Cis Labilization of Ligand Dissociation. 3. Survey of Group 6 and 7 Six-Coordinate Carbonyl Compounds. The Site Preference Model for Ligand Labilization Effects[1]

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Abstract: The results of ^{13}CO exchange and substitution reaction studies on six-coordinate transition metal carbonyl compounds are interpreted in terms of the tendency of a ligand to labilize dissociative loss of CO or other ligand from the position cis to itself. The order of cis-labilizing abilities among ligands seems to be just the reverse of the trans effect order for these same ligands in substitution reactions of square planar complexes. A site preference model is offered to account for these observations; the labilizing effect of a ligand is due to its effect on the energy of the transition state. The cis-labilizing ligand stabilizes the transition state as a result of preferentially occupying a basal site in a square pyramidal or an axial site in a trigonal bipyramidal transition state speies. The site preference model should be useful in rationalizing the relative reactivities of low-valent, six-coordinate transition metal complexes. In addition, it accounts for the substitution patterns seen in several polynuclear metal carbonyl complexes, and may account for variations in effectiveness of transition metal catalysts where dissociative loss of a ligand is an important step in the catalytic cycle.

Thermal substitution reactions in transition metal carbonyl compounds may occur via one or more of several competing pathways:[2,3] (a) dissociation of CO or other departing ligand in the rate-determining step, (b) an associative process involving entering ligand and metal carbonyl, (c) migration of a ligand, particularly of alkyl or hydrogen, to adjacent CO, thus exposing a vacant coordination site at the metal center,[4] (d) a radical chain pathway, in which the metal center is labilized toward substitution by a radical abstraction reaction at the metal center, e.g., abstraction of H from $HRe(CO)_5$.[5]

Dissociation of a metal-bound ligand is the most commonly observed process; the departing ligand is most often CO. In general the rate law for CO substitution in such cases consists of two terms (let R = reactant molecule):

$$\frac{-d(R)}{dt} = (R)[k_1 + k_2(L)] \qquad (1)$$

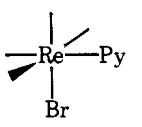
The term in k_2, first order in R and in entering ligand, is often of negligible importance. It has been ascribed to either an associative process, involving an expanded coordination sphere at the metal,[2,3] or to a dissociative interchange.[6] Our concern in this series of papers is with the k_1 term, involving dissociative loss of ligand from the metal in transition metal complexes with singlet ground states, and an electron configuration of 18 electrons in the metal valence orbitals. The experimental results suggest very strongly that dissociation of CO or other ligand from the metal center results in formation of a discrete, reactive intermediate of lower coordination number. The substitution reactions of interest are normally carried out in solvents of low nucleophilicity, e.g., hexane or 1,2 dichloroethane. The several competition ratio studies which have been carried out[6-8] point to the existence of a reactive intermediate with low discriminatory ability. In keeping with this, flash photolysis studies[9] indicate that $Cr(CO)_5$, formed from photodissociation of CO from $Cr(CO)_5$, recombines with CO in hexane with a rate constant of $\sim 3 \times 10^6\ M^{-1}\ s^{-1}$. In perfluoroalkane solvent, the rate constant for recombination is even larger.[10]

Two questions of major importance regarding dissociation of a ligand from a six-coordinate metal center are (a) what are the influences of other ligands in the complex on the rate of dissociation and (b) what is the stereochemical relationship between the departing ligand and those which remain?

Evidences of ligand effects on the rate of CO dissociation from metal carbonyl complexes are widespread. Angelici has summarized the kinetics information available to 1968 by distinguishing between labilizing and nonlabilizing ligands.[3a] The former have donor atoms which are H, N, O, or the halogens, while donor atoms of nonlabilizing ligands are P, As, Sb, S, Mn, Au, etc. The position of hydride in this grouping is anomalous, since hydride is a polarizable, soft base which would be expected to behave as a nonlabilizing ligand in terms of an empirical grouping. The unusual substitution lability of carbonyl hydrides has been accounted for by involing a hydride migration pathway.[2] More recently we have shown that $HRe(CO)_5$ is indeed inert to substitution by CO dissociation, but that substitution may occur rapidly via a radical chain pathway.[5]

Aside from this broad separation of ligands into two groups, and several studies of variation in substitution rates with change in halide,[11] there have been a few attempts to make distinctions among ligands. The question of the stereochemistry of the departing ligand has only recently been addressed. Dobson has offered evidence that halides (and to a lesser extent other ligands) cause relatively more rapid dissociation of cis CO as compared with trans CO groups.[12-14] Studies of the exchange of ^{13}CO with $Mn(CO)_5Br$ or $Re(CO)_5Br$, which proceed by dissociative CO loss, have shown that CO is lost preferentially from the cis position.[8]

