X-Ray Photoelectron Studies of Platinum and Palladium Complexes; Observation of the *trans*-Influence and Distinction Between Terminal and Bridging Chlorine

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Summary Molecular core binding energies have been measured for a series of platinum and palladium complexes; the results show the great potential of *X*-ray photoelectron spectroscopy for studies in structure and bonding.

THE advantage of *X*-ray photoelectron spectroscopy[1,2] is that in principle it is capable of revealing something of the electronic environment of each constituent atom of a molecule and this makes a study of structure and bonding in Pt^{II} and Pd^{II} complexes particularly attractive. The relatively small amounts of sample required coupled with the large ionization cross sections for the Pt(4*f*) and Pd(3*d*) core levels are then additional bonuses. We report here preliminary results concerning bonding between Pt and alkenes and alkynes, the *trans*-influence in square-planar Pt^{II} and Pd^{II} complexes, and distinction between terminal and bridging chlorine in *trans*-$L_2M_2Cl_4$ (L = R_3P or Me-$CHCH_2$; M = Pt or Pd).

Spectra were measured on an A.E.I. ES 100 electron spectrometer for samples studied as thin films on a conducting backing using $MgK\alpha_{1,2}$ radiation. The sensitivity of the technique is illustrated by the spectra shown in the Figure for the Pt(4*f*) and I(3*d*) core levels of *trans*-$(PMe_3)_2PtI_2$ where the sample size was *ca.* 1 mg.

The results are shown in the Table. It may be shown[2] that the binding energy of a given core level of an atom in a molecule is related to the charge distribution by equation (1) where E_0^i is a reference level and the second term

$$E^i = E^i_o + k_{q_i} + \sum_{i \neq j} \frac{q_j}{r_{ij}} \qquad (1)$$

represents the potential from the charge at the atom considered. The third term accounts for the potential from the rest of the molecule (an intramolecular Madelung type potential; for ionic solids however the summation should in principle be extended to all the atoms in the crystal lattice).

Binding energies (in eV)

	L_2	$Pt(4f_{7/2})$	$C(1s)$	$P(2p_{3/2})$	L
cis-$(Ph_3P)_2PtL_2$	$H{-}C{\equiv}C{-}H$	72·3	284·7	131·0	$C(1s)$ $C{\equiv}C$ 283·3*
	$CH_3{-}C{\equiv}C{-}H$	72·4	284·7	130·9	$C(1s)$ $C{\equiv}C$ 283·3*
	$Ph{-}C{\equiv}C{-}H$	72·4	284·7	130·9	$C(1s)$ $C{\equiv}C$ 283·3*
	$H_2C{=}CH_2$	72·4	284·7	131·1	$C(1s)$ $C{=}C$ 283·2*
	$(Cl)_2$	72·2	284·7	131·0	$Cl(2p_{3/2})$ 198·0
	trans-$(Me)_2$	71·2	284·7	130·7	
$(Ph_2P){-}C_2H_4{-}(PPh_2)$	$(Cl)_2$	72·1	284·7	130·9	$Cl(2p_{3/2})$ 198·0
	$(Me)_2$	71·2	284·7	130·5	

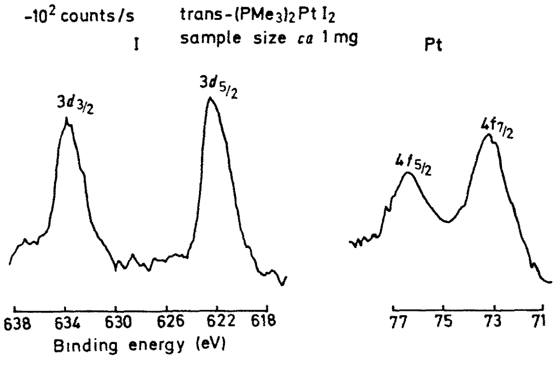
L_2PtX_2				L	
L	X	$Pt(4f_{7/2})$	$Cl(2p_{3/2})$	$P(2p_{3/2})$	$C(1s)$
cis-$Bu^n{}_3P$	Cl	72·0	198·1	131·1	284·7†
trans-$Bu^n{}_3P$	Cl	72·0	199·3	130·7	284·7†
		$Pt(4f_{7/2})$	$I(3d_{5/2})$		
cis-Me_3P	I	72·9	621·4	132·6	285·1
trans-Me_3P	I	72·9	622·1	132·1	285·0
	Pt metal	71·1			
$(PhEt_2P)_2PdCl_2$		$Pd(3d_{5/2})$	$Cl(2p_{3/2})$	$P(2p_{3/2})$	$C(1s)$
cis		338·0	197·4	130·9	284·7†
trans		338·0	198·2	130·6	284·7†

