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CYCLIC COMPOUNDS WITH Pt–C σ-BONDS FORMED BY INSERTION OF AN OLEFINIC PHOSPHINE INTO Pt–H BONDS

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SUMMARY

A novel method for the preparation of compounds containing metal–carbon σ-bonds, stabilised by the chelate effect, is presented. Neutral and cationic complexes of platinum(II) containing such σ-bonds have been prepared by the insertion of the *ortho*-olefinic moiety of a chelate phosphine ligand, (*o*-vinylphenyl)diphenylphosphine, into hydrido–platinum(II) complexes. Reasons for the stability of the insertion products are briefly discussed, as are the mechanism of their formation and some of their reactions.

The structure and stereochemistry of the new complexes have, for the most part, been elucidated, the usual physico-chemical techniques, especially IR and NMR spectroscopy, being employed.

INTRODUCTION

An understanding of the factors affecting the formation and breaking of metal–carbon σ-bonds is important in transition-metal-catalyzed dimerization, oligomerization, polymerization, hydrogenation and isomerization reactions, as well as in hydroformylation of unsaturated organic molecules and in other areas of homogeneous catalysis[1]. In many of these reactions it is believed that the formation of hydrido–metal complexes and their subsequent reactions with unsaturated compounds are key steps in the overall reactions[2].

In a preliminary report[3] of a novel method for the formation of transition metal–carbon σ-bonds, we showed that reaction of (*o*-vinylphenyl)diphenylphosphine (VP) with hydrido-complexes led to insertion of the olefinic part of the ligand into the Pt–H bond, with simultaneous coordination of the tertiary phosphine group to the metal, making use of the chelate effect to stabilize the Pt–C bond formed by the insertion reaction. Since then much interest has been shown in this and closely related areas. The most significant development in transition organometallic chemistry in 1970 was a notable extension in the range of isolable alkyls[4]. This included, in addition to the important work of Lappert[4] and of Wilkinson[4], the extension of our

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work using the chelate effect, initially reported for platinum(II), to manganese(I) by Bennett[5], and insertion into the Pt–H bond in hydrido–phosphine complexes of platinum(II) by simple olefins[6−8] and several dienes[6]. Other subsequent illustrations of the use of the chelate effect have included chelate-stabilized alkyl derivatives of platinum(II) formed by the reaction of platinum(II) complexes with *o*-(diphenylphosphino)benzylpotassium[9] or with the Grignard reagent of *o*-chloroallylbenzene[10].

Here we show various examples of the insertion of the *ortho*-olefinic moiety of the chelate ligand VP into the Pt–H bond in varying types of complex to give compounds with a platinum–carbon σ-bond. Possible mechanisms for this insertion are briefly discussed, as are cleavage reactions of the metal–carbon bond and some attempted oxidations to platinum(IV) complexes.

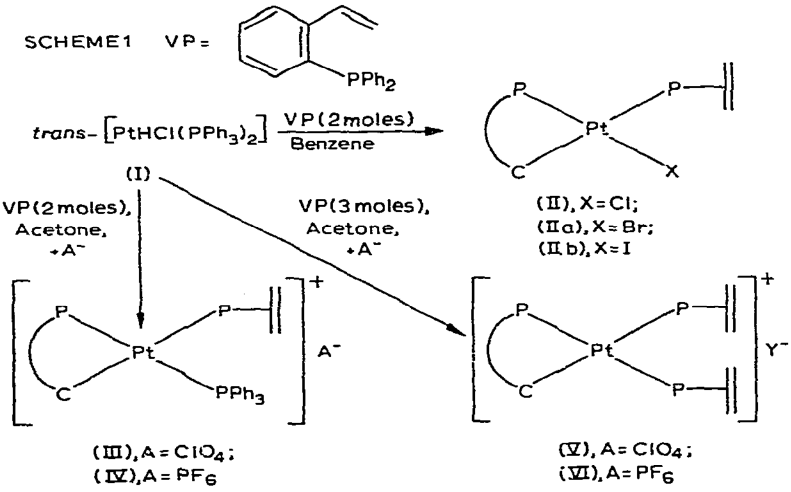
RESULTS AND DISCUSSION

The first observation of insertion of olefins into the platinum–hydrogen bond was by Chatt and Shaw[11], in investigating the forward reaction of the equilibrium:

