Cis Labilization of Ligand Dissociation. 2. Substitution and ^{13}CO Exchange Reactions of Cis Monosubstituted Manganese and Rhenium Carbonyl Bromides[1]

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Abstract: The substitution and ^{13}CO exchange reactions of *cis*-$M(CO)_4BrL$ compounds (M = Mn or Re; L = $P(C_6H_5)_3$, NC_5H_5, or $P(OC_6H_5)_3$) have been studied in hexane and 1,2-dichloroethane. The reactions are first order in metal carbonyl and zero order in entering ligand. The ligand L labilizes the CO groups toward dissociation, in the order $NC_5H_5 > P(C_6H_5)_3 > P(OC_6H_5)_3 \approx CO$. Analysis of the kinetics results reveals that the dissociative loss of the CO groups mutually cis to Br and L is faster than of the other CO groups, and that the five-coordinate intermediate formed is subject to rapid intramolecular rearrangement during its lifetime. The substitution and ^{13}CO exchange results are in good accord. Various possible origins of the cis-labilization observed are discussed. The most attractive explanation is that the ligand L stabilizes the five-coordinate intermediate, by taking up a preferred site in the square pyramidal or trigonal bipyramidal structure.

In paper 1 of this series[2] it was established that the CO groups cis to Br in $Mn(CO)_5Br$ and $Re(CO)_5Br$ are labilized toward dissociation as compared with the trans CO. Furthermore, the cis CO groups are labile relative to those in $Mn(CO)_6^+$.[3] As a means of further exploring the effects of ligands other than CO on the labilities of CO groups we have studied ^{13}CO exchange with *cis*-$M(CO)_4BrL$ compounds, where M = Mn or Re and L = triphenylphosphine (PPh_3), triphenyl phosphite ($P(OPh)_3$), or pyridine, NC_5H_5.

Angelici and Basolo studied the kinetics of reaction of *cis*-$Mn(CO)_4LBr$ compounds with a variety of reagents L′ to form $Mn(CO)_3LL'BR$ compounds.[4] In general these reactions yielded the fac isomer, which upon heating converts to the trans-mer or 2,4-isomer.[5] The rate of formation of the fac isomer was found to be first order in metal carbonyl, zero order in entering ligand. A CO dissociation was postulated as the rate-determining step. Very similar behavior has been noted for the substitution reactions of *cis*-$Re(CO)_4XL$ compounds.[7] In both sets of compounds the rate constant for formation of the disubstituted compound was found to depend on the nature of L. The extent to which the observed rate depends on L′ was not extensively investigated in either study. Table I shows comparisons of substitution rate constants in each metal carbonyl bromide series, relative to the value for $M(CO)_5X$. To facilitate comparisons with data to be presented later, the relative rate constants considered are on a per CO basis, assuming that only the two CO groups cis to both Br and L undergo dissociation.

These data suggest that at least certain ligands, notably PPh_3 and pyridines, are capable of labilizing *cis*-$M(CO)_4LX$ molecules toward CO dissociation relative to $M(CO)_5X$. There is not unequivocal demonstration, however, that such labilization involves the cis CO groups, since the incoming ligands L′ could return to a position different from that vacated by CO. Furthermore, if steric interactions exist between L and L′ the observed rate of incorporation of L′ may be slower than CO dissociation. For example, *cis*-$Mn(CO)_4BrPPh_3$ does not react readily with PPh_3 at 40 °C to yield the fac isomer, as it does with $P(OC_4H_9)_3$. A slow reaction does occur at 55°, yielding 2,4-$(PPh_3)_2Mn(CO)_3Br$.[8] It seems apparent that in this instance steric interactions prevent the PPh_3 from entering in the cis position. The free energy barrier to reaction to give the 2,4-product is sufficiently large so that accumulation of even a very low concentration of free CO serves to cause preferential recombination of CO and the $Mn(CO)_3PPh_3Br$ intermediate to yield starting compound.

To more fully evaluate the extent to which ligands L in *cis*-$M(CO)_4LBr$ labilize the cis CO groups, we have studied the kinetics and stereochemistry of ^{13}CO exchange in several monosubstituted manganese and rhenium carbonyl bromide compounds. In addition a few substitution reactions have been investigated.