The stereochemistry of the departing CO group cannot be inferred rigorously by observing the stereochemistry of substitution of CO by some other ligand such as a phosphine.[8,15] When the entering ligand differs from the departing ligand in terms of steric requirement and electronic properties there is no necessary relation between the stereochemistry it adopts and the original location of the lost CO. Use of ^{13}CO or $C^{18}O$ in exchange studies offers at least a partial answer to the question. By applying the principle of microscopic reversibility[16,17] it follows that the CO group which enters the molecule after loss of a CO must take up the position of the departing CO. The exchange studies prove in the general case to provide only a partial answer, because the five-coordinate intermediate formed by loss of CO is normally fluxional on the time scale of its expected lifetime. This means that as the reaction proceeds label finds its way even into the positions which are inert toward loss of CO, by means of intramolecular rearrangement of intermediates already containing a label. However, it is possible to ascertain in the exchange experiment that a particular position is more labile than another by some factor on the order of 5–10. For example, in the exchange of ^{13}CO with $Mn(CO)_5Br$ and $Re(CO)_5Br$, the results of a careful ^{13}CO exchange study[8] show that the rate constants for loss of CO from the position trans to the bromide could be no larger than about 0.1 of the corresponding rate constants for CO loss from any one cis position. A similar degree of specificity has been seen in other experiments involving ^{13}CO carried out in our laboratory with molecules **1–3**.[15,18] (The bidentate ligands in **2** and **4** are 2,2′-bipyridyl or 1,10-phenanthroline.)



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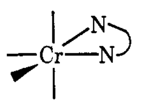

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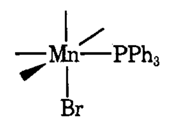

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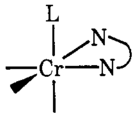
It is not possible to state the precise degree to which the cis position is labilized relative to the trans. However, there are strong indications from substitution studies that ligands which can be shown to labilize the cis positions also have the effect of inhibiting dissociative loss of CO from a trans position. For example, in **4**, when L = PPh_3 the rate of substitution into the molecule of a second PPh_3 is much slower than initial formation of **4**.[19] In **5**, substitution of a second $P(n\text{-}C_4H_9)_3$ in the position trans to L = $P(n\text{-}C_4H_9)_3$ is 40 times slower than for the substitution trans to L = CO.[20] In **6** it has been noted that for L = $P(OCH_2)_3CCH_3$, decarbonylation or rearrangement to the 2,4-isomer, presumably controlled by the rate of dissociative loss of CO, is very slow in comparison with the rate at which the 2,4-isomer is formed from *cis*-$CH_3COMn(CO)_4L$.[21] Similarly, decarbonylation of 2,3-[1,2-bis(diphenylphosphino)ethane]-1-acetylmanganese tricarbonyl is very slow.[22] In these examples there is evidence, already presented in part or discussed later in this paper, that ligands of the kinds involved are labilizing relative to CO.



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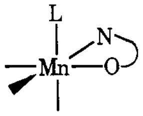

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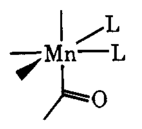

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From the results of molecular orbital calculations[14,23,24] and from ir data for CO stretching mode frequencies,[25–27] it appears that the extent of π bonding between the metal and CO groups trans to a ligand which is a weaker π acceptor than CO is greater than to the CO groups cis to that ligand. On these grounds also, then, it is reasonable to expect that the trans CO groups should be less labile than the cis.

Finally, the characteristics of trans labilization seen in certain low spin d^6 Co(III) complexes suggest that those ligands which are most strongly cis labilizing in metal carbonyls are just those which are least trans labilizing. For example, in bis(dimethylglyoximato)cobalt(III) complexes, the lability of ligands trans to a variety of ligands on the cobalt varies over a large range,[28–32] with ligands such as aquo, halide, and other pseudohalides producing the least labilization, and strongly electron-releasing ligands such as thiourea, alkyl, or sulfite producing the greatest degree of labilization.[33]

It seems reasonable on the basis of all these lines of evidence to hypothesize that ligands which are weaker π acceptors than CO and which upon substitution for CO labilize the complex toward dissociative ligand loss (e.g., $Re(CO)_5Br$ is labile with respect to $Re(CO)_6^+$) preferentially labilize the cis positions.[36]

The electronic and steric properties of a ligand which replaces CO affect both the rate and stereochemistry of successive substitutions. For example, reaction of PPh_3 with *cis*-$Mn(CO)_4BrPPh_3$ is slow[39] and leads to a trans disposition of the two PPh_3. By contrast, exchange of ^{13}CO with *cis*-$Mn(CO)_4BrPPh_3$ is relatively more rapid, and the labeled CO appears cis to PPh_3.[15] However, where substantial steric effects are not present the rate constants for substitution should be the same as those for ^{13}CO exchange. It is therefore possible, with the aid of the hypothesis stated above, to employ the many substitution rate studies which have been reported as a means of establishing an order of ligands with respect to labilization of cis ligand dissociation. So long as dissociative loss of CO is the rate-determining step, the substitution rate constants will never be larger than for CO exchange; they will be smaller only when a large steric requirement makes the labile position inaccessible to the entering ligand, situations which can generally be anticipated on the basis of several well-studied cases.

In the comparisons which follow we have endeavored to place all the available quantitative and semiquantitative rate data on a common footing by estimating the rate constant for CO loss at a common temperature within a given series of like compounds. Fortunately, the activation parameters have been reported for many cases, and extrapolation to the desired temperature can be made with little difficulty. In some cases, however, the extrapolation is rather extended, with an attendant increase in the uncertainty of the rate constant. In cases where no activation parameters have been reported we have assumed a value for E_a based on known values for compounds that are as similar as possible. In all cases the values listed are the specific rate constants per CO group. These were obtained from the first-order rate constants estimated at 30°, by assuming that only the cis CO groups contribute to the observed rate.

