Photoelectron Spectra of Trimethylphosphine-Substituted Tungsten Carbonyls: Ligand Field Effects, Ligand Additivity Effects, and Core−Valence Ionization Correlations

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High-resolution broad-scan gas-phase photoelectron spectra using synchrotron radiation (including valence, inner valence, and core levels) are reported for a series of trimethylphosphine-substituted tungsten carbonyls: $W(CO)_6$, $W(CO)_5PMe_3$, *cis*-$W(CO)_4(PMe_3)_2$, *trans*-$W(CO)_4(PMe_3)_2$, and *fac*-$W(CO)_3(PMe_3)_3$. The inner valence and core level spectra are interpreted by comparison with the published spectra of $W(CO)_6$ and other metal carbonyls. High-resolution valence level spectra of these complexes are also obtained by He I radiation. Fine structure, resulting from spin−orbit splitting, ligand field splittings, and vibrational coupling is resolved in the spectra of both W 5d and W 4f regions. Ligand field splittings on both the W 5d and W 4f levels increase in the order $W(CO)_6 \approx$ *fac*-$W(CO)_3(PMe_3)_3 < W(CO)_5PMe_3 \leq$ *cis*-$W(CO)_4(PMe_3)_2 <$ *trans*-$W(CO)_4(PMe_3)_2$. For the first time, the phosphorus 2p spin−orbit components of the phosphine complexes have been resolved. The binding energies (or ionization potentials) in the spectra of both W 5d valence level and W 4f core level regions are shifted almost linearly to lower energy with each successive step of ligand substitution. The shift per phosphine substitution is 0.66 ± 0.03 eV for the W 5d ionizations and 0.76 ± 0.03 eV for the W 4f ionizations ($\Delta E_{valence}/\Delta E_{core} = 0.86 \pm 0.03$). Similar linear shift trends are also found in the phosphorus 2p core level and phosphorus valence "lone-pair" ionizations. These data confirm the ligand additivity model predictions for these complexes.

Introduction

Electronic structures of the metal carbonyls and their derivatives have been studied extensively using photoelectron spectroscopy, mainly with the laboratory light sources, such as He I/He II, and X-ray radiations. In particular, the $M(CO)_{6-n}L_n$ complexes (M = Cr, Mo, W; L = substituted ligand, such as phosphine etc.; n = 0, 1, 2, 3) have attracted considerable attention.[1] Two models related to the ligand electronic effects on a transition metal center have been found useful in the photoelectron spectroscopic studies of these complexes. The first one, the ligand additivity model proposed by Bursten in 1982,[2] states that the shift in the ionization energies of the metal d valence orbitals is directly proportional to the number and type of ligand substitutions on the metal center. This model was proved to work well in Bursten's electrochemical and photoelectron spectroscopic studies of valence metal d orbitals in $M(CO)_{6-n}(CNR)_n$ (M = Mn, Cr) complexes[2] and in valence photoelectron spectroscopic studies of $Mo(CO)_{6-n}(PR_3)_n$[1b] and $W(CO)_{6-n}(PR_3)_n$.[1c] A similar principle was also found to be valid in the X-ray photoelectron spectroscopic (XPS) studies of core ionization energy shifts of transition metal complexes

in the solid state.[3] The second model, the core−valence ionization correlation model developed by Jolly,[4] states that the binding energy (BE) shift of a nonbonding valence orbital localized on a particular atom of the appropriately chosen molecules should be eight-tenths of that particular atom's core BE shift between two molecules; i.e., $\Delta E_{valence} = 0.8 \Delta E_{core}$. Jolly and co-workers have successfully applied this approach to understand the valence spectra of main-group molecules.[4] This principle was also successfully used for $Fe(CO)_4L$ complexes[5] and for the $Mo(CO)_{6-n}(PMe_3)_n$ series.[1f]

Previous studies[1] have shown that the BE shifts in metal orbitals with ligand substitutions depend on the total donor ability (σ-donation − π-acceptance) or donor:acceptor ratio of the substituted ligand relative to that of parent ligand; while the ligand field splittings in the metal orbitals of low spin d^6 octahedral complexes of a given symmetry depend only on the relative π-accepting ability of the substituted ligand and the parent ligand. For example, BE shifts toward lower energy for the metal d orbitals have been observed in the spectra of $Mo(CO)_{6-n}(PR_3)_n$[1a,b,f,g] and $W(CO)_{6-n}(PR_3)_n$[1a,c,e] when a CO group is replaced by a stronger σ donor but a weaker π acceptor, such as a PR_3 group. The spin−orbit coupling constants (ζ) and valence ligand field splitting ($e-b_2$) separations were

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obtained in the studies of $M(CO)_5L$ (M = Cr, Mo, W; L = PMe_3, PEt_3, $P(NMe)_3$, $P(OMe)_3$, $P(OEt)_3$, PF_3)[1a] and $W(CO)_{6-n}(PR_3)_n$.[1c]

Over the past decade, the application of synchrotron radiation (SR) as the light source for the photoelectron spectroscopic studies of organometallic molecules has been demonstrated.[6] The high-resolution broad-scan photoelectron spectrum of $W(CO)_6$ was obtained using SR.[7a] For the first time, this spectrum covered the valence, inner valence, and core level regions with high resolution. The vibrational structures in the W 4f core level spectrum were also observed.[7b] In this paper, high-resolution broad-scan gas-phase photoelectron spectra are reported for a series of trimethylphosphine-substituted tungsten carbonyls. The inner valence and core level spectra can be interpreted and assigned on the basis of a comparison with the spectra of $W(CO)_6$.[7] The vibrational fine structure and/or broadening due to the ligand field splitting on the W 4f core level of these complexes are observed using SR. Better resolution has been achieved in the newly obtained He I spectra of the valence level and W 5d regions of these complexes. The trend of ligand field splittings observed in the W 5d spectra is in good agreement with that observed in the W 4f region. The phosphorus 2p spin−orbit components of the phosphine-substituted complexes have been resolved for the first time. With ligand substitution, all the metal and ligand orbitals shift with different degrees to lower energy because phosphine is a stronger σ donor and weaker π acceptor than CO. Linear BE shift trends are found in both core and valence levels of metal and phosphorus ionizations, thus confirming the ligand additivity predictions for these complexes. The core−valence ionization correlation principle can be illustrated by comparing the BE shift data between core and valence levels.

