

# Electronic Structure Perturbations of Substituted Ruthenocenes: The First Photoelectron Spectra of Perchloro- and Perfluorocyclopentadienyl Complexes

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The electronic structure perturbations caused by cyclopentadienyl substitutions in the series of complexes  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}$ ,  $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Ru}$ ,  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}$ ,  $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{-Cl}_5)\text{Ru}$ , and  $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{F}_5)\text{Ru}$  are measured by gas-phase photoelectron spectroscopy. The shifts of the valence metal- and cyclopentadienyl-based ionizations give an indication of the overall electronic effects of methyl and halogen substitutions on the cyclopentadienyl rings. The halogen substituent interaction is an admixture of inductive  $\sigma$ -electron-withdrawing and filled–filled  $\pi$ -electron-overlap effects, which act in opposite directions. The  $\pi$ -overlap interaction is relatively weak in the case of chlorine substitution for hydrogen, and the combined  $\sigma$  and  $\pi$  interactions give rise to an overall withdrawal of electron density from the metal center and increase in the metal d-based ionization energies. Fluorine substituents on cyclopentadienyl make the ring only slightly more electron withdrawing than  $\eta^5\text{-C}_5\text{Cl}_5$ , despite the much greater electronegativity of fluorine compared to chlorine. The electron withdrawing ability of  $\eta^5\text{-C}_5\text{F}_5$  is tempered by the greater filled–filled interaction of the fluorine  $p_\pi$  orbitals with the cyclopentadienyl  $p_\pi$  orbitals, which lessens the stabilization of these orbitals and the withdrawal of electron density from the metal. It is interesting that in each case the metal d-based ionizations are stabilized more than the cyclopentadienyl  $\pi$ -based ionizations with halogen substitution for hydrogen, such that these ionizations begin to merge in the lowest ionization energy band.

## Introduction

A rich variety of important organometallic chemistry has developed around transition metal complexes which contain the  $\eta^5$ -cyclopentadienyl ligand. The rates and pathways of the reactions of cyclopentadienyl–metal complexes are often tuned by substitution of the hydrogen atoms on this ligand with other groups. These substitutions perturb the electronic structure and steric properties of the complex.<sup>1,2</sup> The most commonly used substituents on cyclopentadienyl ligands are organic groups, and perhaps the most notable advance in cyclopentadienyl chemistry was the discovery of a facile synthesis for the permethylated ligand, often abbreviated Cp\*. This substitution increases the steric bulk of the ligand and increases the electron richness at the metal center. As an alternative to methylated cyclopentadienyl complexes, the use of halogens as substituents is of interest because of their greater electronegativity, which should reduce the electron density at the metal center and provide for other reactivity possibilities.

The synthesis of substituted cyclopentadienyl complexes commonly employs reaction of the appropriate substituted cyclopentadiene or cyclopentadienyl anion

with a transition metal complex.<sup>3</sup> This method has not proven to be useful for perhalocyclopentadienyls. Reported methods used to prepare  $\eta^5\text{-C}_5\text{X}_5$  complexes (X = Cl, Br, I; the  $\eta^5$  designation will not be used throughout the rest of this paper, but is implied for all complexes discussed) include repetitive metalation/halogenation exchange reactions,<sup>4,5</sup> reaction of diazotetrahalocyclopentadienes with metal halides,<sup>6</sup> and perm-mercuration/perhalogenation of  $\text{C}_5\text{H}_5$  complexes.<sup>7</sup> Only recently has a useful synthetic route to a  $\text{C}_5\text{F}_5$  complex been developed,<sup>8,9</sup> in which flash vacuum pyrolysis of  $(\text{C}_5\text{Me}_5)(\text{C}_6\text{F}_5\text{O})\text{Ru}$  and subsequent CO extrusion yields  $(\text{C}_5\text{Me}_5)(\text{C}_5\text{F}_5)\text{Ru}$ . The synthesis of this novel complex

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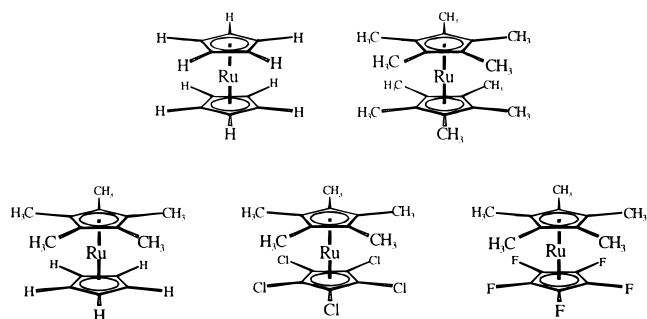
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raises questions as to the effect perfluorination will have on the electronic interaction of a cyclopentadienyl ligand with a metal and how perfluorinated cyclopentadienyl will compare to other perhalogenated cyclopentadienyls. Previous studies of this complex include measures of the solution redox chemistry and gas-phase ionization free energy.<sup>10</sup>

The purpose of this study is to use gas-phase photoelectron spectroscopy (PES) to obtain a measure of the effects of perhalogenation (halogen = Cl, F) upon the electronic properties of cyclopentadienyl ligands coordinated to a metal. The perhalogenated ligands are compared to  $C_5H_5$  as well as to  $C_5Me_5$  (Me =  $CH_3$ ). This study has prompted us to reevaluate the PES of  $(C_5H_5)_2Ru$ . While the PES of  $(C_5H_5)_2Ru$  and various alkyl-substituted ruthenocenes have been reported by others,<sup>11</sup> the increased resolution and better signal-to-noise of the present study allows a more detailed investigation of the electronic structures of these complexes. The specific complexes of this study are depicted below. We



have previously reported portions of this work dealing with  $(C_5Me_5)_2Ru$ .<sup>12</sup>

## Experimental Section

**Preparation of Compounds.** Samples of  $(C_5H_5)_2Ru$  and  $(C_5Me_5)_2Ru$  were purchased from Strem, and spectra were obtained from controlled vaporization of the samples on the photoelectron spectrometer without additional purification. The compounds  $(C_5Me_5)(C_5H_5)Ru$ ,  $(C_5Me_5)(C_5Cl_5)Ru$ , and  $(C_5Me_5)(C_5F_5)Ru$  were synthesized by published methods.<sup>6g,8</sup>

**Data Collection.** Photoelectron spectra were recorded using an instrument that features a 36 cm radius, 8 cm gap hemispherical analyzer (McPherson Instruments), and custom-designed sample cells, excitation source, and detection and control electronics.<sup>13</sup> The excitation source was a quartz capillary lamp that produces both He I and He II radiation, depending on the operating conditions.<sup>14,15</sup> The argon  $^2P_{3/2}$  ionization at 15.759 eV was used as an internal calibration lock of the absolute ionization energy. The difference between the argon  $^2P_{3/2}$  ionization and the methyl iodide  $^2E_{1/2}$  ionization at 9.538 eV was used to calibrate the ionization energy scale. During data collection, the instrument resolution (measured

using fwhm of the argon  $^2P_{3/2}$  peak) was always less than 0.025 eV and was usually less than 0.018 eV. All data were intensity corrected with an experimentally determined instrument analyzer sensitivity function. The He I close-up spectra were corrected for He I  $\beta$  resonance line emission from the source (about 3% of  $\alpha$  line emission at 1.869 eV higher photon energy). The He II data were also corrected for the He II  $\beta$  resonance line emission (about 12% of  $\alpha$  line emission at 7.558 eV higher photon energy).

