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X-RAY PHOTOELECTRON SPECTRA OF INORGANIC MOLECULES

XXX *. ORGANOMETALLIC DERIVATIVES OF TUNGSTEN(0) AND TUNGSTEN(II)

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Summary

The W 4*f* binding energies of various carbonyl-containing complexes of tungsten are reported. Comparisons between W^{II} complexes containing the $[(\eta^3\text{-allyl})W(CO)_2]$ moiety and neutral derivatives of the type $W(CO)_{6-x}L_x$ are made. The absence of a clear-cut correlation between the W 4*f* binding energies and the value of x in $W(CO)_{6-x}L_x$ is discussed and these results compared with those obtained for the analogous molybdenum complexes.

Introduction

The extensive use of X-ray photoelectron spectroscopy (XPS) to probe the electronic and molecular structures of well-defined molybdenum compounds [1—10] has not yet been paralleled by a comparable interest in compounds of tungsten. The few published reports on the latter systems have included one dealing with the dependence of W 4*f* chemical shifts upon the tungsten oxidation state in simple oxide and halide phases [11], a study of satellite structure in the XPS of $W(CO)_6$ [12], a comparison between the metal core electron binding energies of the polyhydride complexes $MH_4(PR_3)_4$ of molybdenum and tungsten [13] and data for K_2WCl_6 and the tertiary phosphine complexes $WCl_4(PR_3)_2$ [14].

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* For part XXIX see ref. 31.

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TABLE 1

X-RAY PHOTOELECTRON SPECTRA OF COMPLEXES CONTAINING THE [(η^3-allyl)W(CO)$_2$] MOIETY [a]

Complex		W $4f_{7/2}$ (eV)	N $1s$ (eV)	Cl $2p_{3/2}$ (eV)	Other B.E.'s (eV)
I	$W(CO)_2(\eta^3\text{-}C_3H_5)(bipy)Cl$	31.5 (1.8)	399.6 (1.9)	197.6 (1.6)	
II	$W(CO)_2(\eta^3\text{-}2\ MeC_3H_4)(bipy)Cl$	31.4 (1.8)	399.4 (1.7)	197.7 (1.8)	
III	$W(CO)_2(\eta^3\text{-}C_3H_5)(bipy)(O_2CCH_3)$	31.6 (1.5)	399.9 (2.1)		
IV	$W(CO)_2(\eta^3\text{-}C_3H_5)(bipy)Br$	31.4 (1.6)	399.4 (1.8)		Br $3d_{5/2}$ = 67.8
V	$W(CO)_2(\eta^3\text{-}C_3H_5)(phen)Cl$	31.7 (1.8)	399.7 (1.9)	197.6 (2.0)	
VI	$W(CO)_2(\eta^3\text{-}2\ MeC_3H_4)(phen)Cl$	31.4 (1.8)	399.6 (2.0)	197.7 (2.0)	
VII	$W(CO)_2(\eta^3\text{-}C_3H_5)(phen)Br$	31.2 (1.7)	399.3 (1.6)		Br $3d_{5/2}$ = 67.7
VIII	$W(CO)_2(\eta^3\text{-}C_3H_5)(dpa)Cl$	32.3 (2.0)	399.9 (2.0)	198.1 (1.8)	
IX	$W(CO)_2(\eta^3\text{-}C_3H_5)(dpa)Br$	31.7 (1.8)	399.7 (1.7)		Br $3d_{5/2}$ = 68.3
X	$W(CO)_2(\eta^3\text{-}C_3H_5)(dpa)I$	31.7 (1.7)	399.7 (1.9)		I $3d_{5/2}$ = 618.8
XI	$W(CO)_2(\eta^3\text{-}C_3H_5)(dpa)(NCS)$	32.1 (1.8)	399.9 (2.1)		S $2p_{3/2}$ = 162.7
XII	$W(CO)_2(\eta^3\text{-}C_3H_5)(dpa)(O_2CCF_3)$	32.0 (1.8)	399.7 (2.3)		
XIII	$[W(CO)_2(\eta^3\text{-}C_3H_5)(dien)]PF_6$	31.5 (1.7)	399.8 (1.8)		P $2p_{3/2}$ = 136.3
XIV	$W(CO)_2(\eta^3\text{-}C_3H_5)(dppe)Cl$	32.0 (1.1)		198.1 (1.2)	
XV	$W(CO)_2(\eta^3\text{-}C_3H_5)(dppe)Br$	32.0 (1.6)			Br $3d_{5/2}$ = 68.7; P $2p_{3/2}$ = 131.4
XVI	$W(CO)_2(\eta^3\text{-}C_3H_5)(dpae)Cl$	32.0 (1.7)		198.1 (1.6)	
XVII	$W(CO)_2(\eta^3\text{-}C_3H_5)(dpae)Br$	31.9(1.4)			Br $3d_{5/2}$ = 68.6

[a] Binding energies are referenced to a C $1s$ binding energy of 285.0 eV for the organic ligands; full-width half-maximum values for the W $4f_{7/2}$, N $1s$ and Cl $2p_{3/2}$ peaks are given in parentheses.