Experimental Section

The compounds $W(CO)_5PMe_3$, cis-$W(CO)_4(PMe_3)_2$, $trans$-$W(CO)_4$-$(PMe_3)_2$, and fac-$W(CO)_3(PMe_3)_3$ were prepared by methods in the literature,[8] with some modifications. For example, a column separation method was used for the purification of cis-$W(CO)_4(PMe_3)_2$ rather than the sublimation method[8] because small amounts of cis-$W(CO)_4(PMe_3)_2$ could be converted to the trans isomer during the sublimation process. For the same reason, the temperature should be kept as low as possible during the sample introduction to the gas cell of the photoelectron spectrometers. A column separation process was also used to purify $trans$-$W(CO)_4(PMe_3)_2$ after the cis to trans isomerization reaction was complete. Two eluents were used in order to separate the trans isomer from the remaining cis isomer and decanting (the heating solvent). The latter was difficult to remove by evaporation[8] because of its high boiling point (>160 °C).

All the samples were introduced into the gas cell of the spectrometer directly via a heatable probe. The less volatile samples required heating to generate sufficient vapor pressure. Temperatures required for these samples were as follows: $W(CO)_6$, 35 ± 5 °C; $W(CO)_5PMe_3$, 50 ± 5

°C; cis-$W(CO)_4(PMe_3)_2$, 90 ± 5 °C; $trans$-$W(CO)_4(PMe_3)_2$, 65 ± 5 °C; fac-$W(CO)_3(PMe_3)_3$, 180 ± 5 °C. The pressure in the sample chamber was controlled to be around 4×10^{-5} Torr, and the pressure in the gas cell was around 5×10^{-3} Torr.

The photoelectron spectra were obtained by using two different photoelectron spectrometers. He I spectra of samples were recorded using a modified McPherson ESCA-36 photoelectron spectrometer.[9] The Ar $2p_{3/2}$ line at a BE of 15.759 eV was used for internal calibration during data acquisition. The spectra at higher photon energies were recorded on the modified ESCA-36 spectrometer with the Grasshopper beamline[10] at the Canadian Synchrotron Radiation Facility (CSRF), which is located at the Aladdin storage ring, University of Wisconsin−Madison.[11] A Quantar model 3395 A position-sensitive detector (PSD) was used together with the ESCA-36 photoelectron spectrometer to enhance the intensity of the signal and minimize the experimental time.[12] The spectra at higher photon energies were calibrated using the Xe 5s line at a BE of 23.397 eV. These spectra were further checked with the He I spectra of the samples. Spectra were deconvoluted with a Gaussian−Lorentzian line shape using a nonlinear least-squares procedure described elsewhere.[13]

Results and Discussion

1. General Features. The high-resolution broad-scan photo-electron spectra of $W(CO)_6$, $W(CO)_5PMe_3$, cis-$W(CO)_4(PMe_3)_2$, $trans$-$W(CO)_4(PMe_3)_2$, and fac-$W(CO)_3(PMe_3)_3$ at 80 eV photon energy are presented in Figure 1. The fitted spectra of cis and trans isomers of $W(CO)_4(PMe_3)_2$ are shown in Figure 2. Table 1 lists the positions, widths, and assignments of bands in the inner valence and core level regions. The spectra of the W 5d region of these complexes have been reported previously, obtained with He I radiation.[1a,c−e] However, the inner valence and core level bands of the phosphine-substituted complexes have not been obtained until now.

One of the important points of recording these broad-scan spectra is that, for each complex, all features can be seen immediately in one spectrum: the relatively intense and narrow valence bands with BE less than 20 eV; the weak, broad inner valence bands with BE between 20 and 40 eV (from S to D); and both very narrow core levels (C_1 and C_2) and a weak, broad core level (C_3) with BE around 40 eV. Another important feature of these broad-scan spectra is that the differences and similarities of these complexes in the whole spectral range can be observed clearly by comparison, which, in turn, can assist in the interpretation and assignment of these spectra, especially based on trends with respect to the spectrum of $W(CO)_6$ (Figure 1a and ref 7). All the phosphine-substituted tungsten carbonyls have similar features in their spectra, except for their shifts in BE and the larger splitting of W 5d orbitals and the phosphorus "lone-pair" bonding orbital in the trans isomer. However, they are different from the starting material $W(CO)_6$, in that they have an extra band P around 10 eV BE which has been assigned previously as the phosphorus lone-pair bonding orbital or $\sigma(W-P)$.[1a,d] Another difference is observed in the inner valence

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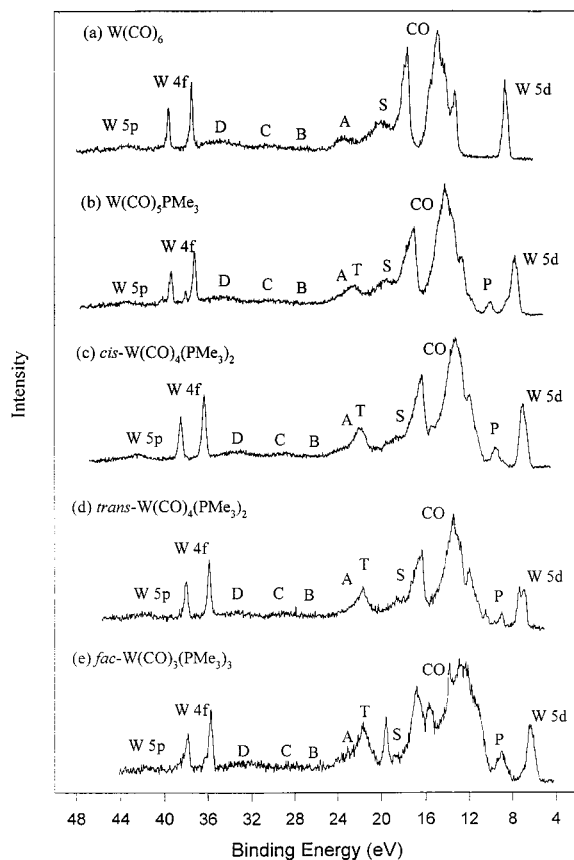
Figure 1. High-resolution broad-scan photoelectron spectra of (a) $W(CO)_6$, (b) $W(CO)_5PMe_3$, (c) *cis*-$W(CO)_4(PMe_3)_2$, (d) *trans*-$W(CO)_4(PMe_3)_2$, and (e) *fac*-$W(CO)_3(PMe_3)_3$ recorded at 80 eV photon energy.

