Cis Labilization of Ligand Dissociation. 5. A Molecular Orbital Investigation[1]

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Abstract: The process of ligand dissociation from a transition metal carbonyl center has been examined using a nonempirical molecular orbital approach. The energy requirements for CO dissociation from $Mn(CO)_6^+$, and from $Mn(CO)_5X$, where X = Br or H, have been investigated. Consideration of the interaction between individual CO groups and the remainder of the molecule in the ground state structures of these species does not provide a rationale for the relative rates of CO dissociations. Instead, the relative energies for CO dissociation appear to depend upon the relative energies of stabilization resulting from geometrical relaxation of the metal carbonyl fragment which remains following CO loss. The cis CO groups of $Mn(CO)_5Br$ are found to be more labile than the trans CO group or than the CO groups of $Mn(CO)_6^+$, because in formation of the transition state more stabilization energy derives from relaxation of the $Mn(CO)_4Br$ fragment. Ligands which have at least one potential π-donor orbital labilize the cis carbonyl groups to the greatest extent, as a result of an improved bonding interaction in the five-coordinate fragment. The calculations suggest that the σ-bonding ability of a ligand such as H is less influential than π-bonding characteristics.

Introduction

Previous papers in this series[2-5] have dealt with the kinetics of thermal substitution reactions of six-coordinate transition metal carbonyl compounds, in which dissociation of a carbonyl ligand is the rate-determining step:

$$M-CO \xrightarrow[\text{slow}]{-CO} M \xrightarrow[\text{fast}]{+L} M-L$$
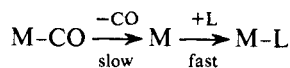
M = metal complex

L = ligand

The information obtained from our studies, as well as from several other investigations of the kinetics of carbonyl substitution reactions,[6-8] have given an indication of the influence of other ligands (heteroligands) in the complex on the rate of CO dissociation and the stereochemical relationship between the departing CO group and the ligands which remain. The reactivity patterns that emerge are not readily understood in terms of current descriptions of the bonding of CO to the metal in the six-coordinate, ground state molecules. We have proposed a site preference model, in which the effect of other ligands than CO on the energy of the transition state plays a crucial role.[4] Experimental support for this model has been discussed in previous papers. The purpose of the present contribution is to examine by means of a theoretical approach the energetics of metal–carbonyl interactions in both the ground and transition states, and their relationships to the kinetics of substitution reactions.

The absence of a relationship between the bonding in the six-coordinate ground state molecule and the kinetics of CO dissociation is exemplified by the kinetics data for exchange of ^{13}CO for ^{12}CO in $Mn(CO)_5Br$.[2] According to the usual π-bonding arguments,[9] the extent of π-back-bonding to a CO group increases as the π-acceptor ability of a heteroligand competing for the back-bonding electrons decreases. In this case the heteroligand is halogen, with filled π orbitals. Because both π-acceptor orbitals of the trans carbonyl are of appropriate symmetry for competition with a π orbital of the heteroligand, as compared with only one of the π-acceptor orbitals of a cis carbonyl, the trans carbonyl should have the stronger π bond to the complex. This is consistent with the experimental result that a trans carbonyl is less labile toward substitution than a cis carbonyl. In addition, however, the cis carbonyls of $Mn(CO)_5Br$ are considerably more labile than the carbonyls of $Mn(CO)_6^+$; this is not consistent with the more intense competition for metal d_π electrons in the hexacarbonyl. Furthermore, labilization of cis carbonyls by a heteroligand is not unique to halogens; other ligands also labilize the cis carbonyl groups to varying degrees.[4] The kinetics data suggest that many ligands which are weaker π acids than CO labilize the cis carbonyl groups, a result at variance with the traditional π bonding concepts.

Before discarding an explanation of cis labilization in terms of ground state properties, the total σ and π bonding of the carbonyl groups to the complex in the ground state must be examined. Ligands which are poorer π acceptors than CO might be expected to cause an increase in negative charge at the metal center, which could weaken the M–CO σ bonds and account for the observed trend in substitution kinetics. The strengths of M–CO σ bonds relative to the π bonds, and the extent to which they change as a function of the bonding capabilities of the heteroligand, must therefore be assessed.

Several other contributions to the energy for dissociation of CO cannot be inferred directly from the ground state description. These contributions arise as the distance between the metal complex and the leaving CO group increases, and the system approaches the transition state. Does charge repolarization in the transition state, as modified by the heteroligand, have important consequences? Similarly, may geometrical rearrangement in the approach to the transition state modify the bonding capabilities sufficiently to alter the energetics of the process? It has been established that CO loss is an essentially dissociative process.[4,6-8,10] This means that the transition state resembles closely in energy and geometry the most stable geometrical form of a five-coordinate intermediate. What is the most stable geometry for the five-coordinate intermediate, and what is the nature of the potential surface connecting energy minima? The answers to these questions require knowledge of the potential energy surfaces of transition metal carbonyl complexes as a function of metal–carbonyl dissociation.

Methods

Considerable insight into the electronic structures of metal carbonyl compounds has already been gained from theoretical investigations employing models at various levels of sophistication. Hillier and his co-workers have reported ab initio (single determinant, slightly extended basis) molecular orbital calculations on several molecules important to this study. Examples include $Cr(CO)_6$,[11] $Mn(CO)_5Cl$,[12] $Mn(CO)_5H$,[12] and

$Cr(CO)_5NH_3$.[13] Unfortunately, it is prohibitively expensive at the present time to examine more than a few points on a potential energy surface using ab initio techniques.