Group 7 Carbonyls. The comparative rates of substitution in several manganese carbonyl species are given in Table I, and the analogous data for rhenium compounds in Table II. (In all cases, the observed substitution rate constants are expressed on a per CO basis. Except in the parent binary carbonyl compounds, the cis positions are assumed to be the labile positions.) In most instances the rate law for the substitution was studied and k_1, the first-order rate constant, was reported. Only these rate constants are of relevance in the present comparisons, and only these values have been employed. It is of some interest to note, however, that the second-order term is not of much significance in the manganese or rhenium systems.

In addition to the comparisons afforded by the data in Tables I and II, there are several other indications of cis-labilizing behavior to be found in the literature. In paper 2 of this series we discussed $M(CO)_4BrL$ compounds[15] and exhibited ^{13}CO data which confirm more qualitative indications[39,40] of cis labilization.

One of the most notable entries in Table II is $HRe(CO)_5$, which has been shown[5] to be exceptionally inert toward substitution. This is the only example of a hydride compound which behaves in this manner. The manganese analogue, $HMn(CO)_5$, cannot be considered in the manganese series, since it is likely that it undergoes substitution by a either hydride migration[2,41] or radical chain process.[5]

Group 6 Carbonyls. A compilation of substitution rate constants for group 6 metal carbonyls is presented in Table III. The range in ligand types is comparable to that available for the group 7 compounds, and the general trends in lability are quite similar in the two families.

It is noteworthy that substitution of a CO in $Cr(CO)_6$ by PPh_3 increases the lability of the cis CO groups by a factor of 300. This result affords additional strong evidence of the labilizing effect of PPh_3. Comparison of the rates of dissociative loss of piperidine from $Mo(CO)_5NC_5H_{11}$[6] and *cis*-$Mo(CO)_4PPh_3NC_5H_{11}$[7b] shows a remarkably similar enhancement in the rate of piperidine dissociation. Thus, cis labilization is not confined to loss of CO. There is at this point, however,

Table I. First-Order Rate Constants at 23° for Substitution of Manganese Carbonyl Compounds

Compound	Substituting ligand	Solvent	$k_1{}^a$ (s^{-1})	Ref
$Mn(CO)_6^+$	^{14}CO	Water	N.R. 15 h	*b*
$Mn(CO)_5AuPPh_3$	^{14}CO	$(n\text{-}C_4H_9)_2O$	N.R. 20 h	*c*
$Mn(CO)_5SnPh_3$	PPh_3	Decalin	$\sim 8 \times 10^{-16}$	*d*1
$Mn(CO)_5GePh_3$	PPh_3	Decalin	4×10^{-14}	*d*2
$Mn_2(CO)_{10}$	PPh_3	*p*-Xylene	1×10^{-11}	*e*
$Mn(CO)_5SO_2CH_3$	$4\text{-}NC_5H_4CH_3$	CH_2ClCH_2Cl	8×10^{-8}	*f*
$Mn(CO)_5I$	$AsPh_3$	$CHCl_3$	2×10^{-7}	*g*1
$Mn(CO)_5Br$	$AsPh_3$	$CHCl_3$	5×10^{-6}	*g*2
$Mn(CO)_5Br$	^{13}CO	Hexane	2.8×10^{-5}	8
$Mn(CO)_5COCH_3$	PPh_3	Toluene	3×10^{-6}	*h*
$Mn(CO)_5Cl$	$AsPh_3$	$CHCl_3$	5.0×10^{-5}	*g*
$Mn(CO)_5NO_3$	PPh_3	CH_3NO_2	10^{-4} to 10^{-5}	*i*

[a] N.R. means no reaction observed. [b] W. Hieber and K. Wollmann, *Chem. Ber.*, **95**, 1552 (1962). [c] S. Breitschaft and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2702 (1966). [d] G. R. Dobson and E. P. Ross, *Inorg. Chim. Acta*, **5**, 199 (1971). (1) Temperature range studied 170–190°, $\Delta H^{\ddagger} = 41.4$ kcal/mol, $\Delta S^{\ddagger} = 14.8$ eu; (2) temperature range studied 150–170°, $\Delta H^{\ddagger} = 39.4$ kcal/mol, $\Delta S^{\ddagger} = 16.1$ eu. [e] Reference 58; Temperature range studied 100–120°, $E_a = 37$ kcal/mol. [f] R. J. Parker and A. Wojciki, unpublished observations; rate constant measured at 66.3°, assumed $E_a = 32$ kcal/mol. [g] R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962). (1) Temperature range studied 30–40°, $\Delta H^{\ddagger} = 32.2$ kcal/mol, $\Delta S^{\ddagger} = 20.7$ eu; (2) temperature range studied 30–48°, $\Delta H^{\ddagger} = 29.8$ kcal/mol, $\Delta S^{\ddagger} = 18.9$ eu. [h] F. Calderazzo and F. A. Cotton, *Chem. Ind. (Milan)*, **46**, 1165 (1964); rate constant measured at 30°, assumed $E_a = 29$ kcal/mol. [i] C. C. Addison and M. Kilma, *J. Chem. Soc. A*, 1539 (1968); rate constant estimated from reaction time at 20 °C.