All samples sublimed cleanly with no detectable evidence of decomposition products in the gas phase or as a solid residue. The sublimation temperatures (in  $^{\circ}C$ , at  $10^{-4}$  torr) were  $(C_5H_5)_2Ru$ , 54–58;  $(C_5Me_5)(C_5H_5)Ru$ , 50–70;  $(C_5Me_5)_2Ru$ , 60–80;  $(C_5Me_5)(C_5Cl_5)Ru$ , 125–150;  $(C_5Me_5)(C_5F_5)Ru$ , 95–120 (monitored using a "K"-type thermocouple passed through a vacuum feedthrough and attached directly to the sample cell).

**Data Analysis.** In the figures of the data, the vertical length of each data point represents the experimental variance of that point. The valence ionization bands are represented analytically with the best fit (program FP<sup>16</sup>) of asymmetric Gaussian peaks.<sup>17</sup> The peaks are defined with the position, amplitude, halfwidth for the high-binding-energy side of the peak, and the halfwidth for the low-binding-energy side of the peak. If an ionization is narrow, the reproducibility of the band position is at least 0.002 eV. The ionization energies for bands comprising overlapping ionizations generally are reproducible to about 0.02 eV. The number of peaks used in a fit was based on the visible features of a given band profile and the minimum number of peaks necessary to give the best statistical fit.<sup>17</sup> The parameters describing an individual ionization peak are less certain when two or more peaks are close in energy and overlap. The confidence limits for the relative integrated band areas are about 5%, with the primary source of uncertainty being the determination of the base line subtracted from the peak. For representation of the He II data, the position and width values of the asymmetric Gaussians were all constrained to He I values because the better signal-to-noise of the He I spectra allows these values to be more accurately determined. The amplitudes were then allowed to vary to account for the different photoionization cross sections for He II. Fitting procedures are described in more detail elsewhere.<sup>17</sup>

## Results

**Valence Ionizations.** The general features of the valence photoelectron spectra of substituted ruthenocenes will be introduced here, while more detailed analysis of these features and trends is reserved for the Discussion. Figure 1 shows the full valence He I photoelectron spectra of the five compounds studied. The general assignments of the ionizations for these compounds follow from numerous previous investigations of the photoelectron spectra of metallocenes.<sup>11,18,19</sup>

The broad region of overlapping ionizations from 12 to 16 eV contains the C–H and C–C  $\sigma$  ionizations as well as the ionizations derived from the two cyclopentadienyl  $a_2'' \pi$  orbitals. In addition, the complexes that contain a  $C_5Me_5$  ligand also contain a distinctive ionization at approximately 11 eV that arises from the e set of methyl C–H  $\sigma$ -bonding orbitals. No attempt has been made to locate the ring  $\pi$  ionizations in this area from the forest of C–C and C–H  $\sigma$  ionizations. Only ioniza-

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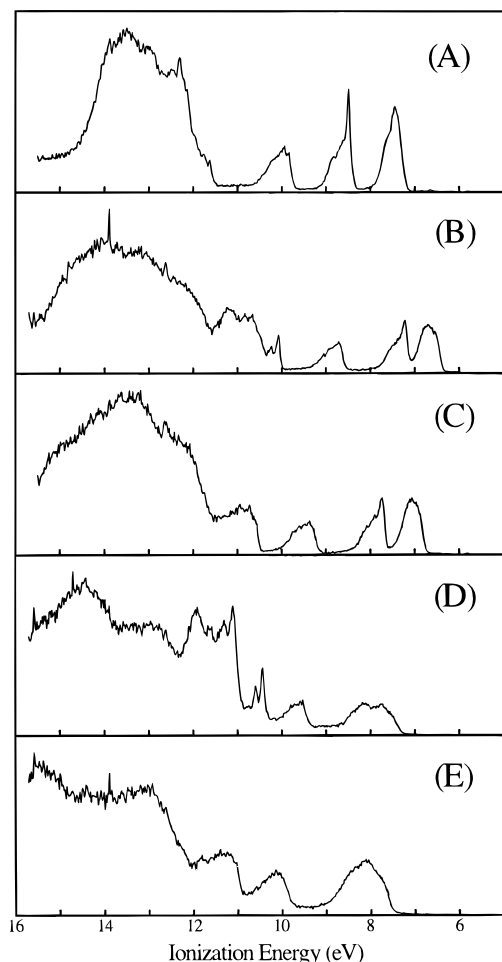
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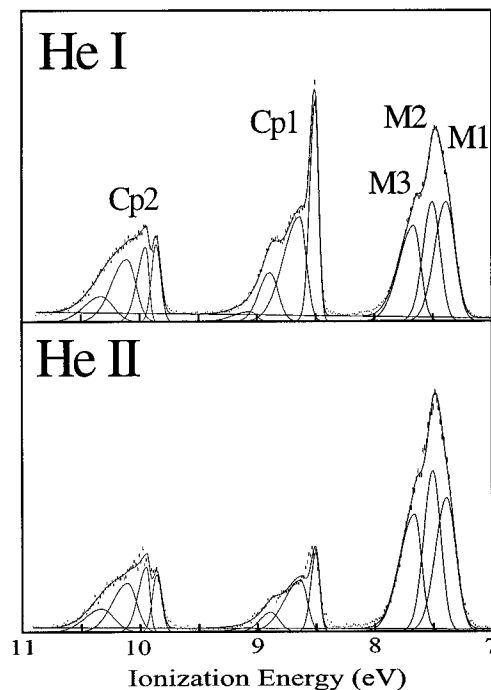
**Figure 1.** Full valence-region He I spectra of (A)  $(C_5H_5)_2Ru$ , (B)  $(C_5Me_5)_2Ru$ , (C)  $(C_5Me_5)(C_5H_5)Ru$ , (D)  $(C_5Me_5)(C_5Cl_5)Ru$ , and (E)  $(C_5Me_5)(C_5F_5)Ru$ .