Several more approximate methods may be used in the attempt to gain information on the energetics of the dissociative process. Hoffmann has employed extended Hückel type calculations to indicate individual orbital contributions to the stability of metal carbonyl complexes.[14,15] Burdett has developed an angular overlap model for predicting the lowest energy geometries of transition metal complex species.[16] Unfortunately, the extended Hückel or simple angular overlap procedures are not suitable for many aspects of the present work. For example, in estimating the relative values of individual electronic terms, such as the σ and π bonding, a particular model assumption or choice of parametrization may significantly prejudice the results.

The Fenske–Hall approximate MO method[17] contains no variable or empirical parameters. The ground states of the systems of interest to this study have already been examined by this method.[18] Results from this model have been found to correlate well with such physical properties of the complexes as carbonyl force constants,[19] which are dependent upon the electron distribution in the complex, and ionization potentials,[20] which are dependent upon the orbital energetics. The method has the further advantage that, although in many instances the results may be compared with extended Hückel studies, the method also maintains sufficient rigor to be compared with ab initio calculations. For instance, the overlap of basis functions is treated exactly, there is a clear distinction between electron–electron interactions and all other energy terms, and the method is iterative on the wave function.

Energy Terms

Total Energy. A full discussion of the molecular energy as determined by the Fenske–Hall model, and its chemical significance, is presented in the Ph.D. Thesis of W. C. Yeakel.[21]

The total molecular energy, E_T, is rigorously defined in the Hartree–Fock–Roothaan (HFR) formalism as

$$E_T = \sum_a \sum_b D_{ab}H_{ab} + \frac{1}{2}\sum_A \sum_B \frac{Z_A Z_B}{R_{AB}} \quad (1)$$

In the first term the sums are over all basis functions a and b. The quantities D_{ab} are the usual density matrix elements defined as

$$D_{ab} = \sum_i \text{occupation}(i) \times C_{ai}C_{bi} \quad (2)$$

where the sum is over molecular orbitals and C_{ai} is the coefficient of orbital a in eigenvector i. The H_{ab} elements are identical with the Fock matrix elements, F_{ab}, with the exception that all electron–electron interactions are counted once instead of twice. The second term in eq 1 represents the nuclear–nuclear repulsions.

The total energy of the approximate method may be defined in an equivalent manner. This is possible because the model makes a clear distinction between contributions to the energy from electron–electron interactions and all other contributions to the energy. An additional term must be added to the approximate total energy to account for the changes in core energy that are not treated explicitly in the variational portion of the problem. Because only differences in energy are significant, it is necessary to include only those portions of the core energy which change with the valence structure. The additional term, E_c, contains the electron repulsions between the core and valence electrons on the same center, and also the electrostatic interactions between each core electron and the nuclei and electrons of other centers. It does not require the calculation of any other integrals than those used in the variational portion of the problem. The energy

$$\tilde{E}_p = \sum_a \sum_b \tilde{D}_{ab}\tilde{H}_{ab} + \frac{1}{2}\sum_A \sum_B \frac{Z_A Z_B}{R_{AB}} + E_c \quad (3)$$

is referred to as the partial approximate total energy. In this expression the sum over a and b refers only to the valence orbitals. The energy is approximate because the $\tilde{H}_{ab}$ and $\tilde{D}_{ab}$ matrix elements are determined by an approximate method, and it is partial because the invariant portions of the core energy have not been included.

The energy units of these calculations are atomic units (1 au = 27.21 eV). It must be emphasized that, because of the approximate nature of the Fock matrix elements, a calculated value for the energy change in any single process is not likely to accurately reproduce the experimentally determined value. This is especially true for the present study, where the process of interest is the breaking of a metal–carbonyl bond. Electron correlation may be expected to significantly influence the energy change predicted for this process.[22] In some instances, as pointed out in later discussion, a single determinant wave function is totally incapable of describing the system. However, the relative values of calculated energies may be expected to have meaning within a closely related series of calculations. It is possible to scale the calculated numbers within a series to obtain familiar values, but this serves no real advantage. We simply report calculated energies in terms of approximate energy units (aeu). The use of these units will stress the comparisons of energy values in a particular series.

Energy Partitioning. So that the calculations may suggest models for the energy changes of these reactions which may be extended to other systems, it is important that the type and behavior of individual contributions to the energy be identified. This analysis is aided if the energy obtained from a calculation is partitioned into separate additive contributions. Many approaches to this problem have been suggested, and several are implemented in the course of this work. The approach commonly used with extended Hückel calculations assumes that the total energy is equal to the sum of the one-electron canonical orbital energies. Diagrams similar to those of Walsh[23] are then used to interpret the total energy. The nature of this approximation, and its limitations, have been discussed extensively. In this study we examine some systems which possess a net charge, and others in which charge repolarization plays an important role. It is under these circumstances that a sum of the orbital eigenvalues has limited value.

Equation 1 suggests that the total energy may be partitioned in terms of the elements of an electronic energy matrix **E**, and a nuclear repulsion matrix, **Z**. The matrix elements of **E** are defined as

$$E_{ab} = D_{ab}H_{ab}$$

The elements of **Z** are defined as

$$Z_{AB} = \frac{1}{2}\frac{Z_A Z_B}{R_{AB}}$$

Thus the total energy is written as

$$E_T = \sum_a \sum_b E_{ab} + \sum_A \sum_B Z_{AB}$$

The element E_{ab} represents the energy obtained from interaction of basis function a with basis function b. When functions a and b are on different centers, a negative E_{ab} term implies a bonding interaction. This partitioning of the energy parallels a Mulliken type of partitioning of the electronic charge.[24] The difference is that a matrix element H_{ab} replaces an overlap matrix element S_{ab} in the definition. The advantage is that the interactions can be analyzed in units of energy which are distinct portions of the total energy. Changes in total energy may then be traced to the most important individual interaction terms.

