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Electronic Structure and Bonding Characteristics of Cyclopentadienyl d^8 Metal–Ligand Complexes. Core and Valence Ionization Study of CpM(CO)$_2$ Where M = Co and Rh and Cp = η^5-C_5H_5 and η^5-$C_5(CH_3)_5$[1]

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A combined investigation of the core and valence ionizations of d^8 cobalt and rhodium complexes of the form CpM(CO)$_2$, where Cp is either η^5-cyclopentadienyl or η^5-pentamethylcyclopentadienyl, is used to reveal the important electronic interactions in these complexes. It is found that, unlike the usual similarity of ionization features of analogous first- and second-row d^6 metal complexes, there are major differences between the valence ionizations of these cobalt and rhodium species. The primary orbital characters associated with each ionization feature are determined by comparing the relative He I/He II intensities, the relative core and valence ionization shifts, and the consistent shifts with ring methylation. Evidence for strong filled-metal with filled-ring orbital interaction is found in the first ionization band and in a band in the region of the cyclopentadienyl e_1'' ionizations. Vibrational fine structure is also observed in the first ionization band, revealing substantial back-bonding into the carbonyls. This band shifts only slightly from cobalt to rhodium. The other predominantly metal ionizations increase substantially in ionization energy from cobalt to rhodium, and the splitting of the ionizations originating from the cyclopentadienyl e_1'' pair of orbitals more than doubles. In contrast to these large changes in the valence ionizations from cobalt to rhodium, there are essentially no changes in the core ionizations, the ground-state geometrical structures, the carbonyl stretching frequencies, and other physical properties. The combined data strongly indicate that the changes in valence ionizations are largely dependent upon excited-state effects in the positive ions. These results have implications for the comparative stability and chemical behavior of cobalt and rhodium complexes.

Introduction

Transition-metal complexes with d^8 electron configurations at the metal are involved in numerous synthetic and catalytic processes.[2] These complexes generally have available coordination sites for interaction with incoming molecules and, in addition, often have readily available oxidation states to allow oxidative additions, rearrangements, reductive eliminations, and other important chemical transformations. Cyclopentadienyl complexes with cobalt, rhodium, and iridium have been receiving increasing attention recently with respect to preparative and catalytic processes.[3]

The reaction chemistry of these complexes can be altered and tuned by changing from Co to Rh to Ir and by changing from cyclopentadienyl to pentamethylcyclopentadienyl groups. The electronic origins and rationale behind these influences are not clearly understood even qualitatively. The best direct experimental approach to investigating the electronic interactions that lead to these properties is photoelectron spectroscopy. We have utilized this approach extensively in the study group 7 (d^6) cyclopentadienylmetal tricarbonyl complexes and numerous related d^6 cyclopentadienylmetal complexes with different metal–molecule and metal–metal interactions. The high-resolution gas-phase He I studies provide precise valence ionization band energies and profiles. In several cases we have observed detailed M–C–O vibrational fine structure that is especially significant because it directly indicates the bonding role of the orbital electrons.[4,5] The relative intensity of ionization bands in the He II excited spectrum in comparison to the relative intensity of bands in the He I spectrum has proven to be a useful method of identifying the predominantly metal ionizations in organometallic complexes.[5–7] Measurement of precise gas-phase core ionization shifts provides additional unique experimental information that allows separation of bonding effects from charge distribution and relaxation effects when used in combination with the valence ionization information.[5,8] It is also useful to compare related cyclopentadienyl and pentamethylcyclopentadienyl complexes to reveal key ionization features and to gain a measure of the fluidity of the electron charge.

The photoelectron spectra of d^8 cyclopentadienyl metal complexes show a richness of valence ionization features not present in the corresponding d^6 complexes.[7,9–11] The

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Table I. Results of Curve-Fit Analysis on Valence Ionization Data

	vert ionizatn energy, eV	half-width, eV		rel integrated peak area		assignmt
		high energy	low energy	He I	He II	
$CpCo(CO)_2$	7.59	0.58	0.30	1.00	1.00	metal I
	7.95	0.59	0.24	0.84	1.09	metal II
	8.51	0.64	0.30	0.89	1.06	metal III
	9.41	0.36	0.44	0.62	0.63	metal IV
	9.87	0.52	0.35	2.35	1.37	ring I
	10.23	0.52	0.35	1.18	0.79	ring II
$Cp^*Co(CO)_2$	6.88	0.45	0.25	1.00	1.00	metal I
	7.37	0.47	0.32	0.84	1.62	metal II
	7.95	0.55	0.35	0.85	1.49	metal III
	8.79[a]	0.66	0.39	3.07	3.48	metal IV, ring I
	9.15	0.66	0.39	0.94	0.76	ring II
$CpRh(CO)_2$	7.64	0.50	0.22	1.00	1 00	metal I
	8.65	0.41	0.16	0.87	1.40	metal II
	9.50	0.43	0.32	1.03	1.62	metal III
	9.82	0.43	0.32	1.22	0.70	ring I
	10.25	0.53	0.34	1.04	0.83	metal IV
	10.59	0.53	0.34	1.02	0.71	ring II
$Cp^*Rh(CO)_2$	6.80	0.54	0.19	1.00	1.00	metal I
	8.12	0.35	0.19	0.69	1.56	metal II
	8.62	0.49	0.35	1.27	1.00	ring I
	9.05	0.49	0.35	0.95	1.35	metal III
	9.63[a]	0.60	0.39	1.79	2.16	metal IV, ring I

[a] Two overlapping peaks under band.

reduced local symmetry and extra electron count at the metal provides for additional complex electronic interactions in these species. Excited-state effects in the form of electron relaxation energies associated with ionization are expected to be more significant in this region of the transition-metal series,[12-14] particularly with the differing degrees of delocalization of the orbital electrons. Splitting of the cyclopentadienyl ionizations due to interaction with the asymmetric metal charge distribution is also expected[15] to be more pronounced than that observed for the d^6 systems.[16] This is a clear example where the combination of core and high-resolution valence ionization studies on a systematic series of complexes is required to obtain a correct evaluation of the different factors influencing the ionizations and chemistry of these species.