Figure 2. Fitted high-resolution broad-scan photoelectron spectra of (a) *cis*-$W(CO)_4(PMe_3)_2$ and (b) *trans*-$W(CO)_4(PMe_3)_2$ recorded at 80 eV photon energy.

level: the intensity of band S decreases with the increase of PMe_3 ligand substitution (or with the decrease of the number of CO ligands); however, the intensity of band T increases with the increase of ligand substitution. This trend clearly illustrates that band S is related to the CO ligand and band T to the PMe_3 ligand. In fact, band T can be assigned to an orbital containing mainly C 2s character of the substituted phosphine groups according to the published results,[14] though a different assignment was proposed for the spectra of $Os(CO)_5$ and $Os(CO)_4$-PMe_3.[15] The intense and very narrow peak between band S and band T, only observed for the fac complex of this study, possibly results from sample decomposition at the high experimental temperature (185 °C). All other bands are similar to those of $W(CO)_6$, and they can be interpreted and assigned as given in Table 1.[7]

For the valence level, band 3 (Figure 2) arises from three MO's ($6t_{1u}$, $4e_g$, and $7a_{1g}$ orbitals) of mainly CO 4σ character. Band 2 is very broad in all cases, with a BE centered around 13 eV. It consists of contributions primarily from the 5σ and 1π orbitals of the CO ligands. Also observed in this region are bands due to $\sigma(C-H)$ and $\sigma(P-C)$ orbitals for phosphine complexes. The other two bands, namely bands P and 1 as shown in Figure 2, are worthy of special attention. First, the bands in the region around 10 eV (shown as P in Figures 1 and
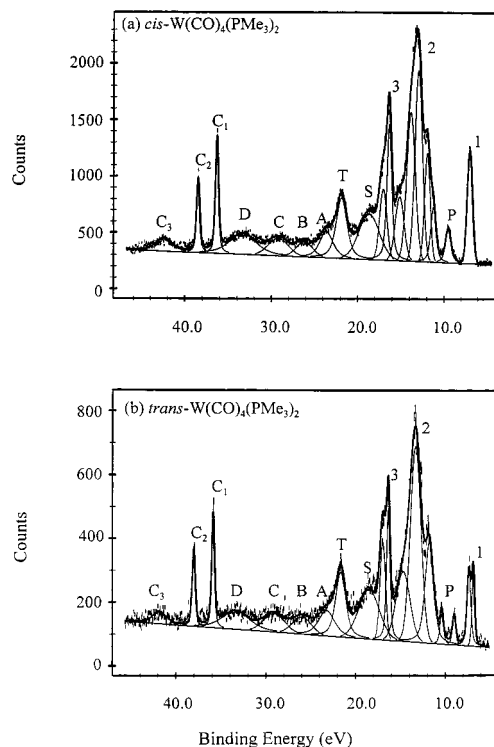
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2) are due to ionizations from the predominantly $\sigma(W-P)$ orbitals. The cis isomer shows only one ionization band in this region, which is broader and more intense than the similar band for the monophosphine complex (shown in Figure 1c and Figure 1d, respectively). The intensity of this band in the spectrum of the cis isomer indicates that the ionizations of the two $\sigma(W-P)$ orbitals are essentially degenerate. However, a large splitting (1.46 eV) can be observed in the ionizations of the two $\sigma(W-P)$ orbitals from the trans isomer, and the two bands are well resolved (see Figure 2b). In the fac complex, these ionizations are again close (only one band can be seen in Figure 1e). These experimental results are very similar to those obtained by Lichtenberger and co-workers in their study of $Mo(CO)_{6-n}(PMe_3)_n$ complexes,[1f] and the large splitting of the $\sigma(W-P)$ band in the trans complex can be explained as due to the energy differences between the d_{z^2} and p_z stabilizations.[1f] Second, band 1 is assigned to ionizations from the W 5d t_{2g}-based orbitals. They all show resolved fine structures, due to spin–orbit coupling, ligand field splitting, and CO vibrational splitting, when higher resolution He I radiation was used (Figure 3). These will be discussed in detail in the next section on the basis of our newly obtained high-resolution W 5d spectra.

2. High-Resolution Close-Up of W 5d Spectra. Our previous photoelectron study[1c] on the W 5d orbitals in $W(CO)_{6-n}(PR_3)_n$ complexes has provided the following findings: (i) there is a good linear correlation between the first ionization potential (IP) or BE for the W 5d levels and the number of ligand substitutions, as predicted by the ligand additivity model; (ii) the experimental ratio of the W t_{2g} splitting (or ligand field splitting) for $W(CO)_5PR_3$, *cis*-$W(CO)_4(PR_3)_2$, *trans*-$W(CO)_4(PR_3)_2$, and *fac*-$W(CO)_3(PR_3)_3$ is in qualitative agreement with the theoretical predictions (1:–1:2:0). In addition, a doublet with a intensity ratio of $\sim$2:1 due to the spin–orbit splitting of the t_{2g} orbital was seen for $W(CO)_6$ and *fac*-$W(CO)_3(PMe_3)_3$; three peaks were observed for cis and trans

