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REACTIONS OF ACETYLENES WITH NOBLE-METAL CARBONYL HALIDES

III *. CHEMICAL AND STRUCTURAL STUDIES OF σ-ALKENYL COMPLEXES OF PLATINUM(II)

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Summary

The reaction of [Pt(CO)Cl(ROOCC=C(Cl)COOR)] and of the anions [*cis*-Pt(CO)Cl_2(ROOCC=C(Cl)COOR)]$^-$ (R = Me or Et) with primary and secondary alcohols (MeOH, EtOH, n-PrOH, i-PrOH, allyl-OH) gives rise to specific alcoholysis of the γ-alkoxy group. The specificity is interpreted in terms of the interaction of the β-carboalkoxy group with platinum.

The crystal structure of (PPN)[*cis*-Pt(CO)Cl_2(EtOOCC=C(Cl)COOPr-i)] has been solved by X-ray analysis.

Introduction

The reaction of dicarbonyldichloroplatinum with symmetrically disubstituted acetylenes gives different products depending on the nature of the substituents on the triple bond. Electron-donating groups such as CH_3 and C_2H_5 favour the cyclodimerisation of acetylenes to cyclobutadiene complexes as well as the insertion of carbon monoxide into the organic dimer to form cyclopentadienone

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[*] For part II see ref. 2b.

derivatives [1]. Conversely, electron-withdrawing groups such as $COOCH_3$ and $COOC_2H_5$ promote the insertion of the acetylene moiety into the Pt—Cl bond, leading to stable σ-chlorovinyl derivatives of platinum(II) [2]. It is worth noting that the asymmetric organic ligand in this last type of compound appears to form a chelate ring by means of a strong Pt←O:COR interaction, and this seems to play an important role in stabilizing these complexes, which otherwise would contain an unsaturated platinum atom.

In this paper we describe the spectroscopic properties and the chemical behaviour of the salt-like compounds (PPN)[*cis*-$Pt(CO)Cl_2$(ROOCC=C(Cl)-COOR')] (R = Me, Et; R' = Me, Et, n-Pr, i-Pr, Allyl), and report the X-ray structural investigation of one of these. We also discuss the specific alcoholysis of the γ-alkoxy group which occurs when these compounds or the neutral β-chlorovinyl derivatives of platinum(II) from which they originate, are dissolved in primary and secondary alcohols.

Results and discussion

Some of us recently described the displacement of the carboalkoxy group bonded to platinum in [Pt(CO)Cl(ROOCC=C(Cl)COOR)] by reaction with chloride ions to give the anions [*cis*-$Pt(CO)Cl_2$(ROOCC=C(Cl)COOR)$]^-$ (I, R = Me; II, R = Et), in which a strong platinum—carbon σ-bond is still present [2]. Quantitative yields of the compounds I and II were obtained on treating the neutral species with an excess of chloride ion in absolute methanol or ethanol. Addition of bulky cations such as PPh_4^+, NR_4^+ and PPN^+ (PPN = μ-nitridobis(triphenylphosphorous)), permitted isolation of the corresponding salts of I and II as colourless needles. The more significant IR absorption bands and the ^1H NMR chemical shifts for these and for other products are listed in Tables 1 and 2, respectively. Compounds I and II are insensitive to oxygen and thermally stable both as solids and in solution. They remain unchanged at room temperature when dissolved in dry THF or chloroform under carbon monoxide; after several hours under reflux partial decomposition is observed, with the formation of a small amount of the green-black carbonyl $[Pt(CO)_2]_n$. No reaction occurred on refluxing I or II in THF or chloroform solutions in the presence of hydrogen. Cleavage of the Pt—C σ-bond in I and II to give $[Pt(CO)Cl_3]^-$ and olefin [3] did not occur on reaction with hydrogen chloride in refluxing benzene or toluene, thus confirming the stability of this bond. Treatment of I and II with chlorine led to platinum(IV) compounds, probably through the oxidative addition of the halogen.

Compounds I and II are quite sensitive to water and react when refluxed in alcohols containing 1—2% of water. The products of this reaction are under investigation, but appear to be derived from the loss of the CH_3 or C_2H_5 of the β-carboalkoxy group and of the chlorine atom bonded to platinum [4]. The reaction of I in methanol and of II in ethanol with LiI or LiSCN resulted only in exchange of the chloride on platinum, giving $[Pt(CO)X_2$(ROOCC=C(Cl)-COOR)$]^-$ ions (X = I, SCN; R = Me, Et), which have been isolated as PPN salts and found to be identical to the compounds obtained in the reaction of [carbonylchloro(1,2-*trans*-dicarboalkoxy-2-chloroethenyl)platinum] with I^- and SCN^- [2]. Conversely, the reaction with neutral donor ligands, e.g. PPh_3, and with

TABLE 1

INFRARED DATA (relative intensities: w = weak, m = medium, s = strong, vs = very strong, (br) = broad, (sh) = shoulder)

Compound		ν(C$\equiv$O)	ν(C=O)	ν(Pt—Cl)
I	(PPN)[*cis*-Pt(CO)Cl$_2$(MeOOCC=C(Cl)COOMe)] [a]	2082vs	1710s(br)	340m [b] 300m
II	(PPN)[*cis*-Pt(CO)Cl$_2$(EtOOCC=C(Cl)COOEt)] [a]	2085vs	1706s(br)	338m [b] 308m
III	(PPN)[*cis*-Pt(CO)Cl$_2$(MeOOCC=C(Cl)COOEt)]	2080vs	1717s 1702s	335m 298m
IV	(PPN)[*cis*-Pt(CO)Cl$_2$(MeOOCC=C(Cl)COOPr-n)]	2080vs	1715s 1700s	335m 295m
V	(PPN)[*cis*-Pt(CO)Cl$_2$(MeOOCC=C(Cl)COOPr-i)]	2080vs	1715m 1702s	330m 297m
VI	(PPN)[*cis*-Pt(CO)Cl$_2$(MeOOCC=C(Cl)COOAllyl)]	2085vs	1710s 1702s	330m 295m
VII	(PPN)[*cis*-Pt(CO)Cl$_2$(EtOOCC=C(Cl)COOMe)]	2080vs	1718s 1708m	330m 295m
VIII	[*cis*-Pt(CO)Cl$_2$(EtOOCC=C(Cl)COOPr-i)]	2080vs	1715s 1700s	335m 298m
IX	[Pt(CO)Cl(MeOOCC=C(Cl)COOEt)]	2115vs	1710vs 1570vs	320m
X	[Pt(CO)Cl(EtOOCC=C(Cl)COOMe)]	2115vs	1700s 1575vs	320m
XI	(PPN)[Pt(CO)I$_2$(MeOOCC=C(Cl)COOEt)]	2065vs	1725s 1710s	
XII	(PPN)[Pt(CO)(SCN)$_2$(MeOOCC=C(Cl)COOMe)]	2080vs	1705s 1695s	2120m [c] 2105m [c]
XIII	[Pt(PPh$_3$)$_2$(SCN)(EtOOCC=C(Cl)COOMe)]		1705s	2100s [c]
XIV	[Pt(bipy)Cl(EtOOCC=C(Cl)COOMe)]		1700vs	340m
XV	[Pt(DPE)Cl(EtOOCC=C(Cl)COOMe)]		1708vs	305m

