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A Photoelectron Spectroscopic Study of Some Pentacarbonylchromium Carbene Complexes

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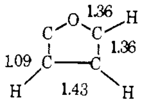
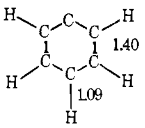
Abstract: Nine pentacarbonylchromium carbene complexes have been studied via photoelectron spectroscopy and molecular orbital calculations. These studies indicate that amino carbenes are poorer π acceptors than methoxy- or thiomethylcarbenes and that all of the carbene ligands studied are poorer π acceptors than the carbonyl ligand. These results are in accord with predictions of relative π acceptor strength based on structural studies of transition metal carbene complexes. In contrast, our results disagree with the generally accepted view of the carbene carbon as an electron deficient center. In every case, the charge on the carbene carbon was found to be less positively charged than the carbonyl carbons. The stability of the chromium–carbene carbon bond was found to depend upon the charge of the carbene carbon and upon the amount of carbon lone pair character in the bond.

In recent years, there has been considerable interest in carbene species, $\ddot{C}(X)Y$, as ligands in transition metal complexes.[1,2] A good deal of attention has been focussed upon the relative ability of the carbene ligand to act as a π acceptor.[3,4] However, no systematic study of the effects of varying X and Y upon the electronic structure of a series of organometallic carbene complexes has been reported. In order to assess these effects, we have obtained the photoelectron spectra of several pentacarbonylchromium carbene complexes, $(CO)_5CrC(X)Y$ ($X = OCH_3, SCH_3, N(CH_3)_2, NH_2, Y = CH_3$; $X = OCH_3, NH_2, Y = C_4H_3O$; $X = OCH_3, N(CH_3)_2, NH_2, Y = C_6H_5$). In addition we have performed molecular orbital (MO) calculations on these molecules. Those aspects of the MO results which are relevant in the interpretation of the photoelectron spectra will be reported here. A fuller discussion of the MO results will be presented in a separate paper.[5]

Photoelectron spectroscopy (PES) has been shown to be a powerful tool for probing the electronic structure of transition metal complexes, especially when combined with molecular orbital calculations[6] and curve-fitting techniques.[7] Interpretation of the photoelectron spectra of large molecules is often difficult. In species with many valence electrons and complex electronic structures, the peaks that appear in the spectrum tend to be broad, with vibrational structure poorly resolved at best. In addition, peaks corresponding to nearly degenerate MO's may merge into one band. As a result, special techniques are needed for the determination of the maxima of all the peaks which contribute to a band. These maxima are the ionization potentials (IP's) of the orbitals to which the peaks correspond.

A single peak in a photoelectron spectrum should have the shape of a Gaussian distribution. Overlapping peaks may give

Table I. Bond Distances Employed in Calculations on (CO)$_5$CrC(X)Y (Å)

	(CO)$_5$Cr Fragment		
Cr–C	1.88	C–O	1.128
	CrC(X)Y Fragment X = OCH$_3$		
	Y = CH$_3$	Y = C$_4$H$_3$	Y = C$_6$H$_5$
Cr–C	2.02	2.02	2.02
C–OCH$_3$	1.32	1.32	1.32
O–CH$_3$	1.48	1.48	1.48
C–C$_4$	1.54	1.47	1.47
C–H	1.09	1.09	1.09
	X = NH$_2$, N(CH$_3$)$_2$		
	Y = CH$_3$	Y = C$_4$H$_3$O	Y = C$_6$H$_5$
Cr–C	2.16	2.16	2.16
C–NR$_2$	1.32	1.32	1.32
N–H	1.03	1.03	1.03
N–CH$_3$	1.50		1.50
C–C$_4$	1.54	1.47	1.47
C–H	1.09	1.09	1.09
	X = SCH$_3$ Y = CH$_3$	C$_4$H$_3$O 	C$_6$H$_5$ 
Cr–C	2.02		
C–SCH$_3$	1.72		
S–CH$_3$	1.88		
C–CH$_3$	1.54		
C–H	1.09		

rise to a variety of band shapes. Although the full spectrum, including argon calibration peak, is needed for assignment of peak positions, expanded spectra of individual bands are helpful for determination of band shape. When a close-up view of a band revealed that it contained distinct shoulders or that it was unusually broad and flat-topped, program GFIT[7] was used to fit the band (in the full spectrum) with two or more asymmetric Gaussian peaks. The reported IP's are the maxima of the smallest number of Gaussian peaks needed for a band to be fit satisfactorily.

After the IP's have been obtained, the nature of the orbitals from which the electrons have been removed must still be determined. Koopmans' theorem provides the link between the photoelectron spectra and the MO calculations, stating that the IP's observed experimentally are the negatives of the eigenvalues of the molecule in its ground state.[8] Although Koopmans' theorem is extremely useful as a guide in interpreting photoelectron spectra, it does neglect electron reorientation, correlation, and relativistic effects. Hence, the ground state eigenvalues of even an ab initio calculation will not correspond exactly to the observed IP's. Nevertheless, it has been shown that quantitative predictions of IP's may be obtained from approximate ground state calculations by applying a method developed by Fenske and Hall.[9] This method assumes that, for a series of reasonably related compounds, the corrections which must be made to the eigenvalues of one compound are transferable to orbitals of similar character in the other molecules of the series. Thus, the spectra for the entire series of carbene complexes may be assigned by coupling an MO calculation for each member of the series with correction factors derived from comparison of the MO calculations and corresponding spectra of a few molecules ((CO)$_6$Cr, (CO)$_5$CrC(OCH$_3$)CH$_3$, (CO)$_5$CrC(N(CH$_3$)$_2$)CH$_3$, C$_4$H$_4$O, and C$_6$H$_6$). The results obtained in this manner are reported below.

Experimental Section

Synthesis. The methoxycarbene complexes, (CO)$_5$CrC(OCH$_3$)Y, were prepared by adding the appropriate lithium reagent, Y$^-$Li$^+$, to chromium hexacarbonyl and methylating the resultant anionic acyl compounds. The other carbene complexes were prepared from methoxycarbene complexes by methods which have been described previously.[10,11] The identity and purity of the compounds were established by infrared, ^{1}H NMR, and/or mass spectroscopy.

Photoelectron Spectra. The photoelectron spectra were obtained using a Varian IEE-15 spectrometer in the UV configuration. Argon was used as a single internal standard. Spectra were obtained at temperatures varying from ambient (for (CO)$_5$CrC(OCH$_3$)CH$_3$) to 80 °C (for (CO)$_5$CrC(N(CH$_3$)$_2$)C$_6$H$_5$). In all cases, separate spectra were taken at different time intervals until the supply of sample introduced into the spectrometer was depleted. There was no sign of sample decomposition in any of the spectra. Reported spectra are plots produced directly by the spectrometer. A typical reported spectra consists of 18 individual scans, of 100-s duration, across a 10-eV region. Peak positions were determined through the use of program GFIT,[7] which permits the fitting of a spectral band with one or more asymmetric Gaussian peaks.

