

# Experimental Quantum Chemistry: Photoelectron Spectroscopy of Organotransition-Metal Complexes

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## Introduction

The chemistry that occurs at transition-metal centers is fundamental to many homogeneous synthesis and catalysis reactions, surface reactions, and bioinorganic processes. Wide-ranging theoretical and experimental studies have contributed greatly in recent years to understanding this chemistry in terms of the basic electronic structure factors that control bonding, geometry, and reactivity at metal centers in molecules and materials. Photoelectron spectroscopy provides the most direct experimental study of electronic structure, and organometallic complexes provide systems with metal-molecule interactions in a variety of electronic environments suitable for detailed investigation. This Account illustrates the electronic structure information directly available from photoelectron spectroscopic studies of organometallic molecules in the gas phase. The information obtained from these experiments provides an understanding independent of theoretical calculations, making photoelectron spectroscopy a true experimental quantum chemical probe of electronic structure.

**Background.** The photoelectron experiment<sup>1-7</sup> is conceptually simple. A photon ( $h\nu$ ) provides the energy to eject an electron from an electronic bound state. The kinetic energy,  $E_K(e^-)$ , of the ejected electron is measured, and the ionization energy ( $E_I$ ) for this event is defined as

$$E_I = h\nu - E_K(e^-) \quad (1)$$

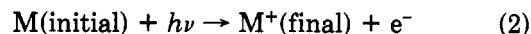
For low-energy photons ( $h\nu$  commonly less than 50 eV) the electrons are ejected primarily from the valence shell, and the technique is called ultraviolet photoelectron spectroscopy (UPS). For high-energy photons ( $h\nu$  commonly greater than 1000 eV) the electrons are ejected primarily from atomic core levels, and the technique is called X-ray photoelectron spectroscopy (XPS). Historically, XPS and UPS developed separately, with early XPS work performed on solids and early UPS experiments performed on gases. More recently, gas-phase XPS results have been correlated with UPS results,<sup>8,9</sup> demonstrating the complementary nature of these two techniques.

The ionization energy, often called the electron binding energy, is viewed as the minimum energy re-

quired to remove an electron from a bound state in the molecule, with the excess energy of the photon converted into the kinetic energy of the ejected electron. At the most fundamental level, the binding energy is a well-defined thermodynamic quantity. Atomic binding energies are often used in thermodynamic cycles and are closely related to the concepts of electronegativity and acid-base behavior. Similarly, molecular ionization energies are related to "electron richness" and bonding. Trends in electron binding energies can be correlated with the electron distribution in the molecule, the strengths of bonds in the molecule, filled-filled orbital interactions, the effective nuclear charge or screening felt by the electrons, and other features of electronic structure.

The first UPS studies of transition-metal complexes appeared in 1969. These studies included  $d^{10}$  Ni(CO)<sub>4</sub> and  $d^8$  Fe(CO)<sub>5</sub><sup>10</sup> and  $d^6$  Mn(CO)<sub>5</sub>X (X = halogen, etc.).<sup>11</sup> The valence spectra clearly reflected the basic  $d$  electronic configurations and electronic symmetry at the metals. The spectra of the Mn(CO)<sub>5</sub>X complexes were also classic in demonstrating the difficulty of definitively interpreting any single spectrum of any single molecule.<sup>11</sup> These systems continued to receive attention through most of the next decade. They contributed to developing the assignment techniques based on the relative ionization intensity changes from He I (21.2 eV) and He II (40.8 eV) sources, ionization shifts with chemical substitutions in the molecules, and spin-orbit effects with heavy atom substitutions in the molecules.

Coincident with the development of these experimental techniques, theoretical electronic structure calculations on organometallic molecules were progressing with improvements in advanced computers and calculational methods. In molecular photoelectron spectroscopy the initial state of the molecule is excited to a final ion state with the ejection of an electron:



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The ionization or binding energy  $E_I$  is the difference in energy between the excited electronic state and the initial state of the molecule.

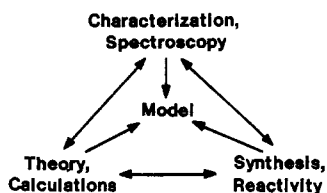
$$E_I = h\nu - E_K(e^-) = E(M^+) - E(M) \quad (3)$$

The formal relationship between this energy difference and the theoretical (one-electron) orbital energies is given by Koopmans' theorem,<sup>12</sup> which states that the ionization energy is the negative of the orbital energy ( $\epsilon_i$ )

$$E_I = -\epsilon_i \quad (4)$$

from a Hartree-Fock molecular orbital calculation, provided that the electron distribution of the final (molecular ion) state does not relax from that of the initial molecular state with one electron missing from orbital  $i$ .<sup>12</sup> The calculated difference in energy between this "frozen" ion state and the energy-optimized or relaxed final state is termed the electronic relaxation energy,  $E_R$ . Extreme care must be exercised in using the results of a given theoretical calculation to assign a given photoelectron spectrum of a transition-metal complex. The electron relaxation energy associated with a metal-based ionization can be several electronvolts and can vary widely for different ionizations of a single molecule.<sup>13</sup> Electron correlation effects can be as significant as relaxation effects and also difficult to treat adequately for many metal complexes. Calculations of ionization energies are often of only limited assistance in giving specific orbital assignments to closely spaced ionizations of transition-metal complexes.

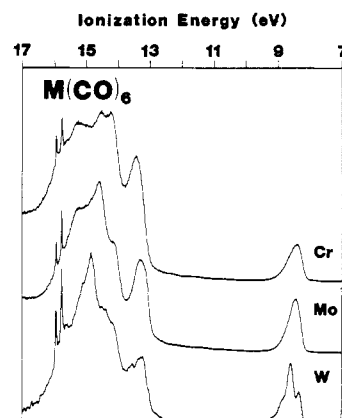
**Approach.** Our experimental efforts have focused on obtaining knowledge of the electronic structure of organometallic molecules from photoelectron spectroscopy. Although we use electronic structure calculations along with our chemical and spectroscopic approaches for the purpose of developing models of the



chemical behavior of transition-metal molecules and fragments, we do not use calculations as the basis for assignment of the photoelectron ionizations. A major theme of this Account is that definitive and chemically significant electron distribution and bonding information can be obtained from photoelectron spectroscopy without necessarily relying on calculations. Thus, photoelectron spectroscopy can independently contribute to the models of electronic structure and can be a true unbiased test of theory. This Account provides a "handbook" of the experimental techniques used to assign and interpret the valence photoelectron spectra of organometallic molecules.

