X-Ray Photoelectron and Mössbauer Spectroscopy of Triphenylphosphine–Iridium Complexes †

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Ir 4*f* core binding energies and ^{193}Ir Mössbauer data have been recorded for a series of $(PPh_3)_2Ir(CO)X$-type complexes and found to be fairly insensitive to variation of X. The Ir 4*f* and N 1*s* photoelectron and Mössbauer spectroscopic results for several iridium–nitrosyl complexes containing iridium in different formal oxidation states with linear and bent Ir–N–O-groups are discussed.

THE chemistry of $(PPh_3)_2Ir(CO)Cl$[1] and its derivatives has attracted much attention in recent years. Nitrosyl complexes have also been extensively studied because of their unique structural and bonding features.[2] We wish to report additional information on the bonding in these compounds as obtained from *X*-ray photoelectron spectroscopy (p.e.) and ^{193}Ir (73 keV) Mössbauer studies.

The combination of both techniques has recently been applied to study transition metal–ligands bonds in gold,[3] iron,[4] and iridium[5] complexes.

EXPERIMENTAL

Photoionisation of core electrons was accomplished by using Al-K_α *X*-radiation (1486·6 eV). The kinetic energies of the photoelectrons were measured on an A.E.I. ES 100 spectrometer. The powdered samples were brushed on a double sided Scotch tape which was pressed onto the copper sample holder. Iridium 4*f* and nitrogen 1*s* core binding energies were determined with reference to the carbon 1*s* line and their positions obtained from different runs agree within ±0·15 eV. The Mössbauer transmission spectra of the 73 KeV γ-transition in ^{193}Ir were recorded with both source and absorber cooled down to 4·2 K. The ^{193}Os activity is obtained by neutron activation of metallic osmium containing 98·7% ^{192}Os. Due to the hexagonal structure of metallic osmium, the source emits a quadrupole split (q.s.) line doublet.[6] This was taken into account during the fitting process. Since the nuclear factor $\Delta\langle r^2\rangle$ is known to be positive in the ^{193}Ir nucleus[7] the isomer shift (i.s.) of the 73 keV γ-line is directly proportional to the difference $\Delta|\psi(0)^2|$ between the total *s*-electron densities at the nucleus in source and absorber. In 5*d* transition metal complexes $|\psi(0)|^2$ mainly depends on the 6*f* and 5*d* populations of the metal orbitals. $|\psi(0)|^2$ is directly increased by the 6*s* population and reduced by the 5*d* population, which shields the *s*-electrons from the nucleus. The quadrupole splitting of the line is a measure of the interaction between the quadrupole moments of the ^{193}Ir nuclear ground state and the electric field gradient (e.f.g.) at the nucleus. In covalent compounds the e.f.g. is mainly produced by the valence electrons. Its sign has not been determined in the present study.

RESULTS AND DISCUSSION

The Mössbauer and p.e. data of the planar complexes *trans*-$(PPh_3)_2Ir(CO)X$[8] (see Tables 1 and 2) show that substitution of Cl^- by other halides and pseudohalides affects only slightly the total electron density on the iridium atom, the *s*-electron density and the electric

TABLE 1

Mössbauer isomer shift and quadrupole splitting data

	I.s./mm s^{-1} [a]	Q.s./mm s^{-1}
$(Ph_3P)_2Ir(CO)Cl$	−0·51 ± 0·02	6·54 ± 0·02
$(Ph_3P)_2Ir(CO)Cl$	−0·49 ± 0·015 [b]	7·74 ± 0·03 [b]
$(Ph_3P)_2Ir(CO)Br$	−0·53 ± 0·015 [b]	6·92 ± 0·03 [b]
$(Ph_3P)_2Ir(CO)N_3$	−0·44 ± 0·02	7·51 ± 0·02
$(Ph_3P)_2Ir(CO)SCN$	−0·46 ± 0·03	7·42 ± 0·06
$(Ph_3P)_2Ir(CO)NO$	−0·57 ± 0·02	2·15 ± 0·02
$(Ph_3P)_3Ir(NO)$	−0·84 ± 0·02	1·27 ± 0·04

[a] The i.s. values are given with reference to an Ir in Os source. [b] Data taken from H. H. Wickman and W. E. Silverthorne, *Inorg. Chem.*, 1971, **10**, 2333.