Table II. First-Order Rate Constants at 30° for Substitution of Rhenium Carbonyl Compounds

Compound	Substituting ligand	Solvent	k_1 (s^{-1})	Ref
$Re(CO)_6^+$	^{14}CO	Water	N. R. 60 h	*a*
$HRe(CO)_5$	PPh_3	Hexane	N.R. 60 days	*b*
$Re_2(CO)_{10}$	PPh_3	Decalin	$<10^{-13}$	*c*
$Re(CO)_5I$	PPh_3	Octane	4×10^{-8}	*d*1
$Re(CO)_5Br$	PPh_3	CCl_4	5×10^{-7}	*d*2
$Re(CO)_5Br$	^{13}CO	Hexane	5×10^{-7}	8
$Re(CO)_5Cl$	PPh_3	CCl_4	2×10^{-6}	*d*3
$Re(CO)_5NCO$	dipy	Toluene	1.5×10^{-6}	*e*

[a] W. Hieber and K. Wollmann, *Chem. Ber.*, **95**, 1552 (1962); experiment conducted at 60 °C. [b] Reference 5; experiment conducted at 27 °C. [c] Reference 58; temperature range studied 130–150°. (The authors propose metal-metal bond cleavage as a rate-determining step. However, loss of CO must be as slow or slower than observed rate.) Assume $E_a = 38$ kcal/mol. [d] D. A. Brown and R. T. Sane, *J. Chem. Soc. A*, 2088 (1971): (1) temperature range studied 80–90°, $E_a = 31.8$ kcal/mol; (2) temperature range studied 60–69°, $E_a = 29.4$ kcal/mol; (3) temperature range studied 55–65°, $E_a = 27.3$ kcal/mol. [e] R. J. Angelici and G. C. Faber, *Inorg. Chem.*, **10**, 514 (1971); temperature range studied 45–60°, $\Delta H^{\ddagger} = 23.5$ kcal/mol, $\Delta S^{\ddagger} = 1.8$ eu.

very little evidence regarding the effect of changing the leaving group. It should be noted that with some bidentate chelate ligands, e.g., diphos, ring strain energies appear to play a role in determining rate of CO loss.[18]

Cis-Labilization Order. In assessing the magnitude of the cis-labilizing effect of a given ligand it is important to distinguish its effect when it replaces a CO of the parent hexacarbonyl and when it acts as a second ligand in an $M(CO)_4XL$ compound. For example, PPh_3 labilizes CO or NC_5H_{11} by a factor of more than 100 when it acts as the primary cis-labilizing ligand. Substituted into $Mn(CO)_5Br$, however, it labilizes loss of the cis CO groups about tenfold. The fact that PPh_3 behaves quantitatively differently in the two cases is, we believe, related to the relative stabilities associated with the placement of the ligands in the five-coordinate intermediate (vide infra). In establishing an order for the cis-labilizing effect, we have attempted as much as possible to make comparisons between ligands in compounds of analogous structure.

Although data which afford the possibility of at least semiquantitative comparisons are few, it is evident from inspection of Tables I–III that substantial cis-labilizing effects do exist. On the basis of the limited data available it is possible to group several ligands in the order of cis-labilizing effect as follows: CO, $AuPPh_3$, H^-, $SnPh_3^-$, $GePh_3^-$, $M(CO)_n$ < $P(OPh)_3$ < PPh_3 < I^-, $CH_3SO_2^-$, NC_5H_5 < CH_3CO^- < Br^- < NCO^-, Cl^-, NO_3^-. In both the group 6 and 7 series, the relative labilizations of cis CO groups toward dissociation span a large range. The range in rate constants in a given metal series is on the order of 10^8. The effects are obviously very large, and compare in magnitude with the range of trans effects seen in the substitution reactions of square planar complexes.[42-45]

Origin of the Cis-Labilization Effect. The process under consideration here involves the loss of CO or other ligand from an octahedrally coordinated metal center with 18 electrons in the valence shell orbitals of the metal. Loss of ligand results in a five-coordinate, 16-electron species which might have either D_{3h} or C_{4v} symmetry (or a lower symmetry derived from those, depending on the other ligands remaining on the complex). For convenience we will refer to these alternative geometries as trigonal bipyramidal (tbp) or square pyramidal (sq-py) without regard to the precise point group symmetry at the metal. Since CO loss presumably occurs with essentially complete metal-CO bond rupture, the transition state should closely resembly the intermediate.[6] Our discussion is therefore couched in terms of the properties of the five-coordinate intermediate.