In this paper the gas-phase XPS and He I/He II UPS of $CpCo(CO)_2$, $Cp^*Co(CO)_2$, $CpRh(CO)_2$, and $Cp^*Rh(CO)_2$ are reported (Cp = η^5-cyclopentadienyl and Cp* = η^5-pentamethylcyclopentadienyl). Just as $CpMn(CO)_3$ has formed the basis for understanding a large number of small molecule and metal electronic interactions in d^6 complexes, study of these group 8 metal carbonyl complexes will form a basis for understanding a variety of interactions within complexes of this class.

Expermental Section

Published procedures were followed for the preparation of $CpCo(CO)_2$,[17] $Cp^*Co(CO)_2$,[15] $CpRh(CO)_2$,[18] and $Cp^*Rh(CO)_2$.[19] He I, He II, and Mg Kα photoelectron spectra were recorded on an instrument with a 36-cm radius hemispherical analyzer and excitation sources and data collection methods that have been described.[5] All spectra were collected under ambient instrument conditions (25 °C for UPS and 35 °C for XPS). All UPS data was intensity corrected for the experimentally known analyzer transmission function.

The UPS data is presented in analytical form in the tables using an asymmetric Gaussian representation for the ionization bands.[5] The functional form is

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

where $C(E)$ is the electron counts at binding energy E, A is the peak amplitude, P is the peak position (vertical IP), $W = W_h$, the half-width when $E > P$ (on the high binding energy side of the peak), or $W = W_l$, the half-width when $E < P$ (on the low binding energy side of the peak), and $k = 4 \ln 2$. Table I lists the fit parameters to two figures past the decimal place to give an accurate analytical representation of the overall valence ionization band contours. The reproducibility of the vertical ionization energies by these techniques is usually about ±0.02 eV. The relative integrated peak areas are reproducible to about 5% in He I and about 10% in He II for individual peaks. If two peaks are overlapping such that there is not a clear inflection betwen their maxima, the peaks are constrained to have the same shape. These situations can be identified in the tables when two peaks have the same high-energy widths W_h and also the same low-energy widths W_l. Overlapping peaks are included in the fit of a band only if they are needed for a statistically significant representation of the band contour and produce experimentally reasonable band shapes. Because of the correlation between peak parameters in an overlapping band, there is greater uncertainty in the true vertical ionization energy for each peak (about ±0.1 eV in worst cases).

The XPS data was collected on the sample while a stable pressure of an internal standard gas was maintained. Two noble gases are used: Ar ($2p_{3/2}$ 248.62 eV) and Ne (1s 870.31 eV) and the standard is chosen to be closest to the desired sample ionization (Ne 1s for Co $2p_{3/2}$ and O 1s; Ar $2p_{3/2}$ for Rh $3d_{5/2}$ and C 1s). A mixture of Ar and Ne is used to calibrate the energy scale. The reported values are an average of 4–8 runs, and the reported uncertainties are the standard deviations from the average.

Calculations. Orbital eigenvalues were calculated by the Fenske–Hall method.[20] The atomic basis functions were taken

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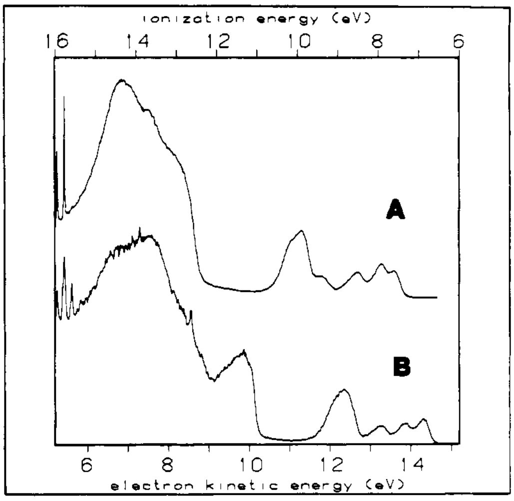

Figure 1. The full He I photoelectron spectra of (A) $CpCo(CO)_2$ and (B) $Cp^*Co(CO)_2$, where Cp = C_5H_5 and Cp* = $C_5(CH_3)_5$.

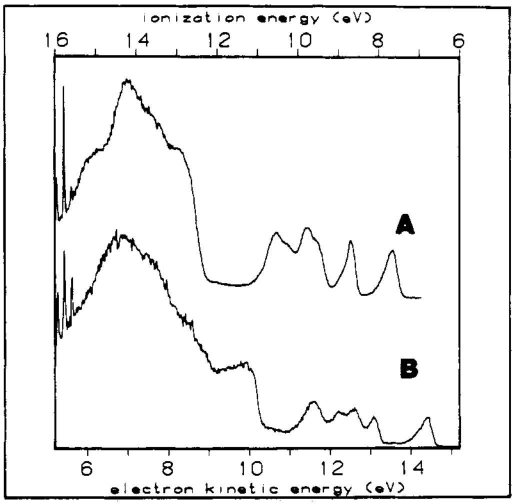

Figure 2. The full He I photoelectron spectra of (A) $CpRh(CO)_2$ and (B) $Cp^*Rh(CO)_2$, where Cp = C_5H_5 and Cp* = $C_5(CH_3)_5$.

from Richardson[21] (Co 1s through 3d with 4s and 4p exponent of 2.0) and Clementi[22] (double-ζ carbon and oxygen functions with the 1s and 2s reduced to single-ζ form). An exponent of 1.2 was used for the hydrogen atom. The atomic positions of $CpCo(CO)_2$ were set according to the crystal structure of $Cp^*Co(CO)_2$.[15]

Ionization Information

The combined experimental results from the different ionization techniques on this series of molecules provides much direct information on the electron distribution and bonding in this class of metal complexes without recourse to theoretical considerations. The experimental results are able to show the delocalization and bonding associated with the first ionization, the ionization energies of the different metal levels, and the nature of the ring-metal and metal-carbonyl interactions. It is also shown how these characteristics are changed with methylation of the cyclopentadienyl ring and with changing from cobalt to rhodium. This section details the information provided solely by the ionizations.

