Electronic Structure of $Os(CO)_4L$ ($L = CO, PMe_3$) Studied by Variable-Energy Photoelectron Spectroscopy

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High-resolution variable-energy photoelectron spectra of $Os(CO)_5$ and $Os(CO)_4PMe_3$ are reported. Using variable-energy synchrotron radiation, both the metal 5p → 5d resonance and the Cooper minimum effect are observed on the osmium 5d orbitals, and they have been successfully used to assign the osmium 5d-based bands. The Xα-SW calculation for $Os(CO)_5$ is used to assign the valence level molecular orbitals. Experimental branching ratios of $Os(CO)_5$ agree well with the theoretical results from both Xα-SW and Gelius methods. The electronic structure of $Os(CO)_5$ from the present study is shown to be similar to that of $Fe(CO)_5$, both of which have a trigonal-bipyramidal structure. The binding energies of the Os 5p core level have been determined, which are shown to be important in the observation of 5p → 5d resonances. Both vibrational and ligand field splittings are shown to be important in the line broadening in the high-resolution Os 4f core level spectra. The chemical shifts of valence and core levels for $Os(CO)_5$ and of $Os(CO)_4PMe_3$ are compared.

Introduction

Since the report of the convenient preparation of the osmium pentacarbonyl in 1983,[1] osmium pentacarbonyl and its monosubstituted derivatives have been extensively investigated. These studies include electron diffraction,[2] site preference of ligand in the monosubstituted $Os(CO)_4L$ complexes,[3] and the extensive use of these complexes as starting materials in various chemical reactions,[4] such as the osmium carbonyl cluster synthesis[5] and the photochemistry studies of metal carbonyl dimers.[6] However, there is still no electronic structural information available on these complexes. The knowledge of the bonding structure and the orbital energies of these complexes is important to the understanding of their chemistry. Furthermore, it has long been recognized that the studies of electronic structures of transition metal carbonyls and their phosphine substituted derivatives are important to surface chemistry, since they serve as model systems for the CO adsorption studies on metal surfaces.[7] Herein, we report the electronic structures of $Os(CO)_5$ and $Os(CO)_4PMe_3$ studied by photoelectron spectroscopy using He I and He II laboratory sources and synchrotron radiation (SR).

Photoelectron spectroscopy has been perhaps the most direct technique for the determination of the electronic structures of organometallic compounds since the first He I studies of $Ni(CO)_4$, $Fe(CO)_5$, and $Mn(CO)_5X$ complexes in 1969.[8] Traditionally, the assignment of the spectra of organometallic compounds has been aided by the increase in intensity of the cross section of the metal d orbitals on going from He I to He II radiation.[9] However, the use of He I and He II radiations sometimes gave indefinitive assignments for some relatively simple molecules, such as $Ni(C_3H_5)_2$[10] and $CpPtMe_3$,[11] even when combined with theoretical calculations. Variable-energy SR studies, on the other hand, provided firm assignments for these molecules.[10c,11b]

By using tunable SR, the variable-energy cross sections of the organometallic complexes can be obtained and, more importantly, the *n*p → *n*d resonance[12] and Cooper minimum[13] effect have been observed for some

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compounds. These two phenomena have been successfully used to assign the metal d based valence orbitals. In the present paper, we report the Fano resonance profile fit for the 5p → 5d resonance of $Os(CO)_4PMe_3$ (this aspect of the study has been reported in a preliminary letter[14]) and the observation of a Cooper minimum on the Os 5d orbitals in $Os(CO)_5$. The observation of these two effects provides firm assignments for the Os 5d valence orbitals. To aid in the complete valence level assignments, an Xα-SW calculation on $Os(CO)_5$ has been carried out. The Xα-SW method has been very successful in the interpretation of the photoelectron spectra of organometallic complexes.[15] We also report the Os−CO vibrational fine structure on the Os 5d orbitals observed by high-resolution He I radiation. In addition to the application of SR to the valence level studies, the high-resolution Os 4f spectra are described. The line broadening is due to vibrational and ligand field splittings.[16]

Experimental Section

Both $Os(CO)_5$ and $Os(CO)_4PMe_3$ were prepared at Simon Fraser University by the published procedures.[1,3]

Photoelectron Spectroscopy. The photoelectron spectra were obtained using two different photoelectron spectrometers. He I and He II spectra were recorded on a McPherson ESCA-36 photoelectron spectrometer.[17] The Ar $2p_{3/2}$ line at 15.759 eV binding energy (BE) was used as internal calibration during data acquisition. The resolution (fwhm of Ar $2p_{3/2}$ line) was about 23 meV for the He I spectra. The variable-energy (22−200 eV) spectra were recorded on the modified ESCA-36 spectrometer[18] at the Canadian Synchrotron Radiation Facility (CSRF) at the Aladdin storage ring, University of Wisconsin—Madison.[19] A 600 g/mm grating gave photon energies between 22 and 72 eV, and a 1800 g/mm grating gave photon energies between 70 and 200 eV. A Quantar no. 36 position sensitive detector[20] was used in this study which enhanced the intensity of the signal by about 20−50 times over the channeltron system. The Xe $4d_{5/2}$ line at 69.541 eV[18b] was used to calibrate the core level spectra at higher photon energies (Figure 1). It is interesting to note that at 110 eV photon energy, the Xe 4d line width was $\leq$ 0.25 eV, but the Os 4f line width was about 0.65 eV.

