

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 d⁶ ML₃⁺ 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 Dicarboxyl(η^5 -(methyl and pentamethyl)cyclopentadienyl)manganese Complexes

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Abstract: The He I and He II valence photoelectron spectra of (η^5 -C₅H_{5-n}(CH₃)_n)Mn(CO)₂L (n = 1 and 5; L = C₂H₄ and C₃H₆) 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_{z²} orbital is found to be accompanied by a comparable interaction with the d_{x²-y²} 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 surfaces⁸ and coordinated to (η^5 -C₅H₅)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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Table I. He I Ionization Data for $(\text{CH}_3)_n\text{C}_5\text{H}_{5-n}\text{Mn}(\text{CO})_2\text{L}$ (L = CO, C_2H_4 , C_3H_6 ; $n = 1, 5$)

	bands	ionization energy, eV	W_h	W_l	rel amplitude	rel area
$\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$	a	7.89	0.65	0.38	1.0	1.0
	b	8.23	0.65	0.38	0.50	0.50
	c	9.57	0.57	0.36	0.96	0.87
	d	10.00	0.57	0.36	0.57	0.52
$\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_2(\text{C}_2\text{H}_4)$	a	7.38	0.66	0.33	1.0	1.0
	b	7.78	0.66	0.33	1.55	1.55
	c	9.32	0.70	0.36	1.49	1.61
	d	9.78	0.70	0.36	0.85	0.90
	e	10.11	0.70	0.36	0.49	0.52
$\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_2(\text{C}_3\text{H}_6)$	a	7.19	0.61	0.35	1.0	1.0
	b	7.59	0.61	0.35	1.40	1.40
	c	9.16	0.66	0.36	1.58	1.69
	d	9.58	0.66	0.36	0.90	0.96
	e	9.75	0.95	0.38	0.45	0.62
$(\text{CH}_3)_5\text{Mn}(\text{CO})_2(\text{C}_2\text{H}_4)$	a	6.94	0.61	0.32	1.0	1.0
	b	7.34	0.61	0.32	1.60	1.60
	c	8.48	0.42	0.28	2.03	1.55
	d	8.81	0.42	0.28	1.15	0.88
	e	9.67	0.71	0.40	1.0	1.19

the systems that have been studied have been hampered either by instability and decomposition of the molecules or by the overlap of key ionization features.

This paper describes a study of the valence ionizations of $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$, $\text{MeCpMn}(\text{CO})_2(\text{C}_3\text{H}_6)$, and $\text{Me}_5\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$, where $\text{MeCp} = \eta^5\text{-C}_5\text{H}_4\text{CH}_3$ and $\text{Me}_5\text{Cp} = \eta^5\text{-C}_5(\text{CH}_3)_5$. The stability and volatility of these systems make them attractive for the gas-phase photoelectron study of coordinated olefin ionizations. The possibility of different methyl substitutions on the olefin and cyclopentadienyl ring is also important. As we have shown, ring methylation causes large shifts in the valence ionizations which are dependent on the orbital character of the band.¹⁶ Knowledge of these shifts, as presented in the previous paper, allows predictable variations in the available UPS spectral window, which is useful in uncovering specific ionization features that are otherwise obscured by overlapping peaks. Peak assignments and interpretations in this study are aided by He I/He II intensity ratio changes and molecular orbital calculations. Particular attention is given to changes in the metal d ionizations in going from the parent tricarbonyls to the olefin complexes, and to the ionization energy shift of the predominantly olefin π orbital upon coordination. A direct comparison of CO and C_2H_4 bonding capabilities in these complexes is provided by these results. It is also shown that distortions of the coordinated olefin, as well as the relative π -donation/ π^* -acceptance, are important in explaining the observed shifts in the ionization energy of the olefin π orbital. These distortions represent a movement toward a metallocyclopropane-type geometry from the classical Dewar-Chart-Duncanson extreme.

Experimental Section

Preparation of Compounds. All solvents were dried and stored in a nitrogen atmosphere until use. Manipulations were carried out using standard Schlenk techniques. The compounds $\eta^5\text{-CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_2(\text{C}_2\text{H}_4)$ and $\eta^5\text{-CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_2(\text{C}_3\text{H}_6)$ were prepared by previously reported methods¹⁷ and the spectra were recorded shortly after preparation and sublimation. The previously unreported $\eta^5\text{-(CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_2(\text{C}_2\text{H}_4)$ was prepared analogously from $\eta^5\text{-(CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_3$, which was obtained by a published route.¹⁶

Infrared spectra were taken in hexane and recorded on a Perkin-Elmer 398 spectrometer; ^1H NMR spectra were recorded in CCl_4 on a Varian EM360L instrument. Elemental analyses were obtained from the University of Arizona Analytical Center. Photoelectron spectra were recorded on a McPherson ESCA 36 instrument which has been described

earlier.¹⁶ Samples were run at room temperature. Curve-fit analysis was done with use of the program GFIT.¹⁶

Preparation of $\eta^5\text{-C}_5(\text{CH}_3)_5\text{Mn}(\text{CO})_2(\text{C}_2\text{H}_4)$. After purging with argon, a Hanovia-type photochemical reactor was charged with 150 mL of THF containing 0.15 g (0.55 mmol) of $\eta^5\text{-C}_5(\text{CH}_3)_5\text{Mn}(\text{CO})_3$. The pale yellow solution was irradiated for 90 min at 0 °C, at which time the IR indicated complete loss of the tricarbonyl starting material and the color had turned deep red. After ethylene was bubbled through the solution for 45 min, the now golden yellow solution showed no IR peaks for the $\eta^5\text{-C}_5(\text{CH}_3)_5\text{Mn}(\text{CO})_2\text{THF}$ intermediate. Evaporation to dryness and multiple sublimations at 45 °C (0.1 mm Hg) gave the bright yellow product (66%). ^1H NMR (CCl_4) δ 1.69 (singlet); IR (hexane) 1958 (s), 1989 cm^{-1} (s).

Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2\text{Mn}$: C, 61.35; H, 6.93; O, 11.68; Mn, 20.05. Found: C, 61.78; H, 7.03; O, 11.59; Mn, 19.6 ± 1.

Calculations. Orbital eigenvalues were calculated by both the extended Hückel¹⁸ and Fenske-Hall methods.¹⁹ The atomic orbital functions and geometry of the $\text{CpMn}(\text{CO})_2$ portion of the molecule were unchanged from previous work.^{19,25,26} The bond distances and angles of the coordinated olefin were taken from the crystal structures of several $\text{CpMn}(\text{CO})_2(\text{olefin})$ complexes.²⁰ The coordinated olefin geometry (Figure 5) was set at a typical C=C bond length of 1.40 Å with the four hydrogen atoms bent away from the metal by 12°.⁷

Results and Ionization Band Assignment

The valence photoelectron spectra of $\text{MeCpMn}(\text{CO})_3$, $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$, $\text{MeCpMn}(\text{CO})_2(\text{C}_3\text{H}_6)$, and $\text{Me}_5\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ are shown in Figure 1. The similarities and differences in the photoelectron spectra of this series of closely related compounds are important to the interpretation of the ionizations. Each spectrum has a broad band of overlapping ionizations from about 11–16 eV ionization energy. The ioni-

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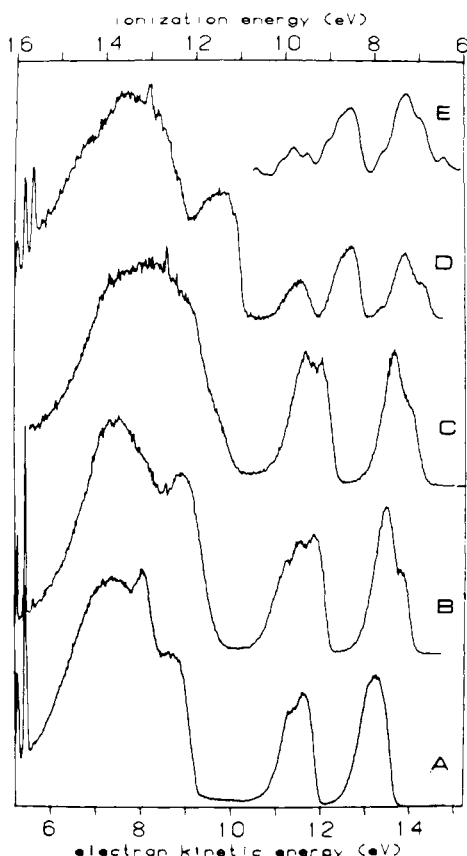


Figure 1. He I photoelectron spectra of (A) $\text{MeCpMn}(\text{CO})_3$, (B) $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$, (C) $\text{MeCpMn}(\text{CO})_2(\text{C}_3\text{H}_6)$, and (D) $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ and (E) He II spectrum of $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$.

zations expected to occur in this region are associated with the carbonyl 5σ and 1π orbitals and the cyclopentadienyl $a_2''(\pi)$ and certain σ orbitals. The most noticeable changes occur on the leading edge of this region. For each of the MeCp complexes there is a visible shoulder at about 12 eV that has been attributed to the methyl group on the ring.¹⁶ For the propylene complex there is an additional inflection at about 11–11.5 eV that is presumably due to the methyl group of this olefin. In the spectrum of the Me_3Cp complex the shoulder now appears as a major ionization feature that has shifted to lower binding energy, consistent with the five cyclopentadienyl methyl groups as discussed previously.¹⁶

The most significant changes are observed in the valence ionization features occurring below 11 eV. This region is shown in greater detail along with the curve analysis of these bands in Figure 2. The vertical ionization energies, shapes, and relative intensities of each band are compiled in Table I. The fit bands are labeled a, b, c, d, and e starting from low ionization energy. A number of very significant changes occur in these ionizations. Consider first comparison of the spectrum of $\text{MeCpMn}(\text{CO})_3$ with that of $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$. Previous comparisons of the ionizations of metal–CO and metal– C_2H_4 complexes found very few differences in the predominantly metal ionizations.^{9,13} We observe distinct differences in these ionizations which will be important in interpreting the olefin interactions. For instance, the broad, unresolved peak at about 8 eV in the spectrum of $\text{MeCpMn}(\text{CO})_3$ becomes a pair of partially resolved peaks with an intensity pattern of approximately 1:2 in the spectrum of $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$. The order of the 1:2 intensity peaks is opposite to that concluded (from evidence discussed in the previous paper)¹⁶ for the first band of the $\text{MeCpMn}(\text{CO})_3$ complex. The ionization band in the region from 9 to 10 eV is considerably more broad in the spectrum of the ethylene complex than in the spectrum of the tricarbonyl complex. The shape of this band for the tricarbonyl complex, shown in detail in Figure 2A, is generally characteristic of predominantly cyclopentadienyl e_1'' ionizations for such complexes.¹⁶