[a] In CHCl$_3$. [b] In nujol mulls (for the other bands see ref. 2). [c] ν(SCN).

chelating ligands, e.g. 2,2'-dipyridine and 1,2-bis(diphenylphosphino)ethane, resulted in displacement of CO and Cl$^-$ and formation of the neutral species [PtL$_2$Cl(ROOCC=C(Cl)COOR)] previously isolated [2].

The most interesting feature of this type of compounds having an alkoxy group in the γ-position is the surprising ease with which it can undergo alcoholysis. Thus I and II undergo complete exchange of the γ-alkoxy group on dissolution in primary alcohols, though it is necessary to reflux for ca. 2 hours for exchange to occur with secondary alcohols:

$$[cis\text{-Pt(CO)Cl}_2\text{(ROOCC=C(Cl)COOR)}]^- + \text{R'OH} \rightarrow [cis\text{-Pt(CO)Cl}_2\text{(ROOCC=C(Cl)COOR')}]^- + \text{ROH}$$

(III, R = Me, R' = Et; VI, R = Me, R' = allyl
IV, R = Me, R' = n-Pr; VII, R = Et, R' = Me
V, R = Me, R' = i-Pr; VIII, R = Et, R' = i-Pr)

This *trans*-esterification reaction was initially observed when I was crystallized from ethanol: colourless crystals were obtained but the ^{1}H NMR spectrum

TABLE 2

NMR DATA (Multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, sp = septet, m = multiplet; solvent = C_3D_6O)

Compound	^{1}H NMR (ppm)			J(Pt—H)	Other resonances
	$\delta(COOC\underline{H}_3)$	$\delta(COOC\underline{H}_2CH_3)$	$\delta(COOCH_2C\underline{H}_3)$		
I	3.67(s) 3.70(s)			2	7.6(m) ($C_6\underline{H}_5$)
II		4.19(q) 4.21(q)	1.25(t) 1.36(t)	2.4	7.6(m) ($C_6\underline{H}_5$)
III	3.67(s)			2	7.6(m) ($C_6\underline{H}_5$)
		4.18(q)	1.35(t)		
IV[a]	3.72(s)			2	4.16(t) ($OC\underline{H}_2CH_2CH_3$) 1.5—2.2(m) ($OCH_2C\underline{H}_2CH_3$) 0.98(t) ($OCH_2CH_2C\underline{H}_3$) 7.6(m) ($C_6\underline{H}_5$)
V	3.67(s)			2	5.03(sp) ($OC\underline{H}(CH_3)_2$) 1.33(d) ($OCH(C\underline{H}_3)_2$) 7.6(m) ($C_6\underline{H}_5$)
VI	3.65(s)			2	6.01(m) ($OCH_2C\underline{H}{=}CH_2$) 4.65(m) ($OC\underline{H}_2CH{=}CH_2$) $\left.\begin{matrix}5.15(m)\\5.26(m)\end{matrix}\right\}$ ($OCH_2CH{=}C\underline{H}_2$) 7.6(m) ($C_6\underline{H}_5$)
VII	3.70(s)				7.6(m) ($C_6\underline{H}_5$)
		4.17(q)	1.24(t)	2.6	
VIII		4.16(q)	1.25(t)	2.5	5.03(sp) ($OC\underline{H}(CH_3)_2$) 1.33(d) ($OCH(C\underline{H}_3)_2$)
IX[a]	3.90(s)			2	
		4.74(q)	1.52(t)		
X[a]	4.26(s)	4.36(q)	1.36(t)		
XI	3.66(s)			2	7.6(m) ($C_6\underline{H}_5$)
		4.16(q)	1.36(t)		
XII	3.83(s)				7.2—7.8(m) ($C_6\underline{H}_5$)
		4.26(q)	1.30(t)	2.5	

[a] $CDCl_3$.

clearly showed the presence of both methoxy and ethoxy groups in the ratio 1/1, due to the formation of III.

The similar reaction of I with n-PrOH, i-PrOH and allyl alcohol produced IV, V and VI, respectively, and the reaction of II with MeOH and i-PrOH gave VII and VIII, respectively. In all cases, alcohol interchange occurs only on one of the two carboalkoxy groups of the molecule: both ^{1}H NMR data, which indicate that α-$COOCH_3$ and α-$COOC_2H_5$ groups are unchanged being coupled with ^{195}Pt (J(Pt—H) 2 Hz) [5], and X-ray studies on VIII (see below) show that γ-alkoxy exchange occurs exclusively. Steric hindrance in the entering group seems to have an important influence on the yield of the final product and on the conditions needed for reaction: practically quantitative exchange occurs with MeOH and EtOH, while the bulkier n-PrOH, i-PrOH and allyl alcohol give only a partial transformation (about 70—80% of the starting product). The lack of reaction of I with t-BuOH even after 24 h can be explained in a similar fashion. The ^{1}H NMR data reported in Table 2 show that there is little variation in the methoxy resonance for III, IV, V and VI, and that the ethoxy resonances in VII and VIII are very similar: this suggests that γ-alkoxy exchange always occurs, the replacement probably being favoured by some sort of interaction with the platinum atom. This replacement does not seem to be dependent on the nature of the leaving alcohol: compound VIII, the crystals of which were particularly suitable for the X-ray study of the structure, was easily obtained from the reaction of VII with i-PrOH.