$$\textit{trans}\text{-}[\mathrm{PtHCl(PEt_3)_2}] + \mathrm{C_2H_4} \rightleftharpoons \textit{trans}\text{-}[\mathrm{PtEtCl(PEt_3)_2}] \qquad (1)$$

under vigorous conditions (90° and 40 atm). The reverse reaction has also been studied[11−13], and it has been shown that the equilibrium position depends both on the nature of the olefin and on the group *trans* to the hydride ligand[12]. This is discussed again below, in connection with the possible mechanism of the insertion.

We now report insertion reactions which go to completion under mild conditions, making use of both the chelate effect and of suitable ligands *trans* to hydride. Thus *trans*-[PtHCl(PPh$_3$)$_2$] [(I); see Scheme 1] reacts with two equivalents of VP in benzene under reflux to give (II): other examples of insertion reactions involving VP are also given in Scheme 1.

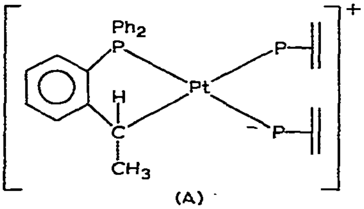


Reaction to give complexes of type (II) appears to be complete [whereas the reaction in eqn. (1) is not] primarily because as well as insertion of the olefinic moiety of the ligand VP into the Pt–H bond of (I) it is possible to substitute the phosphine moiety of the ligand in place of triphenylphosphine, with concomitant formation of a ring: *i.e.*, we obtain a chelate complex. Whatever the stereochemistry of the final product [we favour that shown in (II), as discussed below], the ligand X is *trans* to a group of high *trans*-influence (tertiary phosphine or σ-bonded carbon). Thus in a polar solvent (*e.g.* acetone) in the presence of sodium perchlorate and of *additional* ligand VP (one or two molar equivalents), it is possible to isolate complexes (III) or (V) respectively, the ligand X being displaced as (insoluble) NaX. The lattice energy of this substance contributes much to the driving force to give the perchlorate salts of the cationic alkyl–platinum complexes as shown. Complexes (III)–(VI) show conductivities in agreement with their formulation as 1/1 electrolytes (see Table 2).

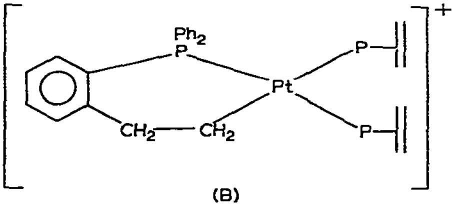
Complex (II) is non-conducting in nitrobenzene. Its IR spectrum in the region 4000–200 cm^{-1} indicates that insertion into the Pt–H bond of (I) has occurred, since the bands in the spectrum of (I) assigned to ν(Pt–H) and δ(Pt–H) have disappeared. Among new bands associated with the ligand VP present in (II), there is absorption at 1620 w cm^{-1} due to a CH_2 scissoring mode[14] [previously assigned to ν(C=C)] showing the presence in compound (II) of a VP ligand coordinated through the phosphorus atom alone. Absorption in the range 595–589 cm^{-1} is present in the IR spectra of the complexes (II)–(VI), assignable to ν(Pt–C), although this vibration probably contains some admixed δ(Pt–C–C) motion[15], making detailed comment on the frequencies unwarranted. By comparison of the spectra of (II) with (IIa) and (IIb) [the bromo- and iodo-complexes respectively, prepared analogously to (II)], ν(Pt–Cl) of complex (II) can be assigned as a band at 289 vs cm^{-1}, which favours PR_3 as the *trans*-ligand rather than σ-bonded carbon[16,17]. Hence we favour the stereochemistry shown for (II) in the Scheme.