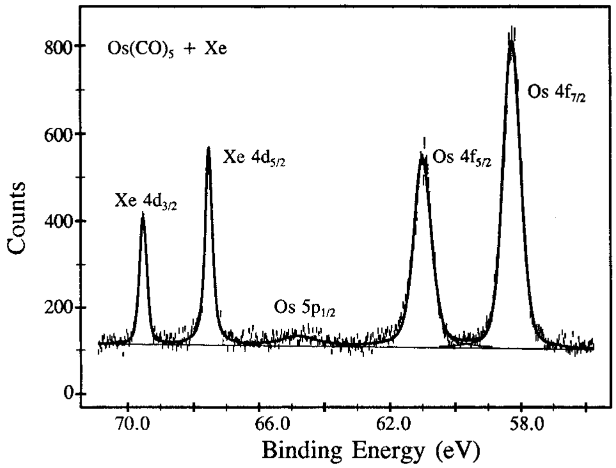

Figure 1. Photoelectron spectrum of $Os(CO)_5$ taken at 110 eV photon energy. It was calibrated with Xe gas, giving the line widths of 0.25 eV for the Xe 4d lines and of 0.65 eV for the Os 4f lines.

The sample of $Os(CO)_4PMe_3$ was introduced through the heatable probe into the gas cell of the spectrometer. It was necessary to heat the sample to 60 ± 5 °C to generate enough vapor pressure. Since $Os(CO)_5$ is very volatile, it was kept in a vessel at 0 °C and leaked into the gas cell. 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. Spectra were deconvoluted with a Gaussian−Lorentzian line shape with a nonlinear least-squares procedure described elsewhere.[21]

Computational Details. The calculation for $Os(CO)_5$ was performed by using the relativistic version of the Xα-SW method.[22] The molecule was idealized to D_{3h} symmetry with the bond distances taken from the structure of $Os(CO)_5$ as determined by electron diffraction.[2] The exchange α parameters were taken from Schwarz's tabulations.[23] The maximum azimuthal numbers, l_{max} of 3, 3, 1, and 1 were used for outer-sphere, Os, C, and O atoms, respectively. The Xα-SW cross sections were calculated using Davenpart's program[24] with a Latter tail[25] added to correct the asymptotic behavior. The resulting partial cross sections (σ_i) were first used to calculate the theoretical branching ratios (BR) ($BR_i = \sigma_i/\Sigma\sigma_i$) for each orbital and then combined to yield the Xα BR's according to the spectral assignment.

BR's of $Os(CO)_5$ were calculated on the basis of the simple Gelius model,[26] using the atomic cross sections calculated by Yeh and Lindau.[27]

Results and Discussion

A. General Features. The broad-scan photoelectron spectra of $Os(CO)_5$ at 120 eV photon energy and of $Os(CO)_4PMe_3$ at 72 eV photon energies are presented in Figure 2. These spectra cover the relatively narrow valence level with BE's less than 20 eV, the weak, broad inner valence level with BE's between 20 and 40 eV, and the core level with BE's greater than 40 eV. Table 1 lists the peak positions and widths for the peaks in the inner valence and core level regions. The Os 4f and $5p_{1/2}$ peaks of $Os(CO)_4PMe_3$ are not shown in Figure 2b because a lower photon energy was used for this

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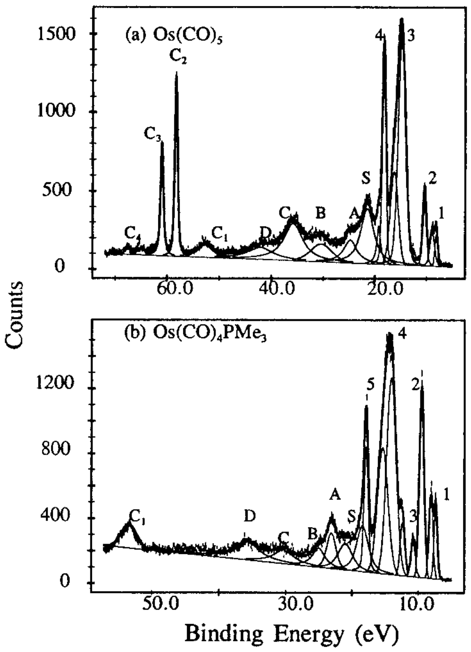

Figure 2. High-resolution broad-scan photoelectron spectra of (a) $Os(CO)_5$ at 120 eV photon energy and (b) $Os(CO)_4PMe_3$ at 72 eV photon energy. See text for explanation of the labeling.

Table 1. Binding Energies, Widths, and Assignments of the Inner-Valence and Core Level Spectra of $Os(CO)_4L$ (L = CO, PMe_3)

	$Os(CO)_5$			$Os(CO)_4PMe_3$		
peak	binding energy (eV)	width (eV)	assgnt	binding energy (eV)	width (eV)	assgnt
S	21.50	3.02	satellite 1	20.52	2.60	P 3s
A	24.78	3.09	satellite 2	22.57	1.63	satellite 1
B	30.38	4.90	satellite 3	24.21	2.27	satellite 2
C	35.82	4.40	CO 3σ	31.31	3.67	satellite3
D	42.13	6.01	satellite 4	36.97	4.47	CO 3σ
C_1	52.70	3.21	Os $5p_{3/2}$	51.91	2.86	Os $5p_{3/2}$
C_2	58.28	0.66	Os $4f_{7/2}$[a]	57.43	0.68	Os $4f_{7/2}$
C_3	61.00	0.66	Os $4f_{5/2}$	60.17	0.67	Os $4f_{5/2}$
C_4	64.90	1.89	Os $5p_{1/2}$	64.03	1.83	Os $5p_{1/2}$

[a] BE's of Os 4f and $5p_{1/2}$ levels are from the spectrum taken at higher photon energy.

spectrum. The valence level region of these spectra will be discussed in the next section, using the *n*p → *n*d resonance and Cooper minimum effect observed by variable-energy SR to aid the assignment.