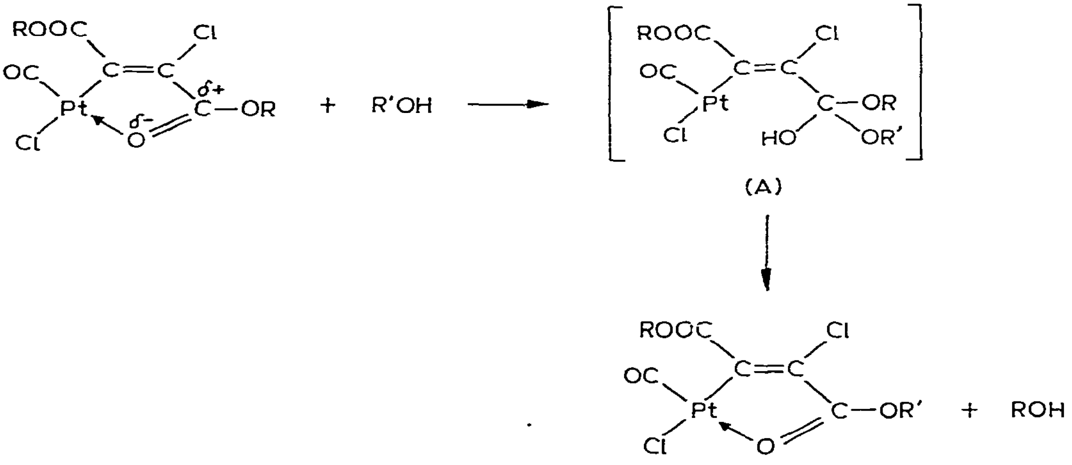
Compounds III, IV, V, VI, VII and VIII have also been obtained by dissolving [carbonylchloro(1,2-*trans*-dicarboalkoxy-2-chloroethenyl)platinum] in the appropriate alcohol in the presence of chloride ions. It is worth noting that selective alcoholysis has been found to occur also with the neutral species [Pt(CO)-Cl(ROOCC=C(Cl)COOR)] (R = Me or Et), when they are dissolved in absolute methanol or ethanol, specific exchange of the alkoxy group occurs:

$$[\mathrm{Pt(CO)Cl(ROOCC{=}C(Cl)COOR)}] + \mathrm{R'OH} \rightarrow$$

$$[\mathrm{Pt(CO)Cl(ROOCC{=}C(Cl)COOR')}] + \mathrm{ROH}$$

$$(\mathrm{IX,\ R = Me,\ R' = Et;\ X,\ R = Et,\ R' = Me})$$

In both cases the fact that substitution of the alkoxy groups occurs easily on the carboalkoxy attached to the β-vinyl carbon atom suggests that the coordination of the carbonyl ester with the metal is important in modifying the activity of the organic moiety bonded to platinum towards nucleophiles. It seems reasonable to assume that electron donation to the metal enhances the electrophilicity of the β-carbonyl ester carbon atom and facilitates the attack of the entering nucleophile, allowing the specific substitution of that particular alkoxy group. That the platinum has acidic character is also supported by the fact that the platinum centre may compete with the carbon atom in the reaction with the entering nucleophile, thus preventing the formation of the intermediate A and leading to coordination on the platinum atom.



(A)

(IX, R = Me, R' = Et;
X, R = Et, R' = Me)

Stronger nucleophiles such as aliphatic and aromatic primary and secondary amines prefer the metal centre, giving unstable derivatives, which slowly decompose to $[Pt(CO)_2]_n$, instead of forming the expected amides.

The chemical behaviour of all the anions obtained by alcohol exchange from I and II does not differ from that observed in the case of the starting compounds. Compound III reacts with I^- in anhydrous ethanol with displacement of the two chlorine atoms bonded to platinum without any modification of the β-chlorovinyl group:

$$[cis\text{-}Pt(CO)Cl_2(MeOOCC{=}C(Cl)COOEt)]^- + 2\,I^- \rightarrow [Pt(CO)I_2(MeOOCC{=}C(Cl)COOEt)]^- + 2\,Cl^-$$

(XI)

Similarly the treatment of VII with LiSCN in MeOH gives $[Pt(CO)(SCN)_2(EtOOCC{=}C(Cl)COOMe)]^-$ (XII), which is readily transformed by PPh_3 into the sparingly soluble neutral species $[Pt(PPh_3)_2(SCN)(EtOOCC{=}C(Cl)COOMe)]$ (XIII). Replacement of CO and of one chlorine bonded to the metal was also observed when (PPN)$[cis\text{-}Pt(CO)Cl_2(EtOOCC{=}C(Cl)COOMe)]$ was treated with neutral chelating ligands such as 2,2′-dipyridine (bipy) and 1,2-bis(diphenylphosphino)ethane (DPE): in alcoholic medium the neutral species [Pt(bipy)Cl(EtOOCC=C(Cl)COOMe)] (XIV) and [Pt(DPE)Cl(EtOOCC=C(Cl)COOMe)] (XV) were precipitated almost immediately.

Description of the crystal structure of (PPN)[*cis*-Pt(CO)Cl$_2$(EtOOCC=C(Cl)-COOPr-i)] (VIII)

The molecular geometry of the anion $[cis\text{-}Pt(CO)Cl_2(EtOOCC{=}C(Cl)COOPr\text{-}i)]^-$ is shown in Fig. 1; the most important bond distances and angles are listed in Tables 3 and 4, respectively. The configuration of the anion shows that platinum maintains the expected square planar coordination, the maximum deviation from the least square-plane being ±0.018 Å, The Pt—C(10) bond length (1.79(2) Å) is in the range of those found in other platinum(II) carbonyls (1.74(4) Å) [6,7]. As expected, the two Pt—Cl bond distances are different. One of the two bond lengths (Pt—Cl(1) 2.297(5) Å) is in good agreement with the sum of the single covalent radii of the atoms and is similar to the mean length (2.305(5) Å) [8] for the Pt—Cl bonds when *trans* to chloride in platinum(II) complexes. This implies that the carbonyl group has a low *trans* influence, consistent with other work in this area [6,9]. On the other hand, the Pt—Cl(3) distance (2.355(7) Å) is 0.040 Å longer than the normal Pt—Cl covalent length, due to the high *trans* influence of the bonded alkenyl group. Furthermore, the molecular geometry of the organic moiety clearly shows that the carboalkoxy groups are *trans* with respect to the double bond, possibly indicating that the γ-methoxy group in VII has undergone exchange. The values of the internal rotation angles C(3)—C(4)—C(5)—Cl(2) (8.5°) and Pt—C(4)—C(5)—Cl(2) (176.5°) show that the unsaturated organic molecule is only slightly misalligned with respect to the coordination plane. No significant intra- or inter-molecular contacts have been found. It is interesting to note that the shortest intramolecular non-bonded distance is that of Pt—O(3) (3.555(3) Å), while that of Pt—O(1)

