hypothesis is that one of the rhenium atoms in the intermediate would become quite exposed, making it more susceptible to subsequent attack by nucleophilic solvents. If such a bridged conformer is indeed the source of the photochemical reactivity of $Re_2Cl_8^{2-}$, then the low quantum yield (amounting in CH_3CN to about 10% of the observed energy loss at 337 nm) implies that expulsion of solvent and return to the symmetrical configuration are competitive with Re_2 dissociation.

Acknowledgment. This research was supported by the National Science Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (D.S.K.).

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(6) We were unable to populate the $\sigma^2\pi^4\delta^1(\delta^*)^1$ state directly for comparison, as the position[4] of the $\delta \rightarrow \delta^*$ band of $Re_2Br_8^{2-}$ falls outside of our available range of excitation energies.

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The Helium(I) Photoelectron Spectra and Electronic Structure of (η^5-Cyclopentadienyl) d^6 Metal Carbonyls

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Abstract: The He(I) photoelectron spectra of $CpMn(CO)_3$, $CpRe(CO)_3$, and $CpFe(CO)_2X$, where Cp = η^5-C_5H_5 and X = Cl, Br, I, and CH_3, are presented. The low energy ionization bands (binding energies from 7 to 13 eV) are found to be sensitive to metal and ligand substitution. The ionizations which are associated primarily with the cyclopentadienyl ring π e_1'' levels display a characteristic band envelope. Interestingly, the degeneracy of the ionizations associated predominantly with the metal d levels in octahedral $M(CO)_6$ complexes and C_{4v} $Mn(CO)_5X$ complexes is not substantially removed in these lower symmetry $CpM(CO)_3$ and $CpFe(CO)_2X$ analogues. In the case of $CpRe(CO)_3$, a distinct spin-orbit splitting of the predominantly metal ionizations is observed. Comparison of the spectra of the $CpFe(CO)_2X$ complexes with the spectra of the corresponding $Mn(CO)_5X$ complexes provides additional information regarding the assignment of the valence ionization bands of the molecules in both of these series. An ab initio calculation on the cyclopentadienide ion and approximate calculations on the transition metal complexes are used to aid in the interpretation of these ionizations. In addition, the details of a method for interpreting the ionizations of a molecule containing an atom with appreciable spin-orbit interaction are presented, and applied to the spectrum of $CpRe(CO)_3$. The combined knowledge provided by this work and earlier investigations leads to a consistent description of the electronic structure and bonding of d^6 metal η^5-cyclopentadienyl carbonyls and indicates that serious errors may result if ionization potentials are interpreted solely on the basis of Koopmans' theorem. The lowered carbonyl force constants in these π-bonded ring complexes (when compared to the corresponding $M(CO)_6$ and $Mn(CO)_5X$ complexes) are not found to be a result of electron donation from the ring, as previously believed. Instead, the carbonyl ligands and the ring interact with metal orbitals of primarily different symmetry, and the lower carbonyl force constants are a direct result of a decrease in competition for the back-bonding electrons from the metal orbitals of appropriate symmetry.

Major advances, both experimental and theoretical, are being made toward the understanding of the electronic structure and properties of transition metal complexes. Developments in the area of He(I) photoelectron spectroscopy (PES) have had a particularly strong impact on the interpretation of molecular electronic structure. With high-resolution electron energy analyzers, it is now possible to determine the successive ionization potentials for removal of electrons from the valence shells of a gaseous molecule. Initial applications of the technique to transition metal complexes have concerned series of transition metal carbonyls[1-9] and bis(η^5-cyclopentadienyl) metal complexes.[1,10-14] Complementing these developments in photoelectron spectroscopy have been equally important advances in the realm of theoretical quantum mechanics. Quantum mechanical calculations on the ground states of molecules coupled with application of Koopmans' theorem[15] have been valuable for qualitative assignment and interpretation of photoelectron spectra. This is exemplified by the role of approximate and ab initio calculations in the assignment of the $Mn(CO)_5X$ spectra.[16] With the development of increasingly efficient computers, it is becoming possible to perform ab initio LCAO-MO-SCF calculations on many transition metal complexes. Hillier and co-workers[5,13,17-20] have performed ab initio calculations on many of the important transition metal carbonyl complexes, and Veillard and his group[21,22] have investigated certain of the π-bonded organometallics by similar procedures. These calculations have contributed much to an understanding of the ionization process, and in some instances[5,13,22] have seriously challenged the traditional concepts concerning the use of Koopmans' theorem and band intensities for assignment of photoelectron spectra.

The present work represents a combination of experimental and calculational techniques for the purpose of interpreting photoelectron ionizations and the electronic structure of transition metal complexes. The aim is to investigate trends in valence shell ionization potentials, band intensities, and band shapes, and to study the relationship of this information to other physical and chemical observables and theoretical models. In this paper we report the results on a selected series of (η^5-cyclopentadienyl) metal carbonyl complexes. There is a rich variety of stable, volatile organometallic molecules in this class, with many interesting ligand systems to be studied. Many of these molecules have intriguing physical and chemical characteristics[23] and have been the subjects of numerous other investigations. The information obtained from study of the series of molecules discussed in this paper will provide a foundation for the study of other related π-bonded organometallics.

The key to understanding the electronic structure of these complexes lies in the analysis of the electronic interactions in $CpMn(CO)_3$ (Cp = η^5-cyclopentadienyl). The photoelectron spectrum of $CpMn(CO)_3$ has been reported earlier in relation to other studies,[24] but no detailed analysis of the spectrum has been presented. $CpMn(CO)_3$ is the central member of the series $Cr(CO)_6$, $CpMn(CO)_3$, and $(Cp)_2Fe$, in which six electrons are assigned as being principally associated with the metal d orbitals. Both $Cr(CO)_6$ and $(Cp)_2Fe$ have been the subjects of previous photoelectron[4,10-12] and ab initio molecular orbital[17,22] studies. The value of the present study is enhanced by the opportunity to both use and contribute to the results of the earlier photoelectron and computational studies on transition metal carbonyls and bis(η^5-cyclopentadienyls). Assignment of the photoelectron spectrum of $CpMn(CO)_3$ is also aided by the spectrum of $CpRe(CO)_3$, in which the ionizations associated with the metal atom display a spin-orbit interaction. Further insight into the bonding in (η^5-cyclopentadienyl) metal carbonyl complexes may be offered by perturbations on the metal-carbonyl portion of the molecule. The series of molecules η^5-$CpFe(CO)_2X$, where X = Cl, Br, I, and CH_3, is interesting in this respect. Again, analysis of the structure of these molecules will necessarily provide a comment on the related molecules, $Mn(CO)_5X$.[6] For example, the spectrum of $CpFe(CO)_2CH_3$, when compared with the spectrum of $Mn(CO)_5CH_3$,[7] is useful for making a definite assignment for ionization from the metal-CH_3 bond, a matter which has received considerable attention.[20,25] This combined photoelectron and theoretical investigation is found to provide some rather unique, reliable, and in some instances surprising information regarding the electronic structure and bonding of an important class of organometallic complexes.

Experimental and Computational Details

Photoelectron Spectra. Spectra were measured using a Varian IEE-15 electron spectrometer in the uv configuration. Simultaneous observation of a number of reference gas ionization peaks showed the energy scale to be linear within less than 0.01 eV over a range of binding energies from 9 to 17 eV. All spectra were determined with an electron analyzer energy of 2 eV, using argon (15.76 eV) as a single internal standard. Under these conditions the half-width of the major argon peak is typically 24 meV at approximately 40000 counts/sec. The $CpFe(CO)_2X$ samples were purified by vacuum sublimation, and identity was established by infrared and mass spectral analysis.[26] The samples were admitted into the spectrometer via the variable temperature inlet system. The spectrum of $CpMn(CO)_3$ was obtained at room temperature. The spectra of $CpRe(CO)_3$, $CpFe(CO)_2Cl$, $CpFe(CO)_2Br$, $CpFe(CO)_2I$, and $CpFe(CO)_2CH_3$ were obtained at 50, 80, 70, 60, and −15°C, respectively. The displayed spectra represent a time-averaged sum of individual sweeps through the binding energy range. The development of each spectrum was carefully observed from its initial occurrence until the supply of sample had been depleted in order to ensure that no transient behavior had occurred. The full spectra are stored in 1000 data channels across a range of 10 eV. In addition, specific regions of the spectra were examined in greater detail for more precise information regarding the band shapes and areas.

Spectral Data Reduction. As is usually the case with large molecules, much of the vibrational fine structure of the ionization bands is not resolved. The ionization band envelopes possess a variety of shapes and intensities, and occasionally are overlapping. In order to describe these band envelopes and ionization potentials precisely and consistently, a program has been developed which efficiently curve fits the spectral data. The functional form used by this program is an asymmetric Gaussian defined as

$$C(\mathrm{E}) = Ae^{-k[(E-P)/W]^2}$$

$$(E > P.\ W = W_{\mathrm{h}};\ E < P.\ W = W_{\mathrm{l}}\ (k = 4 \ln 2))$$

where C(E) is the electron counts computed at binding energy E. A is the amplitude of the peak, P is the position of the peak, and W is either the apparent high binding energy side half-width (W_{h}) if E is greater than P or the apparent low binding energy side half-width (W_{l}) if E is less than P. These parameters, plus the parameters of a linear baseline, are varied to optimize the function fit to the data via a nonlinear regression routine. The program contains options to fix the value of any parameter, place upper or lower bounds on the value of any parameter, or fix the relationship of any one parameter to any other parameter. With these options, it is possible to investigate the different possible fits of a complex band envelope, where the data are not sufficient to uniquely define all of the peak parameters. The parameters of the minimum number of asymmetric Gaussian peaks needed to obtain a fit of each ionization band are reported in the tables, as well as the constraints used for dependent parameters. Each fit is weighted according to the value of each data channel, so that the fit sum represents the data more accurately near the ionization maxima than near the baseline. The most significant fits are displayed.

Molecular Orbital Calculations. Molecular orbital calculations are used to lend additional insight into the interpretation of these spectra. An ab initio calculation on cyclopentadienide was performed with program POLYATOM,[27] which was adapted for the University of Wisconsin Chemistry Department's IBM-7094 by Dr. M. B. Hall. The electronic structures of the transition metal complexes were investigated via the approximate molecular orbital method of Fenske.[28]

For the ab initio calculation on $C_5H_5^-$, the anion was assumed to be planar, belonging to the point group D_{5h}. The carbon-carbon bond distance for this calculation is 1.43 Å, and the carbon-hydrogen distance is 1.09 Å. The calculation used a minimal atomic basis set of contracted Gaussian functions. The carbon 1s and 2s functions correspond to the best atom exponents expanded in three Gaussian functions.[29] The carbon 2p function corresponds to Clementi's atomic function expanded in four Gaussian functions.[30] The three Gaussian expansion for the hydrogen 1s function corresponds to a Slater exponent of 1.2.