Calculations. The MO calculational method used has been described previously.[9,12] The method is approximate, but nonparameterized, requiring as input only the coordinates for the atoms in the molecule and atomic basis functions. The bond distances employed are listed in Table I and are in accord with the crystal structure data for (CO)$_5$CrC(OCH$_3$)C$_6$H$_5$,[13] (CO)$_4$Cr(P(C$_6$H$_5$)$_3$)C(OCH$_3$)CH$_3$,[14] (CO)$_5$CrC(N(C$_2$H$_5$)$_2$)CH$_3$,[15] and (CO)$_5$CrC(SC$_6$H$_5$)CH$_3$.[16] Bond distances for the C$_4$H$_3$O and C$_6$H$_5$ fragments were taken from the reported structures of C$_4$H$_4$O[17] and C$_6$H$_6$.[18] In accord with the crystal structure data, the molecules were oriented so that the plane of the chromium, carbene carbon, and central atoms of groups X and Y lay between the cis carbonyls. The phenyl group was oriented perpendicular to this plane, while the furyl group was taken to be coplanar with it.[19] For the calculation on (CO)$_5$CrC(OCH$_3$)C$_6$H$_5$, the methyl group of the methoxy moiety was placed trans to the metal.[13,14] For (CO)$_5$CrC(N(CH$_3$)$_2$)Y, the carbons of the dimethylamino moiety were taken to be coplanar with the rest of the carbene ligand, as were the hydrogens of (CO)$_5$CrC(NH$_2$)Y.[15] The furyl ring in (CO)$_5$CrC(X)C$_4$H$_3$O was oriented so that the oxygen of the furyl ring faced the X group.[19]

Clementi's double-ζ Slater-type orbitals were used as the basis functions for carbon, oxygen, nitrogen, and sulfur.[20] The 1s and 2s functions for carbon, oxygen, and nitrogen and the 1s through 3s functions for sulfur were curve fit to single-ζ form using the maximum overlap criterion.[21] No 3d orbitals were placed on sulfur. For hydrogen, a 1s exponent of 1.16 was chosen, as this is the minimum energy exponent for hydrogen in methane.[22]

The 1s–3d atomic orbitals given by Richardson et al.[23] for Cr(0) were used as chromium basis functions. The value of 2.1 was used for the exponent of the 4s and 4p orbitals, as this value gives the maximum σ ovelap between the chromium 4p orbitals and the carbon 2p orbitals of the carbonyl group.

The basis functions and bond distances used in this series of calculations differ slightly from those used in a previous calculation on (CO)$_5$CrC(OCH$_3$)CH$_3$.[24] In that calculation, the Cr–C distance for the carbonyl trans to the carbene ligand was made somewhat shorter than the corresponding distance for the carbonyls cis to the carbene. In addition, a 4s exponent of 2.0 and a 4p exponent of 1.6 were employed. Since the 4s and 4p orbitals are involved mainly in σ bonding, it was considered to be more consistent to choose orbital exponents on the basis of σ overlap alone. For this series of molecules, all Cr–CO distances were set to 1.88 Å, since there is no case of statistically significant bond shortening in the carbene complexes for which crystal structures have been performed.[2] It should be noted that the results of the two calculations on (CO)$_5$CrC(OCH$_3$)CH$_3$ do not differ substantially.

Basis Set Transformation. Although the calculations were carried out in an AO basis set, it is easier to discuss the results in terms of appropriate molecular and hybrid orbitals. Therefore, after self-consistency had been reached, the results were transformed to an MO basis derived from the eigenvectors of the free CO group and sp^2 or sp^3 hybrids on the various atoms of the carbene ligand. In order to shorten computing time, the 3σ and 6σ orbitals of the carbonyl groups were deleted from the basis set. Such a deletion has been shown to speed the calculation without significantly altering the results.[25]

Results and Discussion

It is convenient to consider the electronic structure of (CO)$_6$Cr before proceeding to consideration of the carbene complex. An abbreviated MO diagram for chromium hexa-

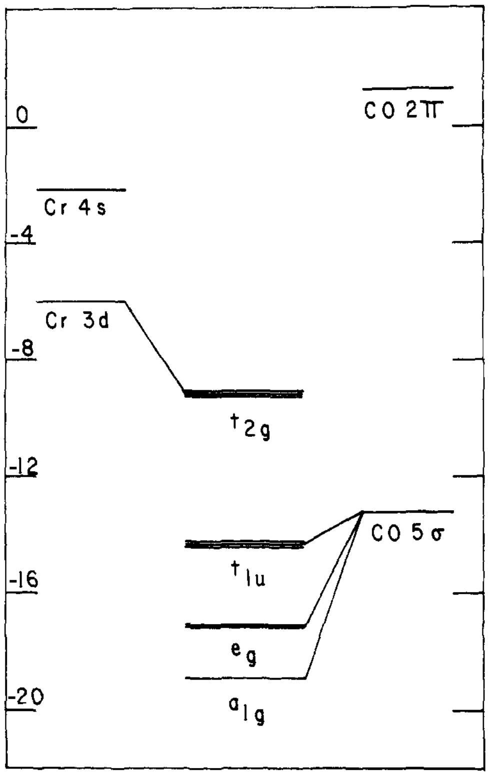


Figure 1. Abbreviated MO diagram for $(CO)_6Cr$.

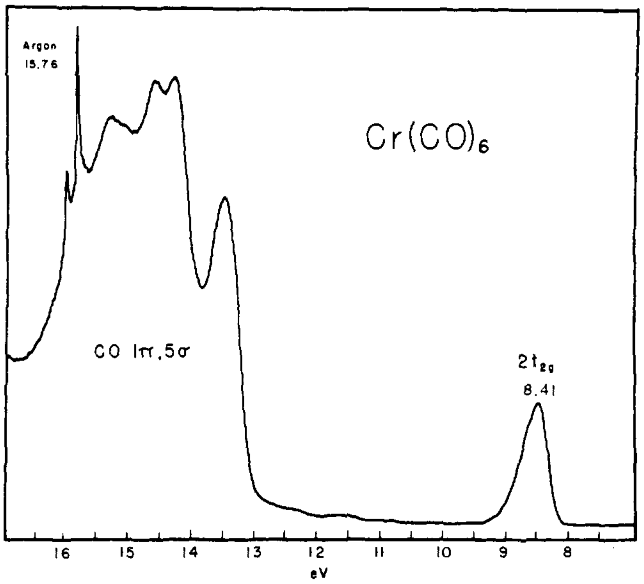


Figure 2. Photoelectron spectrum of $(CO)_6Cr$.

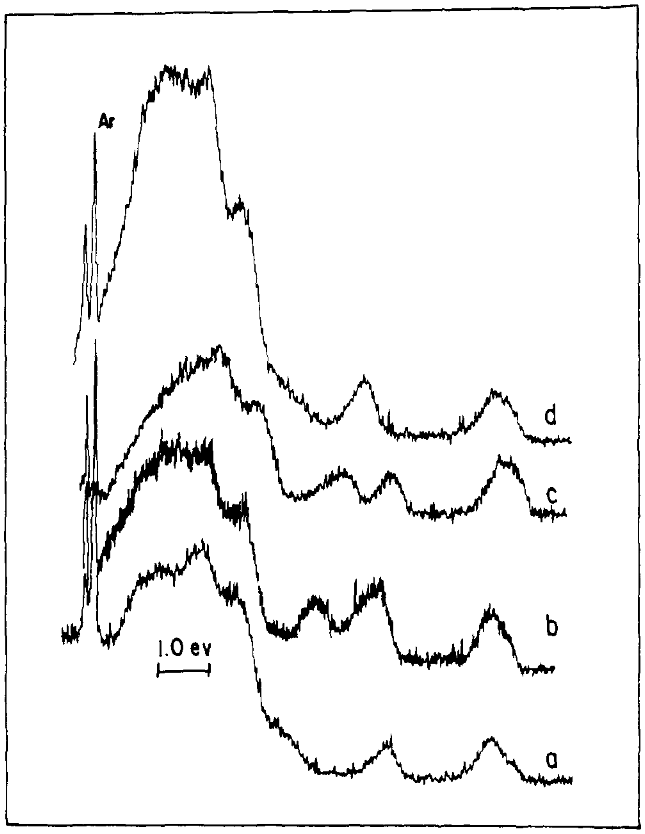


Figure 3. Photoelectron spectrum of: (a) $(CO)_5CrC(OCH_3)CH_3$; (b) $(CO)_5CrC(SCH_3)CH_3$; (c) $(CO)_5CrC(N(CH_3)_2)CH_3$; (d) $(CO)_5CrC(NH_2)CH_3$.

carbonyl is given in Figure 1. The levels labeled Cr 3d and Cr 4s are the Fock matrix diagonal terms for chromium's valence orbitals. The levels labeled CO 5σ and CO 2π are the MO's obtained from a calculation on free CO. The levels in the center of the diagram are the MO's of the complex; they are labeled in accord with O_h symmetry.