**Table 1. Ionization Energies and Relative Areas for Compounds**

compound	position (eV)	relative area			label
		He I	He II	He II/He I	
$(C_5H_5)_2Ru$	7.39, 7.50, 7.66	3	3	1	M1–M3
	8.50	2.52	0.88	0.35	Cp1
	9.86	1.75	1.17	0.67	Cp2
$C_5Me_5(C_5H_5)Ru$	690, 7.06, 7.22	3	3	1	M1–M3
	7.74	2.39	1.04	0.44	Cp1
	9.33	1.90	1.19	0.63	Cp2
$(C_5Me_5)_2Ru$	6.53, 6.74, 6.90	3	3	1	M1–M3
	7.23	2.28	1.11	0.49	Cp1
	8.70	1.66	1.46	0.88	Cp2
$(C_5Me_5)(C_5Cl_5)Ru$	7.54, 7.81	3	3	1	M1–M3
	8.13	3.35	2.12	0.63	Cp1
	9.57	2.29	1.36	0.59	Cp2
$(C_5Me_5)(C_5F_5)Ru$	7.75, 8.06	3	3	1	M1–M3
	8.40	2.30	2.23	0.97	Cp1
	9.99	2.20	1.72	0.78	Cp2

tions below 11 eV will be discussed in detail. Vertical ionization energies for the bands in the close-up spectra from 6 to 11 eV are shown in Table 1.

After corrections for instrument resolution and sensitivity and for other excitation lines in the sources, photoelectron spectra obtained with a He II source differ from spectra obtained with a He I source only in the relative intensities of the ionization bands. This difference is primarily due to the different inherent photoionization cross-sections of atomic orbitals, which vary as the incident photon energy changes. From theoretical estimates, the photoionization cross-section of Ru 4d

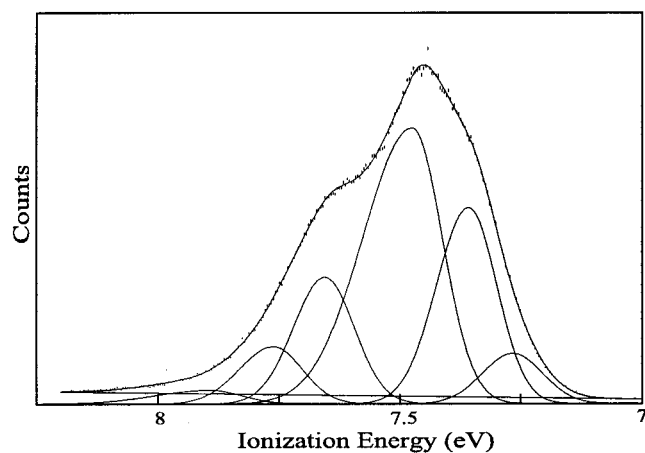


**Figure 2.** He I and He II close-up spectra of  $(C_5H_5)_2Ru$ .

atomic orbitals decrease by a factor of 1.25 when comparing He II to He I.<sup>20</sup> In comparison, the C 2p photoionization cross-section decreases by a factor of 3 when comparing He II to He I. Thus, ionization bands with predominantly metal character should increase relative to bands with predominantly carbon character in the He II spectrum. The F 2p and Cl 3p photoionization cross-sections decrease by factors of 1.1 and 21, respectively, when comparing He II to He I. For  $(C_5Me_5)(C_5F_5)Ru$ , bands containing F character will remain approximately the same in relative intensity with both He I and He II ionization sources as compared to bands which are predominantly metal in character, while for  $(C_5Me_5)(C_5Cl_5)Ru$ , bands containing Cl character will drop substantially on going from He I to He II. Table 1 gives the change in area from the He I to He II spectra for the ionizations of each compound reported relative to the M1 ionizations.

**$(C_5H_5)_2Ru$ .** The He I and He II close-up spectra of  $(C_5H_5)_2Ru$  are shown in Figure 2. The ionizations from 7 to 8 eV primarily derive from the metal d orbitals. The metal-based ionizations represent the  ${}^2E_{2g}$  positive ion state (correlating with removal of an electron from the metal  $e_{2g}$  ( $d_{x^2-y^2}$ ,  $d_{xy}$ ) set) and  ${}^2A_{1g}$  state (removal of an electron from the  $a_{1g}$  ( $d_z^2$ ) orbital). Previously the metal-based ionizations of this complex have been assigned analogously to ferrocene, with the main portion of the band attributed to the  ${}^2E_{2g}$  state and the shoulder to higher binding energy ascribed to the  ${}^2A_{1g}$  state. However, it can be seen from the close-up spectrum presented in Figure 3 that this band has a much more complicated shape that is not defined well with two Gaussian curves. This additional structure is due to spin-orbit splitting of the  ${}^2E_{2g}$  state into  ${}^2E_{2g(5/2)}$  and  ${}^2E_{2g(3/2)}$  states, as well as to the presence of partially resolved vibrational structure, which leads to the need for additional Gaussians to describe the shape of this band, as shown in Figure 3. This observation will be

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**Figure 3.** Close-up of the metal band of  $(C_5H_5)_2Ru$ .

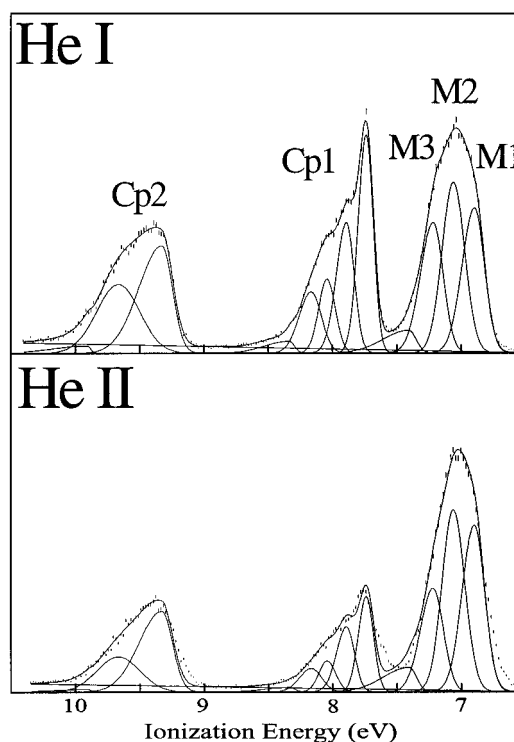
developed further in the Discussion. Because of the large amount of overlap of these bands, it is difficult to assign the three Gaussians used to represent the band in Figure 2 to specific symmetry metal ionizations as done for ferrocene. The Gaussians are labeled simply as M1, M2, and M3 for purposes of discussion.

Ionizations in the region from 8 to 11 eV involve combinations of the  $e_1''$  orbitals of each Cp ring, which are the single-perpendicular-node combinations of the carbon  $p_\pi$  orbitals. For purposes of comparison with the lower symmetry complexes, the ionizations in this region are labeled Cp1 ( ${}^2E_{1u}$  ion state in this case) and Cp2 ( ${}^2E_{1g}$  ion state in this case). These bands show complex features which are quite informative, which will be discussed. The positions of these ionizations reported in Table 1 are taken as the energy of the most intense (vertical) ionization.

