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Substituted metal carbonyls

XVI *. X-Ray photoelectron spectroscopic differentiation of chemically distinct phosphorus environments in unidentate complexes of 1,1′-bis(diphenylphosphino)ferrocene

Hardy S.O. Chan *[,a], T.S. Andy Hor [a], Lai-Tee Phang [a] and Kuang Lee Tan [b]
[a] *Department of Chemistry and* [b] *Department of Physics, Faculty of Science, National University of Singapore, Kent Ridge 0511 (Singapore)*

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Abstract

X-Ray photoelectron spectra of $M(CO)_n(\eta^1\text{-dppf})$ ($n = 5$, M = Cr, **1**, Mo, **2**, W, **3**; $n = 4$, M = Fe, **4**), $(OC)_4Fe(\mu\text{-dppf})Mo(CO)_5$, **5**, $(OC)_5M(\mu\text{-dppf})M(CO)_5$ (M = Cr, **6**, Mo, **7**, W, **8**) and 1,1′-bis(diphenylphosphino)ferrocene (dppf), **9**, suggested that the technique can be diagnostic for pendant and coordinated phosphines, and, in heterometallic cases, be used to differentiate phosphines bound to different metals. The resolution of the $P(2p)$ bands permits a measurement of the relative binding energies for chemically distinct phosphorus sites in the same complex thus eliminating complications in calibration as well as sample charging problems normally associated with X-ray photoelectron spectroscopy in comparative studies.

Introduction

Among the earliest endeavors of X-ray photoelectron spectroscopy (XPS or ESCA) in transition metal chemistry was the probing of free and coordinated phosphines [1]. Despite numerous approaches, efforts towards this directive have consistently been frustrated by the broadness of the $P(2p)$ bands and their insensitivity to shifts for chemically inequivalent nuclei. The core level shifts, if observed, are rarely significant enough to allow one to extract any reliable structural information on the molecules of interest [2]. To complicate matters further, as the binding energies (b.e.'s) are measured separately on the free ligand and the complex, comparison of their values needs judicial considerations in view of the problems in calibration and differences in charging effects. In this paper, we report the first XPS

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* For part XV see ref. 3d.

study of complexes which bear a unidentate diphosphine, a system which allows a direct measurement of the relative b.e.'s of pendant and coordinated phosphines not subjected to differences in surface effects. When this technique is applied to heterometallics, one can also estimate with confidence the shift difference between chemically distinct phosphines.

Results and discussion

The unidentate and heterometallic complexes are represented by $M(CO)_n(\eta^1$-dppf) ($n = 5$, M = Cr, **1**, Mo, **2**, W, **3**; $n = 4$, M = Fe, **4**) and $(OC)_4Fe(\mu$-dppf)$Mo(CO)_5$, **5**, (dppf = 1,1′-bis(diphenylphosphino)ferrocene), respectively. All of these have recently been isolated and characterized [3]. For comparative purpose, the singly bridging dimers $(OC)_5M(\mu$-dppf)$M(CO)_5$ (M = Cr, **6**, Mo, **7**, W, **8**) and free dppf, **9**, are included in the investigation. The b.e.'s for the metal and $P(2p_{3/2})$ levels together with the peak widths are listed in Table 1. The $P(2p)$ b.e. for **9** (131.1 eV) correlates well with those reported for PPh_3 (130.6–132.0 eV) [4]. For compounds **1**–**4**, a broad phosphorus band is observed, which reveals a doublet after extraction of the gaussian components. A representative example is illustrated in Fig. 1 for complex **4**. The 1 : 1 intensity ratio of this doublet confirmed the equal population of the nucleus in two sites. The lower energy bands (130.8–130.9 eV) are consistent with the P peak in free dppf (131.1 eV) whereas the higher energy bands (131.8–132.0 eV) are suggestive of a coordinated dppf moiety with the σ-donating presiding over the π-accepting character. Although the core ionizations found in complexes **1**–**8** span an expectedly narrow region of 131.6–132.0 eV, which restrict the use of $P(2p)$ shift values as diagnostic parameter for the metal to which the P is attached, the coordination shift is sensitive enough to indicate an electronic change on the phosphorus when placed in different metal spheres. This point is best

Table 1

Core level binding energies (eV) [a]