Table 1. BE's,[a] Widths (W_h),[a] and Assignments of the Inner-Valence and Core Level Spectra of $W(CO)_{6-n}(PMe_3)_n$ ($n = 1-3$) Complexes

peak	W(CO)$_5$PMe$_3$		cis-W(CO)$_4$(PMe$_3$)$_2$		trans-W(CO)$_4$(PMe$_3$)$_2$		fac-W(CO)$_3$(PMe$_3$)$_3$		assignment
	BE	W_h	BE	W_h	BE	W_h	BE	W_h	
S	19.61	2.73	18.66	2.80	18.57	2.75	18.51	2.75	valence shake-up
T	22.40	1.33	21.86	1.35	21.68	1.35	21.56	1.36	C 2s
A	24.01	2.12	23.60	2.13	23.18	2.13	23.07	2.14	satellite 1
B	26.92	2.31	26.14	2.33	25.96	2.30	25.55	2.23	satellite 2
C	30.31	2.74	29.21	2.75	29.08	2.75	28.44	2.80	satellite 3
D	34.71	4.12	33.33	4.16	33.30	4.21	32.62	4.30	CO 3σ
C$_1$	37.15	0.38	36.40	0.39	36.38	0.40	35.65	0.40	W 4f$_{7/2}$
C$_2$	39.31	0.38	38.56	0.39	38.54	0.40	37.80	0.40	W 4f$_{5/2}$
C$_3$	43.26	2.20	42.43	2.28	41.82	2.30	41.09	2.30	W 5p$_{3/2}$

^{a} In eV (± 0.02 eV).
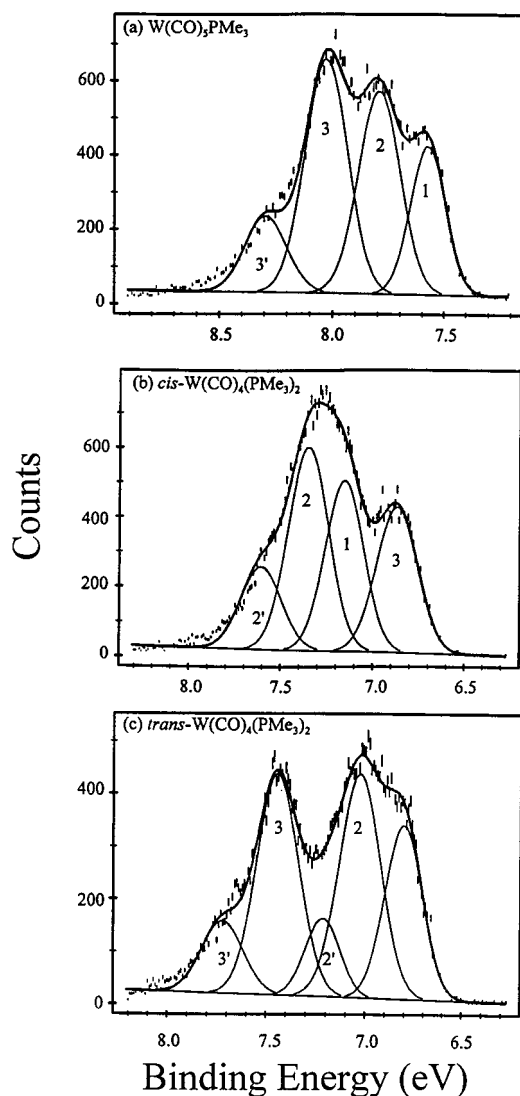
Figure 3. High-resolution He I spectra of W 5d regions for (a) W(CO)$_5$PMe$_3$, (b) cis-W(CO)$_4$(PMe$_3$)$_2$, and (c) trans-W(CO)$_4$(PMe$_3$)$_2$.

complexes due to the ligand field splitting of the t_{2g} level into b_{2g} and e_g (trans) or b_2 and e (cis) and the spin−orbit splitting of the e (or e_g) MO. Because PR$_3$ (such as PMe$_3$) is a poorer π acceptor than CO, the b_2 (or b_{2g}) MO has a larger IP than the e (or e_g) MO in W(CO)$_5$PR$_3$ and trans-W(CO)$_4$(PR$_3$)$_2$, but with the opposite order in cis-W(CO)$_4$(PR$_3$)$_2$.

Our newly obtained spectra of the W 5d region for W(CO)$_5$PMe$_3$, cis-W(CO)$_4$(PMe$_3$)$_2$, and trans-W(CO)$_4$(PMe$_3$)$_2$ (Figure 3) show better resolution than the previously reported spectra.[1c] In addition to the components of spin−orbit splitting (the splitting between band 1 and band 2) and ligand field splitting (the splitting between band 3 and the average of band 1 + band 2), another component (the high-energy shoulder, peaks 2′ and 3′, which are due to the W−CO vibrational stretching) is also clearly resolved in these new spectra. Additional vibrational structure due to the W−C vibration ($\sim$50 meV) has been resolved in the spectrum of W(CO)$_6$.[7b,16] This vibrational structure broadens the spectra in Figure 3 but cannot be fitted readily. Vibrational splitting due to the metal−CO stretching has been reported for the valence spectra of W(CO)$_6$,[7b,16] CpM(CO)$_3$ (M = Re, Mn),[17] and Mo(CO)$_{6-n}$(PR$_3$)$_n$.[1b]

All the bands are fitted with the same width for each spectrum. It is noteworthy that our new spectrum of cis-W(CO)$_4$-(PMe$_3$)$_2$ is slightly different from that previously reported,[1c] which contained a minor component due to the trans isomer (the product was purified by sublimation at high temperature in the previous work,[1c] which evidently caused the conversion of a small amount of cis isomer to the trans isomer). The fitting parameters, together with peak assignments for W 5d spectra, are listed in Table 2. The spin−orbit coupling constants (ζ) and ligand field splittings (Δ) are obtained on the basis of spin−orbit coupling theory[18] and are in rather good agreement with our previous results[1c] and theoretical predictions for this series of phosphine complexes. The ligand field splitting (Δ) in the W 5d region increases in the order W(CO)$_6$ $\approx$ fac-W(CO)$_3$-(PMe$_3$)$_3$ < W(CO)$_5$PMe$_3$ < cis-W(CO)$_4$(PMe$_3$)$_2$ < trans-W(CO)$_4$(PMe$_3$)$_2$, which leads to an increase in width of the whole W 5d spectral envelope in the same order.