trans-$L_2M_2Cl_4$							N.q.r. frequency
$M = Pt$	$Pt(4f_{7/2})$	$Cl(2p_{3/2})$		L			^{35}Cl ν_Q MHz
$L = MeCH{=}CH_2$	72·7	199·4 terminal	$C(1s)$ CH_3	285·0	$C{=}C$	284·2	24·12 terminal[5,8]
		198·4 bridging					15·95 bridging[5,8]
$L = Pr^n{}_3P$	71·9	199·1 terminal	$C(1s)$	284·7†	$P(2p_{3/2})$	130·8	22·36 terminal[5,8]
		198·1 bridging					15·46 bridging
$M = Pd$	$Pd(3d_{5/2})$	$Cl(2p_{3/2})$		L			
$L = MeCH{=}CH_2$	337·9	199·3 terminal	$C(1s)$ CH_3	285·0	$C{=}C$	284·2	
		198·3 bridging					
$L = Bu^n{}_3P$	337·7	198·7 terminal	$C(1s)$	284·7†	$P(2p_{3/2})$	130·7	19·50 terminal[5,8]
		197·7 bridging					12·77 bridging[5,8]
Pd metal	336·3						

* These appear as shoulders on the main peak due to the Ph carbons. Deconvolutions were carried out with a Dupont 310 curve resolver. All levels were calibrated with respect to $Au(4f_{7/2})$ 84 eV binding energy.

† Centroid of relatively broad peak half width 1·8 eV.

In general the *shift* in binding energy of a given core level is dominated by the charge at the atom concerned, the potential from the other atoms being usually much smaller and opposite in sign. In the closely related series of molecules described here, therefore, the shifts in a given core level will qualitatively reflect differences in charge distribution. With large polyatomic ligands such as (Ph_3P) charge migration to or from the ligand has little effect on any individual carbon atom, since it is spread over so many centres, and hence within experimental error the $C(1s)$ binding energy for the phenyl carbons is identical for all samples and consists of a broad peak (half width *ca.* 1·8 eV) centred at 284·7 eV binding energy. Comparison of the core binding energies for *trans*-$(Ph_3P)_2PtMe_2$ and the related chelated phosphine derivative which of necessity has *cis*-stereochemistry indicates that the core levels of the metal are not greatly influenced by the stereochemistry and are comparable in binding energy to the metal itself. On replacement of the strong σ donor CH_3 ligands† by an alkene or alkyne there is considerable electron transfer from metal to ligand. This is shown by the increase in binding energy for the metal core levels and the low binding energy for the alkene and alkyne carbon atoms. [For comparison the $C(1s)$ binding energies for $-C{\equiv}C-$ and $>C{=}C<$ in the free ligands would be *ca.* 284·9 eV]. This result may be understood in terms of the Dewar–Chatt–Duncanson model[3] in which back donation from filled Pt *d* orbitals into the π^* antibonding orbitals of the hydrocarbon is the dominating feature. Siegbahn and his co-workers[4] have also investigated some of these compounds, *e.g.* cis $(Ph_3P)_2$-PtL_2, $L_2{=}PhC{\equiv}CPh$, $CH_2{=}CH_2$, and Cl_2. In general the agreement between our results is satisfactory with the exception of *cis*-$(Ph_3P)_2PtCl_2$ for which a $Pt(4f_{7/2})$ binding energy of 73·4 eV was obtained. This discrepancy is difficult to understand since we have investigated numerous compounds of general formula $(PR_3)_2PtCl_2$ (both *cis* and *trans*) and in each case the binding energies for the $Pt(4f_{7/2})$ levels are close to 72·2 eV.



FIGURE

X-Ray crystallographic data show quite clearly that there is a considerable increase in metal–halogen bond

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† The strong σ-donation from the methyl groups would undoubtedly be reflected in a higher $C(1s)$ binding energy for these ligands. Unfortunately this is obscured by the much higher intensity peak due to the phenyl carbons.

