Cis Labilization of Ligand Dissociation. I. ^{13}CO Exchange and Phosphorus Ligand Substitution with $Mn(CO)_5Br$ and $Re(CO)_5Br$[1]

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Abstract: The exchange of ^{13}CO with $Mn(CO)_5Br$ and $Re(CO)_5Br$ in hexane has been measured using infrared spectral techniques. A complete accounting of the time dependencies of all isotopically labeled species and comparison with the results of phosphorus ligand substitution rates lead to the following conclusions. (a) The rate-determining process is CO dissociation. (b) The rate constant for cis CO dissociation is at least ten times that for trans. (c) The five-coordinate intermediate formed in the dissociation is fluxional. (d) The rate constant for cis CO dissociation in $Mn(CO)_5Br$ is 2.8×10^{-5} sec^{-1} at 23°; for $Re(CO)_5Br$ at 30°, 5.1×10^{-7} sec^{-1}. The labilization of CO toward dissociation by cis ligands which are weaker π acceptors than CO seems general.

The substitution of isotopically labeled CO into $Mn(CO)_5Br$ has been the subject of several investigations;[2-6] substitution of $Re(CO)_5Br$ with ^{14}CO has been the subject of a single study.[7] A question of major interest has been the relative rates of CO dissociation from the positions trans and cis to bromine. It has been fairly well established from studies of substitution reactions of $Mn(CO)_5Br$ with phosphines[8-10] that the process is first order in $Mn(CO)_5Br$ and zero order in substituting ligand. A rate-determining step involving CO dissociation seems likely in both substitution and exchange reactions. Assuming CO dissociation does occur, this raises the additional question of the characteristics of the five-coordinate $Mn(CO)_4Br$ intermediate. If this intermediate recombines with entering ligands with a small free energy of activation, its lifetime should be very short. At the same time, since many five-coordinate species are known to undergo rapid intramolecular rearrangement, the possibility exists that the five-coordinate intermediate may be fluxional during its lifetime. In the most recent study of ^{13}CO exchange with $Mn(CO)_5Br$ all of the above questions were addressed.[6] Analysis of infrared spectral data taken during the course of the exchange reaction suggested that the equatorial CO groups, i.e., those cis to bromine, undergo exchange more rapidly than the axial CO. The results also suggested that the intermediate $Mn(CO)_4Br$ species is fluxional. While this study was considerably more detailed than any previous studies of this type of system, it was unsatisfying in certain respects. The results of subsequent experiments indicated that the experimental arrangement employed may have resulted in an inadequate equilibration of the enriched ^{13}CO with the remainder of the gas phase in the early stages of the reaction. Secondly, analysis of the infrared data was incomplete, partially as a result of the decision to employ fairly low levels of enrichment. Accordingly, we have reinvestigated this system with an improved experimental setup and have employed a more thorough analysis of the infrared spectral data. In addition, we have investigated the exchange of ^{13}CO with $Re(CO)_5Br$. Our conclusions based on the new experimental data and method of analysis are qualitatively the same as those reported previously,[6] but they differ in important quantitative details. We have also investigated the kinetics of the reactions of $Mn(CO)_5Br$ and $Re(CO)_5Br$ with triphenylphosphine and trimethyl phosphite in hexane, to provide a comparison with the ^{13}CO exchange data.

Experimental Section

Manganese and rhenium pentacarbonyl bromide were synthesized by previously described methods.[11] Reagent grade hexane (Fisher Scientific) was washed with concentrated H_2SO_4 and distilled water, passed through a silica gel column, and stored over sodium wire. Carbon monoxide (Bio Rad Laboratories) of 93% ^{13}C isotopic abundance was metered into bulbs fitted with vacuum tight stopcocks, using a vacuum line equipped with a Toepler pump, and then diluted with N_2 to achieve atmospheric pressure.

Kinetics Experiments. Two modifications have been made to the apparatus described previously.[6] A second bulb containing CO of natural ^{13}C enrichment was added to the apparatus in addition to the bulb containing the isotopically enriched CO. The bulb containing natural abundance CO was opened to the system immediately after introduction of the solution containing metal carbonyl, to repress the dimerization reaction during the time the system was being equilibrated to constant temperature. The exchange reaction was then initiated by opening the bulb containing the isotopically enriched material to the system and beginning the circulation of gas. Mass spectrometric analysis of the CO atmosphere in the apparatus previously described[6] showed that in the early stages of the reaction diffusion of CO from the bulb was too slow to permit equilibration within an acceptable time. This may have contributed to some errors in the data in the earlier stages of the reaction as reported previously. The apparatus was modified by circulating the pumped gas directly from and through the bulb to ensure rapid equilibration of all of the gas in the system.[12]