We recently carried out an XPS study of complexes of molybdenum(0) and molybdenum(II) which contain the dicarbonylmolybdenum moiety [15]. In the course of this work we compared our data with that in the literature for complexes of the types $Mo(CO)_5L$, $Mo(CO)_4L_2$ and $Mo(CO)_3L_3$ [2,3]. In contrast to the earlier conclusions of others [3], we found that the Mo $3d_{3/2,5/2}$ binding energies were not dependent in any simple way upon the number of carbonyl groups bound to molybdenum [15].

With the availability in our laboratories of the analogous tungsten carbonyl derivatives, we have now carried out the first in-depth study of the XPS of organotungsten complexes. This has provided us the opportunity to explore further the question of whether for substituted carbonyl complexes of the Group VI elements, $M(CO)_{6-x}L_x$, there is any evidence for a simple correlation between the metal core electron binding energies (Cr $2p$, Mo $3d$ or W $4f$) and the value of x. We describe herein the results of this our most recent study.

Experimental

The X-ray photoelectron spectra were recorded using a Hewlett-Packard Model 5950A ESCA spectrometer. Monochromatic aluminum $K\alpha_{1,2}$ radiation (1486.6 eV) was used as the X-ray excitation source. An electron "floodgun" was used in conjunction with the instrument to eliminate or at least reduce to a minimum surface charging effects.

With the exception of complex XIII all other compounds listed in Tables 1 and 2 were prepared by literature methods or extensions thereof [16—26]. All samples were of acceptable analytical purity and their identity was confirmed further by infrared spectroscopy.

TABLE 2

X-RAY PHOTOELECTRON SPECTRA OF SUBSTITUTED TUNGSTEN CARBONYLS [a]

Complex		W $4f_{7/2}$ (eV)	Other B.E.'s (eV)
XVIII	$W(CO)_2(MeCN)(PPh_2Me)_3$	30.6 (1.6)	P $2p_{3/2}$ = 131.2
XIX	$W(CO)_2(dppe)_2$	30.7 (1.5)	P $2p_{3/2}$ = 131.2
XX	$W(CO)_3(dien)$	30.4 (1.6)	N $1s$ = 399.5
XXI	$W(CO)_3(PMePh_2)_3$	31.0 (1.5)	P $2p_{3/2}$ = 131.3
XXII	$W_2(CO)_6(dppe)_3$	31.0 (1.7)	P $2p_{3/2}$ = 131.1
XXIII	$W(CO)_4(bipy)$	30.4 (1.6)	N $1s$ = 399.3
XXIV	$W(CO)_4(phen)$	30.6 (1.6)	N $1s$ = 399.6
XXV	$W(CO)_4(dpa)$	30.8 (1.8)	N $1s$ = 399.5
XXVI	$W(CO)_4(dppe)$	31.2 (1.5)	P $2p_{3/2}$ = 131.4
XXVII	$W(CO)_4(PPh_3)_2$	31.3 (1.4)	P $2p_{3/2}$ = 131.3
XXVIII	$W(CO)_5(py)$	30.7 (1.6)	N $1s$ = 399.9
XXIX	$W(CO)_5$(iso-nicH)	31.3 (1.4)	N $1s$ = 400.4
XXX	$W(CO)_5(PPh_3)$	31.6 (1.5)	P $2p_{3/2}$ = 131.5
XXXI	$(Et_4N)W(CO)_5Cl$	30.2 (1.8)	N $1s$ = 401.8, Cl $2p_{3/2}$ = 197.8

[a] Binding energies are referenced to a C $1s$ binding energy of 285.0 eV for the organic ligands; full-width half-maximum values for the W $4f_{7/2}$ peaks are given in parentheses.

Preparation of $[W(CO)_2(\eta^3\text{-}C_3H_5)dien]PF_6$

A solution of $WCl(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_2$ (0.40 g, 1 mmol) in nitrogen-saturated acetone (10 cm^3) was treated at 40°C with diethylenetriamine (0.10 g, 1 mmol) followed by excess KPF_6 (0.55 g, 3 mmol) dissolved in water (25 cm^3). After 1 h the yellow product was filtered from the solution, washed with water and dried in vacuo. Yield 0.34 g, 81%. Found: C, 20.3; H, 3.5; N, 7.8. $C_9H_{18}F_6O_2PW$ calcd.: C, 20.4; H, 3.4; N, 8.0%. IR (Nujol): ν (NH) 3300, 3330; ν(CO) 1819, 1918; $\nu(PF_6^-)$ 840 cm^{-1}.