Complex	$P(2p)$	$Fe(2p_{3/2})$ (dppf)	M
$Cr(CO)_5$(dppf), **1**	130.8(1.8); 132.0(1.8)	708.3(1.7)	576.0(1.9) [b]
$Mo(CO)_5$(dppf), **2**	130.8(1.8); 131.9(1.8)	708.2(1.6)	228.4(1.8) [c]
$W(CO)_5$(dppf), **3**	130.9(1.8); 131.8(1.8)	708.3(1.5)	31.9(1.8) [d]
$Fe(CO)_4$(dppf), **4**	130.9(1.8); 132.0(1.8)	708.2(1.6)	709.2(1.6) [e]
$(OC)_4Fe$(dppf)$Mo(CO)_5$, **5**	131.1(1.8); 132.1(1.8)	708.1(1.6)	709.2(1.6) [e]; 228.5(1.9) [c]
$(OC)_5Cr$(dppf)$Cr(CO)_5$, **6**	131.7(2.2)	708.6(2.0)	575.8(2.1) [b]
$(OC)_5Mo$(dppf)$Mo(CO)_5$, **7**	131.6(2.1)	708.2(1.9)	228.5(1.7) [c]
$(OC)_5W$(dppf)$W(CO)_5$, **8**	131.7(2.0)	708.5(1.7)	32.0(1.8) [d]
dppf, **9**	131.1(1.8)	708.5(1.4)	–

[a] Core level binding energies referenced to hydrocarbon peak at 285.0 eV; full-width half-maximum values are given in parentheses. [b] $Cr(2p_{3/2})$. [c] $Mo(3d_{5/2})$. [d] $W(4f_{7/2})$. [e] $Fe(2p_{3/2})$.

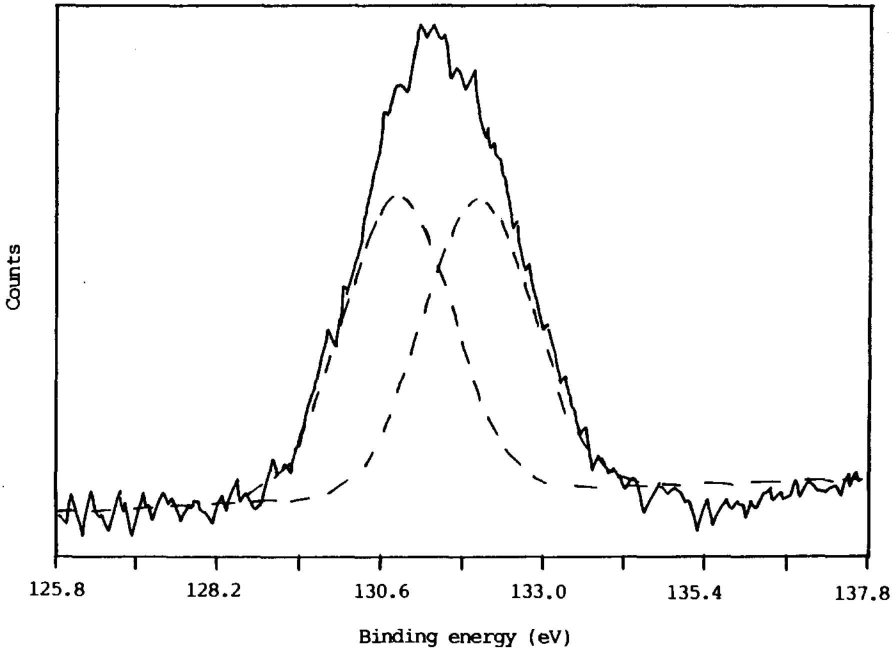

Fig. 1. Curved-fitted P(2*p*) spectrum of Fe(CO)$_4$(dppf).

