of the measurements in supercritical CO_2 were made entirely without stirring, this for a system that is notorious for spurious results due to gas-depletion effects in normal liquids.[31]

IV. Conclusions

The cobalt-catalyzed hydroformylation of propylene works well in supercritical carbon dioxide, is unencumbered with the normal liquid/gas mixing problems that can occur in conventional solvents, while the several reaction variables tested seem to behave normally.

One of the most intriguing aspects of the olefin hydroformylation reaction stems from the observation that the rate of hydroformylation is often faster than the rate of $HCo(CO)_4$ formation from $Co_2(CO)_8$.[20,25] The Heck and Breslow mechanism accounts for this behavior by proposing that the additional hydrogen activation occurs via the intermediate acyl complex.[20,26,27] However, other possibilities exist that might involve olefin complexes, odd-electron species,[32] or clusters[25] in the hydrogen activation mechanism. In future studies, we intend to explore the various possibilities with use of the supercritical fluid/NMR techniques described here.

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Delocalized Electronic Interactions in Chiral Cyclopentadienylrhenium Halide Complexes. Valence Photoelectron Spectra of CpRe(NO)(L)X (Cp = η^5-C_5H_5, η^5-$C_5(CH_3)_5$; L = CO, $P(C_6H_5)_3$; X = Cl, Br, I)

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The electron energies and distributions of the title complexes are investigated by valence photoelectron spectroscopy. Assignment and characterization of the ionization bands are assisted by the trends in He I and He II cross sections for ionization intensities, as well as by the widths and vibrational progressions of certain ionization bands. The shifts of the ionizations, which are key to revealing the nature of the electronic structure interactions in a system, are caused by halogen substitutions on the metal, methyl substitutions on the cyclopentadienyl rings, and phosphine substitutions for the carbonyls. The first three ionizations, corresponding to the three occupied d orbitals of the d^6 Re(I) metal center, are widely separated. This is because each of the three metal d orbitals have very different π interactions with the three different CO, NO, and halogen ligands. The ionizations indicate extensive metal–halogen mixing and a very delocalized electronic structure throughout the metal–ligand system. The first two ionizations correspond to the metal–halogen π^* interaction, which results from the filled–filled interaction, with the first ionization including back-bonding to the carbonyl and the second ionization including back-bonding to the nitrosyl. The third ionization involves back-bonding to both the carbonyl and the nitrosyl. The first two ionizations of the iodide complexes show short vibrational progressions corresponding to the CO and NO stretches. The difference in stabilization of the metal levels by metal–carbonyl and metal–nitrosyl back-bonding is determined from the splitting between the first two ionization bands. The M–X π^* orbitals have increasing halogen character from the chloride complex to the iodide complex, but unlike for the previously studied $Re(CO)_5X$ complexes, where the first ionization shifted from predominantly metal to predominantly halogen in proceeding from X = Cl to X = I, in this case the first three ionizations remain predominantly metal throughout. There is indication in one case of further delocalized interaction of the M–X π electrons with Cp-based electrons. The extent of delocalized and fluid electron density in these systems is in contrast to other systems like $(\eta^5$-$C_5H_5)Fe(CO)_2X$ and $(CO)_5ReX$.

Introduction

Chiral rhenium complexes of the type $CpRe(NO)(L)X$[1-4] provide easily accessed templates in which metal–ligand interactions can be systematically probed. Many of these formally octahedral compounds are readily prepared in optically active form[5,6] and undergo stereospecific or highly stereoselective transformations.[7-9] In particular, the recent discovery of unusual cationic alkyl halide complexes of the formula[10] $[CpRe(NO)(PPh_3)(XR)]^+BF_4^-$ prompted interest

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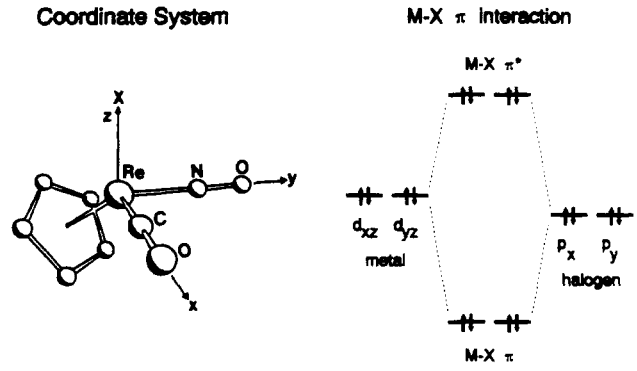
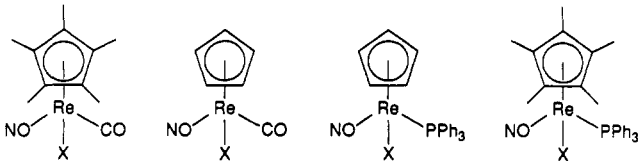


Figure 1. Metal–halogen π interaction in $(\eta^5\text{-}C_5H_5)Re(NO)(CO)X$ systems.

in the corresponding neutral halide complexes CpRe(NO)(PPh_3)X. In an attempt to better understand reaction mechanisms, a detailed knowledge of structure and bonding in these compounds has been sought. As part of this study, the He I and He II photoelectron spectra of CpRe(NO)(L)X complexes (Cp = $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5(CH_3)_5$; L = CO, PPh_3; X = Cl, Br, I) are presented here.



X= Cl, Br, I

In complexes where a halogen is bonded to a transition metal with filled d levels, there is a π interaction between the halogen p_π electrons and the metal electrons. In these cases the filled–filled metal–halogen mixing leads to metal–halogen π and π^* orbitals, as shown in Figure 1. Determination of the predominant metal or halogen character in the highest occupied molecular orbitals of such complexes has been a special challenge. Complexes of the types $(CO)_5ReX$ and $CpFe(CO)_2X$ (where X is Cl, Br, or I) have been thoroughly studied and represent some of the early triumphs of valence photoelectron spectroscopy. The extent of metal–halogen mixing in the $CpFe(CO)_2X$ complexes was estimated by He I/He II intensity trends[11] and in the $(CO)_5ReX$ systems by the extent of spin–orbit coupling.[12] The CpRe(CO)(NO)X complexes are "isoelectronic" with the $CpFe(CO)_2X$ complexes. One would expect the metal levels in the more positive Fe(II) complexes to be stabilized compared to those of the Re(I) complexes. However, the strong back-bonding ability of the nitrosyl ligand will also stabilize the Re complexes compared to the Fe complexes. The amount of metal–halogen mixing depends on the available metal electron density. The delocalization and stabilization of metal electron density by back-bonding to the nitrosyl may reduce the interaction with the halogen p_π electrons. The relative significance of these factors is revealed by valence photoelectron spectroscopy.

The comparison of these complexes with $(CO)_5ReX$ (X = Cl, Br, I) complexes is also enlightening. Hall has performed an excellent spin–orbit analysis applied to the ionizations of these $(CO)_5ReX$ complexes.[12] The CpRe(CO)(NO)X complexes do not have a symmetry-degenerate pair of metal–halogen π^* orbitals to measure the spin–orbit splitting as was done in the case of the $(CO)_5ReX$ complexes. This is because the metal–halogen π^* orbitals are back-bonding to ligands of differing π-acceptor ability (CO and NO) and they split in energy primarily due to this interaction. The He I experiments allow the monitoring of shifts in valence energies with ligand substitution.[13] The effects of Cp ring methylation and carbonyl/phosphine substitution on the metal and ligand ionizations are useful in characterizing these ionizations. This system presents a series of complexes where the ligands around the metal center have varying amounts of σ-donating and π-accepting ability. The trends in He I and He II intensities provide another estimate of the extent of metal–halogen mixing. The predominantly metal ionizations increase in intensity on going from He I to He II compared to the ligand ionizations, whereas the ionizations predominantly halogen in character decrease in intensity in He II because of the low photoionization cross sections of the halogens in He II.[13] Thus, much information relating to the electron distributions and bonding in this series of complexes can be gained from the combination of these experiments.