Applying Koopmans' theorem to the MO results for $(CO)_6Cr$, we would predict that the first peak in the photoelectron spectrum corresponds to removal of an electron from the t_{2g} MO's, which are mainly chromium in character. The maximum of the peak would be predicted to occur at 9.3 eV. This peak should be separated by roughly 5.5 eV from a peak corresponding to the removal of an electron from the first level localized on the carbonyl groups.

The photoelectron spectrum of $(CO)_6Cr$, first reported by Turner et al.,[26] is shown in Figure 2. It is in excellent agreement with the predictions made above. The first peak has its maximum at 8.41 eV, suggesting that the prediction made via Koopmans' theorem is in error by less than 1 eV. The broad band containing peaks corresponding to carbonyl ionizations has its onset at roughly 13 eV, which compares favorably with the calculated t_{1u} eigenvalue of -14.9 eV. As noted on Figure 2, the 15.76 eV peak of argon was used as an energy reference for the IP's. For all the figures of spectra, the ionization potential decreases from left to right.

The spectrum of $(CO)_5CrC(OCH_3)CH_3$ (see Figure 3a) is very similar to that of $(CO)_6Cr$. There are, however, two significant differences. The first band is shifted to lower IP and has a distinct shoulder in the spectrum of the carbene molecule. Furthermore, there is a new band which lies between the metal band and the onset of the broad band. These changes are easily understood when the MO diagram for $(CO)_5CrC(OCH_3)CH_3$ (Figure 4) is compared to the MO diagram for $(CO)_6Cr$.

The levels labeled Cr 3d and Cr 4s in Figure 4 are, once again, the Fock matrix diagonal elements for the chromium atom in the complex. The CO 5σ and CO 2π levels are the free carbonyl MO's, and the $\ddot{C}(OCH_3)CH_3$ π^*, $\ddot{C}(OCH_3)CH_3$ σ^*, $\ddot{C}(OCH_3)CH_3$ σ, and $\ddot{C}(OCH_3)CH_3$ π levels are the free carbene MO's. The MO's of the complex, $(CO)_5CrC(OCH_3)CH_3$, are shown in the center of the diagram and are labeled by their principal contributors.

The differences between the MO diagrams of $(CO)_6Cr$ and $(CO)_5CrC(OCH_3)CH_3$ are more readily understood after examination of the geometry of the carbene complex (see Figure 5). The carbene ligand was placed in the YZ plane, while the carbonyls cis to it were placed between the X and Y axes. The chromium orbitals which would transform as t_{2g}, if the molecule had O_h symmetry, are the $3d_{xz}$, $3d_{yz}$, and $3d_{x^2-y^2}$ AO's. Since the carbene molecule has C_s symmetry, the MO's

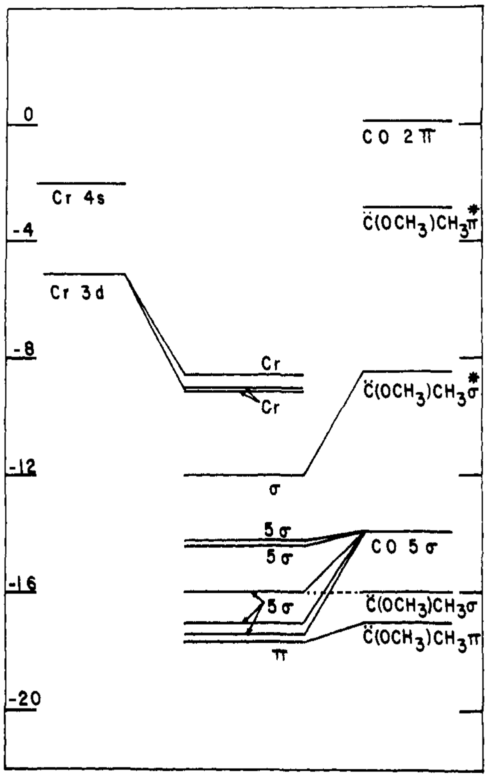


Figure 4. Abbreviated MO diagram for $(CO)_5CrC(OCH_3)CH_3$.

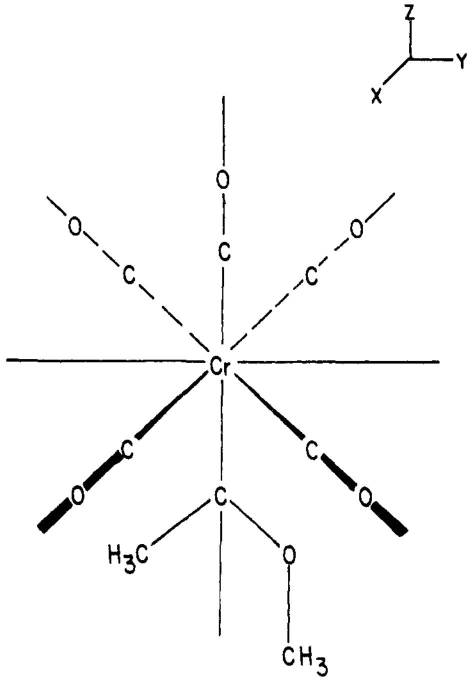


Figure 5. Configuration of $(CO)_5CrC(OCH_3)CH_3$ used in the MO calculation.

to which these orbitals contribute heavily are not degenerate.

The carbene ligand can interact with a metal in much the same way as CO does.[2] The carbene σ^* orbital, with its main component being an sp^2 hybridized orbital localized on the carbene carbon, donates charge to the metal, just as the CO 5σ level does (although the 5σ orbital contains an antibonding interaction between carbon and oxygen, it, too, is principally carbon in character).[27] Similarly, the carbene π^* level (an empty orbital which is also mainly carbon in character) can accept charge from the metal, just as the CO 2π levels do.

Although the π^* level of the carbene is in a better (energetic) position for interacting with the metal d orbitals than the 2π level of the carbonyl, structural studies indicate that carbene ligands, $\ddot{C}(X)Y$, are poorer back acceptors than CO.[13-16] There are several reasons for this. The carbene ligand has only one low-lying empty orbital, while the carbonyl ligand's 2π level is doubly degenerate. Thus, charge accepted by the carbene ligand experiences greater electron-electron repulsion than charge accepted by the carbonyl ligand. Furthermore, the doubly degenerate 2π levels have more opportunity for interaction with the metal than the single π^* orbital. Not only are there twice as many virtual π orbitals per ligand, but the carbonyl's 2π MO's are directed along a straight line connecting chromium, carbon, and oxygen, while the carbene's π^* orbital lies along a bond that makes a 120° angle with the chromium-carbon bond. Hence, M-CO 2π interaction is more favorable for electron transfer than M-C(X)Y π^* interaction.

Replacing CO by the carbene ligand, $\ddot{C}(OCH_3)CH_3$, affects the electronic structure of the complex in several ways. Since the carbene is a poorer backbonder than the carbonyl, chromium's 3d orbitals are destabilized and the degeneracy of the t_{2g} MO's is lifted. For all of the carbene complexes, the MO corresponding to the Cr $3d_{yz}$ orbital, which interacts mainly with the CO $2\pi_y$ MO of the ligand trans to the carbene, is predicted to be the least stable of the three metal MO's. The Cr $3d_{x^2-y^2}$ AO interacts strongly with the cis carbonyls only, while the Cr $3d_{xz}$ AO interacts with the carbene π^* MO and all of the carbonyls. In the methoxycarbenes, the MO corresponding to the Cr $3d_{x^2-y^2}$ orbital is less stable than that corresponding to the Cr $3d_{xz}$ orbital. In the aminocarbenes, the order of these MO's is reversed.

The average of the eigenvalues for the three MO's localized on chromium is less negative than the t_{2g} eigenvalue of $(CO)_6Cr$. Thus, two of the major differences between the electronic structure of $(CO)_6Cr$ and $(CO)_5CrC(OCH_3)CH_3$ lie in the relative stability and degeneracy of the metal MO's. Another major difference is the appearance of a level between the metal and carbonyl levels in the MO diagram of $(CO)_5CrC(OCH_3)CH_3$. This level, at 12.1 eV, results from the interaction of the metal and the $\ddot{C}(OCH_3)CH_3$ σ^* orbital.

