

## COMPLEXES OF PLATINUM WITH TRIPHENYLPHOSPHINE AND 2-METHYL-3-BUTYN-2-OL

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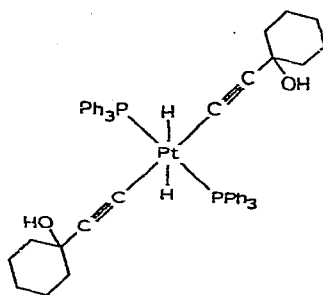
### SUMMARY

Some platinum acetylides *trans*-(PPh<sub>3</sub>)<sub>2</sub>PtCl[C≡C-C(CH<sub>3</sub>)<sub>2</sub>OH] and *cis*- and *trans*-(PPh<sub>3</sub>)<sub>2</sub>Pt[C≡C-C(CH<sub>3</sub>)<sub>2</sub>OH]<sub>2</sub> have been prepared by a new synthetic procedure. The structures have been assigned on the basis of their UV spectra and by a comparison of their spectra with those of the corresponding bis(triphenylphosphine)platinum phenylacetylides.

These platinum acetylides of 2-methyl-3-butyn-2-ol have been identified as intermediate products in the polymerization of 2-methyl-3-butyn-2-ol in the presence of *cis*-(PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>.

### INTRODUCTION

The presence of reactive functional groups in a substituted alkyne restricts the use of lithium or sodium or of Grignard reagents in the synthesis of platinum acetylides, and the first example of a dihydridoplatinum diacetylide, derived from a mono-substituted hydroxyacetylene, was reported only recently by Roundhill *et al.*<sup>1,2</sup>; this compound, (I), was obtained from Pt(PPh<sub>3</sub>)<sub>4</sub> and 1-ethynylcyclohexanol in ether.



(I)

However, other types of platinum complexes derived from dihydroxyacetylenes have been known for many years<sup>3-10</sup>. Their structures are similar either to that of Zeise's salts<sup>11</sup> with the hydroxyacetylene molecule perpendicular to the coor-

dination plane, or to one of the Chatt complexes<sup>12</sup> in which the acetylene bound to the metal, formally Pt<sup>0</sup>, lies in the molecular plane. It is generally accepted that there is a contribution by the hydroxyl groups to the stability of such complexes but the manner in which the hydroxyl groups are involved in bonding with the other atoms is still unsettled<sup>8,9</sup>. Recently Roundhill *et al.*<sup>1,2</sup> reported some Chatt complexes of monosubstituted hydroxyacetylenes. The synthesis and the properties of some new Pt acetylides of 2-methyl-3-butyn-2-ol are described below.

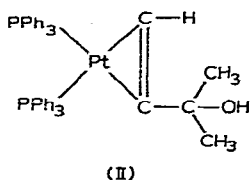
## EXPERIMENTAL

### Apparatus

IR spectra were measured using a Perkin-Elmer model 800 instrument. UV spectra were run on a Beckman DK 2 spectrophotometer. NMR spectra were recorded on a Perkin-Elmer model R 12 instrument.  $\tau$  values are referred to tetramethylsilane (TMS).

### Reagents

2-Methyl-3-butyn-2-ol (commercial product) was distilled under vacuum, dried over Na<sub>2</sub>SO<sub>4</sub>, and redistilled at normal pressure (b.p. 104°) before use. *cis*-(PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub> was prepared according to Jensen<sup>13</sup>. Reagent grade solvents were used.



### Preparation of complexes

*Bis*(triphenylphosphine)(2-methyl-3-butyn-2-ol)platinum (II). This complex was prepared according to Chatt's method<sup>12</sup>: 160.2 mg of *cis*-(PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub> were suspended in 4 ml of absolute ethanol and five drops of 24% hydrazine were added. The mixture was heated to reflux for 2 min, *i.e.* until dissolution was almost complete. The small residue was filtered off, and 0.8 ml of 2-methyl-3-butyn-2-ol were added to the yellow solution. The mixture was heated to reflux and then cooled, and two more drops of hydrazine were added.