TABLE 2

Iridium $4f_{5/2}$ and $4f_{7/2}$ core binding energies of iridium complexes with reference to C 1*s* = 285 eV

$(Ph_3P)Ir(CO)X$	Ir $4f_{5/2}$	$4f_{7/2}$ E_b/eV
X = F [a]	64·6	61·6
Cl	64·6	61·6
Br [a]	64·5	61·4
I [a]	64·5	61·4
N_3 [a]	64·5	61·5
NCO [a]	64·6	61·6
NCS [a]	64·6	61·6
$C(CN)_3$ [b]	64·6	61·6
N_4CCF_3 [c]	64·7	61·7
$(Ph_3P)_3IrNO$ [d]	64·6	61·6
$(Ph_3P)_2Ir(CO)NO$ [d]	65·1	62·1
$(Ph_3P)_2Ir(NO)HCl$ [d]	65·0	62·0
$(Ph_3P)_2Ir(NO)Cl_2$ [e]	65·3	62·4
$[(Ph_3P)_2Ir(CO)(NO)Cl]^+BF_4^-$	66·3	63·5
$[(Ph_3P)_2Ir(CO)(NO)J]^+BF_4^-$ [g]	66·3	63·6
$[(Ph_3P)_3Ir(NO)H]^-ClO_4^-$ [h]	65·5	62·5

[a] Ref. 10. [b] W. Beck, K. Schorpp, C. Oetker, H. S. Smedal, and R. Schlodder, *Chem. Ber.*, in the press. [c] J. Weis, personal communication. [d] Ref. 13. [e] S. D. Robinson and M. F. Uttley, *J. Chem. Soc.* (*A*), 1971, 1254. [f] Ref. 2. [g] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1282. [h] C. A. Reed and W. R. Roper, *Chem. Comm.*, 1969, 155.

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field gradient at the nucleus. On the other hand it has been observed that variation of the anionic ligands X^- has a distinct influence on the i.r. intensity[9] and stretching frequency[10] of the CO band. These p.e. and Mössbauer data point to an essentially unchanged electronic charge distribution around the iridium in these compounds. The electronic changes due to variation of X are obviously compensated by the CO-ligand. The q.s. values for $(PPh_3)_2Ir(CO)X$ ($X = Cl, Br, N_3, SCN$) are the largest so far observed for iridium complexes. The e.f.g. values obtained from the q.s. using the quadrupole moments of the i.r. nuclear ground state, $Q = 1{\cdot}0 \pm 0{\cdot}5b$ compare well with the e.f.g. values for the planar d^8-complex $[Au(CN)_4]^-$, containing strong back bonding cyanide ligands.[12] A different situation occurs, if X = NO. Complexes with a bent metal–NO group have been formulated as complexes of NO^-, whereas linearly co-ordinated nitrosyl ligands are regarded as positively charged NO^+ groups.[2] Thus $(PPh_3)_2Ir(CO)NO$ can either be regarded as an Ir^I d^8-complex containing NO^- or as an Ir^{-I} d^{10}-complex with NO^+ as ligand. The Ir–N–O-angle in $(PPh_3)_3IrNO$ was determined to be 180°.[13] Because of the chemical similarity between $(PPh_3)_2Ir(CO)NO$ and $(PPh_3)_3IrNO$[14] we assume that a $5d^{10}$ configuration also exists in $(PPh_3)_2Ir(CO)NO$. Since NO^+ is known to be a strong π-acceptor, back donation from the metal to the ligand will reduce the effective $5d$ population well below $5d^{10}$ and hence decrease the shielding of s-electrons from the nucleus. Actually the i.s. and thus the s-electron density at the nucleus in $(PPh_3)_2Ir(CO)NO$ have the same values as in the $5d^8$ complex $(PPh_3)_2Ir(CO)Cl$.