### Direct Information from Ionization Band Characteristics

The characteristic features of an ionization band are its energy, width, shape, resolved fine structures, and relative intensity. Each feature is sensitive to the



**Figure 1.** Valence (He I) ionization spectra for  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ , and  $\text{W}(\text{CO})_6$ . The bands between 8 and 9 eV are from ionization of the  $d^6 t_{2g}$  set of orbitals.  $\text{W}(\text{CO})_6$  shows a distinct splitting of this band because of spin-orbit coupling.

electronic structure of the molecule. The ionization energies are most significant in terms of trends between related molecules. This will be the focus of the next section. The other ionization band features can directly reveal information about the electron localization on the metal and the ligands, the bonding or nonbonding nature of the orbitals, and the relationship of the excited positive ion state to the ground state of the molecule.

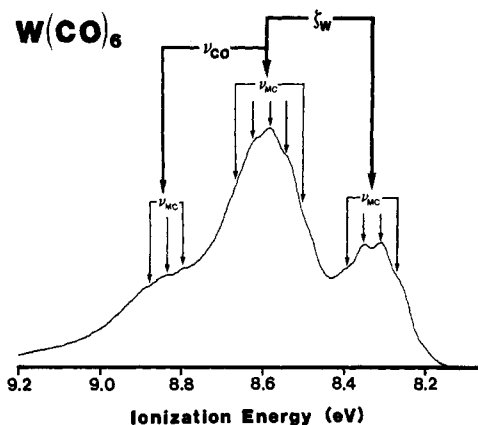
**Ionization Bandshapes and Fine Structure.** For small molecules an important feature of the ionizations is often the resolved vibrational progressions.<sup>1,7</sup> The spacing and intensities of the vibrational components indicate the changes in force constants and bond distances associated with removing the electron to create the particular excited positive molecular ion state. For transition-metal complexes, observation of resolved vibrational fine structure is often less likely because of low metal-ligand vibrational frequencies or because several different vibrational progressions are excited by a single ionization. In these cases the overlapping vibrational components will blend into a single featureless asymmetric Gaussian-shaped ionization band. The breadth of the asymmetric Gaussian indicates the extent of bond distance changes between the ground and ionized states in the molecule. As an example of the ionization bands commonly observed for transition-metal complexes, Figure 1 shows the valence spectra of the metal hexacarbonyls (metal = Cr, Mo, W). The ionizations at greater than 12 eV in Figure 1 derive primarily from the  $5\sigma$  and  $1\pi$  orbitals of the six carbonyls in these complexes. This region is often difficult to interpret in detail for organometallic complexes because of the large number of overlapping ionizations that occur from 12 to 17 eV. Also commonly observed here are C-C  $\sigma$ , C-H  $\sigma$ , and some C-C conjugated  $\pi$  bond ionizations. For these hexacarbonyl complexes one ionization band is observed between 13 and 14 eV that is approximately separated from the other ligand-based ionizations. This ionization correlates with the  $3t_{1u}$  set of CO  $5\sigma$  orbitals, and it displays the distinctive asymmetric Gaussian bandshape. It is broadened relative to the  $5\sigma$  ionization of free CO because of the bonding donation of this combination of the CO  $5\sigma$  orbitals into the empty metal p orbital set.<sup>14,15</sup>

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**Figure 2.** High-resolution close-up and assignment of the  $W(CO)_6$   $t_{2g}$  ionization. Spin-orbit coupling ( $\zeta_w$ ) splits this ionization state into the quadruply degenerate  $^2U'$  ion state at higher ionization energy and the doubly degenerate  $^2E''$  ion state at lower energy. A  $\nu_{CO}$  vibrational fine structure shoulder on the  $^2U'$  band is evident, and ripples due to  $\nu_{MC}$  are shown.

The predominantly metal-based valence d ionizations generally occur at lowest binding energy in a photoelectron spectrum and are separated from the predominantly ligand-based ionizations. Figure 1 shows the  $t_{2g}$  metal ionizations of the hexacarbonyls in the region of 8.5 eV. Figure 2 shows a high-resolution close-up of the  $W(CO)_6$   $t_{2g}$  region obtained with our instrumentation. Tungsten spin-orbit coupling<sup>16</sup> splits the sixfold degenerate  $^2T_{2g}$  ion state ( $t_{2g}^5$ ) into fourfold degenerate  $^2U'$  and twofold degenerate  $^2E''$  states with a separation of  $3/2\zeta$ , where  $\zeta$  is the spin-orbit coupling parameter. The observed splitting between the  $^2E''$  and  $^2U'$  bands is 0.26 eV and corresponds to a  $\zeta$  value of 0.17 eV. This is smaller than the atomic  $\zeta$  value for tungsten of 0.21 eV.<sup>17</sup> The reduction in  $\zeta$  is approximately proportional to the reduction in  $t_{2g}$  density at the metal center, which in this case indicates a 0.1 electron delocalization into each carbonyl  $\pi^*$  orbital.