Experimental Section

Preparation of Compounds. General synthetic and spectroscopic procedures were identical with those given in recent papers.[10,14] Alkylammonium halide salts were obtained from Aldrich and used without purification.

CpRe(NO)(CO)X.[15] The following procedure is representative. A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(CH_3)$ (0.260 g, 0.801 mmol),[1,2] CH_2Cl_2 (10 mL), and a stir bar. The flask was cooled to 0 °C, and CF_3SO_3H (0.071 mL, 0.801 mmol) was slowly added with stirring. After 2 min, $Bu_4N^+Cl^-$ (0.709 g, 2.551 mmol) was added. The orange solution turned red and was stirred for 3 h at room temperature. Solvent was removed under vacuum, and the residue was chromatographed on a 1 × 25 cm silica gel column. A red band eluted with hexane/ethyl acetate (50:50 v/v). Solvents were removed from the eluate by rotary evaporation, and the residue was crystallized from CH_2Cl_2/hexane. Red prisms of CpRe(NO)(CO)Cl formed, which were collected by filtration and dried under vacuum (0.194 g, 0.562 mmol, 70%); mp 104–105 °C dec. Anal. Calcd for $C_6H_5ClNO_2Re$: C, 20.90; H, 1.46. Found: C, 20.63; H, 1.39.

Analogous reactions in benzene using $Et_4N^+Br^-$ and $Bu_4N^+I^-$ gave CpRe(CO)(NO)Br (red prisms; 83%; mp 136–137 °C dec. Anal. Calcd for $C_6H_5BrNO_2Re$: C, 18.51; H, 1.29. Found: C, 18.38; H, 1.33) and CpRe(NO)(CO)I (red prisms; 71%; mp 163–164 °C dec. Anal. Calcd for $C_6H_5INO_2Re$: C, 16.52; H, 1.15. Found: C, 16.58; H, 1.19).

Spectroscopic data (Cl, Br, I): IR (cm^{-1}, KBr) ν_{NO} (s) 1710, 1734, and 1712, ν_{CO} (s) 1975, 1992, and 1975; ^1H NMR (δ, $CDCl_3$) C_5H_5 (s) 5.83, 5.82, and 5.82; ^{13}C NMR (ppm, $CDCl_3$) C_5H_5 (s) 93.51, 93.10, and 93.32, CO (s) 199.46, 199.14, and 199.32.

Cp*Re(NO)(CO)X.[16] The following procedure is representative. A Schlenk flask was charged with Cp*Re(NO)-

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(CO)(CH_3) (0.251 g, 0.636 mmol),[2] CH_2Cl_2 (20 mL), and a stir bar. Then HCl (37% aqueous; 0.160 mL, 2.00 mmol) was added with stirring. After 1 h, the reaction mixture was filtered through a 3-cm pad of silica gel on a coarse fritted funnel. The pad was rinsed with additional CH_2Cl_2, and solvent was removed from the filtrate by rotary evaporation. The residue was dissolved in hexane, and the solution was cooled to −80 °C. Red needles of Cp*Re(NO)(CO)Cl formed, which were collected by filtration and dried under vacuum (0.236 g, 0.569 mmol, 89%); mp 196–198 °C dec. Anal. Calcd for $C_{11}H_{15}ClNO_2Re$: C, 31.84; H, 3.64. Found: C, 31.91; H, 3.65.

Analogous reactions in benzene using HBr (48% aqueous) and HI (47% aqueous) gave Cp*Re(NO)(CO)Br (red microcrystals; 82%; mp 196–198 °C dec. Anal. Calcd for $C_{11}H_{15}BrNO_2Re$: C, 28.76; H, 3.29. Found: C, 28.62; H, 3.31) and Cp*Re(NO)(CO)I (red microcrystals; 90%; mp 205–206 °C dec. Anal. Calcd for $C_{11}H_{15}INO_2Re$: C, 26.09; H, 2.98. Found: C, 26.17; H, 3.00).

Spectroscopic data (Cl, Br, I): IR (cm^{-1}, KBr) ν_{NO} (s) 1682, 1683, and 1703, ν_{CO} (s) 1946, 1949, and 1963; ^1H NMR (δ, $CDCl_3$) C_5Me_5 (s) 2.03, 2.07, and 2.15; ^{13}C NMR (ppm, $CDCl_3$) C_5Me_5 (s) 104.61, 104.28, and 103.70, $C_5\mathit{Me}_5$ (s) 9.90, 10.18, and 10.97, CO (s) 207.08, 206.73, and 206.35.

CpRe(NO)(PPh_3)X. These compounds were prepared as described previously.[17]

Cp*Re(NO)(PPh_3)X. The following procedure is representative. A Schlenk flask was charged with Cp*Re(NO)(PPh_3)(CH_3) (0.169 g, 0.269 mmol),[18] CH_2Cl_2 (25 mL), and a stir bar. Then HCl (37% aqueous; 0.055 mL, 0.69 mmol) was added with stirring. After 0.5 h, the reaction mixture was filtered through a 2-cm pad of silica gel on a coarse fritted funnel. The pad was rinsed with additional CH_2Cl_2 (100 mL), and solvent was removed from the filtrate by rotary evaporation. The residue was dried under oil pump vacuum to give Cp*Re(NO)(PPh_3)Cl as a salmon pink solid (0.148 g, 0.228 mmol, 85%); mp 238–242 °C. Anal. Calcd for $C_{28}H_{30}ClNOPRe$: C, 51.80; H, 4.66. Found: C, 51.58; H, 4.88.

Analogous reactions in benzene using HBr (48% aqueous) and HI (47% aqueous) gave Cp*Re(NO)(PPh_3)Br (brick red powder; 92%; mp 210–215 °C dec. Anal. Calcd for $C_{28}H_{30}BrNOPRe$: C, 48.48; H, 4.36. Found: C, 48.53; H, 4.44) and Cp*Re(NO)(PPh_3)I (red-purple powder; 87%; mp 218–220 °C dec. Anal. Calcd for $C_{28}H_{30}INOPRe$: C, 45.41; H, 4.08. Found: C, 45.56; H, 4.23).

Spectroscopic data (Cl, Br, I): IR (cm^{-1}, KBr) ν_{NO} (s) 1635, 1642, and 1644; ^1H NMR (δ, $CDCl_3$) C_5Me_5 (s) 1.63, 1.66, and 1.73; ^{13}C NMR (ppm, $CDCl_3$) C_5Me_5 (d, J_{CP} = 1.9, 2.0, and 1.8 Hz) 100.36, 100.14, and 99.78, $C_5\mathit{Me}_5$ (s) 9.75, 10.02, and 10.65, PPh_3 ipso (d, J_{CP} = 52.4, 47.9, and 53.4 Hz) 134.59, 135.03, and 131.64, PPh_3 ortho (d, J_{CP} = 10.4, 10.4, and 10.0 Hz) 134.20, 134.28, and 134.40, PPh_3 para (d, J_{CP} = 2.1, 2.2, and 2.2 Hz) 130.04, 130.30, and 130.01, PPh_3 meta (d, J_{CP} = 10.1, 10.0, and 10.2 Hz) 128.12, 128.17, and 128.71; ^{31}P NMR (ppm, $CDCl_3$) 18.2, 16.8, and 14.8 (s).

Photoelectron Spectra. Photoelectron spectra were recorded on an instrument that features a 36 cm radius hemispherical analyzer (10-cm gap) and customized sample cells, excitation sources, detection and control electronics, and data collection methods that have been described previously.[19-22] The He I and He II spectra of Cp*Re(CO)(NO)X and CpRe(CO)(NO)X were measured at sample cell temperatures of 90–110 °C. The Cp*Re(NO)(PPh_3)X and CpRe(NO)(PPh_3)X series of complexes sublimed at sample cell temperatures of 180–200 °C. The compounds sublimed cleanly, and all data collections were repeated at least five times for purposes of examining particular ionization features. No discernible differences were observed between collections.