Experimental Section

Preparations of Compounds. *cis*-$Mn(CO)_4PPh_3Br$. A $CHCl_3$ solution of $Mn(CO)_5Br$ was treated with slight molar excess of PPh_3 at room temperature for 24 h. Solvent was removed under a stream of N_2, and the solid material washed with a minimum of cold hexane. Purification was effected by recrystallization from hexane. The infrared spectrum in the CO stretching region was in good agreement with that previously reported.[9] The frequencies are listed in Table II.

***cis*-$Mn(CO)_4P(OPh)_3Br$.** This previously unreported compound was prepared by bromination of $Mn_2(CO)_8[P(OPh)_3]_2$. The latter compound was prepared by photolysis of $Mn_2(CO)_{10}$ in the presence of $P(OPh)_3$, as previously described.[10] Bromination was carried out under an N_2 atmosphere, by dissolving 1 g of $Mn_2(CO)_8[P(OPh)_3]_2$ (1.0 mmol) in 100 ml of CCl_4. The solution was stirred for 30 min, the volume reduced to 20 ml, and the solution then filtered. Solvent was removed from the filtrate, which was washed with two 5-ml portions of cold hexane. Purification was effected by recrystallization from hexane. The expected four ir bands in the CO stretching region were observed (Table II). Anal. C, 48.5; H, 2.74; Br, 14.5. Calcd C, 47.4; H, 2.71; Br, 14.3. The compound apparently undergoes a solid-state isomerization when stored in air, to yield what appears to be the trans isomer, exhibiting a single strong CO stretching band in the ir at 2015 cm^{-1} in hexane solution. The rearrangement does not occur when the compound is stored under N_2 or under vacuum.

***cis*-$Re(CO)_4PPh_3Br$.** This compound was prepared as previously described,[11] with a reaction time of 35 h at room temperature. The ir CO stretching frequencies are listed in Table II.

***cis*-$Re(CO)_4NC_5H_5Br$.** This compound was prepared as previously described,[11] using a reaction time of 22 h at room temperature. The ir CO stretching frequencies, listed in Table II, are in good agreement with previously reported values.

***cis*-$Re(CO)_4P(OPh)_3Br$.** A 0.45-g sample of $Re_2(CO)_8Br_2$ (0.6 mmol) in 50 ml of CCl_4 was treated with 0.35 ml of $P(OPh)_3$ (1.3 mmol) at 40 °C for 24 h. The solution volume was reduced to 10 ml and the solution filtered. The filtrate was pumped to dryness, and washed with very cold hexane. The sample was pumped on for several days. Anal. C, 37.1; H, 2.39; Br, 10.9. Calcd C, 38.3; H, 2.18; Br, 10.9. The ir spectrum in the CO stretching region gave the expected four bands, as listed in Table II.

Table I. Relative Rates of CO Substitution in *cis*-$M(CO)_4BrL$ Compounds

L		k_1 (s^{-1})
	M = Mn[a]	
CO		1
PPh_3		8.4
$AsPh_3$		2.3
$P(C_4H_9)_3$		1.3
$P(OPh)_3$		0.6
$SbPh_3$		0.6
$P(OC_4H_9)_3$		0.3
	M = Re[b]	
CO	(PPh_3)	1[c]
$PPh_2C_2H_5$	($PPh_2C_2H_5$, NC_5H_5)	1.3
PPh_3	(PPh_3)	4.1
γ-$NC_5H_4CH_3$	(γ-$NC_5H_4CH_3$)	25
NC_5H_5	(NC_5H_5, PPh_3)	24
$P(C_4H_9)_3$	(PPh_3)	0.9

[a] L′ = $P(OC_4H_9)_3$. All data for tetrachloroethane solutions at 40 °C.[4] [b] CCl_4 solution, 60°.[7] L′ varies as indicated in parentheses. [c] Datum for $Re(CO)_5Br$ taken from F. Zingales, M. Graziani, F. Farsone, and U. Belluco, *Inorg. Chim. Acta*, **1**, 172 (1967), since the data for $Re(CO)_4LBr$ are from the same laboratory. D. A. Brown and R. T. Sane, *J. Chem. Soc. A*, 2088 (1971), report a higher value of k_1.