The exchange reactions were allowed to proceed to equilibrium. Much higher levels of ^{13}CO enrichments were used than previously so that at equilibrium the isotopic enrichment was on the order of 40-50%. The extent of ^{13}CO enrichment in the metal carbonyl at equilibrium was deduced from the distribution of intensities in the infrared bands due to isotopically substituted molecules (vide infra). In a few cases samples of the CO atmosphere at equilibrium were withdrawn for mass spectral analysis. The extent of ^{13}C enrichment determined mass spectrometrically was found to be in agreement with the ir results.

Infrared spectral measurements were made using 1-mm path length NaCl window sample cells. A Beckman IR-7 spectrophotometer, frequency calibrated with water vapor, was employed. Data relating to the exchange of the axial CO were obtained from spectra in the frequency range 1920-2020 cm^{-1}. Data relating to the exchange of radial CO groups were obtained from spectral data in the region 2080-2160 cm^{-1}. The CO ir stretching absorption in this frequency region corresponds to the A_1 normal mode consisting mainly of radial CO stretch. Since it is of quite low intensity it was necessary to employ a tenfold ordinate scale expansion, with longer time constants and slower frequency scans to compensate for the added noise levels. Typical spectra obtained in

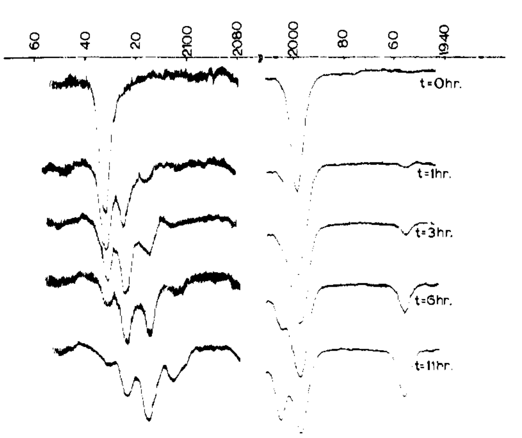


Figure 1. Infrared spectra in the CO stretching region for $Mn(CO)_5Br$ exchange with ^{13}CO. The higher frequency bands were obtained with a 10× ordinate scale expansion.

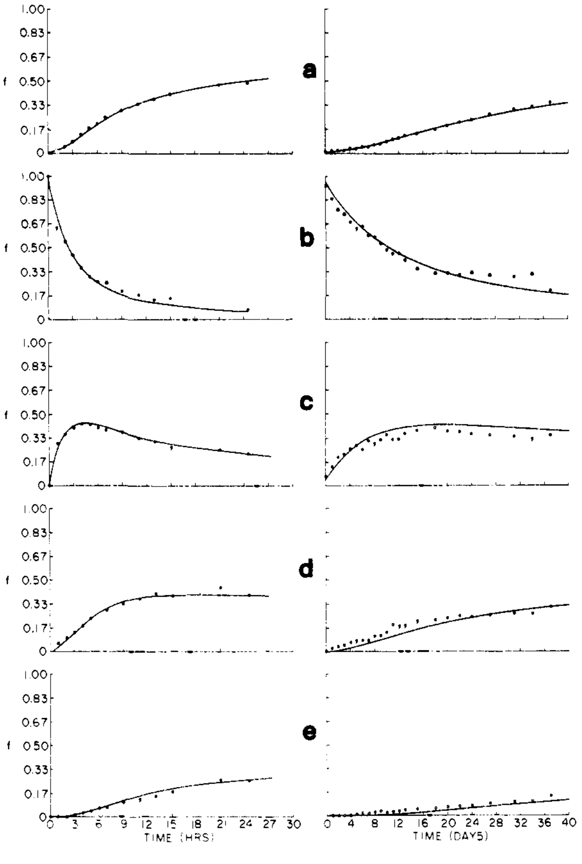


Figure 2. Comparison of calculated fractional abundances of the variously substituted $Mn(CO)_5Br$ (left) and $Re(CO)_5Br$ (right) species with the fractional abundances determined by analysis of the ir data. The circles refer to points determined from the spectra, the continuous lines to the calculated fractions. The fractional abundances represented in each graph are as follows: (a) ^{13}CO in the axial position, (b) all ^{12}CO in radial positions, (c) one ^{13}CO in a radial position, (d) two ^{13}CO groups in radial positions, (e) three ^{13}CO groups in radial positions.

both frequency regions are shown in Figure 1.