The i.s. value of $(PPh_3)_3IrNO$ is by $0{\cdot}27$ mm s^{-1} more negative than that for $(PPh_3)_2Ir(CO)NO$, which is attributed to the stronger π-acceptor property of the carbonyl group compared to that of the phosphine ligand. These different acceptor properties are also confirmed by the higher N 1s binding energy in the carbonyl complex. The q.s. in $(PPh_3)_2Ir(CO)NO$ is smaller by 5 mm s^{-1} than in the planar $(PPh_3)_2Ir(CO)X$ complexes and though larger, well comparable to the q.s. in $(PPh_3)_3IrNO$. In the latter compound, the iridium ion is known to be tetrahedrally surrounded by the ligands, and a recent X-ray structure determination has shown that the complex $(PPh_3)_2Ir(CO)NO$ is a distorted tetrahedron with an almost linear Ir–N–O-group.[15] The Ir 4f binding energies and thus the total electronic charges on the iridium in $(PPh_3)_3IrNO$ and $(PPh_3)_2Ir(CO)NO$ are similar to those of $(PPh_3)_2Ir(CO)X$. In $(PPh_3)_2Ir(CO)NO$ the iridium is found to be even more positive than in the Ir^I complexes, *i.e.*, the effect of the formal oxidation state on the $5d$ population is overcompensated by π-back bonding effects.

The N 1s binding energies of a series of iridium nitrosyl complexes again demonstrate that the electron density on the NO^+ is not necessarily smaller than on the NO^- group. This explains why NO stretching frequencies have proven to be an unreliable tool in determining the bonding mode in nitrosyl complexes (see Table **3**).

TABLE 3

N 1s Core binding energies and NO stretching frequencies (Nujol mulls) of several nitrogen containing iridium complexes. The p.e. data are given with reference to C 1s = 285 eV

	N 1s E_b/eV	$\nu(NO)/cm^{-1}$
$(Ph_3P)_2Ir(CO)N_3$	402·8, 398·5	
$(Ph_3P)_2Ir(CO)NO$ [a]	400·5	1645, 1660
$(Ph_3P)_3IrNO$ [a]	400·2	1600
$(Ph_3P)_2Ir(NO)Cl_2$	400·9	1558
$(Ph_3P)_3Ir(NO)H^+ClO_4^-$	401·1	1777
$[(Ph_3P)_2Ir(CO)(NO)Cl]^+BF_4^-$	403·4	1723
$[(Ph_3P)_2Ir(CO)(NO)J]^+BF_4^-$	403·2	1720
$(Ph_3P)_2Ir(NO)HCl$	401·2	1545

[a] P. Finn and W. L. Jolly (*Inorg. Chem.*, 1972, **11**, 893) report a value of N 1s = 400·3 eV for $(Ph_3P)_3IrNO$ and N 1s = 399·6 eV for $(PPh_3)_2Ir(CO)NO$, which seems to be inconsistent with the interpretation given here.

The Ir–N–O bonding angles in $[(PPh_3)_2Ir(CO)(NO)Cl]^+$ and $[(PPh_3)_3Ir(NO)H]^+$ are known to be **124** and **175°**, respectively.[2,16] The p.e. data, however suggest that there is more negative charge on the linearly co-ordinated 'NO^+' than on the 'bent' NO^- group. Substitution of Cl^- by the stronger σ-donor H^-, and of CO by the weaker π-acceptor PPh_3 increases the electron density on the central iridium ion, which is in part compensated by a strong π-back donation into the antibonding $(NO)\pi^*$-orbitals.

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