2,4-$(PPh_3)_2Mn(CO)_3Br$. This compound was prepared as described earlier.[12] Purification was accomplished by recrystallization from $CHCl_3$ and hexane. The ir spectrum in the CO stretching region (Table II) agrees with that previously reported.[13]

Kinetics. The ^{13}CO exchange reactions were carried out using the techniques previously described.[2] The compound to be studied was dissolved in an appropriate solvent and thermostated under an N_2 atmosphere. The reaction was initiated by opening a bulb containing CO of 93% ^{13}CO enrichment. Each reaction was monitored using ir spectroscopy until complete equilibrium was attained.

Substitution reactions were monitored by following the decrease with time of one of the absorption bands due to the starting compound. All ir spectra were obtained in 1-mm pathlength NaCl window cells, using a Beckman IR-7 instrument operating in the absorbance mode.

Treatment of Data

The ir spectrum of *cis*-$Mn(CO)_4BrPPh_3$, shown in Figure 2, is typical for the compounds under investigation. The CO ir stretching frequencies for all the compounds studied are listed in Table II. The four frequencies of the ir bands due to CO stretching in the all-^{12}CO molecule can be used to calculate three diagonal and one interaction force constant (see Figure 1), using the Cotton–Kraihanzel approximation.[14] The force constants obtained for *cis*-$Mn(CO)_4BrPPh_3$, K_1 = 16.76, K_2 = 16.69, K_3 = 15.60, and interaction constant K_c = 0.27 mdyn/Å, are then used to calculate the CO stretching frequencies in all the possible ^{13}CO substituted molecules. The vibrational analysis also provides L matrix elements which are required to correct measured intensities of bands due to isotopically labeled molecules.

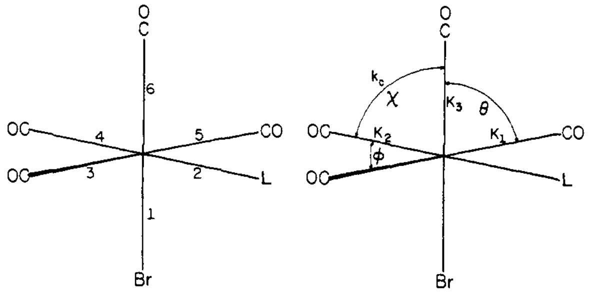

Figure 1. Labeling system and CO stretching force constants assumed for $M(CO)_4LBr$ molecules.

The agreement between calculated frequencies and those assigned from the spectra (Table III) is very satisfactory. We might have chosen to employ some of the frequencies for isotopically labeled molecules to calculate a larger number of force constant parameters, as done by Butler and Spendjian,[15] but the frequency fits are quite satisfactory with the simpler force field, and L matrix elements are not changed significantly. All calculated frequencies are within 2 cm^{-1} of observed values, and nearly all calculated bands can be assigned to observed absorptions. There is, however, considerable overlap of absorptions due to species with varying numbers of ^{13}CO groups.

The bands labeled a and c in Figure 2 arise in large measure from stretching of the two CO groups cis to L and Br, numbered 3 and 5 in Figure 1. Accordingly, these bands exhibit substantial shifts in frequency upon incorporation of ^{13}CO into positions 3 or 5.

Figure 2 shows the ir spectra obtained at various times during the exchange reaction of *cis*-$Mn(CO)_4BrPPh_3$ with ^{13}CO. During the early stages of the reaction there is no evidence of bands in the 1915–1920-cm^{-1} region, which would arise from incorporation of ^{13}CO into position 6. The absorbance of band b is due in large measure to a ^{12}CO stretch in position 4. We also noted the presence of an induction period before the absorbance of this band begins to decrease. These observations suggest that incorporation of ^{13}CO into positions 4 and 6 occurs via intramolecular rearrangement in the five-coordinate intermediate. By analogy with the results obtained for $Mn(CO)_5Br$,[2] this indicates that the five-coordinate intermediate is fluxional. The resulting kinetics scheme is illustrated in Figure 3. The rate constant for dissociation from positions 3 or 5 is labeled k_{cc}, from position 4, k_{ct}, and from position 6, k_t. The expressions for all the rate constants in this reaction scheme, expressed in terms of k_{cc}, k_{ct}, k_t, and f, the fractional abundance of ^{13}CO in the exchanging gas, are given in Appendix B.[16] The coupled differential equations were solved as described previously.[2]

