Electron Emission Spectroscopic Studies of Olefin and Other Complexes of d^8 and d^{10} Metal Ions

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Metal and ligand non-valence electron ionisation energies are reported for a number of complexes of Pt^0, Rh^I, and Ir^I with olefins, substituted olefins, oxygen and other unsaturated ligands. The constancy and magnitude of the metal binding energies in $(Ph_3P)_2Pt(C_2R_4)$ and $(Ph_3P)_2Rh(C_2R_4)Cl$, in contrast to the significant variations observed in $Ir(CO)(PPh_3)_2XY$ (X = Cl or I; Y = olefin, CO, O_2, or NO^+,BF_4^-) is related to the strong π-basicity of the $(Ph_3P)_2Pt$ and $(Ph_3P)_2RhCl$ moieties. Crystallographic and thermodynamic data on some of the complexes are discussed together with observed C(1*s*) satellite peaks.

DIFFRACTION analyses have provided much structural data on complexes of unsaturated molecules with low valent transition metals and therefore have helped in the refinement of valence theories of these molecules. It is, however, desirable that the theoretical interpretations of molecular geometries should be reinforced by information from other methods which, in principle at least, give more direct information on the molecular charge distribution. *X*-Ray-induced electron emission spectroscopy has this potential and Cook *et al.*[1] have recently reported some interesting results for complexes of platinum(0). In the complexes $(Ph_3P)_4Pt$, $(Ph_3P)_2Pt(PhC{\equiv}CPh)$, $(Ph_3P)_2Pt(C_2H_4)$, $(Ph_3P)_2PtCS_2$, $(Ph_3P)_2PtO_2$, and $(Ph_3P)_2PtCl_2$, the phosphorus $2p$ binding energies are sensibly constant and the observed Pt $4f_{7/2}$ ionisation energies were interpreted with the assumption that they reflected only the charge transferred from the metal to antibonding ligand levels. Our concern here is with very similar complexes of Pt^0, Rh^I, and Ir^I; in the case of the d^{10} complexes, the emphasis of our conclusions is somewhat different to that outlined earlier.[1]

EXPERIMENTAL

Binding energies were obtained from e.s.c.a. measurements (Al-K_α) on microcrystalline samples, deposited on adhesive tape, using the A.E.I. ES 100 photoelectron spectrometer. In the case of the olefin complexes of platinum and rhodium, the results in the Table are the mean of data taken on three different samples, with four complete energy scans on each sample, with the exception of the $(Ph_3P)_2Pt(C_2H_4)$ complex for which three separately synthesised samples were used. From each of these, between two and five separate samples were taken and four complete energy scans were then recorded making a total of forty observations of each level. The metal binding energies for the three samples were within a standard deviation of the mean value. In spite of adopting normal precautions for handling these compounds, the presence of a weak O(1*s*) ionisation peak in their spectra may indicate that slight surface oxidation has occurred. However, the unambiguous observation of strong ionisation due to N(1*s*), F(1*s*), and Cl(2*p*) in the spectra of $(Ph_3P)_2PtL$ ($L = C_2(CN)_4$, C_2F_4, C_2Cl_4) indicates that oxidation is not significant in these cases but for $L = C_2H_4$, this is less certain. For the iridium complexes, three complete energy scans of a single sample of each compound were recorded. The binding energies are all relative to C(1*s*) = 285·0 eV and are conservatively estimated to be accurate to ±0·3 eV. The

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

syntheses of the complexes followed standard procedures. All the complexes suffered radiation damage but we have no indications that our results contain systematic errors on account of this.

Binding energies in some platinum, rhodium, and iridium complexes

	$(Ph_3P)_2PtC_2H_4$	$(Ph_3P)_2PtC_2Cl_4$	$(Ph_3P)_2PtC_2F_4$	$(Ph_3P)_2PtC_2(CN)_4$
P(2*p*)	131·7	131·7	131·6	131·8
Pt $4f_{7/2}$	73·0	73·2	73·0	73·2
Pt $4f_{5/2}$	76·1	76·5	76·2	76·5
Cl(2*p*)		199·4 (very broad)		
N(1*s*)				399·4
F(1*s*)			686·3	
Satellite peaks				
Energy	291·4	291·6	291·7	291·5
$I_{sat} : I_{main}$	0·043	0·039	0·021	0·034