The photoelectron spectrum of $(CO)_5CrC(OCH_3)CH_3$ is readily analyzed with the aid of the MO diagram. The first band may be said to result from ionizations of orbitals localized on chromium. Koopmans' theorem predicts that the IP's of these orbitals should be 8.20, 8.95, and 9.08 eV, respectively. If these predictions are fairly accurate, the latter two peaks would probably not be separable. Indeed, the first band in the photoelectron spectrum can be curve fit with two Gaussian peaks, with a relative intensity ratio of 1 to 2. The maxima of these Gaussians occur at 7.47 and 7.89 eV. The difference between the Koopmans' theorem prediction and the observed IP for the first orbital is (8.20 − 7.47 =) 0.73 eV. The difference between the average of the Koopmans' theorem predictions for the second and third peaks and the observed IP is (9.02 − 7.89 =) 1.13 eV. The values 0.73 and 1.13 eV will be used as correction factors in making predictions of the positions of the metal peaks in the photoelectron spectra of the remaining carbene compounds.

The peak lying between the metal and the carbonyl bands may be assigned to ionization of an orbital which is essentially the chromium-carbene σ bond. The principal contributor to this MO is the $\ddot{C}(OCH_3)CH_3$ σ^* level. Koopman's theorem gives a predicted IP of 12.09 eV. The observed IP is 9.89 eV, yielding a correction factor of 2.20 eV for the corresponding peaks in the spectra of the other carbene complexes. (All of the correction factors used are listed in Table VI.)

The degree of interaction between the chromium and carbene ligand, $\ddot{C}(X)Y$, is strongly dependent on the identity of the groups, X and Y. As X and Y are varied, the positions of the peaks corresponding to the metal orbitals and the metal–carbon bond can change considerably. In the discussion to follow, these changes, and their causes, will be considered. For the sake of convenience, the compounds will be divided into three subsets: (1) Y = CH_3, (2) Y = C_4H_3O, and (3) Y = C_6H_5.

Y = Methyl. In addition to $(CO)_5CrC(OCH_3)CH_3$, this subset includes the molecules $(CO)_5CrC(SCH_3)CH_3$, $(CO)_5CrC(N(CH_3)_2)CH_3$, and $(CO)_5CrC(NH_2)CH_3$. The photoelectron spectra for these molecules are shown in Figure 3.

The photoelectron spectrum of $(CO)_5CrC(SCH_3)CH_3$, Figure 3b, has three bands before the onset of carbonyl ionization at ~12.5 eV. The first band, thought to correspond to ionization of orbitals localized on chromium, may be curve fit with three Gaussian peaks. The maxima of these peaks occur at 7.35, 7.59, and 7.79 eV, respectively. The next band may be curve fit with two Gaussians, having maxima at 9.91 and 10.23 eV, respectively. The last band contains a single peak, with maximum at 11.23 eV.

The MO calculation on $(CO)_5CrC(SCH_3)CH_3$ places the chromium–carbene carbon σ bond at 12.10 eV. Applying the correction factor of 2.20 eV to this figure gives the predicted IP: 9.90 eV. This is in excellent agreement with the maximum of the first peak in the second band of the photoelectron spectrum. (A listing of the calculated eigenvalues and predicted and observed IP's for all compounds studied is given in Table VII.)

The remaining peak of the second band is assigned to ionization from a level in which the principal contributor is the C–S π bond of the carbene ligand. The third band is assigned to ionization from a level containing a substantial contribution from the sulfur lone pair. Bands arising from analogous levels in $(CO)_5CrC(OCH_3)CH_3$ are obscured by the onset of carbonyl ionization (see Figure 3a). However, the AO's of sulfur are less stable than those of oxygen, making the bands clearly visible in the spectrum of $(CO)_5CrC(SCH_3)CH_3$. The calculated eigenvalue for the MO corresponding to this third band of the photoelectron spectrum is -13.57 eV; the IP is 11.23 eV, a difference of 2.34 eV. It is gratifying that this correction is close to the correction factor used for predicting the IP of the orbital localized on the chromium–carbene carbon bond because, in $(CO)_5CrC(SCH_3)CH_3$, there is substantial mixing of the carbon and sulfur lone pairs (see Figure 6).

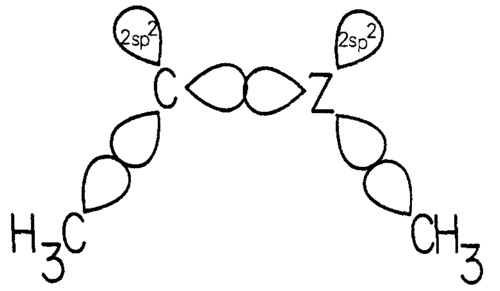


Figure 6. Interaction of lone pairs in $\ddot{C}(ZCH_3)CH_3$ (Z = O, S).

Like the spectrum of $(CO)_5CrC(SCH_3)CH_3$, the photoelectron spectrum of $(CO)_5CrC(N(CH_3)_2)CH_3$ has three bands appearing before the onset of carbonyl ionization (see Figure 3c). Once again, the first band is thought to correspond to metal ionizations and may be curve fit with three peaks. These peaks have maxima at 7.12, 7.35, and 7.61 eV. The remaining bands each contain a single peak, with maxima at 9.72 and 10.67 eV, respectively.

The combination of calculated eigenvalue and correction factor for the MO localized on the chromium–carbene carbon bond gives a predicted IP of 9.66 eV, in excellent agreement with the maximum of the second band. The third band is assigned to ionization of electrons from the C–N π bond of the carbene ligand. The eigenvalue of the appropriate vector is -16.09 eV, giving a correction factor of 5.42 eV for orbitals of this type.

The photoelectron spectrum of $(CO)_5CrC(NH_2)CH_3$ contains only two bands with IP's lower than those of the carbonyl levels (see Figure 3d). The first band, containing peaks with maxima at 7.45 and 7.80 eV, may be assigned to ionization of MO's localized on chromium. The other band contains only one peak, with maximum at 10.31 eV. According to the calculations, the peak corresponds to removal of an electron from the chromium–carbene carbon bond.

Like the C–O π bond of $(CO)_5CrC(OCH_3)CH_3$, the C–N π bond of $(CO)_5CrC(NH_2)CH_3$ is too stable for a band corresponding to its ionization to be visible in the spectrum. Applying the correction factor of 5.42 eV to the appropriate eigenvalue of $(CO)_5CrC(NH_2)CH_3$ gives a predicted IP of 12.66 eV, which is near the value of the onset of carbonyl ionization.

Examination of the MO calculations is necessary if one is to understand why the C–N π bond is 2 eV less stable in $(CO)_5CrC(N(CH_3)_2)CH_3$ than in $(CO)_5CrC(NH_2)CH_3$. The explanation lies with the structure of the ligands, which determines the degree to which the π orbitals may interact with the other orbitals of the carbene moiety. Although the methyl carbons of $\ddot{C}(N(CH_3)_2)CH_3$ lie in the carbene plane, the C–H bonds can interact with the C–N bond, destabilizing it. There is no possibility of such interaction occurring between the π bond and the amino hydrogens, which, like the methyl carbons, lie in a plane perpendicular to the π orbitals.

Y = Furyl. An abbreviated MO diagram for $(CO)_5CrC(OCH_3)C_4H_3O$ is given in Figure 7. Levels labeled Fu π and Fu σ are located primarily on the furyl ring in both the complex and the free ligand.

The three least stable occupied orbitals in $(CO)_5CrC(OCH_3)C_4H_3O$ are localized on chromium. Combining their eigenvalues and the appropriate correction factors yields 7.37 and 7.75 eV as the predicted IP's for MO's. These predictions are in excellent agreement with the observed IP's, 7.37 and 7.68 eV, obtained by curve fitting the first band in the photoelectron spectrum (Figure 8a).

Following the MO's localized on chromium, there is an orbital, σ^*, in which the carbene carbon lone pair is the principal contributor; this MO is the chromium–carbene carbon σ bond. Its predicted IP is 9.71 eV.