The kinetics of substitution of the carbonyl halides by phosphorus ligands in hexane were followed by observing the decrease in the absorbance at 2050 cm^{-1} as a function of time. An experiment to determine the competition ratio between CO and PPh_3 was carried out by mixing hexane solutions of PPh_3 and $Mn(CO)_5Br$ in the reaction vessel employed in studying the exchange reaction with natural abundance CO present at a pressure of about 350 Torr. The vessel atmosphere was continually circulated through the solution to ensure equilibration of dissolved and gaseous CO. The solution CO concentration was estimated from the reported solubility of 0.010 *M* for CO in hexane at 25°,[13] and assuming that Henry's law holds.

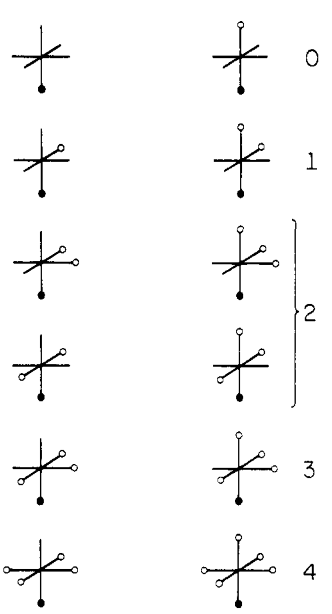


Figure 3. Illustration of the possible arrangements of ^{13}CO groups (represented by open circles) in $M(CO)_5X$. All the molecules containing the same number of radial CO groups, regardless of whether the axial group is ^{12}CO or ^{13}CO (or, in the case of two radial CO groups, regardless of cis or trans geometry), exhibit approximately the same highest energy CO stretch frequency.

Treatment of Data. Data relating to the exchange of the axial CO groups were obtained from observations of a CO ir stretching mode of A_1 symmetry. It occurs for $Mn(CO)_5Br$ at 2000 cm^{-1} when there is a ^{12}CO in the axial position, and at 1958 cm^{-1} when there is a ^{13}CO in that position. For $Re(CO)_5Br$ the absorptions occur at 1982 and 1940 cm^{-1}, respectively. The fraction of ^{13}CO axially substituted was calculated from the relative absorbances of these two absorptions. Typical data sets for both $Mn(CO)_5Br$ and $Re(CO)_5Br$ are shown in Figure 2 at top.

Data pertaining to exchange of radial CO groups were obtained by observation of the higher frequency A_1 CO stretching mode. Replacement of a single radial ^{12}CO by a ^{13}CO results in a shift to lower frequency of this mode on the order of 10 cm^{-1}. Replacement of successive ^{12}CO radial groups results in successive shifts of this totally symmetric, highest frequency CO absorption to lower frequencies, as depicted in Figure 1. Because these absorptions were not fully separated, it was necessary to effect resolution of the multiplet structure with the aid of a Dupont Model 310 curve resolver, or using a program devised by Pitha and Jones for this purpose.[14] At the levels of enrichment corresponding to equilibrium, about 0.5 fractional ^{13}CO enrichment, five absorptions approximately 10 cm^{-1} in separation are seen. These correspond to the five radially substituted species depicted in Figure 3. A vibrational analysis was carried out for all the isotopically substituted species using the complete vibrational force field reported by Ottesen et al.[15] The eigenvalues derived from these calculations permit an unambiguous assignment of the individual components of this high frequency multiplet to the individual radially isotopically labeled species. Further, the eigenvectors revealed the extent to which isotopic substitution changes the mixing of the two CO stretching modes which correspond to those having A_1 symmetry in the all ^{12}CO molecule. Since the overall molecular dipole moment change associated with the two A_1 symmetry coordinates is greatly different, variation in mixing of the CO A_1 symmetry modes results in a change in the molar intensity of the high frequency absorption with changing isotopic substitution. Furthermore, some of the isotopically substituted species have symmetry lower than C_{4v}. When the L matrix elements for mutually trans CO groups are not the same, the change in dipole moment has a horizontal as well as

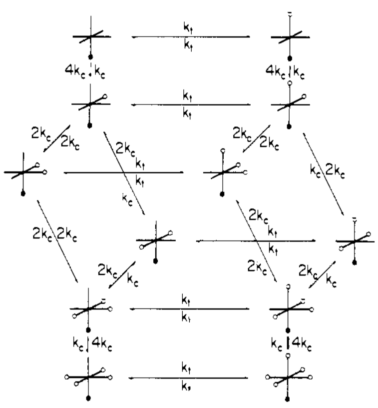


Figure 4. Kinetics scheme for ^{13}CO exchange in $M(CO)_5X$ compounds, assuming that the five-coordinate intermediate is rigid. All interconversion rates are expressed in terms of the two rate constants k_c and k_1, representing respectively dissociation of CO from a position cis or trans with respect to the X group and a number representing the fractional isotopic abundance of ^{13}CO in the carbon monoxide.