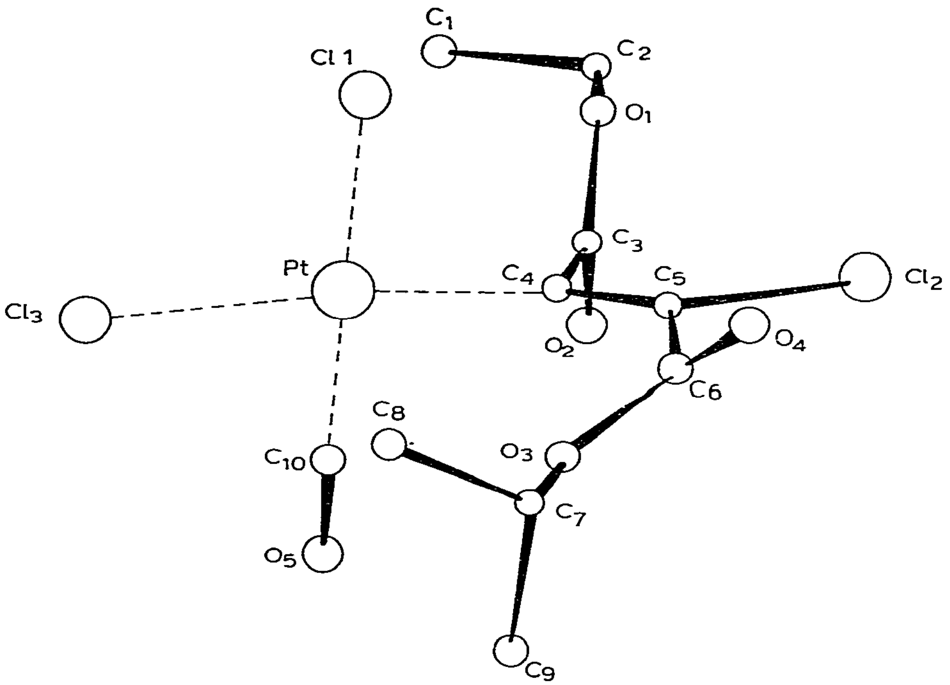


Fig. 1. The molecular geometry of the anion VIII.

is much longer (3.598 Å): this different steric situation may be a factor of some importance in the observed specific replacement of the alkoxy group.

The geometry of the cation is in agreement with that found for other PPN salts of transition metal anions [10]. The average P—N (1.58(1) Å) and P—C (1.79(1) Å) distances compare well with the average values of 1.57(2) and 1.80(2) Å quoted in Handy's paper. Also, the bond angles PNP (137.9(4)°), CPC (108.0(3)°) and NPC (111.01(4)°) are in the expected range for this type of compounds. The conformation of the phenyl rings, as shown by the average

TABLE 3

BOND LENGTHS (Å), (e.s.d.'s on the last significant figure are given in parentheses) FOR THE COMPLEX (PPN)[*cis*-Pt(CO)Cl_2(EtOOCC=C(Cl)COOPr-i)] (VIII)

Pt—Cl(1)	2.297(5)	C(5)—Cl(2)	1.75(2)
Pt—Cl(3)	2.355(7)	C(6)—O(4)	1.19(2)
Pt—C(4)	1.97(2)	C(6)—O(3)	1.32(3)
Pt—C(10)	1.79(2)	C(7)—O(3)	1.47(3)
C(1)—C(2)	1.47(4)	C(7)—C(8)	1.54(3)
C(2)—O(1)	1.54(3)	C(7)—C(9)	1.49(5)
C(3)—O(1)	1.29(2)	C(10)—O(5)	1.14(3)
C(3)—O(2)	1.20(2)	N—P [a]	1.58(1)
C(3)—C(4)	1.56(3)	P—C [a]	1.79(1)
C(4)—C(5)	1.31(2)	C—C [b]	1.40(3)
C(5)—C(6)	1.51(3)		

[a] Average values. [b] Average value for the C—C bonds in the phenyl ring.

TABLE 4

SELECTED BOND ANGLES (°), (e.s.d.'s on the last significant figure are given in parentheses), FOR THE COMPLEX: (PPN)[*cis*-Pt(CO)Cl_2(EtOOCC=C(Cl)COOPr-i)] (VIII)

Pt—C(4)—C(3)	112.6(9)	C(6)—O(3)—C(7)	120.6(6)
Pt—C(4)—C(5)	129.9(1.1)	C(8)—C(7)—C(9)	112.5(1.0)
Pt—C(10)—O(5)	177.8(8)	O(1)—C(2)—C(1)	107.1(9)
Cl(1)—Pt—Cl(3)	90.4(9)	O(1)—C(3)—O(2)	127.2(8)
Cl(1)—Pt—C(10)	177.5(9)	O(1)—C(3)—C(4)	112.7(9)
Cl(1)—Pt—C(4)	89.0(3)	O(2)—C(3)—C(4)	120.1(8)
Cl(3)—Pt—C(4)	179.3(8)	O(3)—C(6)—O(4)	124.4(6)
Cl(3)—Pt—C(10)	89.8(5)	O(3)—C(6)—C(5)	111.6(7)
C(2)—O(1)—C(3)	113.2(7)	O(3)—C(7)—C(8)	105.5(9)
C(3)—C(4)—C(5)	117.4(9)	O(3)—C(7)—C(9)	103.8(9)
C(4)—C(5)—Cl(2)	125.8(1.0)	O(4)—C(6)—C(5)	123.9(9)
C(4)—C(5)—C(6)	124.4(8)	P—N—P	137.9(4)
C(6)—C(5)—Cl(2)	109.8(8)	C—P—C [a]	108.0(4)
		N—P—C [a]	112.5(1.0)

[a] Average value.

TABLE 5

INTERNAL ROTATION ANGLES (°) (e.s.d.'s on the last significant figure are given in parentheses) FOR THE COMPLEX: (PPN)[*cis*-Pt(CO)Cl_2(EtOOCC=C(Cl)COOPr-i)] (VIII)