The MO diagram also shows a number of orbitals with eigenvalues between 13 and 15 eV. Some of them are localized on the carbonyl groups, while others are localized on the furyl ring. In order to predict whether or not peaks corresponding to these (furyl) orbitals will be visible in the photoelectron spectrum of the molecule, we need correction factors for them. Correction factors were obtained by comparing the results of a calculation on C_4H_4O and its published photoelectron spectrum[28] (see Table II). Combining the MO results with the correction factors gives 12.30 eV as the predicted IP for a level localized on the furyl σ framework. This peak is likely to be obscured by peaks arising from ionizations of MO's localized on the carbonyl groups. On the other hand, two peaks corresponding to MO's localized on the furyl π system should be visible in the spectrum, since their predicted IP's are 9.60 and 10.94 eV. Thus, three peaks, arising from ionizations of the Fu π MO's and the σ^* MO, are expected to appear between 9 and 11 eV in the photoelectron spectrum.

The spectrum of $(CO)_5CrC(OCH_3)C_4H_3O$ (Figure 8a) does, indeed, contain three bands lying between the metal and the carbonyl bands. Each contains only one peak. The maxima

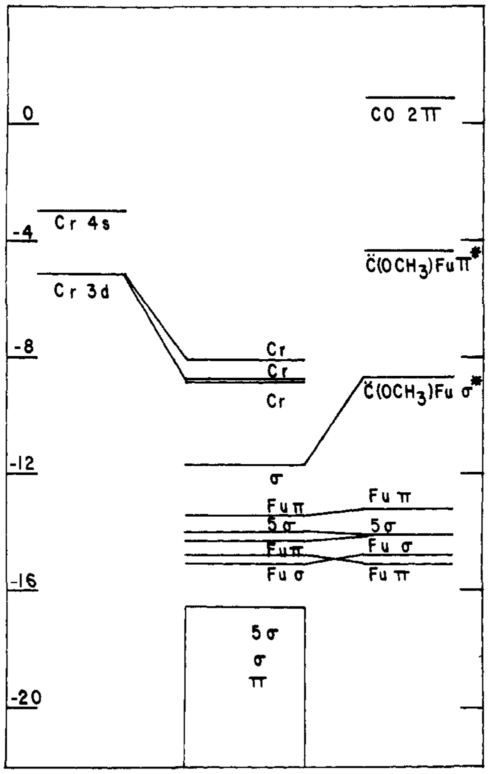


Figure 7. Abbreviated MO diagram for $(CO)_5CrC(OCH_3)C_4H_3O$.

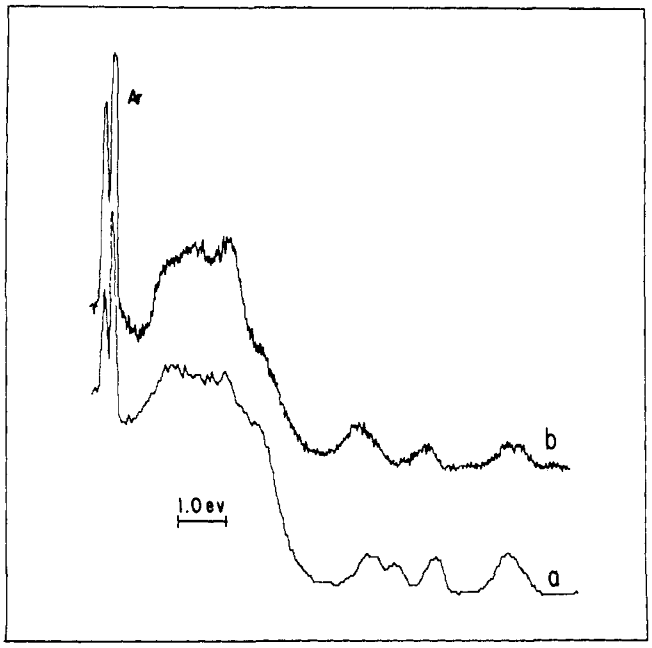


Figure 8. Photoelectron spectrum of: (a) $(CO)_5CrC(OCH_3)C_4H_3O$; (b) $(CO)_5CrC(NH_2)C_4H_3O$.

of these peaks occur at 9.14, 9.92, and 10.51 eV, respectively. Thus, the first and third of these peaks may be assigned to ionizations of the furyl π orbitals. The second peak, which overlaps somewhat with the third, may be assigned to ionization of the σ^* MO.

The photoelectron spectrum of $(CO)_5CrC(NH_2)C_4H_3O$ (see Figure 8b) contains three bands which appear before the onset of carbonyl ionization. According to the MO calculations, the lowest energy band contains peaks corresponding to the metal MO's. The maxima of these peaks occur at 7.22 and 7.52 eV.

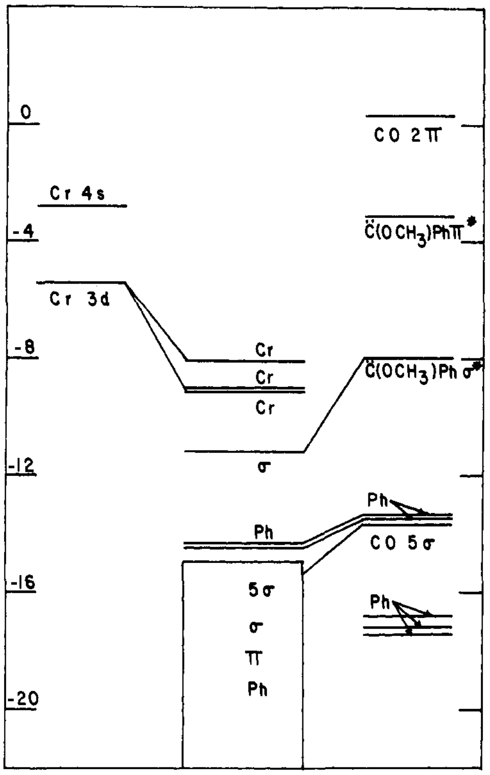


Figure 9. Abbreviated MO diagram for $(CO)_5CrC(OCH_3)C_6H_5$.

Table II. Correction Factors for Orbitals of C_4H_4O

Orbital	Calcd IP,[a] eV	Obsd IP,[b] eV	Δ, eV
$\pi(1a_2)$	12.53	8.90	3.63
$\pi(2b_1)$	14.04	10.32	3.72
$\sigma(9a_1)$	15.67	13.06	2.61

[a] Using Koopmans' theorem, $IP_{calcd} = -\epsilon$. [b] Reference 28.

The second band, containing only one peak, may be assigned to ionization of an MO which is localized on the furyl π system. The IP of this orbital is 9.21 eV.

The third band may be curve fit with two peaks. The peak occurring at higher energy may be assigned to ionization of another furyl-localized MO (IP = 10.68 eV). The remaining peak may be associated with the chromium-carbene carbon σ bond. Its maximum occurs at 10.30 eV.

For $(CO)_5CrC(NH_2)C_4H_3O$ and $(CO)_5CrC(OCH_3)C_4H_3O$, the largest discrepancy between predicted and observed IP is less than 0.5 e (see Table VII). The largest of these small errors in the predictions occurs for peaks localized on the furyl ring in the furyl (methoxy)carbene complex. This is not surprising since the correction factor was calculated for C_4H_4O and replacing one proton by a carbene moiety represents a significant perturbation on the system. The perturbation is less strongly felt, and the discrepancy between predicted and observed IP is smaller in $(CO)_5CrC(NH_2)C_4H_3O$ where the chromium to carbene carbon bond is longer.

Y = Phenyl. An abbreviated MO diagram for $(CO)_5CrC(OCH_3)C_6H_5$ is given in Figure 9. Levels labeled Ph are located primarily on the phenyl ring in both the complex and the free ligand. Note that these orbitals are not given a symmetry designation. Since the plane of the phenyl ring is perpendicular to the symmetry plane of the molecule, the ring's σ and π orbitals are mixed.