To determine the rate of cis CO dissociation we measured the relative integrated absorbances of the bands occurring in

Table II. Infrared Absorption Frequencies in the CO Stretching Region for *cis*-$M(CO)_4LBr$ Compounds

Compound	Band a	Band b	Band c	Band d
$Mn(CO)_4P(C_6H_5)_3Br$[a]	2087 (m)	2022 (s)	2004 (vs)	1958 (s)
$Mn(CO)_4P(OC_6H_5)_3Br$[a]	2097 (m)	2036 (s)	2022 (vs)	1975 (s)
$Re(CO)_4P(C_6H_5)_3Br$[b]	2105 (m)	2013 (s)	2002 (vs)	1948 (s)
$Re(CO)_4NC_5H_5Br$[b]	2110 (m)	2010 (s)	1991 (sh)	1935 (s)
$Re(CO)_4P(OC_6H_5)_3Br$[b]	2114 (m)	2032 (sh)	2016 (s)	1960
$Mn(CO)_3(P(C_6H_5)_3)_2Br$[b]	2036 (w)	1951 (vs)	1917 (s)	

[a] Solvent hexane. [b] Solvent 1,2-dichloroethane.

Table III. Calculated and Observed CO Stretching Mode Absorption Frequencies (cm^{-1}) in $Mn(CO)_4BrP(C_6H_5)_3$ in Hexane

Band a

Obsd freq	2087	2082	...	...	2075	2072	2069	2067	2059	2056	2042	2039
Calcd freq	2087	2085	2082	2080	2075	2073	2067	2065	2060	2057	2044	2041
Possible position of ^{13}CO incorporation	None	6	4	4, 6	3	3, 6	3, 4	3, 4, 6	3, 5	3, 5, 6	3, 4, 5	3, 4, 5, 6

Band b

Obsd freq	2022	2019	...	...	...	1985	1981	...	1977
Calcd freq	2022	2020	2006	1989	1987	1985	1983	1979	1977
Possible position of ^{13}CO incorporation	None; 6	3; 3, 6	3, 5; 3, 5,6	3, 4	3, 4, 6	4	4, 6	3, 4, 5	3, 4, 5, 6

Band c

Obsd freq	2004	1978	1973	...	1961
Calcd freq	2004	1976	1974	1971	1960
Possible Position of ^{13}CO incorporation	None; 4; 6; 4, 6	3	3, 6	3, 4; 3, 4, 6	3, 5; 3, 4, 5; 3, 4, 6; 3, 4, 5, 6

Band d

Obsd freq	1958	1953	...	...	1917	...	...
Calcd freq	1958	1956	1957	1955	1917	1916	1915
Possible Position of ^{13}CO incorporation	None	3, 4, 5; 4; 3, 5	3	3, 4	3, 5, 6; 4, 6; 3, 4	3, 6; 3, 4, 6	3, 4, 5, 6

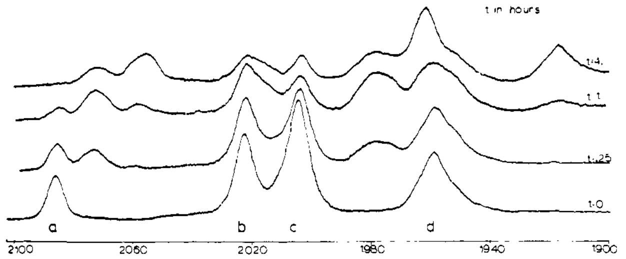

Figure 2. Infrared spectra of *cis*-$Mn(CO)_4BrPPh_3$ in hexane during exchange with ^{13}CO.