The data are represented analytically with the best fit of asymmetric Gaussian peaks (program GFIT).[11,23] The asymmetric Gaussian peaks are defined with the position, the amplitude, the half-width indicated by the high binding energy side of the peak (W_h), and the half-width indicated by the low binding energy side of the peak (W_l). The confidence limits (3σ) of the peak positions and widths are generally ±0.02 eV. The confidence limit of the area of a band envelope is about ±5%, with uncertainties introduced from the baseline substraction and fitting in the tails of the peaks. The individual positions, shapes, and areas of overlapping peaks are not independent and therefore are more uncertain. For evaluation of the He II data, electron counts due to the He IIβ line are substracted from the valence region. The peak positions and shapes are constrained to the values from the He I data, with only the intensities allowed to vary to account for the changes in photoelectron cross sections.

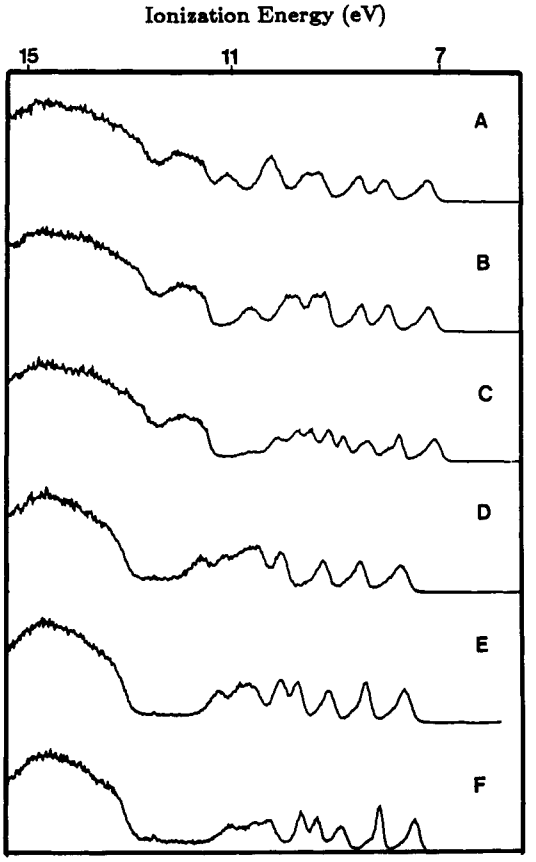

Figure 2. He I spectra of (A) (η^5-$C_5(CH_3)_5$)Re(NO)(CO)Cl, (B) (η^5-$C_5(CH_3)_5$)Re(NO)(CO)Br, (C) (η^5-$C_5(CH_3)_5$)Re(NO)(CO)I, (D) (η^5-C_5H_5)Re(NO)(CO)Cl, (E) (η^5-C_5H_5)Re(NO)(CO)Br, and (F) (η^5-C_5H_5)Re(NO)(CO)I.

Results

The He I spectra of the CpRe(NO)(CO)X and Cp*Re(NO)(CO)X complexes from 5.5 to 15.5 eV are shown in Figure 2. The region from 11.5 to 15.5 eV is a forest of overlapping ionizations comprising the Cp a_1'' ionizations, C–C and C–H σ ionizations, and CO and NO 5σ and 1π ionizations. The additional ionization in the region from about 11.5 to 12.5 eV in the spectra of the pentamethylcyclopentadienyl complexes is due to the e symmetry combination of the C–H bonds of the methyl groups.[19] Attention will be focused on the ionizations from the 7–11-eV region, since these are most informative about the metal–ligand interactions.

PES of Cp*Re(NO)(CO)X Complexes. The valence ionization bands of these pentamethylcyclopentadienyl

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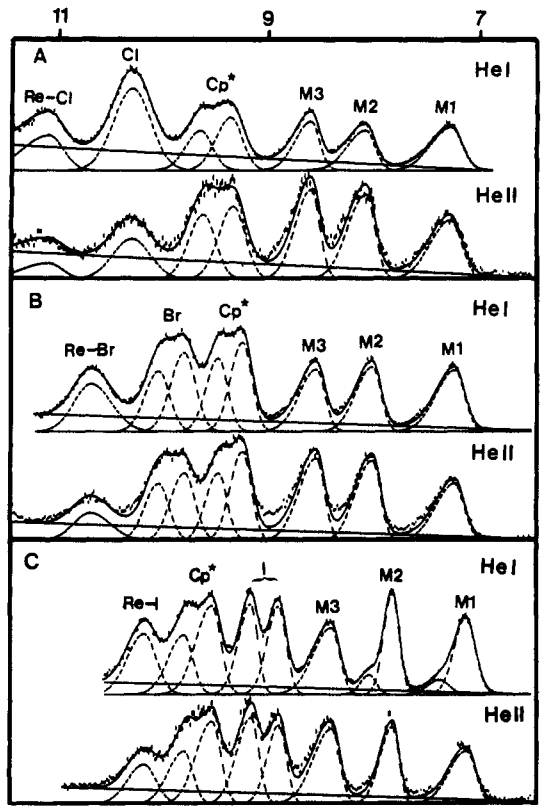

Figure 3. He I/He II intensity trends in (A) $(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(CO)Cl$, (B) $(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(CO)Br$, and (C) $(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(CO)I$.

complexes are well separated and generally straightforward to assign on the basis of comparisons to similar complexes. The He I/He II intensity trends of the complexes are shown in Figure 3. From theoretical estimates of photoionization cross sections, the photoionization cross section of Re falls by a factor of 2 on going from He I to He II.[24] In comparison, the C 2p photoionization cross section decreases by a factor of 3 on going from He I to He II. The Cl 3p, Br 4p, and I 5p photoionization cross sections decrease by factors of 21, 16, and 10, respectively, on going from He I to He II. Thus, ionization bands with predominant metal character should increase relative to all other bands in the spectrum, and ionization bands with predominant halogen character should decrease relative to all other bands. The positions of the various ionizations and their decrease in intensity in He II for the Cp*Re(NO)(CO)X complexes are provided in Table I. For analysis of the relative cross sections, the area of the M3 band is taken as 1.00 and the areas of the M1, the M2, and all other bands are compared relative to it.

As will become apparent from evaluation of the ionization characteristics, there is extensive mixing of metal and ligand character in these ionizations. The assignments and labels in Figure 3 and in the tables are used for the purposes of discussion. They indicate the predominant characters, but the important concern for understanding the electronic structure of these systems involves understanding the mixing and delocalization that is evidenced in each ionization.

The first three ionizations in Cp*Re(NO)(CO)Cl at 7.3, 8.1, and 8.7 eV (labeled M1, M2, and M3) are assigned to

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Table I. $(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(CO)X$ **Valence Ionization Features**[a]

X	orbital character	position	W_h	W_l	rel area	rel decrease in He II area, %
Cl	M1	7.33	0.45	0.25	1.12	24
	M2	8.13	0.40	0.20	0.91	15
	M3	8.65	0.35	0.19	1.00	
	Cp	9.42	0.33	0.26	1.16	17
	Cp	9.69	0.33	0.26	0.88	19
	Cl	10.34	0.42	0.41	2.52	73
	Re–Cl	11.14	0.58	0.33	1.18	75
Br	M1	7.29	0.42	0.22	1.09	29
	M2	8.07	0.36	0.19	0.99	6
	M3	8.59	0.38	0.19	1.00	
	Cp	9.29	0.27	0.21	1.18	25
	Cp	9.53	0.27	0.21	0.98	31
	Br	9.84	0.30	0.25	1.21	36
	Br	10.09	0.30	0.25	0.93	29
	Re–Br	10.73	0.39	0.45	1.13	55
I	M1	7.17	0.21	0.21	1.11	36
	M2	7.87	0.16	0.14	1.11	33
	M3	8.45	0.41	0.18	1.00	
	I	8.95	0.25	0.17	0.96	36
	I	9.21	0.27	0.16	0.99	+20
	Cp	9.58	0.35	0.20	1.25	38
	Cp	9.84	0.35	0.20	0.99	+5
	Re–I	10.22	0.37	0.27	0.84	40

[a] See Experimental Section for explanation of ionization parameters.

primarily metal-based electrons. We will start with the assumption that the first two ionizations represent the M–X π^* ionizations, with back-bonding to the carbonyl and the nitrosyl, respectively, and that M3 represents the predominantly metal level that is back-bonding to both the carbonyl and the nitrosyl. This assumption follows from comparison to the spectra of other similar metal complexes, in which the metal-based ionizations occur at low energy, and from simple considerations of the π interactions of the metal with the ligands. These assumptions will be evaluated throughout the Results and Discussion.

