extensive listing of intrinsic proton binding tendencies at N(1) and N(7) of purines. The N(1)/N(7) intrinsic binding ratio for protons is 2 log units greater for the 6-oxopurines than for adenosine.

The N(1) to N(7) dienPd^{2+} binding ratios in the last column of Table VI have ramifications for the ligand distribution curves. The relatively pronounced favoring of N(1) for IMP and inosine in Figures 9 and 10 results in BM_1 clearly predominating over M_7B^- in basic solutions. In contrast the negative logarithm for GMP in Table VI means that the mole fraction of M_7B^- exceeds that for BM_1 and no crossover occurs; the N(7) metalated complex predominates at all pH values. Basic solutions of GMP and dienPd^{2+} contain a mixture of four species, all present in significant amounts.

The intrinsic N(1)/N(7) binding ratios of Table VI show quantitatively that the tendency to favor N(1) over N(7) is $H^+ > CH_3Hg^+ > Pd(II)$. Indeed for dienPd^{2+}, the binding constant at N(7) is often comparable to or even exceeds that at N(1). For inosine the crossover pH, where the M_7BH_1 and BM_1 mole fractions are equal, occurs at pH 6.1 with dienPd^{2+}, 1.8 log units higher than with CH_3Hg^+, which is due to the lesser N(1)/N(7) binding ratio for dienPd^{2+}.

For AMP the values of log (K_1/K_7) and log (K_1'/K_7') are –0.1 and 0.4, respectively, the primes referring to phosphate protonated species. Compared to the monoanionic phosphate, the dianionic phosphate group favors dienPd^{2+} binding at N(7) over N(1). Thus there are two crossovers between N(7) and N(1) metalated species for AMP in Figure 11. The first crossover appears at pH 2.2 as $M_7BH_1H_P$ gives way to BM_1H_P when dienPd^{2+} successfully competes with H^+ for N(1). The maximum role fraction of BM_1H_P occurs near pH 5. Phosphate deprotonation near pH 6 yields a crossover close to pH 7, above which M_7B predominates marginally over BM_1 according to the –0.1 entry in the last column of Table VI.

We now compare the order of nucleotide binding strengths of dienPd^{2+} with the proton and CH_3Hg^+, the only other metal for which a series of reliable values exists. As previously, we designate the nucleoside by its capitalized first letter and the nitrogen binding site by the usual numbering scheme.[2] The order of decreasing proton binding strengths is then T3 > U3 > G1 > I1 ≫ C3 > A1 > G7 > I7 > A7. The order of CH_3Hg^+ is similar, with a promotion of G7 and I7 to greater than A1. These two sites undergo further significant promotion in the series for decreasing dienPd^{2+} stability constants T3 > U3 > I1 > G7 > G1 > I7 ≫ C3 > A1 > A7 with A1 and A7 now of comparable magnitude. Because of the proton at N(1) in purines and N(3) in pyrimdines the stability order, as opposed to stability constants, is pH dependent. At pH 7 the stability order for dienPd^{2+} becomes G7 > I7 > I1 > G1 > U3 > T3 > C3 > A1 > A7. This order agrees with that observed in neutral solutions of nucleotide mixtures.[7] Thus N(7) of GMP and IMP offers the strongest effective nucleic base binding site for dienPd^{2+} in neutral solutions.

The Effects of Methyl Group Substitution on Metal-Coordinated Cyclopentadienyl Rings. The Core and Valence Ionizations of Methylated Tricarbonyl(η^5-cyclopentadienyl)metal Complexes

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Abstract: Gas-phase He I, He II, and Mg Kα photoelectron spectra are reported for molecules of the type $(\eta^5\text{-}C_5H_{5-n}(CH_3)_n)M(CO)_3$ where n = 0, 1, 5 and M = Mn, Re. The influence of methyl groups on the cyclopentadienyl ring is monitored by shifts in both core and valence ionization energies. This enables effective separation of electron density transfer (inductive) and ring-methyl orbital overlap (hyperconjugative) effects. While the shift in the ring e_1'' ionization is found to be primarily a hyperconjugative effect, the shift in the metal valence ionizations is caused essentially entirely by a shift of electron density toward the metal atom. A greater proportion of this increased density is transferred to the carbonyls in the rhenium complexes than in the manganese complexes, indicating the greater back-bonding ability of the third-row atom. Further evidence of extensive Re–CO back-bonding is provided by the presence of vibrational fine structure on one of the predominantly metal ionizations of the rhenium complexes. This structure is the vibrational progression of the symmetric metal–carbon(CO) stretching mode. The long vibrational progression observed in this band and the frequency of the M–C stretch in the positive ion are direct evidence of considerable π back-bonding from the metal to the carbonyls. The observed vibrational structure in the spin–orbit split rhenium d ionizations also leads to a definitive interpretation of the pattern of metal ionizations in such complexes. The origin of the characteristic splitting of the predominantly ring e_1'' ionization is also considered in detail. The data suggest that the carbon–carbon bond distances in the ring are distorted an average of 0.01 to 0.02 Å from fivefold symmetry when coordinated to a d^6 ML_3 species. This is the first indication from gas-phase spectroscopy for such distortions.

The cyclopentadienyl ring ligand has played an important role in the development of organometallic chemistry since the discovery of ferrocene in 1952. The significance of the cyclopentadienyl ligand has stimulated interest in investigating the chemistry of other closely related ligands, such as rings in which one or more of the hydrogen atoms are substituted by other groups.[1] The most useful developments in this direction have been the synthesis of pentamethylcyclopentadienyl complexes, many of which are analogous to the well-known sandwich and half-sandwich compounds. Although at first glance the permethylation of cyclopentadienyl rings might appear to be a relatively minor alteration, it has proven to be a useful perturbation for mechanistic studies and has uncovered a significantly different chemistry in many systems.[1-3] For instance, the permethylated analogues have

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exhibited altered crystallization characteristics,[4] solubilities,[2a,5] tendencies to form metal–metal bonds,[1,4a,5] stabilities,[2a] susceptibility to attack,[3] sensitivity to oxidation,[6,7] etc. Some of the changes in behavior of pentamethylcyclopentadienyl complexes may be attributed to the steric protection provided by the five ring methyl groups and by the chemically different hydrogen atoms present. Another very important factor is the apparent increased electron density and donor strength of the permethylated ring. One example is the low oxidation potential of decamethylferrocene and its spontaneous oxidation in air, in contrast to the air stability of ferrocene.[7]

