X-Ray Photoelectron Spectroscopic Studies of Tertiary Phosphine Complexes of Heavy Transition Metals

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The *X*-ray photoelectron spectra of 25 complexes of transition metals (including Mo, W, Ru, Os, Rh, Ir, and Pt) are reported. The electron binding energies of ligand atoms are relatively insensitive to changes in the complexes, and the metal electron binding energies must be interpreted with caution.

X-RAY photoelectron spectroscopy (x.p.s.) yields information on the charges of atoms in a compound. The actual charge on an atom usually differs considerably from the charge indicated by the formal oxidation state. There are several x.p.s. studies of palladium and platinum complexes in the literature, and they have been used to infer various ligand properties, such as σ- and π-bonding capabilities. This has often involved rationalisations of differences in binding energies which are smaller than the admitted experimental error. We report here an x.p.s. study of the influence of metal ion, stereochemistry, and oxidation state upon ligands in a series of complexes in order to determine what changes in electron binding energy can be expected in compounds where the molecular properties are accurately known.

The binding energy (B.E.) of an electron in an atom of a molecule is a function of at least four factors [equation (1)]. The simple relationship of B.E. to atomic

$$\text{B.E.} = f_1(\text{atomic charge}) + f_2(\text{Madelung potential}) + f_3(\text{polarisability}) + f_4(\text{M}^n \longrightarrow \text{M}^{n+1}) \quad (1)$$

charge, f_1,† is not adequate to explain the observed chemical shifts. All the atoms present in the crystal or molecule exert some effect on the electron being removed and this can be described as a function (f_2) of the Madelung potential. This contribution to the binding energy may be small, as in molecular crystals, or as large as 5 eV as in some ionic crystals. Finally, the polarisability of the system (f_3) and the different possible states of the charged species produced by the ionisation (f_4) will also affect the measured binding energy. These last two contributions are difficult to calculate at present. One must therefore compare results from compounds which are of very similar structure and with this in mind the compounds in this study were selected.

RESULTS AND DISCUSSION

Cook *et al.*[1] have measured electron binding energies for a series of platinum compounds in which the formal oxidation state of the metal varies from zero to +II. They found that although the Pt($4f_{7/2}$) binding energy in the compounds [$(PPh_3)_2PtX_2$] varies from *ca.* 73·5 in [$(PPh_3)_2PtCl_2$] at one extreme to 71·7 eV in [$(PPh_3)_2Pt(PPh_3)_2$] at the other, the P($2p_{3/2}$) binding energy is sensibly constant. Riggs[2] has examined a somewhat larger range of complexes and has obtained Pt($4f_{7/2}$) binding energies ranging from 76·1 for [$PtCl_4(PEt_3)_2$] to 71·6 eV for [$Pt(PPh_3)_4$]. Throughout 19 complexes, P($2p_{3/2}$) binding energies do not fall outside the range 131·6 ± 0·5 eV and Cl($2p_{3/2}$) binding energies for 11 compounds are in the range 198·8 ± 0·6 eV. A correlation between the platinum electron binding energy and the electronegativity of substituents was established.[2] Moddeman *et al.*[3] reported on a series of 51 platinum(II) and platinum(IV) complexes. The Pt($4f_{7/2}$) binding energies fall in a range of 5 eV with a standard deviation for each value of 0·2—0·3 eV. The Cl($2p_{3/2}$) electron binding energy in the 7 compounds containing chlorine, however, were all within a range 201·6 ± 0·4 eV.

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† f_1 Is intended to include the effects of the electrons and nucleus of the atom being ionised upon the electron being removed.

[1] C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, 1971, **93**, 1904.

[2] W. M. Riggs, Proc. Conf. Electron Spectroscopy, Asilomar, California, 1971, Abstract V 2.

[3] W. E. Moddeman, J. R. Blackburn, G. Kumar, K. A. Morgan, M. M. Jones, and R. G. Allridge, ref. 2, Abstract V 7.

The results were interpreted in terms of the π-accepting character of the ligands other than chlorine.[3]

Clark *et al.*[4] claim that bridging halide ions in platinum complexes have lower electron-binding energies (by *ca.* 1 eV) than terminal halides. Riggs[2] also finds a difference between bridging and terminal halides, as do Moddeman *et al.*,[3] but both groups reported that the bridging halides apparently have the higher electron-binding energies in complexes very similar to Clark's.[4] The resolution of this conflict is not clear. However, no indication is given of how valid comparisons of very different complexes can be made.