In the spectrum of the chloride complex, M1 and M2 decrease slightly in intensity relative to M3 with He II excitation. This indicates substantial ligand character in these ionizations. The M1 and M2 ionizations of the bromide complex also decrease in intensity in He II by similar amounts and are ≈0.05 eV destabilized from the chloride complex. The M1 and M2 ionizations of the iodide complex decrease in intensity in He II more than the chloride and bromide complexes, indicating that, in the iodide complex, there is more halogen character mixed in with these levels. Destabilization of the M1 and M2 ionization bands from the bromide complex to the iodide complex is greater than the destabilization from the chloride complex to the bromide complex, with the M2 ionization destabilizing the most. This suggests more iodide character in the M2 ionization than in the M1 ionization, a point that will be further supported by later evidence. It should also be noted that in the spectrum of the iodide complex, the M1 and M2 ionization bands are narrower than in the spectra of the other complexes. As seen from the spectra of other metal–halogen complexes, sharper ionization bands indicate more halogen character.[11] The M1 and M2 ionizations each also show a weak shoulder ≈0.2 eV to higher binding energy from the main ionization. The energy separation of 0.2 eV corresponds to CO or NO vibrational progression due to back-bonding of the metal electrons into the CO or NO π^* orbitals. Similar shoulders from CO and NO vibrational progres-

sions have been observed in the spectra of other complexes.[25]

The fourth ionization band in the spectra of the chloride and bromide complexes (labeled Cp*) is due to the Cp* e_1'' ring ionizations. This band is assigned from He I/He II intensity trends and comparison with other cyclopentadienyl complexes. It has the characteristic "fingerprint" shape of Cp* e_1'' ionizations of d^6 piano-stool complexes.[19] In the chloride complex, the assignment is very clear, since this band decreases substantially less in intensity than the M–X π ionizations (primarily Cl p_π and labeled Cl), whose intensity falls the most on going from He I to He II. In the bromide complex, however, the assignment of the Cp* and Br ionization bands is less certain, based solely on intensity trends. Both the ionization bands are similar in intensity with He I and He II excitation. The fourth ionization band is assigned to the Cp* electrons and the fifth ionization band to the Br p_π ionizations on the basis of ionization energy shifts. The destabilization of the Br p_π ionizations from the Cl p_π ionizations is 0.37 eV, which is similar in value to that of other chloro and bromo complexes.[11] The "methylation effect" also assists the assignment of the Cp* ionizations, as will be shown later. Both the Cl and Br p_π ionizations do not decrease in intensity in He II as much as predicted, presumably because of the metal character mixing in from the M–X π interaction (Figure 1).

The fourth ionization band in the iodide complex is assigned predominantly to the I p_π orbitals, again primarily because of expected energy trends in halogen ionizations. The I p_π ionizations are 0.9 eV destabilized from the Br p_π ionizations, as expected. The I p_π ionizations do not decrease significantly in intensity in He II. This is again becuase of the metal character mixed in from the M–X π interaction. The narrower widths of these ionizations, like M1 and M2, also point to the iodide character. The Cp* e_1'' ionizations (labeled Cp*) in the iodide complex, however, are 0.3 eV *stabilized* compared to the ionizations in the bromide complex. This is contrary to expectations of the better σ-donor ability of iodide compared to bromide, which should destabilize all ionizations. The destabilization of all other ionizations is observed. The stabilization of the Cp*-based ionizations in this case traces to additional interaction with the halogen lone pairs, which will be a point of the discussion. It is pertinent to note also that the Cp* ionizations decrease in intensity in He II more in the iodide complex than in the bromide complex, indicating some change in their character. The Cp* ionizations in the chloride complex follow normal trends and are 0.1 eV stabilized compared to the same ionizations in the bromide complex.

The sixth ionization band is assigned to the Re–X σ ionizations (X = Cl, Br, I). These ionizations are destabilized as expected on going from the chloride to the bromide to the iodide complex. They also decrease in intensity in He II less from the chloride to the iodide complex, which is expected from the photoionization cross sections of these atoms.

PES of CpRe(NO)(CO)X Complexes. The ionizations of these complexes are assigned on the same basis as those of the Cp*Re(NO)(CO)X complexes. The low-energy ionizations and the labels are shown in Figure 4. The metal-based ionizations, M1, M2, and M3, are destabilized to a much larger extent than those of the methylated complexes on going from the chloride to the iodide complexes. This may be due to greater metal–halogen π interaction. This proposition is substantiated by the relative decrease in intensity in He II of the M1 and M2 ionizations, which is larger than in the methylated complexes. The metal–halogen interaction within the series is, as before, greatest for the iodide complex. The carbonyl and nitrosyl vibrational progressions in the M1 and M2 ionization bands denote the back-bonding of metal electrons into the carbonyl or nitrosyl π^* orbitals. The M2 ionization band in the iodide complex has more iodide character mixed with the metal than the M1 band (from He I/He II intensity trends and the narrower band shape). This is contrary to the chloride and bromide complexes, where M1 has most halide character.

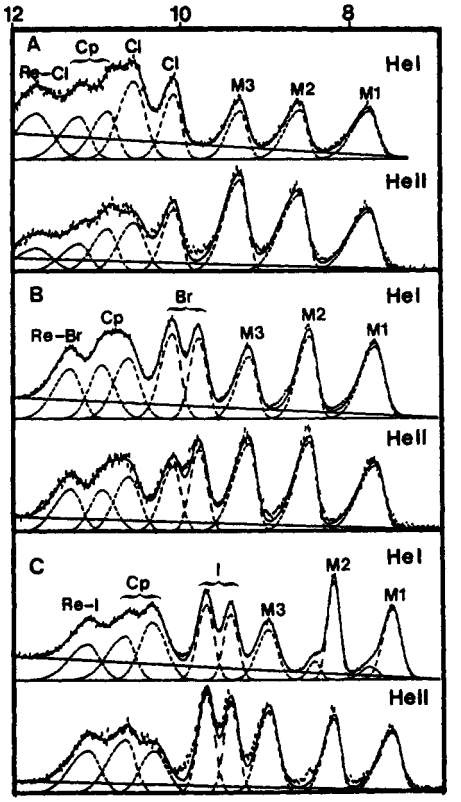

Figure 4. He I/He II intensity trends in (A) (η^5-C_5H_5)Re(NO)(CO)Cl, (B) (η^5-C_5H_5)Re(NO)(CO)Br, and (C) (η^5-C_5H_5)-Re(NO)(CO)I.

The Cp ionizations are destabilized 0.3 eV each time on going from the chloride to the bromide to the iodide complexes. This reflects the increasing σ-donor property of the halogen through this series. The unusual phenomenon of Cp ionization stabilization in the iodide complex as compared to the bromide complex in the pentamethylcyclopentadienyl complexes is not observed in *this* case. The explanation of this phenomenon involves a level crossing and interaction of the Cp* and M–X π ionizations. The details will be left to the Discussion.

The halogen p_π ionizations (M–X π) are destablilized as expected from the chloride to the iodide complex. It is pertinent to mention that the I p_π ionizations are not as destabilized compared to the Br p_π ionizations in these complexes, as in the pentamethylcyclopentadienyl complexes (by 0.6 eV versus 0.9 eV). All of these observations point to Cp–metal–halogen mixing in the case of the pentamethylcyclopentadienyl complexes.