Photoelectron spectroscopy is currently the best method for quantitatively measuring substituent effects on gas-phase oxidation potentials and ionization energies. Some valence-only ionization studies of ring methylation in bis(cyclopentadienyl metal) complexes have recently been reported.[8,9] We have also previously reported the UPS of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$[10] and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$[11] and comments have been made on the change in valence metal and ring ionizations between these complexes.[11,12] These valence ionizations are found to decrease in energy with ring methylation, and this is generally interpreted in terms of a greater electron-releasing or inductive effect of the methyl groups that increase the electron charge in the ring, thereby increasing the ring's net "basicity".[1,8,9] This interpretation is not entirely consistent with theoretical expectations.[13] One problem with the valence-only studies in this regard is that valence ionization energies are sensitive to other factors in addition to the charge distribution in the molecule. In this paper we present a combined core and valence ionization study of a series of cyclopentadienyl metal carbonyl compounds with different degrees of ring methylation. These complexes will illustrate how comparison of gas-phase core and valence ionization energy shifts provides a more detailed and consistent description of the electronic changes that occur. The electron-releasing nature of the methyl groups is found to be a minor effect.

An additional interesting result of these ionization studies concerns the proposed distortion from fivefold symmetry for coordinated cyclopentadienyl rings.[14] Ring distortions have previously been implicated by IR,[15] Raman,[15] NMR,[16] and low-temperature crystal structure results.[18] The valence ionizations examined in this paper indicate that these distortions are also present when the molecules are in the gas phase.

These complexes are the foundation for the description of a significant class of organometallic complexes with different molecules and molecular fragments bound to the metal. A detailed knowledge of the effects of ring methylation on electron distribution, bonding, and ionization characteristics of the present systems is essential for later investigations. The next paper in this series[17] will demonstrate how the spectral changes caused by cyclopentadienyl methylation can be used as a valuable assignment and interpretation aid in related $(\eta^5\text{-cyclopentadienyl})M(CO)_2$(ligand) complexes.

Experimental Section

Photoelectron Spectra. All UPS and XPS spectra were measured with use of a McPherson ESCA 36 electron spectrometer. Different experimental arrangements such as custom designed sample cells, excitation source hardware, differential pumping, etc., were employed according to the individual requirements of the gas-phase He I, He II, and Mg Kα techniques.

He I. Samples were run from a variable temperature sample cell of our own design. Spectra of the Mn compounds were obtained at room temperature, while the Re compounds required heating to 50–60 °C. The argon $2p_{3/2}$ ionization at 15.76 eV was used as an internal lock during data acquisition to ensure that spectral drift was less than ±0.005 eV during time averaging of repetitive scans. The resolution (fwhm of Ar $2p_{3/2}$ ionization) was less than 0.025 eV. Resolution was maintained at 0.017 eV during observation of the vibrational structure in the ionizations of the rhenium complexes.

He II. Samples were handled similarly in the He II studies. The He II radiation source was a differentially pumped, charged particle oscillator-type lamp based on designs previously described.[19]

Mg Kα. For the gas-phase XPS experiments we constructed a windowed, temperature controlled, sample cell that allowed effective vapor isolation from the X-ray source. The temperature was controlled for sample pressures of 0.01–0.05 torr. Argon pressure of 0.01 torr was run simultaneously with all samples as a co-calibrant. The spectrometer was periodically calibrated to the C(1s) and O(1s) ionizations of CO_2.[20,21] The internal argon standarization along with the kinetic energy calibration gives excellent self-consistency and good agreement with core ionization energies for hydrocarbons previously reported.[21] The binding energy of each core ionization peak was determined from a symmetric curve fit of the band, which is more precise than simply locating the top of the band. The standard deviation for each binding energy was determined from repeating each experiment three to six times. The standard deviation in ionization energies was typically 0.02–0.03 eV. In the case of carbon 1s of CO, which partly overlaps with the carbon 1s of Cp and CH_3, the deviation was occasionally as high as 0.05 eV.

Data Reduction. Peak positions and relative intensities were obtained by a previously described[10] asymmetrical Gaussian curve fit with the functional form:

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

where $C(E)$ = electron counts at binding energy E; A = peak amplitude; P = peak position (vertical IP); $W = W_h$, the half-width for $E > P$, or W_l, the half-width for $E < P$; $k = 4 \ln 2$.

Preparation of Compounds. $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ was purchased from Strem Chemical Co., and $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$ was a gift from Ethyl Corp. These compounds were respectively sublimed and distilled prior to recording their spectra. $(\eta^5\text{-}C_5H_5)Re(CO)_3$ was prepared by published methods[22] and was purified by sublimation. Two different methods were used to prepare $(\eta^5\text{-}C_5(CH_3)_5)Mn(CO)_3$. Method A is a high-pressure synthesis completely analogous to the synthetic route for $(\eta^5\text{-}C_5H_5)Mn(CO)_3$.[23] Method B is a variation of an earlier reported route using a sealed-tube reaction.[24] Method B was also used for the preparation of $(\eta^5\text{-}C_5(CH_3)_5)Re(CO)_3$. Pentamethylcyclopentadiene was prepared according to the literature.[25]

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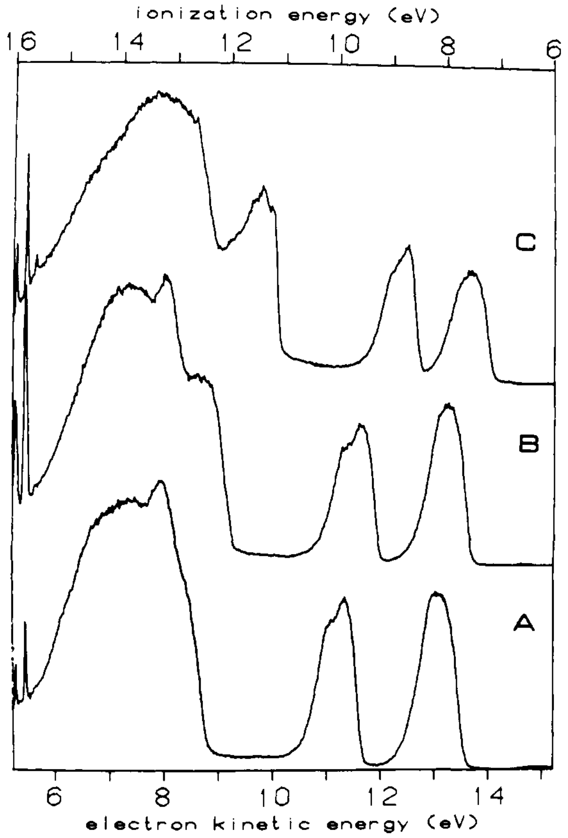

Figure 1. The He I photoelectron spectra of (A) $CpMn(CO)_3$, (B) $MeCpMn(CO)_3$, and (C) $Me_5CpMn(CO)_3$.

