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APPROXIMATE MOLECULAR ORBITAL CALCULATIONS ON CARBENE LIGANDS AND COMPLEXES: THE ABILITY OF THE CARBENE LIGANDS TO ACT AS σ DONORS AND π ACCEPTORS

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Summary

Non-parameterized molecular orbital calculations have been performed on a series of carbene ligands, $\ddot{C}(X)Y$, and carbene complexes, $(CO)_5CrC(X)Y$. In accord with previously obtained experimental data, methoxycarbenes were found to be better π acceptors than aminocarbenes. All of the carbene ligands were found to accept less charge from the chromium than the carbonyl ligand. While the eigenvalues of the highest occupied and lowest unoccupied molecular orbitals were found to be important factors in determining the σ donating and π accepting abilities of the ligands, other factors (such as the spatial localizations and degeneracies of the orbitals) were also found to affect these abilities. An explanation is given for the absence of a significant trans influence in most carbene complexes.

It has long been known that the carbonyl ligand interacts with a metal in two ways: 1) by donating charge to the metal from its filled 5σ orbital, which is mainly carbon in character and 2) by accepting charge into its 2π orbitals, which are also principally carbon in character [1]. A carbene ligand, $\ddot{C}(X)Y$, should also be able to act as both a σ donor and a π acceptor in a transition metal complex [2]. In terms of a valence bond formalism, the atomic orbitals (AO's) of the central carbon can be considered to be sp^2 hybridized. Two of the three sp^2 hybrid orbitals are used in forming single bonds to each of the substituents, X and Y. The remaining sp^2 hybridized orbital is a "lone pair" orbital in the free ligand. It is the orbital from which the carbene carbon will donate charge to the metal in a complex.

In addition to the three hybridized sigma orbitals, the carbene carbon has an empty p orbital which is oriented perpendicular to the sp^2 plane. This orbital can accept charge from the metal in a complex.

The extent to which the carbene ligand will accept charge from, or donate charge to, the metal depends upon the nature of the groups, X and Y. On the basis of ir and nmr spectral studies, Darensbourg and Darensbourg concluded that alkoxycarbene ($X = -OR$) ligands were strong σ donors and strong π acceptors [3]. On the other hand, aminocarbene ($X = -NR_2$) ligands have been classed as poor π acceptors, on the basis of single crystal X-ray studies [4,5,6]. Photoelectron (pe) spectral studies on a series of pentacarbonylchromium carbene complexes have been interpreted as indicating that carbene ligands are less effective at removing charge from chromium than the carbonyl ligand [7]. A recent esca study of platinum and palladium carbene complexes has similarly been interpreted as indicating that carbene ligands of the type $\ddot{C}(NHR)_2$ are poor π acceptors [8].

A good deal of insight into the way a carbene ligand will interact with a metal can be gained by examination of the free ligand itself. A discussion of the electronic structures of the carbene ligands is given below. Following this discussion, the interactions between the carbene ligands and the pentacarbonylchromium moiety in the compounds $(CO)_5CrC(X)Y$, $X = -OCH_3$, $Y = -CH_3$, $-C_4H_3O$, $-C_6H_5$; $X = -NH_2$, $Y = -CH_3$, $-C_4H_3O$, $-C_6H_5$; $X = -N(CH_3)_2$, $Y = -CH_3$, $-C_6H_5$; $X = -SCH_3$, $Y = -CH_3$, will be described.

Experimental

The molecular orbital (MO) calculational method used has been described previously [9, 10]. The method is approximate, but non-parameterized, requiring as input only the coordinates for the atoms in the molecule, and atomic basis functions. The bond distances employed are listed in Table 1 and are in accord with the crystal structure data for $(CO)_5CrC(OCH_3)C_6H_5$ [11], $(CO)_4Cr(P(C_6H_5)_3)C(OCH_3)CH_3$ [12], $(CO)_5CrC(N(C_2H_5)_2)CH_3$ [13], and $(CO)_5CrC(SC_6H_5)CH_3$ [14]. Bond distances for the $-C_4H_3O$ and $-C_6H_5$ fragments were taken from the reported structures of C_4H_4O [15] and C_6H_6 [16]. 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 [17]. For the calculation on $(CO)_5CrC(OCH_3)C_6H_5$, the methyl group of the methoxy moiety was placed *trans* to the metal [11, 12]. For $(CO)_5CrC(N(CH_2)_2)Y$, the carbons of the dimethylamino moiety were taken to be coplanar with the rest of the carbene ligand, as were the hydrogens of $(CO)_5CrC(NH_2)Y$ [13]. The furyl ring in $(CO)_5CrC(X)C_4H_3O$ was oriented so that the oxygen of the furyl ring faced the X-group [17].

In order to facilitate the study of the relative σ donor/π acceptor strengths of the carbene ligands, several calculations were performed in which the chromium-carbene carbon distance was different from the values given in Table I. These changes, and the reasons for making them, are clearly marked in the text.

Clementi's double -ζ Slater type orbitals were used as the basis functions for carbon, oxygen, nitrogen and sulfur [18]. 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 [19]. 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 [20].

The 1s-3d atomic orbitals given by Richardson, et al. [21] 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 sigma overlap 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 $(CO)_5CrC(OCH_3)CH_3$ [22]. 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 sigma bonding, it was considered to be more consistent to choose orbital exponents on the basis of sigma overlap alone. For this series of molecules, all Cr-CO distances were set to 1.88Å, 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 $(CO)_5CrC(OCH_3)CH_3$ 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 the studies on the free ligands containing a furyl or phenyl ring, the MO's were transformed by eigenvectors obtained from calculations on $C_4H_3O^-$ or $C_6H_5^-$. In the studies on the pentacarbonylchromium carbene complexes, the carbonyl 3σ and 6σ MO's were deleted from the basis set. Such a deletion has been shown to speed the calculation without significantly altering the results [23].

Free Ligands

An abbreviated MO diagram for CO is given in Figure 1. The levels labelled C_{2s}, C_{2p} and O_{2p} are the (approximate) Fock matrix diagonal elements for those orbitals. Levels labelled with Greek letters are the MO's. The 1π and 2π orbitals arise from bonding and antibonding interactions of the carbon and oxygen pπ AO's. While the 1π orbitals are mainly oxygen in character, the 2π orbitals are mainly carbon in character. The 4σ and 5σ orbitals correspond roughly to lone pairs on oxygen and carbon, respectively. The carbon-oxygen bond and antibond, having eigenvalues of -42.2 and +126.6 eV, are not shown.

The abbreviated MO diagram for $C(OCH_3)CH_3$, also shown in Figure 1, contains several levels which are similar in localization and energy to the 1π, 4σ, 5σ and 2π orbitals of CO. The carbene π and π* orbitals are, like the carbonyl 1π and 2π

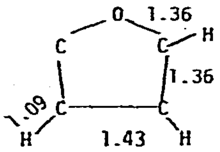
Table 1. Bond Distances Employed in Calculations on $(CO)_5CrC(X)Y$, (Å)

$(CO)_5Cr$ fragment			
Cr-C	1.88		
C-O	1.128		
CrC(X)Y fragment			
X = $-OCH_3$			
	Y = $-CH_3$	Y = $-C_4H_3O$	Y = $-C_6H_5$
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
$C-C_Y$	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 = $-C_4H_3O$	Y = $-C_6H_5$
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
$C-C_Y$	1.54	1.47	1.47
C-H	1.09	1.09	1.09

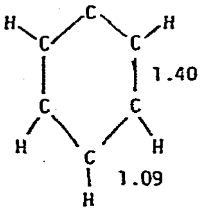
Table 1. continued

	X = -SCH$_3$ Y = -CH$_3$
Cr-C	2.02
C-SCH$_3$	1.72
S-CH$_3$	1.88
C-CH$_3$	1.54
C-H	1.09

-C$_4$H$_3$O



-C$_6$H$_5$



levels, localized on oxygen and carbon, respectively. However, there is an important difference between the two sets of orbitals. The pi-type orbitals of CO are doubly degenerate while the pi-type orbitals of $\ddot{C}(OCH_3)CH_3$ are nondegenerate.

Partly because of charge release by the methyl groups and partly because there is only one pi bond, the carbon-oxygen bond distance is longer in $\ddot{C}(OCH_3)CH_3$ than it is in CO [12,24]. As a result, the magnitude of the interactions between carbon and oxygen is smaller in $\ddot{C}(OCH_3)CH_3$ than in CO. One consequence of the decreased interaction is that there is a smaller splitting between the carbene π and π^* MO's than there is between the carbonyl 1π and 2π MO's (14.25 _vs_ 21.33 eV). In addition, the carbene π^* MO is more highly localized on carbon than a carbonyl 2π MO is. Conversely, the carbene π orbital contains less carbon character than a carbonyl 1π MO does.