3. High-Resolution Spectra of Core Level W 4f. In the past, core level spectra of inorganic and organometallic complexes were recorded by using XPS with low resolution and these spectra could only be used to study chemical shift effects. Recently, however, with high-resolution SR, it has been possible to resolve vibrational and ligand field splittings on the core p and d levels of inorganic molecules[10,19] and on the metal 4f levels of organometallic complexes.[7,15] Studying high-resolution core level spectra of a group of phosphine-substituted tungsten carbonyls is important because we want to know not only the

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Table 2. Band Positions (eV), Widths (eV), Assignments, Spin−Orbit Coupling Constants (ζ), Ligand Field Splittings (Δ = b_2−e or b_{2g}−e_g), Average BE's (eV), and Their Shifts (eV) Relative to W(CO)$_6$ in W 5d Spectra of the Listed Complexes

fitted band	position (±0.02)	width (±0.2)	assignment	ζ (±0.01)	Δ (±0.01)	BE av[a]	BE shift
			W(CO)$_6$				
				0.19		8.44	
1	8.29	0.21	t_{2g}				
2	8.58	0.21	t_{2g}				
2′	8.85	0.21	CO vibration				
			W(CO)$_5$PMe$_3$				
				0.18	−0.29	7.79	−0.65
1	7.56	0.22	e				
2	7.78	0.22	e				
3	8.02	0.22	b_2				
3′	8.29	0.22	CO vibration				
			trans-W(CO)$_4$(PMe$_3$)$_2$				
				0.20	−0.49	7.10	−1.34
1	6.81	0.25	e_g				
2	7.04	0.25	e_g				
2′	7.26	0.25	CO vibration				
3	7.46	0.25	b_{2g}				
3′	7.73	0.25	CO vibration				
			cis-W(CO)$_4$(PMe$_3$)$_2$				
				0.17	0.35	7.13	−1.31
3	6.87	0.24	b_2				
1	7.16	0.24	e				
2	7.35	0.24	e				
2′	7.61	0.24	CO vibration				
			fac-W(CO)$_3$(PMe$_3$)$_3$				
				0.19	0	6.46	−1.98
1	6.31		t_{2g}				
2	6.60		t_{2g}				

[a] Average BE's of all the fitted bands except for the vibrational bands of W 5d spectra.

effect of chemical shifts but also the influence on the width of the core level spectra with ligand replacement.

Figure 4 shows the high-resolution spectra of W 4f levels for W(CO)$_6$ and its phosphine-substituted complexes. These spectra are dominated by the two spin−orbit components W 4f$_{7/2}$ and W 4f$_{5/2}$. The vibrational fine structure due to W−CO stretching is clearly resolved in the high-energy shoulder of the bands for W(CO)$_6$.[7] The small shoulders due to the W−CO vibrational stretching and/or ligand field splitting are also resolved in the spectra of the phosphine-substituted tungsten carbonyls for the first time (Figure 4b−d). Figure 4b was obtained by mixing a small amount of starting material, W(CO)$_6$, with the W(CO)$_5$PMe$_3$ sample and recording the spectra. Since the BE's of the two bands from W(CO)$_6$ are known (Figure 4a), the BE shift of the core level W 4f bands caused by ligand substitution can be seen directly and immediately from Figure 4b [in which bands 1 and 3 belong to W(CO)$_5$PMe$_3$ and bands 2 and 4 belong to W(CO)$_6$]. In addition, the two bands of W(CO)$_6$ can be used for internal calibration of the bands that belong to its monophosphine derivative.

The experimental results and fitting parameters for the BE shifts and the widths of W 4f bands of the studied complexes are listed in Table 3. A greater BE shift than that observed for W 5d valence levels (Table 2) can be seen obviously from these W 4f results with ligand substitutions, and an almost linear correlation is established between the core BE shift and the number of ligand substitutions (~0.76 eV per phosphine for W 4f and 0.66 eV per phosphine for W 5d). In addition, the width of W 4f bands increases slightly from W(CO)$_6$ to *trans*-W(CO)$_4$(PMe$_3$)$_2$, following the order W(CO)$_6$ ≈ *fac*-W(CO)$_3$-

(PMe$_3$)$_3$ (0.30 eV) < W(CO)$_5$PMe$_3$ (0.31 eV) < *cis*-W(CO)$_4$-(PMe$_3$)$_2$ (0.32 eV) < *trans*-W(CO)$_4$(PMe$_3$)$_2$ (0.33 eV). This increase in the width of W 4f bands is due to the ligand field splitting effect, as expected from the ligand field splitting on the W 5d valence levels. For example, W 4f bands of W(CO)$_6$ and *fac*-W(CO)$_3$(PMe$_3$)$_3$ gave the same line width, since the vibrational effect is the only contributing factor and there is no ligand field splitting effect for these molecules due to the symmetry considerations.[20] The broader bands observed for the W 4f core levels of *trans*-W(CO)$_4$(PMe$_3$)$_2$ can be accounted for by the larger ligand field splitting observed on the W 5d orbitals of this molecule. A diagram showing the correlation (with a regression coefficient of r^2 = 0.91) between the ligand field splitting of W 5d spectra and the width of W 4f bands is given in Figure 5. It is worth noting that the increase in the W 4f bandwidth for these complexes is rather small, showing that the 4f$_{7/2}$ splitting into four peaks is less than 0.1 eV.[21] A larger 4f$_{7/2}$ ligand field broadening was seen recently on the Os 4f core levels of the complexes Os(CO)$_4$L (L = CO, PMe$_3$).[7b,15]

