Cyclic Compounds with a Pt–C σ-Bond formed by Olefin Insertion Reactions

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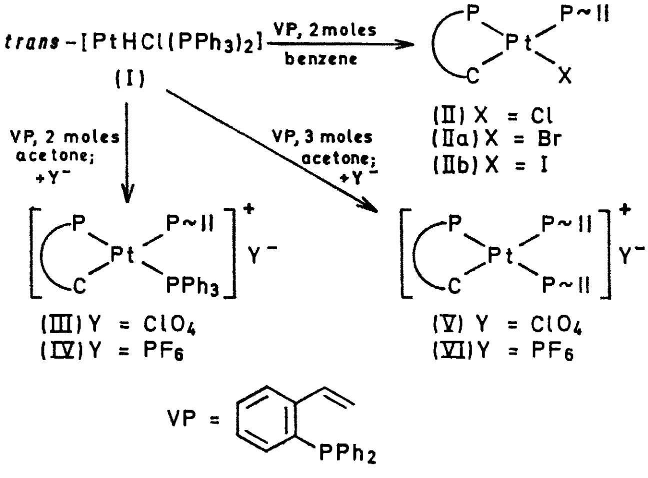
Summary An *ortho*-olefinic moiety of a chelate phosphine ligand (VP) is shown to insert into the hydrido–metal bond of a complex to form compounds containing a metal–carbon σ-bond.

WE report the insertion of the *ortho*-olefinic part of the ligand, (*o*-vinylphenyl)diphenylphosphine (VP) into the platinum–hydrogen bond of *trans*-[PtHCl$(PPh_3)_2$] [(I)→(II): see Chart]. This insertion reaction[1] is of interest since it is often invoked in suggested mechanisms of catalytic olefin hydrogenation,[2] and of oligomerization[3] and isomerization[4] of olefins.

trans-[PtHCl$(PEt_3)_2$] converts olefins into alkanes in the presence of strong acids:[5] this hydrido-platinum complex also reacts with ethylene at 90° and 40 atm. to give[6] *trans*-[PtEtCl$(PEt_3)_2$]: the reverse reaction has also been studied.[6,7] Chatt has pointed out that the position of equilibrium depends on both the nature of the olefin and the group *trans* to the hydride ligand. By the use of VP we have prepared the chelate complexes (II)—(VI), which have been characterized by elemental analysis, and by molecular weight, conductivity, i.r. (4000—200 cm^{-1}), and n.m.r. (^{1}H) studies.

We have not been able to establish unequivocally whether the moiety Pt–CH_2–CH_2– or Pt–$CH(CH_3)$– is present in (II), because of the low solubility of the complex; also, interpretation of the (complex) spectrum is ambiguous because coupling to *cis*- and *trans*- ^{31}P atoms can be comparable in



CHART

TABLE

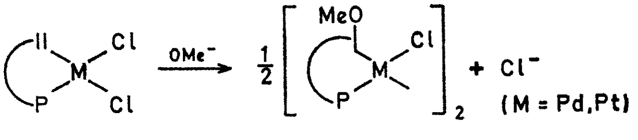
Complex	Colour	M.p.	Molec.[a] weight Calc.	Molec.[a] weight Found	Molec. conductivity[b] (ohm^{-1} cm.^{2} mole^{-1})
(II)	White	210—221°, (decomp.)	808	645	0
(IIa)	White	220—229 (decomp.)	853	695	0
(IIb)	Pale orange	239—248 (decomp.)	900	835	0
(III)	White	decomp. > 160	—	—	20·6
(IV)	White	218—221, (decomp.)	—	—	28·5
(V)	White	decomp. > 170	—	—	25·0
(VI)	White	160—165, (decomp.)	—	—	22·4

[a] Benzene; [*M*] *ca.* 10^{-2}; 25°.
[b] Nitrobenzene; [*M*] = 10^{-3}; 23°.

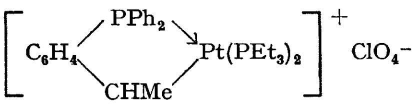
magnitude.[8] However, we favour the Pt–CH(CH$_3$)– structure since (II) shows absorption at 1047 cm.$^{-1}$ (mw), probably due to C–CH$_3$ rocking, which is absent in the spectrum of VP or its complexes.[9] Further, there is no absorption at *ca.* 1200 cm.$^{-1}$ as is found in Pt–CH$_2$–X compounds and assigned to CH$_2$ rocking.[7] The presence in (II) of a VP ligand co-ordinated through the phosphorus atom alone is indicated by a band at *ca.* 1620 cm.$^{-1}$ due to ν(C=C) in some of the compounds and absorption at *ca.* 995 cm.$^{-1}$ due to δ(CH) (vinyl group) in all of them.[10] Absorption in the range 589—595 cm.$^{-1}$ is present in the spectra of (II)—(VI) also, assignable to ν(Pt–C), although this vibration probably contains some admixed δ(Pt–C–C) motion.[11] ν(Pt–Cl) in (II) absorbs at 289 cm.$^{-1}$ (vs), which favours PR$_3$ as the *trans*-ligand rather than σ-bonded carbon.[12] The low solubility of (II) in nonpolar solvents also indicates a *cis*-configuration of phosphorus atoms.

HCl cleaves the metal–carbon bond of (II), forming *cis*-[PtCl$_2$(VP)(EP)] [EP = (*o*-ethylphenyl)diphenylphosphine] in which both phosphine ligands are co-ordinated through the phosphorus atoms alone. The products of bromine oxidation of complexes such as (I) are currently being investigated.

We have also prepared complexes of a bidentate ligand having a σ-bonded carbon atom and a phosphorus atom as bonding atoms by the reaction



Note added in proof. We have now isolated the chelate compound



$$\left[C_6H_4\begin{matrix}PPh_2\\ CHMe\end{matrix}Pt(PEt_3)_2\right]^+ ClO_4^-$$

from the instantaneous reaction between VP and *trans*-[PtH(CO)(PEt$_3$)$_2$]$^+$ClO$_4^-$ in acetone at ambient temperature. This reaction simultaneously involves olefin insertion, loss of the CO group and a *trans* → *cis* reorientation of the two trimethylphosphine ligands.

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