The approximate method of molecular orbital calculation used for the transition metal complexes has been described elsewhere.[25] This method is based on the Hartree-Fock-Roothaan procedure. The basis set is a minimum or slightly extended set of Slater atomic functions. The overlap matrix is treated exactly. The only difference between Fenske calculations and ab initio calculations is that certain portions of the Fock matrix are created with mathematically evaluated integrals which approximate the ab initio elements. Because this method of calculation contains no empirical or variable parameters, it may be used as a separate tool for the investigation of electronic structure. Like ab initio calculations, the results of these approximate calculations are dependent only on the basis set and the internuclear distances, both of which are chosen in a consistent, nonarbitrary fashion. Because wave functions for large molecules are efficiently calculated by this approximate method, and because the Fock matrix elements of this calculation are inherently less complex than those of the ab initio calculation and yet account for the majority of the electronic interactions, these calculations are generally more amenable to detailed study of the primary factors influencing the results obtained.

For purposes of comparison, approximate calculations were also performed on the cyclopentadienide ion. The atomic coordinates are identical with those used in the ab initio calculation, and the

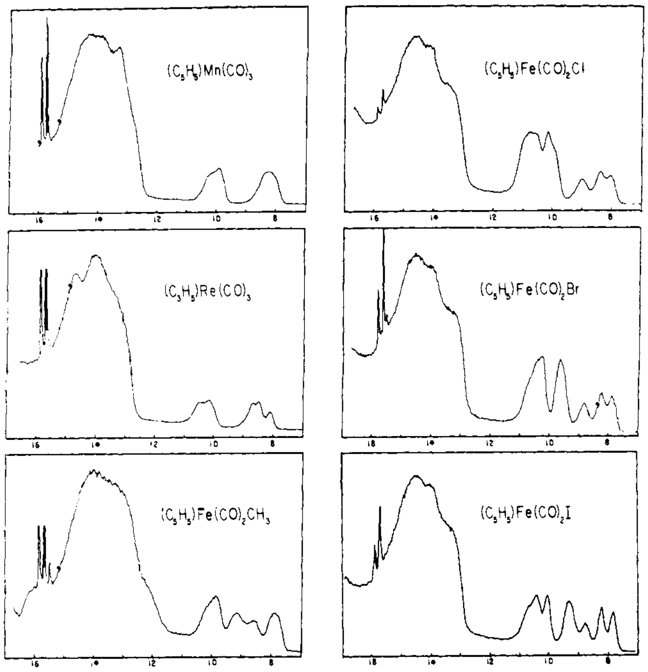

Figure 1. Photoelectron spectra for a binding energy range from 17 to 7 eV. The structure between 15.5 and 16 eV is due to the internal argon standard. In the case of (η^5-C_5H_5)Fe(CO)$_2$CH$_3$, a small amount of nitrogen is also observed.

basis expansion set, although using Slater-type functions, is similar. A hydrogen 1s function exponent of 1.2 was used. The carbon functions have been described previously.[25] Additional calculations with different internuclear distances and with the hydrogen atoms bent out as much as 5° out of the carbon framework plane did not alter the results appreciably. The planar geometry described above was used for all calculations on the transition metal π-cyclopentadienyl complexes so that changes in electronic structure could be ascribed directly to electronic effects.

The structure of CpMn(CO)$_3$ reported by Berndt and Marsh[31] was the basis for the bond distances and angles used in the molecular orbital calculation of that complex. The coordinates of the carbon and oxygen atoms were idealized to C_{3v} symmetry, with an angle of 90° between the ligand groups. The distance between the manganese atom and the carbon atom of each carbonyl group is 1.80 Å, and the distance between the carbon and oxygen atoms of each carbonyl group is 1.15 Å. The distance between the manganese atom and a carbon atom of the cyclopentadienyl ring is 2.165 Å. Small changes in bond distances and angles, including rotation of the Mn(CO)$_3$ portion of the molecule with respect to the cyclopentadienyl ring, did not alter the general conclusions.

Calculations on the CpFe(CO)$_2$X complexes used bond distances derived from the structures of other CpFe(CO)$_2$L[32] and transition metal halide[33] molecules. Again, the bond distances within the ring were left unchanged. The distance between the iron atom and a carbon of the ring is 2.10 Å, a value consistent with the mean value for cyclopentadienyl iron complexes.[34] The angles between the other ligands were again idealized to 90°, with the central axis of the three ligand groups coincident with the C_5 axis of the ring. Although the angle between carbonyl groups may vary as much as 5° from a right angle,[35] this perturbation has no serious consequences for the properties investigated here. The distance between the iron atom and a carbon atom of a carbonyl groups is 1.74 Å, and the distance between a carbon atom and an oxygen atom of a carbonyl group was kept at 1.15 Å. The distances between the iron atom and the chloride, bromide, and iodide atoms were taken as 2.32, 2.47, and 2.66 Å, respectively. Calculations with differenct iron-chloride distances were also performed to observe the sensitivity of the results to this bond length.

The variational basis set used in these calculations is a set of contracted Slater-type atomic valence basis functions. These functions are consistent with those used previously.[36] In addition to the CpFe(CO)$_2$X calculations using halogen best atom functions, a calculation for CpFe(CO)$_2$Cl was also performed using Clementi's[37] chlorine functions to observe the basis set dependence. Manganese and iron 4s and 4p exponents of 2.0 were used throughout.

Results

The He(I) photoelectron spectra recorded for an electron binding energy range of 7-17 eV are presented in Figure 1 for those molecules of principal focus in this study. These displays were produced by the instrument's recorder. The sharp spikes between 15.5 and 16 eV correspond to the internal argon standard. Because of the size and low symmetry of these molecules, the spectra are quite complex. Certain features of the spectra are similar. For instance, the broad intense band from 13 to 16 eV in each spectrum has been assigned as arising from ionization of the carbonyl 5σ and 1π levels in the spectra of transition metal carbonyl complexes,[4] and from ionization of certain of the cyclopentadienyl ring σ and π levels in the spectra of the biscyclopentadienyl metal complexes.[10] This band is generally featureless, undoubtedly because of the large number of overlapping ionizations. The overall shape of the band is similar for each of the iron-halide complexes. The ionization onset of this band is relatively insensitive to changes in the metal atom or to ligand substitution. In each case a sharp ionization onset is observed at approximately 13 eV. The methyl complex displays some additional ionization structure around 12 eV. The spectra also exhibit a common band shape in the binding energy range of 10-11 eV. The ionization bands in the range of about 7-11 eV display a wide range of intensities and shapes which are sensitive to the metal and ligand substitution. These bands will receive primary attention in this study.

The band shapes observed in these spectra may be well represented with the asymmetric Gaussian functional forms described in the experimental section. The results of this analysis are presented in the tables. The positions of the peaks reported in these tables correspond to the vertical ionization potentials. In those instances where the bands are well resolved, these positions are highly reproducible, an upper limit to the uncertainty being approximately ±0.02 eV. When two ionization peaks overlap considerably, the uncertainty may be greater. The tables also include the relative area of each peak. These areas are reported relative to the sum total of the low binding energy ionization area (7-11 eV).

Calculations

Preliminary Considerations. The low binding energy regions of these photoelectron spectra contain specific information regarding the relationships between the low-lying positive ion states and the ground states of the molecules studied. The assignment of these ionization bands is of crucial importance to the interpretation of the electronic structure of these complexes. Several assignment criteria which are based solely upon experimental observables and the most fundamental understanding of electronic structure and the photoionization process may be used to suggest probable assignments. For example, the band shape and relative area of an ionization may suggest that it is associated with a particular positive ion state. Any observed vibrational structure of spin-orbit splitting will also have implications regarding the ionization assignment. In addition, comparison of these spectra with each other through this series of molecules or comparison with the spectra of simpler transition metal complexes may prove useful. All of these criteria will be investigated in the course of obtaining a consistent assignment and interpretation of the ionizations of these complexes.

It is instructive, however, to first consider the results of

Table I. Results of ab Initio Calculation on Cyclopentadienide Ion

Total Energy = 189.948 au Orbital eigenvalues (au) Occupied valence levels		C1s	Population analysis (av) C2s	C2p	H1s
$2a_1'$	−0.916		16	3	1
$2e_1'$	−0.721		13	4	3
$2e_2'$	−0.516		6	8	7
$3a_1'$	−0.488			13	6
$3e_1'$	−0.339			14	6
$3e_2'$	−0.309			17	3
a_2''	−0.301			20	
e_1''	−0.096			20	
Total populations		1.994	1.133	3.017	0.856
Low-lying virtual levels					
e_2''	0.475			20	
$4a_1'$	0.748		3	4	13
$4e_2'$	0.792		12	1	6
$4e_1'$	0.797		2	1	17

the quantum mechanical calculations. These calculations were performed for the purpose of developing a description of the ground state electronic structure of d^6 cyclopentadienyl metal carbonyl complexes. Under the assumptions of Koopmans' theorem,[15] the one-electron orbital eigenvalues of a ground state calculation are related to the ionization potentials. The basic assumption of this theorem is that removal of an electron from a closed shell molecule does not alter the distribution of the remaining electrons. Electron correlation and relativistic effects are also ignored in this theorem.[38] These assumptions certainly are not strictly valid, and the shortcomings of the theorem are well documented. However, in many instances, the description of an ionization in terms of the positive ion states and their relationship to the neutral molecule becomes unnecessarily awkward. The assignment of an ionization in terms of the molecular orbital in the ground state neutral molecule from which the electrons originated is often more efficient and comprehensible. Other factors in the ionization process which are associated with the positive ion, such as electron rearrangement or relativistic effects, will not be ignored, but will be considered subsequent to the orbital description. Besides the descriptive and qualitative value of the ground state molecular orbital representation, certain trends in ionization potentials and cross sections may be produced. This will be possible if the errors in Koopmans' theorem are relatively constant throughout a series. Part of the purpose of this study is to investigate this possibility. In any event, an understanding of the ground state electronic structure of d^6 transition metal (η^5-cyclopentadienyl) carbonyl complexes will facilitate discussion of the photoelectron spectra and prove valuable for the analysis of related substituted complexes.

Unlike the relatively high symmetry transition metal complexes chromium hexacarbonyl and ferrocene, $CpMn(CO)_3$ has, at most, a single symmetry reflection plane. This low symmetry indicates that no ionizations will be exactly degenerate, and therefore a complicated ionization spectrum may result. The low symmetry also suggests that a molecular orbital description of the electronic structure may become very involved. However, the description is greatly simplified if we take advantage of the fact that certain portions of the molecule possess high symmetry locally. The cyclopentadienyl portion of the molecule transforms according to D_{5h} symmetry, and the manganese tricarbonyl portion of the molecule transforms according to C_{3v}. These portions will first be treated separately. It will then be possible to sort out clearly the interactions between the cyclopentadienyl portion and the metal tricarbonyl portion of the molecule. The separate analysis of each portion of the molecule will prove to be of more general value because both the cyclopentadienyl ring and the metal tricarbonyl fragment are common functional groups in organometallic chemistry.

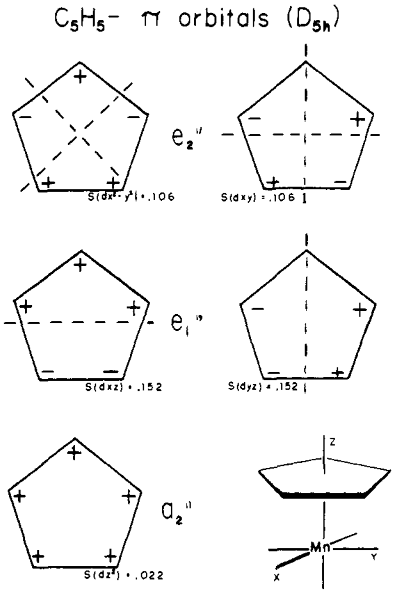

Figure 2. The symmetry orbitals of $C_5H_5^-$. The overlaps with Mn^{+1} d functions correspond to the coordinate system illustrated.