	$(Ph_3P)_2Rh(C_2F_4)Cl$	$(Ph_3P)_2Rh(C_2H_4)Cl$	$(Ph_3P)_3RhCl$	$(Ph_3P)_2RhCl(CO)(C_2(CN)_4)$
Rh $3d_{3/2}$	313·9	313·5	314·0	314·3
Rh $3d_{5/2}$	309·3	308·9	309·4	309·7
P(2*p*)	131·7	131·7	131·8	131·7
Cl(2*p*)	198·9	199·0	198·3	198·5
F(1*s*)	687·1			
N(1*s*)				399·2
O(1*s*)				532·4
Satellite peaks				
Energy	291·6	292·1	291·8	291·5
$I_{sat} : I_{main}$	0·039	0·045	0·042	0·036

	$Ir(CO)(PPh_3)_2XY$								
X	Cl	Cl	Cl	Cl *	Cl	I	I *	I *	$Ir(PPh_3)_2$-$Cl(C_2(CN)_4)$
Y	O_2	CO	C_2F_4	$(NO^+)[BF_4^-]$	$C_2(CN)_4$	O_2	CO	$(NO^+)[BF_4^-]$	
Ir $4f_{7/2}$	61·9	62·1	62·4	63·1	63·4	62·1	62·4	63·7	62·9
Ir $4f_{5/2}$	64·6	64·7	64·9	65·8	65·9	64·6	65·0	66·0	65·8
P(2*p*)	131·9	132·0	131·2	132·0	131·4	131·9	131·7	132·1	131·6
Cl(2*p*)	198·5	198·5	198·2	198·9	198·4				198·3
O(1*s*)	531·9	532·1	532·6	532·5	532·3	532·0	531·8	531·7	
N(1*s*)					399·1				398·9
F(1*s*)			686·2	684·0				684·4	
I $3d_{5/2}$						618·6	618·4	618·8	

* Severe radiation damage.

The main experimental data can be summarised:

(i) The oxygen 1*s*, chlorine 2*p* and phosphorus 2*p* ionisation energies are constant throughout with average values of 532·1 eV (σ = 0·3 eV), 198·5 (0·25) eV and 131·8 (0·3) eV respectively.

(ii) Again within experimental error, the binding energies of the Pt $4f_{5/2}$ and Pt $4f_{7/2}$ electrons in $(Ph_3P)_2Pt$(olefin) are independent of the nature of the substituent groups on the olefin. Our result for the binding energy of the Pt $4f_{7/2}$ electrons in the ethylene complex is about 0·7 eV higher than that observed by Cook *et al.*[1] and, since this point is an important one, we emphasise that the present value is the mean of forty separate observations. The observed binding energies in these zero-valent complexes are also within 0·3 eV or so of those associated with complexes such as $(Ph_3P)_2PtCl_2$ (73·2 eV) [1,2] and K_2PtCl_4 (73·4 eV) [2] where the platinum has a formal charge of +2.

(iii) Although the data are limited, the rhodium binding energies are also independent of olefin substitution or of the nature of the substituent groups on the olefin. In the case of $(Ph_3P)_2RhCl_2(CO)C_2(CN)_4$ it is not possible at present to comment on whether the small increase in the metal binding energy is due to the presence of tetracyanoethylene (tcne) or to the increased co-ordination number; we could not obtain a pure sample of $(Ph_3P)_2Rh(C_2(CN)_4)Cl$.

(iv) The metal binding energies in the iridium(I) chloro-complexes vary significantly. Some caution is needed in relation to the oxygen complexes since these suffer radiation damage. The tetracyanoethylene complex has significantly higher metal binding energies than are found in the remaining complexes. The nitrosyl complexes have similar I.P.'s to those of the tcne adduct and their absolute values approach those of complexes such as $IrCl_3(PMe_2Ph)_3$ in which the iridium has the +3 formal oxidation state.[3] $Ir(PPh_3)_2Cl(C_2(CN)_4)$ has, within experimental error, identical metal binding energies to those of $Ir(PPh_3)_2(CO)Cl(C_2(CN)_4)$.

DISCUSSION

The constancy and absolute values of the platinum binding energies lead to a simple and intuitively likely conclusion: the Lewis basicity of the bis(triphenylphosphine)platinum(0) moiety is so strong that the substituent groups on the olefin play but a minor role in determining the extent to which charge transfer from the metal to ligand antibonding orbitals takes place. A similar argument must be presented for the rhodium(I) complexes although it is now much less convincing in the absence of data on $(Ph_3P)_2RhCl$(tcne). By contrast, we can infer that the Vaska complex $Ir(CO)Cl(PPh_3)_2$,

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[2] W. M. Riggs, Proc. Symp. Electron Spectroscopy, Asilomar, California, 1971, Abstract V. 2 and references therein.