Table II. Observed Effects of Methylation^a

	ring methylation $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ ↓ $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$	olefin methylation $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ ↓ $\text{MeCpMn}(\text{CO})_2(\text{C}_3\text{H}_6)$
metal $1a'$, $2a'$, a'' shifts ^b	0.44	0.19
ring e_1'' shift	0.85	0.18
olefin π shift	0.44	0.36

^a Destabilization of ionization energies in eV. ^b The $1a'$, $2a'$, and a'' shift by the same amount.

The curve analysis of the corresponding band in the olefin complex (Figure 2B) suggests that a similarly shaped ionization may be present in this region along with an additional overlapping band. The intensities are consistent with bands c and d being associated with the $\text{MeCp} e_1''$ ionization. The low intensity band e at 10.11 eV must then be assigned to the predominantly olefin π ionization. This is in the vicinity of the π ionization of free ethylene which occurs at 10.51 eV. However, it should be noted that coordination of a $2e^-$ donor molecule to a metal normally shifts ionization of the ligand donor orbital to higher ionization energy. In the previous photoelectron spectra of a single olefin coordinated to a metal center, the ionizations assigned to the olefin donor orbital are stabilized by 0.05–1.15 eV on coordination.^{9,13} A destabilization of 0.4 eV in the present case should be considered unusual. Also, the fact that the bands in this region are overlapping introduces uncertainty in their true shapes, intensities, and positions. We felt that additional experimental information must be obtained to confirm these results.

One approach is to perturb the electronic structure of the system in a well-defined way and observe the effect on each valence ionization. The change in a particular valence ionization will then give information on the associated orbital character. For example, the electronic structure of the analogous propylene complex may be considered a simple perturbation of the electronic structure of the ethylene complex. The methyl group on the propylene alters the olefin electronic structure precisely as described in the preceding paper.¹⁶ The first ionization of free propylene (9.85 eV) is sufficiently lower than the first ionization of free ethylene (10.51 eV) to alter the interactions with the metal and shift the valence ionizations of the complexes. Comparison of spectra B and C in Figures 1 and 2 show the effects of these perturbations. The most visible change from the ethylene to the propylene complex spectrum is a narrowing and change in contour of the band between 9 and 10 eV. The curve analysis indicates that this is a result of band e shifting closer to bands c and d. The data in Table II show that band e experiences the largest destabilization (0.36 eV), consistent with assigning it to the olefin π ionization. The splitting and intensity pattern of the metal ionizations remains much the same but they are shifted 0.19 eV to lower binding energy by the destabilized olefin levels. Bands c and d, assigned to the cyclopentadienyl e_1'' , are similarly shifted 0.18 eV to lower binding energy. The implications of these shifts will be considered in the Discussion section.

The problem remains that the olefin π ionization has not been clearly resolved in these complexes, leaving some uncertainty concerning its precise ionization energy and intensity. The propylene complex is helpful in supporting band assignment, but the π ionization band is shifted further under the cyclopentadienyl e_1'' ionizations. This observation indicates that methylation of the cyclopentadienyl ring, rather than the olefin, should be helpful in separating these bands. The need to selectively separate overlapping bands in complexes of this type is what originally prompted our study of ring methylation, and led to the synthesis of $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$. The valence ionization spectrum of this complex is shown in Figures 1 and 2. A clearly visible olefin π ionization is observed for this complex. The $\text{Me}_3\text{Cp} e_1''$ ionization (c and d) has the characteristic shape for this band and has shifted 0.85 eV to lower binding energy compared to the corresponding MeCp ionization. The olefin π ionization (9.67 eV) has shifted 0.44 eV. The predominantly metal d ionizations