Cyclopentadienide Ion. The results of the ab initio calculation on the cyclopentadienide ion are listed in Table I. The anion was chosen for calculation because its ground state is a closed shell $^1A_1'$. If the anion is assumed to be effectively planar, it belongs to the point group D_{5h}. In this symmetry the five carbon p_π orbitals transform as a_2'', e_1'', and e_2''. The nodal characteristics of these orbitals are illustrated in Figure 2. From overlap considerations, the relative energy of these symmetry orbitals is expected to be $a_2'' < e_1'' < e_2''$ with the e_1'' orbitals being the highest occupied set and the e_2'' orbitals being the lowest unoccupied set. Previous calculations on this anion using the ab initio SCF-MO-LCGO method[39,40] found that the a_2'' level was more stable than many of the σ levels. In contrast, our ab initio results (Table I) indicate that all the occupied σ levels fall below the π a_2'' level. In addition, the eigenvalues of the occupied orbitals in our calculation are consistently lower than the eigenvalues obtained from the SCF-MO-LCGO calculation. The a_2'' level is over 5 eV below the e_1'' levels. The separation between the e_1'' levels and the lowest virtual levels, the e_2'', is quite substantial in this minimum basis set calculation, being over 15 eV. A more accurate description of the cyclopentadienide ion would require a more extensive basis set. In particular, the neutral atom functions may not be ideally suited for describing the negative ion. However, the primary concern is the C_5H_5 fragment in a transition metal complex, and not as an isolated ion. Also, this minimum basis set calculation is ideally suited for comparison with more approximate methods.

Before further discussion it is appropriate to anticipate the interaction of these ring orbitals with the metal center. The $CpMn(CO)_3$ molecule is assumed to be in a coordinate system (Figure 2) with the metal at the origin and the centroid of the cyclopentadienyl ring directly on the +*z* axis. In this coordinate system the cyclopentadienyl a_2'' orbital may interact with the metal d_{z^2} orbital. Partly because the lobes of the carbon p_π orbitals fall near the nodes of the metal d_{z^2} orbital, the overlap between these orbitals is small. The cyclopentadienyl e_1'' orbitals are of π symmetry with respect

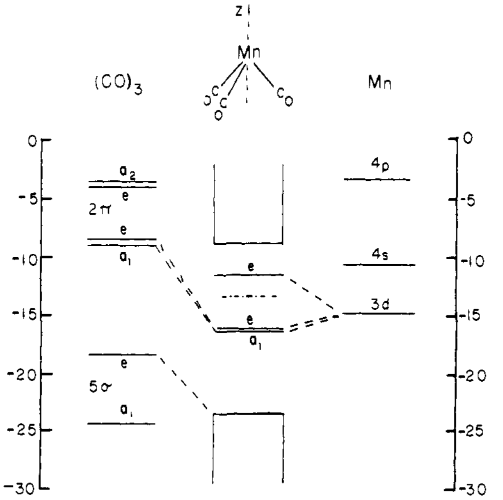

Figure 3. Molecular orbital diagram for $Mn(CO)_3^+$ (energy in eV).

to the metal, and may interact with the metal d_{xz} and d_{yz} orbitals. Because these orbitals are directed toward the same region of space, this interaction is favored by overlap. The e_2'' orbitals have two nodes outside of the molecular plane and have delta symmetry with respect to the metal atom. These orbitals may mix with the metal d_{xy} and $d_{x^2-y^2}$ orbitals.

$Mn(CO)_3^+$. For $CpMn(CO)_3$, the cyclopentadienyl ring is bound to a metal atom with three carbonyl groups on the opposite side. The interactions of these carbonyl groups with the metal atom must be considered carefully in order to understand the total electronic structure of these complexes. For a discussion of the interaction between the $Mn(CO)_3^+$ orbitals and the cyclopentadienyl ring orbitals, it is helpful to consider the $Mn(CO)_3^+$ orbitals in a coordinate system in which the C_{3v} axis is coincident with the master coordinate z axis (Figure 3). In the C_{3v} symmetry of $Mn(CO)_3^+$, the metal d_{z^2} orbital transforms according to the a_1 representation, and the ($d_{x^2-y^2}$, d_{xy}) and (d_{xz}, d_{yz}) sets of metal orbitals both transform according to the e representation. The angle between pairs of carbonyl groups in $CpMn(CO)_3$ is essentially 90°; thus, it is possible to compare the metal-carbonyl bonding in this case with previous interpretations of metal-carbonyl bonding in d^6 octahedral transition metal complexes.[41] For an octahedral complex in this coordinate system, the occupied t_{2g} metal orbitals (which are stabilized through back-bonding to the carbonyl π^* orbitals) are the d_{z^2}, $\sqrt{2/3}d_{x^2-y^2} + \sqrt{1/3}d_{xz}$, and $\sqrt{2/3}d_{xz} - \sqrt{1/3}d_{yz}$ combinations. The virtual e_g metal orbitals (which are destabilized by the carbonyl 5σ orbitals) are the $\sqrt{1/3}d_{x^2-y^2} - \sqrt{2/3}d_{xz}$ and $\sqrt{1/3}d_{xy} + \sqrt{2/3}d_{yz}$. Because the carbonyl groups of $Mn(CO)_3^+$ are at 90° angles with each other, the degeneracy of the orbitals which correspond to the e_g and t_{2g} sets in an octahedral system is only lost through ligand-ligand interaction. The percent characters and energies of these orbitals are also perturbed by the loss of octahedral symmetry in $Mn(CO)_3^+$. These interactions have been discussed previously in terms of overlap considerations.[42]

The molecular orbital diagram for $Mn(CO)_3^+$, based upon our approximate method is shown in Figure 3. The carbonyl orbitals are considered in terms of their symmetry combinations. The interactions between the carbonyl 2π orbitals produce the a_1, 2e, and a_2 representations. The a_1 combination interacts strongly with the metal d_{z^2} orbital. The lower e combination interacts strongly with the metal $d_{x^2-y^2}$ and d_{xy} orbitals. Thus, the highest occupied levels of

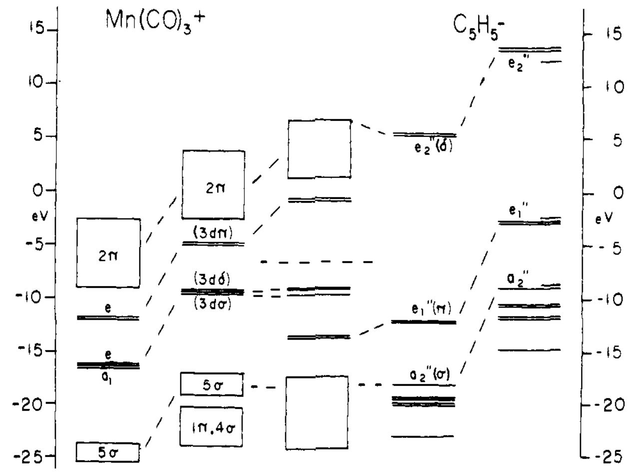

Figure 4. Molecular orbital diagram for $(\sigma^5\text{-}C_5H_5)Mn(CO)_3$. The outside columns represent the orbital eigenvalues of the isolated fragments $Mn(CO)_3^+$ and $C_5H_5^-$. In the case of $C_5H_5^-$, the eigenvalues of the ab initio calculation are also indicated by the shorter horizontal lines. The second and fourth columns represent the fragment orbital energies in the molecular environment, and the center column represents the orbital energies of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$.

$Mn(CO)_3^+$ are predominantly metal $d_{x^2-y^2}$ and d_{xy} in character (with some smaller percentage of d_{xz} and d_{yz} character). The next highest occupied level in $Mn(CO)_3^+$ is the a_1, which is predominantly metal d_{z^2} in character. Because the difference in energy between the occupied a_1 and the occupied e of $Mn(CO)_3^+$ is due to interaction between adjacent carbonyl group 2π orbitals, the splitting is expected to be small. Thus the loss of octahedral symmetry in $Mn(CO)_3^+$ does not significantly split the top three eigenvalues.

The three carbonyl 5σ orbitals transform according to the a_1 and e representations. These a_1 and e orbitals are substantially split by σ-σ interaction. The e(5σ) representation interacts strongly with the metal d_{xz} and d_{yz} orbitals. The a_1 (5σ) representation has only small overlap with the metal d_{z^2} orbital. As a result, the lowest unoccupied orbitals of $Mn(CO)_3^+$ belong to the e representation and are primarily d_{xz} and d_{yz} in character (with some smaller percentage of $d_{x^2-y^2}$ and d_{xy} character). It should be noted that the characters of the predominantly metal levels are intermediate between the characters of a d^6 octahedral complex and those of a d^6 bis(η^5-cyclopentadienyl) complex.

$(\eta^5\text{-}C_5H_5)Mn(CO)_3$. With this understanding of the electronic structure of $C_5H_5^-$ and $Mn(CO)_3^+$, it is now possible to analyze the most important interactions between these two portions of the molecule. The qualitative orbital description of $CpMn(CO)_3$ has been discussed by Orgel.[43] The molecular orbital diagram of $CpMn(CO)_3$ in terms of $C_5H_5^-$ and $Mn(CO)_3^+$ is given in Figure 4. The value of treating the isolated fragments of the molecule separately now becomes evident. That is, although the approximate calculation from which this molecular orbital diagram was derived is a full atomic valence basis calculation, only a few of the highest occupied and lowest unoccupied orbitals of the fragments need be included in this diagram. It was observed in these calculations that the characters of only a few of these orbitals in $CpMn(CO)_3$ are substantially different from the characters determined for the orbitals in the isolated fragments. The low-lying occupied fragment levels behave as though they were ligand core orbitals. Like atomic core orbitals, their form is only slightly perturbed in the molecular environment. This concept of the ligand core was investigated by methods discussed elsewhere.[44] Calculations were performed on $CpMn(CO)_3$ in which certain of the ligand orbitals were frozen to their form determined in the isolated fragments, and perturbation theory analysis was used to judge the validity of the core approximation. In these calculations it was found that the carbonyl 3σ and 6σ orbitals, the first three occupied cyclopentadienyl ring σ orbitals, and all the virtual ring orbitals above the e_2'' level could be deleted from the SCF solution without serious quantitative changes in the results. Of the ring orbitals, only the π combinations were necessary for reproducing the qualitative features of the structure.