The clearly resolved shoulder on the high-energy side of the  $^2U'$  band (Figure 2) is separated from the main feature by 0.26 eV (2090  $cm^{-1}$ ) and correlates with a short progression in the  $\nu_{CO}$  stretch vibrational mode at 1998  $cm^{-1}$ .<sup>18,19</sup> Because ionizing the metal  $t_{2g}$  set has removed an electron with some CO  $2\pi^*$  antibonding character, the C-O bond is stronger in the positive ion. Note that there is still finer detail in our spectrum shown in Figure 2. This structure corresponds to the metal-carbon stretching mode and has a vibrational frequency of 387  $cm^{-1}$ . This is less than the neutral gas-phase  $\nu_{MC}$  of 426  $cm^{-1}$ <sup>20</sup> because removal of a metal  $t_{2g}$  electron weakens the M-C bond. Analysis of the vibrational progression shows that the metal-carbon bond distance increases 0.10 Å with removal of a  $t_{2g}$  electron.<sup>18</sup> Thus, the photoelectron experiment provides a direct measure of back-bonding from the metal  $t_{2g}$  to the CO  $\pi^*$  orbitals by quantitating the effect of the metal  $t_{2g}$  electrons on the metal-carbon force constant and bond distance.

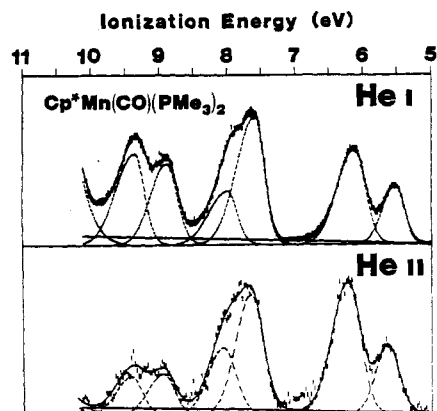
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**Figure 3.** Close-up He I/He II comparison for  $Cp^*Mn(CO)(PMe_3)_2$  where  $Cp^*$  = pentamethylcyclopentadienyl. The six ionization bands correlate (from low energy to high energy) with two metal d, Cp  $e''$   $\pi$ , and two P lone-pair orbitals. The metal ionizations have a substantial He II increase relative to the ring, and the phosphorus lone pairs have a substantial decrease in relative intensity.

**Table I.**  
Band Deconvolution Data for  $Cp^*Mn(CO)(PMe_3)_2$

ionization	vertical ionization energy, eV	half-width, <sup>a</sup> eV		rel intensity	
		$W_h$	$W_l$	He I	He II
M1	5.53	0.43	0.32	0.35	0.48
M2	6.13	0.58	0.38	0.74	1.12
Cp1	7.59	0.63	0.32	1.00	1.00
Cp2	7.99	0.63	0.32	0.42	0.56
P1	8.89	0.55	0.37	0.61	0.33
P2	9.36	0.64	0.34	0.72	0.31

<sup>a</sup>  $W_h$  and  $W_l$  represent the high-energy side and low-energy side half-widths. The full width at half-maximum is  $(W_h + W_l)/2$ .

These observations also can provide experimental band assignment information. There are, to a certain extent, symmetry and electronic constraints that affect the occurrence of vibrational fine structure.<sup>21</sup> Totally symmetric vibrational modes are normally the dominant vibrational progressions observed.<sup>22</sup> A locally symmetric arrangement of ligands interacting equivalently with a metal orbital is more likely to present vibrational fine structure in the valence ionization because fewer normal vibrational modes are activated in the process. Several examples of this observation are illustrated later in this Account.

**Ionization Band Intensities.** The single most widely used experimental technique for identifying predominant metal character in ionizations of organometallic complexes takes advantage of the different relative ionization band intensities obtained with the He I and He II excitation sources. Main-group (C, N, O, P, and S) s and p orbitals generally show relatively large He I intensities and relatively small He II intensities in comparison to transition-metal d orbitals.<sup>26-28</sup>

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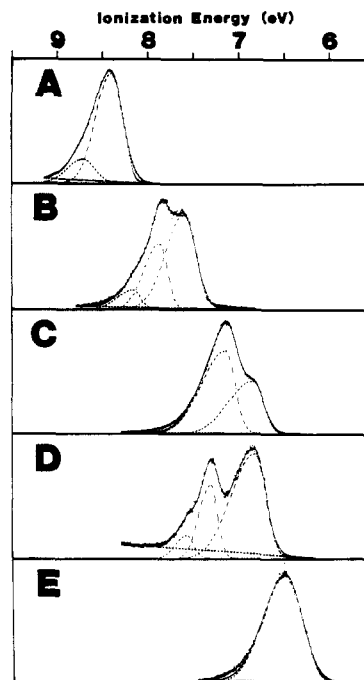
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This empirical relationship of relative He I and He II ionization band intensities provides an invaluable experimental indication of orbital metal or ligand character in the ionization. The physical basis for this empirical band assignment tool has been previously discussed in varying degrees of sophistication.<sup>2,3,29-31</sup> Figure 3 shows He I and He II spectra in the 5–11-eV valence ionization region for Cp\*Mn(CO)(PMe<sub>3</sub>)<sub>2</sub> (Cp\* = pentamethylcyclopentadienyl). The analytical representations for these spectra are listed in Table I. The pair of bands at lowest ionization energy in Figure 3 corresponds to ionization of the predominantly metal d<sup>6</sup> orbitals. These bands have the largest He II relative intensity enhancement. The middle pair of bands are the Cp\* e<sub>1</sub>' set, which show the "trademark" band profile for d<sup>6</sup> piano stool complexes.<sup>32</sup> The highest energy set of bands (between 9 and 10 eV) are predominantly from ionization of the two phosphorus lone-pair donor orbitals. These ionization bands show a substantial relative intensity decrease in He II because of the radial nodal characteristics of the 3p valence orbitals.<sup>29</sup>

### Ionization Energy Trends

The shift in an ionization energy between electronically or chemically related molecules is an especially revealing feature of the electronic structure. In some cases the correlation of ionizations between related molecules simply assists in the assignment of spectra, such as in the comparison of the ionizations of simple molecules with those of increasingly complex molecules as illustrated by the progression of examples in this Account. In other cases, the electronic perturbations caused by chemical group substitutions produce identifiable ionization energy shifts that reveal the localized or delocalized character of the electronic states and the fluidity of charge in the system. We sometimes refer to this as the ESP (electronic structure perturbation) approach to understanding electronic structure through photoelectron spectroscopy. A third application of ionization energy trends is in the correlation of core and valence ionization energy shifts, which allows separation of individual bonding effects from general charge potential and relaxation energy effects.<sup>8,9,32</sup> A more complete experimental and theoretical foundation for these approaches has been developed in recent years which has greatly increased the value of experimental data for providing an understanding of the electronic factors controlling the behavior of organotransition-metal systems. A few of these principles will be introduced in this section.