The carbene σ and σ^* orbitals are, like the carbonyl 4σ and 5σ orbitals, essentially composed of oxygen and carbon lone pairs. The splitting betwen the carbene σ and σ^* levels is somewhat smaller than the splitting between the carbonyl 4σ and 5σ MO's (7.44 eV _vs._ 8.81 eV). Like the carbonyl 4σ and 5σ MO's, the carbene

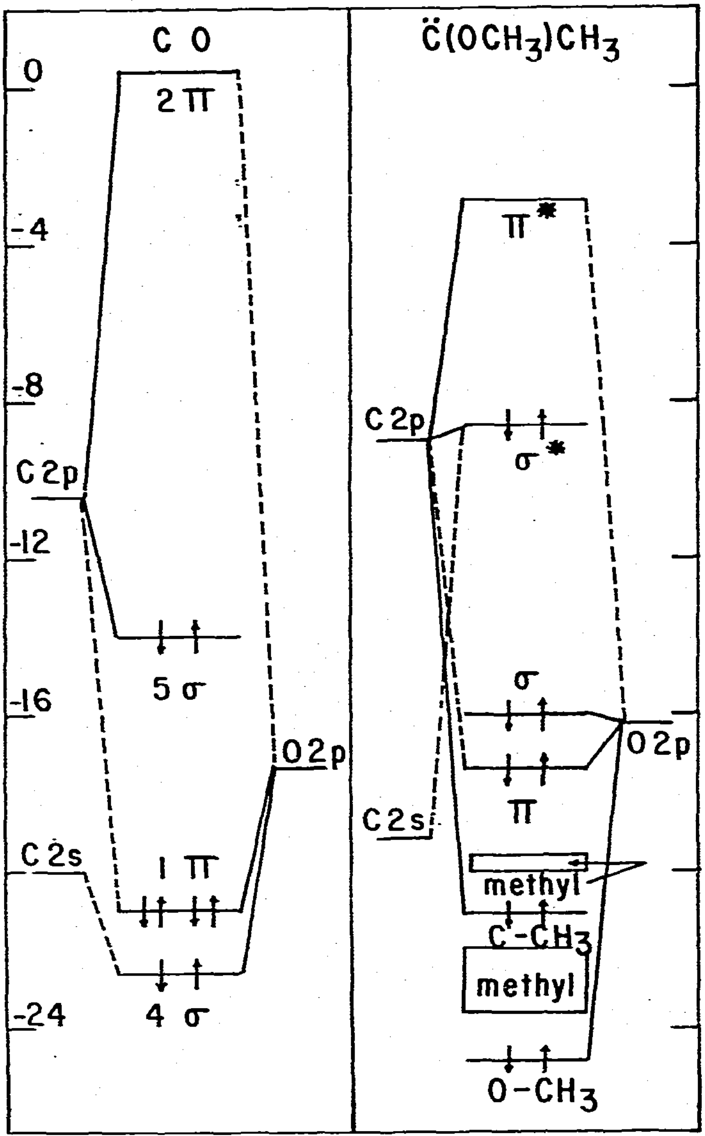


Figure 1. Abbreviated MO Diagrams for CO and $\ddot{C}(OCH_3)CH_3$.

σ and σ^* MO's are not perfectly localized on either oxygen or carbon. The carbene σ MO is bonding in the region between the carbon and oxygen atoms, while the carbene σ^* MO is antibonding in this region.

Just as the degree of interaction between carbon and heteroatom is smaller for $\ddot{C}(OCH_3)CH_3$ than for CO, it is smaller for $\ddot{C}(SCH_3)CH_3$ than for $\ddot{C}(OCH_3)CH_3$. Examination of Table 2 reveals that the π-π^* separation for the methyl(thiomethyl)-

Table 2. Eigenvalues and Per Cent Characters for Some of the MO's of CO and of $\bar{C}(X)CH_3$

CO

Orbital	%Cs	%Cp	%Os	%Op	eiv
2π		66.8		33.2	+0.29
5σ	34.4	47.8	1.0	16.7	-13.79
1π		33.2		66.8	-21.04
4σ	22.5	1.4	12.8	63.2	-22.60

$X = -OCH_3$

Orbital	%Cs	%Cp	%Os	%Op	$\%Me_C$	$\%Me_O$	eiv
π^*		73.1		22.4	3.4	1.2	-2.82
σ^*	13.9	63.2	1.5	9.3	8.7	4.5	-8.55
σ	4.1	16.0	1.3	59.7	12.8	6.2	-15.99
π		20.0		66.0	4.2	9.7	-17.07

$X = -SCH_3$

Orbital	%Cs	%Cp	%Ss	%Sp	$\%Me_C$	$\%Me_S$	eiv
π^*		69.9		26.2	2.9	1.0	-3.74
σ^*	13.6	66.0	2.6	4.4	5.9	7.3	-9.30
σ	0.6	16.1	3.4	69.9	6.4	3.5	-12.73
π		25.1		69.7	2.6	2.6	-13.53

$X = -NH_2$

Orbital	%Cs	%Cp	%Ns	%Np	$\%Me_C$	%H	eiv
π^*		69.5		27.4	3.1	0.0	-1.43
σ^*	14.2	75.8	0.3	0.4	5.5	4.0	-9.38
π		23.8		70.2	6.1	0.0	-16.72

$X = -N(CH_3)_2$

Orbital	%Cs	%Cp	%Ns	%Np	$\%Me_C$	$\%Me_N$	eiv
π^*		64.6		28.8	2.7	3.9	-0.49
σ^*	13.7	74.7	0.2	0.5	5.4	5.4	-8.58
π		29.5		55.6	3.1	11.8	-14.94

carbene ligand is less than 10 eV. It is not surprising that carbon and sulfur should interact less strongly than carbon and oxygen. Sulfur's AO's are less stable than oxygen's. Hence, the sulfur transfers more electron density to the

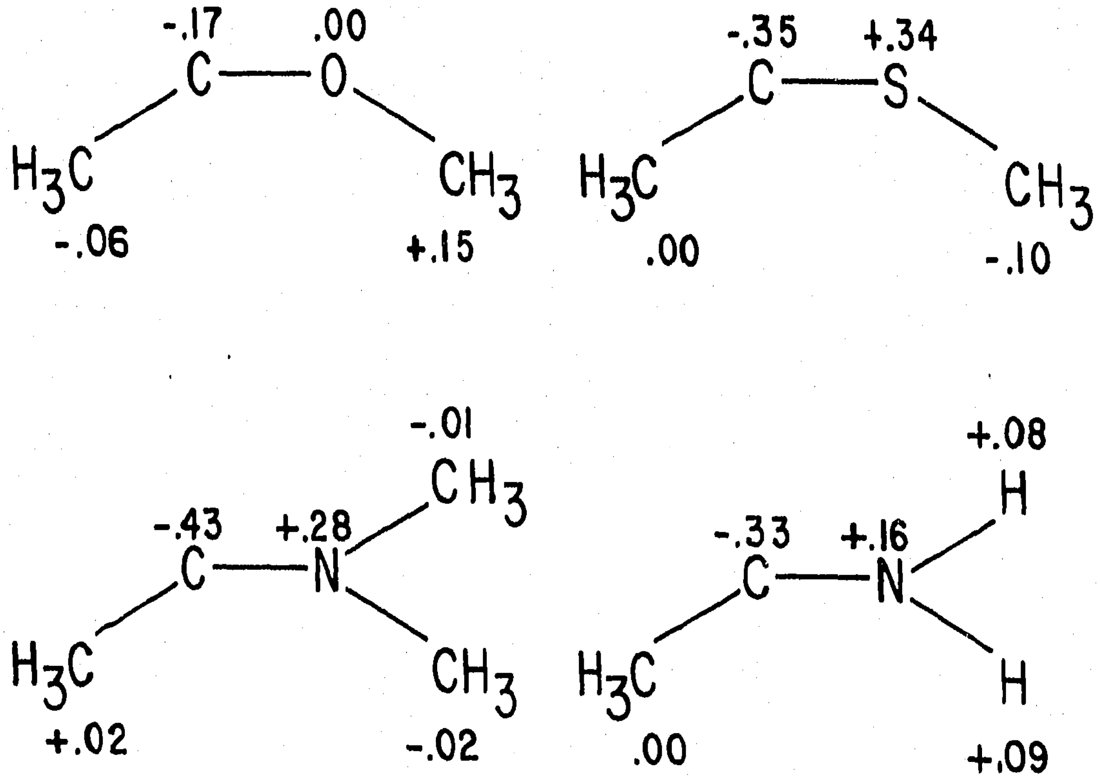


Figure 2. Mulliken Charge Distribution in $\ddot{C}(X)CH_3$.

carbene carbon than oxygen does. As a result, the carbon AO's also become destabilized, leading to a decrease in the magnitude of the interactions between carbon and the heteroatom.

Similarly, the separation between the $\ddot{C}(SCH_3)CH_3$ σ and σ* orbitals is considerably smaller than the separation between the analogous levels of $\ddot{C}(OCH_3)CH_3$ (see Table 2). The sulfur lone pair is less stable than the oxygen lone pair, as expected. Furthermore, the carbon lone pair is *stabilized* in $\ddot{C}(SCH_3)CH_3$, despite the fact that carbon carries a more negative charge in that ligand than $\ddot{C}(OCH_3)CH_3$.

The smaller splitting of the σ and σ* MO's in the methyl(thiomethyl)carbene ligand than in the methyl(methoxy)carbene ligand is caused, in part, by the fact that the (approximate) Fock matrix off-diagonal element between the carbon and sulfur lone pairs of $\ddot{C}(SCH_3)CH_3$ is smaller than the analogous term in $\ddot{C}(OCH_3)CH_3$. In addition, the methyl carbon attached to the carbene carbon is more positively charged in $\ddot{C}(SCH_3)CH_3$ than in $\ddot{C}(OCH_3)CH_3$. Conversely, the methyl carbon attached to sulfur in $\ddot{C}(SCH_3)CH_3$ is more negatively charged than the methyl carbon attached to oxygen in $\ddot{C}(OCH_3)CH_3$ (see Figure 2). Interaction with the methyl carbons should stabilize the carbon lone pair and destabilize the sulfur lone pair in the methyl(thiomethyl) carbene ligand with respect to the analogous orbitals in the methyl(methoxy)carbene ligand. Hence, the σ and σ* MO's of $\ddot{C}(SCH_3)CH_3$ lie closer in energy than the σ and σ* MO's of $\ddot{C}(OCH_3)CH_3$. Conversely, the σ-σ*, and π-π*, separations in the aminocarbene complexes, $\ddot{C}(NH_2)CH_3$ and $\ddot{C}(N(CH_3)_2)CH_3$, are greater than they are in $\ddot{C}(OCH_3)CH_3$ or $\ddot{C}(SCH_3)CH_3$ (see Table 2). Like sulfur, nitrogen donates more charge to carbon than oxygen does (see Figure 2). However, the (approximate) Fock matrix off-diagonal element between the carbon 2p orbitals and the nitrogen 2p orbitals in the methyl(amino)carbene ligands is larger than the analogous term in the methyl(methoxy)carbene ligand, an indication that carbon and nitrogen interact more strongly than carbon and oxygen. This increase in interaction is the opposite of the trend observed when $\ddot{C}(OCH_3)CH_3$ and $\ddot{C}(SCH_3)CH_3$ are compared. The explanation for the difference in trends lies in the geometries of the ligands.

