

Photoelectron Spectra and Reactivity of Methyl(tertiary phosphine)- -platinum and -gold Complexes

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Summary Photoelectron spectra are reported for some methyl(tertiary phosphine) derivatives of platinum(II), gold(I), and gold(III), and it is shown that the data are useful in interpreting trends in chemical reactivity of the complexes.

THE reactivity of alkylplatinum(II) and alkylgold(I) towards oxidative addition reactions and other reactions with electrophiles has been much studied, and the results have often been interpreted in terms of the electronic structures of the complexes.^{1,2} However, no direct investigations of electronic energy levels in these compounds using u.v. photoelectron spectroscopy have been reported. We now report that many alkylplatinum and alkylgold complexes are sufficiently volatile to give good photoelectron (p.e.) spectra and that the results are of considerable interest in interpreting the reactivity of these complexes. Some results are presented in Tables 1 and 2. The

Me₃P. There is evidence from u.v. and n.m.r. spectra and bond angles in tertiary phosphines which supports this series, although different results are found for tertiary amines.⁷ This series is also supported by trends in the $\sigma(\text{MeAu})$ and $5d$ ionisation potentials for complexes [Me₃AuL] (Table 2), which show that the orbital energies follow the series L = MePh₂P > Me₂PhP > Me₃P, and for isostructural platinum(II) complexes [PtXYL₂] for which the orbital energies always follow the series L = Me₃PhP > Me₃P. The reactivity towards oxidative addition of complexes such as *trans*-[IrCl(CO)L₂], *cis*-[PtMe₂L₂], and [AuMeL] generally follows the series L = Me₃P > Me₂PhP > MePh₂P > Ph₃P and, in the past, it has not been possible to determine whether the order is due to electronic or steric effects of the ligands, L.^{1,6,8} Now, since the p.e. data indicate that the opposite series is expected from electronic effects of L, it is clear that steric effects are dominant in this case.

TABLE 1

Vertical ionisation potentials (eV) of some platinum(II) complexes^a

Assignment	<i>t</i> -[PtI ₂ L ₂]	<i>t</i> -[PtImeL ₂]	<i>t</i> -[PtCl ₂ L ₂]	<i>t</i> -[PtClImeL ₂]	<i>c</i> -PtMe ₂ L ₂	<i>t</i> -PtI ₂ L' ₂	<i>t</i> -PtImeL' ₂	<i>t</i> -PtBrMeL' ₂	<i>t</i> -PtClMeL' ₂	<i>c</i> -PtMe ₂ L' ₂
$5d_{xy}$	7.49	7.33	7.86	7.76	7.68	7.39	7.12	7.43	7.54	7.43
$5d_{xz}, 5d_{yz}, 5d_{z^2}$	{ 8.13 8.69	{ 7.80 8.23 8.45	{ 8.43 8.72	{ 8.20 8.48 8.73	{ 8.08 9.36	{ 7.96 8.39	{ 7.51 8.22	{ 7.81 8.08	8.21	{ 7.99 8.24
$\pi(\text{Ph})$	9.25	9.28	9.18	9.21	9.28
$\sigma(\text{MePt})$	9.23	..	9.29	9.13	9.13
$\sigma(\text{PtP})^b$	{ 9.71 10.01	..	{ 9.99 11.50
$\pi(\text{Halogen})^b$	{ 9.57 10.11 10.47	9.64 11.64	{ 10.35 11.06 11.90	10.07 11.85

^a HeI spectra recorded using a Perkin-Elmer P.S. 16 spectrometer. L = PMe₃, L' = PMe₂Ph; *t* = *trans*, *c* = *cis*. ^b Considerable overlap of peaks occurred; assignments are tentative. For L' = PMe₂Ph, bands obscured by phenyl bands.

assignments, which are based on results from photoelectron spectra of other alkyl derivatives of metals,³ on studies of energy levels by electronic spectroscopy,⁴ and on M.O. calculations,⁵ will be discussed more fully elsewhere.

It has generally been assumed that the σ -donor ability of tertiary phosphine ligands follows the series L = Me₃P > Me₂PhP > MePh₂P > PPh₃, decreasing as the more electronegative phenyl groups replace methyl groups.⁶ However, the vertical ionisation potentials (eV) for the lone pair of electrons on phosphorus are Me₃P, 8.58; Me₂PhP, 8.37; MePh₂P, 8.07; and Ph₃P, 8.1, suggesting that the donor ability series should be Ph₃P \approx MePh₂P > Me₂PhP >

the photoelectron spectra are also relevant to the problem of the mechanism of cleavage of alkyl-transition metal bonds by electrophiles. Such reactions can occur either by direct attack of the electrophile at the metal-carbon bond (S_E2 mechanism) or by initial attack at the metal giving an oxidative addition-reductive elimination sequence. An electrophile is expected to attack at the highest occupied M.O., which is a $5d$ orbital in methyl-(tertiary phosphine)platinum(II) complexes but a $\sigma(\text{Me-Au})$ orbital in both methyl-gold(I) and -gold(III) complexes. Hence, the S_E2 mechanism is predicted for electrophilic cleavage of methyl-gold bonds but the oxidative addition-

TABLE 2

Vertical ionisation potentials (eV) of some gold(I) and gold(III) complexes^a

Assignment	[Me ₃ Au(PMe ₃)]	[Me ₂ Au(PMe ₂ Ph)]	[Me ₂ Au(PMePh ₂)]	[MeAu(PMe ₃)]
$\sigma(\text{MeAu})$	{ 7.80 8.63	{ 7.69 8.53	{ 7.64 8.34	8.27
$\pi(\text{Ph})$..	9.49	9.48	..
$5d$	{ 10.18 10.70 11.06	{ 9.99 10.61 10.97	{ 9.98 10.56 10.98	{ 9.34 9.95 10.63 11.45

^a Attempts to obtain p.e. spectra of halogenogold and alkyl(halogeno)gold complexes were unsuccessful owing to their thermal decomposition.

reductive elimination mechanism for cleavage of methyl-platinum bonds in the tertiary phosphine complexes. This is precisely what is observed experimentally.⁹

Other points of general interest are that the lowest ionisation energy for $[\text{Me}_3\text{Au}^{\text{I}}\text{PMe}_3]$ is actually less than that for $[\text{MeAu}^{\text{I}}\text{PMe}_3]$ (no doubt owing to the presence of mutually *trans* methyl groups in the former compound⁵), and that the ionisation energy for *trans*- $[\text{PtXYL}_2]$ appears to be less than that for the *cis*-isomer. This could not be proved directly but is strongly indicated by the series of lowest ionisation energies *cis*- $[\text{PtMe}_2(\text{PMe}_3)_2] > \textit{trans}$ - $[\text{PtI}_2-$

$(\text{PMe}_3)_2] > \textit{trans}$ - $[\text{PtImeL}_2]$, and for several similar series (Table 1). Thus, replacement of a halogen by a methyl group in *trans*- $[\text{PtI}_2\text{L}_2]$ leads to a decrease in ionisation energy as expected, and the ionisation energy for *trans*- $[\text{PtMe}_2\text{L}_2]$ would be expected to be lower still. However, the complex cannot be prepared and the ionisation potential of the isomeric *cis*- $[\text{PtMe}_2\text{L}_2]$ is higher than that for *trans*- $[\text{PtI}_2\text{L}_2]$.

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