**Additivity of Ligand Electronic Effects.** Photoelectron spectroscopy is particularly well-suited for characterizing the electronic effects of ligands on metal complexes. It is important to know the extent that these effects are transferable or additive to new metal complexes. The ligand additivity model as put forth by Bursten<sup>33</sup> proposes that valence metal orbital ionizations



**Figure 4.** Metal region valence ionization (He I) spectra from (A) Mo(CO)<sub>6</sub>, (B) Mo(CO)<sub>5</sub>(PMe<sub>3</sub>), (C) *cis*-Mo(CO)<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>, (D) *trans*-Mo(CO)<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>, and (E) *fac*-Mo(CO)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>. The ionization energies and relative intensities fit the empirical ligand additivity model. The shift to lower ionization energy for increasing phosphine substitution is due to the change in charge potential with ligand replacement. The splittings between the major ionization features of (B), (C), and (D) are due to changes in overlap interactions between the ligands and metal. The high-energy shoulders on the ionization features of (A), (B), and (D) are due to vibrational fine structure (CO stretch).

are systematically and reproducibly shifted in an amount directly proportional to the number of ligand replacements on the metal center. There is no a priori reason to expect additive ligand electronic effects, but recent observations<sup>9,34,35</sup> suggest the model is valid for a wide range of ligands and metal systems. With knowledge of consistent ionization shifts, assignment of complex spectra is simplified and the ionization potentials of unknown species may be empirically predicted.

An ideal system for studying the additivity of ligand electronic effects is the phosphine-substituted hexacarbonylmolybdenum complexes, Mo(CO)<sub>6-n</sub>(PMe<sub>3</sub>)<sub>n</sub>, in which molecules with zero to three phosphines, including *cis*, *trans*, and *fac* isomers, may easily be compared.<sup>9,34</sup> Ionization potentials of the t<sub>2g</sub>-based orbitals of these molecules are described by the following equation:<sup>33</sup>

$$E_n^i = E_0^i + m^i \Delta E_S^i + n \Delta E_Q^i \quad (5)$$

$E_n^i$  is the ionization potential of metal valence orbital  $i$ . The first term on the right,  $E_0^i$ , is the t<sub>2g</sub> ionization potential of the unsubstituted complex Mo(CO)<sub>6</sub> (i.e.,  $n = 0$ ). The second term represents the shift in  $E_n^i$  due to the change in overlap interaction with the substituted ligand, such as the change in metal to ligand back-bonding between CO and PMe<sub>3</sub>. The factor  $m^i$  is the number of these ligand overlap interactions with metal

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orbital  $i$  that have changed with the substitution. The third term represents the shift in  $E_n^i$  due to the change in charge potential, where  $n$  is the total number of  $\text{PMe}_3$  ligands that have replaced CO ligands. The parameters  $E_0^i$ ,  $\Delta E_S^i$ , and  $\Delta E_Q^i$  are empirically determined from ionization data for the series of  $\text{Mo}(\text{CO})_{6-n}(\text{PMe}_3)_n$  complexes.

Figure 4 displays the metal valence region (He I radiation) for these complexes. First note the consistent trend to lower ionization energy with increasing phosphine substitution at the metal. This is the result of a reproducible change in charge potential when a CO is replaced by a  $\text{PMe}_3$ . The  $\Delta E_Q^i$  term of the model represents this Coulombic effect and is  $-0.50 \pm 0.04$  eV per phosphine substitution in this system. The high ionization energy shoulders in the spectra of  $\text{Mo}(\text{CO})_6$  (A),  $\text{Mo}(\text{CO})_5(\text{PMe}_3)$  (B), and *trans*- $\text{Mo}(\text{CO})_4(\text{PMe}_3)_2$  (D) are due to vibrational fine structure from activation of the symmetric CO stretch. Thus, these ionizations are from metal orbitals from the  $t_{2g}$  set that back-bond symmetrically into four carbonyls, and the other lower ionization energy bands are from metal orbitals interacting with a combination of carbonyls and phosphines. This ordering is consistent with the expectation that CO is a better  $\pi$  acceptor than  $\text{PMe}_3$ .<sup>36,37</sup>

The difference between CO and  $\text{PMe}_3$  in the ability to stabilize the metal levels by back-bonding is represented by the  $\Delta E_S^i$  term of the ligand additivity model. In the spectra of Figure 4 this term is observed as the splittings between the  $t_{2g}$ -based ionizations of  $\text{Mo}(\text{CO})_5(\text{PMe}_3)$  (B), *cis*- $\text{Mo}(\text{CO})_4(\text{PMe}_3)_2$  (C), and *trans*- $\text{Mo}(\text{CO})_4(\text{PMe}_3)_2$  (D). For (B) and (C) this splitting represents the contribution of one  $\Delta E_S^i$  factor. For *trans*- $\text{Mo}(\text{CO})_4(\text{PMe}_3)_2$  (D) the splitting corresponds to two  $\Delta E_S^i$  contributions because there is a net change of two in the number of metal/CO vs metal/ $\text{PMe}_3$  interactions with the metal  $a_{1g}$  and  $e_g$  ( $D_{4h}$ ) orbital sets. The empirical value of  $\Delta E_S^i$  calculated from these spectra ( $-0.246$  eV) allows predictions of ionization energies to  $\pm 0.04$  eV.<sup>33,34</sup>