The metal ionizations are in general $\approx$0.5 eV destabilized in the methylated complexes compared to the CpRe(NO)(CO)X complexes. This is the "methylation effect",

(25) Hubbard, J. L.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 2132.

Table II. (η^5-C_5H_5)Re(NO)(CO)X Valence Ionization Features[a]

X	orbital character	position	W_h	W_l	rel area	rel decrease in He II area, %
Cl	M1	7.82	0.46	0.22	1.23	39
	M2	8.62	0.42	0.19	1.14	18
	M3	9.33	0.34	0.20	1.00	
	Cl	10.12	0.32	0.21	1.32	58
	Cl	10.59	0.42	0.31	2.14	72
	Cp	10.88	0.45	0.24	1.27	61
	Cp	11.23	0.50	0.28	1.27	72
	Re–Cl	11.72	0.56	0.42	1.69	78
Br	M1	7.77	0.41	0.22	1.32	38
	M2	8.52	0.34	0.17	1.23	25
	M3	9.23	0.36	0.19	1.00	
	Br	9.83	0.25	0.21	1.08	37
	Br	10.14	0.34	0.23	1.39	53
	Cp	10.65	0.40	0.30	1.23	45
	Cp	10.97	0.35	0.35	1.09	52
	Re–Br	11.34	0.45	0.29	1.07	48
I	M1	7.59	0.25	0.21	1.38	43
	M2	8.26	0.19	0.14	1.37	46
	M3	9.02	0.33	0.23	1.00	
	I	9.47	0.20	0.20	0.95	17
	I	9.75	0.25	0.20	1.21	19
	Cp	10.39	0.35	0.35	1.45	55
	Cp	10.70	0.50	0.25	1.19	26
	Re–I	11.15	0.51	0.33	1.09	28

[a] See Experimental Section for explanation of ionization parameters.

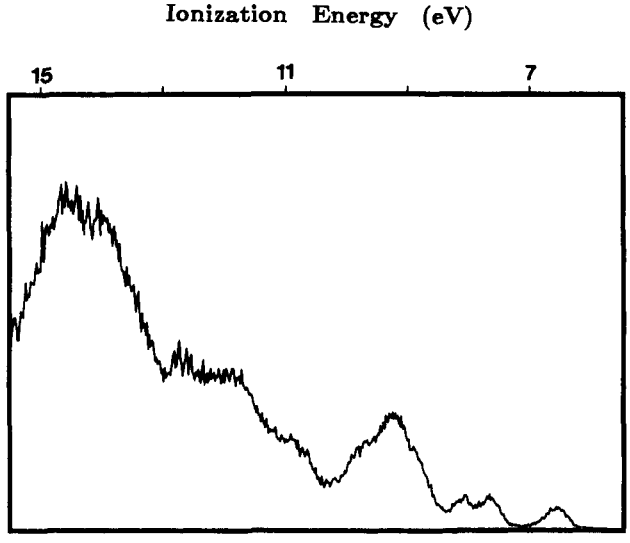

Figure 5. He I spectrum of (η^5-C_5H_5)Re(NO)(PPh_3)Cl.

which has been observed previously in other complexes.[19] Similarly, the Cp ionizations are ≈1.4 eV destabilized in the methylated complexes as a result of this effect (except for the iodide complex) compared to the CpRe(NO)(CO)X complexes. The positions of the ionizations are provided in Table II.

PES of CpRe(NO)(PPh_3)X and Cp*Re(NO)(PPh_3)X Complexes. The effects on the ionizations by the substitution of a phosphine for a carbonyl are observed in this series of complexes. The He I spectrum of CpRe(NO)(PPh_3)Cl from 5.5 to 15.5 eV is shown in Figure 5. The spectra of the other corresponding bromide and iodide as well as the pentamethylcyclopentadienyl analogues are very similar to that of CpRe(NO)(PPh_3)Cl in the higher ionization energy region. There are many overlapping ionizations in the 9–11-eV region due to the Ph π ionizations and the Re–P σ ionizations, as well as the Cp ring

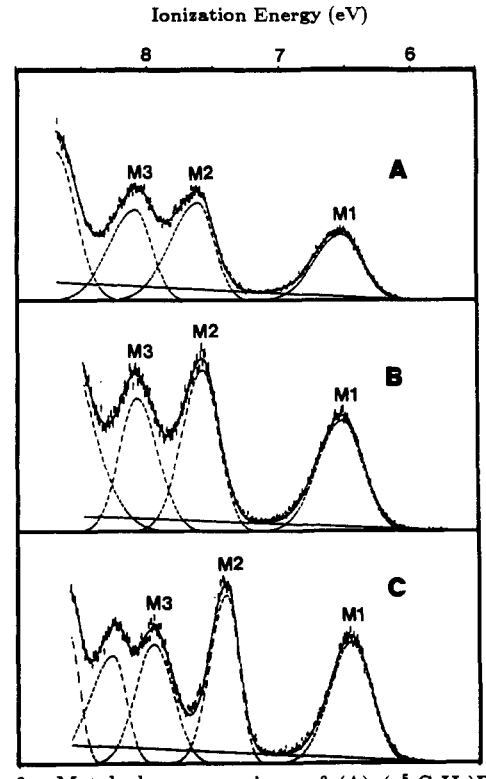

Figure 6. Metal close-up regions of (A) (η^5-C_5H_5)Re(NO)(PPh_3)Cl, (B) (η^5-C_5H_5)Re(NO)(PPh_3)Br, and (C) (η^5-C_5H_5)Re(NO)(PPh_3)I.

Table III. CpRe(NO)(PPh_3)X and Cp*Re(NO)(PPh_3)X Valence Ionization Features[a]

complex	orbital character	position	W_h	W_l	rel area
CpRe(NO)(PPh_3)Cl	M1	6.54	0.47	0.35	1.00
	M2	7.62	0.49	0.29	1.41
	M3	8.09	0.48	0.29	1.29
CpRe(NO)(PPh_3)Br	M1	6.54	0.44	0.36	1.00
	M2	7.59	0.37	0.28	1.19
	M3	8.09	0.32	0.37	1.04
CpRe(NO)(PPh_3)I	M1	6.48	0.40	0.33	1.00
	M2	7.41	0.31	0.19	0.97
	M3	7.96	0.35	0.33	0.91
Cp*Re(NO)(PPh_3)I	M1	6.16	0.39	0.27	1.00
	M2	7.16	0.29	0.29	1.44
	M3	7.66	0.30	0.35	1.03
Cp*Re(NO)(PPh_3)Cl	M1	6.19	0.48	0.33	1.00
	M2	7.32	0.49	0.37	1.92
	M3	7.76	0.49	0.32	2.02
Cp*Re(NO)(PPh_3)Br	M1	6.21	0.45	0.31	1.00
	M2	7.29	0.41	0.34	1.51
	M3	7.74	0.45	0.31	1.60

[a] Cp is η^5-C_5H_5 and Cp* is η^5-$C_5(CH_3)_5$.

ionizations and the halogen lone-pair ionizations. As a result, in these complexes only the metal close-up region shows reasonably separated ionizations. These compounds do not sublime well. Because of the difficulty in obtaining good signal-to-noise ratios in the He I spectra, collections of the He II spectra were not attempted. However, the shift of the metal ionizations in the He I spectra and the width of the bands are sufficient to show the metal–halogen mixing and the general trends.

The metal close-up region of the CpRe(NO)(PPh_3)X complexes is shown in Figure 6. The positions of the ionizations are given in Table III. The assignment of the metal-based ionizations M1, M2, and M3 is the same as for the carbonyl-substituted complexes. Because of the phosphine substitution for carbonyl, the ionizations are

substantially destabilized compared to those of the previous complexes. The M1 ionization bands are destabilized 1.2 eV, M2 1.0 eV, and M3 1.1 eV on the substitution of a carbonyl with a phosphine. Similar destabilizations of metal-based ionizations with this substitution have been observed in other systems.[26,27]

The trends in halogen substitution are similar to those for the carbonyl complexes. The M2 ionization band is destabilized most (0.2 eV) from the bromide to the iodide complex, indicating iodide character in the metal-based ionization. This can also be observed from the narrowness of the ionization band M2 (M2 is 0.2 eV narrower than M1). The M3 ionization band is more destabilized on going from bromide to the iodide as compared to going from chloride to bromide, denoting the better σ-donor ability of the iodide ligand.