The eigenvalues of the $C_5H_5^-$ orbitals as obtained from the approximate calculations are on the right of Figure 4. These eigenvalues are very close to those resulting from the ab initio calculation, which are represented by the short horizontal lines. When the $C_5H_5^-$ ring approaches and interacts with $Mn(CO)_3^+$, its orbital eigenvalues are stabilized by the positive charge of $Mn(CO)_3^+$, as well as by some charge redistribution. Likewise, the closed-shell orbital eigenvalues of $Mn(CO)_3^+$ are destabilized by the negative charge of the cyclopentadienyl ring. The $C_5H_5^-$ and $Mn(CO)_3^+$ orbital energies in $CpMn(CO)_3$ are displayed in the second and fourth columns of Figure 4. The primary symmetries of these orbitals with respect to the metal Cp bond are indicated. These orbitals combine to form the molecular orbitals of $CpMn(CO)_3$, the eigenvalues of which are displayed in the central column. The strongest interaction is seen to be between the lowest unoccupied levels of $Mn(CO)_3^+$ and the highest occupied levels of $C_5H_5^-$. This interaction is favored by overlap considerations. As may be seen from the molecular orbital diagram, the interaction is also favored by the small energy separation between these sets of orbitals. This bonding interaction between the filled $C_5H_5^-$ e_1'' orbitals and the empty $Mn(CO)_3^+$ orbitals, which are primarily d_{xz} and d_{yz} in character, results in a net charge transfer from the $C_5H_5^-$ ring to the metal.

The interactions between the highest occupied $Mn(CO)_3^+$ levels and the suitable ring levels are expected, from this analysis, to be much weaker. The overlap of the $Mn(CO)_3^+$ a_1 orbital with the ring a_2'' is small, and the energy separation is large. The highest occupied $Mn(CO)_3^+$ e orbitals, which have primarily delta symmetry with respect to the ring, are also substantially separated from the ring e_2'' orbitals. The interactions between these sets of orbitals will tend to stabilize the occupied e eigenvalue with respect to the a_1 eigenvalue. These calculations indicate, however, that the e orbital becomes less stable with respect to the a_1 through interaction with the ring. This is because the shift in the eigenvalue of the $Mn(CO)_3^+$ orbitals in forming $CpMn(CO)_3$ is actually dominated by the interaction of these orbitals with the ring e_1'' orbitals, made possible by the small portion of the d_{xz}, d_{yz} character in the e orbitals.

Although $CpMn(CO)_3$ contains only a reflection plane in these calculations, the e orbitals of $Mn(CO)_3^+$ and of $C_5H_5^-$ remain nearly degenerate when they combine to form the orbitals of $CpMn(CO)_3$. These orbitals are not split directly. The metal orbitals which transform according to the e representation for C_{3v} $Mn(CO)_3^+$ also transform according to the e representation for C_{5v} $MnC_5H_5^-$. Any loss in degeneracy is because the carbon and hydrogen atoms in the ring do not all interact equivalently with the carbonyl groups (and vice versa). Again, because these ligand-ligand interactions are small, the predominantly metal orbitals which transform according to the e representation for each local symmetry are not substantially split. Therefore, the orbitals of $CpMn(CO)_3$ which are primarily metal in character will be referred to as the e-type and the a_1-type orbitals in the remaining discussion.

An indication of the relationship of the ground state eigenvalues of $CpMn(CO)_3$ as obtained from this analysis with the eigenvalues of an ab initio calculation, and ultimately with the observed ionization potentials themselves, may be projected from the results of similar studies on $Cr(CO)_6$ and $(Cp)_2Fe$. For example, the approximate calculation of ferrocene places the primarily metal a_{1g} and e_{2g} orbitals at −7.8 and −9.0 eV, respectively. The primarily ring e_{1u} and e_{1g} levels are calculated by this method to be at −14.1 and −14.4 eV. These results are quite similar to the results obtained by the SCF-Xα-SW method.[45] When the results of our approximate calculation are compared with the results of the ab initio calculation on ferrocene,[22] it is found that the approximate calculation places the primarily metal levels higher in energy. Comparison of the approximate calculation of $Cr(CO)_6$ with a similar ab initio calculation[17] indicates the same trend. In addition, the approximate calculation places the eigenvalues of the predominantly ring e_1'' orbitals of ferrocene lower in energy than the corresponding ab initio eigenvalues. In fact, the ab initio calculation on the ferrocene ground state actually places the metal levels below the ring e_1'' levels, which is contrary to the observed order of the ionizations.[10] Further ab initio calculations on the positive ion states of ferrocene show that, from differences in total energy, the initial ionizations are indeed associated with the metal levels. Thus it is not valid to apply Koopmans' theorem to the rigorous results on ferrocene. These results on ferrocene imply that the highest occupied levels of $Mn(CO)_3^+$ and the e_1'' levels of $C_5H_5^-$ are actually much closer in energy than indicated by the approximate calculations, and an ab initio calculation on $CpMn(CO)_3$ may actually reverse the order of the primarily metal levels and the primarily ring e_1'' levels. However, as in ferrocene, the order of the ionization potentials of $CpMn(CO)_3$ should remain the order depicted in Figure 3. Although quantitative comparison of orbital eigenvalues with the ionization potentials is not expected, the qualitative features of the magnitudes of orbital interactions and bonding remain intact. With this background description it is now possible to discuss the ionizations of the cyclopentadienyl metal carbonyl complexes. Further analysis of the theoretical implications will be appropriate during and subsequent to this discussion.

Table II. Ionization Data for $(\eta^5\text{-}C_5H_5)Mn(CO)_3$

Ionization	Binding energy (eV)	Relative amplitude	W_h	W_l	Normalized area
1	8.05	1	0.60	0.37	0.49
2	8.40	0.60	0.60^a	0.37^a	
3	9.90	1.21	0.50	0.33	0.51
4	10.29	0.71	0.50^a	0.33^a	

[a] Indicates constrained parameters.

Assignment and Interpretation of Photoelectron Ionizations

$CpMn(CO)_3$ Ionizations. The results of curve analysis of the low binding energy region of the ionization spectrum of $CpMn(CO)_3$ are presented in Table II. The first ionization band occurs between 8 and 8.5 eV and is assigned as ionizations from the predominantly metal levels. This band is similar in binding energy to the initial ionization of $Cr(CO)_6$, which has a vertical ionization potential of 8.41 eV and has been assigned as ionization from the predominantly metal t_{2g} levels.[4] The overall half-width of this band of $CpMn(CO)_3$ is 0.69 eV, which is considerably greater than the 0.49 eV half-width of the t_{2g} ionizations of $Cr(CO)_6$. This band of $CpMn(CO)_3$ may also be compared with the metal ionizations of $(Cp)_2Fe$, which are split into two distinct ionization peaks. The first ionization peak of ferrocene, at 6.86 eV, represents removal of electrons from the

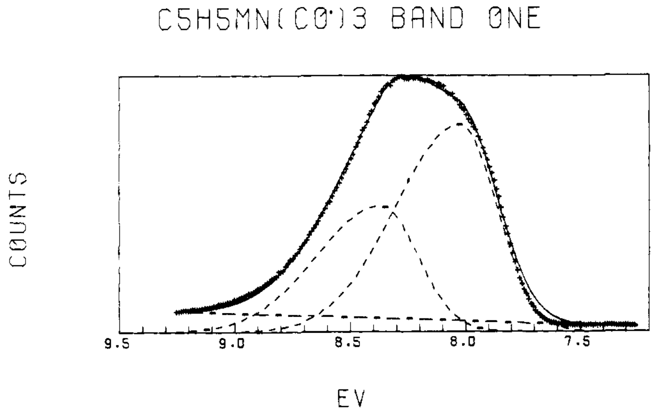

Figure 5. The plus signs are the data values, the dashed lines are the optimized Gaussian peaks and baseline, and the solid line is the fit sum.

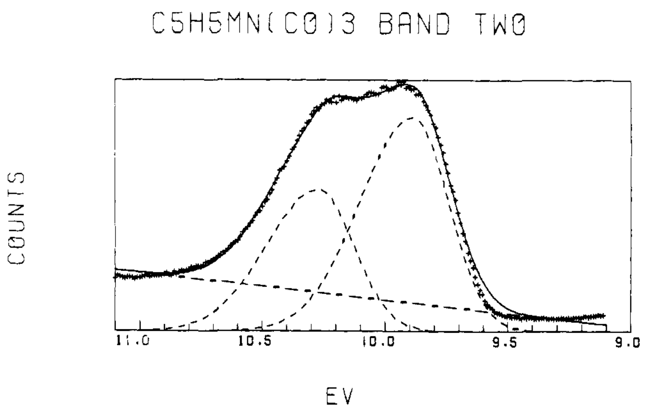

Figure 6. The plus signs are the data values, the dashed lines are the optimized Gaussian peaks and baseline, and the solid line is the fit sum.

e_{2g} orbitals, which are primarily metal d_{xy}, $d_{x^2-y^2}$ in character. The shape and vibrational structure observed for this ionization indicate some bonding interaction with the ring π e_{2g}'' orbitals.[10] The second ionization peak of ferrocene, at 7.23 eV, has been assigned as representing removal of electrons from the primarily metal a_{1g} orbital. The sharpness of this ionization peak reflects the nonbonding nature of the $(Cp)_2Fe$ a_{1g} electrons. From the calculations, the energies of the e- and a_1-type orbitals of $CpMn(CO)_3$ are also expected to be slightly different. Similar to the case of ferrocene, ionization from the singly degenerate a_1-type orbital is expected to occur at higher binding energy than ionization from the e-type orbital. However, because the a_1-type orbital has stronger interaction with the carbonyls, the band envelope for this ionization is expected to be broader than that observed for the a_{1g} ionization in ferrocene.

No vibrational structure or separate ionization peaks could be resolved in the initial ionization band of $CpMn(CO)_3$. However, it is found that this ionization band cannot be adequately represented with a single asymmetric Gaussian peak, suggesting that separate ionization peaks have not been fully resolved. Because knowledge of the exact nature of the ionizations corresponding to this band is important for understanding the electronic structure of this complex and other related molecules, the shape of this band was carefully analyzed. A good representation of the band may be obtained with a minimum of variable parameters when two peaks with equal half-widths are used. This fit is displayed in Figure 5. The fit indicates that the vertical ionization potentials for these peaks are 8.05 and 8.40 eV, and the ratio of their amplitudes is 2:1.2. These results are consistent with the theoretical prediction that ionization from a predominantly metal a_1-type level will occur at slightly higher binding energy than ionization from the predominantly metal e-type levels. Although this evidence is certainly not definitive, the results of this detailed analysis are included here for comparison with other information (vide infra).

The curve fit of the band at approximately 10 eV is shown in Figure 6. The vertical ionization potential of 9.90 eV is lower than that observed in the bis(η^5-cyclopentadienyl) complexes. A distinct shoulder on the band is separated from the vertical ionization potential by 0.39 eV. Additional structure has also been noted in the region of the e_1'' ionizations of the bis(η^5-cyclopentadienyl) complexes but has not been clearly observed. Several processes, such as autoionization or Jahn-Teller effects, could account for this shoulder. The separation of 0.39 eV corresponds to 3140 cm^{-1}, which is in good agreement with the experimental carbon-hydrogen stretching frequency of 3116 cm^{-1} observed for $CpMn(CO)_3$. Therefore it is tempting to ascribe this band shape to a partially resolved vibrational progression.

The ratio of the areas of the band at 8 eV to the band at 10 eV is 0.97:1, whereas the number of electrons accounting for each band (six for predominantly metal levels and four for the predominantly ring e_1'' levels) would suggest a ratio of 1.5:1. As Evans et al. pointed out,[11] this may indicate that the metal d electrons have an intrinsically lower ionization cross section than the ligand e_1'' orbitals.

