine molecules bonded to platinum give rise to two intense multiplets, the positions of which are clearly influenced by the steric requirements of the acetylides. The more intense multiplet is centred at about τ 3 (ppm against TMS in C_6D_6) for all complexes. The lower multiplet is centred at about τ 2 for *trans*-complexes of low dipole moment and at about τ 2.45 for *cis*-complexes of high dipole moment. These observations are in agreement with those of Nelson et al. [10], who proposed that the phenyl resonances are related to the *cis*—*trans* geometry of bis(triphenylphosphine)-palladium or platinum complexes. They used $CDCl_3$ as solvent; we have observed that the distance between the two multiplets increases in C_6D_6, and so the difference between the spectra of complexes of different geometry is more evident.

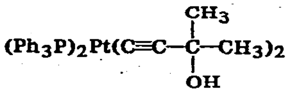
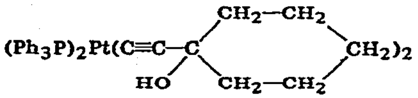
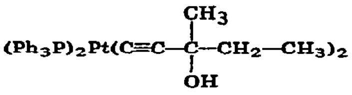
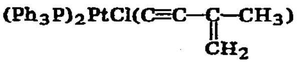
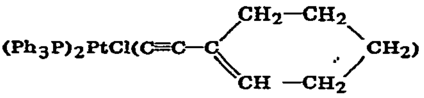
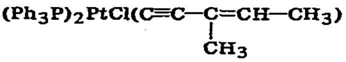
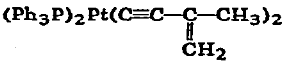
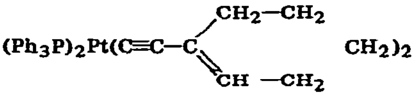
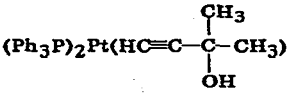
The NMR spectra of complexes I, II and III show the OH resonance at about τ 9.05 as a singlet, which disappears on deuteration. The NMR spectra of dehydrated complexes show resonances in the region of olefinic protons as broad multiplets of low intensity. In the high-field spectra (τ 10—40) no Pt—H resonances were found for any of these complexes, although the Pt—H triplet was clearly detected in a spectrum of *trans*-$(Ph_3P)_2PtHCl$ at the same concentration. We conclude that no hydrides are formed in the reaction of μ-bonded platinum complexes, $(Ph_3P)_2Pt(HC{\equiv}C{-}R)$, with the corresponding alkynes, $H{-}C{\equiv}C{-}R$.

Dehydration reactions

The dehydration of α-hydroxyacetylenes occur after ligand coordination. When

TABLE 2

DIPOLE MOMENTS AND NMR PHENYL RESONANCES FOR *cis*- AND *trans*-BIS(TRIPHENYLPHOSPHINE)PLATINUM COMPLEXES

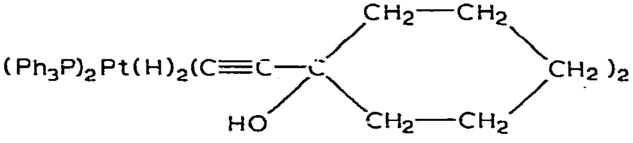
No.	Complex	μ(D) [a]	Phenyl resonances [b] (τ, ppm)	
trans complexes				
I	 $(Ph_3P)_2Pt(C\equiv C-\overset{CH_3}{\underset{OH}{C}}-CH_3)_2$	1.3	2.08	2.93
II		1.9	1.99	2.88
III	 $(Ph_3P)_2Pt(C\equiv C-\overset{CH_3}{\underset{OH}{C}}-CH_2-CH_3)_2$	2.3	2.10	2.95
IV	 $(Ph_3P)_2PtCl(C\equiv C-\underset{CH_2}{\underset{\|}{C}}-CH_3)$		2.04	2.93
V			2.05	2.95
VI	 $(Ph_3P)_2PtCl(C\equiv C-\underset{CH_3}{C}=CH-CH_3)$		2.04	2.94
VII	 $(Ph_3P)_2Pt(C\equiv C-\underset{CH_2}{\underset{\|}{C}}-CH_3)_2$	1.7	2.05	2.93
VIII		1.5	2.07	2.99
IX	$(Ph_3P)_2Pt(C\equiv C-C_6H_5)_2$		2.00	2.97
X	$(Ph_3P)_2PtHCl$		2.10	2.98
cis complexes				
XI	$(Ph_3P)_2Pt(C\equiv C\cdot C_6H_5)_2$	7.1	2.47	2.97
XII	 $(Ph_3P)_2Pt(HC\equiv C-\overset{CH_3}{\underset{OH}{C}}-CH_3)$	6.0	2.44	2.99
XIII	$(Ph_3P)_2Pt(HC\equiv C-C_6H_5)$		2.45	3.10