4. Shift Comparisons and Core−Valence Ionization Correlations. Bursten's ligand additivity model was originally designed for valence metal ionizations. However, it can also be used directly for core level ionizations, as shown in our above experimental data and other published results.[1,3,5] Compared with valence ionizations, the overlap and hyperconjugative interactions between metal core orbitals and ligand valence orbitals are much smaller than those between metal valence orbitals and ligand valence orbitals.[1f,g] Therefore, a greater ionization potential (or BE) shift in core level than in valence level is expected when a change in charge potential on the metal center (due to ligand replacement) occurs. Jolly's core−valence ionization correlation model[4] proposes the following correlation: $\Delta E_{\text{valence}}$ = 0.8 ΔE_{core}, for the nonbonding valence orbital and core level BE shifts of two related molecules. Our experimental BE's and their shifts relative to the starting material, W(CO)$_6$, in both W 5d and W 4f levels of these phosphine complexes are listed in Tables 2 and 3, respectively. A graphical presentation of the core and valence data is shown in Figure 6. The abscissa of the diagram is the number of phosphines in the complex and the ordinate is the shift in electronvolts (eV) relative to the starting material, W(CO)$_6$. The valence metal shifts shown in Figure 6 and Table 2 are obtained by comparing the average W 5d BE values of each phosphine-containing complex with that of W(CO)$_6$.[22] The core level shifts for both W 4f$_{7/2}$ and W 4f$_{5/2}$ components are the same, and therefore, either their average BE values or the BE's of one of the spin−orbit components can be used to compare the shifts. As illustrated in Figure 6 and Tables 2 and 3, the BE's for both valence W 5d and core W 4f levels are shifted almost linearly toward lower energy regions with each successive ligand substitution. The shift per phosphine substitution is −0.66 ± 0.03 eV for W 5d ionizations and −0.76 ± 0.03 eV for W 4f ionizations. These data confirm the validity of ligand additivity predictions for both metal valence and core level shifts in these complexes. The core−valence ionization correlation can be seen

(20) Bancroft, G. M.; Platt, R. H. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 59.

(21) Gupta, R. P.; Tse, J. S.; Bancroft, G. M. *Philos. Trans. R. Soc. London, Ser. A* **1980**, *293*, 535.

(22) By averaging the BE's of all resolved W 5d bands for the phosphine-containing complexes, we treat the valence orbital shifts due to both charge shift and overlap effect together as they are inseparable because of both spin−orbit and ligand field splittings in these complexes. This approach is slightly different from the originally proposed ligand additivity model[1f,2] where only the charge shifts are compared.
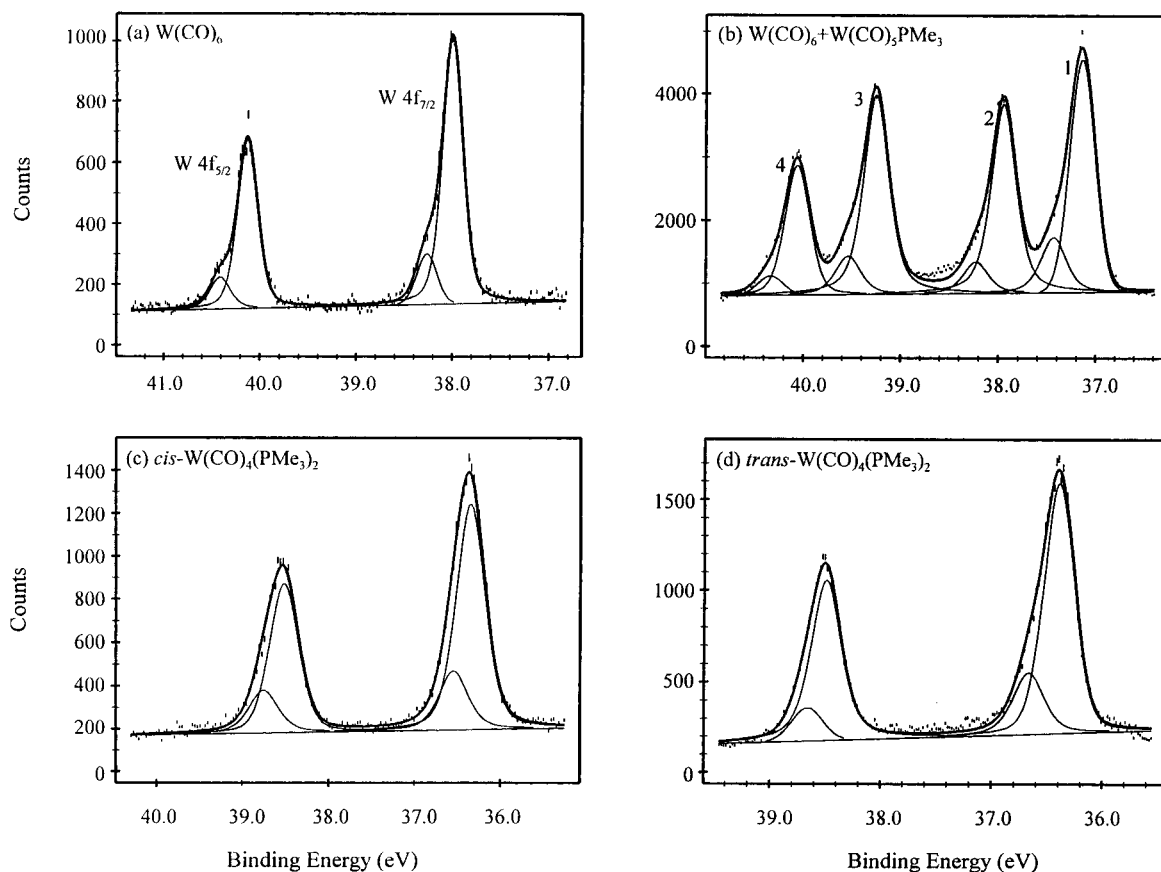
Figure 4. High-resolution W 4f core level spectra of (a) $W(CO)_6$, (b) $W(CO)_6$ + $W(CO)_5PMe_3$, (c) *cis*-$W(CO)_4(PMe_3)_2$, and (d) *trans*-$W(CO)_4$-$(PMe_3)_2$. Spectrum a was recorded at 90 eV photon energy, and spectra b–d were recorded at 102 eV photon energy.