Table I. Overlap Populations between Carbonyl Ligands and the Metal Complex[a]

| | Mn(CO)$_5$Br | | |
	Cis	Trans	Mn(CO)$_6^+$
	A. With Metal 3d Orbitals Only		
π	0.160	0.185	0.143
σ	0.181	0.215	0.188
	0.341	0.400	0.331
	B. With Metal 3d, 4s, and 4p Orbitals		
π	0.124	0.135	0.101
σ	0.331	0.291	0.321
	0.455	0.426	0.422
	C. With Total Metal Complex Fragment		
π	0.106	0.112	0.091
σ	0.162	0.153	0.164
	0.268	0.265	0.255

[a] The symmetry labels refer to the basis of the isolated carbonyl unit.

Table II. Contributions to the Total Energy from Interaction of the Carbonyls with the Metal Complex

| | Mn(CO)$_5$Br | | |
	Cis CO	Trans CO	Mn(CO)$_6^+$
	A. With the Metal		
π	−3.052	−3.356	−2.381
σ	−7.097	−6.463	−6.358
	−10.149	−9.819	−8.739
	B. With the Total Metal Complex Fragment		
π	−4.584	−4.816	−3.586
σ	−6.981	−6.690	−6.483
	−11.565	−11.507	−10.069

Approach to M–CO Dissociation. The major element in the reaction coordinate for CO dissociation is the distance between the leaving carbonyl group and the remaining metal complex. Initially, the analysis will focus on two regions of the potential surface. The first region is the ground state, in which the carbonyl group is at the equilibrium bonding distance to the metal. The second region, the transition state, is approximated as having the carbonyl group removed to infinity from the complex. We refer to the isolated 16-electron five-coordinate metal complex remaining after removal of the carbonyl group as the complex fragment. Because the loss of CO from the six-coordinate ground state molecule is a purely dissociative process, the transition state in the process and the complex fragment should be very close in energy.

Optimization of all the geometrical degrees of freedom in these two regions of the surface would be prohibitively time consuming. A more constrained, but nevertheless revealing, procedure was adopted. This involves successively activating individual degrees of freedom of the system, while constraining all others to remain constant. Thus, important energy changes may be associated with individual stages of the analysis. For instance, a first step is to assume that, other than the distance between metal and departing CO, the geometry of the system remains fixed. The next step is to allow angular distortions within the ground state and also in the complex fragment. Finally, the distances between bonding atoms may also be optimized. As each degree of freedom is activated, the required number of calculations increases immensely.

Results

Attention is focused initially on CO dissociation from the cis and trans positions of Mn(CO)$_5$Br and from Mn(CO)$_6^+$. The results are described in order of the various levels of assumption regarding the constraints placed on the ground and transition states.

The basic features of the ground state electronic structures of octahedral metal hexacarbonyls[18] and metal pentacarbonyl halides[17] have been discussed previously. For the present calculations it is assumed that all metal–carbon distances are 1.85 Å, all carbon–oxygen distances are 1.15 Å, the metal–bromine distance is 2.50 Å, and the angle between all adjacent ligands is 90°.[25] The basis functions are the same as those used previously with the metal 4s and 4p exponents fixed at 2.0.[17]

Contributing Bond Energies in the Ground State. If the dissociation energy is determined by the contributing bond energy[26] between the carbonyl and the complex in the ground state, then a relationship should exist between the dissociation rates and bonding properties. The bonding properties of the

ground state wave function may be assessed in several ways. One method is in terms of Mulliken populations.[24] Population of the carbonyl 2π (π^*) orbitals is a measure of π back-bonding from the metal complex. The carbonyl 2π populations in Mn(CO)$_5$Br are 0.491 e$^-$ for the cis carbonyls and 0.561 e$^-$ for the trans carbonyl. Thus, as indicated in the Introduction, arguments based on the extent of π bonding indicate that the cis carbonyls should be more labile than the trans. However, the carbonyl 2π populations in Mn(CO)$_6^+$ are still lower at 0.434 e$^-$, yet this complex is relatively inert toward dissociation. Thus the variations in CO 2π populations do not account for this reactivity trend.

Reduction of the carbonyl 5σ population is a measure of donation to the metal in the formation of a dative bond from C to metal. σ bonding may be much stronger than the π bonding.[11] The carbonyl 5σ populations in Mn(CO)$_5$Br are 1.529 e$^-$ for the cis carbonyls and 1.485 e$^-$ for the trans carbonyl. While these values are very similar, the variation is in a direction consistent with relative labilities. The carbonyl 5σ populations in Mn(CO)$_6^+$ are 1.490 e$^-$, indicating only slightly better σ donation than the cis carbonyls of Mn(CO)$_5$Br. This trend of σ bonding is consistent with the observed behavior, but it is difficult to judge the significance of these small changes in relation to the larger changes in π populations. This level of population analysis does not indicate the relative magnitude of individual contributions to the bond.

A more direct approach is to examine the various overlap populations between the carbonyl and the complex. This analysis is provided in Table I. The π overlap populations support the comments made previously. The σ overlap populations are more difficult to assess because of the substantial interaction between the carbonyl 5σ and the metal virtual 4s and 4p levels. The σ interaction with the metal d levels is again consistent with the observed kinetics. When the σ and π overlap populations are combined, however, the cis and trans carbonyls of Mn(CO)$_5$Br appear quite similar, and both might be expected to be more inert than the carbonyls of Mn(CO)$_6^+$. Thus analysis of the total overlap populations is either inconclusive or suggests behavior which is not consistent with experimental observation.

The preceding analysis of the metal–carbonyl interaction based upon the ground state wave function still suffers the disadvantage that the overlap populations, in units of electrons, are not a direct measure of the energetics associated with the interaction. σ overlap populations receive the same weighting as π overlap populations, although the stabilization energy associated with each bonding interaction is expected to be different. By contrast, the energy matrix terms between two centers represent the contribution to the total molecular *energy* from overlap interaction of the two centers. Various components of these bonding energies are listed in Table II. Again, the σ and π components are separated for the different metal–carbonyl interactions. Although the relative values have changed, the conclusions concerning the energies of the

metal–carbonyl bonds remain the same. There is little difference between the total bonding of cis and trans carbonyls of $Mn(CO)_5Br$, and both appear to be more strongly bound than the carbonyls of $Mn(CO)_6^+$. Thus, a bonding model based upon ground state structures alone does not provide a plausible explanation for the observed labilization effects.

