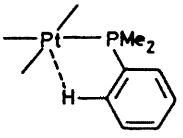
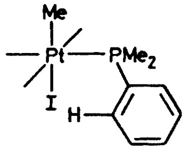
Photoelectron Spectra and Tertiary Phosphine–Metal Complexes

By BERNARD L. SHAW
(*School of Chemistry, University of Leeds, Leeds* LS2 9JT)

Summary Vertical ionization potentials are shown not to be a reliable guide to the donor abilities of tertiary phosphines nor to the electronic tendencies of tertiary phosphine–platinum complexes to undergo oxidative addition reactions.

IN a recent communication[1] it has been proposed that vertical ionization potentials, obtained by photoelectron spectroscopy, are a reliable measure of the electronic donor ability of tertiary phosphines and are also reliable as a means of separating steric from electronic effects in some reactions of tertiary phosphine–platinum(II) complexes, *e.g.* oxidative addition. Thus it was suggested that the donor ability should decrease along the series $Ph_3P \simeq MePh_2P > Me_2PhP > Me_3P$ since the vertical ionization potentials for the lone pair on phosphorus are 8·1, 8·07, 8·37, and 8·58 eV respectively. However, the donor ability towards protons is the reverse of this order, the pK_a's of the conjugate acids being respectively 3·05 (HPh_3P^+), 4·65, 6·25, and 7·85.[2,3] *The proton is small and only has an *s*-orbital available so that this order, though not complicated by π-bonding effects, may include some contribution, unknown in extent, from intramolecular strain release and solvent cage effects. Thus the acid–base equilibria are seen to be unreliable as a measure of donor ability in comparison with the ionization process, in that the latter excludes any contribution from the nature of the acceptor which will vary in different chemical systems. It is probable that change in geometry, especially in systems which include, as here, big differences in resonance effects, may exert a dominant influence. Ionization potentials determined by photoelectron spectroscopy explicitly include changes in geometry, in that the difference between the vertical and ionization potentials which can be inferred from them measure this valuable parameter independent of choice of acceptor.* There is generally a change in geometry of the tertiary phosphine on complexation, *e.g.* C–P–C angles increase; see for example *trans*-$[PtI_2(PMe_3)_2]$[4] where the increase is greater than with $[AuMe(PPh_3)]$.[5] Large changes in n.m.r. parameters of tertiary phosphines which commonly occur on complexation are in part due to changes in geometry (hybridization), *e.g.* ^{31}P shifts, for which the C–P–C bond angle changes which occur on complexation are thought to be dominant,[6] and coupling constants, [*J*(PH) and *J*(PC)], some of which change in sign.[7]


(1)


(2)

Similarly, vertical ionization potentials cannot be assumed to be a reliable guide to the electronic tendencies of tertiary phosphine–transition metal complexes to undergo oxidative addition reactions, to which many factors will contribute, including changes in bond and torsion angles. One factor, which was not considered previously[1] but is probably important, is interaction of the co-ordinatively unsaturated metal with hydrogen(s) on the tertiary phosphine ligands. It has been established that with tertiary phenylphosphine ligands the metal is close to at least one *ortho*-hydrogen, *e.g.* 2·6 Å separation in $[RuCl_2(PPh_3)_3]$[8] and 2·8 Å (for two hydrogens) in $[PdI_2(PMe_2Ph)_2]$.[9] Such interactions promote hydrogen–deuterium exchange[10] and, since the activation energies of these exchanges can be low, *e.g.* 6 kcal mol^{-1} for both aromatic and aliphatic hydrogens in a Pr^nPh_2P–ruthenium system,[10] the energies of interaction may be considerable. It has been estimated that the strength of a similar interaction between molybdenum and the α-hydrogens of an ethyl group in $[\{Et_2B(pz)_2\}Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ (pz = pyrazolyl) is 17—20 kcal mol^{-1}.[11] Thus in *trans*-$[PtIMe(PMe_2Ph)_2]$ there will be an interaction between the platinum and one or two *ortho*-hydrogens of the phenyl ring(s), as shown in (**1**). This will raise the energy of the d_{z^2} orbital and lower the ionization potential. Nevertheless, this *ortho*-interaction will stabilize the square planar complex relative to the platinum(IV) complex (**2**) formed by oxidative addition of methyl iodide, since in the co-ordinatively saturated platinum(IV)

* The section between the asterisks has been included at the suggestion of a referee, to whom the author is grateful.

complex the *ortho*-interaction cannot occur. In *trans*-[PtIMe(PMe$_3$)$_2$] interaction between the platinum and the phosphine hydrogens could occur since metals will activate α-hydrogens on tertiary phosphine ligands to some extent[10,12] but it would be less strong than the *ortho*-interaction just discussed.

(*Received, 6th September* 1978; *Com.* 973.)

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