Nitrogen, like oxygen, is a small atom. The carbon-nitrogen bond length is the same as the carbon-oxygen bond length [2] and both are considerably shorter than the carbon-sulfur bond length is expected to be [25]. In addition, the nitrogen AO's are somewhat more diffuse than the oxygen AO's, and the overlap between the carbon and nitrogen functions is larger than the corresponding overlap for the carbon and oxygen. Since the (approximate) Fock matrix off-diagonal element is overlap dependent, and since it also contains a term which varies as the inverse of the internuclear separation [10], it is larger in $\ddot{C}(NH_2)CH_3$ than in $\ddot{C}(OCH_3)CH_3$ or $\ddot{C}(SCH_3)CH_3$. As a result, the separation of the π and π^* MO's is larger in the methyl(amino)carbenes than in methyl(methoxy)- or methyl(thiomethyl)carbene (14.45 eV for $\ddot{C}(N(CH_3)_2)CH_3$ and 15.29 eV for $\ddot{C}(NH_2)CH_3$ versus 14.25 eV for $\ddot{C}(OCH_3)CH_3$ and 9.79 for $\ddot{C}(SCH_3)CH_3$). Furthermore, the π^* MO in both $\ddot{C}(N(CH_3)_2)CH_3$ and $\ddot{C}(NH_2)CH_3$ is destabilized with respect to its position in $\ddot{C}(OCH_3)CH_3$.

The σ^* MO in the methyl(amino)carbene ligands contains almost no contribution from nitrogen (see Table 2). In $\ddot{C}(OCH_3)CH_3$ and $\ddot{C}(SCH_3)CH_3$, the main contribution to the σ^* MO is the carbene carbon lone pair, but there is also a contribution from the oxygen or sulfur lone pair. However, the nitrogen atom in $\ddot{C}(NR_2)CH_3$ does not have a lone pair; its sp^2 hybridized orbitals are all involved in bonding to either the carbene carbon or the R groups. The N-R bonding MO is more stable than an almost non-bonding orbital would be. Hence, its interaction with the carbon lone pair is much smaller than the interaction between the lone pairs of $\ddot{C}(OCH_3)CH_3$ and $\ddot{C}(SCH_3)CH_3$. Thus, it is not surprising that the σ^* MO in a methyl(amino)carbene ligand is so highly localized on carbon.

The changes in the nature and extent of the carbon-heteroatom interactions also affect the placement of the σ^* MO in $\ddot{C}(NR_2)CH_3$. On the one hand, removal of the interaction with the heteroatom lone pair should stabilize the MO. On the other hand, the increased negative charge on carbon should destabilize it. In $\ddot{C}(NH_2)CH_3$, the first effect is dominant. In $\ddot{C}(N(CH_3)_2)CH_3$, where the methyl groups attached to nitrogen release charge into the system, the two effects are equally balanced and there is no substantial change in the position of the σ^* MO from its position in $\ddot{C}(OCH_3)CH_3$. The methyl groups also affect the pi-type orbitals, so that the π and π^* levels of $\ddot{C}(N(CH_3)_2)CH_3$ are less stable than those of $\ddot{C}(NH_2)CH_3$.

We have seen how varying the X group of $\ddot{C}(X)Y$ can affect the energetics and localizations of the carbene σ and σ^*, and π and π^* MO's. In order to examine the dependence of these quantities on Y, we have examined two Y groups in addition to the methyl group: the phenyl group, $-C_6H_5$, and the furyl group, $-C_4H_3O$.

In studying the phenyl- and furylcarbene ligands, we are attempting to determine how replacing the methyl group of $\ddot{C}(X)CH_3$ with a phenyl or furyl ring affects the carbene carbon-heteroatom pi system and the carbon lone pair. Thus, the $C(X)CH_3\pi$, π^* and σ^* MO's (and the $C(OCH_3)CH_3\sigma$ MO) form an excellent "basis set" for this study. By constructing an MO diagram showing the $\ddot{C}(X)CH_3$ orbitals mentioned above and the phenyl or furyl MO's, we can illustrate the effect of the new Y group in a simple fashion. More traditional MO diagrams, showing the interactions between the carbon and the atoms of the X group explicitly, would be far more complicated and less informative in regard to the effects we wish to examine. It should be noted that the $\ddot{C}(X)CH_3$ "basis set" appears in the MO diagrams strictly as a heuristic device. The $\ddot{C}(X)CH_3$ eigenvectors were not used, in any way, to obtain the eigenvectors or eigenvalues of the furyl- and phenylcarbene ligands.

The use of the new "basis set" is illustrated in Figure 3, which contains abbreviated MO diagrams for $\ddot{C}(OCH_3)C_6H_5$, $\ddot{C}(NH_2)C_6H_5$ and $\ddot{C}(N(CH_3)_2)C_6H_5$. In each MO diagram, the levels on the left are the appropriate MO's of $\ddot{C}(X)CH_3$. The levels on the right are orbitals localized on the C_6H_5 moiety. Those in the center of the diagram are the MO's of $\ddot{C}(X)C_6H_5$.

The crystal structure of $(CO)_5CrC(OCH_3)C_6H_5$ indicates that the plane of the phenyl ring is perpendicular to the symmetry plane of the molecule [11]. This orientation was used for the phenyl ring in performing the calculations on all of the $\ddot{C}(X)C_6H_5$ species. Hence, replacing the methyl group by a phenyl group had only minimal significance for the spatial localization and energetic placement of the carbon-heteroatom pi anti-bond. For each X, the percent composition of the $\ddot{C}(X)C_6H_5\pi^*$ MO is almost exactly the same as the percent composition of the $C(X)CH_3\pi^*$ MO. Similarly, for each X, the eigenvalue of the $\ddot{C}(X)C_6H_5\pi^*$ MO is less than 0.5 eV more negative than the eigenvalue of the $\ddot{C}(X)CH_3$ * MO (see Table 3).

The σ^* level in $\ddot{C}(NH_2)C_6H_5$ and $\ddot{C}(N(CH_3)_2)C_6H_5$ is also slightly stabilized compared to the σ^* MO in $\ddot{C}(NH_2)CH_3$ and $\ddot{C}(N(CH_3)_2)CH_3$. The carbene carbon in the phenylcarbene ligands transfers charge from its lone pair orbital to the phenyl ring. As a result, the carbene carbon is less negatively charged in the phenyl carbenes than in the methylcarbenes and the σ^* MO is stabilized.

Despite similar changes in charge distribution between $\ddot{C}(OCH_3)C_6H_5$ and $\ddot{C}(OCH_3)CH_3$, the σ^* MO is significantly less stable in the phenyl(methoxy)carbene

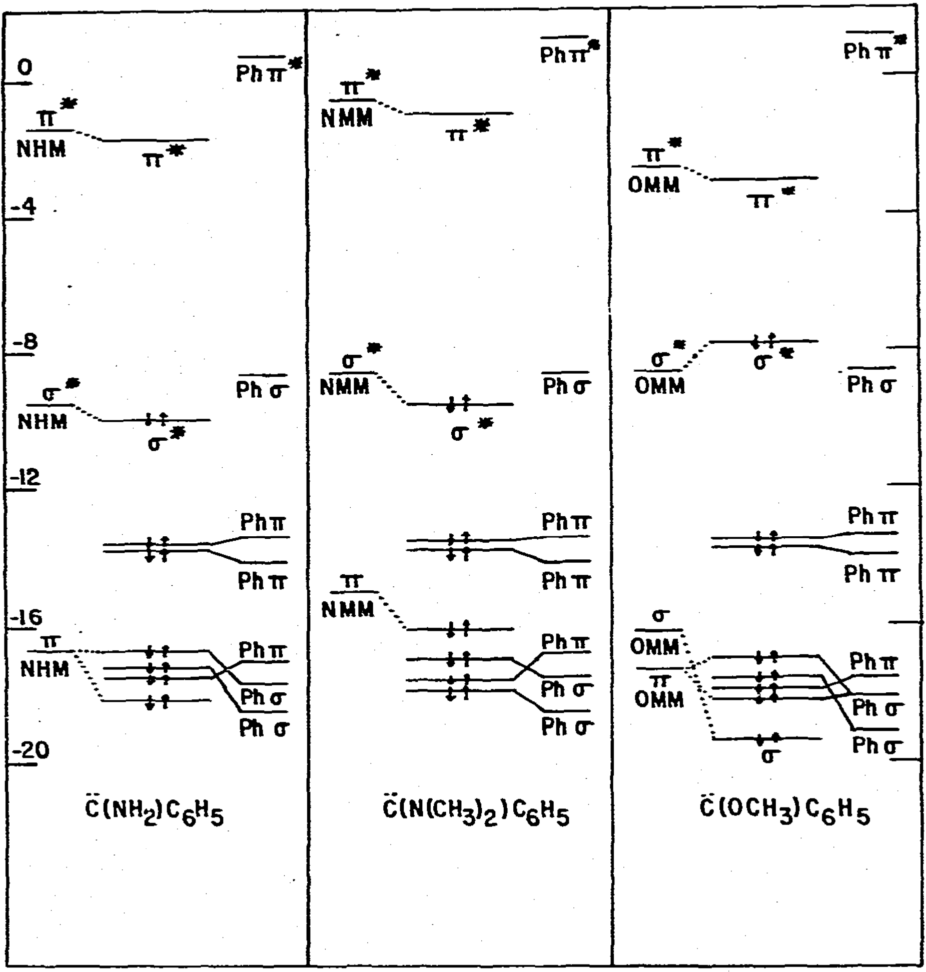
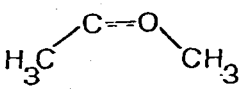
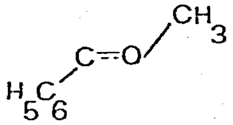


Figure 3. Abbreviated MO Diagrams for $\ddot{C}(NH_2)C_6H_5$, $\ddot{C}(N(CH_3)_2)C_6H_5$ and $\ddot{C}(OCH_3)C_6H_5$. Levels labelled γ_{NHM}, γ_{NMM}, and γ_{OMM} are MO's of $\ddot{C}(NH_2)C_6H_5$, $\ddot{C}(N(CH_3)_2C_6H_5$ and $\ddot{C}(OCH_3)C_6H_5$, respectively, and have symmetry label, γ.

ligand than in the methyl(methoxy)carbene ligand. Crystal structure data indicates that the two methyl groups of $\ddot{C}(OCH_3)CH_3$ are <u>cis</u> to one another, while the phenyl and methyl groups of $\ddot{C}(OCH_3)C_6H_5$ are in a trans configuration [11,12]. The change in configuration results in significant alteration of the σ and σ^* MO's. The largest (approximate) Fock matrix off-diagonal element between the carbene carbon's lone pair and the oxygen's hybrid orbitals occurs between the lone pair





and the oxygen orbital that is *trans* to it. In $\ddot{C}(OCH_3)CH_3$, this oxygen orbital is stabilized by the formation of the bond between the oxygen and the methyl carbon. However, in $\ddot{C}(OCH_3)C_6H_5$, it is the oxygen orbital *cis* to the carbon lone pair that is stabilized by bond formation. Therefore, the *trans* orbital is able to interact very strongly with the carbon lone pair. The ultimate result is increased mixing of carbon and oxygen AO's in the σ and σ^*MO's, and increased splitting of these MO's in $\ddot{C}(OCH_3)C_6H_5$.