The best evidence at present is that the lowest energy form of the 16-electron $Cr(CO)_5$ moiety possesses the sq-py geometry.[46,47] It is not so clear what the lowest energy geometry for $XM(CO)_4$ species might be. Limited evidence based on matrix isolation work suggests the tbp arrangement,[48] but this is among the earliest matrix isolation work on transition metal carbonyls. More recently the C_{4v} geometry has been argued for $Cr(CO)_4PR_3$,[49a] and $Cr(CO)_4CS$.[49b]

In the tbp geometry the relative stability of axial or equatorial location for a ligand vis a vis CO is dependent on its σ and π bonding characteristics, and on the d electron configuration at the metal center.[50,51] In d^8 five-coordinate species of the type $LM(CO)_4$, which possess tbp geometry, ligands such as H, CH_3, Cl, PPh_3, SnX_3, and many others are invariably found in an axial site. When more than two different ligand types are present in the same compound the competition for the axial positions is dependent on both electronic and steric factors. A ligand with a large steric requirement might be driven by steric

Table III. First-Order Rate Constants at 30° for the Substitution Reactions of Group 6 Carbonyl Compounds

Compound	Substituting ligand	Solvent	k_1 (s^{-1})	Ref
$Cr(CO)_6$	PBu_3	Decalin	1×10^{-12}	*a*1
$Cr(CO)_5PR_2R'$	PR_2R'	Octane	1.5×10^{-10}	*b*1
$Cr(CO)_5PPh_3$	^{13}CO	Octane	3×10^{-10}	*c*
$Cr(CO)_5C(OCH_3)CH_3$	PBu_3	Decane	4×10^{-7}	*d*
$Cr(CO)_5I^-$	PPh_3	Diglyme	$<10^{-5}$	*e*1
$Cr(CO)_5Br^-$	PPh_3	Diglyme	2×10^{-5}	*e*
$Cr(CO)_5Cl^-$	PPh_3	Diglyme	1.5×10^{-4}	*e*2
$Cr(CO)_4$(*o*-phen)	$P(OCH_2)_3CCH_3$	CH_2ClCH_2Cl	1×10^{-5}	*f*
$Cr(CO)_4$(bpy)	$P(OC_2H_5)_3$	CH_2ClCH_2Cl	2.5×10^{-5}	*g*
$Cr(CO)_4$(diphos)	$P(OCH_2)_3CCH_3$	Mesitylene	5×10^{-13}	*h*1
$Mo(CO)_6$	PBu_3	Decalin	5×10^{-10}	*a*2
$Mo(CO)_5PR_2R'$	PR_2R'	Octane	2×10^{-8}	*i*
$Mo(CO)_5(4\text{-}NC_5H_4CH_3)$	$4\text{-}NC_5H_4CH_3$	Toluene	5×10^{-8}	*j*
$Mo(CO)_5NC_5H_5$	NC_5H_5	Toluene	4×10^{-8}	*j*
$Mo(CO)_5I^-$	PPh_3	Diglyme	3×10^{-5}	*e*
$Mo(CO)_5Br^-$	PPh_3	Diglyme	1.5×10^{-4}	*e*2
$Mo(CO)_5Cl^-$			$>10^{-3}$	*e*
$Mo(CO)_4$(bpy)	$P(OC_2H_5)_3$	CH_2ClCH_2Cl	7×10^{-6}	*k*1
$Mo(CO)_4$(*o*-phen)	$P(OCH_2)_3CCH_3$	CH_2ClCH_2Cl	1×10^{-5}	*l*1
$Mo(CO)_4$(diphos)	$P(OCH_2)_3CCH_3$	Mesitylene	1×10^{-11}	*h*2
$W(CO)_6$	PBu_3	Decalin	1×10^{-14}	*a*3
$W(CO)_5SbPh_3$	bpy	Mesitylene	1×10^{-12}	*m*
$W(CO)_5PR_2R'$	PR_2R'	Nonane	4×10^{-13}	*b*2
$W(CO)_5Cl^-$	PPh_3	Diglyme	5×10^{-5}	*e*
$W(CO)_4$(*o*-phen)	$P(OCH_2)_3CCH_3$	C_6H_5Cl	5×10^{-9}	*l*2
$W(CO)_4$(bpy)	$P(OC_2H_5)_3$	C_6H_5Cl	5×10^{-9}	*k*2