In the subsequent discussion of the complexes, the following ligand abbreviation will be used (see Tables 1 and 2): py = pyridine; bipy = 2,2'-bipyridyl; phen = 1,10-phenanthroline; dpa = 2,2'-dipyridylamine; dien = diethylenetriamine; dppe = 1,2-bis(diphenylphosphino)ethane; dpae = 1,2-bis(diphenylarsino)ethane; iso-nicH = isonicotinic acid.

Results and discussion

Complexes containing the dicarbonyltungsten moiety

The W $4f_{7/2}$ binding energies of the dicarbonyltungsten derivatives of the types $W(CO)_2(\eta^3\text{-}C_3H_5)L_2X$ and $W(CO)_2L_4$ are listed in Tables 1 and 2 and the spectra of representative examples are presented in Fig. 1. Additional core electron binding energies (N 1*s*, Cl 2*p*, Br 3*d*, I 3*d*, P 2*p* and S 2*p*) which we have recorded for these complexes are also given in Tables 1 and 2. Where comparisons are possible with the analogous molybdenum complexes [15], it is clear that there is good agreement between the two sets of binding energy data for the various ligand atoms. This in turn substantiates our choice of referencing procedure for the binding energies (vide infra). Consequently, we shall not consider further these non-metal binding energies.

The binding energies listed in Tables 1 and 2 have been referenced to a C 1*s* energy of 285.0 eV for the carbon atoms of the ligands. Such a procedure has

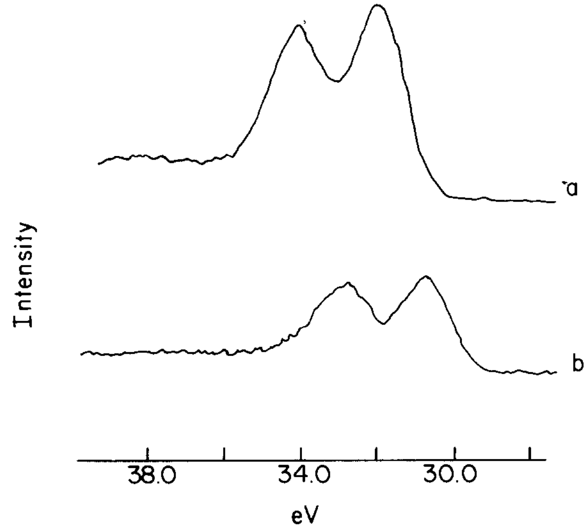

Fig. 1. W 4*f* binding energy spectra of (a) $W(CO)_2(\eta^3\text{-}C_3H_5)(dppe)Br$ and (b) $W(CO)_2(dppe)_2$.

been advocated in the past [2,4,6,8—10,13,27] and is that which we used in our studies on the analogous organometallic molybdenum complexes [15].

For the seventeen η^3-allyl derivatives of W^{II} whose W $4f_{7/2}$ binding energies span the range 31.2—32.3 eV (Table 1), there is no simple correlation of these energies with any systematic variations in the ligand sets. In this regard, these data resemble those for the analogous Mo^{II} complexes [15]. Indeed, where direct comparisons are possible between pairs of complexes of the type $M(CO)_2(\eta^3\text{-}C_3H_5)L_2X$ (M = Mo or W) which contain identical ligand sets, there is a reasonably good linear correlation (within ±0.2 eV) between the Mo $3d_{5/2}$ and W $4f_{7/2}$ binding energies of corresponding pairs (see Fig. 2). Such a result implies that similar ligand sets influence the charge at the Mo^{II} and W^{II} centers to a comparable degree. Similar correlations have been found to exist [5] between the appropriate sets of Mo $3d_{5/2}$ and Re $4f_{7/2}$ binding energies of isoelectronic and isostructural molybdenum and rhenium complexes.

The W 4*f* energies of $W(CO)_2(\eta^3\text{-}C_3H_5)L_2X$ are generally 1 eV or more greater than those of the W^0 dicarbonyl complexes listed in Table 2. A very similar chemical shift was found [15] to pertain to the molybdenum complexes of the types $Mo(CO)_2(\eta^3\text{-}C_3H_5)L_2X$ and $Mo(CO)_2L_4$. These data may be taken to imply that the tungsten atoms are more positively charged in the W^{II}-allyl complexes than in the W^0 dicarbonyls, species which are prepared from the η^3-allyl derivatives by the reductive elimination of C_3H_5X. The values of the W $4f_{7/2}$ binding energies for the η^3-allyl complexes are very similar to those measured for the homoleptic W^{II} isocyanide complexes $[W(CNR)_7](PF_6)_2$ (32.1 ± 0.2 eV) [28]. However, they are, as expected, less than the binding energies encountered for non-organometallic compounds containing tungsten in oxidation states of +3 and above, including such species as $[W_2Cl_9]^{3-}$ (32.4 eV) [29], $W_2Cl_4(OR)_4$-