Table 3. Eigenvalues and Per Cent Characters for Some of the MO's of $\ddot{C}(X)C_6H_5$

X = $-OCH_3$

Orbital	Cs	%Cp	%Os	%Op	%Ph	%Me	eiv	eiv $\ddot{C}(OCH_3)CH_3$
π^*		73.6		21.8	3.4	1.1	-3.16	-2.82
σ^*	9.3	54.0	0.6	18.6	16.1	1.3	-7.82	-8.55
σ	5.2	16.4	2.3	46.0	15.0	15.1	-19.22	-15.99
π		15.2		34.4	43.8	6.6	-18.06	-17.07

X = $-NH_2$

Orbital	Cs	%Cp	%Ns	%Np	%Ph	%H	eiv	eiv $\ddot{C}(NH_2)CH_3$
π^*		69.6		27.0	3.5	0.0	-1.74	-1.43
σ^*	10.6	59.0	0.2	0.3	26.5	3.3	-10.00	-9.38
π		17.3		35.1	47.6	0.0	-18.07	-16.72

X = $-N(CH_3)_2$

Orbital	Cs	%Cp	%Ns	%Np	%Ph	%Me	eiv	eiv $\ddot{C}(NH_3)_2CH_3$
π^*		65.0		28.7	2.4	3.9	-0.93	-0.49
σ^*	10.6	61.0	0.2	0.5	22.7	5.0	-9.36	-8.58
π		23.1		49.6	16.0	11.3	-15.33	-14.94

In contrast to the phenyl ring, the furyl ring is oriented so that its plane coincides with the carbene plane [17]. As a result, the π^* MO in both $\bar{C}(OCH_3)C_4H_3O$ and $\bar{C}(NH_2)C_4H_3O$ is extremely delocalized (see Table 4). The interaction between the carbon-heteroatom pi anti-bond and the virtual furyl pi MO's, which produces this delocalization, also results in a significantly stabilized $\bar{C}(X)C_4H_3O\pi^*$ MO (see Figure 4).

In contrast, the σ^* MO in $\bar{C}(X)C_4H_3O$ has nearly the same eigenvalue as the σ^* MO in $\bar{C}(X)CH_3$. The carbon lone pair orbital is energetically isolated from most of the other orbitals in each of the furylcarbene ligands. There is a furan sigma orbital, with (approximate) Fock matrix diagonal element at ca. -9 eV, which could interact strongly with the carbene carbon lone pair. It does not do so, because it is stabilized by the interaction that leads to the formation of the bond that links the furyl ring to the carbene carbon. Thus, for both $\bar{C}(OCH_3)C_4H_3O$ and $\bar{C}(NH_2)C_4H_3O$, the major perturbation caused by the introduction of the furyl ring is the stabilization and delocalization of the π^* MO.

The MO calculations discussed above indicate that the electronic structure of a carbene liquid is similar to that of a carbonyl ligand. Thus, it may be assumed that a carbene ligand will be able to act as a σ donor and a π acceptor, to some extent, in a transition metal complex. The extent of interaction will be determined by various factors.

In all of the carbene ligands, the $\bar{C}(X)Y\sigma^*$ MO is less stable than the corresponding CO 5σ MO. Conversely, the $\bar{C}(X)Y\pi^*$ MO is more stable than the CO 2π levels. Therefore, solely on the basis of energetics, all the carbene ligands would be predicted to be better σ donors and better π acceptors than the carbonyl ligand. However, the spatial localizations of the carbene σ^* and π^* orbitals vary considerably. For instance, the σ^* MO in the phenylcarbenes is somewhat delocalized, containing contributions from the phenyl ring as well as from the carbene carbon. Similarly, the π^* MO in the furylcarbene ligands contains significantly less carbene carbon character than the π^* MO in the methyl- or phenylcarbene ligands.

All of the carbene ligands compare unfavorably to the carbonyl ligand in terms of the number of orbitals available for accepting charge from a metal. The carbonyl 2π MO's are doubly degenerate. Therefore, CO has two orbitals which are in a good (energetic) position for accepting charge. In contrast, a carbene ligand has only one such orbital.

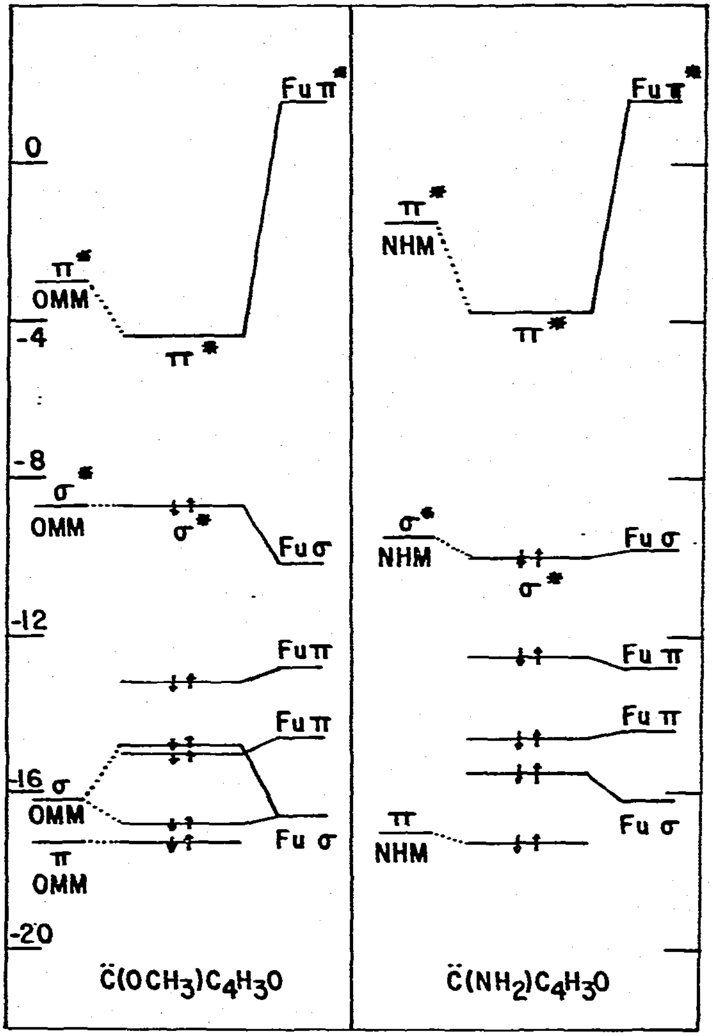


Figure 4. Abbreviated MO Diagrams for $\ddot{C}(OCH_3)C_4H_3O$ and $\ddot{C}(NH_2)C_4H_3O$. Levels labelled γ_{OMM} and γ_{NHM} are MO's of $\ddot{C}(OCH_3)CH_3$ and $\ddot{C}(NH_2)CH_3$, respectively, and have symmetry label, γ.

Thus, there are factors which would tend to make the carbene ligands better π acceptors than CO, and also factors which would tend to make them poorer π acceptors. Only examination of the complexes in which the carbene and carbonyl groups serve as ligands can give a quantitative ranking of the π accepting abilities of the various ligands.

The Complexes

Abbreviated MO diagrams for chromium hexacarbonyl and pentacarbonyl chromium methyl(methoxy)carbene are shown in Figure 5. The levels labelled Cr3d, Cr4s and Cr4p are the (approximate) Fock matrix diagonal elements for the valence orbitals of chromium in each complex. The levels labelled CO5σ and CO2π are the eigenvalues for those orbitals in free CO. Similarly, the levels labelled $\ddot{C}(OCH_3)CH_3\sigma^*$ and $\ddot{C}(OCH_3)CH_3\pi^*$ are the eigenvalues for the corresponding MO's of free $\ddot{C}(OCH_3)CH_3$. The MO's of chromium hexacarbonyl are labelled according to their symmetry in the O_h point group. The MO's of the carbene complex are labelled according to their main contributors.