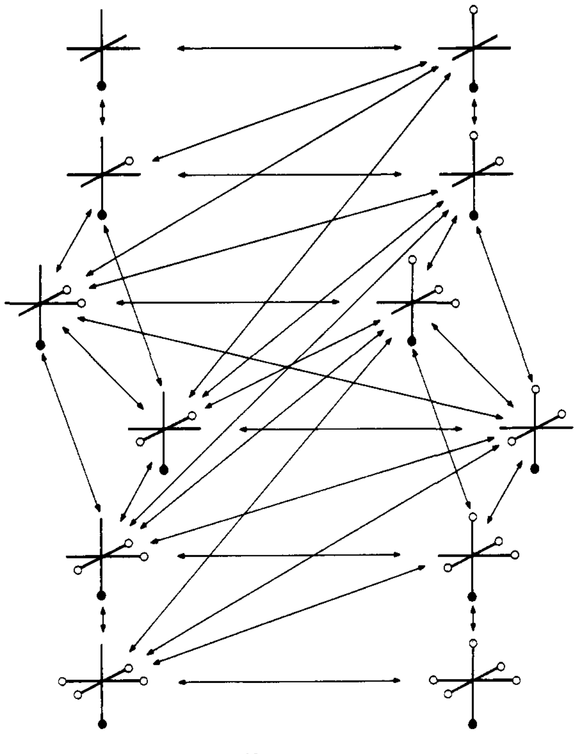


Figure 5. Kinetics scheme for ^{13}CO exchange with $M(CO)_5X$, assuming the five-coordinate intermediate to be fluxional. Expressions for the rates of interconversions are given in Appendix B.[16]

vertical component, and this must be properly accounted for in the analysis. A complete accounting of the analysis of the vibrational system is given in Appendix A in the materials supplied with the microfilm edition of this journal.[16]

Using the results of the vibrational analysis, the observed relative absorbances of the bands due to isotopic substitution could be converted into relative concentrations of the various radially substituted species and the extent of axial substitution as a function of time.

Data Analysis. Figure 4 shows a kinetics scheme for isotopic substitution in $XM(CO)_5$ compounds, corresponding to what we term the rigid mechanism. In this model it is assumed that the five-coordinate intermediate created by dissociation of a CO group is stereochemically rigid, so that the entering CO group takes up identically the same position vacated by the dissociating CO. It is a straightforward process to write down a set of differential equations for the time dependence of the relative concentrations of each of the species shown on the scheme. The expressions involve k_c and k_1, the rate constants for dissociation of CO from the radial and axial sites, respectively, and the fractional abundance of ^{13}CO in the dissolved carbon monoxide.[17] The expressions are provided in Appendix B.[16]

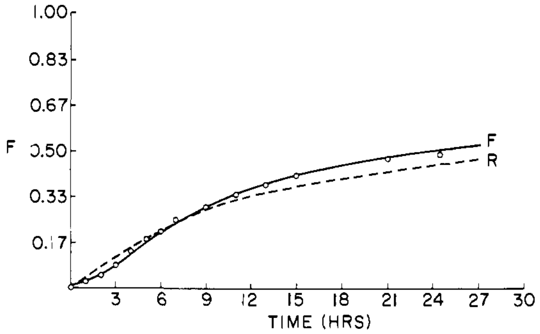


Figure 6. Comparison of the fit between calculated time dependence of the concentration of $Mn(CO)_5Br$ molecules labeled with ^{13}CO in the axial position with points derived from the ir data. Curve R corresponds to the assumption of a rigid five-coordinated intermediate, curve F to the assumption of a fluxional intermediate.

An alternative kinetics scheme, which assumes a completely fluxional intermediate, is shown in Figure 5. In this instance the rate constants for the various interchanges are considerably more complex than those shown in Figure 4 and are omitted from the figure for clarity. All of the rate constants relating to the various species, however, still involve only the quantities k_c and k_t and fractional ^{13}CO abundance.[17] The rate constants, and the equations for the time dependence of each species, are given in Appendix B.[16] The exchange scheme outlined in Figure 5, which we term the fluxional mechanism, involves a complete scrambling of the four CO groups which remain attached to the metal in the five-coordinate intermediate.