[a] In C_6H_6. [b] In C_6D_6, TMS as internal standard, τ values are taken at the centre of the multiplets.

cis-$(Ph_3P)_2PtCl_2$ is warmed with an α-hydroxyacetylene in the presence of NH_4OH the reaction mixture turns yellow in a few minutes. At this stage both the hydrated and dehydrated bisacetylides are present. If warming is continued to a brown colour, only the dehydrated acetylide is obtained. Gas chromatographic analysis of the reaction solution does not indicate the presence of free dehydrated alkyne. The formation of olefin—platinum(II) complexes such as $[n\text{-}Bu_4N]^+$-$[Pt(CH_2{=}CH_2)Cl_3]^-$ from alcohols was previously noted by Hartley [18], but the reaction gave good results only with straight-chain saturated alcohols. In our experiments tertiary alcoholic groups adjacent to triple bonds undergo the dehydration reaction to give enyne complexes with the organic group σ-bonded to the platinum atom. Experiments with isopropenylacetylene showed that such complexes can be prepared from alkenyl/acetylenes only with difficulty because the presence of double and triple bonds in the molecule offers several possibilities of bonding to the platinum atom and complex mixtures of products are obtained.

Conclusions

Our results are in good agreement with those of Nelson et al. [10] and of Shaw et al. [11] on similar palladium and platinum complexes. However, some attempts to repeat the preparation of the complex XIV.



(XIV)

reported by Nelson et al. [7] gave us the complex II. Complex XIV is thus the only example of a dihydridobis(triphenylphosphine) bisacetylide of platinum(IV). The fact that all the complexes synthesised have a *trans* structure confirms that this geometry is preferred for bis(triphenylphosphine)platinum acetylides. IR and NMR spectra can be used to define the steric configurations of complexes of this type.

Complexes IX and XI demonstrate that formation of both *cis* and *trans* isomers is possible.

Experimentals

Reagents and apparatus

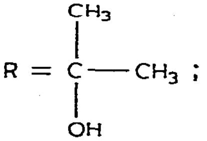
2-Methylbut-3-yn-2-ol, (Fluka), 1-ethynylcyclohexanol (Fluka) and 3-methylpent-4-yn-3-ol (Schuchardt) were used without further purification. Isopropenylacetylene (Fluka) was distilled under reduced pressure. *cis*-$(Ph_3P)_2PtCl_2$ was prepared as described by Jensen [19]. Reagent grade solvents were used.

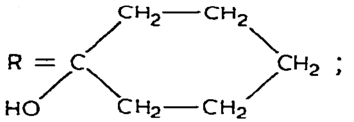
UV spectra were run on a Beckman DK-2A spectrophotometer. Infrared spectra were recorded with Perkin—Elmer 800 and 521 spectrophotometers as Nujol mulls on NaCl or KRS-5 (R.I.I.C.) discs. Proton NMR spectra were run on a Jeol NM-C-60 HL spectrometer using C_6D_6 as solvent and tetramethylsilane (TMS) as internal standard. Mass spectra were obtained with an AEI MS-12 mass spectrometer at 70 eV.

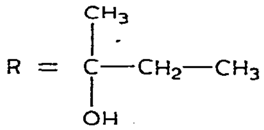
Dipole moments were calculated by the method of Halverstadt and Kumler [20,21]. A DM 01 WTW dipolemeter was used for the determination of the dielectric constants. Densities were measured with an Anton—Paar DMA 02 digital densimeter and refractive indices with a Bausch—Lomb refractometer of the Optical Company (USA).