As has been shown for the other metal carbonyls such as $W(CO)_6$, $Re(CO)_5X$ (X = $Re(CO)_5$, Cl, Br), and $Cr(CO)_6$,[16b,28] the inner valence region of $Os(CO)_5$ is dominated by the contributions from the CO 3σ orbital and satellites due to the shake-up processes from the CO 4σ and 3σ orbitals. Peak S (Figure 2) for $Os(CO)_5$ at 21.50 eV is the shake-up peak from CO 5σ and 1π ionizations, and it has been assigned as satellite 1 in Table 1. Peak A is associated with a normal monopole shake-up state that gains intensity by configuration interaction with the CO $4\sigma^{-1}$ state. Peak B is due to the π^{-2}–π^2 double shake-up process accompanying the 5σ ionization in free CO. Peak C at 30.38 eV BE is broad and intense, and it is due to the contributions from CO 3σ orbitals. The broad but weak peak D at 42.13 eV can be assigned to the shake-up peak from the CO 3σ orbitals.

The inner valence spectrum of $Os(CO)_4PMe_3$ in Figure 2b is slightly different from that of $Os(CO)_5$ because of the contribution from the predominated P 3s orbital. The first peak S at 20.52 eV is unique for $Os(CO)_4PMe_3$, since it is due to mostly the P 3s orbital. The atomic P 3s orbital has a BE of 17.1 eV. It is only possible to observe it with the high intensity of SR at 72 eV photon energy, where the cross section of the atomic P 3s orbital is still relatively high (~0.3 Mb).[27] Peaks A–C can be assigned as satellite peaks from CO 5σ, 1π, and 4σ orbitals and CO 3σ orbitals, respectively. It is worthy to note that the weak and broad satellite peak around 41 eV BE (peak D) in $Os(CO)_5$ is not easily seen for $Os(CO)_4PMe_3$ at the lower photon energy.

The core level region of the two compounds consists of peaks from the ionizations of Os 4f and 5p orbitals. The Os 4f peaks (C_2 and C_3) have a line width of 0.66 eV (Table 1), which is narrower than the other peaks in the core and inner valence region but still much broader than the instrumental resolution (~0.20 eV at 120 eV photon energy). Note the chemical shift of the Os 4f and 5p orbitals of ~0.8 eV on going from $Os(CO)_4PMe_3$ to $Os(CO)_5$. This line broadening on the two Os 4f levels, due to vibrational and ligand field splittings, will be discussed later in the paper. The Os 4f and $5p_{1/2}$ peaks of $Os(CO)_4PMe_3$ are not shown in Figure 2b due to the lower photon energy. We have shown in our preliminary letter that the measurement of the Os 5p BE's is important to observe the 5p → 5d resonance and, hence, to assign the Os 5d valence orbitals.[14]

B. Valence Levels. (a) He I/He II Studies. Up until the mid-80's, valence band photoelectron spectra of organometallic compounds were always taken with the laboratory He I/He II sources. An empirical intensity rule is often used to distinguish metal d-based orbital ionization from the ligand-based orbital ionizations.[9] This rule is based on the assumption that the transition metal d cross sections generally increase from He I to He II radiation in comparison to those of main group s and p orbitals. Figure 3 presents the high-resolution He I/He II photoelectron spectra of $Os(CO)_5$. There are three distinct sets of bands labeled 1, 2, and 3 in Figure 3a and an extra band 4 at higher BE in the He II spectrum shown in Figure 3b. There is no obvious change in relative band intensities from He I to He II spectra of $Os(CO)_5$. It has been shown that the cross section of third-row transiton metal d orbitals, such as of the W 5d orbital in $W(CO)_6$[13a] and of the Os 5d orbital in $Os(CO)_4PMe_3$,[14] actually decreases on going from He I to He II radiation. Furthermore, the interference of peak N (due to the ionization of band 3 by the He IIβ impurity light at 48.37 eV photon energy) on band 1 in Figure 3b makes it even more difficult to apply the above intensity rule to assign the Os 5d orbitals on the basis of the He I/He II spectra alone. Here, we demonstrate the application of SR to the study of the valence levels of these two compounds.