We are not certain whether the structure Pt–CH_2–CH_2– (implying a 6-membered ring involving Pt) or Pt–$CH(CH_3)$– (implying a 5-membered ring) is present in complex (II): we favour the smaller ring. (II) shows absorption at 1047 mw cm^{-1}, possibly due to C–CH_3 rocking, which is absent in the spectrum of VP or its complexes. Also, there is no absorption at ca. 1200 cm^{-1} as is found in Pt–CH_2–X compounds and assigned to CH_2 rocking[12]. ^1H NMR studies on (II) are made difficult by the low solubility of the complex; in addition, interpretation of the (complex) spectrum is ambiguous because coupling to *cis*- and *trans*-^{31}P atoms can be comparable in magnitude[18].

Complex (V) was sufficiently soluble in acetone-d_6 for an NMR spectrum (60 MHz, 34°) to be obtained. The overall stereochemistry is as shown in Scheme 1, but the alternative modes of olefin insertion give either of the structures as shown in (A) and (B). We consider the spectrum to favour structure (A), in agreement with the suggestion already made, but the interpretation of the spectrum is not without possible ambiguity, being complicated by the many nuclei possessing spins which are present in complex (V). As well as signals due to phenyl groups and to olefinic



(A)



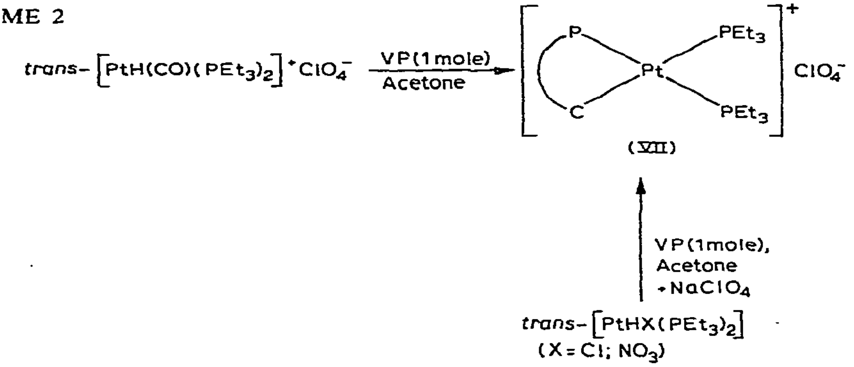
(B)

protons of the monodentate VP ligands, the spectrum contains a complex resonance, symmetrical about its centre which is at τ 9.35 ppm. This is due to protons of the Pt–CH(CH$_3$)– or Pt–CH$_2$–CH$_2$– groups of (A) or (B) respectively. The complex resonance can be interpreted as being due to the CH$_3$ protons of structure (A), with the parameters; J(Pt–H) 36.5 ± 1, J(Pt–P$_{trans}$) *and* J(CH$_3$–H) 7.8 ± 0.5, and J(Pt–P$_{cis}$) ~ 1.5 ± 0.5 Hz. We can assign the spectrum only by this coincidental equal coupling. Further, it was not possible to definitely assign a resonance due to the single methylenic proton of structure (A), but this may be a broad, unresolved peak at τ 8.6 ppm. We suggest that the many splittings affecting this proton give a resonance (in any case only one third as intense as that previously described) so broad that it is not observable above the noise in the spectrum of complex (V).

Some of the factors affecting the formation of five or six membered ring systems in similar insertion reactions have been discussed by Bennett *et al.*[5].

A further example of the use of the olefin insertion reaction to prepare cationic platinum alkyl complexes is shown in the synthesis of (VII) from various hydrido–platinum precursors (Scheme 2).