Preparation of complexes

(a) Complexes trans-$(Ph_3P)_2Pt(C{\equiv}C{-}R)_2$ (I—III):

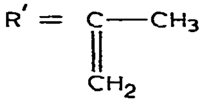
I:

$R = C(CH_3)_2(OH)$

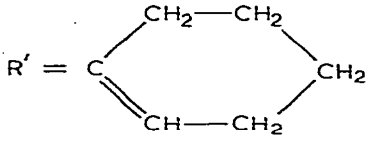
II:


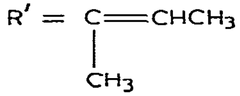
III:

$R = C(CH_3)(OH)CH_2CH_3$

120—150 mg of $(Ph_3P)_2Pt(H{-}C{\equiv}C{-}R)$ [22] were refluxed with 5 ml of $H{-}C{\equiv}C{-}R$ for 15—20 min. The solution turned red-brown. On addition of CH_3OH, complexes I, II or III separated as white crystals (yield about 50%). After filtration, the products were recrystallised from C_6H_6 or $CHCl_3$ by addition of CH_3OH.

(b) Complexes trans-$(Ph_3P)_2PtCl(C{\equiv}C{-}R')$:

IV:

$R' = C(=CH_2)CH_3$

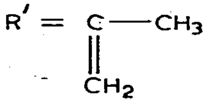
V:


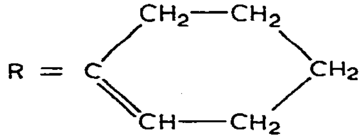
VI:

$R' = C(CH_3){=}CHCH_3$

400 mg of *cis*-$(Ph_3)_2PtCl_2$ were dissolved in 35 ml of $CHCl_3$ by warming; 4 ml of 2-methylbut-3-yn-2-ol was added and the mixture refluxed for about 12 h. The solution, which was green-brown, was evaporated under vacuum and CH_3OH added. On cooling, a green-yellow precipitate of IV separated (yield about 30%). After filtration, the precipitate was dissolved in $CHCl_3$ and Al_2O_3 was added to absorb the green products. The resulting yellow solution was filtered and reduced to a small volume. After addition of CH_3OH, a yellowish microcrystaline powder separated on cooling. This was recrystallised from C_6H_6 by addition of CH_3OH.

V and VI were prepared as above by adding 4 ml of 1-ethynylcyclohexanol or 4 ml of 3-methylpent-4-yn-3-ol to the *cis*-$(Ph_3P)_2PtCl_2$ solution. The addition of Al_2O_3 was not required. Recrystallisation was from the same solvents.

(c) Complexes trans-$(Ph_3P)_2Pt(C{\equiv}C{-}R')_2$:

VII:

$R' = C(=CH_2)CH_3$

VIII:


150 mg of *cis*-$(Ph_3P)_2PtCl_2$ were refluxed with 5 ml of 2-methylbut-3-yn-2-ol and 3—5 drops of NH_4OH (32%) for 20—25 min. The reaction mixture turned brown and yellow microcrystals of VII separated on cooling after addition of CH_3OH (yield about 30%). The solid was recrystallised from C_6H_6.

VIII was prepared as above by using 5 ml of 1-ethynylcyclohexanol. Recrystallisation was carried out as above.

(d) Preparation of complex IV from isopropenylacetylene. To a suspension of 300 mg of *cis*-$(Ph_3P)_2PtCl_2$ in 15 ml of $CHCl_3$ were added 6 ml of isopropenylacetylene and 10 drops of NH_4OH (32%). The mixture was refluxed for about 7 h, and became light brown. After addition of CH_3OH, a yellowish precipitate separated on cooling (yield about 70%). The solid was chromatographed on a silica-gel column using C_6H_6 as eluent. UV analysis of the eluted fractions revealed the presence of complex VII and of some other complexes, but complex IV was the most abundant component.

Fractions containing IV were evaporated to dryness and the solid recrystallised from C_6H_6 by addition of CH_3OH.

(e) Preparation of complex VII from isopropenylacetylene. When the time of the above reaction was increased to 20 h, complex VII became the principal product. Purification of VII was carried out by chromatography on a silica-gel column, followed by recrystallisation from C_6H_6.

The purity of complexes IV and VII was also confirmed by TLC.

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