# Formation of Platinum–Carbon σ-Bonded Complexes from Co-ordinated and Unco-ordinated Olefins and Acetylenes

By W. HEWERTSON* and I. C. TAYLOR

(*Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, P.O. Box* 11, *The Heath, Runcorn, Cheshire*)

*Summary* Nucleophilic attack of methoxide ion on olefinic and acetylenic groups of unsaturated phosphine complexes of $\text{Pt}^{\text{II}}$ occurs even when the group is not co-ordinated to the metal; structures of the resulting cyclic σ-bonded complexes are suggested.

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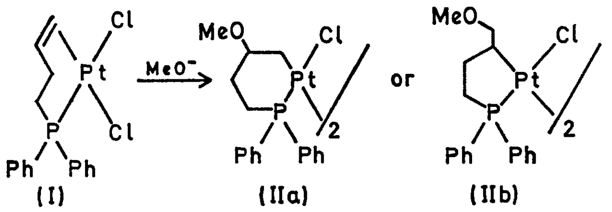
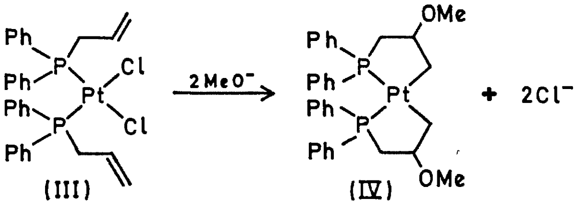
WHEREAS unactivated olefins are not susceptible to nucleophilic attack,[1] olefins complexed to metals with low electron density [*e.g.* $\text{Pt}^{\text{II}}$] react readily with nucleophiles to form σ-bonded complexes.[2] Olefin complexes of $\text{Pt}^0$ undergo electrophilic substitution.[3] We now describe an example of nucleophilic attack on an olefin held in the proximity of, but not initially co-ordinated to, $\text{Pt}^{\text{II}}$. Similar reactions of a co-ordinated olefin and an unco-ordinated acetylene are reported.

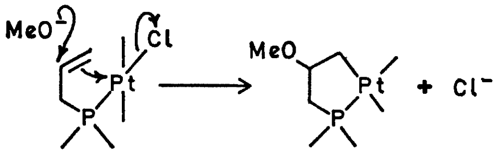
The complex (I) was prepared from but-4-enyldiphenylphosphine and bis(benzonitrile)platinum(II) chloride; its i.r. spectrum indicated the presence of a co-ordinated olefin and a *cis*-arrangement of the chlorine atoms [ν(C=C) shifted from 1639 in the free ligand, to 1503 cm$^{-1}$; ν (Pt–Cl) 330 and 298 cm$^{-1}$]. The $^1$H n.m.r. spectrum was consistent with the suggested structure. When (I) was treated with sodium hydrogen carbonate in methanol, the methoxy-substituted σ-bonded complex (II) was obtained. The ν(C=C) vibration of (I) is not present in (II), a band due to the OMe group appears at 1095 cm$^{-1}$ and the presence of bridging chlorines is confirmed by bands at 271 and 240 cm$^{-1}$. So far we have not established whether 5- or 6-membered rings are formed,† or whether geometrical isomers are present. The $^1$H n.m.r. spectrum is complex.



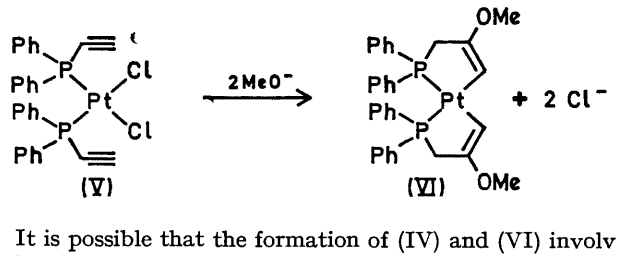
A similar reaction with an unspecified phosphine has recently been mentioned.[4]

*cis*-Bis(allyldiphenylphosphine)platinum(II) chloride (III) was prepared and its i.r. spectrum showed that the double bonds are not co-ordinated to the metal [ν(C=C) 1640 cm$^{-1}$], and that only terminal Pt–Cl bonds are present [ν (Pt–Cl) 315; 292 cm$^{-1}$]. The $^1$H n.m.r. spectrum of the complex is virtually identical to that of the free ligand. The reaction of (III) with methoxide gave a colourless complex which we formulate as (IV). The retention of a *cis*-arrangement of the phosphine ligands is suggested by the high dipole moment (5·2 D) of the complex. The $^1$H n.m.r. spectrum of (IV) has two single lines, of equal intensity and centred around $\tau$ 6·8, separated by 6 Hz at 60 MHz and 17 Hz at 220 MHz, due to the methoxy-protons. It is probable that two geometrical isomers of (IV), differing in the arrangement of the methoxy-groups (*cis* and *trans* with respect to the co-ordination plane of platinum), are obtained, in the ratio 1 : 1. The ease with which (IV) is formed is presumably due to a concerted reaction brought about by the olefinic group being held in close proximity to the metal.





Nucleophilic attack on acetylenes occurs readily, and the prop-2-ynylphosphine complex (V) reacts in a manner entirely analogous to that of (III) to give the corresponding vinylic cyclic complex (VI). The methoxy-peak in the $^1$H n.m.r. spectrum of this compound is a singlet at $\tau$ 6·93 (in benzene). The i.r. spectrum shows that the acetylenic bands [ν (≡C–H) 3225 cm$^{-1}$, ν (C≡C) 2105 cm$^{-1}$] of the complex (V) are absent, and a strong band at 1667 cm$^{-1}$ supports the formulation as a vinylic ether. Although complex (VI) is orange, it is thought to have a *cis*-arrangement of phosphines as the dipole moment of the complex is high (6·7 D).



It is possible that the formation of (IV) and (VI) involve μ-bonded intermediates. 5- rather than 4-membered rings are favoured on steric grounds and nucleophilic attack on the β-carbon atom would lead to such structures.

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† Nucleophilic attack on propene complexes of $\text{Pd}^{\text{II}}$ occurs predominantly at the β-carbon atom, *e.g.* with hydroxide the product is mainly acetone, with acetate an approximately 2 : 1 ratio of isopropenyl and propenyl acetates is formed. (J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition-Metal Complexes," Elsevier, London, 1968, p. 173). It is probable that the 5- and 6-membered rings would have similar stabilities, and attack on the β-position would give (IIa).

The prop-1-ynylphosphine complex, $(MeC{\equiv}CPPh_2)_2PtCl_2$, does not give a $\sigma$-Pt–C bonded product with methoxide; instead simple addition of MeOH to the acetylene groups of the ligand takes place.

Cope[5] has reported the preparation of related chlorine-bridged $Pd^{II}$ complexes from the addition of allyl-amines to palladium(II) chloride in alcohols. Intermediate complexes were not isolated, but it is probable that these reactions involve co-ordinated olefins.[6] Under similar conditions platinum(II) chloride behaves differently.[7] Chlorovinyl cyclic complexes (halogen-bridged) were obtained from the reaction of prop-2-ynyl-amines with palladium(II) chloride and lithium chloride.[8] We find that the addition of lithium chloride to solutions of allyldiphenylphosphine and sodium chloroplatinite and palladite in methanol does not give rise to nucleophilic substitution on the olefinic groups. The complex (III) and its *trans*-palladium analogue were obtained. This difference in reaction path is no doubt due to the greater susceptibility of acetylenes to nucleophilic attack.

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