**Correlation of Core and Valence Ionization Shifts.** The influences of bonding/overlap and charge potential contributions to ionization energies can also be differentiated through use of the core-valence ionization correlation approach of Jolly.<sup>8,38-41</sup> Core ionization potentials are dependent on the charge distribution and relaxation energies. Valence ionization potentials also respond to these factors but in addition are sensitive to bonding (orbital overlap or hyperconjugative) effects. The principle of core-valence ionization correlation states that, when comparing ionization spectra for two related molecules, the binding energy shift of a nonbonding valence orbital localized on an atom present in both molecules should be eight-tenths of the core binding energy shift for that atom between the two molecules. A valence/core shift ratio in excess of the benchmark 0.8 value indicates the contribution of bonding/overlap interactions to the valence shift. For example, the predominantly phosphorus lone-pair valence ionization of free  $\text{PMe}_3$  is

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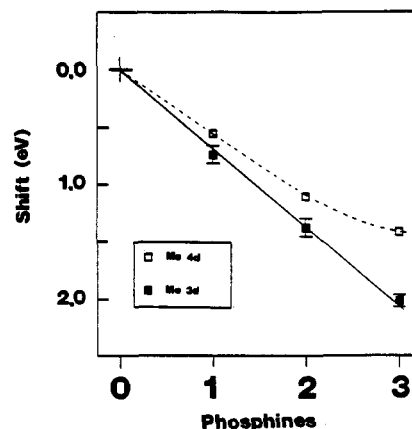


Figure 5. Shift comparison diagram for Coulombic metal ionization shifts for the  $\text{Mo}(\text{CO})_{6-n}(\text{PMe}_3)_n$  complexes, Mo  $3d_{5/2}$  (core), and Mo 4d (valence). The ratio of the valence to core shifts is  $0.74 \pm 0.06$ .

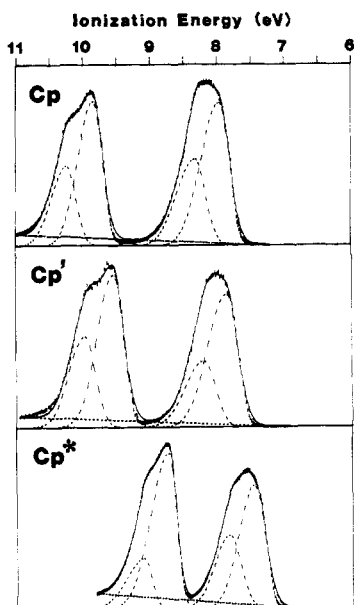
stabilized 1.32 eV when bound to the metal in  $\text{Mo}(\text{CO})_5(\text{PMe}_3)$ . The core phosphorus  $2p_{3/2}$  ionization shifts 0.76 eV from the free phosphine to the coordinated phosphine, indicating that only 0.6 eV (0.8 of 0.76 eV) of the valence shift is due to change in charge potential and relaxation effects. Thus, approximately 0.7 eV of the phosphorus lone-pair ionization stabilization can be attributed to the bonding interaction with the metal center.<sup>11</sup>

Jolly described the "partnership" of core and valence photoelectron spectroscopy in a previous Account<sup>8</sup> and presented several applications of the principle to understanding the valence spectra of main-group molecules. Transition-metal complexes seldom<sup>38</sup> have the strictly nonbonding, lone-pair orbitals necessary for absolute application of the principle, but the correlation can be applied in a relative sense for many metal complexes. The  $\text{Mo}(\text{CO})_{6-n}(\text{PMe}_3)_n$  series is an appropriate system to demonstrate this principle. An experimental measure of the valence/core ionization shift ratio is obtained from these data because the bonding/overlap contribution to the valence shifts ( $\Delta E_S^i$ ) can be removed by using the ligand additivity model. Figure 5 shows the observed core and valence ( $\Delta E_Q^i$ ) ionization shifts from the parent hexacarbonyl as a function of phosphine substitution ( $n$ ). The ratio of the valence/core ionization shifts is  $0.74 \pm 0.06$ , in agreement with Jolly's value of  $0.8 \pm 0.1$ .

### Chemical Modifications for Electronic Structure Perturbation

The example of carbonyl and phosphine complexes discussed above illustrates how the photoelectron experiment can provide detailed and quantitative information on each individual interaction of a ligand with a metal center. The interactions are observed directly in terms of stabilization or destabilization of the "orbital" ionization energies. The interaction of the ligand  $\sigma$  orbital, each  $\pi$  orbital, etc., is a separate effect. The effect of the overall charge potential is also observed. We have applied these principles to the study of a wide range of metal-ligand interactions that are fundamental to many important chemical processes. Examples include alkenes,<sup>42</sup> alkynes,<sup>43</sup> methylenes,<sup>44</sup>

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**Figure 6.** He I valence close-up spectra for ring methylated cyclopentadienylmanganese tricarbonyl complexes. The ring  $\pi$  ionizations at higher ionization energy show a larger shift than the metal ionizations because of an overlap interaction between the ring  $e_1''$  and methyl orbitals.

vinylidenes,<sup>43</sup> dinitrogen,<sup>45</sup> thiocarbonyl,<sup>46</sup> sulfur dioxide,<sup>47,48</sup> halides,<sup>14,49</sup> alkyls,<sup>14,49</sup> cyanide,<sup>49</sup> nitrosyl,<sup>50,51</sup> and thionitrosyl.<sup>50,51</sup> It is not possible to summarize the large amount of information on these systems in this Account. However, there are certain common classes of chemical modifications that occur in these systems that provide a basic framework for understanding the information provided by photoelectron spectroscopy. A few of these types of chemical modification for electronic structure perturbation and the information that is provided will be illustrated here.