The structure of the MO diagram of $(CO)_5CrC(OCH_3)C_6H_5$ is very similar to that of $(CO)_5CrC(OCH_3)$-

Table III. Correction Factors for Orbitals of C_6H_6

Orbital	Calcd IP,[a] eV	Obsd IP,[b] eV	Δ, eV
$\pi(1e_{1g})$	14.47	9.25	5.22
$\sigma(3e_{2g})$	17.95	11.65	6.30

[a] Using Koopmans' theorem, $IP_{calcd} = -\epsilon$. [b] Reference 29.

C_4H_3O. The three highest occupied MO's are localized on chromium. The next MO constitutes the chromium-carbene bond and contains a large contribution from the carbene carbon lone pair. MO's localized on the phenyl ring are found in close proximity to MO's which have the CO 5σ, $\ddot{C}(OCH_3)C_6H_5$ π, and $\ddot{C}(OCH_3)C_6H_5$ σ orbitals as their main contributors.

Combining the MO results with appropriate correction factors yields 7.54 and 8.00 eV for the metal levels' predicted IP's and 9.08 eV for the σ^* orbital's predicted IP. Correction factors for the MO's localized on the phenyl ring were obtained by comparing a calculation on C_6H_6 with the known photoelectron spectrum of that compound[29] (see Table III). Since the degeneracy of the e-type orbitals of benzene is lifted in the carbene complexes, the correction factor for the highest occupied MO(HOMO) of benzene is used to predict the IP's of the first two phenyl-localized MO's. For $(CO)_5CrC(OCH_3)C_6H_5$, these predicted IP's are 9.14 and 9.31 eV, which should be well below the first carbonyl IP. Thus, the spectrum of $(CO)_5CrC(OCH_3)C_6H_5$ may have only two bands appearing before the broad band corresponding to carbonyl ionizations. One band would contain two peaks, in relative intensity ratio of 1:2, and would lie at an energy of 7-8 eV. The other would contain three closely spaced peaks and would lie at an energy slightly above 9 eV.

This is, in fact, precisely what is observed (see Figure 10a). The first band in the photoelectron spectrum may be curve fit with two Gaussian peaks, having maxima at 7.39 and 7.78 eV, and corresponding to the removal of an electron from a metal level. The second band may be curve fit with three Gaussian peaks, having maxima at 9.26, 9.66, and 10.06 eV. The first of these peaks corresponds to removal of an electron from the σ^* MO while the other two arise from phenyl ionizations. The band is somewhat broader than expected from the calculations, which underestimate the splitting of the benzene π levels.

The photoelectron spectrum of $(CO)_5CrC(NH_2)C_6H_5$ (see Figure 10b) contains three bands which appear before the onset of carbonyl ionization. According to the calculations, the first corresponds to the MO's localized on chromium. It may be curve fit with three Gaussians, having maxima at 7.25, 7.52, and 7.73 eV.

The second band may also be curve fit with three Gaussians, having maxima at 9.23, 9.52, and 9.80 eV, respectively. The first two values compare extremely well with the IP's, 9.37 and 9.62 eV, obtained by combining the appropriate correction factor with the eigenvalues for the phenyl MO's. The last value, 9.80 eV, is very close to the IP predicted for the σ^* MO (9.95 eV). Since the peak corresponding to ionization of the σ^* MO generally is more stable in the aminocarbenes than in the methoxycarbenes, it is not surprising that it should now be at higher IP than the phenyl peaks.

The remaining band in the spectrum contains only one peak, with its maximum at 10.50 eV. This peak may be assigned to ionization from an MO localized on the phenyl ring. However, in this case, there is a larger discrepancy between the predicted and observed IP's (1.12 eV) than there had been for the other peaks. This discrepancy may be attributed to the considerable degree of mixing between the more stable σ and π phenyl orbitals that occurs in the complex.

The most complicated photoelectron spectrum obtained in this study is that of $(CO)_5CrC(N(CH_3)_2)C_6H_5$ (see Figure 10c). However, our method, combining MO calculations and correction factors for a series of compounds, makes assignment of the spectrum fairly straightforward.

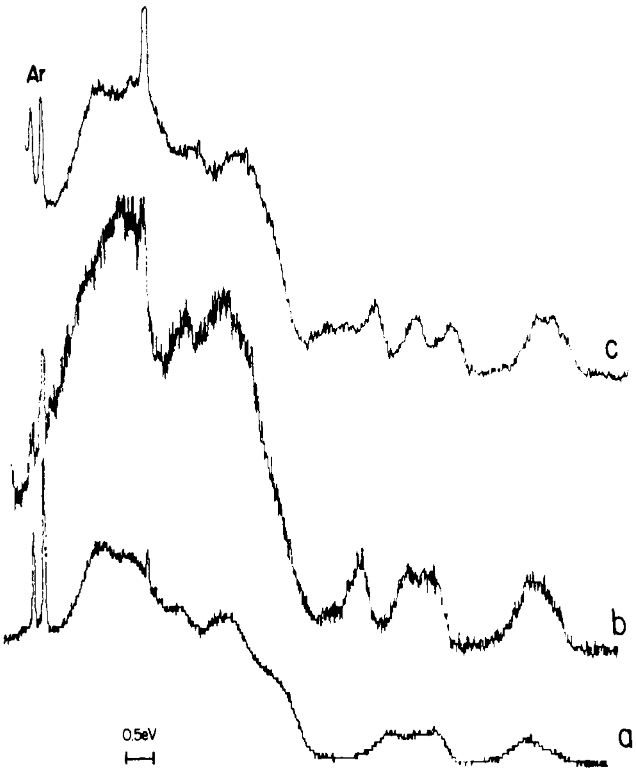


Figure 10. Photoelectron spectrum of: (a) $(CO)_5CrC(OCH_3)C_6H_5$; (b) $(CO)_5CrC(NH_2)C_6H_5$; (c) $(CO)_5CrC(N(CH_3)_2)C_6H_5$.

The first band may be curve fit with three asymmetric Gaussians, having their maxima at 7.02, 7.26, and 7.54 eV. These peaks are thought to correspond to removal of an electron from an MO localized on the chromium. The remaining bands in the spectrum should contain peaks corresponding to the chromium-carbene carbon σ bond, the C-N π bond, and orbitals localized on the phenyl ring.

Combining the MO results and the appropriate correction factor gives 9.54 eV as the predicted IP for the σ^* MO. The third band in the spectrum contains only one peak, with maximum at 9.49 eV. Hence, this band is assigned to ionization of the σ^* MO.

The MO calculations indicate that the $1e_{1g}(\pi)$ orbitals of benzene remain nearly degenerate in $(CO)_5CrC(N(CH_3)_2)C_6H_5$. The IP's predicted for the two MO's to which the phenyl $1e_{1g}(\pi)$ orbitals contribute heavily differ by only 0.02 eV (the predicted IP's are 9.21 and 9.23 eV). Hence, it is likely that these two levels will correlate with a single peak in the photoelectron spectrum. The second band of the photoelectron spectrum contains only one peak (maximum at 8.87 eV), but it has nearly twice the intensity of the peak with maximum at 9.49 eV. The fact that one peak is twice as intense as another does not necessarily indicate that the first peak arises from a doubly degenerate level, since the cross section for ionization is not the same for orbitals of different types.[30] However, analysis of the photoelectron spectra of the carbene complexes has shown that a peak arising from ionization of the σ^* MO and a peak arising from ionization of an MO localized on a phenyl ring generally have roughly the same intensities. Therefore, the peak with maximum at 8.87 eV may be assigned to phenyl ionizations.

The region of the spectrum between 10 and 11.5 eV remains to be accounted for. It has been curve fit with three Gaussian

Table IV. π Acceptance by $\ddot{C}(X)Y$

X	Y	π acceptance, e^-	Av metal IP in $(CO)_5CrC(X)Y$, eV
OCH_3	CH_3	0.36	7.75
NH_2	CH_3	0.22	7.68
$N(CH_3)_2$	CH_3	0.18	7.38
OCH_3	C_4H_3O	0.37	7.52
NH_2	C_4H_3O	0.21	7.42
OCH_3	C_6H_5	0.35	7.65
NH_2	C_6H_5	0.20	7.50
$N(CH_3)_2$	C_6H_5	0.17	7.27
SCH_3	CH_3	0.38	7.58

Table V. Mulliken Gross Atomic Charges for the Carbene Carbon in $\ddot{C}(X)Y$[a]

X	Y	Q
OCH_3	CH_3	+0.04
SCH_3	CH_3	−0.17
$N(CH_3)_2$	CH_3	−0.20
NH_2	CH_3	−0.11
OCH_3	C_4H_3O	−0.07
NH_2	C_4H_3O	−0.23
OCH_3	C_6H_5	+0.03
NH_2	C_6H_5	−0.12
$N(CH_3)_2$	C_6H_5	−0.21

[a] The charge on a carbonyl carbon is typically in the range of +0.05 to +0.08.