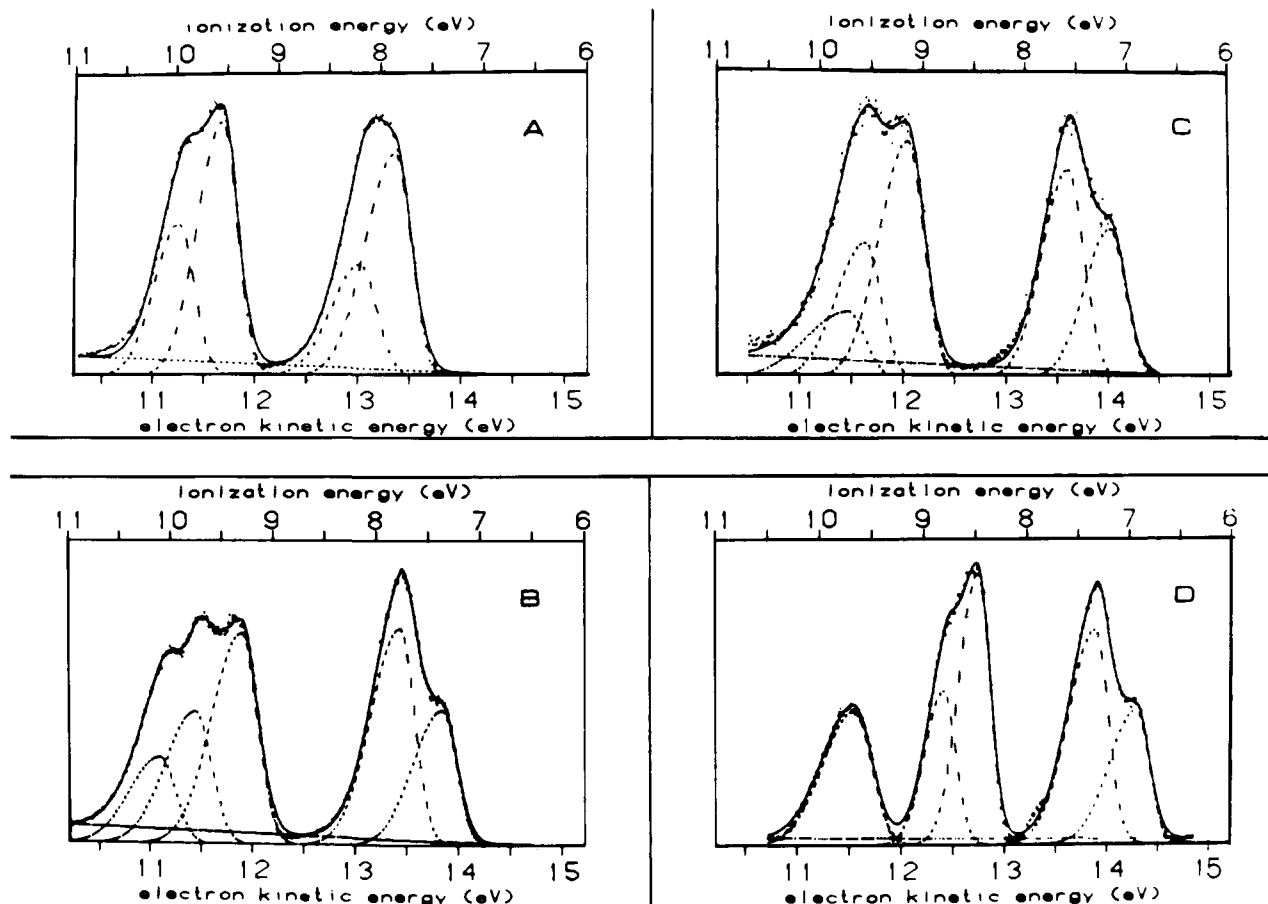


Figure 2. Low-energy (11 → 6 eV) He I spectra of (A) $\text{MeCpMn}(\text{CO})_3$, (B) $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$, (C) $\text{MeCpMn}(\text{CO})_2(\text{C}_3\text{H}_6)$, and (D) $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$.

have shifted 0.44 eV also, and retain the same splitting and intensity pattern.

The olefin π ionization is characterized as rather low in intensity and broad. The He II valence photoelectron spectrum of $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ is shown in Figure 1E. The relative increase in intensity of the first band compared to the next two may be attributed to the high metal d character of the first ionization.²¹ The relative intensity of the $\text{Me}_3\text{Cp} e_1''$ and ethylene π ionizations does not change appreciably, as one would expect for the similar carbon character and nodal characteristics of these orbitals.

Discussion

The experimental observations described in the previous section present two specific challenges for our understanding of the bonding of olefins with metal centers. First, what do the shifts and band contours of the metal and cyclopentadienyl ionizations indicate about the relative strengths of separate olefin orbital interactions with the metal center? Second, why does the olefin π ionization, which forms the $2e^-$ donor bond to the metal center, occur at lower binding energy for the coordinated olefin than for the free olefin? Before addressing these points in detail, it is necessary to be familiar with the relevant molecular orbitals of $\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$. These will provide a basis for the interpretation of the spectral changes which occur throughout this series of compounds.

Orbital Interactions of C_2H_4 with the $\text{CpMn}(\text{CO})_2$ Fragment. The $\text{CpMn}(\text{CO})_2$ fragment is able to coordinate many different kinds of ligand molecules,²² partly because it possesses both donor and acceptor orbitals that are energetically and spatially favorable for bonding interactions. The bonding capabilities of the $\text{CpMn}(\text{CO})_2$ fragment have been described previously and applied to a large number of $\text{CpMn}(\text{CO})_2\text{L}$ compounds.^{19,23-26} These compounds may be considered pseudo-octahedral if the cyclopentadienyl ring is viewed as occupying three coordination sites.