(b) 5p → 5d Resonance. Green and co-workers have observed the *n*p → *n*d resonance in the gas-phase photoelectron studies of some organometallic complexes, using SR.[12] The mechanism of this phenomenon has been recently reviewed by Green.[12] For osmium compounds, the intensity of the bands originating from the

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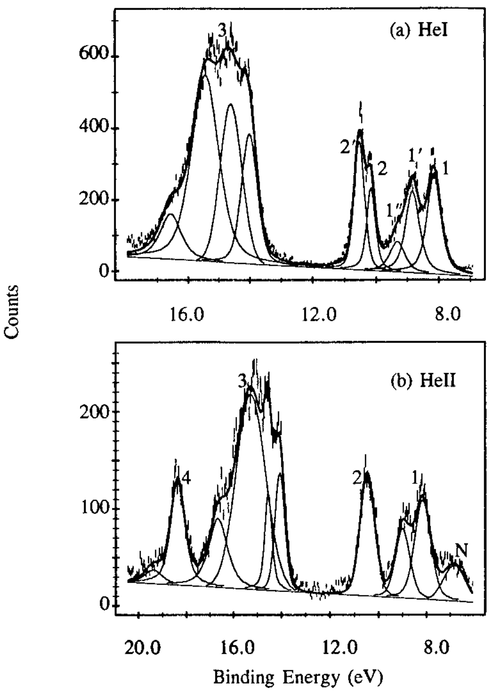

Figure 3. Valence level spectra of $Os(CO)_5$ taken by He I/He II radiation.

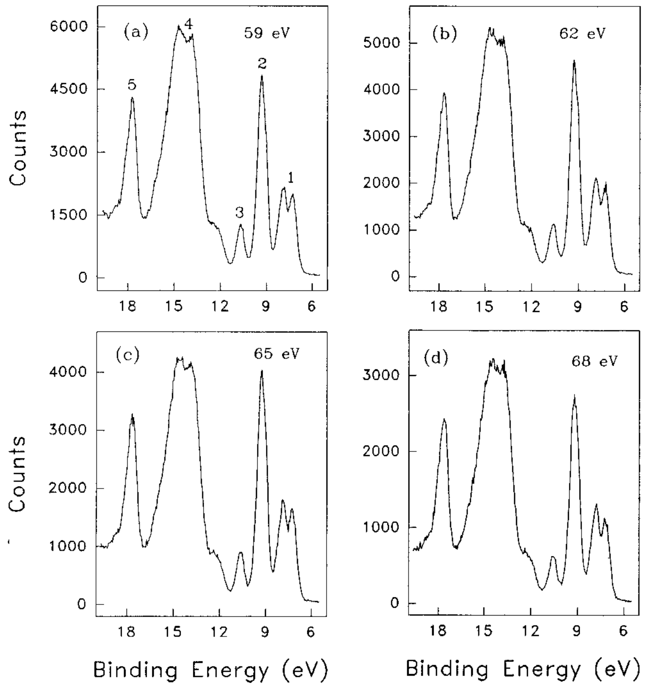

Figure 4. Valence level spectra of $Os(CO)_4PMe_3$ at (a) 59, (b) 62, (c) 65, and (d) 68 eV photon energy, showing the increase of the relative intensities of peaks A and B around 65 eV photon energy.

Os 5d valence orbitals should be enhanced when the incident photon energy is at, or near, the ionization threshold of the Os 5p core orbitals, due to the so-called super Coster−Kronig transition.[29] We have shown that the observation of this resonance is a valuable tool for the assignment of metal d valence orbitals in $CpM(CO)_3$ (M = Mn, Re) complexes[30] and $Os(CO)_4PMe_3$.[14] The Os $5p_{3/2}$ and $5p_{1/2}$ BE's for $Os(CO)_4PMe_3$ have been reported previously at 51.91 and 64.03 eV, respectively.[14] In Figure 4, the valence level spectra of $Os(CO)_4PMe_3$ at 59, 62, 65, and 68 eV photon energy are presented. It is immediately obvious that the peak intensity of bands 1 and 2 display a maximum at around 65 eV photon energy, in good agreement with the BE of Os $5p_{1/2}$ at 64.03 eV. Another resonance corresponding to the Os $5p_{3/2}$ orbital can be also observed around 53 eV photon energy.[14] The observation of the 5p → 5d resonance allows us to assign bands 1 and 2 as due to the ionization from the Os 5d based orbitals without the need of any calculation. Band 1 is separated into two peaks, as is also observed for band 2, but not as clear as 1 (see also the He I spectra in Figure 8). This splitting is due to spin orbit and/or Jahn−Teller splitting,[31] and this also confirms our above assignment of bands 1 and 2 as arising from the valence d orbitals of a third-row transition metal. Peak 3 is assigned as due to the bonding phosphorus lone pair orbital, similar to the assignments for $W(CO)_5PMe_3$[32] and $Fe(CO)_4PMe_3$.[33] Band 4 is broad and intense and is due to the contribution mainly from 1σ and 5π ionizations of CO group, except that the shoulder at 12.23 eV BE is assigned to the P−C σ orbitals.[33]

To better illustrate the 5p → 5d resonance for $Os(CO)_4PMe_3$, experimental branching ratios for bands 1 and 2 between 40 and 85 eV photon energy are plotted in Figure 5. There are two maxima around 53 and 64 eV for both bands 1 and 2. This 11 eV separation is in good agreement with the Os 5p spin−orbit splitting of 11.94 eV. It is interesting to note that band 2 displays two better resolved and more intense maxima, implying that band 2 has more Os 5d character, compared with band 1. This conclusion is supported by the Xα calculation of $Os(CO)_5$ discussed in the next section.