**Ring Methylation.** Large numbers of organometallic molecules contain organic  $\pi$  ring ligands. The most familiar of these ligands is the cyclopentadienyl ( $Cp^-$ ) ring. Many of the systems that have been studied use the  $d^6$   $CpM(CO)_2$  fragment as a common template for interaction with a variety of ligands.<sup>52</sup> Spectral comparisons between complexes with different degrees of ring methylation provide valuable assignment and interpretation information. The methylation is a localized perturbation, and the  $Cp$   $e_1''$  ionizations should show a larger effect than ionizations based on the metal or other ligands. Of more chemical interest, ionization energy shifts due to ring methylation are an experimental indication of electron delocalization and fluidity in the molecule. The effects of ring methylation

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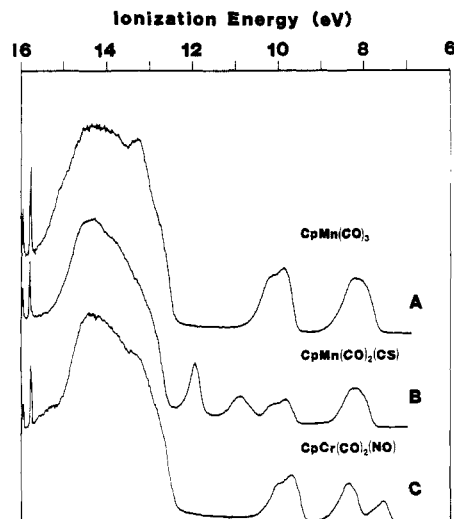
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**Figure 7.** He I valence ionization spectra for (A)  $CpMn(CO)_3$ , (B)  $CpMn(CO)_2(CS)$ , and (C)  $CpCr(CO)_2(NO)$  where  $Cp$  = cyclopentadienyl. The ionization spectrum of (B) shows two additional bands between 10.5 and 12.5 eV from CS  $7\sigma$  and  $2\pi$  orbitals because of the lower electronegativity of sulfur compared to oxygen. (C) shows a splitting of the metal ionizations because NO is a better  $\pi$  acceptor than CO.

on the reactivity and stability of organotransition-metal complexes have been observed.<sup>53-56</sup> Figure 6 shows close-up He I spectra for the cyclopentadienylmanganese tricarbonyls, where  $Cp = C_5H_5$ ,  $Cp' = C_5H_4(CH_3)$ , and  $Cp^* = C_5(CH_3)_5$ . First note that the distinctive bandshape for the higher ionization energy band envelopes identifies these as the cyclopentadienyl  $e_1''$  ionizations as mentioned previously for  $Cp^*Mn(CO)(PMe_3)_2$ . The  $Cp$   $e_1''$  bands show a larger shift between the  $Cp$  and  $Cp^*$  analogues than do the metal ionizations. Application of the core-valence ionization correlation principle separates the Coulombic from the bonding contributions to these shifts.<sup>32</sup> It is found that the  $Cp$  carbon  $1s$  core shift is only about 25% as large as the  $Cp$   $e_1''$  valence shift, showing that the inductive (Coulombic) effect is not the dominant factor. It follows that the bulk of the valence shift is caused by the orbital overlap interaction between the filled  $Cp$   $e_1''$  orbitals and the filled methyl orbitals. To our knowledge this is the only experimental method of separating these effects.

Ring methylation is additive for both core and valence ionizations in the systems studied. The ring-methylated ferrocenes<sup>57,58</sup> show consistent ionization shifts per ring methyl, allowing empirical predictions of ionization potentials for unknown members of the series. More interesting perhaps is the quantitative  $\pi$  delocalization information obtained from these studies. In the  $CpMn(CO)_3$  complexes, the shift of ring ionizations per methyl substitution is about  $-0.24$  eV,<sup>32</sup> and for the  $Cp_2Fe$  system it is about  $-0.14$  eV.<sup>57</sup> A reduction in  $e_1''$  ionization shift per methyl group on a ring is caused by reduced overlap of the filled methyl orbitals

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with the more delocalized ring  $\pi$  orbitals of the complex. The  $\pi$  orbitals in one Cp ring of ferrocene are able to delocalize more effectively because of the energy match with the  $\pi$  orbitals of the other ring.

**Electronegativity and Electron Richness Perturbations.** Comparison of spectra for molecules differing by a ligand or metal substitution can sometimes reveal significant band assignment information if the perturbation includes a large change in atomic electronegativity. This is most common with substitution of atoms down a group of the periodic table, such as the halogen series.<sup>49</sup> As another example, the valence spectra of  $\text{CpMn}(\text{CO})_3$  and  $\text{CpMn}(\text{CO})_2(\text{CS})$  are presented in Figure 7. Sulfur is a second-row element with a lower electronegativity than oxygen, and ionizations correlating with orbitals rich in sulfur character should have lower ionization energies than the analogous oxygen-containing orbitals. The most obvious difference between these two spectra is the two new ionizations of the thiocarbonyl complex (B) at 10.8 and 11.9 eV. These correlate with the CS  $7\sigma$  and  $2\pi$  orbitals.<sup>46</sup> The analogous CO orbitals ( $5\sigma$  and  $1\pi$ ) are much deeper, between 13 and 15 eV. The metal d ionizations show only a slight (0.1–0.2 eV) shift to lower ionization energy in the thiocarbonyl complex, because the improved  $\sigma$  and  $\pi$  donor abilities of CS compared to CO are compensated by the improved  $\pi$  acceptor ability.

Comparison of first-, second-, and third-row transition-metal complexes can provide a wealth of information. The value of spin-orbit splitting effects in the ionizations of third-row complexes has already been mentioned. The shifts in predominantly metal valence ionizations are also useful. In some cases these shifts are more correctly interpreted as changes in electron relaxation energies rather than changes in inherent orbital stabilities. Theory and experiments have shown that relaxation energy differences are particularly significant for  $d^8$  and  $d^{10}$  complexes<sup>13,59–61</sup> and that the relaxation energy associated with first-row metal ionizations is about twice that of second-row metal ionizations.<sup>59</sup> The theoretical interpretation of these shifts is important but of little practical consequence in using these shifts to experimentally reveal the electron distribution and bonding in series of complexes. This is illustrated with the spectra of  $d^8$   $[\text{Cp}]\text{M}(\text{CO})_2$  complexes, where  $[\text{Cp}] = \text{Cp}$  or  $\text{Cp}^*$  and  $\text{M} = \text{Co}$  or  $\text{Rh}$ , shown in Figure 8.<sup>26,62,63</sup> These  $d^8$  metal complexes present a particularly interesting case because of the complexity of the valence ionizations. Twelve of the eighteen valence electrons are ionized below 12 eV. These systems illustrate the utility of He I/He II relative intensity comparisons, ring methylations, the heavy atom effect (relative ionization cross section increases with substitution down the group<sup>64</sup>), and the relaxation energy differences in providing definitive assignment and interpretation of the ionizations. Table