The most convenient coordinate system for describing the orbital interactions of $\text{CpMn}(\text{CO})_2$ places the vacant coordination site along the z axis, with the x axis bisecting the two carbonyls as shown in Figure 3. We have placed a C_2H_4 ligand in the vacant coordination site to illustrate how it interacts with the valence orbitals of the $\text{CpMn}(\text{CO})_2$ fragment. The orbitals shown are calculated eigenvectors of the fragment and not the ethylene complex. The LUMO of the fragment is the $3a'$ orbital, which is high in d_z character and is a good acceptor orbital for incoming ligands along the vacant z axis. The three highest occupied orbitals of $\text{CpMn}(\text{CO})_2$ are the $1a'$, a'' , and $2a'$ orbitals shown in Figure 3. The $1a'$ and a'' both possess π symmetry with respect to the vacant coordination site. The $1a'$ orbital is high in d_{xz} character. The a'' is mostly d_{yz} in nature and is hybridized toward the vacant site. Thus the a'' orbital is the most effective π donor orbital and molecules with single π acceptor orbitals, like olefins, tend to align for interaction with this orbital.²⁴ The remaining HOMO of the fragment is the $2a'$ orbital which is high in $d_{x^2-y^2}$ character (some d_{z^2} also) and has primarily delta symmetry with respect to the vacant site. The correlation of these occupied orbitals with the normal t_{2g} orbitals in octahedral symmetry can be seen.

Coordination of the olefin to $\text{CpMn}(\text{CO})_2$ primarily involves the formation of a $2e^-$ donor bond between the olefin π donor orbital and the empty $3a'$ orbital of the fragment, and the orientation of the olefin to give optimum overlap between its π^* -acceptor orbital and the most effective fragment donor orbital (a''). The olefin has no other comparable acceptor orbitals to interact with the less favorable $1a'$ donor. The remaining $2a'$ fragment orbital has no significant delta overlap with the olefin, but it may have some interaction with the olefin π orbital. The strength of these interactions will affect the ionization energies of the metal d and olefin π orbitals observed in the photoelectron spectrum.

Metal and Cp Ionizations. The He I spectra of the olefin complexes in Figures 1 and 2 show a considerably different

Table III. Effects of CO Substitution by Olefin^a

	Me ₅ CpMn(CO) ₃ ↓ Me ₅ CpMn(CO) ₂ (C ₂ H ₄)	MeCpMn(CO) ₃ ↓ MeCpMn(CO) ₂ (C ₂ H ₄)	MeCpMn(CO) ₃ ↓ MeCpMn(CO) ₂ (C ₃ H ₆)
1a' shift	0.88	0.85	1.04
2a', a'' shifts	0.12	0.11	0.30
ring e ₁ '' shift	0.26	0.24	0.42

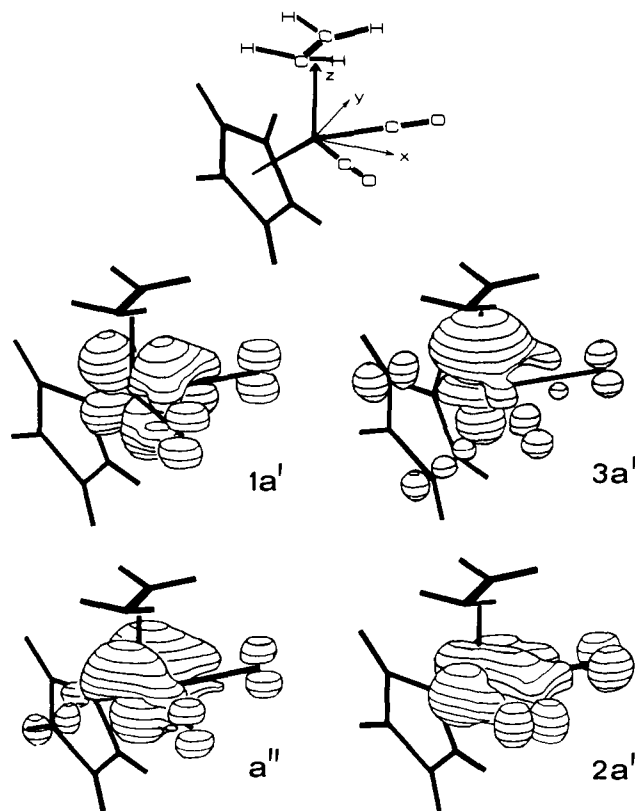
^a Destabilization of ionization energies in eV.

Figure 3. Three-dimensional Fenske-Hall orbital surface plots of the valence molecular orbitals of the CpMn(CO)₂ fragment showing their positions relative to an ethylene ligand. The contour shown is for a 0.05 value of the wave functions.

bandshape in the metal ionization region (7.0–8.0 eV) than that of the MeCpMn(CO)₃ analogue. The ionization energy shifts are summarized in Table III. These shifts furnish the information regarding the relative bonding capabilities of CO and C₂H₄. These shifts are also predicted by simple molecular orbital calculations. A comparison of the calculated and observed ionization energies for MeCpMn(CO)₃ and MeCpMn(CO)₂(C₂H₄) is presented in Figure 4. The predicted values are obtained by applying the calculated shifts between CpMn(CO)₃ and CpMn(CO)₂(C₂H₄) to the observed ionization energies of MeCpMn(CO)₃. This assumes that deviations from Koopmans' theorem, limitations of the approximate method, etc. are reasonably constant for the two systems and that MeCp compared to Cp is a minor perturbation.²⁵ Thus if the calculations reasonably represent the different bonding of CO and C₂H₄ to CpMn(CO)₂, there should be agreement in the shift of the ionization energies. As can be seen, the theoretical prediction is very good in this case.