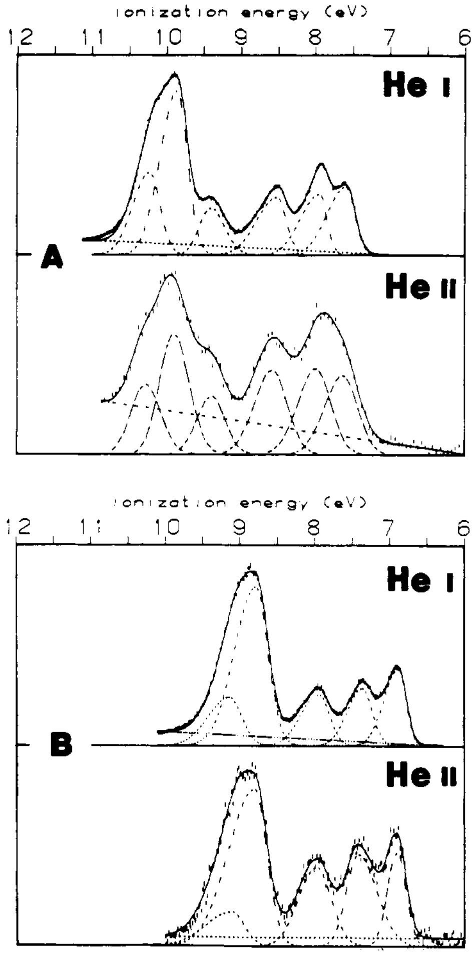

Figure 3. The He I and He II comparison for (A) $CpCo(CO)_2$ and (B) $Cp^*Co(CO)_2$, where Cp = C_5H_5 and Cp* = $C_5(CH_3)_5$.

The valence ionizations below 16 eV of the complexes are shown in the He I photoelectron spectra in Figures 1 and 2. These spectra are similar to those obtained previously.[7,11] As is common with cyclopentadienylmetal carbonyls, the broad, intense band envelope between 15 and 12 eV is due to ionizations from a series of closely spaced ring and CO orbitals including the ring a_2'' π orbital. The permethylated compounds possess an additional peak at around 11.5 eV that has been assigned to ionization from certain methyl group orbitals.[5] The ionization region below 11 eV furnishes much information on the important valence orbital interactions in these compounds and the changes that take place in this region will be a central focus.

$CpCo(CO)_2$ and $Cp^*Co(CO)_2$. The close-up, low-energy He I and He II spectra of these complexes are shown in Figure 3 with the corresponding band-shape analysis listed in Table I. From the results of previous work on cyclopentadienylmetal carbonyls,[5] it is known that only ionizations from the highest occupied ring π orbitals and orbitals that are high in metal d character occur below 11 eV. In these d^8 compounds these orbitals should derive from the four filled metal d orbitals and a pair of orbitals that originate from the e_1'' HOMO of the free cyclopentadienide ring. For the purposes of this discussion we will label the valence ionizations according to their general origins as metal I through metal IV and ring I and ring II. As will be seen, several of these ionizations involve substantial orbital interactions.

In the He I spectrum of $CpCo(CO)_2$ in Figure 3A band-shape features are observed that show the presence of all six ionization peaks. The He I band intensities give the first indication of the character of the ionizations. The fifth ionization band is much more intense in the He I spectrum of $CpCo(CO)_2$ than the other ionization bands, showing that this ionization is largely associated with the

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carbon character in the cyclopentadienyl ring. This band will be labeled ring I. The sixth ionization band is intermediate in He I intensity, suggesting a mixing of ring and metal character. The position of this band suggests that it should be labeled ring II. The first through fourth ionization bands are lowest in He I intensity and therefore presumably highest in metal character. These will be assigned as metal I through metal IV starting at low binding energy. The intensity of the first ionization band, metal I, indicates that analogous to ring II, a significant amount of ring/metal mixing is occurring. This interpretation of metal I is only tentative at this point because overlap of ionization bands metal I and metal II places some uncertainty on the precise intensity of each band. The spectra of the other complexes will clarify the nature of the metal I and ring II ionizations. The He II spectrum shows a very large drop in the relative intensity of band ring I, consistent with its ring character. The bands metal II and metal III are clearly observed to increase in relative intensity with He II excitation, consistent with their metal character. The bands ring II and metal I show an intermediate change between relative He I and He II intensities. They increase in intensity relative to ring I and decrease relative to metal II and metal III.

Comparison of the He I spectrum of $CpCo(CO)_2$ with that of $Cp^*Co(CO)_2$ (Figure 3B) provides peak assignment information from the shift of the ionization bands. In the case of $Cp^*Co(CO)_2$ we can clearly resolve only four ionization features, although two Gaussians are needed for a reasonable representation of the most intense band at 8.8 eV. It is apparent that the most intense ionization band ring I has shifted and merged with the band corresponding to peak metal IV of $CpCo(CO)_2$. The ionization energy shifts that result from ring methylation are listed in Table III. These results show that while all six ionizations shift to lower energy upon ring methylation, the four lowest energy ionizations of $CpCo(CO)_2$ shift much less than peaks ring I and ring II. This is a further indication that peaks labeled ring I and ring II are high in ring π character. It is also observed that band metal I shifts more than metal II, metal III, and metal IV, causing it to move further apart from the other ionizations. This again suggests that this first band is associated with ionization from an orbital with a substantial amount of ring character.