Method A. $(\eta^5\text{-}C_5(CH_3)_5)Mn(CO)_3$. A 300-mL high-pressure reactor was charged with 4.0 g (29.4 mmol) of $C_5(CH_3)_5H$, 7.0 g (24.7 mmol) of py_2MnCl_2, 2.0 g (83.4 mmol) of activated magnesium turnings, and 100 mL of DMF. The reactor was purged with H_2 and then pressurized with 750 psi of H_2 and 1200 psi of CO. The reactor was then heated to 180 °C, pressurized to a total pressure of 4500 psi with CO, and stirred at these conditions for 15 h. After cooling, the dark brown slurry was transferred to a 300-mL, three-neck flask, quenched with 30 mL of water, and steam distilled. The product condensed as either bright yellow crystals or a yellow oil floating on top of the water in the reception flask. The oil was purified by column chromatography (18 × 2.0 cm) in hexane on activated alumina. Further purification was accomplished by vacuum sublimation at 50 °C. Total yield was 0.39 g (5.7%); ν_{CO} (hexane) 2000 (s) and 1915 cm^{-1} (s).

Method B. $(\eta^5\text{-}C_5(CH_3)_5)Mn(CO)_3$. To a 15-mL sealed-tube reactor (Diels–Alder tube) was added a magnetic stirrer bar, 0.5 g (1.28 mmol) of $Mn_2(CO)_{10}$, 5.0 g (36.8 mmol) of $C_5(CH_3)_5H$, and 2.0 mL of cyclooctane. After being sealed and purged with Ar, the tube was heated to 160 °C and stirred with periodic pressure venting. When the ν_{CO} IR bands of $Mn_2(CO)_{10}$ had disappeared, the reaction was stopped (10 h). The brown solution was chromatographed in THF on alumina to give a yellow solution. After solvent removal the product was recrystallized from heptane to yield 0.23 g (32.8%) of the bright yellow, air-stable crystalline product.

Method B. $(\eta^5\text{-}C_5(CH_3)_5)Re(CO)_3$. A sealed tube was charged with 0.5 g (0.77 mmol) of $Re_2(CO)_{10}$ and 4.0 g (29.4 mmol) of $C_5(CH_3)_5H$. After being sealed and Ar purged, the contents of the tube was stirred at 160 °C. After 8 h the ν_{CO} peaks of $Re_2(CO)_{10}$ had disappeared. After the solution was cooled, a white solid precipitated which was recrystallized from hexane to give the colorless, crystalline product ν_{CO} (hexane) 2015 (s) and 1925 cm^{-1} (s).

Results

The He I photoelectron spectra of $CpMn(CO)_3$, $MeCpMn(CO)_3$, and $Me_5CpMn(CO)_3$ are presented in Figure 1. In this notation Cp is $\eta^5\text{-}C_5H_5$, MeCp is $\eta^5\text{-}C_5H_4CH_3$, and Me_5Cp is $\eta^5\text{-}C_5(CH_3)_5$. The general shift of the ionizations to lower binding energy with increasing ring methylation can be seen. All three spectra have three major ionization regions in agreement with expectations based on molecular orbital theory.[10,26,27] The broad, intense band from 16 to 12 eV results from the overlap of CO 5σ and 1π, and ring σ and $a_2''(\pi)$ ionizations. The large number of closely spaced orbitals in this region makes meaningful interpretation difficult. A distinct shoulder between 11 and 13 eV is present in the methyl-substituted compounds. This peak increases in intensity and shifts to lower energy with an increase in the number of ring methyl groups, suggesting ionization from an orbital which is high in ring methyl character. The two lowest binding energy bands at 9.0–10.5 eV and 7.5–8.5 eV exhibit the greatest sensitivity to ring methylation in these systems. The results of curve-fit analyses of these two bands are shown in Figure 2 and the peak parameters are listed in Table I. The ionization

Table I. He I Ionization[a]

	vertical ionization energy, eV	W_h	W_l	relative amplitude	relative area
$C_5H_5Mn(CO)_3$	8.05	0.60	0.37	1.0	0.49
	8.40	0.60	0.37	0.6	
	9.90	0.50	0.33	1.21	0.51
	10.29	0.50	0.33	0.71	
$CH_3C_5H_4Mn(CO)_3$	7.89	0.65	0.38	1.0	0.52
	8.23	0.65	0.38	0.5	
	9.57	0.57	0.36	0.96	0.48
	10.00	0.57	0.36	0.57	
$(CH_3)_5C_5Mn(CO)_3$	7.46	0.54	0.38	1.0	0.50
	7.82	0.54	0.38	0.6	
	8.72	0.64	0.25	1.27	0.50
	9.09	0.64	0.25	1.41	
$C_5H_5Re(CO)_3$	8.05	0.40	0.19	1.0	0.60
	8.44	0.52	0.18	1.30	
	8.72	0.52	0.18	0.53	
	10.11	0.67	0.31	0.84	0.40
	10.54	0.67	0.31	0.41	
$(CH_3)_5C_5Re(CO)_3$	7.57	0.42	0.21	1.0	0.58
	7.92	0.50	0.16	1.13	
	8.23	0.50	0.16	0.59	
	9.07	0.55	0.27	1.08	0.42
	9.42	0.55	0.27	0.48	

[a] W_h and W_l are the high and low binding energy half-widths as defined in the experimental section.