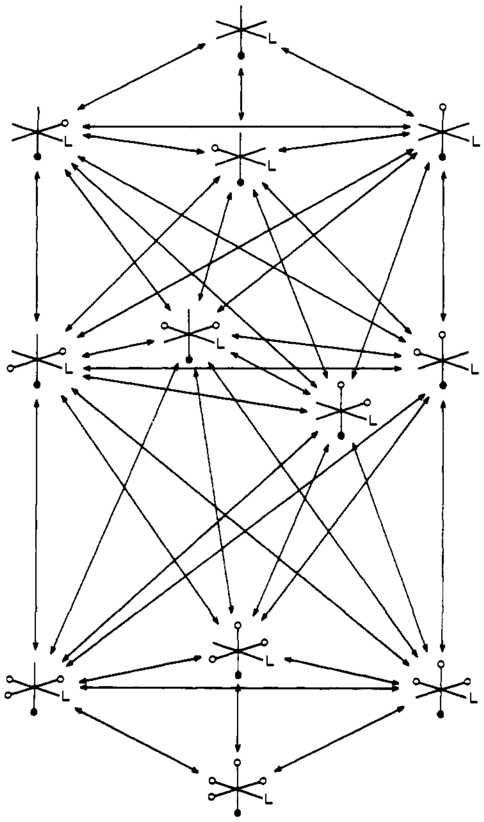

Figure 3. Kinetics scheme for ^{13}CO exchange with *cis*-$M(CO)_4BrL$, assuming a first-order dissociative loss of CO, and rapid intramolecular rearrangement in the five-coordinate intermediate.

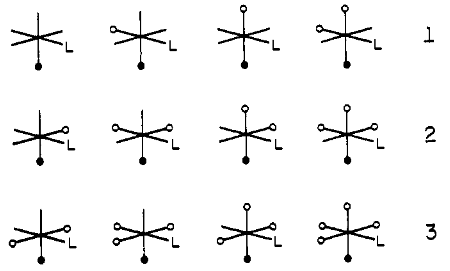

Figure 4. Grouping of all isotopically labeled molecules according to the number of ^{13}CO positions 3 and 5.

the region 2090-2035 cm^{-1}. The bands appearing in this region, at lower frequencies from the 2087-cm^{-1} band due to all-^{12}CO species, are due to molecules with one or two ^{13}CO's in positions 3 or 5. Thus there are three major groupings of bands, corresponding to zero, one, or two ^{13}CO in positions 3 and 5. Within each group there are bands falling at more or less the same frequency, due to molecules with varying degrees of substitution in positions 4 and 6. The groupings of all the possible isotopically labeled species are shown in Figure 4. The integrated absorbance of each band grouping was obtained as a function of time during the exchange reaction. An approximate correction was applied to each grouping to allow for the change in L matrix elements which accompanies the replacement of ^{12}CO by ^{13}CO.[16] This correction could not be precise, because it differs slightly for the various molecules making up each band group. The variation among the different members of each group is not large, however, and an error of no more than perhaps 10% in the correction itself was incurred on this account. From these data it was then possible to obtain reasonably satisfactory estimates of the fractional abundances of molecules with zero, one, or two ^{13}CO groups in positions 3 and 5. The results for a typical exchange study with *cis*-$Mn(CO)_4BrPPh_3$ are shown in Figure 5 as circles. The solid lines show the calculated fractional abundances as a function of time, assuming the kinetics scheme based on a fluxional intermediate, illustrated in Figure 3, and assuming $k_{cc} \gg k_t$, k_{ct}. The agreement between calculated and observed results is not as good as that obtained for $Mn(CO)_5Br$,[2] because of the uncertainties caused by numerous band overlaps and the use of a more approximate force field to obtain L matrix elements. Nevertheless, the derived rate constant $k_{cc} = 2.7 \times 10^{-4}\ s^{-1}$ is probably accurate within about 15%.