The $np \rightarrow nd$ resonance is generally characterized by a Fano-type interaction profile.[34] The typical resonance can be described by the following simple formula:

$$BR = (q + \epsilon)^2/(1 + \epsilon^2) \qquad (1)$$

where $\epsilon \equiv (h\nu - E_r)/0.5\Gamma$, E_r is the resonance energy, Γ is the full resonance width, and q is the line profile index. Band 2 (Figure 5) was fitted to two resonance peaks according to eq 1 with a good fit achieved for q = 4.1, E_r = 53.2, 64.2 eV, and Γ = 3.4, 10.0 eV. Our q value is considerably larger than those obtained for the other organometallic molecules (usually between 0 and 2).[12] Our values of Γ are in good agreement with the values for $Os(\eta\text{-}C_5H_5)_2$.[13b] Our E_r values are 6 eV higher than the values for $Os(\eta\text{-}C_5H_5)_2$ but much closer to the Os 5p BE's for $Os(CO)_4PMe_3$. A good fit could not be obtained for band 1, presumably because band 1 is derived from Os−CO mixed orbitals.

(c) Cooper Minimum Effect. For a subshell orbital with a radial node in the initial wave function, a Cooper minimum is expected in the atomic cross section.[35] The Cooper minimum effect on the Pd 4d ionization has been

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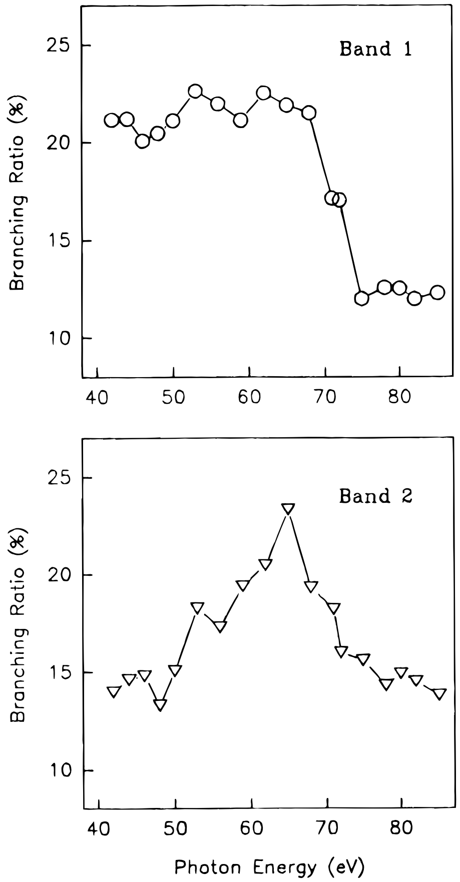

Figure 5. Experimental branching ratios of peaks A and B of Os(CO)$_4$PMe$_3$, showing the Os 5p → 5d resonances around 52 and 64 eV photon energies.

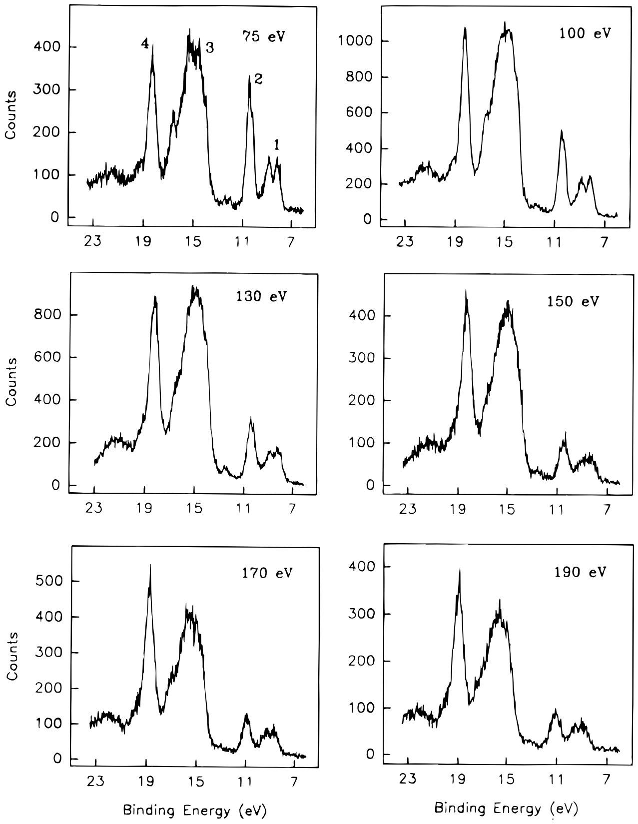

Figure 6. Representative valence level photoelectron spectra of Os(CO)$_5$ at high photon energies.

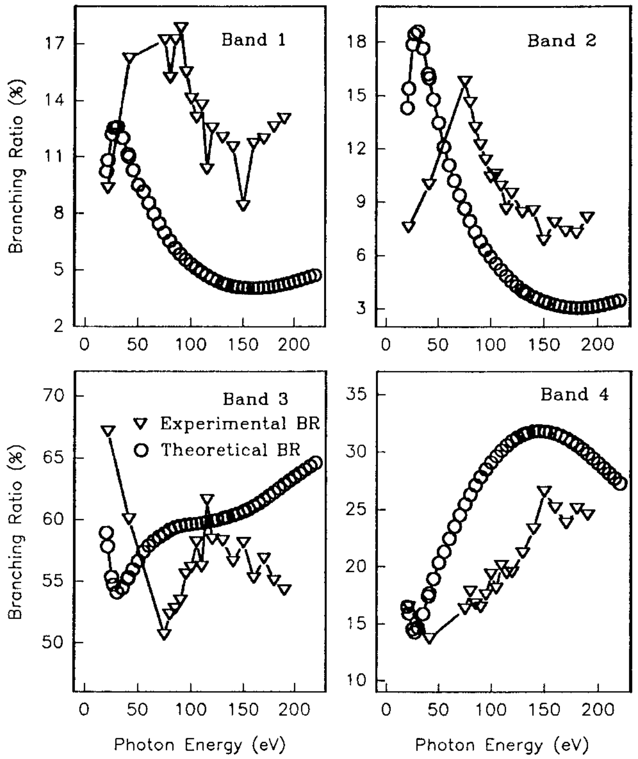

Figure 7. Experimental and theoretical (from the Gelius model) branching ratios of the valence level peaks of Os(CO)$_5$, showing the minimum of peaks A and B around 150 eV photon energy.