Carbonyl Dissociation from the Metal Fragment. The energy separations between the ground states and the states characterized by complete carbonyl dissociation are examined next. The difficulty in theoretically predicting dissociation energies was stressed above. However, we are interested in the comparative energies for cis and trans carbonyl removal from $Mn(CO)_5Br$, and how these compare with the energy of carbonyl removal from $Mn(CO)_6^+$. The quantities of interest are actually second differences in the energy, and many of the errors caused by the approximations or the neglect of configuration interaction largely cancel. This point should be made especially clear for the comparison of cis and trans carbonyl removal from $Mn(CO)_5Br$. Both processes begin at a common ground state, and yield the respective intermediates, as illustrated schematically in Figure 1. For the present the different $Mn(CO)_4Br$ fragments are simply labeled as cis or trans vacant, indicating loss of CO from cis or trans positions, respectively. Although this terminology implies an overall square-based pyramidal (SBP) geometry for the fragments, it does not rule out relaxed geometries for the fragments which appear more closely related to a trigonal bipyramid (vide infra).

The quantity of interest is ΔE(trans loss) $- \Delta E$(cis loss). Any errors in the energies of $Mn(CO)_5Br$ or the free carbonyl group cancel entirely in this comparison. Any contributions to the interactions of the carbonyls with the metal complex that remain relatively constant also vanish. Under the general constraint of rigid geometry in the metal carbonyl fragment, the question of whether a cis or trans CO dissociation is preferred becomes a question of the relative energies of structures **1** and **2**.

cis vacant
1

trans vacant
2

The preferential siting of the heteroligand in an SBP five-coordinate species has been examined in separate studies by Burdett[16b] and Rossi and Hoffmann.[14] The angular overlap model predicts equal stability for the two isomers. Inclusion of the quartic terms in the overlap, rather than just the quadratic terms, leads to the suggestion that weak σ donors prefer the basal site. However, the difference in energies is not expected to be large. Rossi and Hoffmann, using an extended Hückel approach, also find that the apical and basal σ bonds are very similar for d^6 $M(CO)_5$. When the angle between the apical ligand and the basal ligands is $90°$, the basal bonds are slightly stronger. However, as the angle increases the basal bonds rapidly become weaker. The situation is similar for π bonding. When the angle is $90°$ the π interaction is greater in the basal site, but for just slightly greater angles it is greater in the apical site. It is difficult from these results to construct convincing arguments for a preferred site geometry without invoking experimental evidence.[16b]

Our calculations, with all distances and angles in $Mn(CO)_4Br$ constrained to their original values, show a clear preference for the cis-vacant over the trans-vacant structure. Cis-vacant $Mn(CO)_4Br$ + CO is calculated to be 1.20 aeu in energy above $Mn(CO)_5Br$, as compared with 1.51 aeu for trans-vacant $Mn(CO)_4Br$ + CO. However, the energy of $Mn(CO)_5^+$ + CO relative to $Mn(CO)_6^+$ is calculated to be 1.19 aeu. Thus the
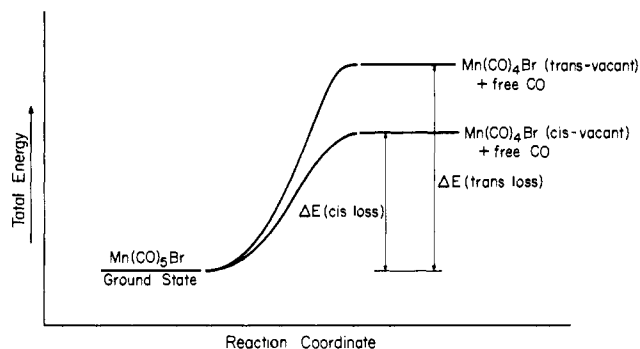
Figure 1. Energy relationships between ground state and metal complex fragment + CO, assuming rigid geometry, for loss of CO from cis or trans positions in $Mn(CO)_5Br$.

assumption of rigid $90°$ angle geometries leads to a clear prediction of preferential cis CO loss from $Mn(CO)_5Br$, but not of an overall labilization relative to $Mn(CO)_6^+$.

Analysis of the possible contributions to the energy changes in proceeding from $Mn(CO)_5Br$ to either **1** or **2** suggests that the major source of the difference in energies arises from an unfavorable energy term due to extensive charge redistribution upon loss of CO. The energy associated with this electron reorganization was identified with the aid of an energy decomposition analysis similar to that of Morokuma,[27] in which the total wave function of $Mn(CO)_5Br$ was created in a stepwise manner from the wave functions of the isolated $Mn(CO)_4Br$ and CO portions. Approximate methods which are not iterative on the wave function fail to reveal this important effect.

Angular Relaxations. Geometrical relaxation in the course of CO loss may play an important role in determining the relative rates of carbonyl dissociation. Consider first the optimized angular geometries of the parent molecules. The ground state of $Mn(CO)_6^+$ has no angular degrees of freedom under the constraint that its symmetry is maintained. The molecule $Mn(CO)_5Br$ has one degree of freedom in C_{4v}, the angle θ between the metal–halogen and the metal–cis carbonyl bond axes, as in **3**. The angle θ has been found to be less than

3
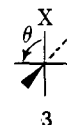
$90°$ for a wide variety of heteroligands.[28] The minimum energy angle in $Mn(CO)_5Br$ as obtained from our calculations, maintaining linear Mn–C–O groups, is $\sim 87°$; the energy is lowered 0.003 aeu from that for the $90°$ geometry. It is not likely that the energy stabilization derived from this degree of freedom is of any serious consequence in cis labilization.