length in going from the *trans* to *cis* isomer in square-planar Pt^{II} and Pd^{II} complexes of the type $(PR_3)_2MX_2$. For $X = Cl$, n.q.r. data suggest[5] that the bond lengthening is accompanied by a considerable electron drift to chlorine. The data in the Table show that in a given *cis–trans* pair the binding energy of the metal is the same but that the binding energy of the halogen is considerably lower in the *cis*-isomer. By contrast the binding energy for the phosphorus atom of the phosphine ligands is somewhat higher in the *trans*-isomers; however, the absolute values for the shift in binding energy within a given *cis–trans* pair is smaller than for the halogen. This undoubtedly arises from the dispersal of any charge over the alkyl and aryl groups of the phosphine ligands. Considering first $(R_3P)_2MCl_2$ (M = Pt or Pd), the results complement and extend the picture of charge distribution in a given *cis–trans* pair suggested by n.q.r. which provides information on only the chlorine atoms. The Pt and Pd core binding energies indicate that the electronic environment about the metal is the same for a given *cis–trans* pair and that an increase in density around chlorine in going from the *trans* to *cis* isomer (as shown by lower binding energies) is compensated by a decrease in density around phosphorus. This is readily understood in terms of the strong σ donor properties of phosphine ligands and a Syrkin type rehybridization scheme.[6] Comparing corresponding isomers‡ $(R_3P)_2MCl_2$ (M = Pt and Pd) for the $Pt(4f_{7/2})$ and $Pd(3d_{5/2})$ core levels the shift with respect to the metal is 0·9 and 1·7 eV, respectively, indicating a positive charge, that on palladium being the larger. By contrast the $Cl(2p_{3/2})$ binding energies are lower for the palladium compounds indicative of a higher electron density compared with the corresponding platinum compound.

For $(R_3P)_2PtX_2$ (X = Cl or I) the binding energies suggest greater positive charge on the platinum and phosphorus atoms for the iodide. This can only reasonably be accommodated by a relatively greater electron density on the halogen atoms in the iodides. This confirms Parshall's[7] order of σ donation of $Cl^- > I^-$ (the π acceptor properties being much smaller) obtained from ^{19}F n.m.r. studies.

The measured molecular core binding energies for *trans*-$L_2M_2Cl_4$ (L = R_3P or $MeCHCH_2$; M = Pt or Pd) are also shown in the Table. In square-planar Pt^{II} and Pd^{II} chlorides, the $Cl(2p)$ core levels appear as spin–orbit-split (*ca.* 1·8 eV) doublets. In the bridged species, however, the $Cl(2p)$ levels appear as broad unresolved peaks, which may be deconvoluted to give four components, corresponding to the spin–orbit-split components for two non-equivalent chlorines. In each case the difference in binding energy between terminal and bridging chlorines is *ca.* 1·0 eV.

On the basis of n.q.r. data [5,8] (also shown in the Table) the chlorine with lower binding energy may be assigned as bridging in each case. For the phosphine complexes, the binding energies of comparable terminal and bridging chlorines is somewhat lower for the palladium compound. This follows the behaviour for the square-planar complexes $[(R_3P)_2MCl_2]$. This reflects the higher electron density around chlorine and is also evident in the n.q.r. results.[5,8] The binding energy of the metal core levels $(4f_{7/2})$ and $Pd(3d_{5/2})$ suggests that in the chlorine-bridged phosphine complexes the electronic environment around the metal is similar to that in the corresponding square-planar complexes.

For the propene complexes, strong interaction between filled metal *d* orbitals and antibonding π^* orbitals is shown by the relatively low $C(1s)$ binding energy of the C=C carbons although comparison with $(Ph_3P)_2PtC_2H_4$ suggests that the interaction is smaller in the bridged complexes. Electron migration to the alkene ligand in the platinum complex is largely at the expense of the metal, since the $Pt(4f_{7/2})$ level binding energy is considerably increased compared with the phosphine complex, the $Cl(2p_{3/2})$ levels being shifted to higher binding energy by a small amount. In the corresponding palladium compound the situation is reversed and electron migration to the alkene is at the expense of chlorine, the binding energy of the palladium being similar in the two compounds. The explanation for this difference in behaviour can be understood by a consideration of the binding energy of the metal core levels with respect to the elements. For the phosphine complexes the shift to higher binding energy amounts to 0·8 and 1·3 eV for $Pt(4f_{7/2})$ and $Pd(3d_{5/2})$ respectively, indicative of considerable positive charge, that on palladium being the greater. Replacement of a strong σ donor ligand by a strong π acceptor ligand in going from the phosphine to alkene complex will therefore be expected to make an increased electron demand on the metal *and* other ligands. The latter will be much larger for the palladium compound since the metal carries a much larger positive charge than in the corresponding platinum complex.

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‡ We are of course comparing compounds with different phosphine ligands, the electronic effects of which will also be different. However these differences will be small as judged by the metal core bonding energies [*cf.* binding energies of *cis*-$(Ph_3P)_2PtCl_2$].

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