The systems of coupled differential equations corresponding to the two reaction schemes shown in Figures 4 and 5 were solved using a computer program which employs the method developed by Matsen and Franklin.[18] Solution of the differential equations for assumed values of k_c and k_1 provides the relative concentration of each isotopically enriched species as a function of time. These could then be converted into a fractional abundance of each species, for direct comparison with the results of infrared analysis. For each mechanism k_c and k_1, the rate constants for cis and trans dissociation, respectively, could be varied to obtain variations in the relative time dependencies of the concentrations of the various species. Calculated values were fit to the relative concentrations derived from the ir data analysis by varying these parameters for each of the two models. An additional criterion in fitting the data to the two models is that the rate constants obtained for the ^{13}CO exchange must be consistent with those obtained for the substitution by triphenylphosphine or other ligand. *A satisfactory fit of observed and calculated results was possible only for the assumption of a fluxional intermediate, with k_c/k_1 large.* Figure 6 illustrates the best fit of the rigid and fluxional models to the $Mn(CO)_5Br$ axial substitution, for the case in which each model is optimized to yield the best overall agreement with the observed axial exchange rate. It is evident that the fluxional mechanism provides a much better fit, especially in the critical early stages of the reaction. A similar result was obtained for $Re(CO)_5Br$. The calculated time dependencies of the fractional abundances of all species assuming the fluxional model are compared with the same quantities derived from the $Mn(CO)_5Br$ and $Re(CO)_5Br$ ir data in Figure 2. Since the time dependencies of the relative concentrations of all the various species obtained in the course of the exchange are rather complex, it was not possible to subject the data to a rigorous least-squares fitting procedure to obtain the best values for the parameters at our disposal. It was evident by inspection, however, that the best fit was obtained by assuming the ratio k_c/k_1 to be large. An increase in the ratio k_c/k_1 above about ten makes no discernible change in the calculated results. On the other hand, a lower value worsens the comparison between calculated and observed results. Thus, on the basis of the present more complete analysis, the ratio k_c/k_1 is substantially larger than the previous estimate.[6] It is important to emphasize that the ratio of radial to axial exchange might be very much greater than the lower limit of about ten set by our observations. The existence of intramolecular rearrangement in the intermediate precludes a more precise determination of this ratio by any means we have so far been able to devise.

Discussion

Comparison of Exchange and Substitution Rates. The reaction under investigation here is the exchange of ^{13}CO for ^{12}CO in $M(CO)_5Br$, forming an equilibrium mixture of the 12 possible isotopically substituted products (Figure 3). The reaction is carried out in hexane solution with circulation of the gas through the solution to ensure that the isotopic composition of the dissolved CO remains that of the gas reservoir. A substantial molar excess of CO with respect to dissolved metal carbonyl is advisable, because the isotopic composition of the gas then remains relatively constant throughout the reaction. Excess CO also serves to suppress the dimerization reaction $2M(CO)_5Br = M_2(CO)_8Br_2 + 2CO$.[19] This reaction occurs in the absence of CO for both the manganese and rhenium system, but is much slower for the rhenium system.

The conditions under which the experiment is carried out preclude our determining the rate law for the reaction. The kinetics of substitution of both $Mn(CO)_5Br$ and $Re(CO)_5Br$ have, however, been studied with other ligands such as phosphines.[8-10]

The substitution rate in a variety of solvents is found to be first order in metal carbonyl and zero order in entering ligand. As a check on the rate constants determined for ^{13}CO exchange, we have measured the kinetics of substitution of $Mn(CO)_5Br$ by PPh_3 and $P(OCH_3)_3$ in hexane at 23° and of $Re(CO)_5Br$ by PPh_3 in hexane at 30°. The substitution rate of $Mn(CO)_5Br$ by PPh_3 was found to be independent of added ligand, in agreement with the earlier work. The first-order rate constant for substitution of $Mn(CO)_5Br$ by PPh_3 was found to be 8.23×10^{-5} sec^{-1} with an uncertainty at the 95% confidence level of 0.27×10^{-5} sec^{-1}. For substitution by $P(OCH_3)_3$ the rate constant was found to be 8.54×10^{-5} sec^{-1}, with an uncertainty at the 95% confidence level of 0.20×10^{-5} sec^{-1}. The rate constant for substitution of $Re(CO)_5Br$ by PPh_3 in hexane at 30° was found to be 1.71×10^{-6} sec^{-1} with a 95% confidence level uncertainty of 0.06×10^{-6} sec^{-1}.