The changes that occur when going to He II are clearer in the initial ionizations for $Cp^*Co(CO)_2$ than for $CpCo(CO)_2$ because of the reduced overlap of ionization bands metal I and metal II. The integrated peak areas listed in Table I indicate that band metal I does not increase in relative intensity nearly as much as bands metal II and metal III, consistent with the greater metal character in these latter ionizations.

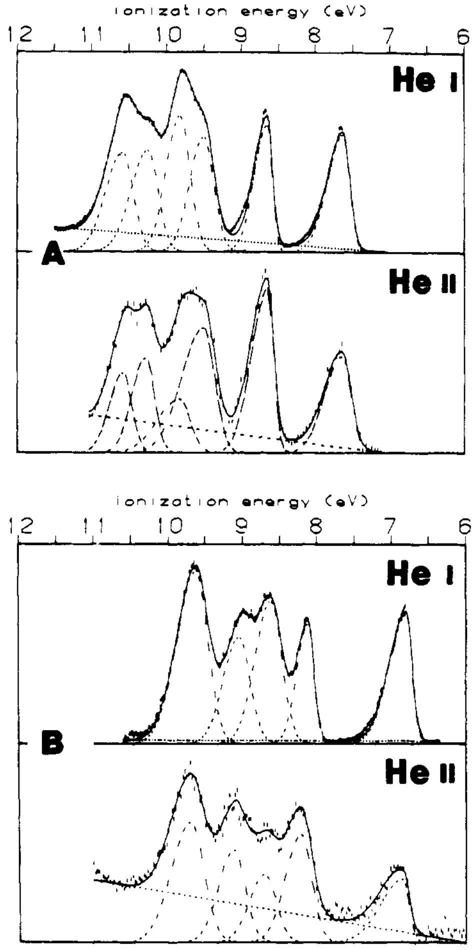

Figure 4. The He I and He II comparisons for (A) $CpRh(CO)_2$ and (B) $Cp^*Rh(CO)_2$, where Cp = C_5H_5 and Cp* = $C_5(CH_3)_5$.

$CpRh(CO)_2$ and $Cp^*Rh(CO)_2$. The He I and He II spectra of the rhodium complexes are shown in Figure 4. In the case of $CpRh(CO)_2$ six individual ionization bands are observed as in the spectrum of $CpCo(CO)_2$. However, the pattern of the ionizations is much different between these two complexes. The He I spectrum of $CpRh(CO)_2$ (Figure 4A) shows that there is not as distinct an energy separation between the metal and ring ionizations as in $CpCo(CO)_2$, although there is a much greater separation between the first and second ionization bands from the following ionizations. The ionization ordering also changes considerably when Co is replaced by Rh. It can be seen in Figure 4 and Table I that the peaks at 9.82 and 10.59 eV (the fourth and sixth ionization bands) both lose intensity compared to the other four peaks in the He II spectrum and correlate with the ring ionizations ring I and ring II of $CpCo(CO)_2$. The splitting of these two peaks is 0.77 eV as opposed to 0.36 eV in $CpCo(CO)_2$. The change in this splitting is an important point in the Dicussion.

Comparison with the spectrum of the permethylated $Cp^*Rh(CO)_2$ analogue in Figure 4B is helpful. As in $Cp^*Co(CO)_2$, we can no longer resolve one of the valence ionizations. The third ionization band in this case clearly loses intensity relative to the other four ionizations in the He II spectrum, indicating the predominantly cyclopentadiene ionization ring I. This band is found to shift very little when Co is replaced by Rh in support of its predominant cyclopentadiene character. The shifts of the other ionizations are such that while ring I is the fifth band of $CpCo(CO)_2$, it merges with the fourth band of $Cp^*Co(CO)_2$, it is the fourth band of $CpRh(CO)_2$, and it is the third band of $Cp^*Rh(CO)_2$. Ring II, which also has substantial cyclopentadiene character, shifts along with ring I in all cases. The fifth band of $Cp^*Rh(CO)_2$ apparently contains ring II and metal IV. The ring II band shifts nearly half an eV when Co is replaced by Rh, again suggesting some metal character associated with this ionization.

The shifts that result from permethylation of the cyclopentadiene ring are shown in Table III. The similarity of the shifts with permethylation of the cobalt and rhodium complexes substantiates the assignments. The two ring ionizations ring I and ring II shift the most as expected. Of the four remaining ionizations, three (metal II, metal III, and metal IV) shift by approximately the same amount while the first ionization band at 7.64 eV shifts more but still less than the ring ionizations.

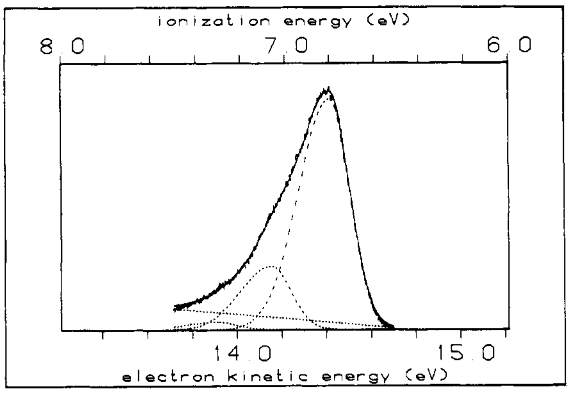

Figure 5. The first ionization band of $Cp^*Rh(CO)_2$.