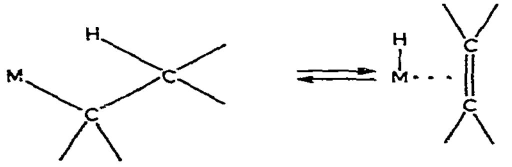
SCHEME 2



In the case of the (instantaneous) reaction between VP and *trans*-[PtH(CO)-(PEt$_3$)$_2$]ClO$_4$ in acetone solution at ambient temperature, we obtain simultaneous olefin insertion, loss of the carbonyl group (as carbon monoxide), and a *trans*→*cis* reorientation of the two triethylphosphine ligands, a requirement which is dictated by the chelate nature of the phosphine–alkyl ligand.

Mechanism of formation of the insertion products

It has been generally accepted that π-accepting supporting ligands directly stabilize metal–carbon σ-bonds against homolysis. Recently however it has been shown that in some cases at least the limiting factors in metal alkyl stability are largely mechanistic[4,19], a facile decomposition route being given by the reaction:



(2)

In the examples of metal alkyl compounds reflected in the complexes under discussion, this equilibrium can be envisaged as being held to the left by the chelate group of the Pt–CH(Me)$C_6H_4(PPh_2)$ ring. Once the Pt–C bond is formed there is no reason to expect it to be weak. The chelate nature of the ligand P–C (o-CH(Me)-$C_6H_4PPh_2$) once formed militates against concerted bond cleavage[20] by either β-elimination [*i.e.* reaction (2) above], reductive elimination (which could occur via Pt^{IV} complexes), or binuclear elimination.

To revert to the insertion process, the sequence of steps is uncertain. A common hypothesis has been that reactions such as (1) take place in both directions via pentacoordinate π-olefinic complexes[12]: however, the observation by Clark[7,8] of insertion reactions such as (3), which occurs when $AgPF_6$ is used only in catalytic amounts, and takes place rapidly at 25° and 1 atm [in marked contrast to the conditions of reaction (1)] suggests that insertion may be achieved easily by a catalytic mechanism, and that the ease of olefin insertion into the Pt–H bond is related to the

$$trans\text{-}[PtHBr(PMePh_2)_2]+AgPF_6 \xrightarrow{Me_2CO}$$

$$trans\text{-}[PtH(PMePh_2)_2(Me_2CO)]PF_6+AgBr \xrightarrow{(i),\ C_2H_4;\ (ii),\ L}$$

$$\longrightarrow trans\text{-}[Pt(Et)(PMePh_2)_2L]^+PF_6 \quad (3)$$

e.g. L = 2,4,6-trimethylpyridine, CO

ease of displacement of the ligand *trans* to the hydride ligand by olefin. The key intermediate in the insertion process is then essentially four- and not five-coordinate[7,8]. The olefin is apparently activated towards insertion into the Pt–H bond once it occupies the position *trans* to hydridic hydrogen, *e.g.* in the very labile intermediate in reaction (3), *trans*-$[PtH(PMePh_2)_2(C_2H_4)]PF_6$, isolable at low temperatures[8].

In the case of the reaction (I)→(II) (see Scheme 1), we postulate displacement of chloride *trans* to hydride as a first step, with concomitant coordination of the VP ligand through its phosphorus donor atom. Displacement of a PPh_3 ligand by the olefinic moiety of the VP ligand and isomerization can give a four-coordinate cationic intermediate $[PtH(PPh_3)(VP)]^+$, having olefin in *trans* position to hydride.

In the reaction leading to complex (VII) (Scheme 2) nitrate is only a weakly bonded ligand, and is in this case also *trans* to the hydride ligand of very high *trans*-influence. With *trans*-$[PtH(CO)(PEt_3)_2]^+$ as the precursor, loss of CO *trans* to H in an irreversible step and coordination of the donor atom of VP gives *trans*-$[PtH(P{-}\|)(PEt_3)_2]^+$ as an intermediate: a twisting mechanism (pyramidal intermediate) could be involved in the formation of the observed final product *cis*-$[Pt(PEt_3)_2(P{-}C)]^+$, since complete loss of the strongly bonded ligand triethylphosphine from the inner coordination sphere of platinum(II) is unlikely.