$CpRe(CO)_3$. Comparison of the ionization spectrum of $CpRe(CO)_3$ with the spectrum of $CpMn(CO)_3$ is valuable because the rhenium d orbitals possess appreciable spin-orbit coupling.[46] The splitting of the ionization band between 8 and 9 eV in the spectrum of the rhenium complex into three distinct peaks is ascribed to spin-orbit interaction in the positive ion. This observation supports the assumption that these ionizations are associated primarily with the metal d electrons. The ionization data for this spectrum are reported in Table III. The separation of the first two peaks is 0.39 eV, and the separation of the second and third peaks is 0.24 eV.

From the spectrum of $CpRe(CO)_3$ alone, the three peaks of the multiplet band cannot be uniquely assigned. However, if one combines the information from $CpMn(CO)_3$, $W(CO)_6$, and $(Cp)_2Os$ with the rhenium spectrum, a particular interpretation is clearly indicated. Since this process relies upon a discussion of spin-orbit coupling matrices, the details are deferred to the appendix. Two of the conclusions of this analysis are appropriate here. First, it is found that the form of the e-type orbitals of $CpRe(CO)_3$ before spin-orbit interaction must be intermediate between the form of the e_{2g} orbitals of $(Cp)_2Os$ and the t_{2g} orbitals of $W(CO)_6$. Second, without spin-orbit interaction, ionization from the a_{1g}-type orbital of $CpRe(CO)_3$ would occur at 0.35-0.45 eV greater binding energy than ionization from the e-type orbitals. This latter conclusion is consistent with the results of curve analysis of the first band of $CpMn(CO)_3$, and both of these conclusions are in agreement with the results of the calculations.

The results of curve analysis of the second band of $CpRe(CO)_3$ are also reported in Table III. The shoulder of this ionization band is slightly stronger than that observed for the similar band in the spectrum of $CpMn(CO)_3$. The splitting of these bands as determined by the curve analysis is 0.41 eV, which is only a slight increase from the value of 0.39 eV determined for $CpMn(CO)_3$. The ratio of the area of the band at 8 eV to the area of the band at 10 eV is 1.04:1. This is not a significant increase over the ratio observed in the spectrum of $CpMn(CO)_3$. From the work of Lloyd et

Table III. Ionization Data for $(\eta^5\text{-}C_5H_5)Re(CO)_3$

Ionization	Binding energy (eV)	Relative amplitude	W_h	W_l	Normalized area
1	8.13	0.51	0.35	0.21	0.51
2	8.52	1	0.44	0.22	
3	8.76	0.66	0.58	0.14	
4	10.18	0.94	0.49	0.35	0.49
5	10.59	0.69	0.49[a]	0.35[a]	

[a] Indicates constrained parameters.

al.[4] on $Cr(CO)_6$ and $W(CO)_6$, it is known that the cross-section for ionization of metal d electrons from third-row transition metals is approximately twice as great as that for first-row transition metals. This characteristic has been termed the "heavy atom effect". That the "heavy atom effect" is not observed in the ratio of these two bands suggests that that band at 10 eV must be associated with some amount of metal character.

The shifts between the bands near 8 and 10 eV in $CpMn(CO)_3$ and the corresponding bands in $CpRe(CO)_3$ are −0.34 and −0.28 eV, respectively. These shifts are consistent with the increased inherent stabilization of the rhenium d orbitals in comparison to the manganese d orbitals and show that the ionizations which are predominantly ring e_1'' in character are also quite sensitive to the metal substitution.

$CpFe(CO)_2X$; X = I, Br, Cl. It is now possible to examine in detail the low binding energy region of the photoelectron spectra of substituted η^5-cyclopentadienyl d^6 metal carbonyl complexes. The spectra of complexes of the series $CpFe(CO)_2X$, where X = I, Br, Cl are discussed first because the spectra of the analogous manganese pentacarbonyl halide complexes have already received considerable attention. The electronic structure of the metal–halogen portion of the $CpFe(CO)_2X$ complexes may be thought of in terms of a perturbation of the C_{4v} electronic structure of the $Mn(CO)_5X$ complexes caused by substituting a cyclopentadienyl ring for three carbon atoms and changing the central metal atom from manganese to iron. From analysis of the ionization spectra of $CpMn(CO)_3$ and $CpRe(CO)_3$, it has been found that the effective symmetry about the metal atom is not greatly altered by this substitution. The results of approximate calculations on molecules of the form $M(CO)_5X$ have been reported previously.[42]

The results of the approximate calculation on $CpFe(CO)_2Cl$ are presented in the form of a molecular orbital diagram in Figure 7. Previous calculations on the transition metal halide complexes employed a best atom basis for the halogen atoms in order to obtain a consistent comparison of trends through the halogen series. The molecular orbital diagram illustrated here was obtained from an approximate calculation using Clementi's atomic functions for the basis set at the chlorine center. Certain features of the diagram are found to be sensitive to this choice of basis. The highest two occupied orbitals correspond to the antibonding metal-halogen e set in the $Mn(CO)_5X$ complexes. The percent metal character in this orbital is increased substantially in this basis. This is no doubt due to the greater inherent stability of Clementi's halogen functions compared to the best-atom functions. In addition, the splitting of these two levels increases to 0.31 eV. This splitting is a sensitive function of the interaction of the tail of the halogen functions with the other ligands, which are in a low symmetry arrangement about the metal atom. The bonding combinations of these π levels are calculated to be split to a lesser degree. Another interesting feature is that the level which corresponds to the primarily metal b_2 orbital in the $Mn(CO)_5X$ complexes now occurs between the bonding and antibonding metal-halogen π levels. The metal-halogen σ bonding orbital is calculated to be more stable than all of these orbitals. This order for these ionizations is contrary to the earlier assignment of the ionizations observed for $Mn(CO)_5X$ complexes. In this earlier assignment, the second ionization, observed as a weak band at 9.56 eV in the $Mn(CO)_5Br$ and $Mn(CO)_5Cl$ spectra, was assigned as the a_1 ionization primarily from simple cross-section considerations. Since that time, careful analysis of the photoelectron data obtained for a series of rhenium pentacarbonyl halide complexes[47] and further consideration of photoelectron cross sections[48] has indicated that this band may actually be due to the b_2 ionization. These points will be considered in the course of assigning the ionizations observed for the $CpFe(CO)_2X$ complexes.

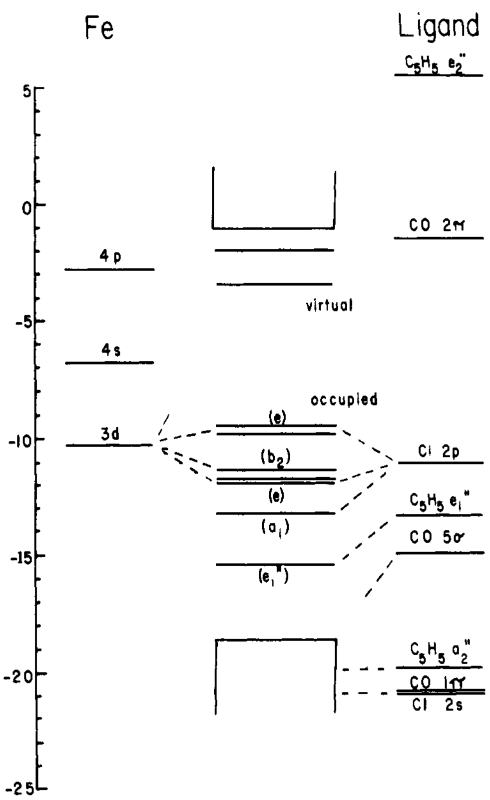

Figure 7. Molecular orbital diagram for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ (energy in eV).

A series of calculations on the complexes $CpFe(CO)_2X$ with X = Cl, Br, and I were performed in order to observe how this description changes with halogen substitution. The qualitative description remains much the same. The most important observation is that the splitting of the metal-halogen π antibonding orbitals decreases as the bond distance increases. These levels also have increasing halogen character. The shifts in ionization potential with halogen substitution are similar to those discussed for the $Mn(CO)_5X$ complexes.[6] Because the degeneracy of the eigenvalues of the $Mn(CO)_5X$ complexes is not substantially lost in the $CpFe(CO)_2X$ complexes, these orbitals will be discussed as though they belonged to the C_{4v} point group.

The results of curve fitting the spectra of the iron complexes are recorded in Tables IV–VI. An example of the fit in this region is displayed in Figure 8. The first two ionization peaks in each spectrum are very nearly equal in amplitude and shape, which is consistent with their being assigned to ionizations from the metal-halogen antibonding π levels. For the chloride complex, the first two ionization

Table IV. Ionization Data for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$

Ionization	Binding energy (eV)	Relative amplitude	W_h	W_l	Normalized area
1	8.00	1	0.40	0.29	0.170
2	8.38	0.99	0.40[a]	0.29[a]	
3	8.99	0.77	0.41	0.36	0.075
4	9.90	1.81	0.47	0.25	0.324
5	10.17	1.81[a]	0.47[a]	0.25[a]	
6–8	10.5–11.1				0.431

[a] Indicates constrained parameters.

Table V. Ionization Data for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$

Ionization	Binding energy (eV)	Relative amplitude	W_h	W_l	Normalized area
1	7.93	1	0.43	0.27	0.212
2	8.30	0.96	0.40	0.21	
3	8.89	0.71	0.44	0.32	0.088
4	9.57	1.36	0.34	0.24	0.261
5	9.78	1.36[a]	0.34[a]	0.24[a]	
6–8	10.4–10.8				0.438

[a] Indicates constrained parameters.

Table VI. Ionization Data for $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$

Ionization	Binding energy (eV)	Relative amplitude	W_h	W_l	Normalized area
1	7.77	1	0.32	0.21	0.237
2	8.17	1.07	0.28	0.21	
3	8.73	0.60	0.38	0.34	0.098
4	9.18	0.77	0.33	0.27	0.208
5	9.37	0.77[a]	0.33[a]	0.27[a]	
6	10.03	1.27	0.29	0.24	0.456
7	10.40	1.21	0.51	0.27	
8	10.76	0.50	0.51[a]	0.27[a]	

[a] Indicates constrained parameters.

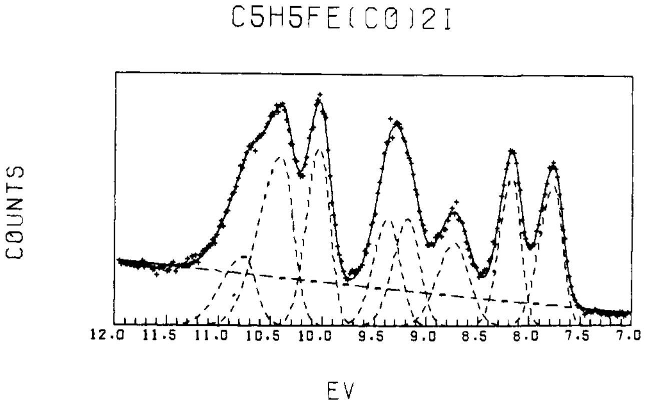

Figure 8. The plus signs are the data values, the dashed lines are the optimized Gaussian peaks and baseline, and the solid line is the fit sum (in eV).

peaks are separated by 0.38 eV. For the bromide and iodide complexes the splitting of these levels is expected to decrease due to the longer metal–halogen bond distance. However, the increasing halogen spin–orbit interaction through this series will tend to hold these levels apart. For the bromide complex the splitting is 0.37 eV while for the iodide complex the splitting is 0.4 eV.