The angular relaxations of the intermediate fragments require more extensive analysis. Loss of CO may reduce the symmetry and greatly increases the number of possible conformations. The fragment $Mn(CO)_5^+$ may maintain C_{4v} symmetry as the angle θ between the apical and basal carbonyl groups changes, **4**. We find the minimum energy geometry of

4

$Mn(CO)_5^+$ to occur for $\theta = 97°$. The total energy is 0.116 aeu below that for the intermediate with $\theta = 90°$. The magnitude of this stabilization is certainly large enough to influence the energetics of carbonyl dissociation.

The $Mn(CO)_4Br$ fragment geometries follow from the $Mn(CO)_5^+$ geometries with bromide substitution for one of the carbonyls. The calculated optimal angle θ in $Mn(CO)_4Br$

in the fragment of C_{4v} symmetry, **5**, is 93.5°. This geometry is 0.027 aeu more stable than the 90° geometry.

5

Bromide substitution in a basal position provides a low-symmetry SBP complex derived from cis carbonyl loss. For this geometry we investigated the energetics as a function of an equivalent angle between the basal ligands (three carbonyls and bromide) and the apical carbonyl group, **6**. The maximum

6

stabilization of 0.194 aeu ($\theta = 101°$) relative to the 90° geometry is a lower limit to what may be obtained from full optimization of a geometry involving Br in a basal position in a distorted SBP.

A geometry which deserves special comment is the C_{2v} structure **7**, characterized by the angles θ and ϕ. Our calcu-

7
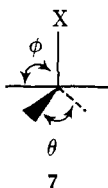
lations suggest that this geometry, with $\theta = 98°$ and $\phi = 85°$, is the most stable $Mn(CO)_4Br$ structure. The energy of the optimal geometry is 0.278 aeu below that of structure **1**.

The origins of the stabilization energy resulting from angular distortions may be understood by examining the bonding interactions of the $Mn(CO)_4^+$ fragment and Br^-. For the C_{2v} geometry depicted in **7**, the $Mn(CO)_4^+$ fragment is near the ideal geometry predicted by extended Hückel calculations.[15] This fragment possesses two low-lying vacant metal levels. The first, of a_1 symmetry, is suitable for σ bond formation with Br^-. The second, of b_2 symmetry, is capable of π interaction with one of the Br 4p orbitals. These interactions are particularly
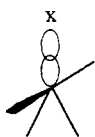
a_1 (σ) interaction $\qquad$ b_2 (π) interaction

interesting in comparison to the bonding interactions in the ground state of $Mn(CO)_5Br$. In both instances Br^- may act as a σ donor into an empty metal level. Br^- may also act as a single π donor to an empty metal level in C_{2v} $Mn(CO)_4Br$, but in $Mn(CO)_5Br$ the same bromide electrons experience antibonding interaction with fully occupied metal levels. It is interesting that the same σ donor properties of the heteroligand which result in a strengthening of the metal–CO bonds in the ground state molecule are also responsible for an increased overall stabilization of the five-coordinate fragment as a whole.

The origins of the stabilization of geometry **6** when θ increases from 90° are the same as those just discussed for geometry **7**, although the lower symmetry of geometry **6** complicates discussion of the nodal surfaces of the individual orbitals. Elian and Hoffmann[15] have shown that when θ increases from 90° in geometry **6**, the π interaction of the basal ligands with a metal ($3d_{z^2}$, 4p) hybrid-type orbital increases. The π interaction in the optimum SBP geometry is not as favorable as for the C_{2v} geometry, and thus the SBP geometry is not as stable.

The magnitude of these interactions may be observed in the energy matrix elements of the calculations. As a computational experiment to test the necessity for invoking π-bonding arguments, the calculations were repeated with the overlap and Fock off-diagonal matrix elements between the bromide π levels and the complex set to zero. Without these π interactions, the stabilization of the C_{2v} fragment compared to the rigid cis-vacant fragment is only 0.06 aeu.

Effects of σ Donor Ligands. It is of interest to compare the labilizing effects of H^- as a ligand with those of Br^-. The substitution kinetics of $HMn(CO)_5$ may not be compared directly with the kinetics of $BrMn(CO)_5$ because substitution of $HMn(CO)_5$ does not proceed through a dissociative mechanism.[7,29] However, in the rhenium series, where the relative substitution behavior is generally similar to that found in the manganese series, the hydride complex is found to be relatively inert toward substitution via a CO dissociative path.[30] The rate of substitution of $HRe(CO)_5$ is several orders of magnitude slower than the rate for $BrRe(CO)_5$. From the results of the preceding sections, it may be anticipated that the lack of π donor capability for H^- is an important factor.

Model calculations on $HMn(CO)_5$ and fragment geometries were performed. The cis-vacant fragment, **1**, of $HMn(CO)_4$ is only 0.04 aeu more stable than the trans-vacant fragment, **2**, for the rigid geometries. This difference is much less than the 0.31 aeu difference found for the corresponding $Mn(CO)_5$-Br geometries. Also, the energy stabilization obtained from relaxation of the SBP fragments is more similar to that obtained for $Mn(CO)_5^+$ than for $Mn(CO)_4Br$. The preferred substitution site is still cis, but based upon the energy of the transition state relative to the ground state, the cis CO groups of $HMn(CO)_5$ are not expected to be significantly more labile through a dissociative mechanism than the carbonyls of $Mn(CO)_6^+$.