The reaction of $Mn(CO)_5Br$ with $P(OCH_3)_3$ proceeds to the cis-disubstituted compound, $Mn(CO)_3[P(OCH_3)_3]_2Br$ as product, whereas the reaction with PPh_3 yields only the monophosphine compound. It seems likely in light of additional experiments we have carried out, and on the basis of Hyde and Darensbourg's demonstration[20] of steric interactions in the formation of cis-disubstituted compounds, that steric repulsions between cis PPh_3 groups, and possibly also between PPh_3 groups and halogen, prevent formation of the disubstituted PPh_3 compound. It is noteworthy that PPh_3 substitution on $Re(CO)_5Br$ leads to $Re(CO)_3[PPh_3]_2Br$ as sole product, a result consistent with the larger radius of Re as compared with Mn.

Since both the CO exchange and phosphorus substitution reactions are presumed to occur via dissociation of CO, the rate of substitution should equal $4k_c + k_t$. This relationship arises because dissociation of any one of the five CO groups from $M(CO)_5X$ in the presence of excess ligand leads to substitution. Our analysis indicates that k_c is much larger than k_t; $4k_c$ for $Mn(CO)_5Br$ at 23° equals $11.1 \pm 2.5 \times 10^{-5}$ sec^{-1}, as compared with 8.35×10^{-5} sec^{-1} for substitution. Similarly, $4k_c$ for $Re(CO)_5Br$ at 30° equals $2.04 \pm 0.3 \times 10^{-6}$ sec^{-1}, as compared with 1.71×10^{-6} sec^{-1} for substitution. The agreement is good, further substantiating the correctness of the fluxional mechanism.

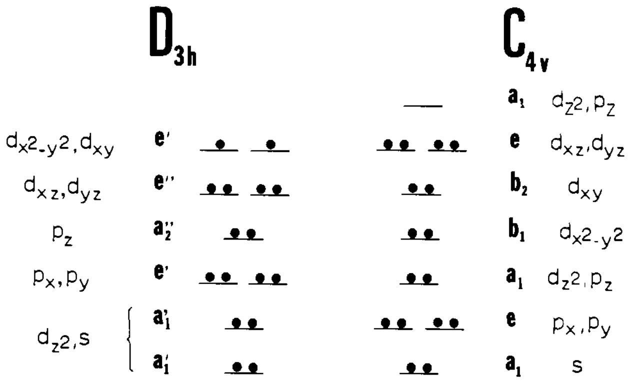
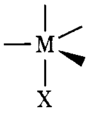


Figure 7. Qualitative ordering of energy levels in $M(CO)_5$ species of D_{3h} and C_{4v} point group symmetry.

Nature of the Five-Coordinate Intermediate. Since the exchange or substitution reaction studied here takes place in a relatively inert hydrocarbon medium, it is reasonable to suppose that solvent does not play a significant role in the reaction. Dissociation of CO from $M(CO)_5X$ leaves a five-coordinate intermediate which might have either C_{3v} symmetry, **1**, or C_{4v} symmetry, **2**, if X assumes an axial position, as expected. The geometry of the analogous pentacoordinate intermediate, $M(CO)_5$, in loss of a CO from the hexacarbonyl, has been the subject of considerable discussion and experimental study.[21-25] It now seems clear that the square pyramidal C_{4v} form of $M(CO)_5$ in solution is lower in energy.[25,26] In either intermediate there are 16 electrons in the molecular orbitals involving the valence atomic orbitals of the metal. The ordering of energy levels (Figure 7) is such that the D_{3h} species should be a ground state triplet of symmetry $^3A_2$.[24] On the other hand, the C_{4v} symmetry species should be spin paired. The qualitative ordering would not be expected to differ in $M(CO)_4X$ unless the orbital labeled d_{z^2} (consisting of antibonding combination of metal d_{z^2} and ligand bonding orbitals) was lowered below the level of the degenerate pair labeled d_{xz}, d_{yz}. This seems quite unlikely.



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The transition state in the dissociative loss of CO from a metal carbonyl probably represents almost complete metal-CO bond rupture; i.e., the metal environment in the transition state very much resembles that in the coordinatively unsaturated intermediate. This conclusion is based on the observation that metal carbonyl intermediates produced by loss of a ligand from the metal show essentially no selectivity in reacting with two different ligands in a competitive situation.[20,27-29] Since no significant differentiation is seen between ligands of widely varying nucleophilicity, it is reasonable to suppose that the free energy of activation for reaction of the five-coordinate species with any ligand is relatively low. This in turn suggests that the transition state closely resembles the final products, the five-coordinate intermediate and free ligand. In the present study, we have measured the competition ratio between PPh_3 and CO for recombination with $Mn(CO)_4Br$, by measuring the rate of substitution of $Mn(CO)_5Br$ in the presence of 0.005 *M* CO and noting the decrease in apparent rate of substitution.