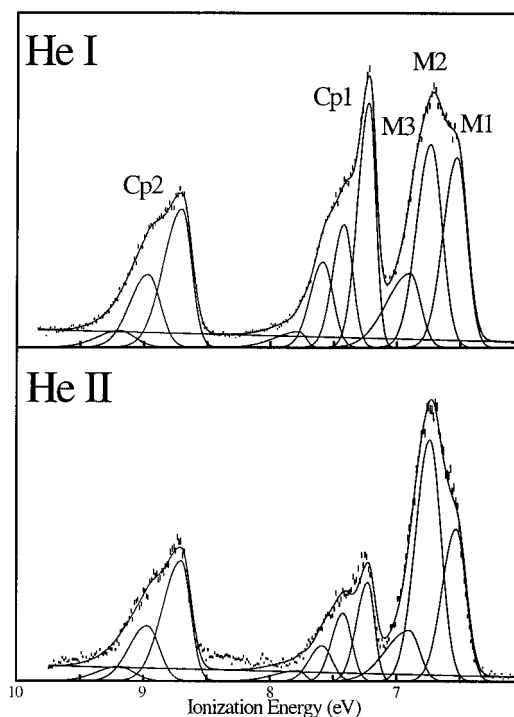
The metal-based ionizations increase dramatically in relative area in the He II spectrum as compared to the ligand ionizations. The He II spectrum also shows the relative increase in the intensity of the ring  $\pi$  ionization labeled Cp2 with respect to the ring  $\pi$  ionization labeled Cp1. Cp2 has the correct *gerade* symmetry to interact with the metal d orbitals, while Cp1 does not. This increase in relative intensity for Cp2 relative to Cp1 illustrates the greater metal involvement with the primarily ligand-based ionization Cp2.

**$(C_5Me_5)(C_5H_5)Ru$ .** The He I and He II close-up spectra of  $(C_5Me_5)(C_5H_5)Ru$  are shown in Figure 4. The shape of the metal band is different than that for  $(C_5H_5)_2Ru$ . The shoulder on the higher binding-energy side of the band is not as prominent as that in  $(C_5H_5)_2Ru$ , and a small shoulder is seen on the lower binding-energy side. All of the ionizations have been shifted to lower ionization energy as compared to  $(C_5H_5)_2Ru$ . However, this destabilization does not affect all of the ionizations equally. The metal bands shift by about  $-0.5$  eV, while Cp1 shifts by  $-0.76$  eV and Cp2 shifts by  $-0.56$  eV. This destabilization is due to interaction and mixing of the filled e set of methyl C-H  $\sigma$ -bonding orbitals, which, as previously mentioned, are located at about 11 eV. These shifts will be analyzed in the Discussion.

The He II spectrum shows the same general trends as that of  $(C_5H_5)_2Ru$ . The Cp bands drop in intensity substantially compared to M1–M3, and Cp1 decreases in intensity more than Cp2. This latter observation indicates that although the molecule does not have a



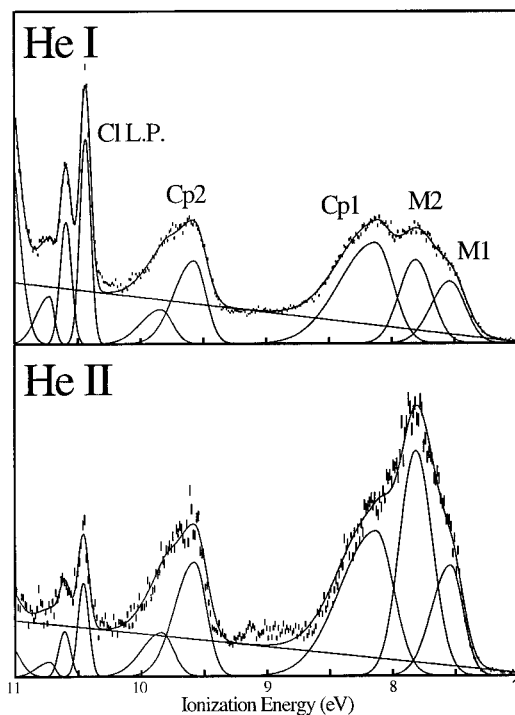
**Figure 4.** He I and He II close-up spectra of  $(C_5Me_5)(C_5H_5)Ru$ .



**Figure 5.** He I and He II close-up spectra of  $(C_5Me_5)_2Ru$ .

formal inversion center of symmetry, the orbital interactions still approximate *gerade* and *ungerade* symmetry, with the metal d orbitals mixing more strongly with the combination of Cp and Cp\* orbitals that contribute to ionization Cp2 than with the combination that contribute to ionization Cp1.

**$(C_5Me_5)_2Ru$ .** The He I and He II close-up spectra of  $(C_5Me_5)_2Ru$  are shown in Figure 5. It is again quite apparent that the metal band has a different shape than that observed for  $(C_5H_5)_2Ru$  or  $(C_5Me_5)(C_5H_5)Ru$ . The ionizations are destabilized further from  $(C_5H_5)_2Ru$  and

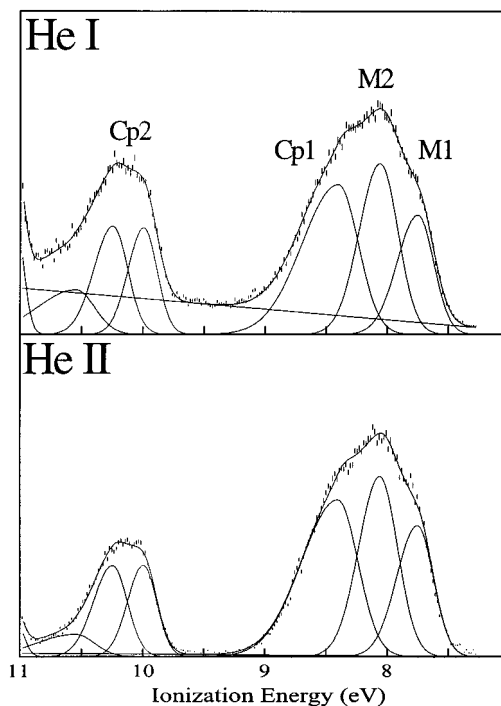


**Figure 6.** He I and He II close-up spectra of  $(C_5Me_5)(C_5Cl_5)Ru$ .

$(C_5Me_5)(C_5H_5)Ru$  as more methyl groups are added. However, the trends in destabilization are not simply additive. The addition of five more methyl groups does not destabilize the M1–M3 and Cp1 ionizations as much as the addition of the first five, but the Cp2 ionization is destabilized more. Permethylation of the second Cp ligand shifts the metal bands by about  $-0.4$  eV, Cp1 by  $-0.51$  eV, and Cp2 by  $-0.63$  eV. The He II spectrum shows the same trends as those seen in the previous compounds.