[a] J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 2082 (1967): (1) temperature range studied 130–144°, $\Delta H^{\ddagger} = 40.2$ kcal/mol, $\Delta S^{\ddagger} = 22.6$ eu; (2) temperature range studied 103–116°, $\Delta H^{\ddagger} = 31.7$ kcal/mol, $\Delta S^{\ddagger} = 6.7$ eu; (3) temperature range studied 146–165°, $\Delta H^{\ddagger} = 39.9$ kcal/mol, $\Delta S^{\ddagger} = 13.8$ eu. [b] J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 347 (1973): $PR_2R' = (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. Reaction studied is chelation: (1) temperature range studied 83–124°, $\Delta H^{\ddagger} = 32.3$ kcal/mol, $\Delta S^{\ddagger} = 6.4$ eu; (2) temperature range studied 123–150°, $\Delta H^{\ddagger} = 37.0$ kcal/mol, $\Delta S^{\ddagger} = 9.6$ eu, [c] J. D. Atwood, M. A. Cohen, and T. L. Brown, to be submitted for publication. Temperature range studied 70–90°; $E_a = 36$ kcal/mol. [d] H. Werner and H. Rascher, *Helv. Chim. Acta*, **51**, 1765 (1968). Temperature range studied 59–68°; $\Delta H^{\ddagger} = 26.0$ kcal/mol, $\Delta S^{\ddagger} = 0.8$ eu. (Essentially identical k_1 using other phosphorus ligands, including PPh_3.) [e] A. D. Allen and P. F. Barrett, *Can. J. Chem.*, **46**, 1655 (1968): (1) reaction reported as slow at 30 °C, in comparison with $Cr(CO)_5Br^-$ or $Cr(CO)_5Cl^-$ rates; (2) rate constant measured at 20°, assumed $E_a = 27$ kcal/mol. [f] Reference 19a. Temperature range studied was 38–58°; $\Delta H^{\ddagger} = 26.4$ kcal/mol, $\Delta S^{\ddagger} = 7.0$ eu. [g] Reference 19b. Temperature range studied was 38–58°; $\Delta H^{\ddagger} = 24.3$ kcal/mol, $\Delta S^{\ddagger} = 1.9$ eu. [h] G. C. Faber and G. R. Dobson, *Inorg. Chim. Acta*, **2**, 479 (1968): (1) temperature range studied was 131–148°, $\Delta H^{\ddagger} = 40.3$ kcal/mol, $\Delta S^{\ddagger} = 19.8$ eu; (2) temperature range studied was 113–136°, $\Delta H^{\ddagger} = 38.0$ kcal/mol, $\Delta S^{\ddagger} = 18.1$ eu. [i] J. A. Connor and G. A. Hudson, *J. Organomet. Chem.*, **73**, 351 (1974). Temperature range studied was 90–126°; $\Delta H^{\ddagger} = 28.7$ kcal/mol, $\Delta S^{\ddagger} = 3.4$ eu. [j] F. Zingales, F. Faraone, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, **7**, 1653 (1968). Rate constants measured at 70°. Assumed $E_a = 31$ kcal/mol. [k] J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, **87**, 5590 (1965): (1) temperature range studied was 38–58°, $\Delta H^{\ddagger} = 24.6$ kcal/mol, $\Delta S^{\ddagger} = 0.48$ eu; (2) temperature range studied was 100–120°, $\Delta H^{\ddagger} = 26.1$ kcal/mol, $\Delta S^{\ddagger} = -7.5$ eu. [l] J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 992 (1967): (1) rate constant reported at 48°, $\Delta H^{\ddagger} = 25.1$ kcal/mol, $\Delta S^{\ddagger} = 2.4$ eu; (2) rate constant reported at 114°, $\Delta H^{\ddagger} = 33.4$ kcal/mol, $\Delta S^{\ddagger} = -10.6$ eu. [m] G. R. Dobson, *Inorg. Chem.*, **13**, 1790 (1974). Rate constant measured at 140°. Assumed $E_a = 40$ kcal/mol.

forces toward an equatorial position, where the number of 90° interactions with adjacent ligands is smaller.[50]

The geometry of the five-coordinate intermediate might also be sq-py. In a d^6 sq-py species, ligands which are relatively weak σ donors are expected to occupy a basal position.[51] The site preference for a ligand which has some π acceptor ability as well is not clear.

The observed cis labilization might be the result of some effect which operates in the ground state of the reactant molecule. On the other hand, it may arise from a stabilization of the transition state due to the presence of a group X as compared with CO. There is little evidence in the observed ground state properties of $XM(CO)_5$ molecules or ions for a weakening of metal–CO bonding in the groups cis to X, as compared with the parent $M(CO)_6$. Crystal structure data, summarized in Table IV, show that there is, if anything, a slight shortening of $M\text{-}C_{cis}$ bonds relative to $M(CO)_6$ in the chromium series. (It is interesting to note, however, that the $Mn\text{-}C_{cis}$ bond length in $ClMn(CO)_5$ is longer than in any of the other Mn compounds.) In both series, there is considerable evidence for a $M\text{-}C_{trans}$ bond shortening for X ligands which are poor π acceptors.

One effect of the introduction of X in place of CO is an opening of the $C_{trans}\text{-}M\text{-}C_{cis}$ bond angle. In $XMn(CO)_5$ compounds, for example, this angle is invariably greater than 90° (Table IV), regardless of the steric requirements of the X group. On the other hand, in the substituted chromium compounds, where π bonding is more extensive, the angular distortions are small and possibly in the opposite sense.

Mason and Bennett have suggested[52] that rehybridization of metal orbitals to permit a greater degree of π bonding to the CO group trans to X, and also to decrease to some extent the σ bond overlap to X, accounts for the increased angle. A similar larger than 90° angle between axial and radial CO groups is seen in five-coordinate $XCo(CO)_4$ species.[53] It thus appears that angular distortions due to differences in the bonding characteristics of X as compared with CO are about the same in six- and five-coordinate complexes with 18-electron configurations.

Dobson has suggested[12,13] that there is some evidence for weaker $M\text{-}C_{cis}$ bonding in $M(CO)_5X$ compounds in the frequencies of the M–C stretching modes. The variation in frequency of the M–C stretching mode of E symmetry appears to correlate with the cis-labilizing properties of X in $XM(CO)_5$.