Calculations were also carried out to investigate the effect of variations in the σ donor ability of the heteroligand. The set of calculations on the various geometries of $HMn(CO)_5$ and $HMn(CO)_4$ were repeated with the Fock matrix element for the hydrogen 1s function lowered by 3 eV from the value determined normally in each calculation. The lowered energy of this term has the effect of decreasing the hydrogen donor ability. The calculations suggest that stronger σ donors *increase* the lability of the cis carbonyls. This result is consistent with the slightly improved σ bonding between the σ donor and the metal complex in the transition state and the tendency of the coordinatively unsaturated $M(CO)_4$ fragment to accept electrons. The sensitivity of the energetics of CO loss to the σ-donor ability of hydrogen is much lower than to the π-donor ability of bromine. A change of 3 eV in the energy of the hydrogen 1s orbital changes the calculated energy requirement for CO loss by only 0.01 aeu, while a change of 3 eV in the energy of the bromine π levels changes it by more than 0.1 aeu.

Pathways for Carbonyl Dissociation. Our calculations suggest that energy changes associated with geometrical relaxation of the five-coordinate complex fragment are of sufficient magnitude to strongly influence the energetics of the CO dissociation process. Furthermore, the fragment resulting from carbonyl loss from $Mn(CO)_5Br$ is capable of achieving significantly more stabilization energy through relaxation to a lowest energy geometry than the fragment obtained from $Mn(CO)_6^+$. If the energy increases smoothly along the path between the ground state and the transition state, then the cis carbonyls of $Mn(CO)_5$ are expected to be labilized relative to those of $Mn(CO)_6^+$. If, however, a maximum value or a discontinuity occurs in the energy in the path between two states, the pathway is forbidden or disallowed in one sense or another. Discussion of the relative kinetics behavior then becomes much more complex.
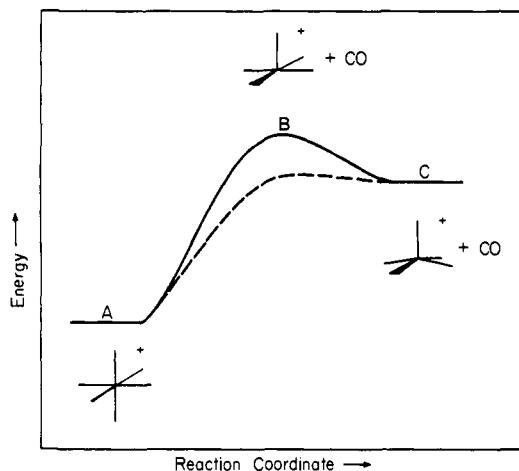
Figure 2. Energy profile for CO dissociation from $Mn(CO)_6^+$. The points A, B, and C represent calculated energies for ground state molecule, and rigid and relaxed geometries following dissociation, respectively. The dotted line represents the expected variation in energy for CO dissociation with concurrent relaxation of the metal complex fragment.

The energy change between two states is expected to be smooth and nearly monotonic if the two states correlate directly. A schematic potential energy surface for dissociation of CO from $Mn(CO)_6^+$ is shown in Figure 2. We have examined three points on this surface: (A) the ground state, identified with the carbonyl at the equilibrium distance, r_e, and with an angle of 90° between adjacent carbonyls; (B) the dissociation product in which 90° bond angles are maintained between M–CO vectors; (C) the dissociation product with lowest energy angular geometry. The minimum energy path of carbonyl dissociation, shown as a dotted line, is that along which removal of the carbonyl is accompanied by the allowed relaxation of the remaining C_{4v} fragment. Analogous considerations apply to carbonyl dissociation from $Mn(CO)_5Br$. As a cis carbonyl is removed, relaxation of the basally substituted SBP fragment, **6**, is allowed. Removal of a trans carbonyl may be accompanied by relaxation of the apically substituted C_{4v} SBP fragment, **5**.

The energy of step 1 for removal of a trans carbonyl from $Mn(CO)_5Br$ was shown to be relatively large, and the stabilization energy associated with relaxation of the $Mn(CO)_4Br$ fragment, with maintenance of C_{4v} symmetry, was found to be small. Therefore, in terms of this model the trans carbonyl is expected to be relatively inert toward dissociative CO loss. The energies for removal of a cis carbonyl from $Mn(CO)_5Br$ or a carbonyl from $Mn(CO)_6^+$ are very similar in the first step, but the SBP relaxation energy in the second step is much larger for the $Mn(CO)_4Br$ fragment than for the $Mn(CO)_5^+$ fragment. Thus a major factor contributing to the labilization of the cis carbonyl groups has been identified, and the model is now capable of accounting for the observed substitution kinetics.

The calculations suggest that the C_{2v} geometry for $Mn(CO)_4Br$, **7**, may be lowest in energy. This geometry can be approached by dissociation of CO from *either* the cis or trans positions. Loss of a cis CO, with concurrent movement of Br, as in **8**, preserves the ordering of energies of highest oc-
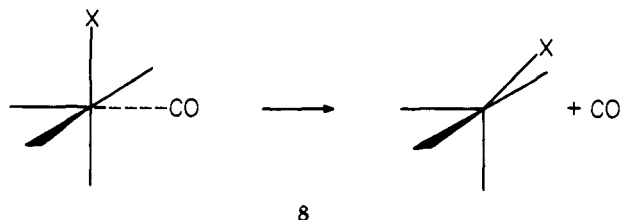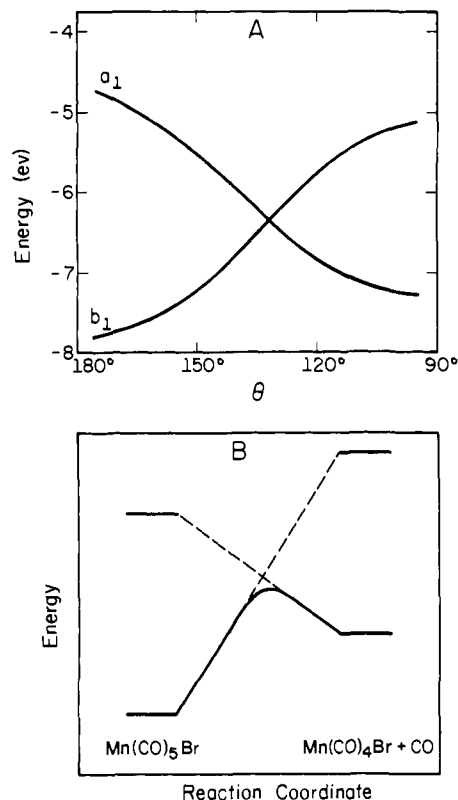