When the mixture was allowed to cool overnight a microcrystalline precipitate (55 mg, 33% yield) was obtained, and this was recrystallized from C<sub>6</sub>H<sub>6</sub> or Cl<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub> by additional CH<sub>3</sub>OH without heating (m.p. 148–150°). Compound (II) decomposes in solution, probably by loss of the methylbutynol molecule, and recrystallization of the crude product from mixtures of benzene or 1,2-dichloroethane with 2-methyl-3-butyn-2-ol was subsequently found to give better yields. The elemental analysis is given in Table 1.

The UV spectrum of (II) in CHCl<sub>3</sub> shows only a shoulder at 255 m $\mu$ . The IR spectrum in Nujol mull is characterized by a band at 1680–1690 cm<sup>-1</sup> and a weak band at 3560 cm<sup>-1</sup>.

TABLE I

UV SPECTROSCOPIC DATA AND ELEMENTAL ANALYSES

Complex	UV spectrum in				M.p. (°C)	Analysis found (calcd.) (%)	
	CHCl <sub>3</sub>		CH <sub>3</sub> OH			C	H
	λ(mμ)	log ε	λ(mμ)	log ε			
$\begin{array}{c} \text{H} \\   \\ (\text{PPh}_3)_2\text{Pt}-\text{C} \\    \\ \text{C} \\   \\ \text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array}$	255 (sh)				148-150	60.8 (61.0)	4.8 (4.7)
<i>trans</i> -(PPh <sub>3</sub> )PtCl[C≡C-C(CH <sub>3</sub> ) <sub>2</sub> OH]	330 (sh) 309		330 (sh) 302		195-198	59.2 (58.7)	4.5 (4.4)
<i>trans</i> -(PPh <sub>3</sub> )PtCl(C≡C-Ph)			257 335 (sh) 314 264	3.94 4.64 4.12 4.60			
<i>trans</i> -(PPh <sub>3</sub> ) <sub>2</sub> Pt[C≡C-C(CH <sub>3</sub> ) <sub>2</sub> OH] <sub>2</sub>	341 288 (sh)	4.08 4.13				63.3 (62.5)	5.2 (5.0)
<i>trans</i> -(PPh <sub>3</sub> ) <sub>2</sub> Pt(C≡C-Ph) <sub>2</sub>			348	4.39			
<i>trans</i> -(PPh <sub>3</sub> ) <sub>2</sub> Pt[C≡C-C(CH <sub>3</sub> ) <sub>2</sub> OH] <sub>2</sub> ·C <sub>6</sub> H <sub>6</sub>			290 (sh) 266	4.51 4.69	222-225	64.9 (64.9)	4.8 (5.2)
<i>cis</i> -(PPh <sub>3</sub> ) <sub>2</sub> Pt[C≡C-C(CH <sub>3</sub> ) <sub>2</sub> OH] <sub>2</sub>	322	3.76	317 245	3.76 4.45	247-250	62.2 (62.5)	5.0 (5.0)
<i>cis</i> -(PPh <sub>3</sub> ) <sub>2</sub> Pt(C≡C-Ph) <sub>2</sub>			314 254	4.41 4.64			

*trans*-Bis(triphenylphosphine)(3-hydroxy-3-methyl-1-butyryl)platinum chloride (III) 400 mg of *cis*-(PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub> were refluxed with 35 ml of CHCl<sub>3</sub> and 4 ml of 2-methyl-3-butyne-2-ol for 7 h and the green solution was then evaporated under vacuum. Addition of 20 ml of CH<sub>3</sub>OH to the gummy residue gave a yellow green microcrystalline powder, which was filtered off and dissolved in CHCl<sub>3</sub>. The CHCl<sub>3</sub> solution was treated with a small amount of Al<sub>2</sub>O<sub>3</sub>, on which the green products were adsorbed. The resulting yellow solution was filtered and reduced to a small volume. Methanol was then added to give a yellow microcrystalline powder (III) (130 mg, 31% yield) which was recrystallized from acetone and then precipitated from CHCl<sub>3</sub> by addition of CH<sub>3</sub>OH (m.p. 195-198°). The elemental analysis was consistent with the formula (PPh<sub>3</sub>)<sub>2</sub>PtCl[C≡C-C(CH<sub>3</sub>)<sub>2</sub>OH] (see Table 1).

