background counts, B_R is the ratio of background time to scan time ($B_R = 0.67$ for this data set), and T_R is the 2θ scan rate in degrees per minute. The standard deviation of I was calculated as $\sigma(I) = T_R\{S + (B_1 + B_2)/B_R^2 + q(I)^2\}^{1/2}$ where q in this case was set equal to 0.003.

(28) "International Tables for X-Ray Crystallography", Vol. I, 2nd ed, The Kynoch Press, Birmingham, England, 1965, p 98. The coordinates of equivalent positions for $P2_1/N$ are $\pm[X,Y,Z; \frac{1}{2} - X, \frac{1}{2} - Y, \frac{1}{2} + Z]$.

(29) All crystallographic programs used in structural determination and least-squares refinement were written by J. C. Calabrese. The absorption correction program DEAR (J. F. Blount) uses the Gaussian integration method of Busing and Levy. Plots were made using ORTEP (C. K. Johnson).

(30) $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100\%$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2] \times 100\%$.

MO Calculations on Metal Carbene Complexes and Metal Acyl Complexes. The Importance of the LUMO in Determining the Site of Nucleophilic Attack

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Abstract: Molecular orbital calculations have been performed on $(CO)_5CrC(OCH_3)CH_3$ and $(CO)_5MnCOCH_3$ in order to discover which factors determine the site of nucleophilic attack in metal carbene complexes and metal acyl complexes. The reaction of a nucleophile with either $(CO)_5CrC(OCH_3)CH_3$ or $(CO)_5MnCOCH_3$ is frontier, rather than charge, controlled. The differences in the energies and localization properties of the LUMO's of the two compounds indicate that attack of nucleophiles at coordinated CO is much more likely for the acyl species than for the carbene complex.

The factors which determine the site of nucleophilic attack on a polyfunctional organometallic compound are not well understood. The kinetically controlled site of nucleophilic attack of CH_3Li on $(CO)_5MnCOCH_3$ was found to be the cis CO ligand and not the acyl carbon.[1] In contrast, the kinetically controlled site of nucleophilic attack upon metal-carbene complexes, such as $(CO)_5WC(OCH_3)C_6H_5$, is the carbene carbon atom[2-4] and not the CO ligand. To gain an understanding of the differing reactivities of these structurally related compounds, we have carried out molecular orbital (MO) calculations on $(CO)_5MnCOCH_3$ and $(CO)_5CrC(OCH_3)CH_3$. The results of our calculations indicate that charge is not the factor determining the site of nucleophilic attack in the acyl and carbene complexes.[5a] Rather, the calculations indicate that there is a correlation between the site of nucleophilic attack and the location of the lowest unoccupied molecular orbital (LUMO) in the metal complexes.

Experimental Section

Parameter-free molecular orbital calculations, which have been described elsewhere,[6] were carried out on $(CO)_5CrC(OCH_3)CH_3$ and $(CO)_5MnCOCH_3$.

Clementi's double $-\zeta$ functions for neutral atoms were used as basis functions for carbon and oxygen.[7] The 1s and 2s functions were curve-fit to single $-\zeta$ form using the maximum overlap criterion.[8] For hydrogen, a 1s exponent of 1.16 was chosen, as this is the minimum energy exponent for hydrogen in methane.[9]

For the metal basis functions, the 1s-3d atomic orbitals given by Richardson et al.[10] for Cr(+) and Mn(+) were used. A 4s exponent of 2.0, and a 4p exponent of 1.6, were used for each of the metals.[11] One calculation in which a 4d orbital, with exponent 1.6, was placed on chromium was also performed. This latter expansion of the basis set had the effect of stabilizing all molecular orbitals by roughly the same amount. Since it is the separation of the energy levels (and not the actual magnitude of the eigenvalues) which is important in predicting the reactivity of the compounds, it was concluded that it was unnecessary to include the 4d orbital in the rest of the calculations.

Although the calculations were carried out in the atomic orbital basis set, it is easier to discuss the results in terms of appropriate molecular and hybrid atomic 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 carbon and oxygen atoms of the acyl and carbene ligands.