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Figure 3. A. Energies of highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals in $Mn(CO)_4Br$ as a function of relaxation of $Mn(CO)_4Br$ fragment following axial CO loss, as in **9**. The symmetry species are those of the C_{2v} point group. B. Energy profile (shown by the solid line) for trans CO loss from $Mn(CO)_5Br$, with concurrent angular relaxation of the fragment. The ground state electron configuration of $Mn(CO)_5Br$ correlates with a doubly excited configuration in $Mn(CO)_4Br$.

cupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively), and is thus a thermally allowed process. On the other hand, loss of a trans CO, with relaxation of the remaining CO groups as illustrated in **9**, results in a crossing in energies of the HOMO and LUMO.
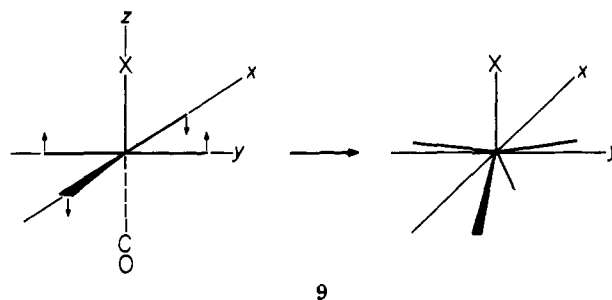
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Figure 3A shows the energies and C_{2v} point group symmetry species of the HOMO and LUMO in the $BrMn(CO)_4$ fragment, as a function of the extent of distortion along the coordinate shown in **9**. The HOMO, of b_1 symmetry, consists predominantly of d_{xz} character when θ is near 180°; the LUMO, of a_1 symmetry, consists mainly of d_{z^2}. The HOMO intersects the LUMO at a point along the distortion coordinate. Salem and co-workers refer to this situation as a type C avoided crossing.[31] Because mixing of configurations is not properly incorporated in the molecular orbital model, the model does not adequately describe the electronic structure of the molecule in the vicinity of an orbital crossing as illustrated in Figure 3. Thus, although the model does not preclude a crossing of orbitals of different symmetries, inclusion of interelectronic re-
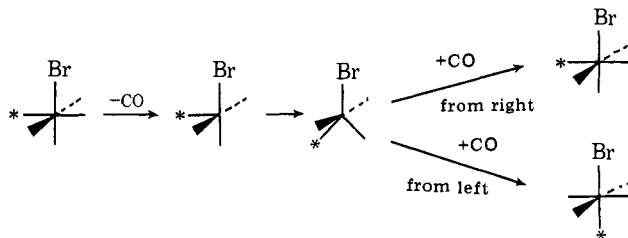
Table III. Relative Energies of CO Dissociation from Metal Complexes

Parent molecule	Basic symmetry	Geometry of M(CO)$_4$X (text diagram)	Angles	Energy relative to parent, aeu
Mn(CO)$_5$Br	C_{4v}	5	$\theta = 90°$	1.51
			$\theta = 94°$	1.48[a]
	SBP-basal X	6	$\theta = 90°$	1.20
			$\theta = 101°$	1.01[a]
	C_{2v}	7	$\theta = 90°, \phi = 90°$	0.96
			$\theta = 98°, \phi = 90°$	0.93
			$\theta = 98°, \phi = 85°$	0.92[a]
Mn(CO)$_6$$^+$	C_{4v}	4	$\theta = 90°$	1.19
			$\theta = 97°$	1.07[a]
	C_{2v}	7	$\theta = 150°, \phi = 90°$ [b]	1.10[a]
Mn(CO)$_5$H	C_{4v}	5	$\theta = 90°$	1.28[a]
	SBP-basal X	6	$\theta = 90°$	1.24
			$\theta = 98°$	1.13[a]
	C_{2v}	7	$\theta = 100°, \phi = 90°$ [b]	1.12[a]

[a] Minimum energy near optimum angles of geometry. [b] The angle θ was not optimized for these fragments.
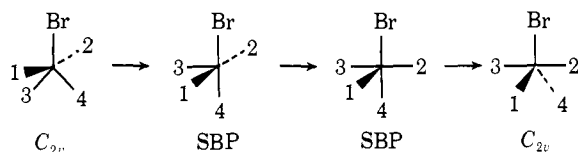
pulsions results in some degree of mixing of the two orbitals, and thus in an avoided crossing. The energy surface for the concurrent trans CO loss and rearrangement of the Mn-(CO)$_4$Br fragment has the character shown schematically by the lower solid line in Figure 3B. Attainment of the lowest energy configuration of Mn(CO)$_4$Br via loss of trans CO is thus a thermally disallowed process.

Although trans carbonyl loss in a thermal reaction is not favored, exchange studies with isotopically labeled carbonyl indicate that the label does eventually find its way to the trans position.[2] This occurs only after an induction period, indicating that the label is first substituted to a cis position, and then finds its way to the trans position in subsequent substitution steps. Assuming the C_{2v} geometry for the five-coordinate intermediate, a mechanism by which the cis carbonyl finds its way into the trans position is described in the following steps.