Table II. The Measured Splittings in the Cp e_1'' Ionization (eV)

complex	splitting, eV	reference
$CpMn(CO)_3$	0.39	this work
$MeCpMn(CO)_3$	0.43	this work
$Me_5CpMn(CO)_3$	0.37	this work
$CpRe(CO)_3$	0.43	this work
$Me_5CpRe(CO)_3$	0.35	this work
$MeCpMn(CO)_2(C_2H_4)$	0.46	17
$MeCpMn(CO)_2(C_3H_6)$	0.42	17
$Me_5CpMn(CO)_2(C_2H_4)$	0.38	17
$CpMn(CO)_2SO_2$	0.43	11
$MeCpMn(CO)_2SO_2$	0.42	11
$CpMn(CO)_2N_2$	0.39	28
$CpMn(CO)_2CS$	0.36	29
$CpFe(CO)_2I$	0.36	10
$CpFe(CO)_2CH_3$	0.36	10
$CpCr(CO)_2NO$	0.38	30
$CpCr(CO)_2NS$	0.42	30

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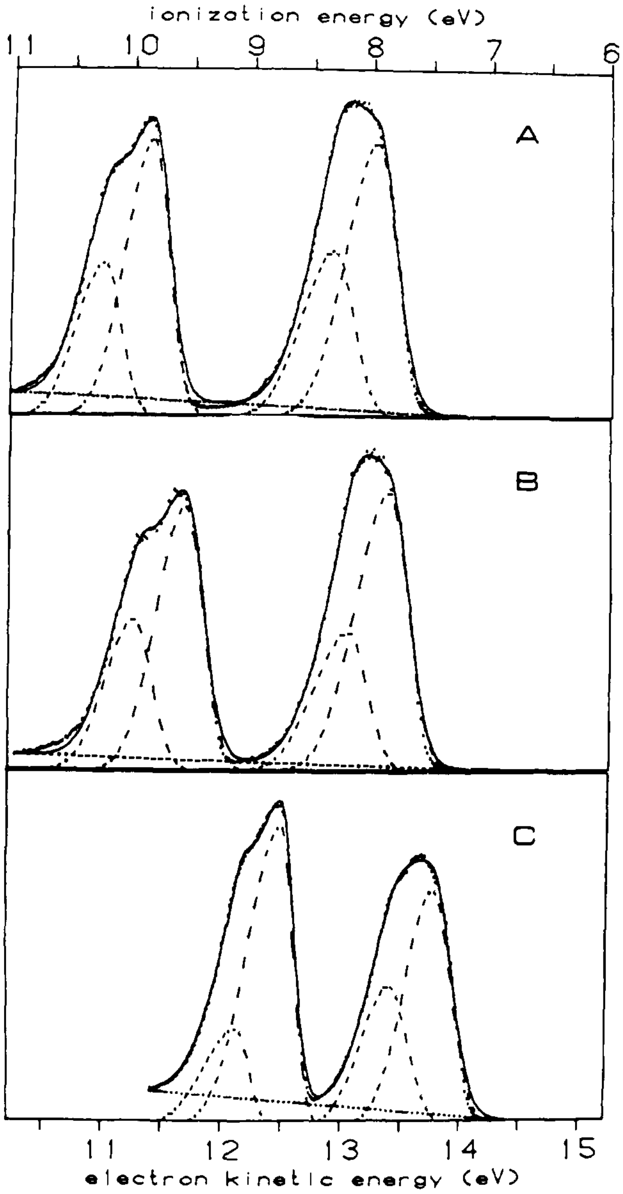

Figure 2. Low ionization energy He I spectra of (A) $CpMn(CO)_3$, (B) $MeCpMn(CO)_3$, and (C) $Me_5CpMn(CO)_3$.

band at 9.0–10.5 eV has previously been assigned to the predominantly ring e_1'' ionization. This band has a shoulder on its high binding energy side that has been observed in the spectra of a large number of cyclopentadienyl-containing compounds. The consistency of the splitting in this band for a variety of d^6 $CpM(CO)_2L$ complexes is shown in Table II. This distinctive bandshape will be one focal point of the discussion.

Figure 3 illustrates the differences in relative band intensities in the He I and He II spectra of these complexes. In Figure 3 the He I and He IIα spectra are corrected for the increased analyzer transmission at higher spectra energy. The He IIα spectrum is also corrected for secondary He IIβ and He IIγ emissions in the source. It is clear that the first ionization band, from 7.5 to 8.5 eV, increases in intensity relative to the band in the 9.0 to 10.5 eV region. By analogy with the spectra of other metal complexes, this indicates that the first band is from an orbital which is high in metal d character.[31]

The He I spectra of $CpRe(CO)_3$ and $Me_5CpRe(CO)_3$ in Figure 4 provide further peak assignment information. These spectra have the same general features as their Mn analogues except for the considerable splitting observed in the lowest energy ionization. This splitting can be attributed to spin–orbit coupling in the third-row metal,[10,32] and is an additional indication of high metal character in this ionization. The increased relative intensity of this band also reflects the known larger metal d ionization cross-section for third-row metals compared to first-row metals.[33]

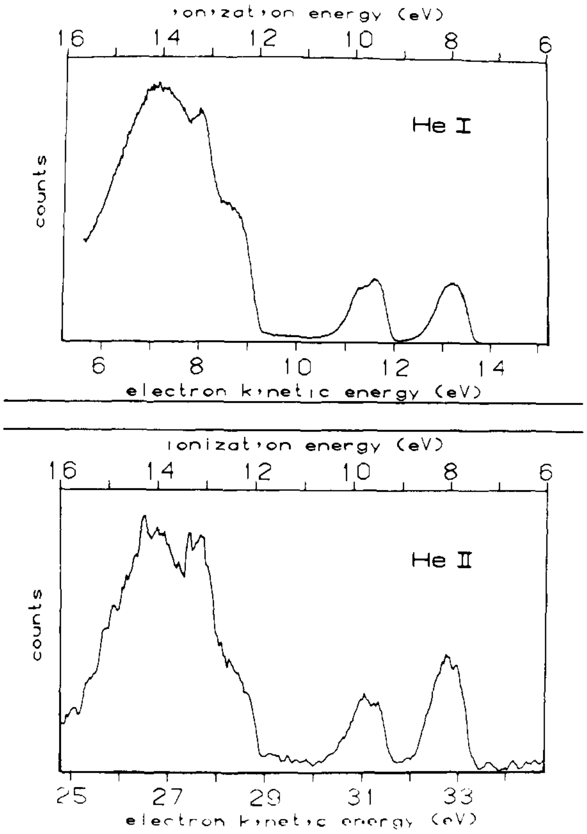

Figure 3. He I and He II photoelectron spectra of $MeCpMn(CO)_3$.