The bond distances and angles employed are shown in Table I. The carbonyl C-O distance was kept constant at 1.128 Å, the distance observed in free CO.[12] This was done so that a single set of ligand basis functions could be used for all carbonyls and is in accord with the insensitivity of the carbon-oxygen bond length for the bond order range 2-3.[13] The other bond lengths for $(CO)_5CrC(OCH_3)CH_3$ represent a synthesis of the crystal structure data for $(CO)_5CrC(OCH_3)C_6H_5$ and $[(C_6H_5)_3P]$-$(CO)_4CrC(OCH_3)CH_3$.[2] The bond distances for $(CO)_5MnCOCH_3$ are in agreement with those found for *cis*-$[(CH_3CO)(C_6H_5CO)Mn(CO)_4]^-$.[1]

Results

The possibility that nucleophilic attack on $CH_3COMn(CO)_5$ and $(CO)_5CrC(OCH_3)CH_3$ might be charge controlled was considered first. Examination of the resonance forms for $(CO)_5MnCOCH_3$ and $(CO)_5CrC(OCH_3)CH_3$ does not allow an estimation of the relative positive charge on the acyl and the carbene carbon atoms. Both the acyl carbon and the carbene carbon have π electron density donated from an oxygen atom and from a metal atom. While the oxygen atom of the acyl complex is a better π-donor to carbon than the methoxy oxygen of the carbene complex, the manganese atom of the acyl complex is a poorer π-donor to carbon than the chromium atom of the carbene complex. Since the relative magnitude of these opposing effects is not readily evaluated, resonance theory cannot be used to determine the relative positive charges on

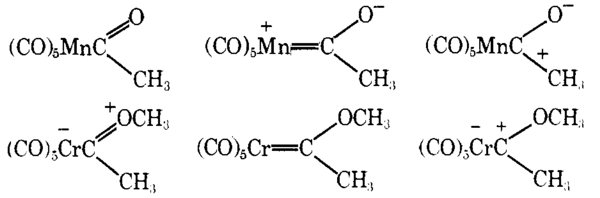
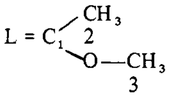
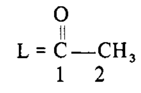


Table I. Bond Distances (Å) and Bond Angles (deg) for $(CO)_5CrC(OCH_3)CH_3$ and $(CO)_5MnCOCH_3$

	M(CO)$_5$ Moiety	
M = Cr		M = Mn
1.85	M–C$_{trans\ carbonyl}$	1.79
1.88	M–C$_{cis\ carbonyl}$	1.83
1.128	C–O	1.128
90	C$_{ax}$–M–C$_{eq}$	90
180	M–C–O	180
	M–L Moiety	
		
1.50	C$_1$–C$_2$	1.50
1.32	C–O	1.17
1.48	O–C$_3$	—
1.09	C–H	1.09
2.02	M–C$_1$	2.10
129	M–C$_1$–C$_2$	120
117	M–C$_1$–O	120
125	C$_1$–O–C$_3$	—

the acyl and on the carbene ligands in these different complexes.

The gross atomic charges derived for $(CO)_5CrC(OCH_3)CH_3$ and $(CO)_5MnCOCH_3$ via Mulliken population analysis[14] are shown in Figure 1. The results for the carbene complex, in agreement with the ESCA data of Perry et al.,[15] indicate that the carbene carbon atom is somewhat less positive than the carbonyl carbons. Nevertheless, the carbene carbon in $(CO)_5CrC(OCH_3)CH_3$ is the preferred site for nucleophilic attack. For $(CO)_5MnCOCH_3$, the acyl carbon is the most positive in the compound; yet, it is the cis carbonyl of the acyl complex that is attacked by nucleophiles. Clearly, charge is not the factor which distinguishes the carbene or acyl carbon from the carbonyl carbons.

An explanation of the reactivities of $(CO)_5MnCOCH_3$ and $(CO)_5CrC(OCH_3)CH_3$ may, however, be obtained from the theory of frontier control,[16,17] which emphasizes the importance of a compound's HOMO or LUMO in determining which sites in the molecule will be most susceptible to attack by an electrophile or a nucleophile. A striking result of the MO calculations on the carbene complex (see Figure 2) is the marked separation of the LUMO from all of the other MO's. The LUMO lies 4.6 eV below the next lowest unoccupied MO and 6.6 eV above the highest occupied MO (HOMO). The LUMO is localized on the carbene carbon: the LUMO's major component is the carbene carbon $2p_x$ orbital which constitutes 60% of the level. The preference for nucleophilic attack at the carbene carbon can be explained as a result of the spatial localization and energetic isolation of the LUMO of the complex.

On the other hand, the LUMO of $(CO)_5MnCOCH_3$ lies very close to a series of empty MO's, most of which are essentially pure carbonyl levels. Unlike the spatially localized LUMO of the carbene complex, the LUMO of $(CO)_5MnCOCH_3$ is diffuse and contains substantial amounts both of acyl carbon character (24%) and of carbonyl character (a total of 50% 2π character from the four equatorial CO groups). Thus, for $(CO)_5MnCOCH_3$, examination of the LUMO alone does not permit a prediction of the preferred site of attack. There are too many closely spaced empty levels of various character for an unequivocal prediction of the compound's reactivity to be made.