TABLE 1

Electron binding energies (eV) for complexes $K_2[MCl_6]$

	$M(4f_{5/2})$	$M(4f_{7/2})$	$Cl(2p_{3/2})$	$K(2p_{3/2})$	$M(4f_{5/2})$ *	$M(4f_{7/2})$ *
W	36·8	35·1	199·2	293·5	37	34
Re	46·9	44·5	199·5	293·9	47	45
Os	56·4	53·7	198·9	293·2	52	50
Ir	66·0	63·2	198·8	293·0	63	60
Pt	78·8	75·6	199·1	293·2	74	70

* Taken from ref. 8; values apply to metal in zero oxidation state.

We first investigated the series $K_2[MCl_6]$ (M = W, Re, Os, Ir, or Pt). These complexes are of known similar structure, so that surface charging, Madelung, and polarisability effects are likely to be constant. The metal–halogen bond lengths change slightly from 2·37 in $K_2[ReCl_6]$[5] to 2·33 Å in $K_2[PtCl_6]$.[6] The estimated charge on the metal decreases from 1·72 at W to 0·70 at Pt.[7] The metal–halogen stretching force constants change from 1·45 for Re to 1·59 mdyn eÅ^{-1} for Pt.[7] The σ and π covalent contributions to the metal–halogen bonds, as judged by n.q.r. and i.r. data, change from 0·28 and 0·100, respectively, at W to 0·55 and zero, respectively, at Pt.[7] We thus had good reason to expect to see some reflection of this in the $Cl(2p_{3/2})$ electron binding energies.

TABLE 2

Electron binding energies (eV) in $[MCl_4(PEt_3)_2]$ and $[MCl_4(PMe_2Ph)_2]$

	PEt_2				PMe_2Ph			
	$M(4f_{5/2})$ and	$M(4f_{7/2})$	$Cl(2p_{3/2})$	$P(2p_{3/2})$	$M(4f_{5/2})$ and	$M(4f_{7/2})$	$Cl(2p_{3/2})$	$P(2p_{3/2})$
W	36·8	34·8	199·5	131·5	36·5	34·3	199·3	131·8
Re	45·9	43·5	199·4	131·6	46·3	43·8	199·4	132·1
Os	55·3	52·8	199·1	131·2	55·5	53·2	199·1	131·7
Ir	66·5	63·8	199·3	131·7	66·5	63·7	199·0	131·8
Pt	78·8	75·5	199·3	131·8	78·4	75·8	198·5	132·1

The results in Table 1 are quoted relative to C(1s) estimated at 285 eV. No attempt has been made to determine 'absolute values'. The values have uncertainties of *ca.* ±0·3 eV which is the practical limit imposed by calibration errors, reproducibility, and the instrumental resolution. The significance of the metal binding energies is not clear because of the lack of reference data although comparison with Siegbahn's values[8] indicates increasing positive charge on the metal in the series W $\longrightarrow$ Pt (*cf.* ref. 7). More important, the $Cl(2p_{3/2})$ binding energies are constant through the series within the limits of experimental error despite large changes in other physical quantities in the series. The $K(2p_{3/2})$ electron binding energy is roughly constant. For KCl, $Cl(2p_{3/2})$ has been shown to be *ca.* 200·7 (ref. 9) or 200·2 eV,[3] suggesting that ionic chloride is more positive than complexed chloride. This, intuitively, cannot be correct, and is probably a consequence of Madelung and polarisability effects.