The carbonyl ligand interacts with chromium in two ways. The CO5σ orbital, which is more stable than the Cr3d level, donates charge to the metal by interacting with the empty e_g orbitals, $3dz^2$ and 3dxy, as well as the 4s and 4p AO's. The CO2π orbitals, which are less stable than the Cr3d level, accept charge from the metal, by interacting with the filled t_{2g} orbitals, $3dx^2$-y^2, 3dxz and 3dyz. (Note that, in all of these calculations, the carbonyl ligands were placed between the X and Y axes. The plane of the carbene ligand was the YZ plane.) Other ligands may also interact with a metal as CO does. The

Table 4. Eigenvalues and Per Cent Characters for Some of the MO's of $\ddot{C}(X)C_4H_3O$

X = $-OCH_3$

Orbital	%Cs	%Cp	%Os	%Op	%Fu	%Me	eiv	eiv $\ddot{C}(OCH_3)CH_3$
π^*		44.8		18.5	35.6	1.0	-4.08	-2.82
σ^*	13.9	62.6	1.6	11.5	5.5	4.9	-8.59	-8.55
σ	0.9	8.2	1.0	35.5	53.9	0.5	-16.59	-15.99
π		27.6		55.4	8.9	8.1	-17.07	-17.07

X = $-NH_2$

Orbital	%Cs	%Cp	%Ns	%Np	%Fu	%H	eiv	eiv $\ddot{C}(NH_2)C_4H_3O$
π^*		41.0		22.5	36.5	0.0	-3.11	-1.43
σ^*	14.49	76.4	0.3	0.4	4.2	3.8	-9.72	-9.38
π		30.6		58.8	10.6	0.0	-17.05	-16.72

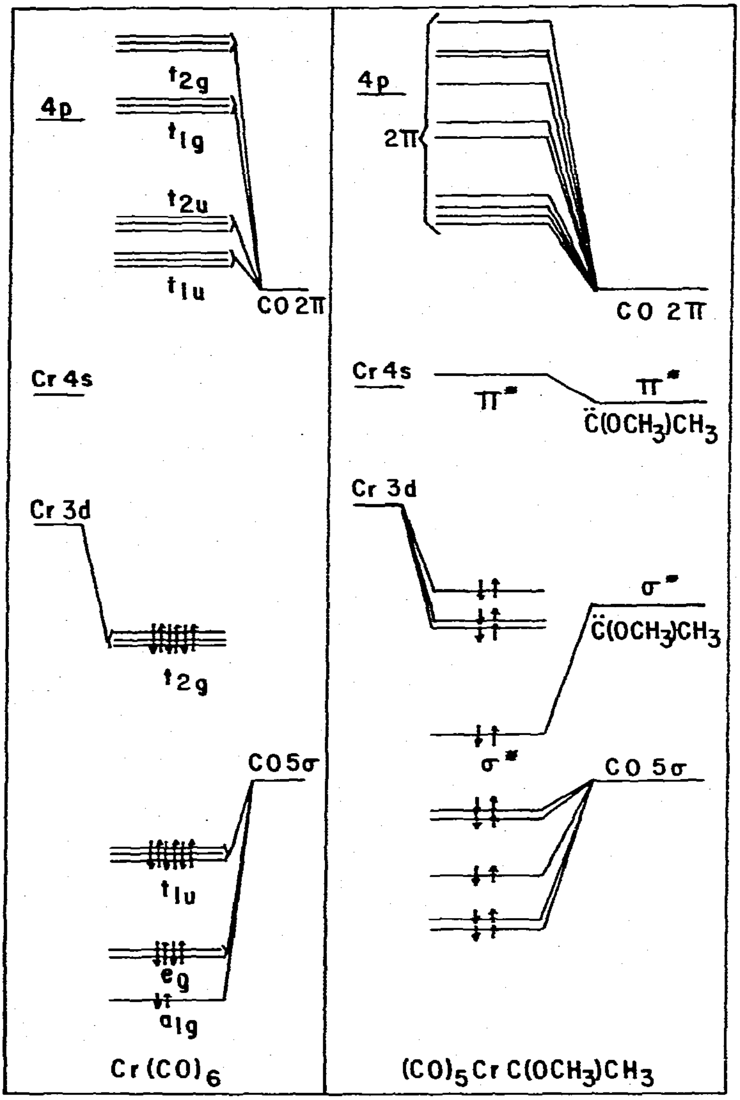


Figure 5. Abbreviated MO Diagrams for $(CO)_6Cr$ and $(CO)_5CrC(OCH_3)CH_3$.

transfer of charge in each direction is appreciable only when the energies of the metal and ligand orbitals are reasonably close and the interaction between the orbitals is large.

Examination of the MO diagram for $(CO)_5CrC(OCH_3)CH_3$ confirms the prediction that the $\ddot{C}(OCH_3)CH3\sigma^*$ and π^* levels would be able to interact with chromium in much the same way as the $CO_5\sigma$ and 2π orbitals. However, it seems that the carbene ligand is a poorer π acceptor than the carbonyl ligand. Notice, for

Table 5. σ Donation and π Acceptance by CO and $\ddot{C}(OCH_3)CH_3$

Complex	Ligand	Orbital	Population Free Ligand	Population Complex	Δ	Population Free Ligand	Population Complex[***]	Δ
$(CO)_6Cr$	CO	2π	0.00	0.49[*]	+0.49	0.00	0.51	+0.51
	CO	5σ	2.00	1.51[*]	-0.49	2.00	1.48	-0.52
$(CO)_5CrC(OCH_3)CH_3$	CO,cis	2π	0.00	0.52[**]	+0.52	0.00	0.51	+0.51
	CO,cis	5σ	2.00	1.49[**]	-0.51	2.00	1.49	-0.51
$(CO)_5CrC(OCH_3)CH_3$	CO,trans	2π	0.00	0.54[**]	+0.54	0.00	0.54	+0.54
	CO,trans	5σ	2.00	1.48[**]	-0.52	2.00	1.48	-0.52
$(CO)_5CrC(OCH_3)CH_3$	$\ddot{C}(OCH_3)CH_3$	π^*	0.00	0.36[**]	+0.36	0.00	0.43	+0.43
	$\ddot{C}(OCH_3)CH_3$	σ^*	2.00	1.48[**]	-0.52	2.00	1.41	-0.59

[*] The Cr-CO was taken as 1.92 Å.

[**] The Cr-CO was taken as 1.88 Å. The Cr-$\ddot{C}(OCH_3)CH_3$ distance was taken as 2.02 Å.

[***] The central carbon of each ligand was placed 1.88 Å from chromium in the calculations for which results are reported here.

instance, that the (approximate) Fock matrix diagonal element for the Cr3d orbitals is less negative in $(CO)_5CrC(OCH_3)CH_3$ than in $(CO)_6Cr$. This is an indication that less charge is being removed from the metal in the carbene complex than in the hexacarbonyl.

Examination of the central columns of Table 5 permits a quantitative comparison of $\ddot{C}(OCH_3)CH_3$ and CO as σ donors/π acceptors. Although the ligands have essentially the same σ donating ability, the carbonyl ligand is a significantly better π acceptor, gaining ∿0.5 electron upon complexation compared to 0.36 electron accepted by the methyl(methoxy)carbene ligand. It should be noted, however, that the CO2π levels are doubly degenerate. A single CO2π orbital accepts roughly 0.25 electron, which is significantly less than the 0.36 electron accepted by the (non-degenerate) $\ddot{C}(OCH_3)CH_3\pi^*$ orbital. Thus, the presence of two low-lying virtual orbitals in CO outweighs the energetic advantage of the $\ddot{C}(OCH_3)CH_3\pi^*$ level, and the carbonyl ligand accepts more charge from chromium than the carbene ligand does.

It should also be noted that the amount of π acceptance by CO is slightly higher in $(CO)_5CrC(OCH_3)CH_3$ than in $(CO)_6Cr$. However, the amount of π acceptance by the carbonyl <u>trans</u> to the carbene ligand is essentially the same as the amount of π acceptance by a carbonyl <u>cis</u> to the carbene ligand. Replacing a carbonyl ligand by a ligand which is a poorer π acceptor frequently has more of an effect on the carbonyl <u>trans</u> to the new ligand than on the other carbonyls [24]. The reason for the absence of a significant <u>trans</u> influence [26] in $(CO)_5CrC(OCH_3)CH_3$ will be explored later.

To a certain extent, our results reflect the crystallographic data which we used to determine the internuclear separations for the calculations. The relative amounts of σ donation and π acceptance which we observed may simply be functions of differing orbital overlaps. In order to determine whether $\ddot{C}(OCH_3)CH_3$ was an inherently weaker π acceptor than CO, we performed calculations on $(CO)_6Cr$ and $(CO)_5CrC(OCH_3)CH_3$ with all the ligands' central carbons placed 1.88 Å from chromium (1.88 Å is the chromium to carbonyl carbon distance for $(CO)_5CrC(OCH_3)CH_3$ as indicated crystallographically). Pertinent results from these calculations are shown in the last columns of Table 5.

When all ligands are equidistant from chromium, the carbonyl ligands and the metal transfer virtually the same amount of charge among themselves in both $(CO)_6Cr$ and $(CO)_5CrC(OCH_3)CH_3$. With the carbene carbon at the same distance from the chromium as the carbonyl carbons, the methyl(methoxy)carbene ligand is a slightly better σ donor, and a slightly poorer π acceptor, than the carbonyl ligand is.

Examining the interactions between the metal and the central carbon of the ligand is helpful in understanding the differences in the σ donating and π accepting abilities of CO and $\ddot{C}(OCH_3)CH_3$. Table 6 contains populations for the AO's of the carbonyl carbon and of the carbene carbon, both in the free ligands and in the complexes. The change in the carbonyl's $C(2s+2p_z)$ population represents charge removed from the $CO5\sigma$ level. Nearly all of the charge donated to the metal by the carbonyl ligand comes from the carbon, in accord with the designation of the 5σ level as principally a carbon lone pair. Similarly, almost all of the charge donated to chromium by the carbon ligand is removed from the $C2sp^2$ orbital, the carbene ligand's carbon lone pair. The lone pairs of both the carbonyl and carbene ligands have the same degeneracy and roughly the same orientation with respect to the metal. The factor determining which lone pair donates more charge to chromium is the energetic separation between the Cr3d level and the lone pair level. Since the carbene lone pair is destabilized with respect to the carbonyl lone pair, the carbene ligand is the better σ donor.

Roughly 0.3 electron is transferred to the carbon p_π AO's of each carbonyl ligand. The same amount of charge is transferred to the carbon p_x AO of the carbene ligand. Thus, a greater percentage of the charge accepted by the ligand remains on the carbon atom in $\ddot{C}(OCH_3)CH_3$ than in CO. This is as would be expected since the $\ddot{C}(OCH_3)CH_3\pi^*$ MO is more strongly localized on carbon than the $CO2\pi$ orbitals are.