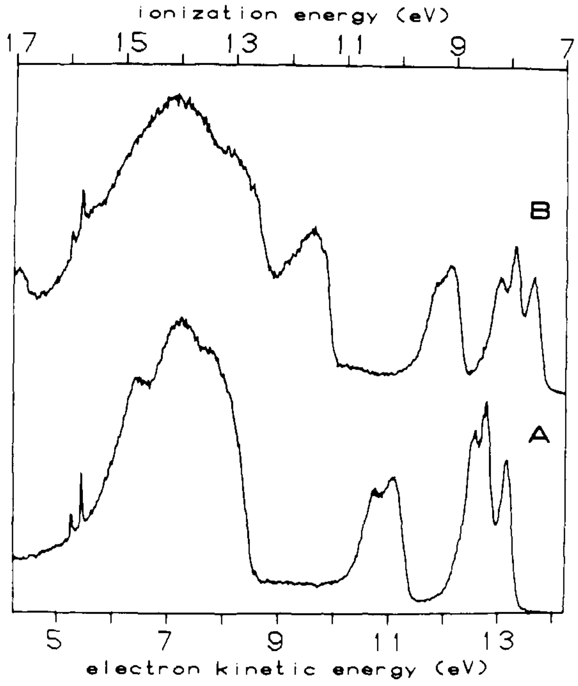

Figure 4. The He I photoelectron spectra of (A) $CpRe(CO)_3$ and (B) $Me_5CpRe(CO)_3$.

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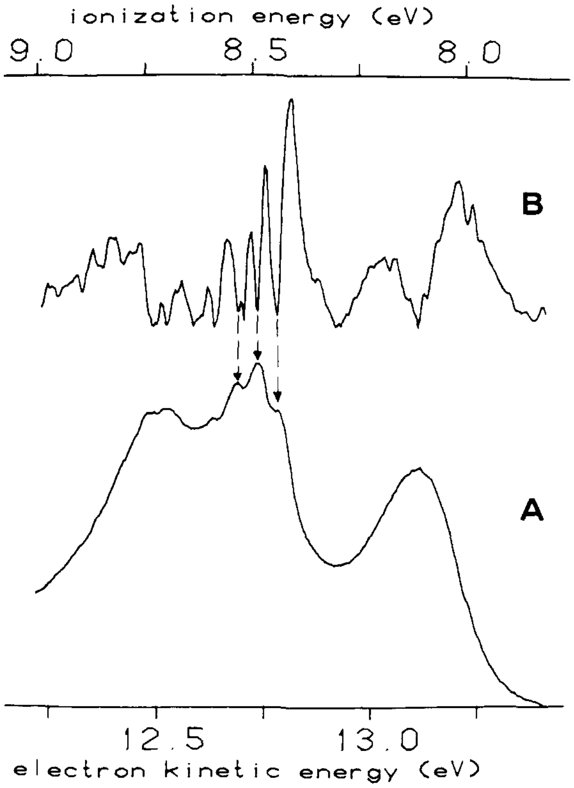

Figure 5. (A) Closeup of the metal ionization region of $CpRe(CO)_3$. (B) Absolute value of the first derivative of A.

The closeup of this ionization for $CpRe(CO)_3$ is shown in Figure 5. The plot of the absolute value of the first derivative of the spectrum accentuates the vibrational fine structure which can be observed on the middle peak and extends into the third peak. The measured vibrational splitting is 400 ± 5 cm^{-1}. The observation of this vibrational fine structure has important consequences for the detailed description of the metal orbital interactions in these complexes (vide infra).

The core ionizations of these complexes are listed in Table III. The carbon 1s ionizations of the carbonyl ligands are observed as a shoulder on the high binding energy side of the carbon 1s ionizations of the Cp ring with an intensity ratio close to the expected value of 3:5. In the spectra of the methylated ring complexes, the ring carbon 1s ionization region increases in intensity without appreciable increase in band half-width, indicating that the ring carbon 1s ionizations and the methyl carbon 1s ionizations are close in energy.

Discussion

Tricarbonyl(η^5-cyclopentadienyl)metal complexes have been the subject of several previous theoretical and ionization studies.[10,26,27] These studies agree in their general interpretation of the ionizations and electronic structure of these species, such as the observation that the first ionization band is predominantly associated with metal d orbital electrons and the second ionization is associated with the Cp e_1'' orbital electrons. However, there are some very important questions that could not be answered from previous experiments. One concerns a definitive determination of the pattern of valence metal ionizations. Reasonably precise knowledge of these ionizations is needed for understanding the relative bonding characteristics of other small molecule ligands in similar complexes. Another question concerns the unusual but characteristic band envelope of the Cp e_1'' ionization. The experimental results reported here provide information for interpreting these features. These points will be discussed before focusing on the effects of Cp ring methylation.

Metal Ionization Pattern. The occupied metal d orbitals of a d^6 $Mn(CO)_3^+$ fragment transform as a_1 (mostly dz^2) and e (mostly $d_{x^2-y^2}$, d_{xy}) representations.[34] Molecular orbital calculations show that the a_1 orbital is only slightly more stable than the e orbitals in the $Mn(CO)_3^+$ fragment, and that these orbitals are perturbed very little by the addition of the Cp^- ring.[10] The a_1 and e ionizations are not fully resolved in the spectra of the manganese complexes, but bandshape analysis (Figure 2) does show that the bandwidths and profiles are at least consistent with the expected e before a_1 pattern. Additional evidence is provided by the spin–orbit splitting of these ionizations which is easily observed in the spectra of the rhenium complexes (Figure 4). Analysis of the spin–orbit terms gives one interpretation that assigns the outer metal ionizations to the spin–orbit components of the e orbitals. The middle ionization band then derives from the a_1 orbital, which has only slight spin–orbit mixing with the e components. The pattern of the ionizations is obtained if the e orbitals are about 0.4 eV less stable than the a_1 orbital before spin–orbit splitting. This interpretation is consistent with the theoretical expectations. However, it was not possible in earlier studies to rule out other interpretations based on different assignments of the rhenium ionizations.[10]

Table III. Core Ionization Data

	orbital	ionization energy, eV	full width at half maximum, eV
$CpMn(CO)_3$	C_{1s} (Cp)	291.01	1.54
	C_{1s} (CO)	292.76	1.30
	O_{1s}	538.85	1.58
	$Mn_{2p_{3/2}}$	646.76	1.33
$MeCpMn(CO)_3$	C_{1s} (Cp)	290.89	1.56
	C_{1s} (CO)	292.58	1.30
	O_{1s}	538.79	1.65
	$Mn_{2p_{3/2}}$	646.69	1.26
$Me_5CpMn(CO)_3$	C_{1s} (Cp)	290.71	1.63
	C_{1s} (CO)	292.35	1.30
	O_{1s}	538.37	1.59
	$Mn_{2p_{3/2}}$	646.08	1.34
$CpRe(CO)_3$	C_{1s} (Cp)	291.07	1.65
	C_{1s} (CO)	292.80	1.30
	O_{1s}	538.59	1.79
	$Re_{4f_{7/2}}$	49.97	1.71
$Me_5CpRe(CO)_3$	C_{1s} (Cp)	290.70	1.60
	C_{1s} (CO)	292.24	1.30
	O_{1s}	538.05	1.52
	$Re_{4f_{7/2}}$	49.46	1.81