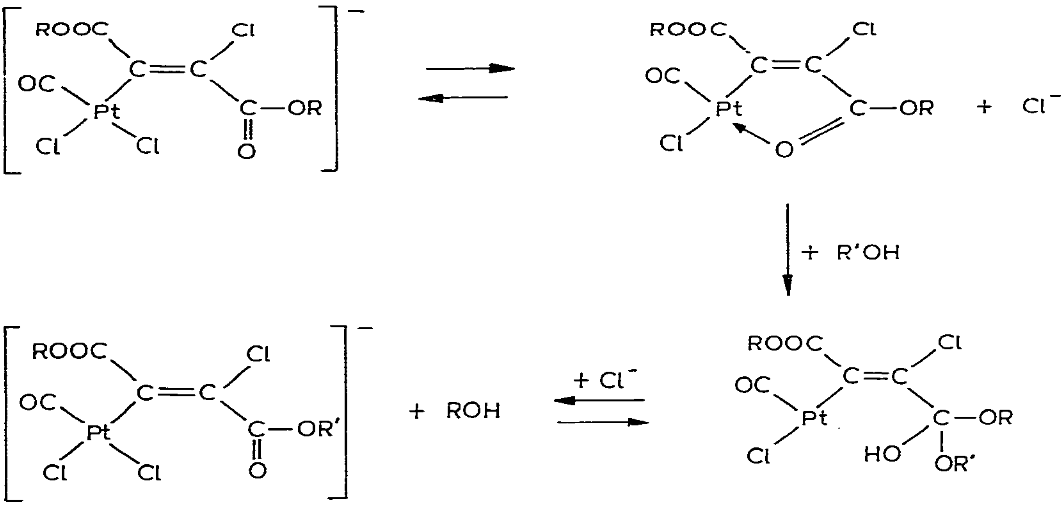
Pt—C(4)—C(5)—Cl(2)	−176.4(1.0)
Pt—C(4)—C(5)—C(6)	0.4(8)
Cl(1)—Pt—C(4)—C(3)	−107.5(9)
Cl(1)—Cl(3)—Pt—O(5)	178.6(9)
Cl(3)—Pt—C(10)—O(5)	−95.4(7)
Cl(3)—Pt—C(4)—C(3)	−95.7(8)
Cl(3)—Pt—C(4)—C(5)	89.0(9)
O(1)—C(3)—C(4)—Pt	94.3(8)
O(2)—C(3)—C(4)—C(5)	90.2(8)
O(2)—C(6)—C(5)—O(3)	−178.5(8)
O(3)—C(7)—C(8)—C(9)	−112.6(1.1)
O(4)—C(6)—C(5)—C(4)	159.7(9)
O(5)—C(10)—Pt—C(4)	84.7(1.2)

values of the angles reported in Table 5, are in agreement, with those discussed previously [10].

Conclusions

In the light of the behaviour reported previously [2] for the neutral β-chlorovinyl derivatives of platinum(II), the reactivity of these β-chlorovinyl anions is not surprising. Their stability towards carbon monoxide or weak bases appears to be higher than that of the parent neutral compounds, the relatively strong bond of the β-carbonylcarboalkoxy group towards platinum being replaced by the chloride strong bond. Alcohol exchange in platinum(II) complexes has been observed on [*trans*-PtX(COOR)$(PPh_3)_2$] in the presence of X^-, and in this case an anionic mechanism was proposed [11]. The specificity of the alcohol exchange observed when the anions were treated with various alcohols may be interpreted in terms of interaction with the metal of the β-carboalkoxy group, already proposed for the neutral compounds. This interaction enforces the presence of a positive charge on the γ-carbon atom, which is further stabilized by the conjugate bond system of the organic moiety. On the other hand, such stabilisation of the positive charge on the γ-carbon implies that the fourth coordination position of the square-planar platinum(II) may be freed by dissociation of the Cl⁻ group according to Scheme 1.

SCHEME 1



The fact that the crystal structure of VIII shows that the carbon monoxide molecule is located on the same side as the γ-i-propoxy group, indicates that on chloride dissociation free rotation around the Pt—vinylcarbon bond will be possible in solution. The isolation, in the solid state of the particular rotamer of VIII examined seems to be due to steric hindrance by the α-carboethoxy group, as it can be seen from the scale-model of VIII. On the other hand, preliminary structural data of other σ-alkenyl derivatives of platinum [4] indicate that when the less hindered carbomethoxy group is present on the α-vinyl carbon atom, the other possible rotamer is preferentially formed in the solid state.

The importance of the β-carboalkoxy group interaction with the central metal in the alcoholysis is supported by the fact that compounds XII, XIII, XIV and XV, in which the coordination sphere is filled by stable π-donor ligands, do not undergo alcohol exchange even on refluxing in the alcohols for several hours.

Experimental

Solvents were purified and dried by standard methods. Infrared spectra were recorded on a Perkin—Elmer 457 grating spectrometer, the samples being prepared as nujoll mulls between NaCl or CsI plates. The spectra were calibrated with polystyrene. Nuclear magnetic resonance spectra were recorded on a NEVA NV 14 spectrometer using chloroform-*d* or acetone-*d* solutions. Chemical shifts (δ) are reported in ppm, downfield from internal TMS, and coupling constants are given in Hz. Conductivity was determined on a Philips PR 9500 bridge. The [Pt(CO)Cl(ROOCC=C(Cl)COOR)] (R = CH_3, C_2H_5) complexes were prepared as previously described [2].

(PPN)[cis-Pt(CO)Cl_2(MeOOCC=C(Cl)COOMe)] (I)

[Carbonylchloro(1,2-*trans*-dicarbomethoxy-2-chloroethenyl)platinum] (0.41 g, 0.954 mmol) was added to a solution of PPNCl (1.15 g, 2 mmol) in absolute methanol (10 ml). The solution was stirred vigorously for 1 h and then cooled at —20°C. The white crystalline solid which separated was filtered off, washed with cold methanol (5 ml), dried, and recrystallized from absolute methanol (8 ml). (0.77 g, yield 80%), Λ_M 103.8 ohm^{-1} cm^2 mol^{-1} (10^{-3} *M* acetone), m.p. 131°C. The compound is soluble in acetone, chloroform and dichloromethane and insoluble in benzene, toluene and hydrocarbons. Found: C, 51.83; H, 3.68; Cl, 10.25; N, 1.44. $C_{43}Cl_3H_{36}NO_5P_2Pt$ calcd.: C, 51.13; H, 3.59; Cl, 10.53; N, 1.38%.

(PPN)[cis-Pt(CO)Cl_2(EtOOCC=C(Cl)COOEt)] (II)

[Carbonylchloro(1,2-*trans*-dicarboethoxy-2-chloroethenyl)platinum] (0.466 g, 1 mmol) was added with stirring to absolute ethanol (20 ml) containing PPNCl (1.0 g, 1.74 mmol). After evaporation to reduce the volume to 10 ml, the solution was cooled to —20°C. White crystals separated, and were filtered off, washed with cold ethanol (10 ml), and dried. (0.88 g, yield 85%). Λ_M 106.7 ohm^{-1} cm^2 $mole^{-1}$ (10^{-3} *M* acetone), m.p. 130°C. Found: C, 52.42; H, 3.75; Cl, 10.20; N, 1.40. $C_{45}Cl_3H_{40}NO_5P_2Pt$ calcd.: C, 52.06; H, 3.88; Cl, 10.25; N, 1.35%.