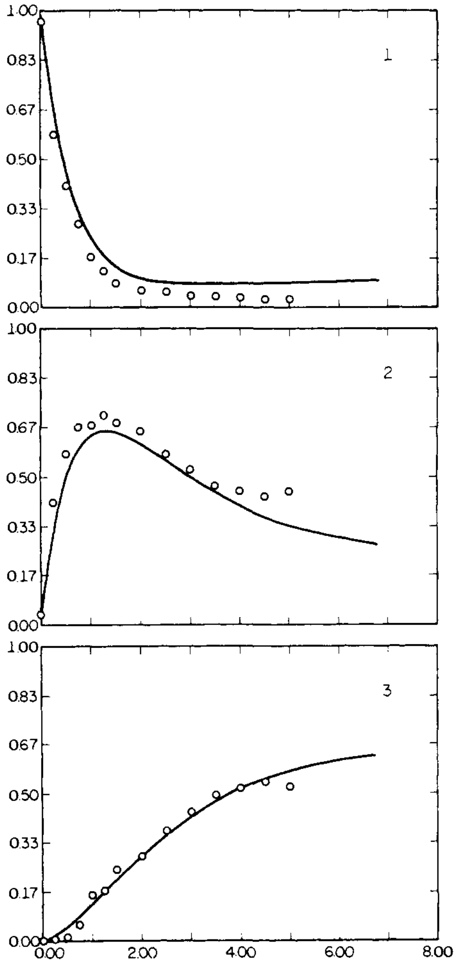

Figure 5. Fractional abundances of *cis*-$Mn(CO)_4BrPPh_3$ molecules containing zero (a), one (b), or two (c) ^{13}CO in positions 3 and 5, as derived from absorbances (circles) or calculated, solid line.

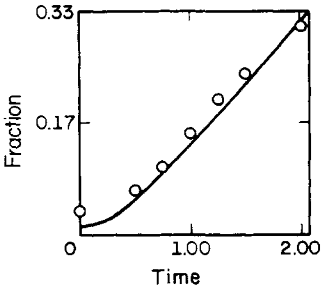

Figure 6. Fractional incorporation of ^{13}CO into position 6 in *cis*-$Mn(CO)_4BrPPh_3$ as a function of time. Circles represent estimates from ir spectra; the solid line represents calculated results.

Table IV. Rate Constants for Substitution Reactions of *cis*-$Mn(CO)_4BrPPh_3$ in hexane at 23°.

Substituting ligand	$k_1(\times 10^4\ s^{-1})$
CO^a	5.4
$P(OC_4H_9)_3$	4.2
$P(OC_4H_9)_3{}^b$	2.0
$P(OPPh)_3$	3.6

[a] $k_1 = 2k_{cc}$. [b] Tetrachloroethylene solvent.

Table V. Rate Constants for Exchange of ^{13}CO with *cis*-$M(CO)_4BrL$ Compounds

	M = Mn (23°, hexane)	
L	$k_{cc}\ (\times 10^5\ s^{-1})$	$k_{cc}(L)/k_{cc}(CO)$
CO^a	2.8	1.0
$P(OPh)_3$	3.1	1.1
PPh_3	27.0	9.6
	M = Re (30°, 1,2-dichloroethane)	
L	$k_{cc}\ (\times 10^7\ s^{-1})$	$k_{cc}(L)/k_{cc}(CO)$
CO	1.0	1.0
$P(OPh)_3$	1.1	1.1
PPh_3	9.8	9.8
NC_5H_5	72	72

[a] Reference 2.

Further evidence that the model of a fluxional intermediate, with $k_{cc} \gg k_t$, k_{ct}, is correct is found in the growth of absorbance in the 1915-1920-cm^{-1} region. The fractional integrated absorbance in this region in relation to the absorbance of band d from which it derives gives a measure of the extent of incorporation of ^{13}CO into position 6. As shown in Figure 6, there is a decided induction period in agreement with the calculated results based on the fluxional model, shown as the solid line.