The complex (III) is slightly soluble in hot C<sub>6</sub>H<sub>6</sub>, CH<sub>3</sub>COCH<sub>3</sub>, CCl<sub>4</sub>, Cl<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>CHOHCH<sub>2</sub> and CS<sub>2</sub> and insoluble in *n*-hexane. UV spectroscopic data are given in Table 1. The IR spectrum shows a doublet at 2095-2110 cm<sup>-1</sup>.

*trans*-Bis(triphenylphosphine)bis(3-hydroxy-3-methyl-1-butyryl)platinum (IV)

To 250 mg of *cis*-(PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub> were added 5 ml of 2-methyl-3-butyne-2-ol and two drops of NH<sub>3</sub> (32%). The mixture was warmed at reflux for 20 min. In a few minutes the *cis*-(PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub> dissolved and a yellow precipitate (IV) separated, the

solution turning yellow-brown. After cooling the solid was filtered off (70 mg, 25% yield).

The product (IV) is very slightly soluble in hot  $\text{Cl}_2\text{CH}_2\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ ,  $(\text{CH}_3)_2\text{SO}_2$ ,  $\text{C}_6\text{H}_5\text{CH}_3$ ,  $\text{CCl}_4$  and  $\text{CS}_2$ . It is insoluble in  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{COCH}_3$  and n-hexane and was recrystallized from boiling  $\text{C}_6\text{H}_6$  (m.p. 222–225°). The elemental analysis of complex (IV) corresponds with a monobenzene adduct  $(\text{PPh}_3)_2\text{Pt}[\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{OH}]_2 \cdot \text{C}_6\text{H}_6$  (see Table 1). The product loses one equivalent of benzene on recrystallization from  $\text{CCl}_4$  (Table 1).

UV data are reported in Table 1. The IR spectrum in Nujol mull exhibits a doublet at 2088–2105  $\text{cm}^{-1}$ .

*cis-Bis(triphenylphosphine)bis(3-hydroxy-3-methyl-1-butynyl)platinum (V)*

*Method I.* To 150 mg of  $\text{cis}-(\text{PPh}_3)_2\text{PtCl}_2$  were added 5 ml of 2-methyl-3-butyn-2-ol and 15 mg of NaOH. The mixture was refluxed for 15 min, during which it turned yellow. After 15 min the excess of 2-methyl-3-butyn-2-ol was evaporated under vacuum and the residue treated with  $\text{CHCl}_3$ ; NaOH and unreacted  $\text{cis}-(\text{PPh}_3)_2\text{PtCl}_2$  were filtered off and the  $\text{CHCl}_3$  solution evaporated to dryness. The residue was dissolved in a small volume of  $\text{C}_6\text{H}_6$  and  $\text{CH}_3\text{OH}$  was then added and white crystals (V) separated after a few hours in the cold. The product was recrystallized from  $\text{C}_6\text{H}_6$  by addition of  $\text{CH}_3\text{OH}$  (m.p. 247–250°) (37 mg, 22% yield). The elemental analysis of compound (V) is consistent with the formula  $(\text{PPh}_3)_2\text{Pt}[\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{OH}]_2$  (see Table 1).

*Method II.* 220 mg of complex (II) were refluxed with 6 ml of 2-methyl-3-butyn-2-ol for 15 min. The mixture was then reduced to a small volume and  $\text{CH}_3\text{OH}$  was added. After cooling overnight white crystals separated. The product was taken up in  $\text{C}_6\text{H}_6$  and reprecipitated by addition of  $\text{CH}_3\text{OH}$  (m.p. 247–250°) (113 mg, 47% yield).

