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Preliminary communication

X-RAY PHOTOELECTRON SPECTRA OF INORGANIC MOLECULES

XXIX*. THE CHARACTERIZATION OF MIXED PHOSPHIDO-PHOSPHINE AND PHOSPHIDO-PHOSPHITE COMPLEXES OF TRANSITION METAL CARBONYL CLUSTERS USING X-RAY PHOTOELECTRON SPECTROSCOPY*

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Summary

X-ray photoelectron spectroscopy has been found to provide a useful means of studying the electronic structure of the phosphorus atoms in PPh, PPh_2, PPh_3, PHPh and $P(OMe)_3$ ligands in a number of polynuclear cobalt and iron complexes.

Elucidation of the electronic structures of Groups IV—VI atoms intimately associated with transition metal clusters can help to predict whether their reactivity is electrophilic or nucleophilic in character. From this an understanding of the relationship between such clusters and pure transition metal clusters can emerge and the potential of such clusters as homogeneous catalysts can be evaluated. We are currently investigating the synthesis, structure and reactivity of transition metal carbonyl clusters containing the phenylphosphido moiety.

During the course of this work we discovered that X-ray photoelectron spectroscopy (XPS) offers a convenient and useful means of probing the electronic structure of the reactive phosphorus atom. Since these results are of relevance to the characterization of a broad range of carbonyl clusters we now communicate the preliminary details of our work.

The appropriate core electron binding energies of a selection of iron carbonyl dimers and trimers and cobalt carbonyl tetramers are presented in Table 1*. Since each P 2*p* binding energy peak consists of a closely spaced

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*For part XXVIII see ref. 1.

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TABLE 1

CORE ELECTRON BINDING ENERGIES OF CARBONYL CLUSTERS OF COBALT AND IRON CONTAINING PHOSPHORUS LIGANDS [a]

Compound		P 2p		Co $2p_{3/2}$/Fe $2p_{3/2}$
$Co_4(CO)_{10}(PPh)_2$	I		130.4(2.0)	
$Co_4(CO)_8(PPh_2)_2[P(OMe)_3]_2$	II	133.4(2.1)	130.6(2.0)	780.1
$Co_4(CO)_9(PPh)_2[P(OMe)_3]$	III	133.2(2.2)	130.6(2.1)	780.2
$Co_4(CO)_9(PPh)_2(PPh_3)$	IV		130.8(2.6)	780.1
$Fe_3(CO)_9(PPh)_2$	V		130.3(2.1)	709.3
$Fe_3(CO)_8(PPh)_2[P(OMe)_3]$	VI	132.7(2.2)	129.8(1.9)	
$Fe_2(CO)_6(PPh_2)_2$	VII		130.8(2.2)	709.2
$Fe_2(CO)_6(PHPh)_2$	VIII		131.2(2.3)	709.3

[a] Binding energies are internally referenced to a C *1s* energy of 285.0 eV for the phenyl groups of the phosphine ligands: full-width half-maximum values (fwhm) for the P 2*p* peaks are given in parentheses.

$2p_{1/2,3/2}$ doublet ($\Delta E \approx 0.5$ eV) the energies reported in Table 1 refer to the peak maximum and therefore correspond most closely to the energy of the P $2p_{3/2}$ components. In the case of the iron phosphide cluster V the progressive growth of a peak at ca. 132.8 eV during prolonged irradiation is in accord with X-ray induced oxidation of the μ-PPh units. This probably occurs through reaction with chemisorbed oxygen. Reduction of the X-ray beam powder from 1 kW to 400 W resulted in a dramatic reduction in the rate of growth of the 132.8 eV peak.

A comparison of carbonyl clusters containing only the phenylphosphido moiety with clusters substituted with trimethyl phosphite or triphenylphosphine allows an unambiguous assignment of the P 2*p* binding energies. The P 2*p* peak at ca. 133 eV is due to the phosphorus of trimethyl phosphite while the P 2*p* binding energies of PPh_3 (in complex IV) and the bridging PPh unit occur between 130.8 and 129.8 eV **. As a consequence, complex IV which contains both μ_4-PPh and PPh_3 exhibits a single P 2*p* band envelope containing the binding energy peaks of both these phosphorus sites. However, since the full-width at half-maximum (fwhm) value of the P 2*p* peak of IV is the largest for the complexes listed in Table 1 it is apparent that the P 2*p* binding energies of PPh_3 and μ_4-PPh differ by a few tenths of an eV. In the case of the mixed phosphido—phosphite clusters, the relative intensities of the well resolved P 2*p* peaks are in good agreement with those expected on the basis of the ligand stoichiometric ratios (μ-PPh/$P(OMe)_3$ equal to 2/1 or 2/2).

The P 2*p* binding energy spectra of the phosphido-bridged iron dimers VII and VIII show that relative to the iron trimers V and VI there is a positive chemical shift of ca. 1 eV. However, whether this difference is entirely due to ground state charge differences or owes its origin, at least in part, to differences in relaxation energy cannot yet be discerned.

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*XPS measurements were carried out using a Hewlett—Packard 5950A ESCA spectrometer with Al-K_α radiation (1486.6 eV). Data were usually collected at ambient temperature using an X-ray beam power of 1 kW, and an electron "flood-gun" was employed to eliminate, or reduce to a minimum, surface charging effects. Full details of our experimental procedure is described elsewhere [2].

**The chemical shift between the P 2*p* binding energies of coordinated $P(OMe)_3$ and PPh_3 is in accord with that noted by Lindberg and Hedman [3] for free $P(OEt)_3$ and PPh_3 (1.7 eV).

The most significant result of the present study concerns the value of the P 2*p* binding energies of the μ-PPh, μ-PHPh and μ-PPh_2 units. In an earlier study by Jolly and co-workers [4] it was found that the P 2*p* chemical shift between PPh_3 and phosphorus in the phosphide phases CrP and MnP was ca. — 1.8 eV, implying that the phosphorus atoms in the latter phases were very electron rich. In contrast to this situation the P 2*p* energies of the μ-PPh unit (formally derived from PPh^{2-}) in complexes I—VI, and the μ-PR_2 units (formally derived from PR_2^- in complexes VII and VIII) are comparable to the binding energy of coordinated triphenylphosphine, in which form the phosphorus atom is generally unreactive. Lampin [5] has reported that compound V is unreactive towards butyllithium and we have found it to be unreactive towards anhydrous HCl. It is reported [6] that $NaBH_4$ converts compound V to VIII though it is not clear from that result whether the phosphorus is the center of reactivity. Reaction of compound I with $NaBH_4$ leads to $Co_4(CO)_9(\mu\text{-PPh})_2(\mu\text{-H})^-$ without disruption of the iron—phosphorus bonds [6]. Collman [7] has reported that compound VII can be cleanly reduced with sodium dispersion to $Fe_2(CO)_6(\mu\text{-PPh}_2)_2{}^{2-}$ without disruption of the phosphido bridges. The XPS results, therefore, are clearly consistent with the generally unreactive nature of the cluster-bound phosphido moieties.

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