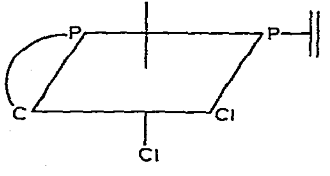
Some reactions of the insertion products

We have shown that compound (IIa) probably contains a five-membered ring. Attempts to form a cyclic acyl complex by reaction with CO in various solvents at ambient temperature and above but only at 1 atm pressure of CO were unsuccessful. Insertion of CO (to give an acyl complex) into *trans*-$[PtMeCl(PEt_3)_2]$ requires vigorous conditions (90°, 50–100 atm): in our case the reluctance to acyl formation may be steric and/or electronic in nature. The reaction would involve an increase in ring size from 5 to 6, and also the π-acceptor capacity of the acyl group once formed may reduce the electron density at the platinum atom, so reducing the back donation to other ligands, facilitating their replacement which may be a decomposition pathway.

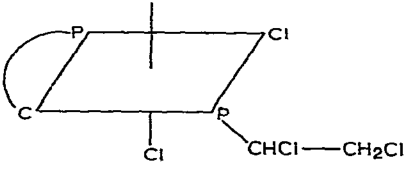
HCl cleaves the metal–carbon bond of compound (II), forming *cis*-[$PtCl_2$(VP)(EP)] [EP = (*o*-ethylphenyl)diphenylphosphine] in which both the phosphine ligands are coordinated through the phosphorus atoms alone. The overall effect on the ligand VP of (*a*) insertion into the Pt–H bond [(I)→(II)] and (*b*) cleavage of the Pt–C bond of (II) by HCl is thus simply hydrogenation of the olefinic moiety of the ligand VP: stage (*a*) can be seen as hydride attack at the β-carbon of the vinyl group, and (*b*) as proton attack at the α-carbon atom. The *cis*-stereochemistry of [$PtCl_2$(VP)(EP)] is suggested by its far IR spectrum (see Table 1) which shows the expected two ν(Pt–Cl) absorptions in the region anticipated[16,17] for chlorine *trans* to phosphine ligand; further, the complex is white in colour and insoluble in non-polar solvents.

It has recently been shown[21] that the complex [PtCl(P′–C) P(t-Bu) (*o*-tolyl)$_2$] [P′–C = $CH_2C_6H_4$P(t-Bu) (*o*-tolyl)] is unaffected by dry hydrogen chloride in ether at 20° for three days, and similar resistance has been observed with related complexes[22]. *trans*-[Pt(P′–C)$_2$] with hydrogen chloride gives *trans*-[PtCl(P′–C) P(t-Bu) (*o*-tolyl)$_2$], *i.e.* *one* of the platinum–carbon bonds is cleaved. Non-chelate complexes of the type *cis*-[PtR_2L_2], *cis*-[$PtClRL_2$], or *trans*-[$PtClRL_2$] (R = alkyl, CH_2Ph, or aryl; L = tertiary phosphine or tertiary arsine) are easily attacked by hydrogen chloride to give [$PtCl_2L_2$][17,23]: the rate of cleavage of the second Pt–C bond is however, slower than that of the first[24]. Factors important in such a cleavage of the chelate complexes would include the basicity of the metal atom (an oxidative addition reaction to a platinum(IV) hydride is a likely intermediate step); and the fact that with very bulky substituents on the phosphorus donor atom, the platinum(II) reactant may in fact be acting as a pseudo-octahedral complex.