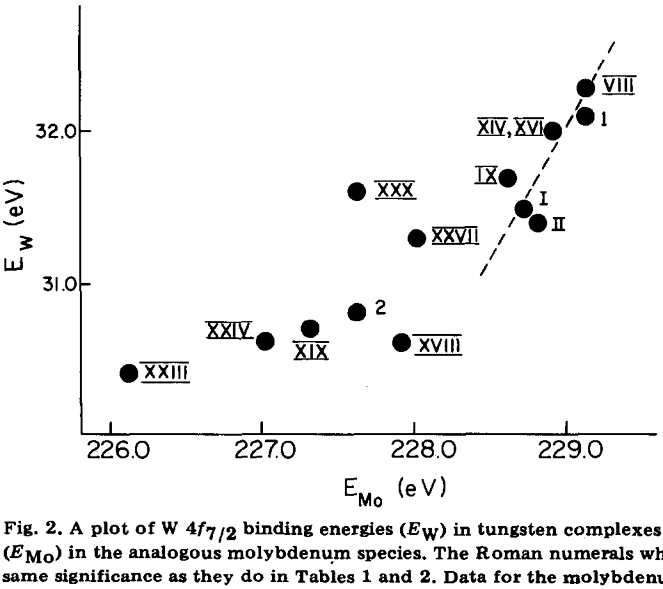

Fig. 2. A plot of W $4f_{7/2}$ binding energies (E_W) in tungsten complexes vs. Mo $3d_{5/2}$ binding energies (E_{Mo}) in the analogous molybdenum species. The Roman numerals which label the data points have the same significance as they do in Tables 1 and 2. Data for the molybdenum complexes are taken from ref. 15. Data for the points labeled **1** ($MH_4(PPh_2Me)_4$) and **2** ($[M(CNR)_7](PF_6)_2$) are taken from refs. 13, 28 and 32.

$(ROH)_2$, where R = Me or Et, (33.8—33.6 eV) [30], K_2WCl_6 and $WCl_4(PR_3)_2$ (35.1—34.3 eV) [14], WBr_5 (36.5 eV) [11] and WCl_6 (37.1 eV) [11].

Carbonyl complexes of the type $W(CO)_{6-x}L_x$

The data available in Table 2 for complexes of the type $W(CO)_{6-x}L_x$ reveal that there is no simple clear-cut correlation between the values of the W 4*f* binding energies and the value of x. In fact, the overall range of W $4f_{7/2}$ energies is surprisingly small (31.6—30.4 eV); the ranges of W $4f_{7/2}$ energies for $x = 2$, 3, 4 and 5 being 30.6—30.7, 30.4—31.0, 30.4—31.2 and 30.7—31.6 eV, respectively. This result reinforces our previous conclusions [15] concerning the molybdenum complexes $Mo(CO)_{6-x}L_x$, and confirms that for these metals at least the metal core electron binding energies do not decrease smoothly in the order $M(CO)_5L > M(CO)_4L_2 > M(CO)_3L_3 > M(CO)_2L_4$ irrespective of the nature of L. Of course the ideal comparison is for a series of complexes for which L remains unchanged. Such a comparison is not yet possible for the $Mo(CO)_{6-x}L_x$ systems where the closest we come is for the series $Mo(CO)_5(PPh_3)$, $Mo(CO)_4$(dppe), $Mo(CO)_3(dppe)[P(OBu)_3]$ and $Mo(CO)_2(dppe)_2$, whose Mo $3d_{5/2}$ binding energies are 227.6, 226.7, 227.0 and 227.3 eV, respectively [15]. In the case of $W(CO)_{6-x}L_x$, we have recorded data for $W(CO)_4$(dppe), $W_2(CO)_6(dppe)_3$ and $W(CO)_2(dppe)_2$ for which the values of W $4f_{7/2}$ decrease from 31.2 to 31.0 to 30.7 eV (Table 2). This trend is indeed that which is expected if upon substitution of CO by ligands which are better σ donors and poorer π acceptors than CO leads to a build-up of electron density at the metal center. However, the spread of W 4*f* binding energies is only 0.5 eV, which is smaller than the uncertainty in the individual values (±0.2 eV). At this time it appears that trends in the Mo 3*d* and W 4*f* energies of $M(CO)_{6-x}L_x$ complexes are unlikely to be useful in identifying the value of x in complexes of unknown structure.

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