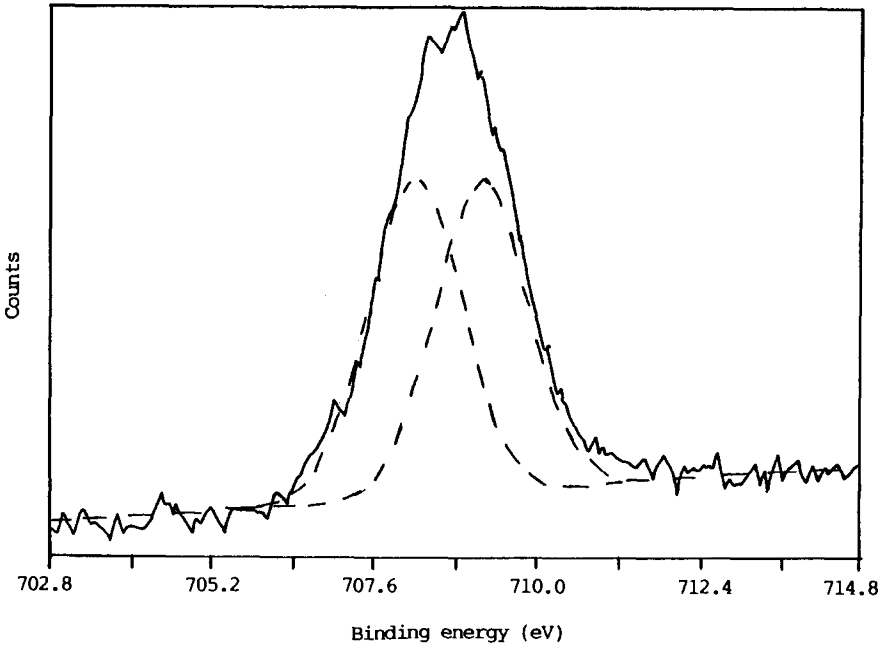

Fig. 2. Curved-fitted Fe(2*p*) spectrum of Fe(CO)$_4$(dppf).

illustrated in complex **5** where the P(2*p*) band is successfully resolved into two peaks. On the other hand, the relatively smaller breath of the homonuclear bridging complexes **6–8** does not allow for such exercise thus lending support to the existence of a homonuclear dimer. The P(2*p*) b.e.'s are fully consistent with those registered in **1–3** for the coordinated sites. The slightly greater half widths in the P(2*p*) bands of these homonuclear dimers may be originated from some slight distortions [3d] on the dppf bridging unit in the lattice structures.

The present analysis gives the relative b.e.'s between the phosphorus in its free and coordinated state which are free from interferences of sample charging and other surface effects and calibration problems which are normally associated with XPS. Though the P(2*p*) shift values are found to be insensitive towards the metal to which the phosphine is attached, the resolution of the P peaks on different metal spheres revives fresh hope in using XPS as a structure elucidation technique. These systems also permit a direct comparison of a metal in two structurally nonequivalent sites within the same complex. The Fe($2p_{3/2}$) peak in **4** can be deconvoluted to two peaks of equal intensity separated by 1.0 eV, as illustrated in Fig. 2. The lower and higher energy band correspond to the ferrocenyl and iron carbonyl moieties, respectively. Even though the ferrocenyl iron is of two units higher than its carbonyl counterpart in its formal oxidation state, the lower core ionization of the former gives unambiguous support to the dependence of b.e. in XPS on the charge of the metal, which in turn can be raised significantly by the presence of strong π-acceptors such as CO. All the other metal b.e.'s recorded are in good agreement with those reported for other Group 6 M(0) carbonyls [5].

Conclusion

With the advent of XPS and its instrumentation, it is our belief that the technique can play a more central role in the characterization of organometallic complexes. Its ability in distinguishing intrinsically nonequivalent nuclei within a complex is prompting us to examine other phosphine carbonyl systems which previously had been thought to be spectroscopically indistinguishable. The possible use of XPS as a "super NMR" [6] in general, and as a probe for heterometallics in particular provides the necessary impetus for our research.

Experimental

All the preparations were carried out in standard Schlenk flasks under a dry argon or nitrogen atmosphere according to the methods previously described [3]. The identity and purity of the samples were checked by IR, NMR and microanalyses. Core level spectra were obtained on VG ESCA/SIMSLAB MK II spectrometer using Mg-K_α radiation, operating on a fixed retardation of 40, and covered the energy region for all the elements contained. The sample in powder form was sprinkled onto a double-sided Scotch tape mounted onto a standard VG holder. The binding energies were referenced to the hydrocarbon component in the C_{1s} envelope defined at 285.0 eV to compensate for surface charging. The b.e. of each core ionisation peak was determined from a symmetric curve fit of the band and is estimated to have an uncertainty of ±0.3 eV. Surface atomic stoichiometric ratios were measured from peak area ratios corrected with appropriate experimentally determined sensitivity factors. Deconvolution of the overlapping spectral components was performed on VG software. No strenuous effort was made to resolve the P($2p$) sub-levels. However, literature data [7] suggested that $2p_{1/2}$ is rarely registered whilst the $2p_{3/2}$ is commonly recorded and reported for phosphine complexes.

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