In the carbonyl ligand, the extra charge received from the metal is divided between two orbitals. In the carbene ligand, all of the additional charge is placed in one orbital. As a result, the electron-electron repulsion caused by π acceptance is much greater for the carbene ligand than for the carbonyl ligand. The lowest unoccupied MO (LUMO) of $(CO)_5CrC(OCH_3)CH_3$, in which the carbene π^* MO is the main contributor, has an eigenvalue of -1.15 eV in the calculation being discussed now. When the calculation is done with the molecule in its crystallographically determined geometry, the LUMO is considerably stabilized (eigenvalue: -2.14 eV).

Having only one p_π orbital affects the carbene ligand's ability to inter-

Table 6. σ Donation and π Acceptance by the Central Carbons of CO and $\ddot{C}(OCH_3)CH_3$*

Complex	Ligand	Orbital	Population		Δ
			Free Ligand	Complex	
$(CO)_6Cr$	CO	C2px+2py	1.33	1.65	+0.32
	CO	C2s +2pz	2.77	2.27	-0.50
$(CO)_5CrC(OCH_3)CH_3$	CO,cis	C2px+2py	1.33	1.64	+0.31
	CO,cis	C2s+2pz	2.77	2.29	-0.48
$(CO)_5CrC(OCH_3)CH_3$	CO,trans	C2px+2py	1.33	1.66	+0.33
	CO,trans	C2x+2pz	2.77	2.27	-0.50
$(CO)_5CrC(OCH_3)CH_3$	$\ddot{C}(OCH_3)CH_3$	C2px	0.50	0.80	+0.30
	$\ddot{C}(OCH_3)CH_3$	C1sp^2 **	0.73	0.75	+0.02
	$\ddot{C}(OCH_3)CH_3$	C2sp^2 **	1.97	1.41	-0.56
	$\ddot{C}(OCH_3)CH_3$	C3sp^2 **	0.97	0.97	0.00

*The central carbon of each ligand was placed 1.88Å from chromium in the calculations for which results are reported here.

**The carbon s and p orbitals were transformed into an sp^2 hybrid basis, in which the px orbital was left unchanged. The C1sp^2 orbital is used in bonding to the oxygen, while the C3sp^2 orbital is used in bonding to the central carbon of the methyl group. C2sp^2 is the carbon lone pair.

act with a metal in another way as well. The orbital has a non-zero (approximate) Fock matrix off-diagonal term with only the chromium 3dxz orbital. The carbon of the <u>trans</u> carbonyl, since it has both p_x and p_y orbitals of pi symmetry, can interact with both the chromium 3dxz and 3dyz orbitals. The <u>cis</u> carbonyls interact with the chromium 3dx^2-y^2 orbital, in addition to the chromium 3dxz and 3dyz orbitals. Thus, the carbonyl ligands have more opportunity for accepting charge from the metal than the carbene ligand does.

The non-degeneracy and spatial localization of the carbon p_π AO are common to all of the carbene ligands. Therefore, all of them may be expected to be poorer π acceptors than CO. However, the eigenvalues of the π^* level vary considerably in the carbenes. We turn now to a consideration of the relative π acceptor (and σ donor) strengths of the various carbene ligands, $\ddot{C}(X)Y$.

Experimental evidence [3-5] indicates that aminocarbenes are poorer acceptors than alkoxycarbenes. This is in agreement with our calculations on the free ligands, which showed that, for a given Y, the π^* level of the species C(X)Y was always more destabilized with X = $-NH_2$ or $-N(CH_3)_2$ than with X = $-OCH_3$. In order to make a more direct comparison of amino- and methoxycarbenes as π acceptors, we performed calculations on $(CO)_5CrC(NH_2)CH_3$ and $(CO)_5CrC(OCH_3)CH_3$ in which the central carbon of each of the carbene ligands was placed 2.02 Å from the chromium. (Crystallographic data indicates that this is an appropriate chromium to carbene carbon distance for a methoxycarbene complex). The relevant results of these calculations are shown in Table 7.

Given a chance for equal interaction with the metal, $\ddot{C}(NH_2)CH_3$ becomes essentially as good a σ donor as $\ddot{C}(OCH_3)CH_3$ but remains a slightly poorer π acceptor. The latter result is in accord with the result that the π^* level of $\ddot{C}(NH_2)CH_3$ has roughly the same per cent composition as the π^* level of $\ddot{C}(OCH_3)CH_3$ and is 1.4 eV less stable.

Table 7. σ Donation and π Acceptance by $\ddot{C}(OCH_3)CH_3$ and $\ddot{C}(NH_2)CH_3$ *

Ligand	Orbital	Population Free Ligand	 Complex	Δ
$\ddot{C}(OCH_3)CH_3$	Cpx	0.50	0.77	+0.27
	Cpx+Opx	2.03	2.39	+0.36
	$C2sp^2$	1.97	1.48	-0.49
$\ddot{C}(NH_2)CH_3$	Cpx	0.57	0.77	+0.20
	Cpx+Opx	2.02	2.31	+0.29
	$C2sp^2$	1.96	1.50	-0.46

*The central carbon of each of the carbene ligands was placed 2.02 Å from chromium.

Since the σ* level of $C(NH_2)$ is more stable than that of $\ddot{C}(OCH_3)CH_3$, the aminocarbene's σ* level is in a poorer energetic position for interacting with the empty chromium 3d orbitals. However, the σ* level is also more strongly localized on carbon in the aminocarbene, resulting in enhanced metal- σ* interaction. This partially compensates for the less favorable energetic position of the ligand orbital.

Although the identity of the X group seems to be more important than the identity of the Y group in determining the σ donor/π acceptor strength of the carbene ligand, the Y group may not be totally unimportant. In the discussion to follow, the effect of varying Y (from $-CH_3$ to $-C_6H_5$ to $-C_4H_3O$) while keeping X fixed will be examined.

We will begin by considering the methoxycarbene complexes (see Table 8A). In all of the calculations on $(CO)_5CrC(OCH_3)Y$ to be discussed here, the chromium-carbene carbon bond distance employed was 2.02 Å.

The amounts of σ donation and π acceptance by $\ddot{C}(OCH_3)CH_3$ and $\ddot{C}(OCH_3)C_6H_5$ are virtually identical. This is somewhat surprising since we observed small, but significant, differences in the electronic structures of the two ligands.

The σ* level is less stable in $\ddot{C}(OCH_3)C_6H_5$ than in $\ddot{C}(OCH_3)CH_3$ while the π* level is more stable. Thus, the phenyl(methoxy)carbene ligand should be a better σ donor and a better π acceptor than the methyl(methoxy)carbene. Yet it is not a better π acceptor, because the chromium 3d level is more stable in $(CO)_5CrC(OCH_3)C_6H_5$ than in $(CO)_5CrC(OCH_3)CH_3$.

One of the causes of the stabilization of the metal level in $(CO)_5CrC(OCH_3)C_6H_5$ is the low electron density in the carbene carbon's lone pair orbital. The chromium experiences less nearest neighbor repulsion in the phenyl complex than it does in $(CO)_5CrC(OCH_3)CH_3$. Furthermore, the "partially depopulated" lone pair orbital donates less charge to the metal than the lone pair orbital in $C(OCH_3)CH_3$. This also contributes to the relative stability of the metal level in $(CO)_5CrC(OCH_3)C_6H_5$.

That $\ddot{C}(OCH_3)C_4H_3O$ should donate the same amount of charge to chromium as $\ddot{C}(OCH_3)CH_3$ comes as no surprise. The eigenvalue and spatial localization of the σ* MO are nearly identical for the two ligands. Conversely, the eigenvalue and localization of the π* MO of $\ddot{C}(OCH_3)C_4H_3O$ differ substantially from those of the π* MO in $\ddot{C}(OCH_3)CH_3$. Nevertheless, the π accepting ability of $\ddot{C}(OCH_3)C_4H_3O$ does not differ significantly from that of $\ddot{C}(OCH_3)CH_3$.

Table 8. σ Donation and π Acceptance in $(CO)_5CrC(X)Y$

A. X = $-OCH_3$*

Y	Ligand	Orbital	Population Free Ligand	 Complex	Δ
CH_3	CO,cis	2π	0.00	0.52	+0.52
	CO,cis	5σ	2.00	1.49	-0.51
	CO,trans	2π	0.00	0.54	+0.54
	CO,trans	5σ	2.00	1.48	-0.52
	$\ddot{C}(OCH_3)CH_3$	Cpx	0.50	0.77	+0.27
	$\ddot{C}(OCH_3)CH_3$	Cpx+Opx	2.03	2.39	+0.36
	$\ddot{C}(OCH_3)CH_3$	$C2sp^2$	1.97	1.48	-0.49
C_6H_5	CO,cis	2π	0.00	0.53	+0.53
	CO,cis	5σ	2.00	1.50	-0.50
	CO,trans	2π	0.00	0.55	+0.55
	CO,trans	5σ	2.00	1.47	-0.53
	$\ddot{C}(OCH_3)C_6H_5$	Cpx	0.50	0.76	+0.26
	$\ddot{C}(OCH_3)C_6H_5$	Cpx+Opx	2.04	2.39	+0.35
	$\ddot{C}(OCH_3)C_6H_5$	$C2sp^2$	1.88	1.46	-0.42
C_4H_3O	CO,cis	2π	0.00	0.52	+0.52
	CO,cis	5σ	2.00	1.49	-0.51
	CO,trans	2π	0.00	0.55	+0.55
	CO,trans	5σ	2.00	1.48	-0.52
	$\ddot{C}(OCH_3)C_4H_3O$	Cpx	0.62	0.84	+0.22
	$\ddot{C}(OCH_3)C_4H_3O$	Cpx+Opx	2.16	2.48	+0.32
	$\ddot{C}(OCH_3)C_4H_3O$	$C2sp^2$	1.97	1.49	-0.48

B. X = $-NH_2$**

CH_3	CO,cis	2π	0.00	0.53	+0.53
	CO,cis	5σ	2.00	1.50	-0.50

Table 8 (continued)