The competition ratio, i.e., the rate of recombination of $Mn(CO)_4Br$ with CO as compared to PPh_3, is found to be 1.7. This value is consistent with the competition ratios near one obtained for ligands of widely varying nucleophilicity reacting with other metal carbonyl and substituted metal carbonyl intermediates containing 16 electrons in the valence orbitals of the metal. It supports the contention that $Mn(CO)_4Br$ is a strongly electrophilic species which reacts with any available nucleophile with small free energy of activation. Unfortunately, there is very little direct evidence regarding the rates of reaction of coordinatively unsaturated metal carbonyl intermediates with nucleophiles. Kelley et al. have reported[30] that $Cr(CO)_5$, generated in a flash photolysis experiment, reacts with CO in solution with a bimolecular rate constant of $3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$. This is only about three orders of magnitude lower than the diffusion-controlled encounter rate.[31] Thus, even if all the departure from the diffusion controlled rate of collisions between $Cr(CO)_5$ and CO were enthalpic in nature, a small activation energy is involved. The evidence therefore suggests that the intermediates in metal carbonyl dissociation reactions containing 16 electrons in the valence orbitals of the metal are reactive and combine with nucleophiles in reactions characterized by small energies of activation.

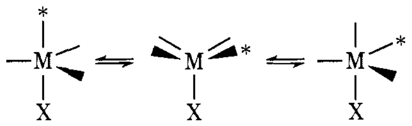
It seems most likely that the $M(CO)_4X$ intermediate possesses C_{3v} symmetry. This follows in part from the fact that the cis CO groups dissociate preferentially. A reaction coordinate involving least motion of other parts of the molecule leads naturally to a transition state in which the environment at the metal is essentially of C_{3v} symmetry. It should be noted also that matrix isolation studies of the five-coordinate species derived by photolytic loss of CO from $HMn(CO)_5$,[32] $CH_3Mn(CO)_5$,[33] and $CH_3COMn(CO)_5$[33] all indicate nominal C_{3v} site symmetry at the metal.

Since the kinetics results indicate that the five-coordinate intermediates are fluxional, it is of some interest to estimate their average lifetime in solution. Assuming that the bimolecular rate constant for reaction of $M(CO)_4X$ with CO is about that found[30] for reaction of $Cr(CO)_5$ with CO, i.e., about $3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$, we obtain for the inverse characteristic lifetime of the intermediate, $1/\tau_i$

$$1/\tau_i = \frac{-d[M(CO)_4X]}{[M(CO)_4X]dt} = 3 \times 10^8[CO]$$
$$\approx 3 \times 10^4\ \text{sec}^{-1}$$

where we have inserted the measured molar solubility of CO in hexane, 0.01 M, at 1 atm pressure. This average reciprocal lifetime may be compared with the observed rates of exchange of axial and radial CO groups in carbonyl and substituted carbonyl systems with 18 electrons in the metal orbitals. The classic system is $Fe(CO)_5$; it has not been possible to stop the axial-radial exchange of ^{13}CO as seen in the ^{13}C NMR spectra, even at temperatures to −170°.[34] Recently Mahnke et al.[35] have estimated the rate of axial-radial exchange in $Fe(CO)_5$ at −20° to be $1.1 \times 10^{10}\ \text{sec}^{-1}$; this seems extraordinarily large. Axial-radial exchange in $(C_6H_5)_3PFe(CO)_4$ appears fast at −110°,[36] and Cotton and Troup report[37] that they were unable to observe slow exchange in $Fe(CO)_4NC_5H_5$, at temperatures to −100°. We have studied the ^{13}C NMR spectra of tribenzyltintetracarbonylcobalt;[38] axial-radial exchange is slow at −140°. From these low temperature observations, and assuming an enthalpy of activation of perhaps 6 kcal mol^{-1}, it can be estimated that the *lower bound* for the rate constant for intramolecular exchange of axial and radial CO groups in these systems at room temperature is on the order of $10^6\ \text{sec}^{-1}$. This is clearly much faster than the average lifetime expected for the five-coordinate intermediate generated in the dissociation reaction. Unless there is some special barrier to the intramolecular rearrangement inherent in the fact that the intermediate is a 16-electron rather than an 18-electron system, it is expected that the intermediate will undergo intramolecular scrambling of CO groups during its lifetime.