The exchange of 2,4-$(PPh_3)_2Mn(CO)_3Br$ with ^{13}CO was determined by procedures very similar to those used for the $Mn(CO)_4LBr$ compounds. The asymmetric stretch of CO groups 3 and 5 yields the expected grouping of three bands corresponding to incorporation of zero, one, or two ^{13}CO molecules. The fractional absorbances of the three bands as a function of time were employed to calculate the value for k_{cc}, the dissociation rate constant for CO groups 3 and 5. The CO stretching mode occurring at 2036 cm^{-1} shifts to 1975 cm^{-1} upon ^{13}CO incorporation into position 6. The time dependence of absorbance at 2036 cm^{-1} shows an induction period, consistent with the assumption that $k_{cc} \gg k_t$, and assuming a fluxional five-coordinate intermediate.

Results and Discussion

The reactions under consideration here are the substitution and exchange processes:

$$M(CO)_4BrL + L' \rightarrow M(CO)_3BrLL' + CO$$

$$M(CO)_4BrL + {}^{13}CO \rightarrow M(CO)_3({}^{13}CO)BrL + CO$$

The substitution reaction has been observed previously[4,7] to follow a first-order rate law, with no dependence on the incoming ligand. We have studied the substitution reactions of *cis*-$Mn(CO)_4BrPPh_3$ by tributyl phosphite, $P(OC_4H_9)_3$, and triphenyl phosphite $P(OPh)_3$ in hexane for direct comparison with the ^{13}CO exchange rate constants. The results are shown in Table IV. The value for ^{13}CO as ligand, derived from the exchange studies is also listed for comparison. The factor of two arises since the kinetics analysis employed in analyzing the exchange data is formulated in terms of a specific rate constant for CO dissociation at each position. The agreement between the exchange and substitution results is sufficiently close to provide confidence that the exchange kinetics have been properly analyzed.

Table V lists the results of exchange reaction studies involving both manganese and rhenium compounds. The choice of 1,2-dichloroethane as solvent for the rhenium compounds was dictated by their low solubility in hexane. In addition to the values listed in this table, a comparative study was carried out in 1,2-dichloroethane to determine the relative exchange rates for *cis*-$Mn(CO)_4BrPPh_3$ and 2,4-$(PPh_3)_2Mn(CO)_3Br$. The choice of solvent was in this instance also dictated by the insolubility of the latter compound in hexane. Values of k_{cc} for

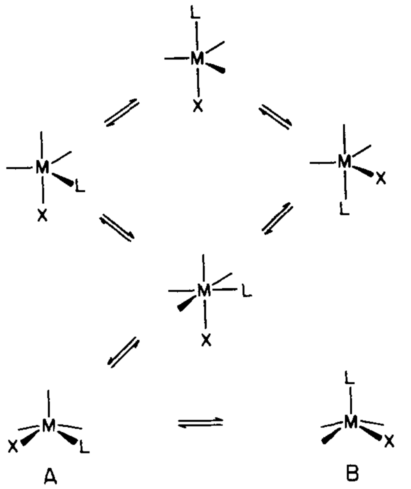

Figure 7. Intermediates formed by loss of CO from *cis*-$M(CO)_4XL$.

these two compounds in 1,2-dichloroethane at 23° were found to be 0.96×10^{-4} and $2.5 \times 10^{-4}\ s^{-1}$, respectively.

The most obvious conclusion from the exchange studies is that PPh_3 and NC_5H_5 are cis labilizing. To the extent that comparison is possible the manganese and rhenium compounds show the same relative rates of exchange as a function of ligand L. It was not possible to determine the exchange rate for *cis*-$Mn(CO)_4BrNC_5H_5$, because all attempts to prepare this compound resulted in formation of the disubstituted compound, 2,3-$(NC_5H_5)_2Mn(CO)_3Br$.[13] Clearly, in this case also the pyridine is strongly cis labilizing.

It is of interest to note that although $P(OPh)_3$ is not strongly cis labilizing, the *cis*-$M(CO)_4BrP(OPh)_3$ compounds undergo faster exchange in the cis than in the trans position, as evidenced by induction periods in the growths of absorbances due to ^{13}CO in positions 4 or 6. It is noteworthy that the labilizing effect of phosphine extends to multiple substitution, as evidenced by the larger specific rate constant for exchange into 2,4-$(PPh_3)_2Mn(CO)_3Br$ as compared with *cis*-$Mn(CO)_4BrPPh_3$.