The third ionization peak in these spectra is somewhat less intense than the first two, although its total cross section is not as low relative to the other peaks as the cross section of the corresponding peak at 9.56 eV in the $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ ionization spectra.[6] Also, whereas this weak intensity band was not observed in the spectrum of $Mn(CO)_5I$, it is now clearly discernible in the spectrum of $CpFe(CO)_2I$. The approximate calculations on $CpFe(CO)_2Cl$ suggest, via Koopmans' theorem, that this band should be assigned to ionization from the predominantly metal b_2-type orbital. However, as mentioned, it is also quite possible that this band results from ionization of the metal–halogen σ bond, the a_1-type orbital. It is not possible to base a choice for either of these assignments upon the appearance of the spectra.

The next distinct ionization band exhibits a definite shoulder in the spectra of the chloride and bromide complexes and is an unresolved broad band in the spectrum of the iodide complex. These observations lend further support to the assignment of this band as representing ionizations from the metal–halogen π-bonding orbitals. In order to be consistent, this band was fit in each case with two separate peaks which were constrained to have the same shapes and amplitudes. The 0.27 eV splitting determined for these bands in the spectrum of the chloride complex decreases to 0.21 and 0.19 eV splitting for the bromide and iodide complexes.

The remaining ionization bands in the spectra of $CpFe(CO)_2Cl$ and $CpFe(CO)_2Br$ are somewhat amorphous. In the photoelectron spectra of $CpFe(CO)_2I$ two separate peaks are observed between 10 and 11 eV. The first peak near 10 eV is sharp and well defined. If the peak at 8.73 in the spectrum of $CpFe(CO)_2I$ is assigned as ionization from the metal b_2-type level, then the peak at 10 eV must be assigned as ionization from the metal–halogen σ bond. In the spectrum of $CpFe(CO)_2Br$, the increased stabilization of this peak to approximately 10.4 eV results in a convergence of this ionization with those of predominantly ring e_1'' levels, yielding the complex band envelope observed between 10 and 11 eV. In the spectrum of $CpFe(CO)_2Cl$, this ionization may now actually be at a higher binding energy than the e_1'' ionizations.

The ionization band of $CpFe(CO)_2I$ at 10.4 eV has much the same shape as those near 10 eV in the spectra of $CpMn(CO)_3$ and $CpRe(CO)_3$. The shoulder on the high binding energy side of this band is separated from the main peak by 0.36 eV. Again, this ionization band is assigned as originating from the primarily ring e_1'' orbitals.

The comparison of the ionization potentials of the $Mn(CO)_5X$ complexes with the ionization potentials of the $CpFe(CO)_2X$ complexes is presented in Table VII. All ionization potentials of the $CpFe(CO)_2X$ complexes have shifted approximately 0.5 eV to lower binding energy. These shift data do not provide a definitive assignment for the a_1-type and b_2-type ionizations. All of the trends in ionization potentials and ionization cross sections observed for the $Mn(CO)_5X$ species are also observed for the $CpFe(CO)_2X$ species. Because the lower symmetry of the $CpFe(CO)_2X$ complexes causes a slight splitting in the e levels, and because small differences in the shift of each peak may remove accidental peak degeneracies (as in the case of $Mn(CO)_5I$), the study of the spectra of the cyclopentadienyl iron complexes is a valuable parallel to the study of the corresponding manganese complexes.

The integrated area of each ionization band relative to the total integrated area for ionizations in a binding energy range from 7 to 12 eV is also listed in the tables. The "heavy atom effect" is evident in the comparison of these relative cross sections through the series of halogen complexes. Ionization bands 1 and 2 account for an increasing portion of the total ionization area from the chloride complex to the iodide complex. This observation is consistent with the assignment of these bands to ionization from the

Table VII. Comparison of Ionization Potentials (eV) between $Mn(CO)_5X$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$

$Mn(CO)_5Cl$	11.15	10.52		9.56	8.89	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$	>10.5	10.17	9.90	8.99	8.38	8.00
Δ	<0.65	0.35	0.62	0.57	0.51	0.89
$Mn(CO)_5Br$	10.79	1.13		9.57	8.83	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$	>10.4	9.78	9.57	8.89	8.30	7.93
Δ	<0.39	0.35	0.66	0.68	0.43	0.80
$Mn(CO)_5I$	10.42	9.69		<9.3	8.73	8.41
$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$	10.03	9.37	9.18	8.73	8.17	7.77
Δ	0.39	0.32	0.51	0.57	>0.56	0.64

Table VIII. Ionization Data for $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$

Ionization	Binding energy (eV)	Relative amplitude	W_h	W_l	Normalized area
1	7.79	1	0.45	0.34	0.265
2	8.03	1[a]	0.45[a]	0.34[a]	
3	8.61	1[a]	0.45[a]	0.34[a]	0.132
4	9.23	1.21	0.58	0.57	0.232
5	9.90	1.81	0.48	0.32	0.370
6	10.26	0.93	0.48[a]	0.32[a]	

[a] Indicates constrained parameters.

metal–halogen π antibonding orbitals, which have increasing halogen character from the chloride complex to the iodide complex. Bands 4 and 5, which have been assigned to ionizations from the metal–halogen π bonds, account for a successively smaller portion of the total area from the chloride to the iodide spectrum. This is consistent with the decreasing halogen character associated with these ionizations. Again, no definitive assignment for the a_1- and b_2-type ionization may be made from these considerations because both the relative area of band 3 and the combined relative area of bands 6, 7, and 8 increase.

$CpFe(CO)_2CH_3$. As with the halide complexes, the electronic structure in the metal and methyl portion of $CpFe(CO)_2CH_3$ may be thought of in terms of a perturbation of the electronic structure of $Mn(CO)_5CH_3$ caused by substituting a cyclopentadienyl ring for three carbon atoms and changing the central metal atom from manganese to iron. Molecular orbital calculations have been performed at various levels of approximation for the purpose of investigating the electronic structure of $Mn(CO)_5CH_3$. The assignment of the low binding energy ionizations of $Mn(CO)_5CH_3$ has been a problem of considerable difficulty. Recently, three separate ionization peaks have been observed between 8.5 and 10 eV.[7]

In terms of the local C_{4v} symmetry of the $Mn(CO)_5$ portion of the molecule, all calculations predict one peak to be associated with ionization from the primarily metal e orbitals which are π in symmetry with respect to the metal–methyl bond. A second peak should correspond to ionization from the metal b_2 orbital, and a third to ionization from the metal–methyl σ bond, the a_1. All three ionization potentials are predicted to be close in energy, so that small deviations from Koopmans' theorem could reverse the order predicted by the eigenvalues of a ground state calculation. Also, two of the ionization peaks between 9 and 9.5 eV overlap substantially, and this precludes any opportunity of studying the separate ionization peak shapes. No definitive assignment could be made from these data.

In the photoelectron spectrum of $CpFe(CO)_2CH_3$, all the ionization bands are separated to a much greater extent. The curve fit photoelectron spectrum of $CpFe(CO)_2CH_3$ is illustrated in Figure 9. These results are summarized in Table VIII. The first ionization band is broadened and displays a distinct asymmetry. Like the band assigned as metal e ionizations in the $CpFe(CO)_2X$ spectra, this band is well represented by two equivalent peaks which are separated by 0.24 eV. Curve analysis of the next two ionization peaks indicates the band at 9.23 eV is relatively more symmetric and more intense than the band at 8.61 eV. This is consistent with assigning the band at 9.23 eV to ionization from the a_1-type orbital, and assigning the band at 8.61 eV to ionization from the metal b_2-type orbital. The shifts in ionization potential for these orbitals from $Mn(CO)_5CH_3$ to $CpFe(CO)_2CH_3$ are shown in Table IX. The ionization potentials of the peaks which are associated with primarily metal orbitals are observed to be shifted to lower binding energy by 0.6 eV or more. The ionization peak which is ascribed to ionization from the a_1 orbital shifts only 0.3 eV, thus providing further support for this assignment.

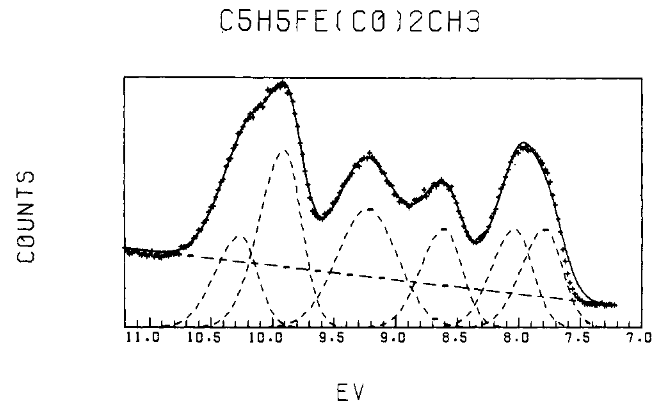

Figure 9. The plus signs are the data values, the dashed lines are the optimized Gaussian peaks and the baseline, and the solid line is the fit sum.

Table IX. Shifts in Ionization Potential (eV) from $Mn(CO)_5CH_3$ to $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$

$Mn(CO)_5CH_3$	9.56	9.22	8.65	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	9.23	8.61	8.03	7.99
Δ	0.33	0.61	0.62	0.86

The band at 10 eV has the characteristic shape which has been observed in the spectra of these complexes for ionization from the orbitals which are primarily e_1'' in character. The shoulder on this band is represented by a peak which is separated by 0.36 eV from the primary component. This separation is the same value that was found for this band in the spectrum of $CpFe(CO)_2I$.

Also recorded in Table IX are the areas of each ionization band relative to the total band area. The greater integrated intensity of the band assigned to ionization from the methyl a_1 orbital relative to individual peaks assigned to ionizations from orbitals which are primarily metal d in character is evident in this table. By either assignment this spectrum shows that ionization from an a_1-type orbital is not necessarily weak in intensity compared to ionizations from other orbitals. This has also been observed in the spectra of transition metal carbonyl amine and phosphine complexes.[9] Also, the total relative area of bands associated with metal d levels to bands associated with ring e_1'' levels is 1.07 to 1. This represents only a slight increase over the value of 0.94 to 1 observed for $CpMn(CO)_3$.

Discussion

Theoretical calculations, as shown in this work, are a valuable tool for providing insight into the ionization process. The implications of ionization data to molecular electronic structure must be carefully analyzed. Ab initio molecular orbital calculations on fundamental molecules provide a firm basis for interpretation. This knowledge may be expanded efficiently into new areas with approximate molecular orbital methods. Analysis of the spin-orbit multiplet observed in the ionization spectra of complexes containing third-row transition metal atoms is also found to give valuable additional information concerning ionizations which are associated primarily with the metal d electrons. The information obtained from these photoelectron spectra, quantum mechanical calculations, and previous studies of related systems has been combined to provide a consistent assignment of the ionizations of these d^6 transition metal cyclopentadienyl complexes. The fundamental bonding and electronic structure characteristics of these complexes have been outlined. It is helpful to review briefly the major points.