Table VI. Correction Factors Used in Assignment of the Photoelectron Spectra of $(CO)_5CrC(X)Y$

Molecule	Orbital	IP, eV Calcd[a]	 Obsd	Δ, eV
$(CO)_5CrC(OCH_3)CH_3$	Cr $3d_{yz}$[b]	8.20	7.47	0.73
$(CO)_5CrC(OCH_3)CH_3$	Cr $3d_{x^2-y^2}$[b]	8.95	7.89	1.13
$(CO)_5CrC(OCH_3)CH_3$	Cr $3d_{xz}$[b]	9.08		
$(CO)_5CrC(OCH_3)CH_3$	σ^*	12.09	9.89	2.20
$(CO)_5CrC(N(CH_3)_2)CH_3$	C–N π	16.09	10.67	5.42
C_4H_4O	$\pi(1a_2)$	12.53	8.90	3.63
C_4H_4O	$\pi(2b_1)$	14.04	10.32	3.72
C_6H_6	$\pi(1e_{1g})$	14.47	9.25	5.22
C_6H_6	$\sigma(3e_{2g})$	17.95	11.65	6.30

[a] Using Koopmans' theorem, IP = $-\epsilon$. [b] The carbene ligand lies in the YZ plane. The cis carbonyls lie between the X and Y axes; as a result, the chromium orbitals which would transform as t_{2g} in octahedral symmetry are the $3d_{yz}$, $3d_{x^2-y^2}$, and $3d_{xz}$ orbitals.

peaks, having maxima at 10.16, 10.58, and 10.96 eV. This area of the spectrum should contain a peak arising from ionization of the C–N π bond (predicted IP = 10.56 eV). In addition, it contains two peaks arising from MO's to which the phenyl $3e_{2g}(\sigma)$ orbitals contribute heavily.

The MO calculation gives −17.71 and −18.16 eV as the eigenvalues for these levels. Application of a correction factor of 6.30 eV yields 11.41 and 11.86 eV as the predicted IP's. These predicted IP's could be too high, since this was the case for the predicted IP's for the first set of phenyl peaks. In addition, the predicted IP for the analogous phenyl σ orbital in $(CO)_5CrC(NH_2)C_6H_5$ was also too high. Hence, it is reasonable to assign the peak at 10.58 eV to the C–N π ionization and the peaks at 10.16 and 10.96 eV to phenyl ionization.

For peaks other than those associated with the MO's localized on the phenyl ring, the discrepancy between predicted and observed IP is no more than 0.25 eV in these complexes. For peaks associated with phenyl ionizations, the discrepancy varies, being very small for the low IP phenyl levels in $(CO)_5CrC(NH_2)C_6H_5$ and quite large for the higher IP phenyl levels in $(CO)_5CrC(NH_2)C_6H_5$ and $(CO)_5CrC(N(CH_3)_2)C_6H_5$. This is not totally unexpected. The phenyl $1e_{1g}(\pi)$ orbitals are energetically isolated from the other orbitals of the ring. The major discrepancy between their predicted and observed IP's comes from the perturbation introduced by replacing a hydrogen atom with a pentacarbonylchromium carbene moiety. This perturbation is somewhat greater in the methoxycarbene complex than in the aminocarbene complexes. The phenyl $3e_{2g}(\sigma)$ orbitals are energetically close to a number of other orbitals with which they mix strongly. Hence, the correction factor obtained from the spectrum of benzene may not be the most appropriate for these levels.

General Trends. The first band in the photoelectron spectrum of each of the carbene complexes arises from removal of electrons from orbitals localized on chromium. In each complex, the metal levels are nondegenerate. Accordingly, the metal band in the photoelectron spectrum often shows dictinct shoulders and can always be curve fit with two or three Gaussian peaks. The maxima corresponding to the first IP's are in excellent agreement with the first IP's obtained by mass spectral analysis of $(CO)_5CrC(OCH_3)CH_3$, $(CO)_5CrC(NH_2)CH_3$, $(CO)_5CrC(N(CH_3)_2)CH_3$, and $(CO)_5CrC(SC_6H_5)CH_3$.[31]

Although the splitting pattern of the metal band is not always predicted accurately, the predicted average IP is never more than 0.35 eV away from the average of the observed IP's. For a given Y, the correct trend for the variation in the average metal IP is predicted as X is varied from OCH_3 to NH_2 to $N(CH_3)_2$. This is gratifying since a major factor in determining the stability of the metal MO's is the degree of π acceptance by the ligand and the nature of X is more important than the nature of Y in determining the ability of $\ddot{C}(X)Y$ to act as a π acceptor (see Table IV). Since all of the carbene ligands are poorer π acceptors than CO, the average metal IP in each of the carbene complexes is lower than the IP of the t_{2g} level of chromium hexacarbonyl.

The largest discrepancies between observed and predicted IP occur for peaks associated with MO's localized on the phenyl or furyl rings. Agreement between the predicted and observed peak positions is generally better for the furyl levels than for the phenyl levels. Since the furyl plane coincides with the symmetry plane of the carbene complex, the σ–π separation of its MO's is not disrupted. On the other hand, the σ and π MO's of the phenyl ring are mixed, because the phenyl ring is perpendicular to the carbene plane. Hence, the furyl MO's bear more resemblance to furan MO's than the phenyl MO's do to those of benzene.

The least accurate predictions are made for those MO's of $(CO)_5CrC(N(CH_3)_2)C_6H_5$ which are related to the benzene $3e_{2g}$ level. In the carbene complex, these MO's mix strongly with other MO's localized on the ring. Yet, the discrepancy between predicted and observd IP remains reasonable (on the order of 1 eV), underscoring the usefulness of our method.

The IP for the peak corresponding to the σ^* MO varies over a range of 1 eV, from 9.26 eV in $(CO)_5CrC(OCH_3)C_6H_5$ to 10.30 eV in $(CO)_5CrC(NH_2)CH_3$ and $(CO)_5CrC(NH_2)C_4H_3O$. It is gratifying that, despite the number of factors which influence the position of the σ^* peak, its observed IP is, at most, 0.2 eV different from the predicted IP. When either X or Y is held constant as the nature of the other group is varied, the correct trend in the position of this peak is generally predicted.