A definitive assignment is now possible because of our ability to observe fine structure in the central ionization of the rhenium metal band. We have developed this ability from separate high resolution ionization studies of metal–carbonyl complexes.[35] This is the first report of such structure in the spectrum of an organometallic complex. Briefly, the structure is associated with the symmetric metal–carbon (of CO) stretch in the positive ion. We have found that this structure is observable in the ionization of a predominantly metal d orbital that is symmetrically back-bonding to the carbonyls. In $CpRe(CO)_3$ this would be that a_1 orbital, which is mostly d_{z^2} in character. This orbital is directed between the tricarbonyl tripod with the carbonyls near the nodal surface, so that it back-bonds equally to the three carbonyls. The observation of strong structure on the central ionization and very little structure on the outer ionizations is direct support for assigning the middle component of the spin–orbit split band to the predominantly a_1 ionization.

Two features of the vibrational fine structure also provide direct evidence for the magnitude of back-bonding from the rhenium

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to the carbonyls in this orbital. First, the measured vibrational spacing in the positive ion is 400 ± 5 $\mathrm{cm^{-1}}$. The decrease of this frequency from 502 $\mathrm{cm^{-1}}$ in the neutral molecule[36] reflects the decrease in Re–C(O) bond order when one metal π electron is removed. If back-bonding were not significant one would expect a slight increase in bond energy from the improved σ donation of the carbonyls. The other important feature is that a true progression in the vibrations is obtained. If the orbital were truly nonbonding, then the first or adiabatic vibrational mode would be most intense.[37] The vertical transition is actually to the third or fourth vibrational mode, indicating an increase in the equilibrium Re–C(O) distance in the positive ion compared to the neutral molecule.

Cyclopentadienyl e_1'' Ionization. In all of the spectra reported in this paper and those of the compounds listed in Table II, the predominantly Cp e_1'' ionization displays a shoulder on its high binding energy side separated 0.40 ± 0.05 eV from the main peak. Although the consistency of this bandshape has made it a very useful peak assignment aid in the photoelectron spectra of complexes of this type, the origin of this bandshape has not been explained. The lack of symmetry of the complexes seems to have some relationship to the observed splitting. For instance the MeCp species generally have slightly larger splittings, while the $\mathrm{Me_5Cp}$ complexes generally have smaller splittings. However, the differences between these splittings are fairly small. It appears that the general splitting and characteristic bandshape must be a more fundamental consequence of the coordination of $\mathrm{Cp^-}$ to a $\mathrm{d^6}$ $\mathrm{ML_3}$ group.

In previous studies it was noted that the separation in the e_1'' ionization is consistent with the frequency of the carbon–hydrogen stretching mode, and that perhaps this splitting is a short progression in this vibrational mode.[10] This possibility is now eliminated because the same bandshape is found in the spectrum of $\mathrm{Me_5CpM(CO)_3}$, in which there are no ring carbon–hydrogen bonds. Autoionization is another process that can give rise to unusual band envelopes, but this process is now ruled out because the shoulder is still observed when He II excitation is used.[37]

The degenerate Cp e_1'' ionization might also be split by strong Jahn–Teller forces in the positive ion. This possibility is always present when the positive ion is in a degenerate or nearly degenerate electronic state.[38] Observation of this effect is also dependent on the energy coupling of the ground and excited electronic states to the nuclear motions of the molecule.[37] If the Jahn–Teller coupling is important in this case it should also be important in other high-symmetry Cp–metal complexes. A splitting is not observed in the spectrum of CpNiNO,[39] and current assignments are not in favor of Jahn–Teller splittings in metallocenes.[8] In addition, a Jahn–Teller splitting is generally dependent on the vibrational energy of the molecule.[38,40] We have recorded ionization spectra of $\mathrm{MeCpMn(CO)_3}$ from 25 to 150 °C without any detectable change in the bandshape. The excited state Jahn–Teller type effect may still contribute to the total splitting, but it is difficult to support as the dominant factor.

Since excited state or positive ion effects are unable to satisfactorily account for the bandshape of the predominantly Cp e_1'' ionization, it is appropriate to consider certain ground state effects in more detail. In particular, the possibility of a ground state distortion of the coordinated $\mathrm{Cp^-}$ ring, which would split the e_1'' ionization, should be carefully considered. Over the past 10 years an increasing amount of spectroscopic evidence has accumulated which indicates that distortions of the coordinated $\mathrm{Cp^-}$ ring do occur,[15,16,18] but the distortions are apparently small and have been difficult to unambiguously observe within the certainty of crystal structure determinations.[14,18] The additional problems of packing forces and other solid-state electronic effects further complicate the issue. An advantage of our gas-phase ionization experiments is that there are no solid-state effects. Also, the time scale of the electronic transitions is fast compared to nuclear motions, so thermal and librational motions are not a concern. It should be noted that small distortions in the coordinated $\mathrm{Cp^-}$ ring might be easily detected by UPS since the splitting of the e_1'' eigenvalues will have an even greater effect on the separation of the positive ion states than on the stability of the ground state.

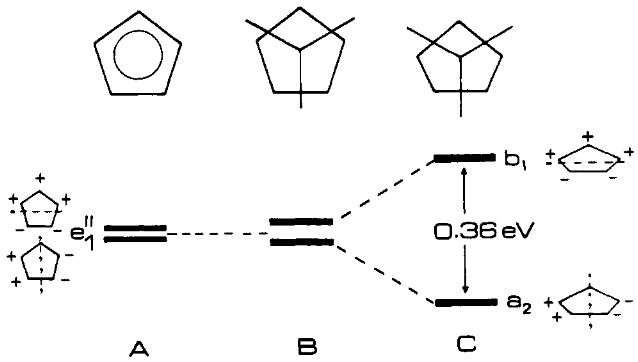

Figure 6. The effects of coordination and the loss of fivefold symmetry on the e_1'' HOMO of free $\mathrm{C_5H_5^-}$: (A) free $\mathrm{C_5H_5^-}$, (B) $\mathrm{CpMn(CO)_3}$ in which the local fivefold symmetry of the ring is maintained (splitting in e_1'' is 0.04 eV), (C) $\mathrm{CpMn(CO)_3}$ in which two of the ring C–C bond lengths have been shortened by 0.03 Å.