The Cp*Re(NO)(PPh_3)X complexes (Figure 7) follow a trend similar to that of the CpRe(NO)(PPh_3)X complexes. The methylation effect is prevalent in these sets of complexes and M1, M2, and M3 ionizations are destabilized 0.3 eV in the Cp*Re(NO)(PPh_3)X complexes compared to the CpRe(NO)(PPh_3)X complexes. The substitution of a carbonyl by a phosphine is seen in the destabilization of M1 by 1.1 eV, M2 by 0.8 eV, and M3 by 0.9 eV. The positions of the ionizations are given in Table III. The M2 ionization band in the iodide complex is again more destabilized than that from the chloride to the bromide complexes, indicating more metal–halogen mixing. This is also substantiated by the width of M2, which is 0.1 eV narrower than band M1.

Discussion

Basic Metal–Ligand Orbital Interactions. As is evident from the results described in the previous section, the valence ionizations provide a wealth of information on the electron distribution and energies in this class of complexes. We will discuss the basic metal–ligand orbital interactions in CpRe(NO)(CO)X systems, especially the metal–halogen π interaction. In order to simplify the valence orbital details for these piano-stool molecules, the molecule is oriented with the coordinate system as shown in Figure 1. In this geometry, it is seen that the d^6 metal levels of t_{2g} heritage transform as predominantly d_{xz} and d_{yz}, which are of π symmetry with respect to the halogen, and the predominantly d_{xy} orbital, which is oriented for π back-donation into the cis carbonyl and nitrosyl ligands. In this coordinate system, the nitrosyl is placed along the y axis and the carbonyl along the x axis.

In the $CpFe(CO)_2X$ systems with this coordinate system, the d_{xz} and d_{yz} orbitals are back-bonding to one carbonyl each and the small split between them is the difference in the symmetric and antisymmetric combinations from lack of true C_{4v} symmetry. The d_{xy} orbital is back-bonding to two carbonyls. In the CpRe(NO)(CO)X systems, the d_{xy} orbital is back-bonding to both the nitrosyl and the carbonyl, the d_{xz} is back-bonding to the carbonyl, and the d_{yz} is back-bonding to the nitrosyl. This different back-bondings of the three metal-based orbitals are evidenced by the separation in energy between the first three ionizations in the photoelectron spectra. M1 is back-bonding to a carbonyl, M2 to a nitrosyl (which is a better π acceptor than CO), and M3 to both a carbonyl and a nitrosyl. From the difference in the split of the M1 and M2 ionizations, the different back-bonding stabilization of a carbonyl compared to a nitrosyl is $\approx$0.8 eV. This difference in stabilization of the ionization is consistent with that observed in the photoelectron spectra of $CpCr(CO)_2NO$ systems.[22] Since the degeneracy of the metal d_{xz}/d_{yz} orbitals is broken by bonding effects, the spin–orbit splitting of the Re metal d and halogen ionizations cannot be used as a measure of the metal–halogen interaction as was done by Hall in the $(CO)_5ReX$ systems.[12]

The filled halide (X) p_π levels are of the correct symmetry to interact with the filled d_{xz} and d_{yz} levels (see Figure 1). This filled–filled interaction gives rise to ionizations corresponding to the symmetric M–X π combination and an antisymmetric M–X π^* combination. The compositions of the M–X π and M–X π^* levels are dependent on the relative stability of the metal and halogen levels. For example, as X varies from Cl to Br to I and the halogen p_π levels become less stable, the M–X π^* combination (M1 and M2 bands) is observed to gain in halide character, while the symmetric π combination gains in metal character. Another factor that comes into play is the closer energy match and greater delocalization of the more ligand-based (because of NO back-bonding) M2 level compared to the M1 level. The results show that even though the M2 level is more delocalized to the nitrosyl, the closer energy match of the M2 level compared to the M1 level with the I p_π levels dominates in causing the M2 level to mix more than M1 with the iodide lone pairs. This greater iodide character in M2 than in M1 is evidenced by the width of the bands and the shifts with ligand substitution. The opposite trend occurs with the chloride and bromide complexes. Here, the energy proximity of M2 to the halide lone pairs is not close enough to dominate the delocalization due to nitrosyl back-bonding with M2, and M1 can pick up slightly greater halogen character.

The Cp e_1'' ring orbitals and the iodide e orbitals have similar symmetries, and they both interact with the metal d_{xz} and d_{yz} orbitals. In the Cp* complexes, the e_1'' ring orbitals and the M–X π orbitals are also close together in energy. The Cp* series of complexes is the only case in which a level crossing of the M–X π and Cp e_1'' ionizations appears to take place with halogen substitution. The M–X π ionizations of the chloride and bromide complexes are more stable than the Cp* ionizations, while the reverse order occurs for the iodide complex. The Cp* electrons and the M–I π electrons interact with each other, and as a result, the M–I π ionizations are destabilized and the Cp* ionizations are stabilized. This accounts for the 0.3-eV stabilization of the Cp* ionizations of the iodide complex compared to those of the bromide complex. The I p_π (M–I π) ionizations are 0.8-eV destabilized compared to the Br p_π (M–Br π) ionizations, which is similar to the case of CH_3Br and CH_3I.[28] The extra destabilization experienced by the I p_π electrons as a result of the interaction with the Cp* electrons is compensated by the stabilization as a result of interaction with the metal d electrons. This level crossing of the metal–halogen π and Cp* e_1'' ionizations does not occur in the CpRe(NO)(CO)X series of complexes because the Cp e_1'' ionizations are substantially more stable than in the pentamethylcyclopentadienyl complexes.

Halogen Substitution in CpRe(NO)(CO)X Systems As Compared to Other Systems. The $CpFe(CO)_2X$ system is isoelectronic with the CpRe(NO)(CO)X system. In both cases, the first two ionizations (M1 and M2) are the M–X π^* ionizations and the third ionization (M3) is back-bonding into the two π-acceptor ligands.[11] The ion-

(26) Kellogg, G. E. *Diss. Abstr. Int., B* **1986**, *46*, 3838.
(27) Lichtenberger, D. L.; Rai-Chaudhuri, A. *Inorg. Chem.* **1990**, *29*, 975.
(28) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Halsted Press: New York, 1980.

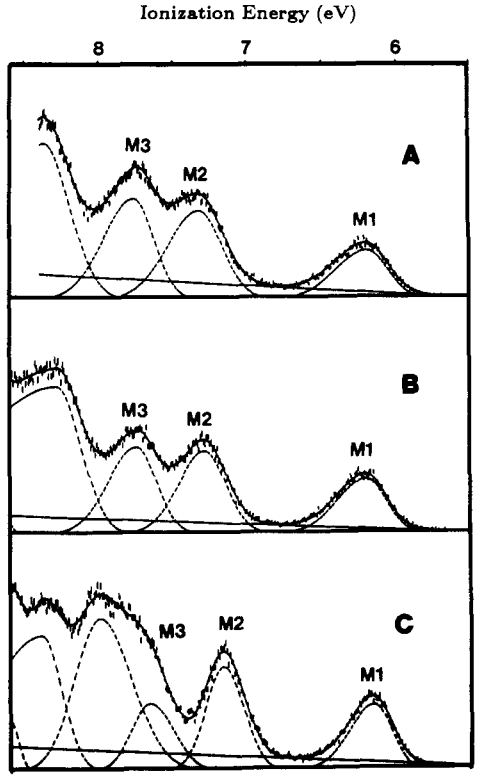

Figure 7. Metal close-up regions of (A) (η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)Cl, (B) (η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)Br, and (C) (η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)I.

ization energies of the two series of complexes are very similar. The M1 ionization differs from the other ionizations in that it is less stable in the rhenium complexes compared to the iron complexes. The M1 ionization does not mix with the nitrosyl back-bonding orbitals. The ionization features show that the M–X π^* ionizations are mostly metal in character in the chloride complex and the M–X π are mostly the Cl lone pairs in both cases. The splitting of the Cl p_π ionizations in the rhenium complexes shows that there is still substantial mixing. In both cases, the bromide complex shows more metal–halogen mixing than is seen in the chloride complex. Both the chloride and the bromide complexes in the two systems interact to a similar extent, as seen from the shifts in the bands and their relative He I/He II areas.