used to confirm the assignment of the photoelectron spectrum of Pd(η^3-C$_3$H$_5$)$_2$.[13c] The Cooper minimum for the atomic Os 5d orbital is predicted to occur around 200 eV photon energy.[27] At high photon energies, Green and co-workers have observed a decrease of the cross section of the Os 5d orbitals in Os(η^5-C$_5$H$_5$)$_2$.[13b] However, only photon energies up to 115 eV were used, and the complete minimum was not covered. Representive high-energy photoelectron spectra at 75, 100, 130, 150, 170, and 190 eV of Os(CO)$_5$ are shown in Figure 6. It is obvious that the relative intensities of bands 1 and 2 decrease continuously in comparison to the intensities of bands 3 and 4, on going from 75 to 130 eV photon energy. This decrease in intensity slows down on going from 150 to 190 eV photon energy, reaching a minimum in intensities for bands 1 and 2 in this energy range.

Branching ratios of the valence peaks of Os(CO)$_5$ from experiment and from the Gelius model are plotted in Figure 7. It is clear from the experimental results that the BR's of bands 1 and 2 increase on going from low energy up to about 70 eV photon energy and begin to decrease from 70 eV, reaching a minimum at the photon energy of 150 eV. The BR's calculated by the Gelius method have been successfully used to aid in the interpretation of experimental BR's of organometallic molecules.[10c,11b] The atomic cross sections and the Xα compositions were combined to calculate the BR's of bands 1−4, using the Gelius approach. From the plot of BR's (Figure 7) obtained by the Gelius model, a minimum of BR's of bands 1 and 2 can be found around 150 eV photon energy, in good agreement with the experimental results. The observation of the Cooper minimum confirms the assignment of bands 1 and 2 as arising from Os 5d orbitals in Os(CO)$_5$. It is interesting to note that better agreement is found for the BR's of

Table 2. Valence Level Assignment and Xα-SW Ground-State Valence Orbital Compositions of $Os(CO)_5$

orbital	Xα energy (eV)	IP (eV)	band assgnt	Os (%) 5d	Os (%) 5p + 5s + 4f	CO (%) (ax)	CO (%) (eq)
6e′	−6.85	8.05/8.82	1	52	8	4	36
3e″	−9.23	10.20/10.52	2	82	0	9	9
$4a_2''$	−12.80	14.01	3	0	12	75	13
5e′	−13.63			2	2	3	94
$1a_2'$	−13.68			0	0	0	100
2e″	−13.73			1	0	13	86
$3a_2''$	−13.82			0	2	9	89
4e′	−14.27	14.61	3	2	0	91	7
1e″	−14.46			4	0	86	10
3e′	−14.76	15.45	3	32	4	6	58
$6a_1'$	−14.91			2	22	13	63
$5a_1'$	−16.06	16.57	3	41	1	49	9
$4a_1'$	−18.99	18.27[a]	4	0	0	0	100
2e′	−19.00			0	0	0	100
$2a_2''$	−19.64	19.28	4	0	0	100	0
$3a_1'$	−19.68			0	0	100	0

[a] BE's of band 4 are taken from the spectrum in Figure 3b, since there are two well-separated peaks under band 4.

band 2, consistent with the view that band 2 results from a nonbonding Os 5d orbital, while band 1 results from an orbital with substantial ligand character, as our Xα calculation results reported below shows. In addition to qualitative agreement between the experimental results and the Gelius model BR's of bands 1 and 2, qualitative agreement can also be found for the BR's of bands 3 and 4.

(d) Xα-SW Calculation of $Os(CO)_5$. By using the 5p → 5d resonance and the Cooper minimum effect, we have assigned the first two bands (with lowest BE) in the valence level spectra of $Os(CO)_4PMe_3$ and $Os(CO)_5$ to the Os 5d derived orbitals for both osmium carbonyls. The rest of the valence level peaks can be assigned with the aid of the Xα-SW calculation. The Xα orbital energies, compositions, and the PES band assignment of $Os(CO)_5$ are listed in Table 2. The calculated results show that two e orbitals (6e′ and 3e″) are filled with eight Os 5d electrons. From the composition results, it is clear that band 1 arises from a Os−CO π bond orbital and band 2 is due almost entirely to a Os 5d nonbonding orbital since it has over 80% Os 5d character. This provides a rationalization that both the Cooper minimum effect and 5p → 5d resonance is better observed for band 2. Both the 6e′ and 3e″ orbitals lose their degeneracy because of the larger spin-orbit/Jahn−Teller splitting for the Os 5d orbitals, as two peaks are seen in Figure 3 for both bands 1 and 2 (Table 2). Band 3 arises from 10 CO-based orbitals, and it should be noted that the fitting of band 3 into four peaks is somewhat arbitrary, due to the number of the orbitals involved. Band 4 is also assigned to a CO based band, with almost pure O character.