Both X and Y are important in determining the IP of the σ^*

Table VII. Predicted and Observed Ionization Potentials (eV) for $(CO)_5CrC(X)Y$[a]

X = SCH_3				Y = CH_3 X = $N(CH_3)_2$				X = NH_2			
Orbital	Calcd	Pred	Obsd	Orbital	Calcd	Pred	Obsd	Orbital	Calcd	Pred	Obsd
Cr $3d_{xy}$	8.18	7.45	7.35	Cr $3d_{yz}$	7.79	7.06	7.12	Cr $3d_{yz}$	8.03	7.30	7.45
Cr $3d_{x^2-y^2}$	8.93	7.80	7.59	Cr $3d_{xz}$	8.18	7.05	7.35	Cr $3d_{xz}$	8.51		
										7.52	7.80
Cr $3d_{xz}$	9.04	7.91	7.79	Cr $3d_{x^2-y^2}$	8.60	7.47	7.61	Cr $3d_{x^2-y^2}$	8.79		
σ^*	12.10	9.90	9.91	σ^*	11.86	9.66	9.72	σ^*	12.41	10.21	10.31
σ	13.57		11.23	C-N π	16.09		10.67	C-N π	18.08	12.66	*b*
C-S π	13.76		10.23								

X = OCH_3				Y = C_4H_3O X = NH_2			
Orbital	Calcd	Pred	Obsd	Orbital	Calcd	Pred	Obsd
Cr $3d_{xy}$	8.10	7.37	7.37	Cr $3d_{yz}$	7.96	7.23	7.22
Cr $3d_{xz}$	8.86			Cr $3d_{xz}$	8.39		
		7.75	7.68			7.43	7.52
Cr $3d_{x^2-y^2}$	8.90			Cr $3d_{x^2-y^2}$	8.73		
σ^*	11.91	9.71	9.92	σ^*	12.44	10.24	10.30
Fu π	13.23	9.60	9.14	Fu π	12.96	9.33	9.21
Fu π	14.66	10.94	10.51	Fu π	14.62	10.90	10.68

X = OCH_3				Y = C_6H_5 X = NH_2				X = $N(CH_3)_2$			
Orbital	Calcd	Pred	Obsd	Orbital	Calcd	Pred	Obsd	Orbital	Calcd	Pred	Obsd
Cr $3d_{xz}$	8.27	7.54	7.39	Cr $3d_{yz}$	8.12	7.39	7.25	Cr $3d_{yz}$	7.94	7.21	7.02
Cr $3d_{x^2-y^2}$	9.11			Cr $3d_{xz}$	8.60	7.47	7.52	Cr $3d_{xz}$	8.33	7.20	7.26
		8.00	7.78								
Cr $3d_{xz}$	9.15			Cr $3d_{x^2-y^2}$	8.89	7.76	7.73	Cr $3d_{x^2-y^2}$	8.75	7.62	7.54
σ^*	11.28	9.08	9.26	σ^*	12.15	9.95	9.80	σ^*	11.74	9.54	9.49
Ph	14.36	9.14	9.66	Ph	14.59	9.37	9.23	Ph	14.43	9.21	
											8.87
Ph	14.53	9.31	10.06	Ph	14.84	9.62	9.52	Ph	14.45	9.23	
Ph	17.90	11.30	*b*	C-N π	18.83	13.41	*b*	C-N π	15.98	10.56	10.58
Ph	18.22	11.92	*b*								
				Ph	17.92	11.62	10.50	Ph	17.71	11.41	10.16
				Ph	18.65	12.35	*b*	Ph	18.16	11.86	10.96

[a] The calculations indicate that there are a series of orbitals localized on the carbonyl ligands and having eigenvalues of ca. 14-15 eV. The onset of the photoelectron bands corresponding to the ionization of these closely spaced levels occurs between 11 and 12 eV. Since the eigenvalues do not change much from compound to compound, and since the structure of the carbonyl band in the spectrum is quite complex, no predictions or observations are given for the carbonyl peaks. [b] Peak obscured by the onset of the carbonyl band.

peak. When X = NH_2 or $N(CH_3)_2$, the σ^* eigenvector in $(CO)_5CrC(X)Y$ is 55-60% carbon, but when X = OCH_3 or SCH_3, the carbon contribution decreases to 35-40% and a contribution from the oxygen or sulfur lone pair appears in the eigenvector. Since the interaction between the lone pairs is antibonding in nature, the σ^* MO tends to be destabilized in the methoxy- and thiomethylcarbene complexes.

The contribution of the carbon lone pair to the σ^* MO is lowest for the phenylcarbenes and highest for the methylcarbenes. The carbon lone pair in the phenyl complexes donates charge to the phenyl ring, resulting in a decrease in the amount of donation to the metal. Hence, for a given X, the peak corresponding to the σ^* MO appears at lower IP in $(CO)_5CrC(X)C_6H_5$ than in $(CO)_5CrC(X)CH_3$ or $(CO)_5CrC(X)C_4H_3O$.

The IP of the peak corresponding to the σ^* MO is also lower when X = $N(CH_3)_2$ than when X = NH_2. In both cases, the percent composition of the σ^* level is the same. However, the carbene carbon is more negatively charged in the dimethylaminocarbene complexes, which destabilizes the σ^* MO (see Table V).

In compounds containing both carbonyl and carbene carbons, the carbene carbon is preferentially attacked by nucleophiles.[2,32] In addition, carbene carbons have highly deshielded ^{13}C NMR shifts.[33] These data have led many workers to conclude that carbene carbons are electron deficient centers, in contrast to the results reported here. We have previously attributed the reactivity of carbene carbons with nucleophiles to the nature of the LUMO in carbene complexes.[24] It is possible that energy considerations may also be important in explaining the ^{13}C NMR data.[34] Efforts to obtain a quantitative correlation between ^{13}C NMR chemical shifts and orbital transition energies are continuing in our laboratory.

Conclusion

The combination of nonparameterized MO calculations and appropriate correction factors has been shown to be a valuable aid in making assignments for the photoelectron spectra of closely related molecules. Although small shifts in IP may not be predicted correctly, major trends are forecast accurately. Because correction factors vary in magnitude, our method may succeed in predicting the structure of a photoelectron spectrum accurately in cases where simple application of Koopmans' theorem would fail.

In general, the observed IP's are within 0.5 eV of the IP's predicted by our method. Agreement is even better for orbitals in which the percent composition remains most constant throughout the series.

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Intermolecular and Intramolecular Cycloaddition Reactions of Azirines by Group 6 Metal Carbonyls and by Titanium Tetrachloride

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Abstract: Reaction of 2-arylazirines with an equimolar amount of a group 6 metal carbonyl [$M(CO)_6$, M = Cr, Mo, W] gives 2,5-diarylpyrazines and isomeric dihydropyrazines in good combined yields. Isoxazoles, pyrazoles, and pyrroles can be synthesized in high yields, and under very mild conditions, by intramolecular cycloaddition of 3-phenyl-2-substituted-2*H*-azirines with molybdenum hexacarbonyl. These reactions occur via carbon–nitrogen bond cleavage of the azirine ring. Pyrazines, pyridazines, α-chloro ketones, and monoketones were formed in low yield by titanium tetrachloride induced cleavage of the azirine ring.

Transition metal carbonyls can effect a number of useful reactions in organic chemistry.[1] Two particularly elegant transformations are the cyclocoupling of α,α'-dibromo ketones with olefins or dienes and diiron enneacarbonyl,[2] and the cleavage of strained ring compounds by di-μ-chloro-tetracarbonyldirhodium(I) [e.g., quadricyclane].[3]

Azirines have been shown to undergo carbon–nitrogen bond cleavage on thermolysis, while photolytic ring opening of these unsaturated heterocycles usually occurs via rupture of the carbon–carbon bond.[4] It is also known that metal carbonyls can effect photolytic-type reactions of organic substrates (e.g., santonin)[5] under nonphotolytic conditions. These findings raise the following questions: will metal carbonyls cleave the azirine ring in a synthetically useful manner; and does such an anticipated reaction take place by carbon–nitrogen or carbon–carbon bond cleavage of the azirine ring? This paper describes the reactions of group 6 metal carbonyls [$M(CO)_6$, M = Cr, Mo, W], principally molybdenum hexacarbonyl, with azirines.[6]

It was of interest to compare the group 6 metal carbonyl results with those obtained for an early transition metal, titanium. Therefore, the cleavage of azirines by titanium tetrachloride is also reported in this paper. This titanium compound is a good Lewis acid[7] and can chlorinate aromatics in the presence of pertrifluoroacetic acid,[8] although chlorination does not occur with $TiCl_4$ alone.

Results and Discussion

Treatment of 2-arylazirines (**1**, R = H, CH_3, OCH_3; R′ = H) with an equimolar quantity of group 6 metal carbonyls in tetrahydrofuran at room temperature, for 24 h, affords 2,5-diarylpyrazines (**2**) generally as the major product. Also formed in most instances were the isomeric 2,5-diaryl-3,6-dihydro- (**3**) and 2,5-diaryl-1,6-dihydropyrazines (**4**).[9] The combined yields for **2–4** are very good, and are listed in Table I.

All of the pyrazines, and several of the dihydropyrazines, are known compounds and were identified by comparison of