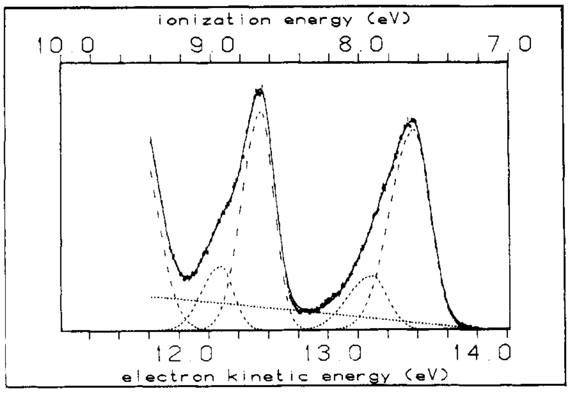

Figure 6. Close-up He I spectra of the first two ionization bands of $CpRh(CO)_2$.

Because of these ionization energy shifts, the first ionization band in $Cp^*Rh(CO)_2$ is now well-separated from the other ionization energy bands and the first two ionizations of $CpRh(CO)_2$ are well-separated from the other ionizations. The detailed examination of these band profiles is especially informative. Figure 5 shows that a vibrational progression in the CO stretching mode is clearly observed in the first ionization band of $Cp^*Rh(CO)_2$. A progression of this sort is expected when ionization of a predominantly metal electron with substantial back-bonding to carbonyls activates the symmetric stretching mode.[5,23,24] In our studies of d^6 metal carbonyls only two members of the CO vibrational progression are observed (the main peak and a shoulder). In the present d^8 case three members are clearly obtained, indicating more extensive delocalization of the metal electrons into the carbonyls and a more substantial change in CO bond distance when this electron is removed. The first two ionization bands of $CpRh(CO)_2$ also show CO vibrational structure (Figure 6). The frequency here is 2270 ± 80 cm^{-1}. The second ionization band is narrower and therefore has less bonding character than the first ionization. The CO vibrational structure is clearer in the second band than in the first because of the narrowness of each vibrational component.

Table II. Core Ionization Data for $CpM(CO)_2$ and $Cp^*M(CO)_2$

	orbital	ionization energy, eV Cp	 Cp*
M = Co	C 1s(Cp)	290.61 (6)	290.44 (3)
	C 1s(CO)[a]	292.77 (15)	292.12 (10)
	O 1s	538.92 (3)	538.41 (3)
	Co $2p_{3/2}$	785.95 (4)	785.32 (5)
M = Rh	C 1s(Cp)	290.59 (3)	290.36 (1)
	C 1s(CO)[a]	293.09 (14)	292.21 (10)
	O 1s	538.99 (5)	538.43 (4)
	Rh $3d_{5/2}$	315.03 (7)	314.37 (3)

[a] The uncertainty for these numbers is large because of partial overlap with the more intense cyclopentadienyl carbon 1s ionizations.

Table III. Shifts in Core and Valence Ionizations Energies (eV[a]) Resulting from Ring Methylation

	$CpCo(CO)_2$ to $Cp^*Co(CO)_2$	$CpRh(CO)_2$ to $Cp^*Rh(CO)_2$
carbon core 1s (Cp)	−0.17	−0.23
carbon core 1s (CO)	−0.65	−0.88
oxygen core 1s	−0.51	−0.56
metal core	−0.63[b]	−0.66[c]
valence band metal I	−0.71	−0.84
valence band metal II	−0.58	−0.53
valence band metal III	−0.56	−0.45
valence band metal IV	−0.62[d]	−0.62[d]
valence band ring I	−1.08[d]	−1.20
valence band ring II	−1.08	−0.96[d]

[a] Shifts to lower binding energy are negative. [b] Cobalt $2p_{3/2}$. [c] Rhodium $3d_{5/2}$. [d] Bands overlap in the pentamethylcyclopentadienyl complexes.

Table IV. Shifts in Core and Valence Ionization Energies (eV[a]) from Cobalt to Rhodium

	$CpCo(CO)_2$ to $CpRh(CO)_2$	$Cp^*Co(CO)_2$ to $Cp^*Rh(CO)_2$
carbon core 1s (Cp)	−0.02 (9)	−0.08 (4)
carbon core 1s (CO)	+0.3 (3)	+0.1 (2)
oxygen core 1s	+0.07 (8)	+0.02 (7)
valence band metal I	+0.05	−0.08
valence band metal II	+0.70	+0.75
valence band metal III	+0.99	+1.10
valence band metal IV	+0.84	+0.84
valence band ring I	−0.05	−0.17
valence band ring II	+0.36	+0.48

[a] Shifts to lower binding energy are negative. [b] Bands overlap in pentamethylcyclopentadienyl complexes and increase uncertainty in shifts to about 0.2 eV.

Core Ionization Information. The gas-phase core ionization data for these complexes are listed in Table II. The core level shifts with ring methylation assist in a different way with assignment and interpretation of the valence ionizations. It is known from previous core ionization studies that the basically inductive effect of ring permethylation causes a 0.2–0.3 eV shift of the carbon 1s binding energies to lower energy.[5] The valence ring ionizations derived from the e_1'' set of π orbitals shift about 1 eV or more to lower binding energy because of an additional hyperconjugative (overlap) interaction with methyl group orbitals. The methyl group orbitals responsible for this interaction are observed to ionize in the region of 11 eV. The shifts of valence band ring I (Table III) in all spectra are as expected for ionizations from these ring levels.