The spectrum of $Os(CO)_5$ is similar to that of $Fe(CO)_5$.[36] The structure of $Fe(CO)_5$ has been established as trigonal bipyramidal in the solid state by X-ray crystallography.[37] The pentacarbonyls of the iron subgroup all have a trigonal-bipyramidal configuration of D_{3h} symmetry in the gas phase for which 8 d electrons fill two HOMO e orbitals. A comparison of Os 5d BE's in $Os(CO)_5$ and in $Os(CO)_4PMe_3$ (Table 3) shows that the latter is destablized by substitution of a CO group by a PMe_3 group. This can be readily explained since PMe_3 is a better σ-donor, but a weaker π-acceptor, than CO.

Table 3. Vibrational Fitting Parameters of Os 5d Spectra of $Os(CO)_5$ and $Os(CO)_4PMe_3$

compd	peak	binding energy (eV)	Jahn−Teller splitting (eV)	ν_{expl} (eV)	ν(C−O) (cm^{-1})
$Os(CO)_5$	1	8.05	0.76	0.30	2035/1993
	2	10.20	0.32	0.25	
$Os(CO)_4PMe_3$	1	7.31	0.64	0.27	2061/1978
	2	9.09	0.29	0.25	

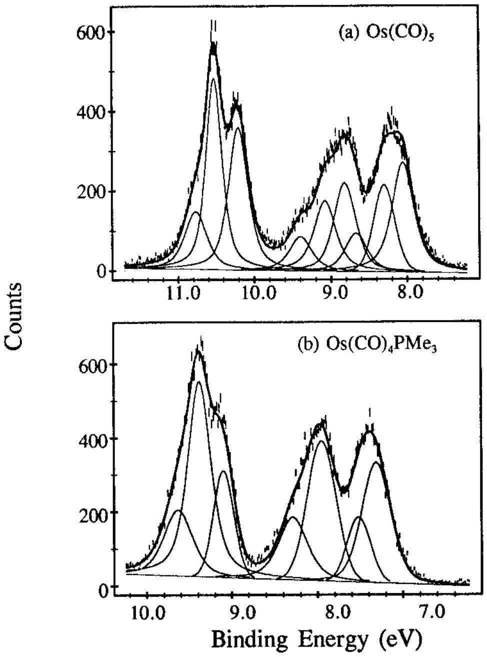

Figure 8. Vibrationally resolved He I spectra of (a) $Os(CO)_5$ and (b) $Os(CO)_4PMe_3$.

(e) High-Resolution Os 5d Spectra. Vibrational fine structure has been previously observed in the valence level of transition metal carbonyls, such as $W(CO)_6$[38] and $CpRe(CO)_3$[39] by Lichtenberger and coworkers. It has been shown to be valuable for the metal d band assignment and in the study of the metal carbonyl bonding. In Figure 8, the high-resolution He I spectra of the first two bands of $Os(CO)_5$ and $Os(CO)_4PMe_3$ are presented. These spectra have the same general features except the spectrum in Figure 8b shifts to lower binding energy due to the substitution of one axial CO by a PMe_3 group in $Os(CO)_4PMe_3$. As shown above, band 1 and band 2 in both molecules are due to the e′ and e″ orbitals, respectively, with mainly Os 5d character. The e′ orbital is primarily $d_{x^2-y^2}$ and d_{xy}, while the e″ orbital consists of d_{xz} and d_{yz} orbitals. The splitting of band 1 into 1′ and 1″ and of band 2 into 2′ and 2″ can be attributed to the Jahn−Teller and/or spin−orbit splitting. It is interesting to note that the splitting of peak 1 (~0.7 eV) is much larger than in peak 2 (~0.3 eV). The large difference of this splitting has also been observed in the corresponding Fe 3d bands of

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$Fe(CO)_5$. It has been explained that the e′ orbital has stronger vibrational coupling with low-frequency CO vibrations, which produces a larger Jahn–Teller effect.[36]

In addition to the Jahn–Teller/spin–orbit splitting, the fine structure caused by the vibrational progressions is clearly observed the spectra shown in Figure 8. The vibrational fitting parameters of Figure 8 are listed in Table 3. A three-element progression was necessary to obtain a satisfactory fit for peak 1 of $Os(CO)_5$, while the other bands in Figure 8 show fewer vibrationally resolved structures. The frequency obtained from the fitting varies from 0.25 to 0.30 eV or 2016 to 2420 cm^{-1} (Table 3). This is close to or slightly larger than the ground-state CO stretching frequencies for $Os(CO)_5$ and $Os(CO)_4PMe_3$ that are 1978 and 2061 cm^{-1}.[1,3]

C. Core Levels. Traditionally, core level spectra of inorganic and organometallic complexes have been recorded using XPS with a resolution of >1 eV, and XPS was mainly employed to study chemical shifts. 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[40] and on the 4f level of organometallic molecules like $W(CO)_6$.[16] High-resolution core level spectra of $Os(CO)_5$ and $Os(CO)_4PMe_3$ are important because with a knowledge of Os 5p BEs the Os 5p → 5d resonance can be accurately predicted to aid in the valence spectrum assignment. Furthermore, we wanted to show that the line broadening of Os 4f levels is due to both vibrational and ligand field splittings in $Os(CO)_5$ and $Os(CO)_4PMe_3$. These spectra also allowed a comparison of the Os 4f chemical shifts of the two molecules and a comparison of these core level shifts with the Os 5d shifts in the valence spectra.