The UV characteristics are listed in Table 1. The IR spectrum of the product is characterized by bands at 3620 and 2120  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

The synthesis of platinum acetylides of 2-methyl-3-butyn-2-ol was of special interest because of the light it threw upon polymerization of this acetylene in the presence of platinum complexes. In the polymerization reaction of phenylacetylene in the presence of certain bis(triphenylphosphine)platinum complexes we have identified *trans*- $(\text{PPh}_3)_2\text{PtCl}(\text{C}\equiv\text{C}-\text{Ph})$  and *cis*- and *trans*- $(\text{PPh}_3)_2\text{Pt}(\text{C}\equiv\text{C}-\text{Ph})_2$  as active intermediates<sup>14</sup>. [These previously unknown acetylides were also synthesized independently from *cis*- $(\text{PPh}_3)_2\text{PtCl}_2$  and  $\text{Na}-\text{C}\equiv\text{C}-\text{Ph}$  in liquid ammonia<sup>15</sup> and were characterized by their UV and IR spectra.] We then studied the polymerization reaction of 2-methyl-3-butyn-2-ol in the presence of *cis*- $(\text{PPh}_3)_2\text{PtCl}_2$  (ref. 16), following the course of the reaction by taking aliquots of the polymerization mixture, chromatographing then on silicagel columns and eluting first with  $\text{C}_6\text{H}_6$  and then with  $\text{CHCl}_3$ . The eluted fractions were analyzed spectroscopically and shown to contain compounds with UV and IR spectra similar to those of the complexes mentioned above. It thus seems that this reaction produces analogous intermediates.

Attempts to prepare *trans*- $(\text{PPh}_3)_2\text{PtCl}[\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{OH}]$  and *cis*- and *trans*- $(\text{PPh}_3)_2\text{Pt}[\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{OH}]_2$  by the method used for the preparation of

phenylacetylides<sup>15</sup> were unsuccessful and a mixture of  $(PPh_3)_2Pt[O(CH_3)_2C-C\equiv CH]_2$  and  $(PPh_3)_2Pt[O(CH_3)_2C-C\equiv CH]Cl$  was probably obtained.

On the assumption that complexes with metal carbon  $\sigma$ -bonds are formed in the course of the alkyne polymerization, we tried to prepare the butynol acetylides under reaction conditions similar to those used for the polymerization. We found that in  $CHCl_3$  solution *cis*- $(PPh_3)_2PtCl_2$  reacts with 2-methyl-3-butyn-2-ol to give a monochloro acetylide (III), so that only one chlorine atom of the starting complex is replaced by a methylbutynol molecule. The complex (III) probably has a *trans* structure since its UV spectrum is very similar to that of *trans*- $(PPh_3)_2PtCl(C\equiv C-Ph)$  (see Table 1).

The same complex (III) is present in the  $CHCl_3$  fractions of the chromatographed polymerization mixture of 2-methyl-3-butyn-2-ol; *trans*- $(PPh_3)_2PtCl(C\equiv C-Ph)$  was found in the corresponding fractions obtained from the polymerization of phenylacetylene.

If bases are added to the *cis*- $(PPh_3)_2PtCl_2$  and 2-methyl-3-butyn-2-ol reaction mixture, both chlorine atoms are replaced by 2-methyl-3-butyn-2-ol. In the presence of  $NH_3$  complex (IV) is formed which exhibits an UV spectrum analogous to that of *trans*- $(PPh_3)_2Pt(C\equiv C-Ph)_2$ , and which must thus be *trans*- $(PPh_3)_2Pt[C\equiv C-C(CH_3)_2OH]_2$ . Complex (IV) can also be obtained from the polymerization of 2-methyl-3-butyn-2-ol by elution with  $C_6H_6$ . [The complex *trans*- $(PPh_3)_2Pt(C\equiv C-Ph)_2$  is obtained from phenylacetylene under similar conditions.]