For levels that are localized on the metal the core ionization shifts should be similar to the valence ionization shifts,[5,8,25] because there is no overlap interaction with the methyl orbitals. This is reasonably correct for valence bands metal II, metal III, and metal IV. The first ionization band metal I, as noted previously, consistently shifts more than bands metal II, metal III, and metal IV, indi-

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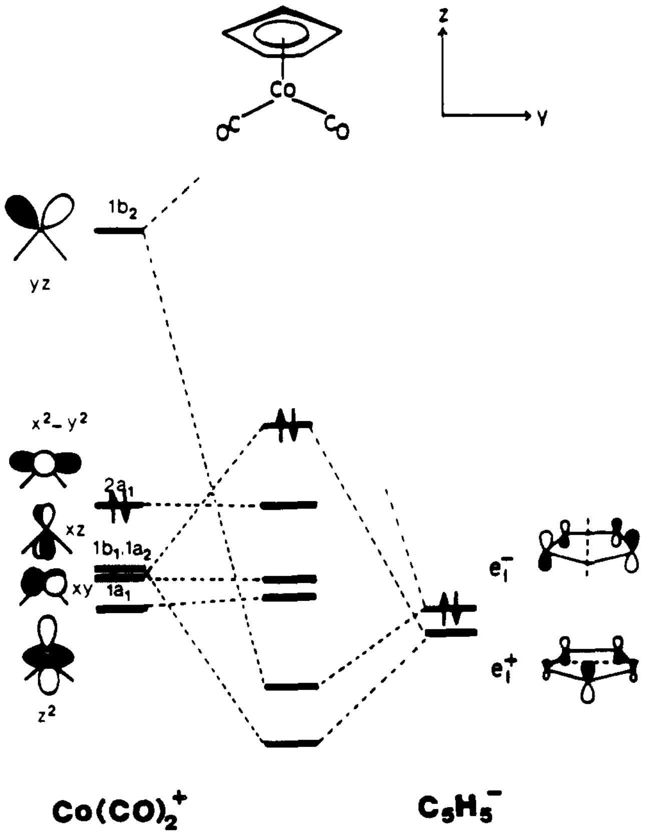

Figure 7. The Fenske–Hall molecular orbital diagram of $CpCo(CO)_2$. The HOMO is indicated.

cating delocalization into the cyclopentadienyl ring π system. Thus the first ionization in these complexes exhibits substantial delocalization into both the ring and the carbonyl groups.

It is also interesting to compare the core and valence ionization energy shifts between analogous cobalt and rhodium complexes shown in Table IV. The first point to be noted is that there is essentially no shift in the core ionizations for the cyclopentadienyl and carbonyl groups. This indicates that the charge distribution and potential that these groups experience is not significantly altered by rhodium in place of cobalt. The first valence ionization energy is also relatively constant, presumably in part because of the delocalization of this level into the cyclopentadienyl and carbonyl ligands. The remaining valence metal levels metal II, metal III, and metal IV show substantial shifts, and the predominantly cyclopentadienyl levels ring I and ring II shift by different amounts and in different directions. The very large changes in these valence ionizations, in contrast to the negligible changes in the core ionizations of the ligands, are important for comparing the nature of these cobalt and rhodium complexes.

Discussion

Qualitative discussions of the orbital interactions in d^8 cyclopentadienylmetal dicarbonyls have appeared previously.[26,27] A more detailed understanding of these levels is now possible on the basis of this experimental study. A molecular orbital diagram obtained from a Fenske–Hall calculation for $CpCo(CO)_2$ is shown in Figure 7. The four occupied predominantly metal orbitals of the $Co(CO)_2^+$ fragment are the $1a_1$, $1a_2$, and $1b_1$ which are stabilized by back-bonding to the carbonyls, and the $2a_1$, which can also back-bond to the carbonyls but in addition is slightly destabilized by some σ antibonding. This will slightly enhance the delocalization of the $2a_1$ into the carbonyls, and this is observed in the CO vibrational structure in the ionization of this level. The empty metal orbital is the $1b_2$, which is directed for sigma interaction with the two carbonyls.

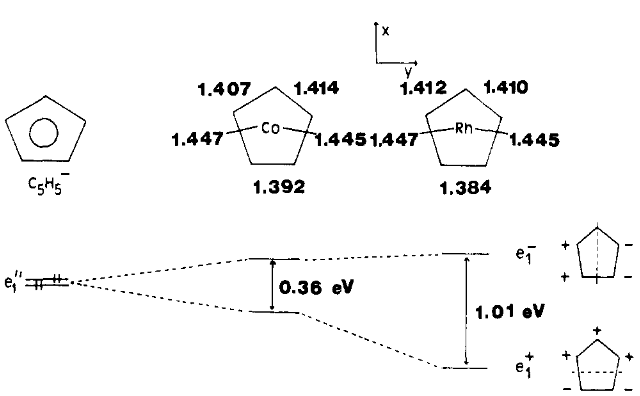

Figure 8. Observed loss in degeneracy in the ring e_1'' orbitals upon coordination, in comparison to the crystallographically determined bond lengths in the cyclopentadienyl rings.

One metal–ring interaction is between the metal $1b_1$ and the ring orbital labeled e_1^+ (according to its Cp^- origin and the symmetry with respect to the mirror plane).[15] This is a filled–filled orbital interaction that does not result in net bonding, but it does serve to stabilize the bonding combination of the interaction. The ionization associated with this bonding combination has been labeled ring II because of its primary origin. The strong metal–ring mixing in this ionization is evidenced by the He I/He II intensity comparisons, and the ionization energy shifts from cobalt to rhodium. The antibonding counterpart of this filled–filled interaction is labeled metal I and is the first ionization of the complexes. The first ionization of these complexes will be discussed later. It should be noted that this filled–filled interaction does not directly result in a change of charge distribution in the vicinity of the metal and the ring.

The primary bonding interaction between the ring and the metal occurs through electron donation from the ring e_1^- orbital to the empty metal $1b_2$ orbital. The interactions of the e_1^+ and e_1^- orbitals with the metal are clearly different, and this will serve to lift the degeneracy of the resultant ionizations. A Fenske–Hall calculation on the cyclopentadienyl ring fragment using the distortion found in the crystal structures shows that the e_1^+ orbital should be separated by 0.65 eV below the e_1^- orbital *before* overlap interaction with the metal. Interaction with the metal will further separate the energies. It can be seen that the expected large splittings are observed in these ionizations for the rhodium compounds ($CpRh(CO)_2$, 0.77 eV; $Cp^*Rh(CO)_2$, 1.01 eV).