(PPN)[cis-Pt(CO)Cl_2(MeOOCC=C(Cl)COOEt)] (III)

(a) [Carbonylchloro(1,2-*trans*-dicarbomethoxy-2-chloroethenyl)platinum] (0.45 g, 1.03 mmol) was added with stirring to a solution of PPNCl (1.145 g, 2 mmol) in anhydrous ethanol (10 ml). Heating 1 h at 50°C and cooling to —20°C gave white crystals, which were filtered off, washed with cold ethanol (10 ml) and dried (0.79 g, yield 78%), Λ_M 115.7 ohm^{-1} cm^2 $mole^{-1}$ (1.05 × 10^{-3} *M* acetone), m.p. 128°C. Found: C, 51.75; H, 3.63; N, 1.43. $C_{44}Cl_3H_{38}NO_5P_2Pt$ calcd.: C. 51.60; H, 3.74; N, 1.37%.

(b) I (0.93 g, 0.92 mmol) was dissolved in anhydrous ethanol (20 ml) and kept at 50°C for 1 h. On cooling at —20°C white crystals separated (0.66 g, yield 70%). Found: C, 51.81; H, 3.65; N, 1.41%.

(PPN)[cis-Pt(CO)Cl_2(MeOOCC=C(Cl)COOPr-n)] (IV)

This compound was prepared as described for III but using dry n-propanol (10 ml) for dissolving [carbonylchloro(1,2-*trans*-dicarbomethoxy-2-chloroethenyl)platinum] (0.436 g, 1 mmol) and PPNCl (1.147 g, 2 mmol) or I (0.856 g, 0.85 mmol) (0.53 g, yield 51%; 0.34 g, yield 40%), m.p. 115°C. The integration of the signals of the NMR spectrum showed that the alcohol exchange resulted in about 80%. Found: C, 51.88; H, 3.73; N, 1.32. $C_{46}Cl_3H_{42}NO_5P_2Pt$ calcd.: C, 52.06; H, 3.88; N, 1.35%.

(PPN)[cis-Pt(CO)Cl_2(MeOOCC=C(Cl)COOPr-i)] (V)

This compound was prepared similarly by dissolving in isopropanol (10 ml) [carbonylchloro(1,2-*trans*-dicarbomethoxy-2-chloroethenyl)platinum] (0.44 g, 1 mmol) and PPNCl (1.147 g, 2 mmol) or I (0.82 g, 0.81 mmol). It was recrystallized from anhydrous isopropanol (0.6 g, yield 58%; 0.45 g, yield 53%), m.p. 133°C. Found: C, 51.40; H, 3.50; N, 1.29. $C_{46}Cl_3H_{42}NO_5P_2Pt$ calcd.: C, 52.06; H, 3.88; N, 1.35%.

(PPN)[cis-Pt(CO)Cl$_2$(MeOOCC=C(Cl)COOAllyl)] (VI)

This compound was prepared similarly by refluxing for 2 h in allyl alcohol (20 ml) [carbonylchloro(1,2-*trans*-dicarbomethoxy-2-chloroethenyl)platinum] (0.4 g, 0.91 mmol) and PPNCl (1.1 g, 1.91 mmol) or I (0.78 g, 0.77 mmol), (0.46 g, yield 45%; 0.38 g, yield 48%). Λ_M 106.6 ohm^{-1} cm^2 $mole^{-1}$ (1.16×10^{-3} *M* acetone), m.p. 104°C. Found: C, 53.09; H, 3.69; N, 1.41. $C_{45}Cl_3H_{38}NO_5P_2Pt$ calcd.: C, 52.16; H, 3.70; N, 1.35%.

(PPN)[cis-Pt(CO)Cl$_2$(EtOOCC=C(Cl)COOMe)] (VII)

This compound was prepared similarly by dissolving in absolute methanol (10 ml) [carbonylchloro(1,2-*trans*-dicarboethoxy-2-chloroethenyl)platinum] (0.42 g, 0.9 mmol) and PPNCl (0.88 g, 1.53 mmol) or II (0.77 g, 0.74 mmol) (0.534 g, yield 58%; 0.356 g, yield 47%), m.p. 97°C. Found: C, 52.35; H, 3.57; N, 1.51. $C_{44}Cl_3H_{38}NO_5P_2Pt$ calcd.: C, 51.60; H, 3.74; N, 1.37%.

(PPN)[cis-Pt(CO)Cl$_2$(EtOOCC=C(Cl)COOPr-i)] (VIII)

This compound was prepared by refluxing in isopropanol (20 ml) for 2 h VII (0.36 g, 0.35 mmol) and PPNCl (0.172 g, 0.3 mmol) (0.233 g, yield 64%), m.p. 91°C. Found: C, 53.00; H, 3.90; Cl, 10.35; N, 1.33; Pt, 19.01. $C_{46}Cl_3H_{42}NO_5P_2Pt$ calcd.: C, 51.96; H, 4.07; Cl, 10.22; N, 1.35; Pt, 18.75%.

[Pt(CO)Cl(MeOOCC=C(Cl)COOEt)] (IX)

A solution of [carbonylchloro(1,2-*trans*-dicarbomethoxy-2-chloroethenyl)-platinum] (0.260 g, 0.596 mmol) in absolute ethanol (10 ml) was stirred under nitrogen for 20 min at 50°C. The yellow solution was evaporated to dryness and the solid residue redissolved in hot toluene (20 ml) and filtered off. The filtrate was evaporated in vacuum to 10 ml and then cooled to −10°C. The golden-yellow needles were filtered off, washed with cold toluene (15 ml), and dried (0.164 g, yield 61.2%). Found: C, 21.92; H, 1.87. $C_8Cl_2H_8O_5Pt$ calcd.: C, 21.35; H, 1.79%.

[Pt(CO)Cl(EtOOCC=C(Cl)COOMe)] (X)

A solution of [carbonylchloro(1,2-*trans*-dicarboethoxy-2-chloroethenyl)-platinum] (0.506 g, 1.09 mmol) in absolute methanol (30 ml) was kept at 40°C for 30 min under nitrogen. The yellow solution was then evaporated to dryness and the solid residue treated with toluene (20 ml). The suspension was filtered and the filtrate evaporated in vacuum to reduce the volume to 10 ml. Cooling at −10°C gave yellow needles, which were filtered off, washed with cold toluene (10 ml) and cold hexane (20 ml), and dried, (0.294 g, yield 60%). Found: C, 21.76; H, 1.85. $C_8Cl_2H_8O_5Pt$ calcd.: C, 21.35; H, 1.79%.

(PPN)[Pt(CO)I$_2$(MeOOCC=C(Cl)COOEt)] (XI)

III (0.137 g, 0.133 mmol) and NaI (0.346 g, 2.3 mmol) dissolved in anhydrous ethanol (10 ml) were heated at 70°C for 2 h. On cooling to −20°C pale-yellow crystals separated which were filtered off, washed with cold ethanol (5 ml), and dried, (0.0835 g, yield 52%), m.p. 120°C. Found: C, 43.67; H, 3.23, Cl, 3.07; I, 21.57; N, 1.10. $C_{44}ClH_{38}I_2NO_5P_2Pt$ calcd.: C, 43.77; H, 3.17; Cl, 2.94; I, 21.03; N, 1.16%.