In our view, the most reasonable pathway for interconversion of axial and radial CO groups in $M(CO)_4X$ species, whether 16 or 18 electron in character, is an "umbrella" process.



Such a process has the advantage over the pseudorotation pathway (as one of several alternatives) that it does not require strongly σ donor and/or weakly π acceptor X groups to move from the axial position in which they are at lowest energy.[39] The suggested interconversion would apply regardless of whether the C_{3v} or C_{4v} form were lower in energy.

Cis Labilization of CO Dissociation. Simple arguments regarding the competition of CO groups for π bonding with the (predominantly) d_{xz}, d_{yz}, and d_{xy} orbitals of the metal serve to account for the fact that the cis CO groups in $M(CO)_5X$ are more labile toward dissociation than the CO trans to the halogen.[40] The trans CO competes with two other CO groups for π bonding with either the d_{xz} or d_{yz} orbital. Each radial CO group, on the other hand, competes with two other CO groups for π bonding with either the d_{xz} or d_{yz} orbital and with three others for π bonding with d_{xy}. Hence π bonding is stronger to the axial CO. This is reflected in the relative values for CO stretching force constants in $Mn(CO)_5Br$,[15] and in the results of molecular orbital calculations,[41,42] which show higher CO bond orders in the radial CO groups and higher M-C bond order to the axial CO.

While these considerations account for the relative labilities of the cis and trans CO groups, they do not account for the fact that the cis CO groups of $Mn(CO)_5Br$ and $Re(CO)_5Br$ are considerably more labile toward dissociation than those of $Mn(CO)_6^+$ and $Re(CO)_6^+$, respectively. There is no evidence whatever of CO exchange in $Mn(CO)_6^+$ and $Re(CO)_6^+$, even after extended periods of time.[43] With due allowance for temperature, the observations suggest that CO dissociation is at least two orders of magnitude slower than the rates of radial CO dissociation from the corresponding carbonyl halides. Furthermore on the basis of substitution data,[8] the cis CO lability in $M(CO)_5X$ compounds increases in the order $X = I < Br < Cl$, i.e., in the order of decreasing σ donor character of the axial ligand. There is no evidence, however, in the ground state properties of the pentacarbonyl halides for a weakening of the bond from metal to the cis CO groups. Indeed, the simple π bonding arguments alluded to above suggest that the cis CO groups should also be stabilized by replacement of a CO by a non-π-acceptor ligand such as halide, albeit to a lesser degree than the trans.

The phenomenon of cis labilization, in the sense that the position cis to a designated ligand is labilized as compared with when that ligand is CO, is in fact widespread in reactions involving dissociative loss of a ligand from six-coordinate low-valent metal species. Since cis labilization is as important, and even more diverse in its manifestations than the much studied trans effect,[44,45] it is surprising that it has not been more fully and systematically explored. There are observations scattered throughout the literature to the effect that replacement of CO by another ligand in a given situation leads to labilization of the compound as a whole toward substitution.[46-48] There has, however, been only limited evidence that the greater overall lability is in fact due to loss from the cis position.[6,49,50] Indeed, this fact can be established with rigor only when an isotopic replacement of the type reported on in this paper is carried out, for only then is the free energy profile for the reaction the same in both directions,[5] so that the stereochemistry of the product mirrors precisely the stereochemistry of the dissociative process. Nevertheless, once the systematics of cis labilization have been established by sufficient exemplary isotopic exchange studies, it is possible on reasonable grounds to interpret many substitution reactions in terms of a cis labilization.

In subsequent papers in this series we intend to present further established examples of cis labilization and to show how it depends on the nature of the cis-labilizing ligand.

Supplementary Material Available. Appendices listing all rate expressions for the two mechanisms and an account of the corrections to absorption intensities based upon vibrational analyses will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3380.

References and Notes

(1) This research was supported by the National Science Foundation through contract DMR-7203026 with the Materials Research Laboratory, University of Illinois, and research Grant MPS-71-03201.
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(16) See paragraph at end of paper regarding supplementary material.
(17) The CO is present in the exchange vessel in considerable molar excess over the Mn(CO)$_5$Br. Nevertheless, during the course of the reaction the extent of ^{13}CO enrichment in the CO changes, from an initial value of (typically) about 50 to about 40%. The calculations were made so as to take into account the changing isotopic enrichment of the CO during the reaction.
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