Figure 4 shows that the highest occupied, mostly metal d orbitals of MeCpMn(CO)₃ (1e and a₁) switch their relative ordering in MeCpMn(CO)₂(C₂H₄). The a₁ orbital of the tricarbonyl is greatly destabilized (0.85 eV) when a CO ligand is replaced by C₂H₄, and becomes the 1a' HOMO of MeCpMn(CO)₂(C₂H₄).²⁷ This destabilization is expected since the 1a' orbital of MeCpMn-

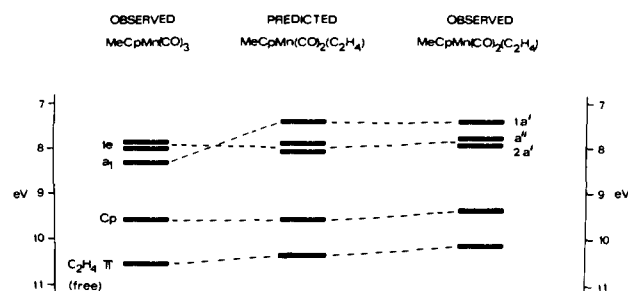


Figure 4. Predicted vs. observed orbital ionization energies for MeCpMn(CO)₂(C₂H₄).

(CO)₂(C₂H₄) is no longer stabilized by back-bonding as it was in the tricarbonyl. The single C₂H₄ π* acceptor prefers to interact with the a'' donor of CpMn(CO)₂, as explained above.

The 1e HOMO of the tricarbonyl correlates primarily with the a'' and 2a' orbitals of the ethylene complex. These orbitals remain nearly degenerate and experience only a slight shift (0.11 eV) to lower ionization energy. In the absence of unusual olefin orbital interactions with the 2a' orbital (vide infra), the 2a' and a'' orbitals can remain nearly degenerate only if the ethylene stabilization of the a'' orbital is similar to the carbonyl π-back-bonding stabilization of this orbital. This has been illustrated for a wide range of good and poor acceptor ligands in CpMn(CO)₂(ligand) complexes.^{19,23,25,26,28} The near degeneracy of the a'' and 2a' orbitals in this complex indicates that the single C₂H₄ acceptor orbital is comparable in back-bonding ability to a single CO acceptor orbital.

The 2a' orbital is the correct symmetry to interact with the olefin π bond. Although this interaction has been invoked in the discussion of other metal-olefin properties,²⁹ it does not appear to be important in determining the shifts of the ionizations in these complexes. An interaction of this type would be most directly manifested in a destabilization of the 2a' ionization. One example in which an extra destabilization of the 2a' ionization would be observed is given by comparison of the ethylene and propylene complexes. The greatest difference between ethylene and propylene is the ionization energy of the olefin π bond, which is 0.66 eV less stable in the case of propylene and would interact more strongly with the 2a' orbital. However, Table II shows that the 1a', 2a', and a'' ionizations all shift identically from the ethylene to the propylene complex, indicating that any difference in the 2a' interaction is negligible on the energy scale of these experiments.

The slight decrease in ionization energy of the 2a' and a'' orbitals when a CO is replaced by ethylene reflects the slight increase of charge density on the metal center of the ethylene complex compared to the carbonyl complex. This increase is primarily the result of the increased localization of the 1a' orbital on the metal center due to lack of a suitable ethylene a' acceptor orbital. In the case of propylene the greater destabilization of the 2a' and a'' ionizations shows that propylene is a better donor than ethylene, while the remaining degeneracy of these ionizations indicates that the single acceptor of propylene is still comparable to the single acceptor of CO.

Effects of Methylation. The sensitivities of the ionizations to both methylation of the cyclopentadienyl ring and methylation

(27) For clarity we have retained the labels of the CpMn(CO)₂ fragment orbitals shown in Figure 3.

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of the olefin are summarized in Table II. The shift of the metal and ring valence ionizations with methylation of the ring is as expected from the results of the previous paper.¹⁶ Specifically, the shift of the ring e_1'' ionization (0.85 eV) is about twice as large as the shift of the metal ionizations (0.44 eV). In addition, the olefin π level allows observation of the shift in a ligand ionization. It is interesting to note that the olefin π ionization shifts by the same amount as the metal ionizations when the cyclopentadienyl ring is methylated. Similarly, when the olefin is methylated the olefin π ionization shifts twice as much as the metal ionizations. In this case the metal and the ring ionizations shift by the same amount.

As shown in the previous paper, the shift in the π ionization of the methylated group is largely due to the hyperconjugation effect, which is accompanied by some charge induction. The shifts in other ionizations are directly due to the resulting charge rearrangement throughout the molecule. Thus the π ionization of the methylated group is destabilized more than the other ionizations. The similarity of the metal and olefin π shifts when the ring is methylated, and the similarity of the metal and ring shifts when the olefin is methylated, illustrate the very fluid electron density in these systems. This is apparently another reason that the $\text{CpMn}(\text{CO})_2$ fragment is able to form stable molecules with a large number of different ligand types. The fluid electron density is able to accommodate a wide range of different bonding needs.