**$(C_5Me_5)(C_5Cl_5)Ru$ .** The He I and He II close-up spectra of  $(C_5Me_5)(C_5Cl_5)Ru$  are shown in Figure 6. As compared to  $(C_5Me_5)(C_5H_5)Ru$ , all of the ionizations have been stabilized. However, unlike methyl substituents that destabilize the Cp-based ionizations more than the metal-based ionizations, here the metal ionizations are affected greater than the Cp ionizations. The metal ionizations have been stabilized by about 0.7 eV, while Cp1 has been stabilized by 0.39 eV and Cp2 by 0.24 eV. As a result of the greater stabilization of the metal ionizations than Cp1, the metal ionizations and Cp1 have almost merged into one band. The metal ionizations appear to be partially obscured and are defined by only two Gaussians, labeled M1 and M2. There are also additional ionizations due to chlorine lone pairs located from 10–11 eV.

In the He II spectrum, the Cp1 and Cp2 ionizations still decrease compared to M1–M3 by about the same amount. This indicates that there is not substantial chlorine character associated with these ionizations. If there were substantial chlorine character, the intensity of these ionizations would decrease much more dramatically with He II excitation, as seen for the sharp chlorine lone pair ionizations near 10.5 eV which fall by nearly 90%. It is not possible to clearly determine if the Cp1 ionization decreases more than the Cp2 ionization as it does for the other complexes because of the close proximity of the Cp1 ionization to the M1–M3



**Figure 7.** He I and He II close-up spectra of  $(C_5Me_5)(C_5F_5)Ru$ .

ionizations. Examination of the integrated peak areas in Table 1 indicates that metal-based ionization intensity is coincident with the Cp1 ionization.

The chlorine lone pair ionizations located near 10.5 eV are very sharp and have a well-resolved vibrational progression. The adiabatic ionization is at 10.44 eV and is also the vertical ionization. The spacing between the vibrational components is 0.16 eV or  $1300\text{ cm}^{-1}$ . There are several vibrations observed in the vibrational spectroscopy of the ground-state molecule, but they have not been fully assigned.<sup>6</sup> It is also interesting to note that a similar looking set of ionizations is seen in the spectrum of  $(C_5Me_5)_2Ru$  (see Figure 1), starting at 10.23 eV with a spacing of 0.15 eV. In addition, a similar sharp ionization is observed in the spectrum of  $(C_5Me_5)_2Fe$  at 10.12 eV.<sup>21</sup> Extended Hückel calculations<sup>22</sup> indicate that these ionizations derive from the  $e_{2u}$ -symmetry set of substituent-based orbitals that have  $\pi$  symmetry with respect to the Cp rings. A through-space interaction between the two rings pushes this completely antisymmetric orbital to higher energy so that its ionization is clearly observed. A corresponding ionization is not seen for  $(C_5Me_5)(C_5F_5)Ru$  because the fluorine ionizations are at too great an ionization energy.

**$(C_5Me_5)(C_5F_5)Ru$ .** The He I and He II close-up spectra of  $(C_5Me_5)(C_5F_5)Ru$  are shown in Figure 7. These spectra are very similar to those for  $(C_5Me_5)(C_5Cl_5)Ru$ . All of the ionizations have been stabilized as compared to those of  $(C_5Me_5)(C_5H_5)Ru$ , and the metal bands have been stabilized the most, by about 0.85 eV as compared to 0.66 eV for both Cp1 and Cp2. This has caused the metal bands and Cp1 to merge even further than for  $(C_5Me_5)(C_5Cl_5)Ru$ . In the He II spectra, all of the valence ionizations stay relatively constant to each other in area.

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## Discussion

The previous section presented the general assignments of the valence photoelectron spectra in terms of metal d-based and cyclopentadienyl  $\pi$ -based ionizations and the effects of methyl, chlorine, and fluorine substitutions on these ionizations. In this section, the shifts, shapes, and intensity changes of the ionizations will be examined in more detail in terms of the orbital interactions and electron distributions in these systems. To begin, a brief review of the symmetry of these molecules and an explanation of the symmetry labels used in this discussion are presented.

**Symmetry Designations.** The two cyclopentadienyl rings of a metallocene may be oriented in the two extremes of either an eclipsed ( $D_{5h}$ ) or a staggered ( $D_{5d}$ ) conformation. Crystal structures of ruthenocene<sup>23</sup> and decamethylruthenocene<sup>24</sup> show the rings to be in an eclipsed orientation. We have chosen to use the  $D_{5d}$  point group irreducible representations in our discussion of these molecules. There is very little difference in the electronic structure between the  $D_{5h}$  and  $D_{5d}$  symmetries, and much of the literature employs the  $D_{5d}$  point group with reference to ferrocene. In addition, the *gerade* and *ungerade* notation of the  $D_{5d}$  point group allows for a rapid grasp of symmetry matching with metal orbitals that is not as accessible with the prime and double prime notation of the  $D_{5h}$  point group. When spin-orbit coupling is discussed, the double group notation for  $D_5$  will be used. The notation of the point groups converge when spin-orbit effects are taken into consideration, as double group  $D_5$  is a subset of both the  $D_{5d}$  and  $D_{5h}$  point groups.

Crystal structures of  $(C_5Me_5)(C_5H_5)Ru$ ,<sup>25</sup>  $(C_5Me_5)(C_5Cl_5)Ru^{6g}$  and  $(C_5Me_5)(C_5F_5)Ru^9$  show these molecules also to be in eclipsed conformations. Because of the reduction of symmetry due to substitution of a single ring, these molecules belong to the  $C_{5v}$  point group, but for clarity and ease of comparison they will also be labeled as  $D_{5d}$ , which is still the local symmetry at the metal, as indicated by features of the ionizations that were presented in the previous section.

**PES of  $(C_5H_5)_2Ru$ .** This study has shown that the structure of the metal ionizations of  $(C_5H_5)_2Ru$  is more complex than previously thought. The shape of this band can be seen most clearly in Figure 3, which is a close-up of only the metal-based ionizations. The metal ionizations of ferrocene give rise to a simple band structure, with the  ${}^2A_{1g}$  and  ${}^2E_{2g}$  states separated by 0.36 eV ( ${}^2A_{1g} > {}^2E_{2g}$ ). Previous work on  $(C_5H_5)_2Ru$ <sup>11</sup> resulted in the assignment of the metal band in an analogous manner, with the discernable shoulder on the high-energy-binding side representing the  ${}^2A_{1g}$  state. However, it is apparent from the data presented here that the metal band of  $(C_5H_5)_2Ru$  has a more complicated structure.