The cobalt analogues are found to have much smaller splittings ($CpCo(CO)_2$, 0.36 eV, $Cp^*Co(CO)_2$, 0.36 eV). These splittings are comparable to or even smaller than the splittings we have observed for d^6 cyclopentadienylmetal tricarbonyls (0.36–0.46 eV), in which geometrical and electronic perturbations are known to be much smaller.[5] The possibility that these ionization differences between Co and Rh are due to ground-state bonding differences was partly the reason that we undertook a careful structural comparison of the cobalt and rhodium complexes.[15,19] The decreased population of the e_1^- orbital relative to the e_1^+ orbital is reflected in a geometrical distortion of the ring from fivefold symmetry. The pertinent results of this

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Table V. CO Stretching Frequencies and ^{1}H NMR

	CO stretch, cm^{-1}	^{1}H NMR, τ
$CpCo(CO)_2$	2033, 1972[a]	5.00[b]
$CpRh(CO)_2$	2040, 1975[c]	5.12[d]
$Cp^*Co(CO)_2$	2010, 1950[e]	8.11[f]
$Cp^*Rh(CO)_2$	2012, 1947[g]	7.95[h]

[a] Cyclohexane: King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287. [b] CS_2: footnote *a*. [c] CCl_4: this work. [d] Benzene: Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. [e] Hexane: Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277. [f] CS_2: footnote *a*. [g] Hexane: this work. [h] $CDCl_3$: Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *26*, 393.

study are shown in Figure 8. For the pentamethylcyclopentadienyl complexes of Co and Rh the distortion of the rings is nearly identical, indicating no significant change in ground-state bonding of the e_1^- orbital to the metals. The similar electron distribution in the vicinity of the ring is also reflected in the constant carbon core ionization energies. There is no evidence of substantial changes in the ground-state electron distribution and bonding in these complexes, but splitting of the ionizations derived from e_1^+ and e_1^- interactions with the metal nearly triples between the Co and Rh complexes.

These results point to excited-state effects associated with electron relaxation in the positive ions. It has been found both experimentally[28-31] and theoretically[12,32] that electron relaxation energies can be substantial for transition-metal complexes, particularly for first-row metals to the right of the transition-metal series and for d^8 configurations.[12,13] In addition, electron relaxation energies are expected to decrease while descending a column of the periodic table. Ab initio calculations show that cobalt 3d ionizations will have almost twice the relaxation of rhodium 4d ionizations.[12] This will have an important influence on the observed splitting of the ionizations if the metal character obtained in the mixing with e_1^+ and e_1^- is different. The He I/He II intensity comparisons and valence ionization shifts indicate that the ring II ionization (the bonding combination of the filled–filled ring e_1^+/metal $1b_1$ interaction) has greater metal character than ring I. This is largely because of the closer energy proximity of the ring e_1'' orbitals to the filled metal $1b_1$ than the empty $1b_2$ orbital. This metal character in ring II produces a greater relaxation energy with ionization in the case of cobalt than in the case of rhodium, leading to the decreased splitting in the ring I and ring II bands in the cobalt spectra.

The importance of this relaxation is even more evident in the predominantly metal ionizations. The ionizations metal II, metal III, and metal IV show the largest shifts between the cobalt and rhodium complexes. These shifts, which are between 0.7 and 1.1 eV, are very large in comparison to the nearly constant ionization energies observed for first- and second-row d^6 complexes. For instance, the t_{2g} ionizations of $Cr(CO)_6$ and $Mo(CO)_6$ are within 0.05 eV.[4] If the metal atomic orbital energies of rhodium were on the order of 1 eV more stable than those of cobalt in the ground state of these molecules, this would substantially decrease the ability of the rhodium relative to cobalt to back-bond to the carbonyls and would alter the bonding of the metal with other ligands. However, as the core ionization data in Table IV shows, the electron potential experienced by the carbonyl and cyclopentadienyl ligands is not changed between the Co and Rh complexes. Furthermore, Table V shows that neither the carbonyl stretching frequencies nor the proton NMR shifts change significantly between the cobalt and rhodium complexes. It is apparent once again that changes in ground-state electron distributions are not primarily responsible for the shifts in the valence ionizations between these cobalt and rhodium complexes. The greater electron relaxation energy associated with cobalt 3d ionizations is a major factor for their lower ionization energies in comparison to the rhodium complexes.

This same result is found from examination of the simple Co^+, and Rh^+ ions. Ab initio atomic SCF calculations on the Co^+ and Rh^+ ions (d^8 configurations) place the valence d orbital energies the same within a few tenths of an electronvolt (with Co having the higher ionization energy).[33] Experimentally, the Rh^+ ion has the higher ionization energy by 1.0 eV,[34] just as we find for the predominantly metal ionizations of these organometallic complexes.

The first ionization of these complexes, labeled metal I, is essentially constant in ionization energy in the Co and Rh complexes. This is an interesting contrast to the shift of the other ionizations associated with metal character. The metal I band is the antibonding counterpart of the interaction between the metal $1b_1$ and the ring e_1^+, and this serves to reduce the metal character associated with the ionization. This delocalization of metal character from metal I to ring II accounts for most of the shift in the ring II ionization when the metal is changed from Co to Rh, but it is not sufficient to account for the nearly constant metal I ionization energy. An additional factor must be associated with further delocalization of metal I into the π^* of the carbonyls. The width and vibrational fine structure of the first ionization band shows that it is not associated with a simple antibonding orbital. Because of the metal–ring mixing it does include some carbon–carbon bonding within the ring. In addition, the destabilization of the metal b_1 density through antibonding interaction with the ring increases the donor ability of this orbital to the π^* of the carbonyls. This gives rise to the substantial CO vibrational progression observed with this ionization. Thus this additional delocalization of metal character releases antibonding interaction between the ring and the metal into bonding with the carbonyls and is partly responsible for the very small shift of this ionization when cobalt is replaced by rhodium.