There are subtle changes in the case of the iodide complexes. M2 has more iodide character than M1 in the Re system and is consequently more destabilized on going from the bromide to the iodide complex than in the corresponding Fe system. This follows from the closer energy proximity of the M2 level to the I p_π levels. Overall, however, the Fe–iodide system has more halogen character in the M–X π^* orbitals on the basis of He I/He II intensity trends and more metal character in the M–X π orbitals. This is due to the fact that the nitrosyl ligand present in the Re systems removes π metal electron density from the M–X π^* orbitals. As a consequence, metal–halogen π interaction can be a little less. Both systems can be said to show metal–halogen π interaction that increases with the higher halides.

It is interesting to compare the CpRe(NO)(CO)X systems to the $(CO)_5$ReX systems. Hall has carried out a detailed spin–orbit coupling analysis to assign the ionizations of these complexes. The spin–orbit coupling shows that, in the chloride complexes, the M–X π^* ionizations are predominantly metal, in the bromide complexes the M–X π and π^* ionizations have equal amounts of bromide and metal character, and in the iodide complex, the M–X π^* ionizations are nearly all I p_π in character, while the M–X π ionizations are predominantly metal in character.[12] This contrasts with the present study in which the M–X π^* ionizations are always predominantly metal. The reason for the dissimilarity in the ionization compositions between the two Re systems lies in the ligands around the metal center. If one compares $CpRe(CO)_3$ and $HRe(CO)_5$, the metal IP's are ≈0.6 eV destabilized in the Cp complex because of the loss of two carbonyls and thus the loss in the stabilization by back-bonding. For $(CO)_5$ReBr, the metal levels are close in energy to the Br p_π levels and extensive mixing occurs, giving equal amounts of metal and bromide character to the M–X π and M–X π^* ionizations. For the $(CO)_5$ReI complex, the I p_π ionizations are at a lower ionization energy than the metal ionizations to start with, and as a result, the M–X π^* ionizations are predominantly I p_π in character. In the CpRe(NO)(CO)X systems, even in the case of the iodide, the I p_π ionizations occur at a higher ionization energy than the metal levels to start with. Therefore, the M–X π^* orbitals are predominantly metal in character. The $(CO)_5$MnX systems are similar to the $(CO)_5$ReX system.[29] $ClMn(CO)_5$ has predominantly metal character in the M–X π^* ionizations, $BrMn(CO)_5$ has equal metal and bromide character in the M–X π and π^* ionizations, and $IMn(CO)_5$ has predominantly iodide character in the M–X π^* ionizations.[29] In the bromide complex, the M–X π band at higher ionization energy splits when a CO cis to the bromide is replaced by $CNCH_3$, suggesting its metal character. In this context, in the Cp*Re(NO)(CO)X complexes, the split in the M–X π band of the complexes increases from the bromide to the iodide complex. This is because these ionizations are gaining in metal character and interacting preferentially with CO and NO and also because there is increased spin–orbit splitting of the higher halides (iodine has a spin–orbit split of 0.6 vs 0.3 in bromine).

Halogen Substitution in Cp*Re(CO)(NO)X Complexes. The trends in the pentamethylcyclopentadienyl complexes are similar to those in the CpRe(NO)(CO)X complexes. The M–X π^* ionizations (M1 and M2) shift most from the bromide to the iodide complexes. At the same time, M2 shifts more than M1. The Br p_π ionizations shift 0.4 eV from the Cl p_π ionizations vs 0.6 eV in the CH_3X systems. The smaller shift is due to the M–X π interaction. A 0.8-eV destabilization occurs from the Br to the I p_π ionizations, which is the same as in the CH_3X systems. Although the M–X π interaction is important here, it is offset by the destabilization that the M–X π ionization incurs on crossing over and interacting with the Cp electrons. This Cp–iodide interaction can also be observed from the He I/He II intensity trends, which show a greater decrease in intensity in He II in one of the Cp bands compared to the chloride and the bromide complexes because of the I p_π ligand character mixing in.

Carbonyl/Phosphine Substitution and Halogen Trends. The metal ionizations in the CpRe(NO)(PPh_3)X and Cp*Re(NO)(PPh_3)X complexes show the effect of substituting a phosphine for a carbonyl on the energy of the ionizations. The electronic effects of replacing CO with PPh_3 on the metal and Cp ionizations have been well documented.[26,30,31] The metal ionization shifts play an

(29) Lichtenberger, D. L.; Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1973**, *12*, 702.
(30) Lichtenberger, D. L.; Calabro, D. C.; Kellogg, G. E. *Organometallics* **1984**, *3*, 1623.
(31) Bursten, B. E.; Darensbourg, D. J.; Kellogg, G. E.; Lichtenberger, D. L. *Inorg. Chem.* **1984**, *23*, 4361.

important role in the assignment of the ionizations in the corresponding Cp*Re(NO)(CO)X and CpRe(NO)(CO)X complexes.

The phosphine substitution in place of a carbonyl places extra negative charge potential at the metal center, which destabilizes all ionizations. In addition, there is extra destabilization felt by the metal orbitals that were back-bonding to the removed carbonyl. The latter destabilization is ≈0.3 eV, as found from other systems,[26] while the charge effect at the metal center results in ≈1-eV destabilization.[27] The M1 and M3 bands in the CpRe(NO)(CO)X and Cp*Re(NO)(CO)X complexes arise from orbitals that are back-bonding to the carbonyl ligand, as mentioned before. M2 primarily feels the charge effect. These ionizations shift as expected to lower IP due to both the charge effect and removal of CO back-bonding. In Cp*Re(NO)(PPh_3)Cl, M1 destabilizes 1.2 eV, M2 0.81 eV, and M3 0.89 eV from the corresponding Cp*Re(NO)(CO)Cl complex. M1, M2, and M3 ionizations shift 1.1, 0.78, and 0.85 eV to lower IP on going from Cp*Re(NO)(CO)Br to Cp*Re(NO)(PPh_3)Br complexes. In the Cp*Re(NO)(PPh_3)I complex, M1, M2, and M3 ionizations are destabilized 1.01, 0.71, and 0.79 eV compared to those of the Cp*Re(NO)(CO)I complex. M2 is the least destabilized in each case, as it does not back-bond to the removed carbonyl. All of the shifts are less than the 1.3 eV observed for the shifts in other systems, reflecting the more delocalized nature of the metal-based ionizations.

The CpRe(NO)(PPh_3)X complexes show trends similar to those of the Cp*Re(NO)(PPh_3)X complexes on substitution of the phosphine for the carbonyl. The M1 ionization destabilizes 1.2 eV for the chloride, 1.2 eV for the bromide, and 1.1 eV for the iodide complexes as the carbonyl is substituted by the phosphine. The M2 ionization destabilizes 1.0 eV for the chloride, 0.9 eV for the bromide, and 0.85 eV for the iodide complexes. The M3 ionizations are destabilized 1.2 eV for the chloride, 1.1 eV for the bromide, and 1.1 eV for the iodide complexes. The width of the metal band also helps to characterize its primary character. The M2 bands of the iodide complexes of these phosphine-substituted species are narrower than the other metal bands. As discussed before, M2 interacts most with the I p_π and this halogen lone-pair character cause the narrowness of this band. As mentioned before, the difference in the M1 and M2 energies in these complexes also reflects the difference in back-bonding stabilization by the nitrosyls and carbonyls. Previous studies have found the substitution of a nitrosyl for a carbonyl splits the metal ionizations by 0.8 eV,[22] and this is the difference in energy between M1 and M2 in Cp*Re(NO)(CO)Cl. The substitution of a phosphine for a carbonyl induces a relative destabilization of 0.3 eV due to the loss of back-bonding.[26] Therefore, in Cp*Re(NO)(PPh_3)Cl, M1 and M2 should be separated by 1.1 eV (0.3 eV + 0.8 eV). The experimental energy split is 1.13 eV, which is in excellent agreement. This magnitude of split is seen in all the CpRe(NO)(PPh_3)X and Cp*Re(NO)(PPh_3)X complexes.