We next investigated two series of complexes $[MCl_4(PR_3)_2]$ (M = W, Re, Os, Ir, or Pt; $PR_3 = PEt_3$ or PMe_2Ph). Spectroscopic measurements show that all these complexes have a *trans*-configuration, and a crystallographic study showed that $[MCl_4(PMe_2Ph)_2]$ (M = W, Re, Os, or Ir) have C_i symmetry, with four equal metal–chlorine bond lengths, as does $[PtCl_4(PEt_3)_2]$.[10] The metal–halogen bond length is sensibly constant throughout the series $[MCl_4(PMe_2Ph)_2]$ (2·329 ± 0·010 Å) but the metal–phosphorus bond length changes quite dramatically [W 2·550(3), Re 2·505(3), Os 2·448(3), Ir 2·392(5), and Pt 2·393(5) Å].[10] A reflection of this would certainly be expected, *a priori*, in x.p.s. measurements. The results are shown in Table 2. The following conclusions can be drawn. (i) The binding energies of the metal electrons are independent of the type of phosphine ligands. (ii) The chlorine electron binding energies do not differ significantly from each other, or from the values measured for $K_2[MCl_6]$. There may be a trend evident in the series $[MCl_4(PMe_2Ph)_2]$ suggesting a decrease of electron transfer from chlorine to the metal with decrease of metal electron deficiency. However, this is only just outside experimental error and is not evident in the series $[MCl_4(PEt_3)_2]$. (iii) The phosphorus electron binding energies are constant within experimental error. (iv) Comparison with Table 1 shows that the metal electron binding energies are unchanged upon substitution of chlorine by the tertiary phosphine for tungsten, iridium, and platinum, and decrease by *ca.*

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[4] D. T. Clark, D. B. Adams, and D. Briggs, *Chem. Comm.*, 1971, 602.

[5] B. Aminoff, *Z. Krist.*, 1936, **94**, 246.

[6] G. Engel, *Z. Krist.*, 1935, **90**, 341.

[7] T. L. Brown, W. G. McDugle, and L. G. Kent, *J. Amer. Chem. Soc.*, 1970, **92**, 3645.

[8] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johannson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, 'Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy,' Almqvist and Wiksells Boktryckeri AB, Uppsala, 1967.

[9] C. K. Jørgensen, personal communication.

[10] L. Aslanov, R. Mason, A. G. Wheeler, and P. G. Whimp, *Chem. Comm.*, 1970, 30.

1 eV for rhenium and osmium. (v) Comparison of Tables 1 and 2 shows that, within the limitations of the x.p.s. experiment, the replacement of two chlorides in $[MCl_6]^{2-}$ by tertiary phosphines does not change the $Cl(2p_{3/2})$ electron binding energy. This was also found by Cook *et al.*[1] Thus phosphorus and chlorine appear to withdraw from (or supply to) the metal the same amount of charge. This constancy of values for chlorine is a nice demonstration of the electroneutrality principle.

TABLE 3

Electron binding energies (eV) in *mer*- and *fac*-$[MCl_3(PMe_2Ph)_3]$

	$M(4f_{5/2}$ and $4f_{7/2})$ or $M(3d_{3/2}$ and $3d_{5/2})$	$Cl(2p_{3/2})$	$P(2p_{3/2})$
mer-Mo	232·6, 229·6	198·2	131·1
mer-Re	44·4, 42·0	198·8	131·4
mer-Ru	281·1, 276·8	198·2	131·3
mer-Os	54·4, 51·8	198·4	131·3
fac-Rh	314·2, 309·5	197·9	131·8
mer-Ir	65·3, 62·4	198·0	131·6
fac-Ir	65·5, 62·7	198·8	132·0

In order to study steric influences, a series of complexes $[MCl_3(PMe_2Ph)_3]$, of both *meridional* and *facial* configurations, was investigated for several metals, M (see Table 3). For complexes *mer*-$[MCl_3(PMe_2Ph)_3]$ (M = Re, Os, or Ir) the metal–halogen bond length changes very little, whether for chlorine *trans* to chlorine or *trans* to phosphorus, but the metal–phosphorus bond lengths of both kinds (*trans* to chlorine and *trans* to phosphorus) change by >0·1 Å.[10] The results are shown in Table 3. The following conclusions can be drawn. (i) The metal electron binding energies are *ca.* 1—2 eV lower for oxidation state +(III) compared to oxidation state +(IV). This is to be expected. The separation of the spin doublets appears unchanged by the change in oxidation state. (ii) The $P(2p_{3/2})$ electron binding energies are constant throughout the series. They are also substantially the same as for the M^{IV} compounds. The spectra are generally very sharp with no indication of a resolution into two kinds of phosphorus even when, as in the *meridional* complexes, there are formally two kinds present. The phosphorus findings parallel those of Cook *et al.*[1] (iii) The $Cl(2p_{3/2})$ electron binding energies are all *ca.* 1 eV lower than in the M^{IV} complexes. The signals for chlorine are always broader than those of phosphorus but if there is any separation due to non-equivalent chlorines, it is certainly <*ca.* 0·6 eV. The situation is complicated because the closely spaced chlorine $2p$ doublet (separation 1·4 eV) cannot be fully resolved. In addition the linewidth in the solid state is a function of the method of sample preparation and of surface properties, and the determination of ' absolute ' linewidths is not reliable.