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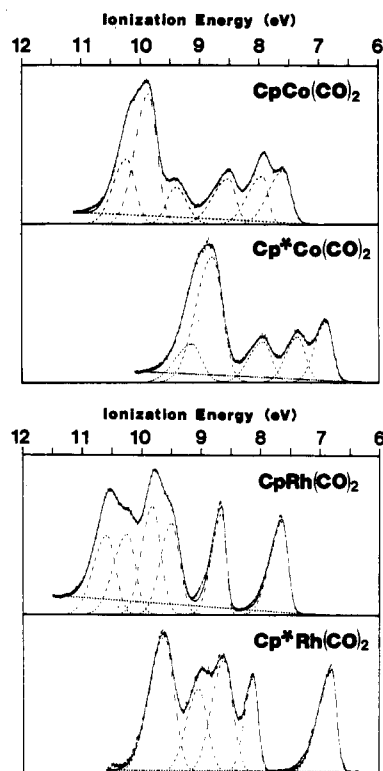


Figure 8. He I close-up spectra for  $\text{CpCo}(\text{CO})_2$ ,  $\text{Cp}^*\text{Co}(\text{CO})_2$ ,  $\text{CpRh}(\text{CO})_2$ , and  $\text{Cp}^*\text{Rh}(\text{CO})_2$  where Cp = cyclopentadienyl and  $\text{Cp}^*$  = pentamethylcyclopentadienyl.

Table II.  
Shifts in Valence Ionization Energies (eV) between  
 $[\text{Cp}]\text{Co}(\text{CO})_2$  and  $[\text{Cp}]\text{Rh}(\text{CO})_2$

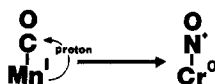
ionization <sup>a</sup>	$[\text{Cp}] = \text{Cp}$	$[\text{Cp}] = \text{Cp}^*$
M1	+0.05	-0.08
M2	+0.70	+0.75
M3	+0.99	+1.10
M4	+0.84	+0.84
Cp1	-0.05	-0.17
Cp2	+0.36	+0.48

<sup>a</sup> Ionization bands are listed in the order observed (from low to high ionization energy) for the  $[\text{Cp}]\text{Co}(\text{CO})_2$  complexes. The ionization ordering for the Rh complexes is somewhat different because of relaxation energy.

II lists the ionization energy shifts between analogous cobalt and rhodium ionization bands for the  $\text{CpM}(\text{CO})_2$  and  $\text{Cp}^*\text{M}(\text{CO})_2$  complexes. One particularly useful feature of these shifts is that larger shift magnitudes indicate more metal character for the ionization and less electron density delocalization.<sup>59</sup> A key result in this case is the small shift of the lowest ionization band (M1), which indicates extensive delocalization of the lowest positive ion state to the ligands. This ionization would formally be assigned to the metal in these  $d^8$  complexes, but the extensive delocalization of this ionization to the ligands leaves only three ionizations (M2, M3, M4) that can clearly be assigned to the metal. This is just one example in which the photoelectron experiment can provide key information on actual electron distributions in contrast to simple formal oxidation state and d-electron count descriptions.

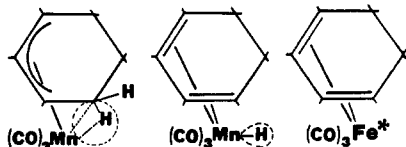
**Proton/Hydride Shift.** In addition to information from comparisons down a group of the periodic table, it is also possible to make comparisons across the rows of the periodic table. In some cases the atomic substitutions can be envisioned as the shift of a proton from

one atomic center to another, and the related molecules remain isoelectronic. For example, imagine removing a proton from the metal of  $\text{CpMn}(\text{CO})_3$  and "shifting" it to a carbon of one of the carbonyl ligands. Thus,



instead of a  $d^6 \text{Mn}^I$ , the metal center is  $d^6 \text{Cr}^0$ , and instead of a CO, the ligand is  $\text{NO}^+$ . The photoelectron information then shows how the electronic structure is able to adjust to the shift in charge potential. Figure 7 displays the valence spectrum of  $\text{CpCr}(\text{CO})_2(\text{NO})$ .<sup>50,51</sup> The metal ionizations of the NO complex are the two bands between 7 and 9 eV, and the Cp  $e_1'' \pi$  ionization is at 9.7 eV. Two competing effects are influencing the metal ionizations. First, the reduced metal positive nuclear charge for the NO complex destabilizes the predominantly metal ionizations. The shift of the first ionization band reflects this destabilization. CO vibrational fine structure on this band shows that this orbital is symmetrically back-bonding to the carbonyls.<sup>51</sup> The other two metal orbitals are the correct symmetry to back-bond to the nitrosyl. Second, because of the greater  $\pi$ -accepting ability of the nitrosyl, these d  $\pi$  electrons partially "follow" the proton and are stabilized by the back-bonding interaction.