The primary cause of this structure is spin-orbit splitting of the  ${}^2E_{2g}$  state into  ${}^2E_{2(5/2)}$  and  ${}^2E_{2(3/2)}$  states. Spin-orbit splitting has previously been observed for the third-row metallocenes. The PES of  $(C_5H_5)_2Os$ <sup>19</sup> shows a 0.66 eV separation between the  ${}^2E_{2(5/2)}$  and

${}^2E_{2(3/2)}$  states due to the large spin-orbit coupling constant for Os ( $\zeta = 0.378$  for atomic  $Os^{26}$ ). The energy splitting between the  ${}^2E_{2(5/2)}$  and  ${}^2E_{2(3/2)}$  states is  $2\zeta$ , giving a spin-orbit coupling parameter  $\zeta_{obs}$  of  $0.330 \pm 0.003$  eV for the  ${}^2E_{2g}$  ionizations of  $(C_5H_5)_2Os$ , which is  $(87 \pm 3)\%$  of the neutral atomic spin-orbit coupling constant. From a zero differential overlap (ZDO) approximation, this result suggests that the  $e_{2g}$  orbital of  $(C_5H_5)_2Os$  is 87% metal in character. On the basis of a similar estimate for the metal character of the  $e_{2g}$  orbital of  $(C_5H_5)_2Ru$  and the reported spin-orbit coupling constant of neutral Ru ( $\zeta \approx 0.11$  eV<sup>27</sup>), a splitting of approximately 0.2 eV is expected. The separation between M1 and M3 of  $(C_5H_5)_2Ru$ , as shown in Figure 2, is 0.26 eV. The lower binding-energy side of the metal band of  $(C_5H_5)_2Ru$  can be assigned to the  ${}^2E_{2(5/2)}$  ionization state, the higher binding-energy side of the metal band is assigned to the  ${}^2E_{2(3/2)}$  ionization state, and the center portion is assigned to the  ${}^2A_{1g}$  ionization state. Due to the overlap of the ionizations and the presence of vibrational fine structure on all of these ionizations, it is not possible to accurately assign the positions of the vertical ionizations of these three ionization states. The position of M1 is probably the most accurate of any of the metal bands, and this band will be used as the best approximation of the position of the metal bands and their relative shifts when comparing compounds.

The ionization band at 8.5 eV is due to the cyclopentadienyl-based  ${}^2E_{1u}$  ion state. This state arises primarily from ionization of the particular combination of Cp  $e_1''$  carbon  $p\pi$  orbitals on either side of the metal, which is symmetric to a mirror plane between the rings. This combination of the Cp orbitals may not interact, by symmetry, with the metal d orbitals and, therefore, is expected to be predominantly ligand based. The complex structure of the band indicates the activation of several vibrational progressions upon ionization. Although this ionization envelope shows discernible structure, the resolution between the individual vibrational levels is not adequate for a detailed modeling of the individual bands.  $(C_5H_5)_2Ru$  has four symmetric  $A_{1g}$  vibrations that can be activated by photoionization,<sup>28</sup> giving the observed complicated band shape due to overlapping vibrational progressions.

In contrast to the Cp1 ( ${}^2E_{1u}$ ) ionization, the Cp2 ( ${}^2E_{1g}$ ) ionization beginning at 9.8 eV arises from an orbital of correct symmetry to interact with the metal d orbitals. The large stabilization of Cp2 from Cp1 is the first indication of metal character in the  $e_{1g}$  orbital. There is a 1.36 eV split between the two ionizations, compared to 0.74 and 1.4 eV for  $(C_5H_5)_2Fe$  and  $(C_5H_5)_2Os$ , respectively. The similar splitting observed for  $(C_5H_5)_2Ru$  and  $(C_5H_5)_2Os$  illustrates the similar bonding capabilities of the second- and third-row metals.

The second indication of greater metal character in the  $e_{1g}$  orbital is seen in the He II spectrum of  $(C_5H_5)_2Ru$ . As pointed out in the results, ionizations that arise from orbitals containing a greater amount of Ru 4d character are expected to increase in intensity relative to ionizations from orbitals that do not contain metal

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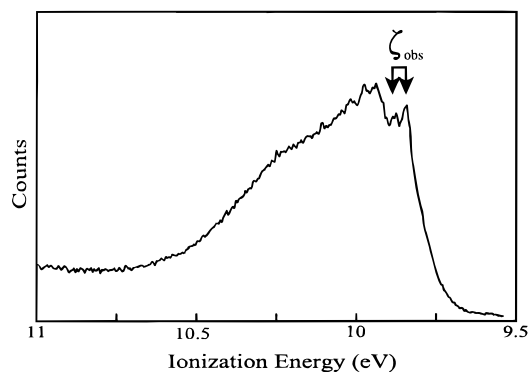
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**Figure 8.** He I close-up of the ligand  ${}^2E_{1g}$  ionization of  $(C_5H_5)_2Ru$ .

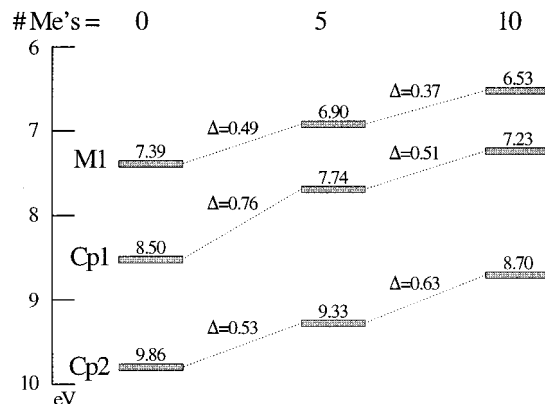
character. The He II spectrum clearly shows an increase in the intensity of the  ${}^2E_{1g}$  ionization relative to the  ${}^2E_{1u}$  ionization.

A further close-up of the ionization resulting from the  ${}^2E_{1g}$  state is shown in Figure 8. This band shows a complicated structure similar to  ${}^2E_{1u}$ . However, the leading edge of the  ${}^2E_{1g}$  ionization shows two distinct, sharp ionization features. These two features are ascribed to spin-orbit splitting caused by the metal character in this ionization. The magnitude of the splitting ( $0.036 \pm 0.007$  eV) determines the extent of metal character in the corresponding orbital, estimated to be  $(33 \pm 6)\%$  using the ZDO approximation for atomic contributions to spin-orbit splitting and the 0.11 eV  $\zeta$  value reported for ruthenium previously. Estimates of the metal character based on synchrotron studies are 17%, while SCF-LCAO-MO calculations predict 33% metal character.<sup>11c</sup> A similar approximation based on the observed spin-orbit splitting for this ionization of  $(C_5H_5)_2Os$ <sup>19</sup> gives  $(27 \pm 1)\%$  metal character.