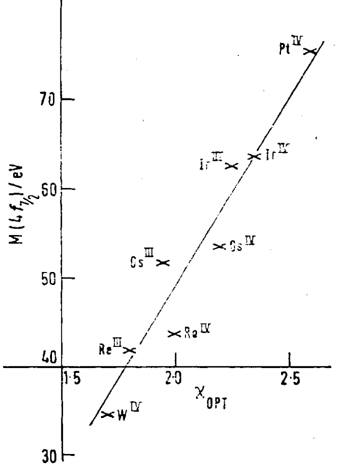
TABLE 4

Effect of changing metal oxidation state upon electron binding energies (eV)

	Re			Os		
	$M(4f_{7/2} + 4f_{5/2})$	$Cl(2p_{3/2})$	$P(2p_{3/2})$	$M(4f_{7/2} + 4f_{5/2})$	$Cl(2p_{3/2})$	$P(2p_{3/2})$
trans-$[MCl_4(PMe_2Ph)_2]$	46·3, 43·8	199·4	132·1	55·5, 53·2	199·1	131·7
mer-$[MCl_3(PMe_2Ph)_3]$	44·4, 42·0	198·8	131·4	54·6, 52·0	198·6	131·6
trans-$[MCl_2(PMe_2Ph)_4]$	43·0, 40·7	198·4	131·3	53·4, 50·7	198·3	131·5
trans-$[MCl(N_2)(PMe_2Ph)_4]$	42·9, 40·5	198·7	131·8			

The difference in behaviour between chlorine and phosphorus in these M^{III} and M^{IV} complexes probably arises because phosphorus in a tertiary phosphine has three additional organic groups which may also be polarised to take up charge whereas chlorine has none. In other words, the phosphine as a whole is more polarisable than chlorine. In none of the complexes studied did the C(1*s*) appear as other than a single strong peak with no indication of fine structure.

The most significant changes in electron binding energy upon changing the formal oxidation state of the metal are shown by the metal ion itself (Table 4). The $Cl(2p_{3/2})$ and $P(2p_{3/2})$ electron binding energies are relatively independent of metal and oxidation state with the reservations already stated above. The metal electron binding energies change with formal oxidation state but there is no reason to believe that the relationship is necessarily linear. There is a rough correlation between metal $4f_{7/2}$ binding energies and optical electronegativity (see Figure) but this is only significant in so far as f_1 presumably makes the major contribution to the chemical shifts in the complexes under investigation. Changes in ligands can upset such relationships entirely. Thus $[ReCl(N_2)(PMe_2Ph)_4]$ contains formal rhenium(I) but its



Correlation between $M(4f_{7/2})$ binding energies and optical electronegativity electronic condition is more akin to rhenium(II) to judge from the electron binding energies (Table 4). This suggests that complexed dinitrogen carries considerable negative charge, but also indicates that x.p.s. data should not be used to determine metal oxidation states without considerable care.

The above results indicate that the main use of x.p.s. in complex chemistry at present will be in the study of metal ions and also of those ligands which contain atoms capable of carrying considerable negative charge, such as oxygen or nitrogen.

EXPERIMENTAL

Spectra were measured by use of a Varian IEE 15 spectrometer using both Mg-$K_{\alpha 1,2}$ and Al-$K_{\alpha 1,2}$ as exciting radiation. The binding energies were measured with respect to internal C(1*s*) (in Scotch tape for the hexahalogenometallates, and otherwise in the tertiary phosphine) taken as 285 eV. The values tabulated are the mean of at least two, and generally four, measurements, and are accurate in the best cases to ±0·2 eV. Some hexahalogenometallates were obtained commercially. All other complexes were prepared according to literature methods,[11] except for $[MCl_2(PMe_2Ph)_4]$ (M = Re [12] or Os [13]), which have yet to be described in detail.

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