Discussion

The results of the MO calculations on $(CO)_3CrC(OCH_3)CH_3$ and $(CO)_5MnCOCH_3$ may be more easily understood after a brief examination of the nature of the carbene and acyl ligands. Since the C–O bond in CH_3CO^- is shorter than that in $CH_3\ddot{C}(OCH_3)$, the MO's of the acyl anion which are bonding in the CO region are relatively more stable than the corresponding levels of the carbene (the opposite being true for antibonding MO's). Furthermore, there is more π bonding between carbon and oxygen in CH_3CO^- than in $CH_3\ddot{C}(OCH_3)$. As a consequence of this, there is a greater separation of the π and π^* levels for the acyl ligand than for the carbene. In the carbene, the π level is essentially an oxygen lone pair, while the π^* level is largely localized on the carbon atom. These differences in electronic structure and charge distribution (Figures 3 and 4) influence the way in which the ligands act in the pentacarbonyl complexes. The relative placement of the HOMO and LUMO of each ligand is especially significant, since the Fock matrix diagonal terms,[18] shown in Figure 2, reflect the order of the orbital energies of the free ligands.

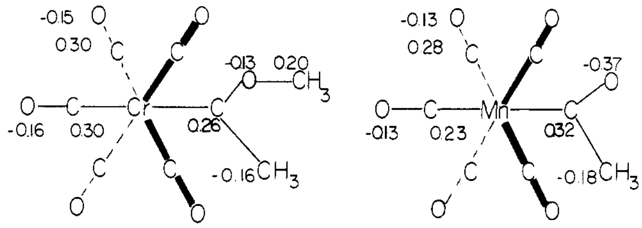


Figure 1. Gross atomic charges for $(CO)_5CrC(OCH_3)CH_3$ and $(CO)_5MnCOCH_3$.

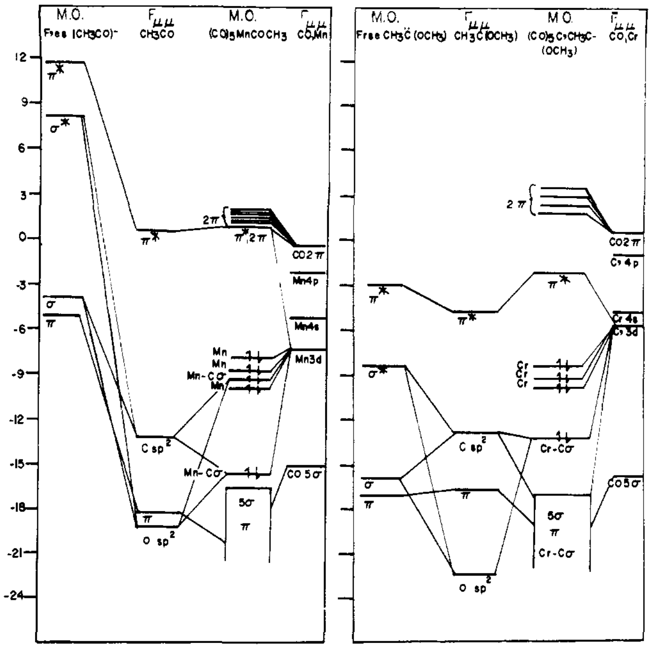
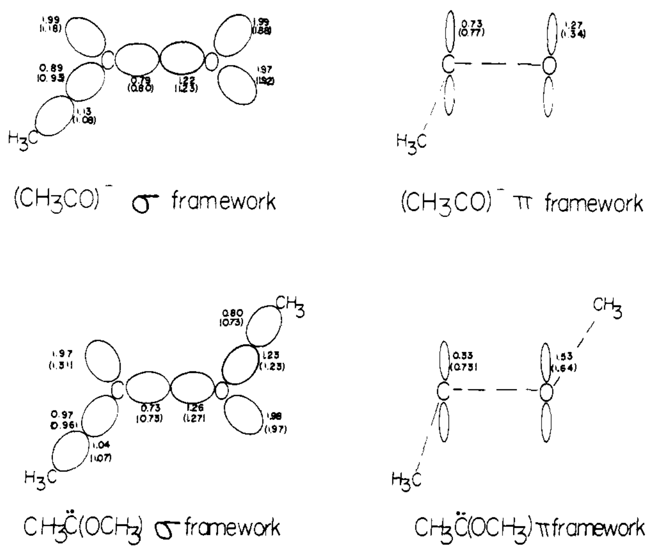


Figure 2. Selected molecular orbitals of $(CO)_5MnCOCH_3$ and $(CO)_5CrC(OCH_3)CH_3$. Molecular orbitals for the free acyl and carbene ligands are labeled by their symmetry with respect to the C–O bond. Fock matrix diagonal elements correspond to functions in the transformed (ligand molecular or hybridized) basis. Molecular orbitals of the complexes are designated by their major component or bonding function.