(PPN)[Pt(CO)(SCN)$_2$(EtOOCC=C(Cl)COOMe)] (XII)

A solution of [carbonylchloro(1,2-*trans*-dicarboethoxy-2-chloroethenyl)-platinum] (0.31 g, 0.67 mmol) in anhydrous methanol (10 ml) containing LiSCN (0.3 g, 5 mmol) was refluxed for 3 h. The solution was cooled to room temperature, and addition of PPNSCN (0.48 g, 0.84 mmol) gave a microcrystalline white solid, which was recrystallized from anhydrous methanol, (0.230 g, yield 32%), m.p. 91°C. Found: C, 52.16; H, 3.60; N, 3.93. $C_{46}ClH_{38}N_3O_5P_2PtS_2$ calcd.: C, 51.66; H, 3.58; N, 3.93%.

[Pt(PPh$_3$)$_2$(SCN)(EtOOCC=C(Cl)COOMe)] (XIII)

XIII (0.49 g, 0.46 mmol) in 10 ml $CHCl_3$ was treated with PPh_3 (0.28 g, 1.06 mmol). Cooling gave a white solid, which was filtered off, washed with methanol (10 ml) and toluene (10 ml), and dried, (0.258 g, yield 58%), m.p. 210°C. Found: C, 53.99; H, 3.96; N, 1.54. $C_{44}ClH_{38}NO_4P_2PtS$ calcd.: C, 54.52; H, 3.93; N, 1.44%.

[Pt(bipy)Cl(EtOOCC=C(Cl)COOMe)] (XIV)

When a solution of VII (0.41 g, 0.4 mmol) in $CHCl_3$ (10 ml) was treated with 2,2′-bipyridine (0.187 g, 1.2 mmol) the solution immediately became pale-yellow. Addition of methanol (10 ml) at −10°C gave a yellow-green microcrystalline solid which was filtered off, washed with methanol (10 ml) and toluene (10 ml), and dried, (0.157 g, yield 68%). Found: C, 36.19; H, 2.38; N, 4.97. $C_{17}Cl_2H_{16}N_2O_4Pt$ calcd.: C, 35.50; H, 2.78; N, 4.84%.

[Pt(DPE)Cl(EtOOCC=C(Cl)COOMe)] (XV)

VII (0.407 g, 0.4 mmol) in $CHCl_3$ (20 ml) was treated with 1,2-bis(diphenylphosphino)ethane (DPE) (0.2 g, 0.5 mmol). After stirring for 1 h at 40°C the volume was reduced to 5 ml. Addition of methanol (20 ml) gave a white solid, which was filtered off and washed with methanol (10 ml), (0.250 g, yield 77%), m.p. >240°C. Found: C, 48.50; H, 3.38. $C_{33}Cl_2H_{32}O_4P_2Pt$ calcd.: C, 48.30; H, 3.93%.

Crystallographic data collection

A crystal of prismatic shape (approximate dimensions 0.35 × 0.23 × 0.19 mm) obtained by slow evaporation from an isopropanol solution of VIII was used. From systematic absences the space group was determined as $P2_1/n$ with 4 molecules in the unit cell. The lattice constants a 33.593(3), b 9.164(1), c 15.170(2) Å, β 101.14(5)° were obtained from diffractometer data by least squares refinement of the values of the setting angles for 25 reflections. The value for D_{calc} is 1.51 g cm^{-3}, while the observed density D_{obs} is 1.50(2) g cm^{-3}.

5956 reflections were collected on an automatic diffractometer up to sin θ 0.5385 (Mo-K_α radiation, graphite monochromated, λ 0.7169 Å) using the ω

(continued on p. 211)

TABLE 6

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR COMPLEX VIII (e.s.d.'s on the last significant figure are given in parentheses; anisotropic temperature factor $T = \exp - 1/4(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)$

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	−0.11407(2)	0.05430(8)	0.02855(5)	5.79(3)	3.08(2)	4.51(3)	−0.86(8)	2.90(5)	−1.18(7)
Cl(1)	−0.1711(2)	0.1816(6)	0.0446(3)	6.4(3)	6.9(3)	6.1(3)	3.9(5)	1.5(4)	−3.1(5)
Cl(2)	−0.0870(2)	0.0282(6)	0.3400(3)	8.6(3)	7.1(3)	4.9(2)	−0.7(5)	3.3(4)	0.8(4)
Cl(3)	−0.1251(2)	0.1163(6)	−0.1249(3)	9.7(4)	4.7(2)	5.3(3)	−0.2(5)	4.6(5)	−0.4(4)
O(1)	−0.1515(4)	−0.1797(16)	0.1848(10)	7.7(8)	6.0(7)	9.1(9)	−1.5(10)	6.6(8)	0.8(6)
O(2)	−0.0894(5)	−0.2513(16)	0.1727(11)	10.4(10)	5.1(7)	11.0(10)	1.2(10)	6.8(9)	0.3(7)
O(3)	−0.0564(4)	0.2584(13)	0.1587(9)	8.3(8)	3.3(5)	8.3(8)	−3.2(10)	8.3(9)	−3.3(9)
O(4)	−0.0838(6)	0.3324(16)	0.2734(11)	10.4(10)	6.8(9)	10.6(10)	−6.7(10)	7.0(10)	−6.9(8)
O(5)	−0.0397(5)	−0.1032(19)	0.0127(13)	10.1(10)	10.9(12)	11.5(10)	1.6(10)	6.8(8)	−1.8(9)
C(1)	−0.1622(8)	−0.3800(24)	0.0918(16)	11.3(12)	5.8(12)	7.9(7)	−3.4(10)	5.1(10)	−1.0(9)
C(2)	−0.1636(8)	−0.3419(25)	0.1847(17)	11.1(12)	4.6(13)	9.9(7)	−5.2(10)	6.5(8)	1.8(8)
C(3)	−0.1150(6)	−0.1598(22)	0.1727(12)	6.6(11)	5.0(10)	5.4(9)	0.8(8)	5.0(8)	1.6(7)
C(4)	−0.1054(5)	0.0033(18)	0.1569(11)	4.7(9)	3.4(7)	5.2(9)	0.2(7)	1.3(9)	0.1(6)
C(5)	−0.0909(4)	0.0826(19)	0.2278(11)	3.3(8)	4.9(9)	4.9(8)	0.6(7)	1.2(9)	1.0(7)
C(6)	−0.0767(6)	0.2385(10)	0.2243(12)	5.6(9)	5.4(9)	5.2(9)	−0.6(8)	4.1(9)	−1.2(8)
C(7)	−0.0423(7)	0.4050(21)	0.1393(15)	8.8(14)	4.5(10)	7.8(13)	−4.6(9)	5.1(8)	0.5(9)
C(8)	0.0011(7)	0.3790(32)	0.1243(17)	7.0(14)	10.7(7)	9.9(12)	−4.0(10)	6.2(8)	−2.3(10)
C(9)	−0.0702(8)	0.4345(27)	0.0564(18)	9.1(15)	6.1(1)	10.2(17)	1.6(8)	−3.3(2)	2.9(2)
C(10)	−0.0683(7)	−0.0394(26)	0.0194(14)	7.7(12)	6.0(8)	9.1(12)	−1.5(9)	6.6(7)	0.8(9)