Now that a firm understanding of the PES of  $(C_5H_5)_2Ru$  has been established, we can examine the effect of substituents.

**Methyl Substituent Effects.** There have been numerous PES studies of the effects of methyl substitution on the electronic structure of  $d^6$  metallocenes.<sup>11a,b</sup> Most of these studies have considered the methyl group as an inductive electron donor to the Cp ring. However, the group electronegativity of methyl is actually greater than that of H in all electronegativity scales (for example, 2.3 for methyl compared to 2.2 for hydrogen on the Pauling scale), which would qualitatively indicate that methyl has about the same if not slightly less  $\sigma$  inductive donor ability than hydrogen.<sup>29</sup>

Our previous valence and core PES studies of methyl-substituted Cp ligands<sup>18,30,31</sup> have given evidence that the primary electronic perturbation of a methyl group in place of hydrogen in a metal-coordinated, unsaturated organic ligand is a hyperconjugative  $\pi$  interaction rather than a  $\sigma$  inductive one. The three C-H bonds of a methyl group transform as e and  $a_1$  symmetry orbitals. The ionizations related to the methyl e symmetry orbitals begin around 11 eV in the spectra of these complexes, which is only a few electronvolts greater



**Figure 9.** Correlation diagram illustrating the shifts observed upon methylation of the cyclopentadienyl ligands.

energy than the ionizations of the Cp  $e_1''$  orbitals. With the methyl bound to the cyclopentadienyl ring, one of the methyl e orbitals can interact in a  $\pi$ -fashion with the Cp ring  $\pi$  orbitals. This Cp-methyl  $\pi$  interaction is a filled-filled interaction that destabilizes the highest occupied Cp-methyl  $\pi$  orbital. The primary difference in the interaction of a methyl group with an unsaturated bond in comparison to a hydride is due to this type of orbital interaction, not a difference in inductive,  $\sigma$ -type donation. Upon coordination to a metal center, the destabilized  $\pi$  orbitals of the methyl-substituted Cp are then closer in energy to the empty metal  $e_{1g}$  orbitals, making electron donation to the metal center more favorable and destabilizing the metal-based orbitals.

A correlation diagram showing the shifts of the ionizations M1, Cp1, and Cp2 upon Cp methylation is shown in Figure 9. Several points are evident from this diagram. First, methylation does not affect the ionizations equivalently. The overall shifts upon complete methylation are in the order Cp1 ( $-1.27$  eV) > Cp2 ( $-1.16$  eV) > M1 ( $-0.86$ ). The ligand-localized Cp1 ionization is destabilized 0.11 eV more than the delocalized Cp2 ionization upon complete methylation of the Cp rings. The metal orbitals are affected the least by Cp methylation.

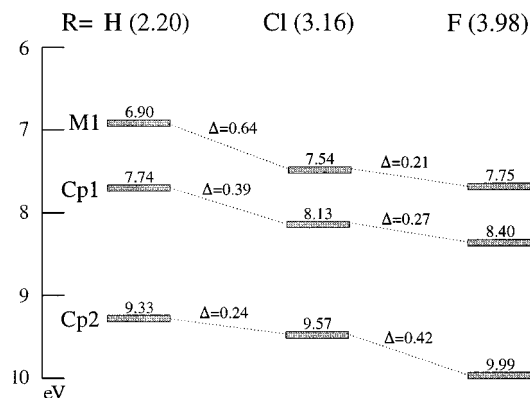
It can also be seen that the effect of the methyl substituents is not simply additive for this series of compounds. The methyl substituents are added to the molecules in an unsymmetric way, and this nonadditivity is due to the reduction of symmetry for  $(C_5Me_5)(C_5H_5)Ru$ . As the first five methyl groups are added to one Cp ligand, the contribution of the methylated Cp ring to the Cp1 orbital will be increased at the expense of the contribution of this ring to the Cp2 orbital and the Cp1 ionization will be shifted more. As the next five methyls are added, methyl character will again be more evenly distributed between the Cp1 and Cp2 orbitals. The observed trend is that the lower energy Cp2 ionization "catches up" to the ionization that felt the effect of the first five methyls.

**Halide Substituent Effects.** A correlation diagram comparing the ionization energies for  $(C_5Me_5)(C_5H_5)Ru$ ,  $(C_5Me_5)(C_5Cl_5)Ru$ , and  $(C_5Me_5)(C_5F_5)Ru$  is shown in Figure 10. All of the ionizations for the halogenated compounds are stabilized compared to  $(C_5Me_5)(C_5H_5)Ru$  due to the higher electronegativities of the halide substituents. The ionizations of the fluoro-substituted compound are stabilized the most due to fluorine's greater electronegativity. However, based solely on

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**Figure 10.** Correlation diagram illustrating the shifts upon halogenation of the Cp ligand. Electronegativities of the Cp ligand substituents are in parentheses.

electronegativities, a much larger stabilization of the ionizations would be expected, particularly as comparison is made between the chloro- and fluoro-substituted compounds. This discrepancy from the results expected based on electronegativities is due to the additional ability of the chloro and fluoro lone pairs to have filled- $\pi$ -overlap interactions with the Cp  $\pi$  orbitals. This interaction *destabilizes* the antibonding  $\pi$  combination with the Cp  $\pi$  orbitals, acting opposite to the  $\sigma$ -inductive electron withdrawal in shifting the energies of the valence Cp-based ionizations. As discussed for the methyl substituents, the destabilization of the Cp  $\pi$  orbitals brings them closer in energy to the unoccupied  $e_{1g}$  orbitals of the metal, which increases electron donation to the metal. Thus, the halogen lone pairs become electron donors to the metal through the Cp  $\pi$  orbitals. This donation acts counter to the halogen  $\sigma$ -inductive effect, and the metal ionizations are not stabilized as much as expected based on the  $\sigma$  electronegativity.

For  $(C_5Me_5)(C_5Cl_5)Ru$  compared to  $(C_5Me_5)(C_5H_5)Ru$ , the amount of stabilization of the ionizations is  $M1 > Cp1 > Cp2$ . The Cp2 ionization is stabilized the least because it is very close in energy (within 1 eV) to the Cl lone pairs, causing it to feel the majority of the filled- $\pi$  overlap interaction with these lone pairs. In addition to being further separated in energy, the Cp1 ionization has a majority of Cp\* character so it is not held up in energy as much by the  $\pi$ -overlap interaction with Cl. The relative intensities of the ionizations from He I to He II excitation also reflect the chlorine character in the Cp2 ionization. In the ruthenocene and methylated ruthenocene spectra, the Cp2 ionization gains in intensity relative to the Cp1 ionization with He II excitation because of the partial metal character in this orbital. In the spectrum of the chloro complex, the chlorine  $\pi$  character in the Cp2 ionization, with the diminishing cross-section for chlorine, offsets the increasing cross-section of the metal character. The chlorine  $\pi$  character is relatively small, or otherwise the Cp2 ionization would greatly diminish in intensity. The largest stabilization is seen for the metal-based ionizations, which have essentially no direct overlap with the Cl lone pairs and reflect the full change in charge potential.