The action of one molar equivalent of chlorine in CCl_4 on (II) gives a product analysing for "$PtCl_3(VP)_2$". The action of halogens in various proportions on complexes similar to (II) in low oxidation states and having coordinated double bonds or double bonds in proximity to the metal (as here) can variously give[25] (*i*) formation (by an oxidation process) and (*ii*) cleavage of metal–carbon σ-bonds, or (*iii*) saturation of the carbon–carbon double bonds, as well as (*iv*) simple oxidative addition to the metal. In the present instance the halogenated product shows three very strong bands (see Table 1) in the region associated with ν(Pt–Cl), and we consider that simple oxidative addition has occurred, giving (VIII) [or another isomer which would show three ν(Pt–Cl) bands]. Any of the other possibilities, (*i*)–(*iii*) above give products for which fewer bands would be predicted. The three bands assigned to ν(Pt–Cl) in (VIII) occur at 344, 318 and 296 cm^{-1}, which suggests the isomer shown in (VIII), the first



(VIII)



(IX)

TABLE 1

IR SPECTRAL DATA FOR THE NOVEL PLATINUM COMPLEXES IN NUJOL (cm^{-1})

Complex[a]	"*ν(C=C)*"[b]	*$\nu_{as}(ClO_4)$*	*ν(P–F)*	*ν(Pt–C)*	*ν(Pt–Cl)*
PtCl(P–C)(VP)[c]	?			591m	289vs, 284s,(sh)[d]
PtBr(P–C)(VP)[c]	?			595m	
PtI(P–C)(VP)	?			591m	
$[Pt(P–C)(PPh_3)(VP)]ClO_4$[e]	1620w	1094w		589m	
$[Pt(P–C)(PPh_3)(VP)]PF_6$	?		838vs	592w	
$[Pt(P–C)(VP)_2]ClO_4$[e]	1620w	1094vs		591m	
$[Pt(P–C)(VP)_2]PF_6$	1625w		840vs	589w	
$[Pt(P–C)(PEt_3)_2]ClO_4$		1093vs		591m	
$PtCl_2(VP)(EP)$[f]	?				323vs, 296vs
"$PtCl_3(VP)_2$"	?			?	344vs, 318s, 296s
PtMeClI(P–C)(VP)[c]	?			?	289vs

[a] For abbreviations, see text. [b] See ref. 14. [c] Absorption due to solvating benzene at 680 s cm^{-1}. [d] Probably due to $\nu(Pt–^{37}Cl)$. [e] Absorption due to H_2O at 3450 w (br) and 1580 m cm^{-1}. [f] Absorption due to solvating CH_2Cl_2 at 1279 m and 748 vs cm^{-1}.

two bands being assignable[16,17] to the pair of *trans* Cl ligands, and the third band to Pt–Cl *trans* to P.

The action of *ca.* six molar equivalents of chlorine in carbon tetrachloride solution on (II) leads (incompletely) to chlorination to "$PtCl_5(VP)_2$", which has not yet been completely characterised. The far infrared spectrum of this product shows a very strong band at 343 cm^{-1}, with a shoulder at 330 cm^{-1}, assignable to a pair of *trans* Cl ligands, and a strong band at 263 cm^{-1} assignable to ν(Pt–Cl) *trans* to carbon. Configuration (IX) explains these results satisfactorily: saturation of the double bond has occurred, in addition to an apparent isomerization. If this interpretation is correct, then the Pt–C bond is abnormally resistant to cleavage.

By the action of a large excess of bromine on (IIa), the bromo-analogue of (II), a product "$PtBr_5(VP)_2$", was obtained again poorly characterized. The band assigned to ν(Pt–C) at 595 cm^{-1} in its precursor is not present in the product, which shows a new band at 545 vs cm^{-1}, possibly assignable to ν(C–Br). [It is not likely to be a ν(Pt–C) band shifted on oxidation since for closely comparable methyl complexes of Pt^{II} and Pt^{IV}, it has been shown[17] that ν(Pt–C) is unchanged, provided that the *trans*-ligand is unaltered.]

By reaction of (II) with pure methyl iodide over several days at room temperature in the absence of light, an addition product was obtained, *i.e.* [PtMeClI(P′–C)(VP)]. This product was insufficiently soluble for its NMR spectrum to be studied. The far IR spectrum showed an absorption at 289 vs cm^{-1} assignable to ν(Pt–Cl) *trans* to phosphine[16,17]; it is not possible to deduce the overall stereochemistry.