Table IV. Decrease in Valence and Core Ionization Energies (eV) with Methyl Substitution

	$\mathrm{CpMn(CO)_3} \downarrow \mathrm{MeCpMn(CO)_3}$	$\mathrm{CpMn(CO)_3} \downarrow \mathrm{Me_5CpMn(CO)_3}$	$\mathrm{CpRe(CO)_3} \downarrow \mathrm{Me_5CpRe(CO)_3}$
valence			
ring e_1''	0.31	1.19	1.08
metal	0.16	0.59	0.50
core			
$\mathrm{C_{1s}}$	0.09 (Cp)	0.30 (Cp)	0.37 (Cp)
	0.14 (CO)	0.41 (CO)	0.56 (CO)
$\mathrm{O_{1s}}$	0.06	0.48	0.54
$\mathrm{Mn_{2p}}$, $\mathrm{Re_{4f}}$	0.11	0.68	0.50

This point is supported by molecular orbital calculations on these systems. Figure 6 illustrates the results of parameter-free Fenske–Hall calculations for the coordination of the $\mathrm{Cp^-}$ ring. When the free $\mathrm{Cp^-}$ ring with D_{5h} symmetry is coordinated to $\mathrm{Mn(CO)_3^+}$ with C_{3v} symmetry, the initially degenerate e_1'' orbital eigenvalues split by just 0.04 eV from the descent to C_s symmetry of the full complex. Thus, just as there is no evidence for the splitting of the e orbitals of $\mathrm{M(CO)_3^+}$ in coordination to the $\mathrm{Cp^-}$ ring (previous section), the calculations show that the e orbitals of the $\mathrm{Cp^-}$ ring are not significantly split upon coordination to $\mathrm{M(CO)_3^+}$. An important observation is that the five carbon–carbon overlap populations in the ring are no longer the same. The carbon–carbon bonds that are not eclipsed by carbonyls of $\mathrm{Mn(CO)_3}$ have clearly larger overlap populations, and there will be a tendency for these bonds to be shorter than the others. The $\mathrm{Cp^-}$ ring will be susceptible to small distortions because one component of the e_1'' will be stabilized while the other is destabilized with little net change in total energy. A model calculation was performed in which two C–C bond lengths were shortened by 0.03 Å. The e_1'' orbitals in this calculation are split into b_1 and a_2 orbitals with a separation of 0.36 eV, in good agreement with the measured splittings in Table II. This distortion is similar in symmetry and in magnitude to that found from low-temperature crystal-structure determinations of $\mathrm{CpMn(CO)_3}$ and CpRe-

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Table V. Decrease in C_{1s} and HOMO Ionization Energies (eV) with Methyl Substitution of Free Olefins

	$H_2C{=}CH_2$ ↓ $H_2C{=}CHCH_3$	$H_2C{=}CH_2$ ↓ $CH_3HC{=}CHCH_3$-*trans*	C_5H_6 ↓ $(CH_3)_5C_5H$	C_6H_6 ↓ 1,3,5-$(CH_3)_3C_6H_3$	C_6H_6 ↓ $C_6(CH_3)_6$
C_{1s}	0.20	0.31	0.23	0.23	0.43
HOMO	0.79[a]	1.29[a]	1.26	0.85[a]	1.39[a]

[a] Reference 42.

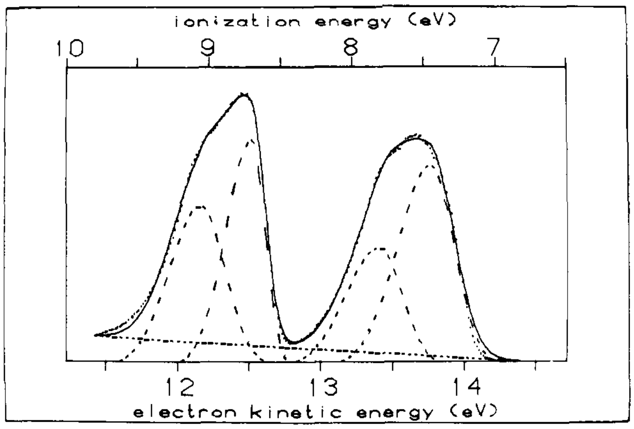

Figure 7. Curve-fit analysis of $Me_5CpMn(CO)_3$ in which the ring e_1'' ionization between 8.5 and 9.5 eV is fit with two gaussians of equal area.

$(CO)_3$.[18] Although complete optimization of the ring geometry was not pursued in our calculations, it is clear that an average deviation of C–C bond distances of only about 0.01–0.02 Å is sufficient to account for the observed splitting in the e_1'' ionization.

The intensity pattern of the two individual bands in the Cp e_1'' ionization envelope is also consistent with this analysis. A shortening of two ring C–C bonds, as shown in Figure 6, increases the bonding nature of the a_2 orbital while decreasing that of the b_1 orbital. Orbitals with more bonding character generally have broader vibrational envelopes.[37] Figure 7 shows a fit of the Cp e_1'' ionization in which the two components are constrained to have equal ionization areas. The greater half-widths of the higher bonding energy component is evident.

The Electronic Effects of Cp Ring Methylation. When an atom or group is substituted on a molecule, it is useful to view the perturbation on the electronic structure as a combination of two contributing factors. The first involves the different direct orbital overlap interactions in the valence shell of the molecule (conjugation or hyperconjugation). The second involves the electron flow or charge redistribution throughout the molecule (induction). These two effects are generally difficult to separate experimentally. A complete ionization study of a molecular system, however, provides a natural means of distinguishing between the two influences. Shifts in the atomic core ionization energies, as measured by gas-phase XPS, are generally understood as changes in the electronic potential or charge distribution in the vicinity of the atom (often interpreted as atomic charges or oxidation states). Theoretical and experimental studies on related systems indicate that electron relaxation energies or excited state effects will not be important for the trends examined here.[41] The valence ionizations also sense the charge redistribution according to their atomic composition, but in addition, reflect the different valence orbital overlap interactions. Thus a careful comparison of the gas-phase valence and core ionization shifts allows a more detailed understanding of the changes in electronic structure that have occurred.