Comparing  $(C_5Me_5)(C_5F_5)Ru$  to  $(C_5Me_5)(C_5H_5)Ru$  shows some similar effects to the chloro substitution. The metal-based ionizations are stabilized more (0.88 eV)

than the Cp-based ionizations (0.66 eV each). This is strong evidence of the overlap effects with the fluorine lone pairs, even though the fluorine lone pair ionizations are well-separated in energy from the outer valence levels. Fluorine lone pairs in organofluorine molecules ionize in the region of 17–20 eV. The fluorine lone pair mixing in the Cp1 and Cp2 ionizations is relatively similar and substantial. Both ionizations are stabilized to the same amount, and both show only small changes in intensity from He I to He II excitation. The large energy separation to the fluorine lone pairs apparently reduces the difference in the contribution to the Cp1 and Cp2 ionizations. Compared to the chloro-substituted compound, the metal and Cp1 ionizations are stabilized to a much lesser extent, indicating that fluorine has much better  $\pi$  overlap than chlorine. The Cp2 ionization is stabilized the most, which reflects the much worse energy match between the Cp  $\pi$  orbitals and the much more stable F p orbitals.

The first ionization energies of the chloro- and fluoro-substituted compounds are very similar. This is caused by the balance between the different electronegativities of these two halides and the different  $\pi$ -donor abilities to the metals through the Cp  $\pi$  orbitals, which act in opposite directions. A Cl p orbital is best described as a weak  $\pi$  donor to C because the long C–Cl bond length (1.72 Å for this compound) results in relatively poor overlap of the 2p orbitals of C and the 3p orbitals of Cl. Fluorine is a much better  $\pi$  donor than Cl because the shorter C–F bond lengths (1.24 Å) allow better overlap of C 2p and F 2p orbitals. At these bond distances, the aryl  $\pi$ -p  $\pi$  overlap is calculated to be 0.229 for Cl and 0.254 for F for typical atomic functions.

While the greater  $\pi$ -donor ability of fluorine than chlorine may be counterintuitive to some, this conclusion is in agreement with the general reactivity of fluoro- and chloro-substituted aromatic compounds. For example, while all the halogens are ortho- and para-directing and deactivate aromatic rings toward electrophilic aromatic substitution, fluorine is the *least* deactivating of the halogens.<sup>32</sup> In addition, the Hammett parameters for fluorine and chlorine indicate that fluorine is less electron withdrawing than chlorine.<sup>33</sup>

The PES of perfluorinated unsaturated and aromatic organic compounds show a similar trend, which has been dubbed the “perfluoro effect”.<sup>34,35</sup> To be specific, the perfluoro effect is recognized as the much larger stabilizing effect on the  $\sigma$  ionizations as compared to the  $\pi$  ionizations of planar molecules. For example, the  ${}^2E_{1g}$   $\pi$  ionization of hexafluorobenzene is stabilized 0.88 eV from that of benzene, while the  $\sigma$  ionizations are stabilized by 2.5–3 eV. The 0.66 eV stabilization of the Cp  $\pi$ -based ionizations of  $(C_5Me_5)(C_5F_5)Ru$  are consistent with the characters of these orbitals and the effects of  $\pi$  interactions with the fluorine substituents.

**Comparison with Previous Studies.** A few other studies that address the electronic structure of these compounds have been reported. Core level ionizations

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of the compounds studied here (other than  $(C_5Me_5)(C_5F_5)Ru$ ) have been measured by surface XPS.<sup>6</sup> The XPS study has shown that  $Cp^*$  and  $C_5Cl_5$  have almost equal but opposite effects upon the Ru core ionizations, such that the Ru  $3d_{5/3}$  binding energy of  $Cp_2Ru$  and  $(C_5Me_5)(C_5Cl_5)Ru$  are the same, within the uncertainty of that experiment ( $\pm 0.1$  eV). This same balanced electronic effect is reflected in the first ionizations of  $Cp_2Ru$  and  $(C_5Me_5)(C_5Cl_5)Ru$  reported here, with the higher precision of this experiment showing that the shift is only  $0.15 \pm 0.05$  eV. The similarity of the core and valence results shows that the metal-based ionizations are controlled by the charge potential at the metal and not by overlap effects. Solution electrochemistry has shown  $C_5Cl_5$  and  $C_5F_5$  to have very similar overall electronic effects at the metal.<sup>10</sup> Cyclic voltammetry experiments show that both  $(C_5Me_5)(C_5Cl_5)Ru$  and  $(C_5Me_5)(C_5F_5)Ru$  exhibit diffusion-controlled, irreversible two-electron oxidations with  $E_{pa} = +1.11$  and  $+1.07$  V (versus Fc), respectively. Thus, the characteristics observed in the gas-phase experiments of the present study also apply to solution measurements. The  $\Delta G_{et}^\circ$  has been measured by gas-phase ionization energetics by Richardson et al.<sup>10</sup> Richardson has also developed a  $\gamma$  parameter to describe the electronic effects of Cp derivatives on the ionization free energy of  $LL'Ru$  complexes, where L is the ligand of interest and L' is another Cp ligand with a known  $\gamma$  parameter, anchored to  $\gamma = 0$  for Cp and  $\gamma = -1.0$  for  $Cp^*$ .<sup>36</sup> The  $\gamma$

parameters for  $C_5Cl_5$  and  $C_5F_5$  are close, with  $\gamma(C_5Cl_5) = 1.06$  and  $\gamma(C_5F_5) = 1.5$ . The magnitude of these  $\gamma$  parameters agree with the magnitude of the stabilization of the first ionizations seen in the gas-phase PES of this series of compounds.

### Conclusions

The primary electronic effect of methyl groups as substituents of Cp ligands is a hyperconjugative interaction that destabilizes the Cp  $\pi$ - and metal-based ionizations. Halide substituents show an admixture of  $\sigma$ -inductive electron-withdrawing and  $\pi$ -electron-overlap effects, which balances to an overall slight electron-withdrawing ability from the metal. The fluoro-substituted Cp is only slightly more electron withdrawing than the chloro-substituted Cp. The electron-withdrawing ability of the fluoro-substituted ring is tempered by the greater  $\pi$ -donor capability of fluorine than chlorine. Further studies are currently underway in our laboratories to evaluate the influence of halocyclopentadienyl substituents on other metal complexes.

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