Preliminary experiments have shown that compounds containing iridium–carbon bonds can similarly be prepared by insertion of the ligand VP into hydrido–iridium(III) complexes[26].

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus, and are corrected. Other physical measurements and the preparation of the ligands were carried out as described previously[27]. The hydrido–platinum(II) precursors were prepared by established methods.

Microanalyses were performed in the laboratories of Alfred Bernhardt, Elbach über Engelskirchen, West Germany, and the Department of Chemistry, University College London. Analytical data and physical properties for the new complexes are given in Table 2. All reactions were carried out in an atmosphere of dinitrogen.

TABLE 2

ANALYTICAL AND OTHER DATA FOR THE NOVEL PLATINUM COMPLEXES

Complex[a]	*M.p. (°C)*	*Colour*	*Molar conductivity*[b] *ohm^{-1}·cm^2·mol^{-1}*	*Analysis found (calcd.) (%)*				
				C	*H*	*Cl*	*F*	*P*
PtCl(P–C)(VP)[c]	210–221 decomp.	White	0	64.5 (64.75)	4.9 (4.9)	3.7 (3.7)		6.35 (6.4)
PtBr(P–C)(VP)[d]	220–229 decomp.	White	0	60.4 (60.6)	5.05 (4.55)	7.95[e] (8.3)[e]		6.6 (6.4)
PtI(P–C)(VP)	239–248 decomp.	Pale orange-pink	0	54.1 (53.5)	4.45 (3.9)	14.2[f] (14.1)[f]		7.05 (6.85)
$[Pt(P–C)(PPh_3)(VP)]ClO_4$[g]	decomp. >160	White	20.6	60.0 (59.7)	4.6 (4.6)	3.3 (3.05)		7.85 (8.0)
$[Pt(P–C)(PPh_3)(VP)]PF_6$	218–221 decomp.	White	28.5	59.15 (59.1)	4.55 (4.25)		9.75 (9.65)	10.65 (10.5)
$[Pt(P–C)(VP)_2]ClO_4$[g]	decomp. >170	White	25.0	60.15 (60.2)	4.55 (4.7)	3.3 (3.0)		
$[Pt(P–C)(VP)_2]PF_6$	160–165 decomp.	White	22.4	60.3 (59.75)	4.9 (4.3)		9.55 (9.45)	10.15 (10.25)
$[Pt(P–C)(PEt_3)_2]ClO_4$	decomp. >210	White	23.4	46.8 (46.8)	6.1 (5.85)	4.15 (4.35)		11.25 (11.4)
$PtCl_2(VP)(EP)$[h]	>210 decomp.	White	0	54.75 (54.7)	4.35 (4.2)	12.85 (12.0)		6.85 (7.0)
"$PtCl_3(VP)_2$"	decomp. >235	Pale cream	0	54.5 (53.1)	4.0 (4.15)	12.1 (11.3)		
PtMeClI(P–C)(VP)[i]	208–217 decomp.	Pale buff	0	54.4 (54.7)	4.4 (4.3)	3.9 (3.5)	13.2[f] (12.5)[f]	

[a] For explanation of abbreviations, see text. [b] Nitrobenzene; $[M] = 10^{-3}$; 25°. [c] As dibenzene solvate. [d] As sesquibenzen solvate. [e] Bromine analysis. [f] Iodine analysis. [g] As dihydrate. [h] As 0.5 CH_2Cl_2 solvate. [i] As mono-benzene solvate.

Preparation of $[Pt(CHMeC_6H_4PPh_2)Cl(VP)]$

trans-$[PtHCl(PPh_3)_2]$ (0.390 g) and the ligand VP (0.294 g) were dissolved in benzene (15 ml): after heating the solution under reflux for 2 h, light petroleum (b.p. 60–80°) was added to precipitate the product as a white crystalline solid (0.287 g), which could be recrystallised from the same mixture of solvents.