The primary bonding interaction between the metal and the ring is a π-type interaction. The orbitals that are involved are the filled e$_1''$ orbitals of $C_5H_5^-$ and the virtual metal d$_{xz}$-type and d$_{yz}$-type orbitals. The bonding combination of this interaction, which is largely localized on the ring, ionizes to produce a characteristic band envelope between 10 and 11 eV for these complexes. The sensitivity of the ionization potential of this band and the lack of sensitivity of the band area relative to the metal band area upon metal substitution is evidence that this ionization is also associated with appreciable metal character.

The ionizations associated predominantly with the metal d electrons are described as a$_1$-type and e-type ionizations. Analysis of the band shape in CpMn(CO)$_3$ and the spin-orbit splitting in CpRe(CO)$_3$ reveals that these ionizations must occur close in energy, with the a$_1$-type ionization at slightly higher binding energy than the e-type ionizations. The characters of these orbitals are expected to be intermediate between those of an octahedral metal carbonyl complex and those of a bis(η^5-cyclopentadienyl) complex. The slight lifting of degeneracy and the small shift in the metal ionizations relative to the ligand ionizations are helpful for providing a definitive assignment for the CpFe(CO)$_2$X ionizations. The trends within the series of complexes CpFe(CO)$_2$X parallel the trends in the series of complexes Mn(CO)$_5$X. It is for this reason that the study of the (η^5-cyclopentadienyl) complexes serves an important complementary role in the assignment and interpretation of the photoelectron ionizations of transition metal complexes. All these conclusions are predicted by the calculations and supported by experiment.

There is one final facet of the bonding descriptions of mixed (η^5-cyclopentadienyl) and carbonyl complexes which deserves mention. The relationship of carbonyl force constants to the σ-donor and π-acceptor ability of the carbonyl groups is well established.[36] In general, the force constant is lowered with increasing charge at the metal center and instability of the metal functions. The carbonyl force constants of the (η^5-cyclopentadienyl) complexes studied here are lower in each case than those of the hexacarbonyl or pentacarbonyl analogues. It has previously been concluded, therefore, that a net charge has been donated into the Mn(CO)$_3$ portion of the molecule from the ring.[49]

It would appear that the photoelectron ionizations of Cr(CO)$_6$ and (Cp)$_2$Fe would support this latter contention of strong electron donation from the ring since the ionization energies of the 3d iron electrons are lower than those of the 3d chromium electrons. However, ab initio calculations on the ground states of the neutral molecules[17,22] do not concur with this assumption. The iron atom is found to have a greater positive charge than the chromium atom, and the eigenvalues of the metal a$_{1g}$ and e$_{2g}$ levels of ferrocene are calculated to be 3-6 eV below the metal t$_{2g}$ levels of Cr(CO)$_6$. Most probably the trend in ionization potentials is a consequence of limitations in Koopmans' theorem. It is important to keep in mind that the calculations are a description of the ground state and the ionization potentials are dependent upon the ionic states as well.

Table X. Comparison of Carbonyl Force Constants and Calculated Carbonyl 2π Occupations

		Occupation[a]	Force constant[b]
Cr(CO)$_6$		0.512	16.49
Mn(CO)$_5$Cl[36]	cis	0.429	17.49
	trans	0.572	16.28
Mn(CO)$_5$Br[36]	cis	0.440	17.39
	trans	0.572	16.32
Mo(CO)$_5$I[36]	cis	0.453	17.29
	trans	0.572	16.37
Mn(CO)$_5$CH$_3$[25]	cis	0.468	16.82
	trans	0.549	16.11
(η^5-C$_5$H$_5$)Mn(CO)$_3$		0.618	15.84
(η^5-C$_5$H$_5$)Fe(CO)$_2$Cl[50]		0.517	16.58
(η^5-C$_5$H$_5$)Fe(CO)$_2$Br[50]		0.530	16.51
(η^5-C$_5$H$_5$)Fe(CO)$_2$I[50]		0.546	16.45
(η^5-C$_5$H$_5$)Fe(CO)$_2$CH$_3$[50]		0.535	15.77

[a] Via Mulliken analysis. [b] In mdyn/Å.

In actual fact, the trends in carbonyl force constants can be understood without invoking strong ring donation by examination of the results of the approximate calculations. In each case, the approximate calculations indicate that, in comparison to the carbonyl analogues, the metal orbitals of the (η^5-cyclopentadienyl) complexes are more stable and the metal center has a more positive charge, and yet the 2π occupations of the carbonyls have increased. These results are shown in Table X. In fact, from the results of the approximate calculations on Cr(CO)$_6$, Mn(CO)$_5$X, CpMn(CO)$_3$, and CpFe(CO)$_2$X, where X = Cl, Br, I, it is possible to estimate the force constants from the 2π occupations with a standard error of 0.11 mdyn/Å, which is on the order of the error in the force constants themselves.

The reason for this trend in force constants and populations becomes evident from a careful analysis of the interactions in the cyclopentadienyl complexes. As described earlier, the ring e$_1''$ levels interact strongly with the metal d$_{xz}$ and d$_{yz}$ orbitals. The interactions of the ring a$_{1u}''$ and e$_{2g}''$ levels with the metal d$_{z^2}$ and (d$_{x^2-y^2}$, d$_{xy}$) orbitals are relatively weak. The carbonyl π^* orbitals, on the other hand, accept primarily from the metal d$_{z^2}$ and (d$_{x^2-y^2}$, d$_{xy}$) orbitals. Thus, the cyclopentadienyl ring and the carbonyl groups are competing for back-bonding electrons from largely dissimilar metal orbitals. The replacement of three carbonyl groups with a cyclopentadienyl ring reduces the competition of the remaining carbonyl groups for π-back-bonding electrons. Thus, although the metal levels are stabilized, the π^* orbitals of the carbonyl groups are able to accept additional charge.

It is concluded, therefore, that the trends in ground state orbital eigenvalues indicated by these calculations are entirely reasonable. As also indicated by ab initio calculations on the positive ion states of ferrocene,[22] the trends in ionization potentials between these two series must be a result of a breakdown in the assumptions of Koopmans' theorem, most probably caused by electron rearrangement upon ionization. This is a point which requires further consideration. Nonetheless, these results indicate that special care must be exercised when interpreting the ionization spectra of transition metal complexes. Quantum mechanical calculations are especially helpful in sorting out those properties which are characteristic of the ground state electronic structure from those properties which are peculiar to the positive ion. Despite the fact that Koopmans' theorem is not exactly satisfied, a consistent description of the electronic structure of

Table XI. Spin–Orbit Interaction Matrix for d Functions in Units of ζ (+ and – refer to electron spin)

	$d_{z^2}{}^+$	$d_{x^2-y^2}{}^+$	$d_{xy}{}^+$	$d_{xz}{}^+$	$d_{yz}{}^+$	$d_{z^2}{}^-$	$d_{x^2-y^2}{}^-$	$d_{xy}{}^-$	$d_{xz}{}^-$	$d_{yz}{}^-$
$d_{z^2}{}^+$	0								$-\sqrt{3}/2$	$i\sqrt{3}/2$
$d_{x^2-y^2}{}^+$		0	$-i$						$1/2$	$i/2$
$d_{xy}{}^+$		i	0						$-i/2$	$1/2$
$d_{xz}{}^+$				0	$-i/2$	$\sqrt{3}/2$	$-1/2$	$i/2$		
$d_{yz}{}^+$				$i/2$	0	$-i\sqrt{3}/2$	$-i/2$	$-1/2$		
$d_{z^2}{}^-$				$\sqrt{3}/2$	$i\sqrt{3}/2$	0				
$d_{x^2-y^2}{}^-$				$-1/2$	$i/2$		0	i		
$d_{xy}{}^-$				$-i/2$	$-1/2$		$-i$	0		
$d_{xz}{}^-$	$-\sqrt{3}/2$	$1/2$	$i/2$						0	$i/2$
$d_{yz}{}^-$	$-i\sqrt{3}/2$	$-i/2$	$1/2$						$-i/2$	0

these complexes may be obtained from the sum total of information. Many interesting ligand systems bond with (η^5-cyclopentadienyl) metal complexes to form compounds which are stable and volatile enough to allow study by He(I) photoelectron spectroscopy. This work opens the door for the investigation of these species.

Acknowledgment. The authors wish to thank Dr. M. B. Hall for his assistance in analyzing the spin–orbit interactions and for many additional helpful discussions. The authors also wish to thank Dr. T. H. Whitesides for supplying the sample of η^5-$C_5H_5Re(CO)_3$. This work was supported by the National Science Foundation (Grant GP-27636). D.L.L. also acknowledges an NDEA Title IV Fellowship (Grant 69-03546.1).

Appendix

Interpretation of the Effects of Spin–Orbit Interaction in Photoelectron Spectra. The spin–orbit interaction in transition metal ions has been discussed previously.[46] Here we are concerned with interpreting the multiplet of ionization peaks which result from ionization of a neutral closed-shell ground-state molecule. In this case, the multiplet structure is due to the interaction of spin and orbital angular momentum in the positive ion states. For transition metal complexes, this interaction becomes important for metals in the third row. The observed multiplet pattern is dependent upon the magnitude of the spin–orbit coupling and the characters and relative energies of the positive ion states. Often, the multiplet pattern will provide unique information regarding these latter quantities.

Within the framework of Koopmans' theorem, an analysis of the spin-orbit interaction in terms of a molecular orbital description of the ground-state wave function is equivalent to an analysis in terms of a configuration interaction treatment of the positive ion states.[51] In the first case, Koopmans' theorem is used to relate the orbital eigenvalues to the ionization potentials, and in the second case the ion configurations are Koopmans' configurations. As will be seen, the role of electron rearrangement in the positive ions may also be partially incorporated into the orbital description. We will limit ourselves to the case of a complex with a single transition metal atom with an appreciable spin-orbit coupling parameter, ζ, and apply these results to the spectrum of $CpRe(CO)_3$.

The full d-d spin-orbit interaction matrix is given in Table XI. If the atomic value of ζ is known, and if the orbital description of the ground state of the molecule before consideration of the spin-orbit interaction is known, the multiplet structure may be predicted. This is accomplished by first forming a matrix C, the columns of which are the atomic expansion coefficients of each molecular spin orbital. (The spin-up component of a particular orbital defines one column, and the spin-down component defines a second.) The full spin-orbit interaction matrix is then transformed to this basis. The Fock matrix may be added to this interaction matrix. By the definition of these canonical orbitals, the Fock matrix contributes to the diagonal elements only. The eigenvalues which result from diagonalization of this matrix occur in degenerate pairs. These eigenvalues are interpreted in the usual manner via Koopmans' theorem.

Generally, however, the exact value of ζ or the character of the orbitals is not known. For these cases, the solution of the problem may be slightly reformulated so that the multiplet pattern provides information regarding these quantities. First of all, only those orbitals with appreciable metal character are treated explicitly, for these are the only orbitals with appreciable spin-orbit interaction terms. Secondly, these orbitals are treated as though they are completely localized metal d in character and are normalized. The delocalization of these orbitals is accounted for by allowing each spin-orbit coupling parameter between orbitals to be a variable. The variation of this parameter also allows for some differences between the ground state and the positive ion states. The matrix equations are then solved with the variables defined by a particular problem to reproduce the observed splitting pattern.