[3] G. J. Leigh and W. Bremser, *J.C.S. Dalton*, 1972, 1216.

has a relatively low basicity and that metal to ligand charge transfer is significantly determined by the nature of the adduct: it is only with the strong π-acid, tcne, that the metal binding energies approximate to those of formal iridium(III) systems.

Crystallographic and equilibrium constant data are available which seem to bear out these general propositions although some only constitute circumstantial evidence.

In $IrCl(CO)(PPh_3)_2O_2$, the bond length in the co-ordinated dioxygen molecule is accurately established as 1·31 Å.[4] Cook *et al.*[1] pointed out that the corresponding value in $(Ph_3P)_2PtO_2$ apparently varies in a way which reflects the solvent of crystallization. The values observed of 1·45 Å for the benzene-solvated complex[5] and 1·50 Å for the chloroform-solvated species[6] are identical within experimental error, but appear to be significantly different from that in the toluene-solvated complex (1·26 Å).[7] The latter result seems inconsistent with the behaviour of the co-ordinated oxygen molecule and if we accept the other results, the strong π-basicity of $(Ph_3P)_2Pt$ *vis à vis* $Ir(CO)Cl(PPh_3)_2$ is established. The O–O bond length of 1·50 Å[8] in $Ir(CO)I(PPh_3)_2(O_2)$ indicates the sensitivity of the acidity of the iridium(I) species to relatively small ligand perturbations. In $(Ph_3P)Pt(C_2(CN)_4)$[9] and $(Ph_3P)_2Pt$-$C_2(H_2(CN)_2)$[10] the carbon–carbon (olefin) bond lengths are identical at 1·52 Å and the average metal–carbon bond lengths are only slightly different at 2·11 and 2·13 Å respectively. A knowledge of the geometries of the ethylene and tetrafluoroethylene complexes would be of obvious interest.

The equilibrium constants for the reactions of $IrX(CO)(PPh_3)_2$ with unsaturated molecules[11] relate strongly to the π-acidity of the adduct; in the case of the chloro-complexes, K_{eq} varies from <1 for the ethylene adduct to $1{\cdot}4 \times 10^5$ for the tcne complex. The equilibrium constant for the reaction of C_2H_4 with $RhCl(PPh_3)_2$ is *ca.* 100 times greater than that for the comparable reaction with $IrCl(CO)(PPh_3)_2$. Ugo reports[12] that $Pt(PPh_3)_2$ reacts 100 times more quickly with dioxygen than $IrCl(CO)(PPh_3)_2$, which we take to reflect the greater π-basicity of the platinum complex. Finally, Cenini *et al.*[13] have suggested, on the basis of i.r. and n.m.r. data, that the bisphosphineplatinum(0) fragment is a better π-base than Vaska's complex.

It has long been accepted that a platinacyclopropane canonical structure contributes significantly to a valence bond description of the ground state of a π-olefin complex of platinum.[14] While the absolute metal binding energies are consistent with this view, it should not lead on to assuming that the metal ion has an actual charge approaching +2. In many respects, our results add to, rather than subtract from, the credibility of the Pauling Electroneutrality Principle which would imply also that structures involving the olefin in a (formal) dicarbene complex such as $L_2Pt(CR_2)_2$ are relatively unimportant. In molecular orbital terms the latter implies that there is back donation from the metal to the ligand σ^* orbitals; the e.s.c.a. results indicate that this process cannot be significant.

Table 1 shows that for the platinum- and rhodium-olefin complexes, there are satellite C(1*s*) peaks positioned at *ca.* 6 eV to higher binding energy with respect to the main C(1*s*) peak; the integrated intensities of these satellite peaks ranges from 2—6% of the main absorption, but it is clear that they cannot be transitions associated with the olefin as such, even if the ratio of intensities corresponds roughly to the ratio of olefin carbon atoms to phenyl carbon atoms (*ca.* 4%), since the splitting of *ca.* 6 eV is too large for such an assignment. At first sight, the situation appears very similar to that observed in the e.s.c.a. spectra of some transition metal carbonyls[15] where carbon and oxygen (1*s*) satellites were separated by 5—6 eV from the normal ionisation peaks. The origin of these satellites is not fully understood, but, in addition, it would be unwise to follow the arguments of Barber *et al.*[15] in detail since we have recently observed satellite peaks in triphenylphosphine itself; further data on other phosphine-olefin complexes are being collected and we shall discuss these at some later time.

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