Table IV. Structural Parameters of Six-Coordinate Metal Carbonyl Systems

Compound	$M-C_{trans}$[a]	$M-C_{cis}$[a] (av)	$C_{trans}-M-C_{cis}$ (av)	Ref
$(CO)_4Fe[Mn(CO)_5]_2$	1.81	1.86	94	*b*
$C_5H_5(CO)_2FeMn(CO)_5$	1.748	1.825	93.4	*c*
$Ph_3SnMn(CO)_5$	1.752 (7)	1.750 (7)	93.3	*d*
$(CH_3)_3SnMn(CO)_5$	1.823 (13)	1.802 (12)	95	*e*
$HMn(CO)_5$	1.822 (9)	1.845 (9)	97	*f*
$CFHCFMn(CO)_5$	1.73 (3)	1.79 (3)	94	*g*
$SnCl_3Mn(CO)_5$	1.826 (43)	1.888 (44)	91.6	*h*
$ClMn(CO)_5$	1.807 (9)	1.892 (6)	92	*i*
$Cr(CO)_6$	1.909 (7)	1.909 (7)	90	*j*
$PPh_3Cr(CO)_5$	1.845 (4)	1.880 (4)	88.4	*k*
$P(OPh)_3Cr(CO)_5$	1.861 (4)	1.893 (4)	88.4	*k*
trans-$[P(OPh)_3]_2Cr(CO)_4$	—	1.878 (7)	90	*l*
$(CH_3)_3PSCr(CO)_5$	1.815 (8)	1.900 (7)	88.9	*m*

[a] Numbers in parentheses refer where shown to standarized uncertainties in bond length. [b] P. A. Argon, R. D. Ellison, and H. A. Levy, *Acta Crystallogr.*, **23,** 1079 (1967). [c] P. J. Hansen and R. A. Jacobson, *J. Organomet. Chem.*, **6,** 389 (1966). [d] H. P. Weber and R. F. Bryan, *Acta Crystallogr.*, **22,** 822 (1967). [e] R. F. Bryan, *J. Chem. Soc. A*, 696 (1968). [f] S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3,** 1491 (1964); S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davison, *ibid.*, **8,** 1928 (1969). [g] F. W. B. Einstein, H. Luth, and J. Trotter, *J. Chem. Soc. A*, 89 (1967). [h] S. Onaka, *Bull. Chem. Soc. Jpn.*, **48,** 319 (1975). [i] P. T. Greene and R. F. Bryan, *J. Chem. Soc. A*, 1559 (1971). [j] A. Whitaker and J. W. Jeffery, *Acta Crystallogr.*, **23,** 977 (1967). [k] H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, **12,** 265 (1973). [l] H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, **11,** 161 (1972). [m] E. N. Baker and B. R. Reay, *J. Chem. Soc., Dalton Trans.*, 2205 (1973).

It is not evident, however, that the observations are generally applicable, nor is it clear how the M–C stretching coordinate of E symmetry is related to the nuclear configuration changes which lead to loss of CO. In general, however, it is reasonable to look for a lower potential energy gradient along the nuclear configuration coordinate which leads to CO dissociation.[54,55]

Our tentative conclusion from the available evidence is that there are no compelling reasons for supposing that X is cis labilizing as a result of ground-state effects. On the other hand, there are clear indications that $M-CO_{trans}$ bonding is strengthened in the ground state when X is cis labilizing. More data relevant to the question at hand are needed, but we conclude tentatively that cis labilization is due in most instances to the effect of X in stabilizing the transition state.

The magnitude of the cis labilization, and the observed order of ligands invites a comparison with the much-studied trans effect in square planar substitution reactions.[42–45] At first sight there would seem to be little basis for comparison, but in fact the two processes are remarkably opposite in character. Square planar substitution occurs via an associative step, in which the four-coordinate, 16-electron square planar metal complex goes to a five-coordinate, 18-electron transition state, probably always of tbp geometry.[56] In considering substituent effects it is important to keep in mind that the trans-labilizing ligand in square-planar substitution necessarily finds itself in the trigonal plane in the tbp transition state.

Analysis of all the observations regarding the trans *influences* of ligands in square planar complexes, coupled with kinetics data regarding their trans effects, can be roughly incorporated into a few statements which take account of the obvious differences in trans influences[58] of strongly σ donor ligands and those which are strong π acceptors: Ligands which are strong σ donors weaken the metal–ligand bond in the position trans to them in the ground state of the square planar system. Such ligands probably suffer a weakening of their own bonding to metal between the ground and transition states. (Often the transition state has a disadvantageous geometry for such ligands, e.g., H^-, because they preferentially occupy the axial position rather than the equatorial position they must occupy if they are to be trans labilizing.)[56] Thus, the effect of such ligands (e.g., H^-, PBu_3, etc.) is largely one of ground state weakening of the trans metal–ligand bond. On the other hand, ligands which are strong π acceptors do not directly weaken the trans metal–ligand bond, except where that ligand is itself a π acceptor ligand, a rare situation in square planar systems. Rather, the influence of the strongly π acceptor ligands seems to be due to their relative stabilizing influence on a transition state of tbp geometry in which they are in the equatorial plane, and thus relatively more strongly bonded to the metal.[51]