Any shifts in valence ionization energies caused by changes in ground-state orbital interactions and bonding between the Co and Rh complexes are on a much smaller scale than the large shifts in the predominantly metal ionizations. Differences in ground-state bonding and electron distribution in these complexes are beyond the discrimination level of a variety of experiments. The charge potential at each atom is the same within the confidence limits of the core ionization data (within 0.1 eV). Ground-state bonding features as indicated by carbonyl stretching frequencies, proton NMR, and structural

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distortion of the cyclopentadienyl ring are also the same within the uncertainty of these experiments. It is not surprising that many classes of analogous cobalt and rhodium complexes have been prepared. It is also not surprising that different synthetic routes are sometimes required for the preparation of these complexes and that they can have very different chemistries. The excited-state effects evidenced here in the shifts of the predominantly metal valence ionizations can have substantial consequences for oxidation and reduction processes, as well as the stability of key intermediates and products. In these complexes it is clear that delocalization of the highest occupied orbital into the carbonyls is having a significant influence on the character and stability of the first ionization level.

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Registry No. $CpCo(CO)_2$, 12078-25-0; $CpRh(CO)_2$, 12192-97-1; $Cp^*Co(CO)_2$, 12129-77-0; $Cp^*Rh(CO)_2$, 32627-01-3.

Concerted [4π + 2π] Cycloaddition of (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5) with the Isomeric 2-Butenedinitriles

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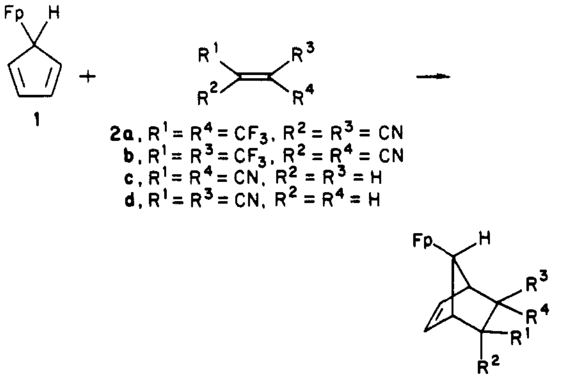
Fumaronitrile and maleonitrile rapidly cycloadd to (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5) with comparable rates to afford 7-*syn*-[(η^5-C_5H_5)Fe(CO)$_2$]bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*endo*-dicarbonitrile (**3b**) and a 1:1 mixture of 7-*syn*-[(η^5-C_5H_5)Fe(CO)$_2$]bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*exo*-dicarbonitrile (**3c**) and 7-*syn*-[(η^5-C_5H_5)Fe(CO)$_2$]bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarbonitrile (**3d**), respectively, in excellent yield. Mechanistic studies strongly support a concerted [4π + 2π] cycloaddition for these reactions.

Introduction

Cycloaddition of transition-metal η^1-allyl complexes to unsaturated electrophilic molecules has been much studied recently.[1] Correlation of the stereochemistry of the starting alkene with the stereochemistry of the product can provide mechanistic insight into this reaction. Williams and Wojcicki[2] reported that Fp(η^1-C_5H_5) (1), where Fp = (η^5-C_5H_5)Fe(CO)$_2$, reacts with both *trans*- and *cis*-1,2-bis(trifluoromethyl)-1,2-dicyanoethylene, **2a** and **2b**, respectively, to give the same cycloadduct **3a** in which the trifluoromethyl groups are trans to each other. Fumaronitrile **2c** also yields a 1:1 cycloadduct with undetermined stereochemistry.[2] This paper reports the stereochemistry of the cycloadducts obtained by reaction of fumaronitrile and its geometric isomer maleonitrile **2d** with Fp(η^1-C_5H_5) and the mechanism for these reactions.



2a, $R^1 = R^4 = CF_3$, $R^2 = R^3 = CN$
b, $R^1 = R^3 = CF_3$, $R^2 = R^4 = CN$
c, $R^1 = R^4 = CN$, $R^2 = R^3 = H$
d, $R^1 = R^3 = CN$, $R^2 = R^4 = H$

3a, $R^1 = R^4 = CF_3$, $R^2 = R^3 = CN$
b, $R^1 = R^4 = CN$, $R^2 = R^3 = H$
c, $R^1 = R^3 = CN$, $R^2 = R^4 = H$
d, $R^2 = R^4 = CN$, $R^1 = R^3 = H$
e, $R^1 = R^4 = CO_2Me$, $R^2 = R^3 = H$

Results and Discussion

As reported by Williams and Wojcicki,[2] fumaronitrile and Fp(η^1-C_5H_5)[3] rapidly react at room temperature. After chromatography, analytically pure cycloadduct is obtained in 85% yield. The IR and ^{1}H NMR spectra of this compound agree with the data previously reported. Especially instructive for assigning the stereochemistry of this cycloadduct as **3b** is analysis of its ^{1}H NMR spectrum at 250 MHz.[4] The key absorptions are at δ 3.04 (dd, 1, J = 3.8, 3.9 Hz) and 2.55 (d, 1, J = 3.8 Hz) that are assigned to the *exo*- and *endo*-CHCN protons, respectively. Double irradiation demonstrates that they are coupled to each other (J = 3.8 Hz), and the upfield signal due to the endo hydrogen atom is not coupled to the adjacent bridgehead proton whereas the downfield resonance due to the exo-hydrogen atom is (J = 3.9 Hz).

Surprisingly, maleonitrile[5] rapidly reacts with Fp(η^1-C_5H_5) at room temperature. Indeed, allowing maleonitrile and fumaronitrile to compete for Fp(η^1-C_5H_5) reveals the two alkenes to be of comparable reactivity. This dramatically contrasts with the results with dimethyl fumarate

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