TABLE 7. ATOMIC FRACTIONAL COORDINATES AND THERMAL FACTORS FOR THE PPN$^+$ GROUP

	x/a	y/b	z/c	B_{iso}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P(1)	−0,4010(1)	0,645(5)	0,1050(3)	4,1(3)	3,4(2)	2,4(2)	3,9(2)	−0,3(3)	1,4(3)	0,4(3)
P(2)	0,3157	0,0494	0,0122	3,4(3)	4,1(2)	2,5(2)	3,7(2)	0,1(3)	2,2(3)	0,3(4)
N	0,3610	0,1081	0,0395	5,5(4)	2,8(5)	3,6(5)	4,3(5)	−1,1(7)	2,2(9)	0,8(9)
C(1P1)	0,3940(5)	−0,0362(19)	0,2023(10)	7,3(5)						
C(2P1)	0,4280(5)	0,2290(17)	0,1428(10)	7,0(5)						
C(3P1)	0,4571(6)	0,2330(21)	0,2214(12)	6,0(5)						
C(4P1)	0,4706(7)	0,3665(26)	0,2443(15)	3,3(3)						
C(5P1)	0,4696(7)	0,4818(25)	0,1871(14)	4,7(4)						
C(6P1)	0,4419(6)	0,4816(22)	0,1121(13)	4,3(3)						
C(7P1)	0,4327(4)	−0,0421(17)	0,0474(9)	6,2(4)						
C(8P1)	0,4684(5)	−0,1062(17)	0,0935(11)	5,3(4)						
C(9P1)	0,4213(5)	−0,0580(20)	−0,0453(10)	5,3(4)						
C(10P1)	0,3730(6)	−0,0384(23)	0,3468(13)	5,4(4)						
C(11P1)	0,4802(6)	−0,2104(21)	−0,0444(12)	6,1(5)						
C(12P1)	0,4460(6)	−0,1449(21)	−0,0925(12)	6,3(5)						
C(13P1)	0,4927(6)	−0,1926(22)	0,0446(12)	5,9(5)						
C(14P1)	0,3767(6)	−0,1893(23)	0,3493(13)	5,1(4)						
C(15P1)	0,3869(6)	−0,2655(24)	0,2780(14)	4,7(4)						
C(16P1)	0,3959(6)	−0,1918(23)	0,2014(13)	3,6(3)						
C(17P1)	0,3820(5)	0,0359(21)	0,2710(11)	5,0(4)						
C(18P1)	0,4191(5)	0,3515(20)	0,0856(11)	7,0(5)						
C(1P2)	0,2833(5)	0,1223(18)	0,0820(10)	6,7(5)						
C(2P2)	0,3013(5)	0,2224(20)	0,1486(12)	6,9(5)						
C(3P2)	0,2744(7)	0,2852(25)	0,2035(15)	5,9(4)						
C(4P2)	0,2342(6)	0,2388(25)	0,1938(14)	3,4(3)						
C(5P2)	0,2184(7)	0,1354(25)	0,1285(14)	5,0(4)						
C(6P2)	0,2438(6)	0,0757(23)	0,0715(13)	5,2(4)						
C(7P2)	0,2977(5)	0,1028(16)	−0,1019(10)	5,5(4)						
C(8P2)	0,2597(5)	0,0548(22)	−0,1472(11)	5,5(4)						
C(9P2)	0,2463(6)	0,0964(20)	−0,2389(12)	5,0(4)						
C(10P2)	0,2708(6)	0,1792(22)	−0,2823(12)	4,4(4)						
C(11P2)	0,3077(6)	0,2257(22)	−0,2340(12)	5,0(4)						
C(12P2)	0,3225(5)	0,1921(21)	−0,1437(12)	7,5(4)						
C(13P2)	0,3283(5)	−0,2260(19)	−0,0515(11)	7,9(5)						
C(14P2)	0,3278(5)	−0,3780(21)	−0,0492(12)	8,9(7)						
C(15P2)	0,3108(7)	−0,4484(23)	0,0123(15)	3,2(3)						
C(16P2)	0,2947(7)	−0,2165(27)	0,0751(16)							
C(17P2)	0,2920(8)	−0,3757(32)	0,0770(18)							
C(18P2)	0,3129(4)	−0,1471(17)	0,0120(10)							

scan mode (scan width 1.00°, scan speed 0.05° $\sec^{-1}$) and by averaging two background counts at both sides of the peak for each reflection (5 sec each). During the data collection three standard reflections were measured every hour to check the experimental conditions, and no significant variations or decay of the crystal were detected. The data were corrected for Lorentz and polarisation effects but no absorption corrections (due to the small size and regular shape of the crystal) or extinction corrections were necessary. 3142 reflections having a net intensity $I \geqslant 3\sigma(I)$ were considered as observed. The structure was solved by Patterson and Fourier methods and refined by block diagonal least squares with anisotropic temperature factors for the Pt, P, N and O atoms and the carbons of the acetylenic moiety, while isotropic factors were used for the carbons of the phenyl rings. No attempt was made to locate the hydrogen atoms, but their contribution, calculated from fixed idealized atomic position (C—H bond length 1.05 Å) was added during the last part of the refinement. The final agreement factor $R_1 = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$ for the observed reflection was 0.054. A final difference map showed no significant features. For the non-hydrogenic atoms the scattering factors from reference [12] corrected for the real part of the anomalous scattering [13] were used, while for the hydrogen atoms the values in reference [14] were used. The final atomic coordinates and temperature factors are listed in Table 6 while a perspective view of the anionic part of the molecule showing the numbering of the atoms is shown in Fig. 1. In Table 7 are given the atomic fractional coordinates and thermal factors for the PPN^+ group.

Acknowledgements

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