The Effect of Coordination on the Olefin π Ionization. Figure 4 shows that the C_2H_4 donor orbital is destabilized upon coordination. In the case of coordinated olefins, there are three distinct factors which affect their π orbital ionization energies. As pointed out in the results section, such donor orbitals are normally stabilized by bond formation. This can result simply from the overlap of a filled ligand donor orbital with an appropriate metal orbital to give M-L bonding and antibonding combinations. The magnitude of this stabilization depends on both the amount of overlap and the energy separation between the metal and ligand orbitals. A second factor in the orbital energy is the charge redistribution which accompanies olefin coordination. Since olefins possess both donor and acceptor capabilities, the relative dominance of these two interactions will determine the direction of net charge flow in the M-olefin bond. If the olefin behaves primarily as a donor ligand, then it will acquire a partial positive charge upon coordination and charge redistribution will exert a stabilizing influence on the olefin π orbital. If the olefin acceptor ability dominates, the olefin will experience a build up of negative charge which will have a destabilizing effect on its π ionization energy. It is tempting to interpret shifts in the olefin π ionization energy solely in terms of these charge-transfer mechanisms so as to give an indication of the relative donor/acceptor strength of the olefin ligand.^{12,15} This line of reasoning is valid only under certain circumstances.

For most other ligand molecules the effects of M-L overlap and the accompanying charge redistribution are sufficient for explaining shifts in the ligand ionization energies upon coordination. However, in the case of olefin ligands the donor and acceptor orbitals are π bonding and antibonding with respect to the C-C bond. As a result both π -donation and π^* -acceptance serve to reduce the C=C bond order and lengthen the C-C bond. In addition, some rehybridization of the carbon centers toward sp^3 occurs which partially destroys the σ - π separability. These points have been discussed by other authors.²⁹ Crystal structures of coordinated olefins in complexes of this type show lengthening of the C=C bond from 1.34 to about 1.40 Å, and a bending of the four substituent groups or atoms away from the metal atom.⁷

Figure 5 shows how the calculated orbital energies and overall strength of the metal-olefin interaction are sensitive to these olefin distortions. In reconstructing the metal-olefin bond we first bring a free ethylene molecule within bonding distance of a $\text{CpMn}(\text{CO})_2$ fragment while maintaining the olefin at its free geometry (Figure 5b). The calculated relative orbital energies which result at this hypothetical geometry are not in agreement with the observed He I spectrum. For instance the a'' and $2a'$ orbitals are not approximately degenerate. Also, the C_2H_4 π orbital has been weakly stabilized. This initial stabilization of the olefin π orbital cor-

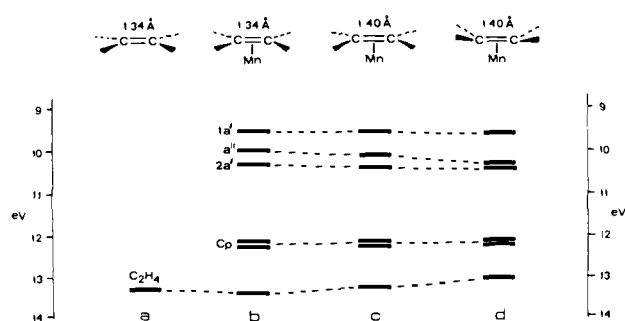


Figure 5. Stepwise effects of olefin distortions on the metal d and olefin π orbitals.

Table IV. The Effect of Metal-Olefin Interactions on Olefin π Ionization Energy^a

orbital interaction with metal	effect of metal-olefin overlap energy	effect of charge redistribution	effect of decrease in C=C bond order
olefin π -donation	stabilization	stabilization	destabilization
olefin π^* -acceptance	0	destabilization	destabilization

^a Stabilization in this sense refers to a shift of the ionization to greater ionization energy.

responds to the normal stabilization of a donor orbital due to M-L overlap. Stepwise relaxation of the olefin to its favored coordination geometry is shown in Figures 5c and 5d. Lengthening of the C=C bond to 1.40 Å (Figure 5c) decreases the π - π^* separation and destabilizes the olefin π orbital. This improves the π -donation to the metal and increases π^* -acceptance from the metal into the more stable olefin π^* orbital. This increased back-bonding is evidenced by the stabilization of the metal a'' donor orbital. These trends are continued with the partial rehybridization of the ethylene carbon atoms such that the four hydrogen atoms are bent away from the metal. This further destabilizes the olefin π orbital and also strengthens the M-olefin interaction by increasing orbital overlaps. The increased back-bonding to the olefin now stabilizes the a'' to approximate degeneracy with the $2a'$ as observed experimentally. Thus the free olefin sacrifices some of its own carbon-carbon bond strength to form a stronger metal-olefin bond. It should be emphasized again that the ability of the eigenvalues of both the extended Hückel and Fenske-Hall calculations to reproduce the shift in the olefin π -ionization indicates that excited state, relaxation, and other effects are not of primary importance for this trend.