Figure 3 shows the effects of complexation on the electronic distribution of the ligands. Comparison of the populations of the various hybrid atomic orbitals in the free ligands and in the complexes reveals that charge is donated from the central carbon's σ lone pair and accepted into the antibonding (π^*) combination of the p orbitals (Op_x and Cp_x). The acyl ligand is a better σ donor and a poorer π acceptor than the carbene ligand; this has a marked effect on



$(CH_3CO)^-$ σ framework

$(CH_3CO)^-$ π framework

$CH_3\ddot{C}(OCH_3)$ σ framework

$CH_3\ddot{C}(OCH_3)$ π framework

Figure 3. Mulliken populations of some of the atomic orbitals of the acyl and carbene ligands. The atomic orbitals of the oxygen and central carbon atoms have been combined into sp^2 hybrids. The numbers in parentheses represent the orbital populations for the ligands in the complexes; the other numbers are the populations for the free ligands.

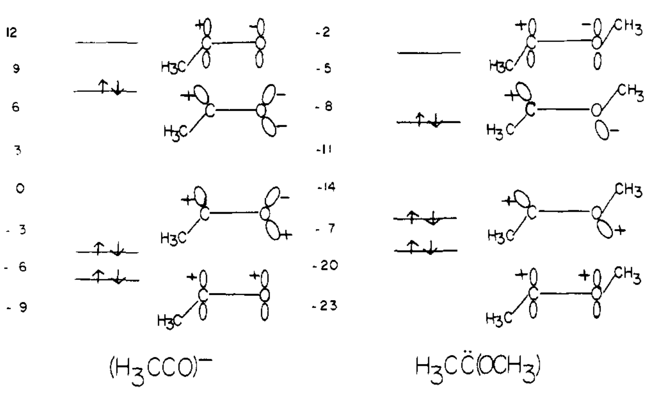


Figure 4. Some molecular orbitals of CH_3CO^- and $CH_3\ddot{C}(OCH_3)$. Note that the energy scales differ by 14 eV, a consequence of the difference in charge between the ligands.

the electronic structures of the $M(CO)_5$ moieties of the complexes.

The charge which the acyl ligand initially donates to manganese is passed to the carbonyl 2π levels, stabilizing them. Thus, the M_{3d}–$CO_{2\pi}$ separation is roughly the same for both the manganese and chromium complexes. This separation generally increases as the atomic number of the metal increases,[19] with a consequent lowering in the amount of back-bonding from M to CO. For $(CO)_5MnCOCH_3$ and $(CO)_5CrC(OCH_3)CH_3$, the populations of the CO 2π orbitals are virtually identical (see Table II), and the eigenvalues of the unoccupied, mainly CO 2π levels are nearly the same.

In $(CO)_5MnCOCH_3$, these 2π levels are found in very close proximity to the acyl π* level. However, the carbene π* level, which is essentially a carbon p orbital, is far more stable than the corresponding acyl level, which is truly a π* orbital. Thus, the LUMO of the carbene complex is energetically distinct from its other low-lying empty orbitals, while the LUMO of $(CO)_5MnCOCH_3$ lies in a band of closely spaced, unoccupied levels with various localization properties.

Table II. Mulliken Populations of CO 5σ and 2π Levels

	Free ligands		$(CO)_5CrC(OCH_3)CH_3$	$(CO)_5MnCOCH_3$
5σ	2.00	Cis	1.36	1.36
		Trans	1.34	1.34
2π	0.00	Cis	0.48	0.50
		Trans	0.55	0.55

Conclusion

Our molecular orbital calculations on $(CO)_5CrC(OCH_3)CH_3$ reveal that the LUMO is energetically isolated and spatially localized on the carbene carbon atom. Frontier orbital control of nucleophilic attack on the carbene complexes predicts attack at the carbene carbon atom. Our calculations for the acyl complex $(CO)_5MnCOCH_3$ indicate that there are too many closely spaced empty levels associated with both the acyl carbon and coordinated CO to make a prediction of the site of nucleophilic attack based on the location of the LUMO. Comparison of the calculations for the carbene complex and for the acyl complex indicates that attack of nucleophiles at coordinated CO is much more likely for the acyl complex than for the carbene complex. Thus, while our calculations do not allow a prediction of the site of attack on an acyl complex, they allow an understanding of the differences in the reactivity of metal-carbene complexes and of metal-acyl complexes.

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