Y	Ligand	Orbital	Population Free Ligand	Complex	Δ
	CO,trans	2π	0.00	0.56	+0.56
	CO,trans	5σ	2.00	1.47	-0.53
	$\ddot{C}(NH_2)CH_3$	Cpx	0.57	0.73	+0.16
	$\ddot{C}(NH_2)CH_3$	Cpx+Npx	2.02	2.24	+0.22
	$\ddot{C}(NH_2)CH_3$	$C2sp^2$	1.96	1.58	-0.38
C_6H_5	CO,cis	2π	0.00	0.52	+0.52
	CO,cis	5σ	2.00	1.50	-0.50
	CO,trans	2π	0.00	0.56	+0.56
	CO,trans	5σ	2.00	1.47	-0.53
	$\ddot{C}(NH_2)C_6H_5$	Cpx	0.58	0.71	+0.13
	$\ddot{C}(NH_2)C_6H_5$	Cpx+Npx	2.03	2.23	+0.20
	$\ddot{C}(NH_2)C_6H_5$	$C2sp^2$	1.87	1.57	-0.30
C_4H_3O	CO,cis	2π	0.00	0.53	+0.53
	CO,cis	5σ	2.00	1.52	-0.48
	CO,trans	2π	0.00	0.57	+0.57
	CO,trans	5σ	2.00	1.49	-0.51
	$\ddot{C}(NH_2)C_4H_3O$	Cpx	0.66	0.80	+0.14
	$\ddot{C}(NH_2)C_4H_3O$	Cpx+Npx	2.12	2.32	+0.20
	$\ddot{C}(NH_2)C_4H_3O$	$C2sp^2$	1.96	1.60	-0.36

C. $X = -N(CH_3)_2$**

Y	Ligand	Orbital	Free Ligand	Complex	Δ
CH_3	CO,cis	2π	0.00	0.54	+0.54
	CO,cis	5σ	2.00	1.50	-0.50

Table 8 (continued)

Y	Ligand	Orbital	Population		Δ
			Free Ligand	Complex	
	CO,trans	2π	0.00	0.58	+0.58
	CO,trans	5σ	2.00	1.47	-0.53
	$C(N(CH_3)_2)CH_3$	Cpx	0.66	0.80	+0.14
	$C(N(CH_3)_2)CH_3$	Cpx+Npx	2.02	2.20	+0.18
	$C(N(CH_3)_2)CH_3$	$C2sp^2$	1.96	1.58	-0.38
C_6H_5	CO,cis	2π	0.00	0.54	+0.54
	CO,cis	5σ	2.00	1.50	-0.50
	CO,trans	2π	0.00	0.58	+0.58
	CO,trans	5σ	2.00	1.47	-0.53
	$C(N(CH_3)_2)C_6H_5$	Cpx	0.67	0.79	+0.12
	$C(N(CH_3)_2)C_6H_5$	Cpx+Npx	2.03	2.20	+0.17
	$C(N(CH_3)_2)C_6H_5$	$C2sp^2$	1.86	1.57	-0.29

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*The Cr-CO distance was taken as 1.88 Å. The Cr-C(X)Y distance was taken as 2.02 Å.

**The Cr-CO distance was taken as 1.88 Å. The Cr-C(X)Y distance was taken as 2.16 Å.

Although the π* MO of the furyl(methoxy)carbene ligand is considerably more stable than the π* MO of the methyl(methoxy)carbene ligand, it is not very strongly localized on the carbene carbon. Energetics and localization properties work in opposite directions with the result that the carbene carbon and methoxy oxygen accept somewhat less charge from chromium in $\ddot{C}(OCH_3)C_4H_3O$ than in $\ddot{C}(OCH_3)CH_3$.

However, it would not be accurate to characterize the furyl(methoxy)carbene ligand as a poorer π acceptor than the methyl(methoxy)carbene ligand. Since the π* MO of $\ddot{C}(OCH_3)C_4H_3O$ is delocalized over the ring, changes in the population of the furyl p_x orbitals, upon complexation, must also be considered in assessing the π accepting ability of $\ddot{C}(OCH_3)C_4H_3O$. When this change (0.07 e^-) is considered, the furyl(methoxy)carbene ligand is seen to be a somewhat better acceptor than its methyl analog.

Table 8B lists the amounts of σ donation and π acceptance for the aminocarbene ligands, $\ddot{C}(NH_2)CH_3$, $\ddot{C}(NH_2)C_6H_5$ and $\ddot{C}(NH_2)C_4H_3O$. The chromium to carbene carbon distance in the calculations used to obtain this data was 2.16 Å, the crystallographically determined value for dialkylaminocarbene complexes [2]. This bond distance was employed since there have been no crystal structures reported for complexes containing an aminocarbene ligand of the type, $\ddot{C}(NH_2)Y$.

Examination of Table 8B reveals that $\ddot{C}(NH_2)CH_3$, $\ddot{C}(NH_2)C_6H_5$ and $\ddot{C}(NH_2)C_4H_3O$ are all very poor π acceptors, taking from 0.2 to 0.22 e^- from chromium. In fact, each of these carbene ligands accepts less than half the charge accepted by a carbonyl ligand in the same complex. Thus, the π* MO of an aminocarbene ligand does a poorer job of removing charge from chromium than a single carbonyl 2π MO.

In $(CO)_5CrC(NH_2)C_4H_3O$, the delocalization of the π* MO completely cancels the advantage of energetic stabilization. Only 0.01 e^- is added to the furyl pi system by complexation, so that $\ddot{C}(NH_2)C_4H_3O$ remains a poor backbonder despite having additional AO's which may accept charge.

For both cases studied, the dimethylaminocarbene ligands were found to be poorer backbonders than their unmethylated counterparts (see Table 8C). This is hardly startling, since the π* MO is destabilized by 0.8-0.9 eV when the hydrogens of $\ddot{C}(NH_2)Y$ are replaced by methyl groups.

It is surprising, however, that the σ donating abilities of $\ddot{C}(NH_2)Y$ and $\ddot{C}(N)(CH_3)_2Y$ are identical. The σ* MO is 0.7-0.8 eV less stable in the latter series. However, because the dimethylaminocarbene ligands are such poor acceptors, the chromium levels are also destabilized in $(CO)_5CrC(N(CH_3)_2)Y$. Hence, the amount of σ donation remains the same as it was in $(CO)_5CrC(NH_2)Y$.

The data presented in Table 8 agree with experimental evidence that interactions between the carbene carbon and the X group are more important in determining the ability of the carbene ligand to act as a π acceptor than interactions with the Y group. The amount of π acceptance by the methoxycarbene ligands ranges from 0.35 e^- for $\ddot{C}(OCH_3)C_6H_5$ to 0.39 e^- for $\ddot{C}(OCH_3)C_4H_3O$.

The variation in amount of π acceptance is even smaller for the aminocarbene ligands. On the other hand, when $\ddot{C}(OCH_3)CH_3$ and $\ddot{C}(NH_2)CH_3$ are placed at the same distance from the $(CO)_5Cr$ moiety, the methyl(methoxy)carbene ligand accepts 0.07 e^- more than the methyl(amino)carbene ligand. Calculations performed using the crystallographically appropriate geometries (with the central carbon of $\ddot{C}(OCH_3)CH_3$ 2.02 Å from the metal and the central carbon of $\ddot{C}(NH_2)CH_3$ 2.16 Å from the metal) accentuate these findings--the methyl(methoxy)carbene ligand accepts nearly twice as much charge as the methyl(amino)carbene ligand.

The importance of the X group is underscored when complexes of the type $(CO)_5CrC(X)_2$ are examined. Table 9 shows the amounts of σ donation and π acceptance for $(CO)_5CrC(SCH_3)CH_3$ and $(CO)_5CrC(SCH_3)_2$. In the calculations for which results are shown, the carbene carbon was placed 2.02 Å away from the chromium, in accord with the crystal structure of $(CO)_5C(SC_6H_5)CH_3$ [10,27].

Examination of the table reveals that $\ddot{C}(SCH_3)CH_3$ is a slightly poorer σ donor and a slightly better π acceptor than $\ddot{C}(OCH_3)CH_3$. The σ^* and π^* MO's of $\ddot{C}(SCH_3)CH_3$ have roughly the same localization properties as the corresponding levels in $\ddot{C}(OCH_3)CH_3$ and are more stable. Hence, the trends in σ donation and π acceptance are readily explained.

In contrast to $\ddot{C}(SCH_3)CH_3$, $\ddot{C}(SCH_3)_2$ is a very poor π acceptor. The carbene carbon's p_x orbital has a relatively high population in the free ligand, because charge density is donated to it by two sulfur atoms. Interaction between these sulfur atoms and the carbene carbon results in significant destabilization of the π^* MO (see Table 10). As a result, $\ddot{C}(SCH_3)_2$ accepts only 0.23 e^- from chromium. The σ^* MO of $\ddot{C}(SCH_3)_2$ is also destabilized compared to the corresponding MO in $\ddot{C}(SCH_3)CH_3$. Yet, $\ddot{C}(SCH_3)_2$ is a poorer σ donor than $\ddot{C}(SCH_3]CH_3$, donating only 0.39 e^- to the metal. The replacement of a good π acceptor by a poor one destabilizes the metal AO's, cancelling the advantage of $\ddot{C}(SCH_3)_2$ in having a less stable σ^* MO.