In some cases it is best to view the shift in terms of an electron pair that completely follows the proton. This then becomes a "hydride" shift. An example of this would be the comparison of  $\text{HMn}(\text{CO})_5$  to  $\text{Fe}(\text{CO})_5$ , where the  $d^6 \text{Mn}^I$  becomes a  $d^8 \text{Fe}^0$  center by the shift of the hydride to the metal center. We have used this approach to help reveal the electronic factors that are operating in carbon-hydrogen bond activation processes. The initial molecule used in these studies was cyclohexenylmanganese tricarbonyl, which displays an agostic interaction of a C-H bond with the metal center.<sup>65</sup> Complete breaking of the carbon-hydrogen bond produces the hydrido(cyclohexadiene)manganese tricarbonyl complex, which is only inferred as an NMR intermediate and is not available for photoelectron study.<sup>66</sup> One important application of the hydride shift approach is to probe the electronic structure of molecules that are not accessible for photoelectron spectroscopy. Cyclohexenylmanganese tricarbonyl is related to (cyclohexadiene)iron tricarbonyl by the hydride shift, as shown in the following structures:<sup>67</sup>

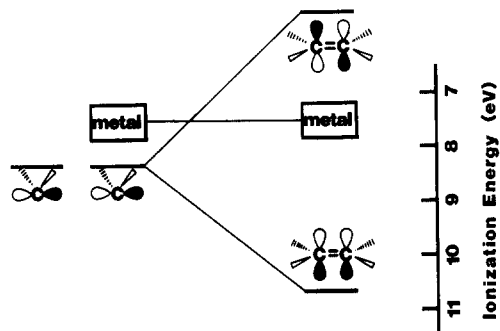


The latter molecule is stable and can be studied with photoelectron spectroscopy. In fact, the electronic structure of these three molecules differ for the most part by the hydride-shifted pair of electrons. The photoelectron spectra show that the stability gained from the agostic interaction in the cyclohexenyl-

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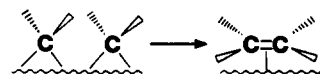
**Figure 9.** Ionization correlation for methylene coupling to form an ethylene. Metal-bound methylene ionizations are modeled by the ionizations of  $[\text{CpMn}(\text{CO})_2]_2\text{-}\mu\text{-CH}_2$  and metal-bound ethylene ionizations are modeled by the ionizations of  $\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ . The greater ionization energy of the ethylene  $\pi$  than the methylene  $b_1$  shows the driving force for the coupling. The level crossing of the methylene metal orbitals shows that the coupling will be forbidden for particular symmetries and electron counts.

manganese tricarbonyl complex follows from the stabilization of this electron pair through interaction with empty metal d levels.<sup>67</sup> The Mn-H structure is not favored because of the destabilization of this electron pair in a metal-hydride bond in comparison to a carbon-hydrogen bond.

### Ionizations and Chemistry

The importance of the chemical approach to understanding and interpreting valence ionizations cannot be overemphasized. Development of consistent band assignments requires careful design of related experiments in order to fully utilize the information content of the ionizations. A single spectrum yields unambiguous information only in special cases of resolved fine structure or other identifiable ionization features. Carefully controlled comparisons with variable ionization sources and appropriately related molecules lead to definitive interpretation of the ionizations and description of the electronic interactions in the systems. With this approach, it is rarely necessary to invoke calculations to discuss the information provided by a photoelectron spectrum.

The kinds of detailed electronic structure information we have been able to experimentally obtain from valence ionizations also contributes directly to an understanding of important chemical processes. In a way directly analogous to theoretical Walsh diagrams, the electronic structure factors that contribute to the favorability of a structure or a reaction path can be explored by correlation of the ionizations of molecules that model important intermediates. Ionization energies are actually well-defined thermodynamic quantities and can contribute to construction of Born-Haber type cycles for chemical reactions. As the "library" of well-understood molecular ionizations and electronic structure principles is building, we are finding additional correlations that provide models for chemical behavior. For example, the coupling of methylenes on a surface to form ethylenes is an important catalytic C-C chain growth step. We have examined in separate studies



the electronic structure of bridging methylenes  $[\text{CpMn}(\text{CO})_2]_2\text{-}\mu\text{-CH}_2$ <sup>44</sup> and  $\pi$ -bound ethylene  $\text{CpMn}$ -



(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>).<sup>42</sup> Because these organic species are bound to the same metal fragment, CpMn(CO)<sub>2</sub>, comparison of the spectra reveals the important bonding interactions and a pathway for methylene coupling. Figure 9 shows an ionization correlation for the bridging methylene and  $\pi$ -bound olefin frontier orbitals. An important observation is that the methylene b<sub>1</sub> ionizations are found below the metal ionizations. The methylene b<sub>1</sub> orbitals correlate with the bonding and antibonding ethylene orbitals. The coupling is energetically reasonable if the methylene electron pair is transferred to the metal rather than the ethylene  $\pi^*$  in the process. However, when the metal levels are occupied, the coupling involves a level crossing that is symmetry-forbidden. Thus, d-electron-rich metals will generally not favor methylene coupling. The same conclusion was reached in a theoretical study by Hoffmann.<sup>68</sup> Similar correlations have assisted understanding the oligomerization of acetylenes to vinylidenes,<sup>43</sup> the activation of carbon-hydrogen bonds in organometallic molecules,<sup>67</sup> and the formation of metallacyclopropanes,<sup>69</sup> metallacycloprenes,<sup>43</sup> and dimetallacyclobutadienes.<sup>70</sup>

Current developments in the area of photoelectron spectroscopy are providing new approaches to the understanding of the electronic structure of organo-transition-metal complexes. Molecular Auger electron

spectroscopy (AES) has been discussed by Rye in a previous Account.<sup>71</sup> AES can be a local probe of valence electronic structure in the positive ion state. These experiments also reveal information about the electronic structure of chemically important excited states.<sup>72</sup> Synchrotron radiation provides a continuum of ionization sources rather than the discrete set (He I, He II, etc.) that are commonly used, leading to additional cross-section information as a function of source energy, angular distribution, and resonance effects.<sup>73</sup> The bridge between gas-phase and surface photoelectron spectroscopy is being built with surface experiments on transition-metal species.<sup>74</sup> The field of photoelectron spectroscopy promises to have an increasing impact on developing models of metal-assisted chemistry.

*It has been extremely enjoyable and rewarding to be able to interact with the many co-workers and collaborators who have enthusiastically contributed to the development of this research. Their names are included in the references. This work has been supported by the U.S. Department of Energy (Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research), The National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, Research Corporation, and the Department of Chemistry, University of Arizona.*

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