Methylation Effect on Metal and Ligand Ionizations. The effect of placing five methyl groups on the cyclopentadienyl ring has been studied in detail.[13,19,32] Metal ionizations are destabilized by ≈0.5 eV and the Cp e_1'' ring ionizations (which interacts with the filled methyl orbitals) by 1.4 eV. In some of the CpRe(NO)(CO)X and Cp*Re(NO)(CO)X complexes, the assignment of the ionizations on the basis of He I/He II intensity trends is ambiguous. In all cases, the methylation effect aids the assignment of the ionizations. Again, M1, M2, and M3 ionizations are seen to be metal-based, since they destabilize 0.5, 0.5, and 0.7 eV, respectively, for the chloride, 0.5, 0.5, and 0.6 eV, respectively, for the bromide, and 0.4, 0.4, and 0.5 eV, respectively, for the iodide complex in the CpRe(NO)(CO)X series on pentamethylation. In the CpRe(NO)(PPh_3)X series, M1, M2, and M3 destabilize 0.4, 0.3, and 0.3 eV, respectively, for the chloride complex, 0.3, 0.3, and 0.4 eV, respectively, for the bromide complex, and 0.3, 0.3, and 0.3 eV, respectively, for the iodide complex on methylation.

The Cp e_1'' ring ionization shift is the key to the assignment of ionizations in many cases. In the Cp*Re(NO)(CO)X complexes, the ionizations are 1.4 eV (Cl), 1.4 eV (Br), and 0.9 eV (I) destabilized compared to the same ionizations in the CpRe(NO)(CO)X complexes. Especially in the bromide complex, Cp*Re(NO)(CO)Br, the Cp and Br ionizations are difficult to assign from He I/He II intensity trends. In the iodide complex, Cp*Re(NO)(CO)I, the unusual shift again shows substantial metal–halogen–Cp mixing.

Conclusions

The interaction of the Re metal with various ligands like X, NO, CO, Cp, and PPh_3 is demonstrated by the photoelectron study of this series of complexes. The difference in back-bonding stabilization of metal electrons into the nitrosyl, carbonyl, and phosphine ligands is shown in the M1 and M2 ionization bands. Nitrosyl is 0.8 eV more effective than carbonyl at stabilizing the metal ionizations by back-bonding, and carbonyl is 0.3 eV more effective than triphenylphosphine. The additivity of the electronic effects is shown in the case where the nitrosyl is 1.1 eV more effective than the triphenylphosphine at stabilizing the metal ionizations through back-bonding. The effects of pentamethylation of the cyclopentadienyl ring show the interaction of the Cp and Cp* ligands with the metal and also a Cp–iodide p_π interaction that has not been recognized previously. Most attention is given to the metal–halogen π interaction, which determines the character of the highest occupied orbitals. The M–X π^* ionizations are metal-based in every case but have increasing halogen character with the higher halides. The M2 ionization shows more halogen character than band M1 in all the iodide systems. As compared to that of the $CpFe(CO)_2X$ systems, there is less metal–halogen interaction in the Re systems because of the presence of the nitrosyl ligand, which removes and stabilizes metal π-electron density, which would otherwise have interacted with the halogen lone-pair electrons. The $(CO)_5ReX$ system is different from the CpRe(NO)LX systems, especially for the higher halides like iodide, where the lowest ionization band of $(CO)_5ReI$ is predominantly the I p_π ionizations. The CpRe systems are unique in presenting a very fluid electron system with extensive delocalization of metal electrons on surrounding ligands of a type not encountered before.

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Reaction Chemistry of $[M(R_3SiOCCOSiR_3)(dmpe)_2Cl]$ (M = Ta, Nb): Isolation and Structural Characterization of the First (Dihydroxyacetylene)metal Complexes and Removal of the Disiloxyacetylene Ligand as an Alkene

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The reaction of $[M(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ (M = Ta, Nb) with aqueous HCl results in oxidative addition of H^+ to the metal center and protiolysis of the trimethylsiloxy groups to afford $[MH(HOCCOH)(dmpe)_2Cl]Cl$ complexes, which contain the novel dihydroxyacetylene ligand. Single-crystal X-ray diffraction studies were performed on the tantalum analogue **5**. The geometry about the metal center is pentagonal-bipyramidal, with the four phosphorus atoms and the hydride ligand defining the equatorial plane and the axial positions being occupied by the chloride ion and the midpoint of the acetylene ligand. Reaction of $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ with $HBF_4{\cdot}Me_2O$ yields the related hydride complex $[TaH(Me_3SiOCCOBF_3)(dmpe)_2Cl]$ (**7**), which was also structurally characterized. The bis(*tert*-butyldimethylsiloxy)acetylene ligand in $[Ta(t\text{-}BuMe_2SiOCCOSiMe_2\text{-}t\text{-}Bu)(dmpe)_2Cl]$ was removed with the C–C bond intact by hydrogenation with either pure hydrogen or synthesis gas in the presence of 5% palladium on carbon or $[RhCl(PPh_3)_3]$. The product of this hydrogenation is bis(*tert*-butyldimethylsiloxy)ethylene, which was characterized by mass spectrometry and by comparison with an authentic sample prepared by an alternate route. Spectroscopic evidence supports a cis geometry for the alkene. Crystal data: compound **5**, orthorhombic, $P2_12_12_1$, a = 8.777 (2) Å, b = 14.856 (2) Å, c = 18.154 (5) Å, Z = 4; compound **7**·(toluene), monoclinic, $P2_1/c$, a = 10.776 (3) Å, b = 17.066 (2) Å, c = 19.414 (6) Å, β = 92.18 (2)°, Z = 4.

Introduction

The reductive coupling of carbon monoxide has been known since 1834 when Justus Liebig reported the formation of "potassium carbonyl" upon exposure of carbon monoxide to molten potassium.[1] In 1963 Büchner correctly identified "potassium carbonyl" as the potassium salt of acetylenediolate, $K_2(^-O{-}C{\equiv}C{-}O^-)$,[2] which is the first member in a series of aromatic oxocarbon polyanions,[3] $C_nO_n^{2-}$. While hydroxyacetylene,[4] phenylhydroxyacetylene,[5] and even dihydroxyacetylene[6] have been reported recently in the literature, they are very unstable and have been observed only in the gas phase, by matrix isolation, or by using pulsed laser techniques. These compounds can be stabilized, however, by bonding to one or more metal centers, as evidenced by the isolation and structural characterization of a trinuclear cobalt hydroxyacetylene complex.[7]

Carbon monoxide can be transformed into organic products containing more than one carbon atom by using the Fischer–Tropsch[8] reaction. This process is complicated, however, since a complex mixture of alkanes, olefins, aldehydes, acids, alcohols, and aromatics is obtained from the reaction. The selective conversion of carbon monoxide to ethylene glycol has been achieved with a variety of group 8 or 9 catalysts;[9] however, these transformations require high temperatures and pressures and have slow turnover rates. Alternative routes for reductively coupling carbon monoxide are therefore very desirable. Indeed, reports of the reductive coupling of carbon monoxide with the use of alkali metals and reagents,[1,2,10] by electrochemical techniques,[11] or by employing soluble lanthanide, actinide,

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