The exchange results reported here are in reasonable agreement with the substitution data summarized in Table I. The exchange results provide firmer support than can be obtained from the substitution studies[4,17] that certain of the ligands L in *cis*-$Mn(CO)_4BrL$ are capable of labilizing the cis CO groups toward dissociation. The exchange results also provide strong evidence that the five-coordinate intermediates formed in CO dissociation undergo rapid intramolecular rearrangement during their lifetime.

Since the ligands which give rise to cis labilization of CO dissociation are poorer π acceptors than CO, it is to be expected that the CO groups in *cis*-$M(CO)_4BrL$ are involved in more extensive π bonding with the metal than in $M(CO)_5Br$. The observed crystal structures for $Mn(CO)_4ClPPh_3$[18] provide no evidence of Mn–CO bond weakening which might account for the more facile dissociative loss of CO. Neither is there evidence in the crystal structure data for a large repulsive interaction between PPh_3 and the cis CO groups which would give rise to a steric acceleration of CO dissociation. Additional arguments against steric acceleration as the source of cis labilization are (a) pyridine, which is the most strongly cis labilizing of the L groups studied, does not have a particularly large steric requirement; (b) the relative degrees of cis labilization are comparable in the Mn and Re series, in spite of a substantial difference in metal covalent radii.

We defer until the following paper a general discussion of cis labilization. It is useful, however, to consider the possibility that cis labilization in the compounds studied here arises through a stabilization of the transition state by L as compared with CO in the same position. The geometry of the lowest energy form of the intermediate formed by loss of CO from *cis*-$M(CO)_4BrL$ is not known. The two extreme possibilities are a trigonal intermediate, with idealized C_{3v} symmetry (or a lower symmetry derived from that), and idealized C_{4v} symmetry (or a lower symmetry derived from that). The possibilities are indicated in Figure 7. We assume that only the CO groups cis to both X and L undergo dissociation. Whichever geometry is lower in energy, the kinetics results require that the various forms be connected by fairly low energy barriers, since rapid intramolecular rearrangement occurs during the presumably short lifetime of the intermediate.

The most important point to be made is that, whichever form the intermediate assumes, there exist nonequivalent sites. If groups X and L exhibit a preference for a particular site, then the particular CO dissociation which leads without further rearrangement to a geometry with X and L in those sites will be most facile. From this point of view the most attractive possibility seems to be loss of CO to form the intermediate A, with both X and L in basal positions of an approximately square-pyramidal species. Barring excessive steric repulsion an incoming nucleophile will trap intermediate A, leading to the 2,3-geometry product. Where steric interactions for this geometry are large, for example, when both L and incoming ligand are PPh_3, the barrier to entry of the ligand is too large. In this case, a competition is set up between the very small quantity of CO in solution formed by CO dissociation and the much more abundant PPh_3. Since the intermediate B is in equilibrium with A, but present in much smaller amounts, B may interact with PPh_3 to form the more stable 2,4-$(PPh_3)_2Mn(CO)_3Br$. The rate of formation of this compound, however, is quite slow if intermediate B is higher in energy than A, as expected.

The relative cis-labelizing abilities of ligands can be correlated reasonably well with their expected degree of site preference in the five-coordinate intermediate, as discussed in the following paper. In the present paper we have shown that cis labilization of CO dissociation may be cumulative, in the sense that introduction of a second cis-labilizing ligand into a molecule already containing a cis-labilizing group results in additional labilization. In addition, it has been shown that the degree of labilization is reflected in the rate constants for substitution as well as exchange reactions, in the absence of large steric repulsions which prevent entry of the incoming ligand.

Supplementary Material Available: Appendices listing rate expressions and an account of the corrections to absorbance intensities based upon vibrational analyses (10 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This research was supported by The National Science Foundation through Grant MPS 71-03201 and contract DMR 7203026 with the Materials Research Laboratory, University of Illinois.
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(4) R. J. Angelici and F. Basolo, *Inorg. Chem.*, **2**, 728 (1963).
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