In this mechanism loss of carbonyl from the cis-labeled complex leads to the C_{2v} geometry in which either the vacated position may be substituted, leading to the original complex, or the position opposite to the vacated position may be substituted, moving the label to a position trans to the bromide.

This mechanism accounts for migration of labeled CO to the trans position without requiring fluxionality of the five-coordinate intermediate and without complete scrambling of the carbonyls.[2] However, if the C_{2v} geometry 7 and the basally substituted SBP geometry 6 are close in energy, as expected, complete scrambling of the carbonyls is allowed through a distorted Berry-type mechanism:[32]

In contrast to the normal Berry mechanism for intramolecular scrambling of five equivalent ligands, complete intramolecular exchange in M(CO)$_4$X species also requires interconversion of the two SBP geometries.

Discussion

The calculations have successfully provided a consistent rationale for the relative rates of CO dissociation from Mn(CO)$_6$$^+$, Mn(CO)$_5$Br, and Mn(CO)$_5$H. A summary of the important results is given in Table III. The approach obviously has several limitations, as discussed in the Methods and Results sections. More sophisticated theoretical treatments may modify some of our conclusions. The present model includes the constraint that, for all positions on the reaction coordinate, the distances between directly bonded atoms remain constant and the M–C–O bond angles remain 180°. Variation of the bond distances may significantly affect calculated energies. Unfortunately, full optimization of bond distances requires many times more calculations than have already been performed. However, in most instances, longer or shorter bond distances are a direct result of the lesser or greater bonding capabilities, and will not alter the relative stabilizations which have been described. It does, however, make comparisons of calculated activation energies with observed kinetics more tenuous. Optimization of bond distances could also influence predictions based upon the ground state wave functions. The M–CO distances in both cis and trans positions were constrained at 1.85 Å from the metal. Full geometry optimization would in all likelihood place the trans CO closer to the metal than a cis carbonyl, and bond order analysis for this geometry would then reveal a stronger trans bond. Thus ground state considerations of this sort are capable of accounting for the site of substitution. However, the overall labilization of the cis CO groups in Mn(CO)$_5$Br is based substantially on stabilization associated with reorganization in the complex accompanying the change in metal–carbonyl distance. Thus, cis labilization is best understood in terms of the preferred geometry of the five-coordinate fragment.

The molecular orbital results support prior conjecture that variations in ground state properties are not directly related to the effect identified as cis labilization. The calculations indicate that ligands which are good electron donors, particularly π donors, tend to labilize the cis carbonyls through stabilization of the coordinatively unsaturated, metal complex fragment representing the transition state.

Other ligands such as NO$_3$$^-$, Cl$^-$, NCO$^-$, CH$_3CO^-$, CH$_3SO_2$$^-$, and NC$_5H_5$ are potentially capable of the same type of behavior. However, we are not in a position to predict the relative cis labilizing effectiveness among these ligands. For example, the relative rates of CO loss from Mn(CO)$_5$X vary in the order Cl > Br > I,[33] whereas the halogen σ and π orbital energies vary in the order Cl < Br < I. On the other

hand, photoelectron studies indicate that the interaction of the halide orbitals with the metal in the ground state molecule decrease in the order Cl > Br > I.[34]

Ligands such as triphenylphosphine, which are not capable of acting as relatively good π donors toward the metal following CO loss, are nevertheless observed to behave as cis-labilizing ligands.[3,4] In these instances there may be some steric contribution to the rate enhancement.[35] Additional experimental work is required to separate electronic and steric factors. Calculations of the type performed here are not sufficiently reliable when applied to kinetics processes to permit distinctions between ligands such as various phosphines, or even between phosphines and CO.

References and Notes

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(25) Care was taken that the important results derived from comparing the calculations are not strongly dependent upon the particular basis functions or bond distances used. For the calculations on $Mn(CO)_5Br$ and $Mn(CO)_5^+$, the use of the same basis functions and bond distances for both may not appear advisable since one molecule is neutral and the other is positively charged. The potential difficulties caused by charge may be eliminated by considering $Cr(CO)_6$ instead of $Mn(CO)_6^+$. Calculations on $Cr(CO)_6$ provide essentially the same conclusions, indicating that the results are not altered, so long as the basis functions and bond distances are within realistic limits.
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Application of ab Initio Molecular Orbital Calculations to the Structural Moieties of Carbohydrates. 3[1]

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Abstract: Ab initio RHF/4-31G level molecular orbital calculations have been carried out on dimethoxymethane as a model compound for the acetal moiety in methyl pyranosides. The calculations are consistent with the predictions of the *anomeric effect* and the *exo-anomeric effect*. They reproduce very successfully the differences in molecular geometry observed by x-ray and neutron diffraction of single crystals of the methyl α-D- and methyl β-D-pyranosides. Calculations carried out at the 6-31G* level for methanediol confirm the earlier calculations at the 4-31G level, with smaller energy differences between the four staggered conformations.

Dimethoxymethane as a Model Compound for the Acetal Moiety in Pyranosides

In pyranoses, pyranosides, pyranosyl halides, furanoses, furanosides, nucleosides, and nucleotides, two of the four atoms bonded to the anomeric carbon atom C(1) are more electronegative than carbon, and necessarily have lone-pair electrons. The electronic transfer, which arises from these electronegative differences, is compensated for by a feedback from the lone pairs to the antibonding (σ^*) orbitals of adjacent bonds, as suggested by the application of Pauling's rule concerning the essential electroneutrality of atoms.[3] In consequence, there is a difference in the electronic structure between molecules with the α configuration, **1**, and those with the β configuration, **2**, at the anomeric center, C(1), because of the different geometrical relationship between the carbon 2p orbitals and the distribution of the lone pairs on the ring oxygen and the substituent X. This difference is believed to be responsible for the difference in the stability of pyranosides and furanosides to acid hydrolysis, the preferred α configurations in glycosyl fluoride