It is interesting to note that, while all of the carbene ligands are poorer acceptors than the carbonyl ligands, only in the complex, $(CO)_5CrC(SCH_3)_2$, does the trans carbonyl interact much more strongly with the chromium than a cis carbonyl. There is a substantial trans influence even when the carbene carbon of $\ddot{C}(SCH_3)_2$ is placed 2.02 Å from chromium. Yet, in that geometry, the carbene ligand accepts more charge density than the carbene ligands of $(CO)_5CrC(N(CH_3)_2)CH_3$ and $(CO)_5CrC(N(CH_3)_2)C_6H_5$. This is an indication that

Table 9. σ Donation and π Acceptance in $(CO)_5CrC(SCH_3)CH_3$ and $(CO)_5CrC(SCH_3)_2$*

Compound	Ligand	Orbital	Population		Δ
			Free Ligand	Complex	
$(CO)_5CrC(SCH_3)CH_3$	CO,cis	2π	0.00	0.51	+0.51
	CO,cis	5σ	2.00	1.50	-0.50
	CO,trans	2π	0.00	0.54	+0.54
	CO,trans	5σ	2.00	1.48	-0.52
	$C(SCH_3)CH_3$	Cpx	0.56	0.81	+0.25
	$C(SCH_3)CH_3$	Cpx+Spx	2.03	2.41	+0.38
	$C(SCH_3)CH_3$	$C2sp^2$	1.95	1.49	-0.46
$(CH)_5CrC(SCH_3)_2$	CO,cis	2π	0.00	0.52	+0.52
	CO,cis	5σ	2.00	1.50	-0.50
	CO,trans	2π	0.00	0.60	+0.60
	CO,trans	5σ	2.00	1.46	-0.54
	$C(SCH_3)_2$	Cpx	0.73	0.87	+0.14
	$C(SCH_3)_2$	Cpx+2(Spx)	3.99	4.22	+0.23
	$C(SCH_3)_2$	$C2sp^2$	1.91	1.52	-0.39

*The Cr-C(X)Y and $Cr\text{-}C(X)_2$ distance was taken as 2.02Å.

more than the π acceptor ability of a ligand must be considered in determining why the metal-carbonyl bond _trans_ to it is strengthened.

The _cis_ carbonyls of $(CO)_5CrC(SCH_3)_2$ accept less charge density than the _cis_ carbonyls of the other complexes containing carbenes (_i.e.,_ $\ddot{C}(NH_2)Y$ and $\ddot{C}(N(CH_3)_2Y)$ which are also poor backbonders. Figure 6 shows the amount of π acceptance by the _cis_ carbonyls in all of the compounds studied. Note that there are two sets of _cis_ carbonyls in each of the complexes--one set consisting of the carbonyls closest to the X group of the carbene and the other set consisting of carbonyls closest to the Y group. In the complexes containing a carbene with a

Table 10. Eigenvalues and Per Cent Characters for Some of the MO's of $\ddot{C}(SCH_3)_2$

Orbital	%Cs	%Cp	%Ss	%Sp	%Me	eiv.	eiv. $\ddot{C}(SCH_3)CH_3$
π*		63.5		35.2	1.4	-1.05	-3.74
σ*	13.6	61.8	5.5	5.5	13.7	-8.57	-9.30
π		0.0		97.2	2.7	-10.20	-12.73
σ	5.5	0.0	4.0	84.8	5.6	-10.67	-13.53

heteroatom lone pair, the populations of the two sets of carbonyls are nearly identical, when the lone pair points toward the cis carbonyls. However, when a hydrogen or methyl group is pointed toward the carbonyls, the ligands nearest the X group accept more density than those nearest to the Y group. The interaction between the cis carbonyls and the comparatively positive hydrogen or methyl group stabilizes the oxygen atom of the carbonyl group. More of the charge accepted by the carbonyl group flows to the oxygen and the group can accommodate additional charge density more readily. Thus, although $\ddot{C}(SCH_3)_2$ and the aminocarbene ligands have similar σ donor and π acceptor abilities, their overall interactions with the $(CO)_5Cr$ moiety are somewhat different in nature. All of the carbonyls participate in "soaking up" the electron density that the $C(NR_2)Y$ ligands cannot accept. Only the trans carbonyl of $(CO)_5CrC(SCH_3)_2$ is able to take the charge density not accepted by the carbene in that complex.

Throughout this discussion, we have been concerned primarily with the amounts of σ donation and π acceptance by the carbene and carbonyl ligands. Let us now consider the effect of these processes upon the ligands.

Although the carbonyl ligand accepts roughly as much charge from chromium as it donates to the metal, the carbonyl carbon becomes positively charged as a result of σ donation and π acceptance. This happens because nearly all the charge donated by CO comes from the carbon, but a fair amount (~40%) of the charge accepted by the ligand goes to the oxygen.

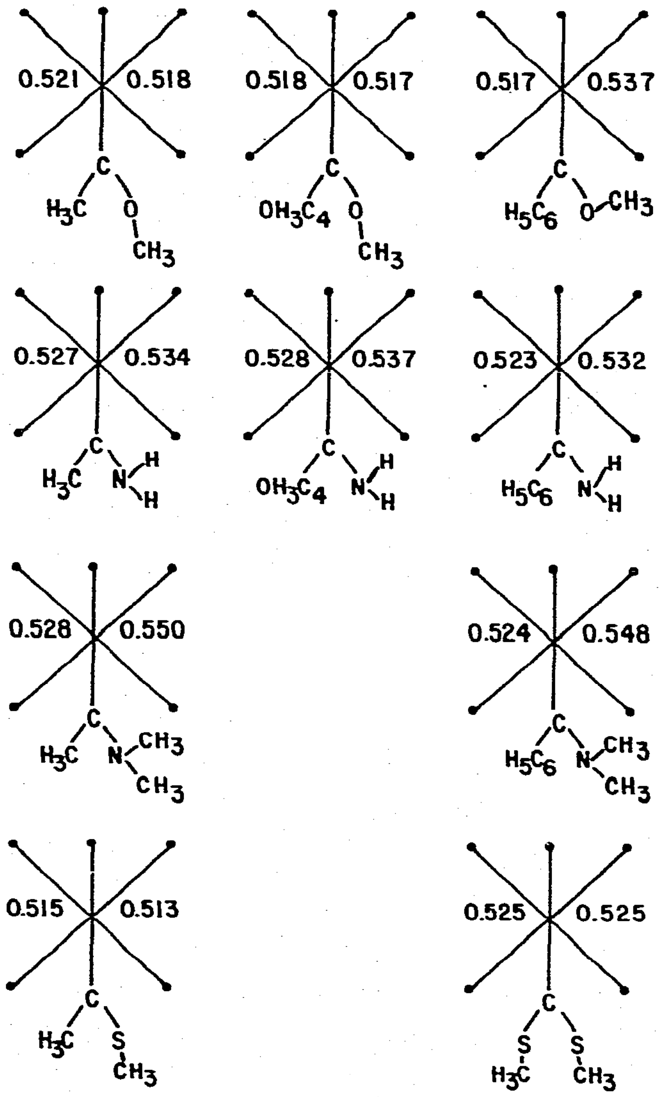

Figure 6. Acceptance by *cis* Carbonyls in $(CO)_5CrC(X)Y$.

Interaction with chromium also lowers the negative charge on the carbene carbon. Once again, nearly all of the charge donated to the chromium comes from the carbene carbon. However, less of the charge accepted (∿20-25%) flows to the heteroatom. Nevertheless, the carbene carbon loses electron density, since the total amount of charge accepted by the carbene ligand is smaller than the amount it donates to the metal.

The carbonyl carbon atom and the carbene carbon atom lose roughly the same amount of electron density in their interactions with chromium. However, a carbonyl carbon in the pentacarbonylchromium carbene complexes, $(CO)_5CrC(X)Y$, will generally be more positively charged than the carbene carbon. This is so because the carbene carbon in the free ligand, $\ddot{C}(X)Y$, is more negative than the carbon in free CO. The difference in charge is slight for methoxycarbenes but quite significant for amino- and dimethylaminocarbenes.

Our results concerning the relative charges of the carbonyl and carbene carbons are at odds with the traditional interpretation of experimental evidence (e.g., reactivity [2,28,29] and ^{13}C nmr data [30,31]) which attributes a high positive charge to carbene carbons. The observed preference of nucleophiles for attack at the carbene carbon has been explained as being the result of frontier control of the site of attack [22]. The deshielding of the ^{13}C nmr resonances of carbene carbons may also be due, in part, to the energetic isolation and spatial localization of the LUMO's of the carbene complexes. Efforts at obtaining quantitative correlations between chemical shifts and orbital energy differences are being pursued in our laboratory.

Conclusion

We have seen that there is a good deal of variation in the σ donating/π accepting abilities of the carbene ligands we have studied. The variations we have observed are in accord with the crystallographic [11-14] and spectral data [3,8] available for carbene complexes. This is gratifying, since our results are not dependent upon the input of any experimental data (the variations in σ donor/π acceptor strength are seen even when the geometries are changed in an attempt to eliminate them).

In general, our calculations on the free ligands, discussed earlier, permitted us to understand the results of the calculations on the complexes readily. However, predictions of the degree to which a ligand will interact with an organometallic moiety must be made carefully. No single characteristic of the ligand's electronic structure is the sole determinant of the ligands' σ donor/π acceptor strength.

For instance, the energetic placement of the ligands' highest occupied MO (HOMO) and LUMO is a very important factor in determining the ability of the ligand to donate charge to, or accept charge from, a metal. However, it is not the only factor. The spatial localization, degeneracy and symmetry properties of the HOMO and LUMO must also be considered. Even a substantial energy advantage may not be sufficient to overcome a disadvantage. For instance, the nondegenerate π^* MO of $\bar{C}(OCH_3)CH_3$ is $\sim$3 eV closer to the Cr3d level in $(CO)_5CrC(OCH_3)CH_3$ than the doubly degenerate 2π level of CO is. Consequently, the carbene ligand accepts more charge "per accepting orbital" than the carbonyl ligand does, but the total amount of charge accepted by $\bar{C}(OCH_3)CH_3$ is less than that accepted by CO. In complexes such as $(CO)_5CrC(NH_2)CH_3$, where the energy advantage of the carbene π^* orbital is considerably less than 3 eV, the carbene ligand accepts less charge than the carbonyl ligand, even on a "per orbital" basis.

Another factor that cannot be ignored in predicting the relative σ donor/π acceptor strengths of a series of ligands is the synergistic relationship between σ donation and π acceptance [32]. The extent to which a ligand donates charge to a metal affects the stability of the metal orbitals, altering the tendency of the metal to give charge back to the ligand. The dimethylaminocarbene ligands are poor σ donors largely because they are poor π acceptors.

Indirect measures of σ donor/π acceptor strength must also be viewed critically. For example, we have seen that the tendency of a species to have more of an effect on a ligand *trans* to it than on a ligand *cis* to it is not dependent solely on that species' π accepting ability.

In short, there are many factors which influence the ability of a ligand to interact with other groups in a complex. One must be careful to avoid oversimplification in attempting to predict how a ligand will behave when it is bonded to an organometallic moiety.

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