Consider for the moment a d^6 metal system in C_{3v} symmetry in which the metal orbitals have the form

$$a_{1g}\text{-type } d_{z^2}$$

and

$$\begin{aligned}\text{e-type } &\sqrt{1/(1+x)}\,d_{x^2-y^2} + \sqrt{x/(1+x)}\,d_{xz}\\ &\sqrt{1/(1+x)}\,d_{xy} - \sqrt{x/(1+x)}\,d_{yz}\end{aligned} \qquad \text{(A-1)}$$

where x is variable.

The full spin-orbit interaction matrix is, in units of ζ,

$$\begin{array}{cccc} & e^+{}_{(x^2-y^2,xz)} & e^+{}_{(xy,yz)} & a_1{}^- \\ e^+{}_{(x^2-y^2,xz)} & 0 & -\frac{i}{2}\frac{2-x}{1+x} & \frac{\sqrt{3}}{2}\frac{x}{1+x} \\ e^+{}_{(xy,yz)} & \frac{i}{2}\frac{2-x}{1+x} & 0 & i\frac{\sqrt{3}}{2}\frac{x}{1+x} \\ a_t{}^- & \frac{\sqrt{3}}{2}\frac{x}{1+x} & -i\frac{\sqrt{3}}{2}\frac{x}{1+x} & 0 \end{array} \qquad \text{(A-2)}$$

Where + and – signs on the orbitals refer to electron spin. The block of opposite spin has elements which are the negative of these.

These spin–orbit interactions are more easily understood if an initial step in the diagonalization is taken. In terms of the combinations

$$\begin{aligned} e'^+ &= \frac{1}{\sqrt{2}}e^+{}_{(x^2-y^2,xz)} + ie^+{}_{(xy,yz)}\\ e''^+ &= \frac{1}{\sqrt{2}}e^+{}_{(x^2-y^2,xz)} - ie^+{}_{(xy,yz)} \end{aligned} \qquad \text{(A-3)}$$

the spin-orbit interaction matrix, in units of ζ, is

$$\begin{array}{cccc} & e'^{+} & e''^{+} & a_1^{-} \\ e'^{+} & \frac{1}{2}\frac{2-x}{1+x} & 0 & \sqrt{3/2}\sqrt{x/(1+x)} \\ e''^{+} & 0 & -\frac{1}{2}\frac{2-x}{1+x} & 0 \\ a_1^{-} & \sqrt{3/2}\sqrt{x/(1+x)} & 0 & 0 \end{array} \qquad \text{(A-4)}$$

It is interesting to note that this single spin-orbit interaction matrix embodies the interactions observed for both osmocene and tungsten hexacarbonyl. The orbitals represent the a_{1g} and e_{2g} combinations of osmocene when the value of x equals zero. The spin-orbit interaction matrix for this case, including the diagonal elements of the Fock matrix, becomes

$$\begin{array}{cccc} & e'^{+} & e''^{+} & a_{1g}^{-} \\ e'^{+} & \epsilon(e_{2g}) + \zeta & 0 & 0 \\ e''^{+} & 0 & \epsilon(e_{2g}) - \zeta & 0 \\ a_{1g}^{-} & 0 & 0 & \epsilon(a_{1g}) \end{array} \qquad \text{(A-5)}$$

Thus the e_{2g} components are split by 2ζ, and the a_{1g} component does not interact directly. From the multiplet pattern in the spectrum of Cp_2Os,[12] the most reasonable assignment appears to be that the highest and lowest peaks of the multiplet correspond to the split e_{2g} states, giving a spin-orbit coupling parameter for osmium in the complex of 0.31 eV. This value is slightly smaller than the expected atomic value of 0.33 to 0.43 eV, presumably because of orbital delocalization in the complex.

If the value of $x = 0.5$, the orbitals form a set which corresponds to the t_{2g} combinations of $W(CO)_6$. In this case the interaction matrix, with the diagonal elements of the Fock matrix, is

$$\begin{array}{cccc} & e'^{+} & e''^{+} & a_1^{-} \\ e'^{+} & \epsilon(t_{2g}) + {}^{1}/_{2}\zeta & 0 & \sqrt{1/2}\zeta \\ e''^{+} & 0 & \epsilon(t_{2g}) - {}^{1}/_{2}\zeta & 0 \\ a_1^{-} & \sqrt{1/2}\zeta & 0 & \epsilon(t_{2g}) \end{array} \qquad \text{(A-6)}$$

Thus the e′ and e″ levels are initially split by ζ. Further interaction of the e′ level with a_1^- produces an e″ level which is separated by ${}^{3}/_{2}\zeta$ from the u′ level (e″ and a_1^- originally). The observed separation of these levels in $W(CO)_6$[4] of 0.26 eV corresponds to a spin-orbit coupling parameter of about 0.18 eV. This example may be extended to C_{4v} complexes by allowing the diagonal energy of the a_1^- level to be different than the diagonal energies of the other two. This introduces the additional parameter, Δ, which represents the difference in energy between the e and b_2 levels of a C_{4v} complex before spin-orbit interaction. This example has been discussed in detail by Hall.[47]

In the more complex case of $CpRe(CO)_3$, the exact value for x for the e-type orbitals is not known. In addition, the separation in energy between the a_1-type and e-type orbitals before spin-orbit interaction is not known, and the value of the spin-orbit coupling parameter for rhenium is uncertain. Furthermore, three different assignments for the origins (whether primarily from e-type or primarily from a_1-type orbitals) of the three peaks in the multiplet pattern are conceivably possible. With these four degrees of freedom, an infinite number of solutions for the observed three-peak multiplet pattern are possible.

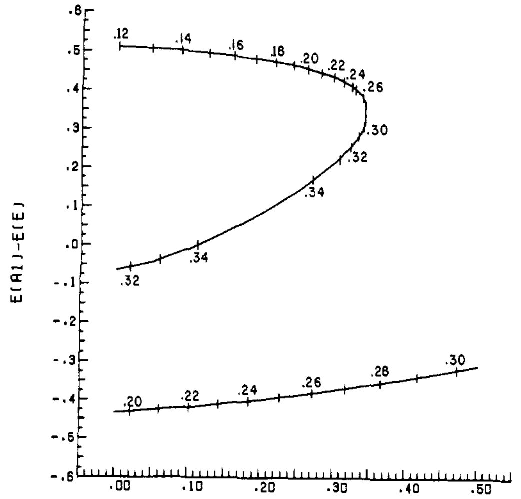

Figure 10. Solutions for the multiplet pattern in the ionization spectrum of $(\eta^5\text{-}C_5H_5)Re(CO)_3$. The values on the curves correspond to the spin-orbit coupling parameter ζ. The variable x defines the (e_{2g},t_{2g})-type orbitals $\sqrt{1/(1+x)}d_{xy} + \sqrt{x/(1+x)}d_{xz}$ and $\sqrt{1/(1+x)} - \sqrt{x/(1+x)}d_{yz}$. The ordinate represents the difference in eigenvalues of the e- and a_1-type orbitals before spin-orbit interaction.

In Figure 10 the solutions of the multiplet pattern of $CpRe(CO)_3$ for values of x ranging from 0 to 0.5 are illustrated. The ordinate represents the difference in energy between the e-type and a_1-type orbitals before spin-orbit interaction, and the spin-orbit coupling parameter is indicated along each curve. It should be stressed that the parameters associated with each point on these curves reproduce the observed splitting pattern.

Many of the solutions depicted in Figure 10 may be ruled out by considering the likely range of parameter values. First, consider the spin-orbit coupling parameter. From photoelectron studies[47] on $Re(CO)_5X$ complexes where X = H, CH_3, $COCF_3$, Cl, Br, and I, the spin-orbit coupling parameter for rhenium is found to range from 0.23 to 0.26 eV. This is also intermediate between the value of 0.18 for tungsten from $W(CO)_6$ and the value of 0.31 for osmium from $(\eta^5\text{-}C_5H_9CH_3)_2Os$. From the solutions illustrated in Figure 10, this value of ζ does indeed indicate that the e-type orbitals are intermediate in character from e_{2g}-type of osmocene to t_{2g}-type of $W(CO)_6$. Two solutions are possible for the ordering of the a_1- and e-type orbitals which are consistent with this range of spin-orbit coupling values. One solution places the a_1-type orbital above the e-type orbital by about 0.4 eV, and the character of the e-type orbital tends toward the t_{2g}. The solutions in this region are extremely sensitive to small perturbations in the variables. The other solution places the a_1-type orbital below the e-type by about 0.4 eV, and the character of the e-type orbital tends toward e_{2g}. As discussed previously, the interactions of the metal with the carbonyl groups and the cyclopentadienyl ring indicate that the e-type orbitals will tend toward the e_{2g} character. Also, experience with the $Re(CO)_5X$ photoelectron spectra has indicated that the splitting pattern of the ionizations before spin-orbit interaction in these complexes closely reproduces the splitting pattern in the analogous $Mn(CO)_5X$ spectra.[47] If the a_1-type ionization occurred 0.3–0.4 eV before the e-type ionization in $\eta^5\text{-}C_5H_5Mn(CO)_3$, the splitting of the ionization peaks would probably be resolved and would certainly not account for the band shape observed in this spectrum.

The solutions displayed in Figure 10 may be altered somewhat if the positive ions have much different localization properties from each other. The calculations on the ground state of $CpMn(CO)_3$, however, indicate that the characters should be quite similar, and ab initio calculations on positive ions formed by removal of a d electron from ferrocene indicate that the positive ions have more similarly localized d orbitals than ferrocene itself. Interactions with other orbitals and higher-order effects have also been assumed to be small in this analysis. In any event, the bulk of the evidence indicates that ionizations from orbitals which are primarily metal d in character occur close in energy, and that ionization from the a_1-type orbital probably follows ionization from the e-type orbitals by no more than a few tenths of an electron volt.

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Thermolysis of Diene Iron Tricarbonyl Complexes. Cis–Trans Isomerization and Hydrogen Scrambling Reactions in Cyclic and Acyclic Complexes

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Received March 24, 1975

Abstract: The thermolysis of several cyclic and acyclic diene iron tricarbonyl complexes has been investigated. On heating (*trans,cis*-1,5-diphenylpentadiene)iron tricarbonyl (*cis*-**3**) in benzene two competing reactions were observed: metal epimerization (leading to racemization and exo-endo scrambling) and isomerization to the trans,trans isomer (*trans*-**3**). On the basis of kinetic and labeling studies a mechanism for these reactions involving a coordinatively unsaturated dihapto iron tricarbonyl complex is proposed. Only 1,3-shifts of hydrogen were detected, presumably due to the formation of a π-allyl metal hydride intermediate. When the cyclic species were subjected to the same reaction conditions, 1,5-hydrogen shifts were observed. When the cyclic complex contained an aromatic substituent, metal epimerization was observed as well. These reactions are postulated to involve consecutive 1,3-hydrogen migrations and coordination of the iron to the aromatic ring, respectively. As suggested by earlier work, there is no necessity to postulate any concerted $[1,n]$, $n = 3, 5$, sigmatropic migration of hydrogen: all of the reactions can be consistently explained on the basis of known intermediates.

The question of the mechanism of hydrogen migrations catalyzed by transition metals is of substantial practical and theoretical interest. Hydrogen migration reactions can either be a limitation on the synthetic usefulness of a given catalytic process, leading to mixtures of products,[1] or a powerful synthetic tool,[2] allowing novel transformations not