The bromo- and iodo-complexes were prepared analogously, using *trans*-$[PtHX(PPh_3)_2]$ (X = Br or I, respectively) as precursors: yields 85 or 70%, respectively).

Preparation of $[Pt(CHMeC_6H_4PPh_2)(PPh_3)(VP)]ClO_4$

A solution of *trans*-$[PtHCl(PPh_3)_2]$ (0.276 g) and VP (0.211 g) in acetone (30 ml) was heated under reflux for 30 min. $NaClO_4 \cdot H_2O$ (0.060 g) was added to the cold reaction mixture, which was then stirred for 30 min and filtered to remove sodium chloride. Evaporation of the solution to low bulk under reduced pressure and addition of ether containing a little water precipitated the required product (0.26 g) which was filtered off and washed with ether. It was recrystallised from acetone/ether to give white crystals.

The hexafluorophosphate salt was prepared analogously, using ammonium hexafluorophosphate. The product was recrystallised from methanol by addition of ether and water. Yield 85%.

Preparation of $[Pt(CHMeC_6H_4PPh_2)(VP)_2]A$ $(A = ClO_4$ *or* $PF_6)$

These salts were prepared analogously to the salts of the $[Pt(CHMeC_6H_4PPh_2)(PPh_3)(VP)]^+$ cation described immediately above, but using three molar equivalents of VP/Pt atom instead of two molar equivalents. Yields 70% or 95%, respectively.

Preparation of $[Pt(CHMeC_6H_4PPh_2)(PEt_3)_2]ClO_4$

The ligand VP (0.057 g) was added to a solution of *trans*-$[PtH(CO)(PEt_3)_2]ClO_4$ (0.109 g) in acetone (2 ml). Carbon monoxide was immediately given off. The reaction mixture was put aside for 10 min, and ether was then added to precipitate the product as colourless, highly refractive crystals (0.134 g), which were washed with water and ether.

This complex was also prepared by the action of one molar equivalent of VP on *trans*-$[PtHX(PEt_3)_2]$ $(X = NO_3$ or Cl) in acetone solution in the presence of $NaClO_4 \cdot H_2O$ over 1 h at ambient temperature. The identity of the product in each case with that prepared from *trans*-$[PtH(CO)(PEt_3)_2]ClO_4$ was established by analysis, IR spectrum (4000–200 cm^{-1}) and by conductivity measurements.

Action of hydrogen chloride on $[Pt(CHMeC_6H_4PPh_2)Cl(VP)]$

Hydrogen chloride gas was bubbled through a stirred suspension of the complex (0.169 g) in hot benzene (20 ml). After passage of gas for 5 min, the solution was evaporated to dryness under reduced pressure. Recrystallisation of the residue from dichloromethane/ethanol gave colourless crystals of *cis*-dichloro[(*o*-ethylphenyl)-diphenylphosphine][(*o*-vinylphenyl)diphenylphosphine] (0.128 g).

Action of chlorine on $[Pt(CHMeC_6H_4PPh_2)Cl(VP)]$

A solution of chlorine (one molar equivalent) in carbon tetrachloride (0.28 ml) was added in drops to a stirred solution of the complex (0.095 g) in chloroform (10 ml) over 10 min. Addition of ethanol to the solution under reduced pressure precipitated a product analysing as $[PtCl_3(VP)_2]$, in the form of pale cream crystals which were recrystallised from chloroform/ethanol to give the product (0.037 g).

Action of methyl iodide on $[Pt(CHMeC_6H_4PPh_2)Cl(VP)]$

A solution of the complex (0.210 g) in methyl iodide (10 ml) was put aside at ambient temperature for 4 days. The reaction solution was evaporated to dryness under reduced pressure, and the residue was recrystallised from benzene/light petroleum (b.p. 60–80°) to give the methyl iodide addition product as a very pale buff coloured solid (0.121 g).

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