The shifts in valence and core ionizations with Cp ring methylation are shown in Table IV. A large amount of information is provided by these numbers. The most dramatic shift occurs for the valence Cp e_1'' ionization, which is destabilized more than 1 eV from $CpM(CO)_3$ to $Me_5CpM(CO)_3$. This is a relatively large shift for any valence ionization between two similar molecules. Knowledge of this shift will prove valuable for study of a number of other Cp–metal complexes, as illustrated in the next paper.[17] This shift is not simply due to the different inductive effect of a methyl group compared to a hydrogen atom, as implied in most other discussions of the methyl substitution effect.[1,8] That this is not a purely inductive effect can be seen in the core carbon 1s ionizations of the ring, which shift only about one-fourth the amount of the valence orbital. The majority of the shift in valence ioniation must be caused by overlap interaction of the e_1'' orbital with methyl group orbitals. The theoretical aspects of this methyl orbital interaction have been discussed in detail elsewhere.[13] The methyl group orbitals that are involved can be seen in the valence photoelectron spectrum (Figure 1C). The ionization band between 11 and 12 eV is primarily the e combination of the methyl carbon–hydrogen bonds. One combination of these orbitals has the correct symmetry to interact with the e_1'', which is less than 3 eV away. Thus the symmetry and energy separation are favorable for this orbital destabilization (hyperconjugation) of the e_1'' ionization.

We have also collected valence and core shift information for uncoordinated methylated olefins, cyclopentadiene, and benzene. This information is collected in Table V. The trends in valence and core ionization shifts for the free molecules are basically the same as for the coordinated cyclopentadiene. There may be a slight decrease in the shift of the Cp e_1'' ionization when the ligand is coordinated, but the different symmetries of the coordinated Cp and free cyclopentadiene must also be taken into account.

The shift of the metal valence ionizations (Table IV) is only about half the shift of the Cp e_1'' ionization. In this case the shift of the metal core ionizations is nearly the same as the shift of the metal valence ionizations, indicating that the dominant factor is the charge redistribution toward the metal center. Of course, the metal is not expected to have any appreciable direct orbital overlap with the methyl orbitals, so this result is expected. The metal will sense the increased charge on the ring and the increased donation from the destabilized e_1'' orbitals into the empty metal levels. This is also further evidence that the filled metal levels that are observed in the valence photoelectron spectra are basically nonbonding with respect to the ring and will monitor the charge redistribution in much the same way as the metal core levels.

The relative shifts of the Mn and Re complexes give a clue to the greater bonding capability of the Re atom. The shift of the Cp e_1'' ionization in the Re system is less than in the Mn system, indicative of the greater overlap of the e_1'' orbitals with the empty Re acceptor orbitals. In addition, the shift of the Re valence and core ionizations is less than the shift of the corresponding Mn ionizations, while the shift of the core carbon (of CO) and oxygen ionizations is greater. These shifts indicate that the rhenium atom is more effective at transferring charge from the Cp ligand to the coordinated carbonyl ligands.

Conclusions

The cyclopentadienyl ring methylation is a chemical modification of the complex that perturbs the electronic structure, and thereby provides much information on the orbital characters, sensitivies, and bonding capabilities. The effects of the chemical modification on electronic structure are best monitored by combined core and valence ionization studies, which allows separation of various inductive and orbital overlap influences. The magnitudes of the valence ionization energy shifts for the permethylated compounds are large on the energy scale of these

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experiments. This is an indication of considerable change in the electronic structure of these compounds and shows that electronic effects should, in general, receive equal attention to steric effects in explaining reactivity differences between substituted and unsubstituted cyclopentadienyl complexes.

In the course of this investigation we have obtained additional fundamental experimental observations relating to coordinated cyclopentadienyls and carbonyls. The Cp e_1'' ionization bandshape is probable evidence of small (0.01–0.02 Å) distortions from fivefold symmetry of the Cp^- ring when coordinated to d^6 ML_3^+ groups in the gas phase. The observation of Re–(CO) vibrational fine structure in the spin–orbit split valence metal ionizations, and the trends in core binding energies, provide direct evidence of the extent of rhenium to carbonyl π back-bonding. These observations also allow definitive interpretation of the pattern of metal ionizations that will be important to the following investigations.

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Valence Ionizations of Olefins Coordinated to Metals. Olefin Dicarbonyl(η^5-(methyl and pentamethyl)cyclopentadienyl)manganese Complexes

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Abstract: The He I and He II valence photoelectron spectra of $(\eta^5\text{-}C_5H_{5-n}(CH_3)_n)Mn(CO)_2L$ (n = 1 and 5; L = C_2H_4 and C_3H_6) are presented. The synthesis of the pentamethylcyclopentadienyl metal ethylene complex is reported for the first time. This complex is particularly helpful in revealing the ionization characteristics of the metal–olefin complexes. In each case the ionization that is associated primarily with the olefin π bond ($2e^-$ donor to the metal) is shifted to *lower* binding energy in the complex compared to the binding energy of the free ligand. Molecular orbital calculations are reported that agree very well with the shifts in ionization energies. The relative magnitudes of individual metal–olefin orbital interactions are evaluated. It is found that the ionizations and stability of the complexes are sensitive to the geometry changes that accompany coordination of the olefin. These distortions are associated with a lowered carbon–carbon bond strength and an increased metal–olefin bond strength through increased π-donor/π^*-acceptor interactions.

Interactions that are basically π in symmetry between metals and coordinated molecules are a common occurrence in inorganic and organometallic chemistry. The most important examples are perhaps the interactions of metals with unsaturated hydrocarbons and other carbon-containing species. The Dewar–Chatt–Duncanson model has provided a long-standing qualitative picture of the bonding in olefin-type systems.[1] However, recent theoretical treatments have called attention to a number of other potentially significant considerations.[2-6] For instance, in one study the classical donation from the olefin π orbital to the empty metal d_{z^2} orbital is found to be accompanied by a comparable interaction with the $d_{x^2-y^2}$ orbital.[3] The prediction of considerable metal interaction with the olefin σ and σ^* orbitals has also appeared.[4,5] There is considerable disagreement between different theoretical methods as to the relative importance of the different bonding interactions. Experimental information relating to these interactions is obtainable from high-resolution valence photoelectron spectroscopy of particular metal–olefin complexes. The application of this technique to the study of the electronic structure of coordinated olefins has been receiving increasing attention. Early studies have reported the He I spectra of ethylenes adsorbed on metal surfaces[8] and coordinated to $(\eta^5\text{-}C_5H_5)_2Mo$ (and W)[9] and $Fe(CO)_n$.[10-14] More recently the gas-phase He I and He II spectra of some Rh and Ir complexes have been reported.[15] Many of

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