These results are in agreement with bond energy calculations by Sakaki et al. on $\text{Pt}(\text{PH}_3)_2\text{C}_2\text{H}_4$.⁶ They found that olefin distortion causes a strengthening of the M-C and C-H bonds, and a weakening of the C=C bond. As we have shown, our Mn system exhibits the same trends in M-C and C=C bond strengths with olefin distortion. Sakaki also obtained a net transfer of electron density onto the olefin with bond formation in their d^{10} system. The shifts in ionization energies for the d^6 $\text{Mn-C}_2\text{H}_4$ system do not indicate a net transfer of electron density when the olefin is coordinated.³⁰ Also, if charge redistribution were significant in this system the noniterative extended Hückel calculations would not be successful in predicting the correct ionization shifts. Distortion of the olefin upon coordination, and the resulting destabilization of the olefin π ionization, is enhanced by both π -donation and π^* -acceptance by the olefin, but does not necessarily require a net charge transfer. Instances in which the donation and acceptance essentially balance may be envisioned as a coordinated olefin effectively experiencing a partial $\pi \rightarrow \pi^*$

(30) Although it is difficult from these measurements to absolutely determine the charge density on the coordinated ethylene, comparison of metal and ring ionization energies for the CO and ethylene complexes does show that the net charge density on coordinated ethylene is less than the charge density on coordinated CO. The net charge density is even less on a coordinated propylene.

excitation. Several authors have noted the similarity between the geometry of coordinated olefins and the geometry adopted by olefins in their lowest electronically excited state.^{31,32}

As can be seen, the relationship between olefin binding energy shifts and metal-olefin interactions is complex. The important factors which determine the ionization energy of the coordinated olefin π orbital are summarized in Table IV. The three columns show how each contributing factor affects the olefin π ionization energy if the π -donation and π^* -acceptance interactions are considered individually. For instance, π -donation has a stabilizing effect on the olefin π orbital as a result of overlap stabilization and the buildup of positive charge on the olefin, but a destabilizing effect due to a decrease in C=C bond order. The π^* -acceptance has strictly a destabilizing effect on the olefin π orbital. The π^* -acceptance results in an accumulation of negative charge on the olefin and also reduces the C=C bond order. The overall shift in olefin π ionization energy upon coordination is determined by both the relative dominance of the π -donation/ π^* -acceptance interactions and the relative magnitudes of each contributing factor.

The small charge redistribution upon ethylene coordination in $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ indicates that, in this system, the π -donation and π^* -acceptance interactions are approximately of equal importance, resulting in no significant overall charge transfer between the metal and olefin. The observed 0.40 eV destabilization of the ethylene π orbital in $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ from free ethylene results from the combined reduction in C=C bond order of both π -donation and π^* -acceptance, which more than compensates for the small metal-olefin overlap stabilization. In this

compound one cannot conclude that the decrease in olefin ionization energy implies a buildup of electron density on the olefin resulting from a dominant π^* -acceptance interaction.

The $\text{MeCpMn}(\text{CO})_2(\text{C}_3\text{H}_6)$ and $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ compounds provide convenient perturbations which help illustrate the usefulness of Table IV. In $\text{MeCpMn}(\text{CO})_2(\text{C}_3\text{H}_6)$ the coordinated propylene π orbital has been destabilized by only 0.10 eV relative to free propylene. This molecule has the largest energy separation between the filled metal levels and the olefin π^* level, and therefore has the least amount of π^* -acceptance. In addition, the enhanced π -donation of propylene, due to its electron-donating methyl group, makes propylene an overall stronger donor than acceptor ligand in this system. In this case the donor and acceptor charge-transfer mechanisms do not cancel, but instead, furnish a stabilizing influence which reduces the overall destabilization of the propylene upon coordination. The $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ complex presents a perturbation in the opposite direction. The five ring methyl groups destabilize the ring e_1'' orbital and supply an increased amount of electron density to the metal.¹⁶ This decreases the energy separation between the metal levels and the C_2H_4 π^* orbital which enhances olefin π^* -acceptance, and diminishes olefin π -donation to the more electron rich metal. The charge-transfer contribution now furnishes a further destabilization which helps to shift the C_2H_4 π orbital to lower ionization energy by 0.85 eV in $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$.

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The Valence Electronic Structure of Bridging Methylene: UV Photoelectron Spectroscopy of μ -Methylene- bis(dicarbonyl(η^5 -cyclopentadienyl)manganese)

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Abstract: The He I photoelectron spectrum of $\mu\text{-CH}_2\text{-}[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2]_2$ in the ionization energy range below 11 eV is reported and compared with the ionizations of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2(\text{C}_2\text{H}_4)$. Excellent agreement is found between the observed ionizations and the predictions of parameter-free molecular orbital calculations. The valence orbitals of the $\mu\text{-CH}_2$ group appear to have near ideal matching with the frontier orbitals of the $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2$ fragments to produce the bonding and stability of this cyclopropane analogue. An effective charge transfer from the metals to the methylene occurs in this interaction which results in a high negative charge on the methylene carbon and formation of a net metal-metal bond. The bonding of the bridging methylene in this complex is also compared with the bonding of a terminal methylene with the analogous $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2$ species. It is concluded that the formation of the metal-metal bond is an important factor in the greater stability of the bridging system.

Since the first identification of a CH_2 moiety stabilized as a bridging group between two metal centers,² such compounds have been increasingly recognized for their importance in organometallic chemistry. The metal-methylene unit may be an intermediate

in olefin metathesis reactions, and it recently has been implicated as significant in certain Fischer-Tropsch type reactions.³⁻⁵ A growing number of μ -alkylidene complexes have been synthesized in recent years and an understanding of the stabilities and reactivities of these species is beginning to unfold.^{6,7} This paper

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