In the presence of a stronger base as NaOH complex (V) is obtained. The elemental analysis of (V) is similar to that of (IV). Its UV spectrum is very similar to that of *cis*- $(PPh_3)_2Pt(C\equiv C-Ph)_2$ , and complex (V) seemed likely to be *cis*- $(PPh_3)_2Pt[C\equiv C-C(CH_3)_2OH]_2$ . However, since complex (V) can also be obtained from bis-(triphenylphosphine)(2-methyl-3-butyn-2-ol)platinum (II) and 2-methyl-3-butyn-2-ol it could be a dihydridoplatinum diacetylide, analogous to the dihydridoplatinum complex (I) reported by Roundhill *et al.*<sup>1,2</sup>, but this was ruled out by a consideration of the IR and NMR spectra of the two products. The IR spectrum of complex (V) exhibits a band due to OH stretching at  $3620\text{ cm}^{-1}$  and a  $C\equiv C$  band at  $2120\text{ cm}^{-1}$ . Bands at the same frequencies have been given for (I) by Roundhill *et al.* (a unique band at  $2120\text{ cm}^{-1}$  was reported by those authors, although two bands might be expected owing to the presence of Pt-H and  $C\equiv C$  bonds in the complex). The NMR spectrum of complex (I) shows two resonances at low fields: a multiplet centered at  $\tau$  2.39, due to phosphine protons, and a multiplet at  $\tau$  9.05 ppm, due to methylenic protons. A third resonance from the metal hydride occurs at  $\tau$  32.88 ppm. No separate resonance of the hydroxy groups was observed. Roundhill *et al.* suggested that the resonance was shifted to the methylene region. The NMR spectrum of complex (V) in  $CDCl_2$  solution shows a multiplet at  $\tau$  2.65, (phosphine protons) and a singlet at  $\tau$  9.18 ppm (due to methyl protons and probably to OH protons, if the ratio of the areas of the first and second resonance is considered). No resonances at higher fields (up to 40 ppm) were observed in the spectrum of complex (V).

Although the IR and the low field NMR spectrum of complex (V) are very similar to those of Roundhill's complex<sup>1,2</sup>, complex (V) is not a dihydride because no Pt-H resonances are present in the NMR spectrum at high fields. The *cis* structure thus seems then to be the most probable.

The IR spectra of complexes (II), (III) and (IV) also require some comments.

The spectrum of complex (II) is characterized by a band at 1680–1690  $\text{cm}^{-1}$ , due to the C=C stretching vibration which appears at a similar frequency in Chatt's complexes. A weak band at 3560  $\text{cm}^{-1}$  is present in the spectra in Nujol mull, while two bands at 3560 and 3605  $\text{cm}^{-1}$  are present in hexachlorobutadiene (HCB) mulls. The appearance of an additional band at the stretching frequencies of free OH in the HCB spectra shows that some hydrogen bonds of the OH groups are broken in HCB. At present we cannot define the nature of such bonding, but several possible modes exist<sup>8,9</sup>.

The IR spectra of complexes (III) and (IV) show no bands in the region 3000–3600  $\text{cm}^{-1}$ . The absence of bands in this region must be the result of strong solid state interactions, probably involving intermolecular bridging by OH groups. The NMR spectrum of complex (III) in  $\text{CCl}_4$  shows a resonance at  $\tau$  6.65 ppm, which disappears on deuteration and which must be ascribed to the hydroxyl group proton. A weak band at 3580  $\text{cm}^{-1}$  is present in the IR spectrum of complex (III) in  $\text{CCl}_4$ . Interactions of OH groups are thus greater in the solid state than in solution. Similar spectra of complex (IV) could not be obtained because of its very low solubility at room temperature.

The IR spectra of complexes (III) and (IV) are characterized by doublets at 2095–2110 and 2088–2105  $\text{cm}^{-1}$ , respectively. In this region the corresponding phenylacetylides show singlets at 2125 and 2110  $\text{cm}^{-1}$ , respectively, due to the C $\equiv$ C stretching vibrations. To explain the doubling of the band at about 2100  $\text{cm}^{-1}$  in these complexes we have considered the possibility of intramolecular hydrogen bonding between the hydrogen atom of the OH group and the metal atom (involving the  $d_{z^2}$  orbital of the Pt atom); the Pt–H stretching frequency in the Pt hydrides does, in fact, occur at about 2100  $\text{cm}^{-1}$ . No proton resonances were observed, however, in the NMR spectra of complex (II) below 40 ppm relative to TMS, where the resonances of hydride protons are normally found<sup>8–17</sup>. The IR spectrum of complex (II) in  $\text{CCl}_4$ , in the presence of 20% of pyridine showed the same doublet at 2095–2110  $\text{cm}^{-1}$ . A strong base such as pyridine, should influence any Pt atom hydrogen bonding and the absorption spectrum in the 2100  $\text{cm}^{-1}$  region as well, but this was not observed. The doublet at 2100  $\text{cm}^{-1}$  must thus be ascribed to C $\equiv$ C stretching; the reason for the splitting into a doublet is uncertain.

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