Table 3. Fitting Parameters[a,b] for W 4f Spectra of the Listed Complexes

complex	BE of $4f_{7/2}$ (eV)	shift (eV)[c]	width (eV)
$W(CO)_6$	37.94		0.30
$W(CO)_5PMe_3$	37.15	−0.79	0.31
cis-$W(CO)_4(PMe_3)_2$	36.40	−1.54	0.32
trans-$W(CO)_4(PMe_3)_2$	36.38	−1.56	0.33
fac-$W(CO)_3(PMe_3)_3$	35.65	−2.30	0.30

[a] Fitting error for $4f_{7/2}$ BE 0.02 eV and for width ±0.005 eV. [b] The spin−orbit splitting for all the listed complexes is 2.165 ± 0.005 eV. [c] The shift is calculated using the BE's of W $4f_{7/2}$ orbitals, referenced to $W(CO)_6$.

immediately for these complexes when the W 5d shift is plotted against the W 4f shift (Figure 7). In very good agreement with Jolly's model, the ratio of the valence metal d level shifts to the core metal shifts is 0.86 ± 0.03.

5. Phosphorus 2p Bands. Up to now, we have studied the ligand additivity principle and core−valence ionization correlation for metal-based orbitals, i.e., W 5d and W 4f orbitals, for these phosphine-substituted tungsten carbonyls. The high-resolution SR also allows us to study the ligand-based phosphorus ionizations, i.e., the $\sigma(W-P)$ lone-pair valence orbital and phosphorus 2p core orbitals. This would enable us to study the application of the ligand additivity model and Jolly's core−valence ionization correlation using exclusively the ligand-based ionization potentials.

The photoelectron spectrum of *cis*-$W(CO)_4(PMe_3)_2$ obtained at 152 eV photon energy is shown in Figure 8. The high-energy shoulder around 137.5 eV is probably due to the impurity of free PMe_3; this shoulder was not included in the peak fitting. Similar spectra for the other phosphine-substituted complexes
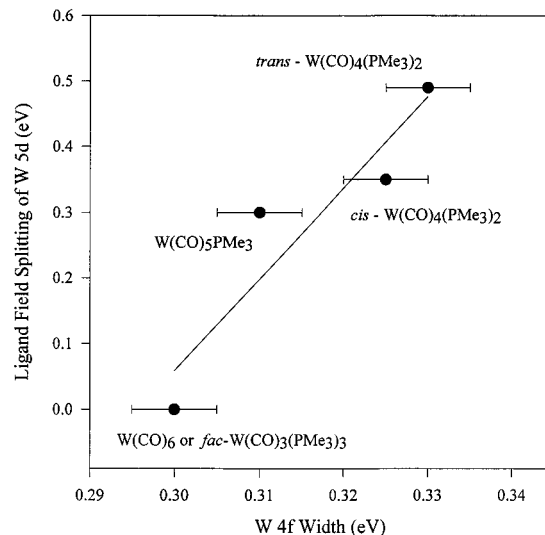

Figure 5. Diagram showing the correlation between the ligand field splitting of W 5d bands and the width of W 4f bands.

were obtained but not presented. The phosphorus 2p bands are broadened by vibrational splittings as for our previously published Si 2p spectra of $Si(CH_3)_4$.[10d] Table 4 gives the BE's and widths of the phosphorus 2p bands of $W(CO)_{6-n}(PMe_3)_n$ together with the mean BE of the valence $\sigma(W-P)$ orbital. These data show that the P lone pair is stabilized by 1.51 (10.09 − 8.58) eV and the P $2p_{3/2}$ orbital by 0.48 (136.58 − 136.10) eV, when the first phosphine bonds to the metal, in good agreement with the shifts (1.32 and 0.78 eV, respectively) observed for the $Mo(CO)_{6-n}(PMe_3)_n$ series of complexes.[1f] This large increase in phosphine BE's when the first phosphine bonds to the metal

Table 4. Phosphorus Lone-Pair or σ(W−P) and Phosphorus 2p Ionizations in $W(CO)_{6-n}(PMe_3)_n$ Complexes

complex	σ(W−P) mean BE (eV)	phosphorus $2p_{1/2}$		phosphorus $2p_{3/2}$	
		BE (eV)	width (eV)	BE (eV)	width (eV)
$W(CO)_5PMe_3$	10.09(2)	137.43(5)	0.47(3)	136.58(5)	0.48(3)
cis-$W(CO)_4(PMe_3)_2$	9.62(2)	136.76(8)	0.50(3)	135.90(8)	0.50(3)
trans-$W(CO)_4(PMe_3)_2$	9.64(2)	136.78(5)	0.51(3)	135.93(5)	0.52(3)
fac-$W(CO)_3(PMe_3)_3$	9.18(2)	136.19(5)	0.49(3)	135.34(5)	0.50(3)
free PMe_3a	8.58			136.10(14)	