The 4f spectra of $Os(CO)_5$ and $Os(CO)_4PMe_3$ taken at 110 eV photon energy are shown in Figure 9. The fitting parameters are summarized in Table 4. The experimental line width of the Os 4f levels is 0.64 eV, which is much larger than our instrumental resolution of these spectra (~0.20 eV; also see Figure 1). It has been shown that the line broadening of the W 4f levels in $W(CO)_6$ was dominated by the contribution from the vibrational progression due to the CO stretching mode.[16] Similarly, we fitted one CO vibrational series into the Os 4f spectra in Figure 9, in an attempt to explain this line broadening. But the resultant line widths (0.53 eV) are still unreasonably large, compared with that of the theoretical inherent line width[41] (~0.15 eV) and the total experimental W 4f width (0.25 eV).[16] We believe that the ligand field splitting from these low-symmetry molecules is the major cause of this 4f line broadening. This splitting is proportional to the nuclear quadrupole splitting as normally observed by Mössbauer spectroscopy or nuclear quadrupole resonance.[16b]

The chemical shift of the Os 4f levels between the reference $Os(CO)_5$ and $Os(CO)_4PMe_3$ is −0.85 eV (Table 1). It is interesting to compare this shift to that of the average valence Os 5d chemical shift (−0.93 eV) between these two molecules (Table 3). Jolly and coworkers have developed the following approach to study the bonding character of MOs, using the chemical shift information of both core and valence levels of related compouds:[42]

$$\Delta = [\mathrm{IP} - \mathrm{IP(ref)}]_{\mathrm{valence}} - 0.8[E_{\mathrm{B}} - E_{\mathrm{B}}(\mathrm{ref})]_{\mathrm{core}} \quad (2)$$

where IP, E_B and IP(ref), E_B(ref) are the vertical potential of the Os 5d level and the Os 4f binding energy of $Os(CO)_5$ and $Os(CO)_4PMe_3$, respectively. A positive Δ value corresponds to bonding character in the MO, and a negative value of Δ corresponds to antibonding character. Our value of −0.25 eV indicates that these d orbitals are slightly antibonding and that PMe_3 is a weaker π-acceptor than CO.[42]

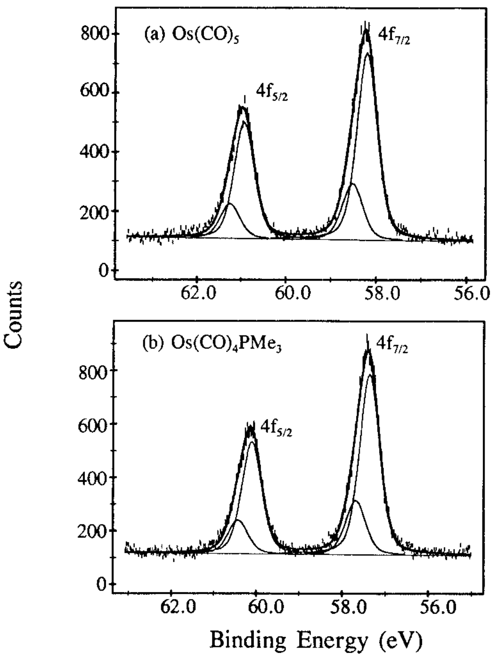

Figure 9. High resolution Os 4f core level spectra of (a) $Os(CO)_5$ and (b) $Os(CO)_4PMe_3$ at 110 eV photon energy.

Table 4. Vibrational Fitting Parameters of Os 4f Spectra of $Os(CO)_5$ and $Os(CO)_4PMe_3$

compd	BE $4f_{7/2}$ (eV)	spin–orbit splitting (eV)	SO intensity ratio	Γ_{expl} (eV)	ν(C–O) (cm^{-1})
$Os(CO)_5$	58.20[a]	2.73	0.62	0.53	2035
$Os(CO)_4PMe_3$	57.37	2.73	0.62	0.55	2061

[a] Value of 58.02 eV in the previous paper (ref 16b) was a typographical error.

Conclusions

High-resolution photoelectron spectra of two mononuclear Os carbonyls have been investigated. The Os 5p → 5d resonances of $Os(CO)_4PMe_3$ were observed using variable-energy synchrotron radiation, and a good Fano fit was obtained for these resonances. The Cooper minimum effect was observed for $Os(CO)_5$. These effects have been successfully used to assign the Os 5d valence orbitals. Vibrational splitting due to Os–CO stretching was resolved on the Os 5d bands in the high-resolution He I spectra. The Xα-SW calculation of $Os(CO)_5$ confirmed our experimental MO ordering of this molecule.

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Good agreement was found between the experimental BR's and the theoretical results (by both Xα-SW method and the Gelius model). Both experimental and theoretical results are consistent with the trigonal-bipyramidal structure for these molecules.

The high resolution and high intensity of SR is critical for the study of the inner-valence and core level spectra. The inner-valence level of both molecules was shown to be dominated by the contribution from the CO group, with the exception of the P 3s orbital in $Os(CO)_4PMe_3$. The high-resolution Os 4f spectra were shown to be broadened by both vibrational and ligand field splittings. The Os 4f chemical shift between $Os(CO)_5$ and $Os(CO)_4PMe_3$ was compared with the Os 5d chemical shift, using Jolly's treatment. The shifts are consistent with PMe_3 being a weaker π-acceptor than CO.

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