[a] Reference 1f.
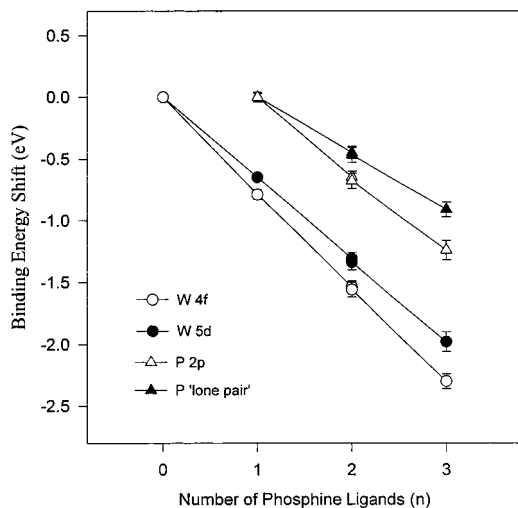
Figure 6. Shift comparison diagram for tungsten and phosphorus BE shifts, W 5d (valence), W 4f (core), P lone pair (valence), and P 2p (core).
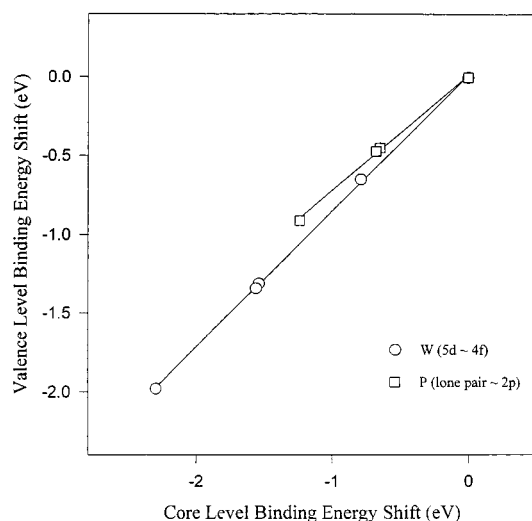
Figure 7. Core−valence shift correlation for tungsten and phosphorus ionizations. W 5d ~ W 4f; P lone pair ~ P 2p.

occurs because the W 5d orbitals can accommodate some of the electrons from the phosphorus lone pair. The additional stabilization of the P lone pair is mainly due to the strong bonding interaction with the metal center. With further substitutions after the monophosphine complex, the phosphine levels show a destabilization trend which is additive like that in the metal levels with shifts of −0.46 ± 0.02 eV for the phosphorus valence lone pair or σ(W−P) orbital and −0.62 ± 0.06 eV for core level phosphorus $2p_{1/2}$ and $2p_{3/2}$ orbitals. Also, as for the metal levels, further evidence of additivity is that cis and trans isomers of $W(CO)_4(PMe_3)_2$ have almost identical phosphorus ionizations (although the lone-pair BE's for the cis and trans isomers of $W(CO)_4(PMe_3)_2$ are quite different, the averages of
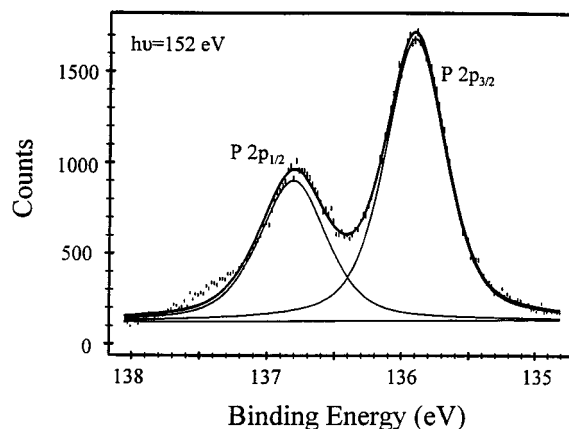
Figure 8. High-resolution photoelectron spectrum of *cis*-$W(CO)_4$-$(PMe_3)_2$ recorded at 152 eV, showing the phosphorus 2p region.

the two lone-pair BE's for each complex are very similar). The shift comparison of phosphorus lone-pair and 2p ionizations of the studied phosphine complexes is illustrated graphically in Figure 6, and their correlation is shown in Figure 7. The ratio of the lone-pair shifts to the 2p shifts is 0.73 ± 0.04. A similar core−valence correlation was also found in the study of $Mo(CO)_{6-n}(PMe_3)_n$.[1f]

From the above discussion (and Figures 6 and 7), it is interesting to note that the metal-based ionizations and the ligand-based ionizations show very similar additivity shift trends. This is because these shifts are caused by the changing charge potential when the CO ligands are systematically substituted. And the change in charge potential is determined by both the extremely fluid electron density in this system and the substantial two-center effects from ligand substitutions, as originally proposed by Lichtenberger et al. for the $Mo(CO)_{6-n}(PMe_3)_n$ series of complexes.[1f] It is also important to point out that both the metal- and ligand-based core−valence correlations agree well with Jolly's model for a ratio of 0.80.[4] However, Jolly's model is only strictly applicable when the localized nonbonding valence orbitals are used, and a ratio higher than the empirical value of 0.80 would suggest a bonding character in the chosen valence orbitals.[23] Therefore, a higher ratio (0.86) obtained using metal BE's of this series of phosphine-substituted complexes indicates the strong W 5d back-bonding into the carbonyls, as is generally accepted for metal carbonyl systems.

Conclusions

High-resolution photoelectron spectra of $W(CO)_6$, $W(CO)_5$-PMe_3, *cis*-$W(CO)_4(PMe_3)_2$, *trans*-$W(CO)_4(PMe_3)_2$, and *fac*-$W(CO)_3(PMe_3)_3$ have been reported. The advantages of monochromatized SR for studying the electronic structure of organometallic complexes have been demonstrated. The spin−orbit components of phosphorus 2p orbitals have been resolved in these phosphine complexes. Spin−orbit splittings, ligand field

(23) Jolly, W. L. *J. Phys. Chem.* **1981**, *85*, 3792.

effects, and vibrational structures are observed in the spectra of both W 5d and W 4f regions.

As the CO ligands are systematically replaced by phosphines on the metal center, all the metal and ligand orbitals shift. The linear shift of BE in both metal valence and core levels and in phosphorus valence and core levels prove the validity of the ligand additivity principle for these complexes. The core−valence ionization correlation is established between valence and core levels in both tungsten and phosphorus ionizations. Ligand field splittings on both the W 5d and W 4f levels increase in the order of $W(CO)_6 \approx fac\text{-}W(CO)_3(PMe_3)_3 < W(CO)_5PMe_3 \leq cis\text{-}W(CO)_4(PMe_3)_2 < trans\text{-}W(CO)_4(PMe_3)_2$.

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