We cannot be certain of the geometries of the transition states or intermediates resulting from CO dissociation from the six-coordinate complexes. Nevertheless it is possible to proceed in an empirical manner to account for the cis-labilizing effects of ligands in terms of a site preference model. In this model the labilizing effect of a ligand is ascribed to its ability to stabilize a transition state of particular geometry. That is, the (approximately) five-coordinate transition state is stabilized as a result of replacement of one or more CO groups by other ligands. We will assume that the most stable geometry in the five-coordinate species is sq-py, in which ligands other than CO may occupy preferentially either a basal or axial position. Assume further that the ligand L in $M(CO)_5L$ is preferentially sited in the basal position in square-pyramidal $M(CO)_4L$. Then, as illustrated in Figure 1, the free energy for CO dissociation from the cis position may be lowered, not only relative to trans CO dissociation but also relative to CO dissociation from $M(CO)_6$. In the site preference model, the cis labilizing ligands are relatively more stable than CO in the basal position of the 16-electron, five-coordinate species as compared with the six-coordinate complex. The degree of labilization observed for a given L is determined by the magnitude of the difference between CO and L. Ligands which are weak σ donors and non-π-acceptors are likely to be strongly oriented toward occupancy of the basal position in the sq-py intermediate, and are thus strongly cis labilizing. It is just such ligands which are highest in the cis-labilizing order shown above.

Ligands which are moderately good σ donors, but which are more weakly π acceptor in character than CO (e.g., NC_5H_5, PPh_3) are also more stable in the basal position than CO, but the difference in stabilities diminishes as the ligands become more strongly σ donating or π accepting. Thus in the case of H^-, for example, there is apparently only a very low site preference, with the result that H^- is not a labilizing ligand. A ligand which is a strong σ donor ligand and a weak π acceptor, and which possesses only a low site preference (e.g., $SnPh_3^-$, or $Sn(CH_3)_3^-$) may in fact *stabilize* the six-coordinate species with respect to CO dissociation. This would be the case because such a ligand, upon substitution for CO, causes increased π bond interaction between metal and cis CO groups in the starting six-coordinate species. However, in the extreme case of a ligand which is a stronger π acceptor ligand than CO (e.g., NO) the trans ligand may become labile toward dissociation, as already noted.[36]

A ligand may exert a strong site preference, leading to stereospecific substitution, even when there is no overall labilization of the complex as compared with the chosen reference ligand, in our examples CO. This would occur when the lower energy configuration, while considerably lower in energy than for the alternate siting of the ligand, is nevertheless not relatively lower than for CO as ligand. Triphenyl phosphite, which is not strongly labilizing relative to CO, but which causes preferential cis CO dissociation,[15] may be an example.

A rationale for the observed cis-labilizing effects could alternatively be formulated on the basis of an assumed tbp geometry for the five-coordinate species. There is at this point perhaps some slight basis for preferring the sq-py geometry, but in either case the geometry of the transition state/intermediate is such that a clear distinction exists between nonequivalent positions. This fact makes it possible for the transition state/intermediate to adopt a configuration which places L in the lower energy location.

This brief discussion of the site preference model is intended to serve only as an introductory basis for relating the properties of ligands to their ability to cis or trans labilize.Considerably more experimental kinetic data, and more systematic spectroscopic and structural studies, are needed to reveal more clearly the factors common to ligands which are responsible for labilization and to establish that the labilization is indeed with respect to a particular position. In this connection, however, it should be noted that the site preference model is probably more amenable to detailed test and understanding than the trans effect. The process involved is dissociative and essentially nonpolar in character, and thus relatively independent of solvent effects. There is no entering group to add a further dimension of complexity to the system. Thus far the most extensive comparative data are those for metal carbonyl systems in which most of the ligands on the metal are CO. As a result, since CO is a strongly π acceptor ligand, the labilization resulting from CO replacement by most other ligands is in the cis position. However, the model is applicable to systems with a great variety of other ligands on the metal, and leaving groups other than CO are open to consideration.

Applications. The recognition that there exists a general tendency of many ligands to labilize other ligands toward dissociation should help to systematize the reactivity patterns observed in the low-valent transition metal complexes. In addition, it may help to account for many previously unexplained observations in the chemistry of six-coordinate transition metal organometallic systems. For example, there are several reports in the literature that polynuclear metal carbonyl compounds undergo ligand substitution with rate constants which increase with the degree of substitution. Thus, $Mn_2(CO)_{10}$ has been observed to undergo substitution by phosphorus ligands to yield the axially substituted $Mn_2(CO)_9L$.[59] The rate law contains both first- and second-order terms. The first-order term is thought to correspond at least in part, to a rate-determining dissociation of CO.[59-61] Substitution of triphenylphosphine into $Mn_2(CO)_9L$ occurs at the other metal center; the rate law contains only a first-order term.[59] The magnitude of the rate constant is larger than for the first substitution, in the order $L = PPh_3 > P(n\text{-}C_4H_9)_3 > P(OPh)_3 > CO$. When $L = PPh_3$, k is about 50 times larger than when $L = CO$. This large increase is difficult to account for in terms of a labilization of the other metal center as a result of PPh_3 substitution on the first metal. On the other hand, the results are readily rationalized in terms of a labilization of dissociation of the four CO groups which are cis to PPh_3 in $Mn_2(CO)_9PPh_3$. Loss of a cis CO is expected to occur much more readily than CO dissociation from $Mn_2(CO)_{10}$. But the incoming PPh_3 cannot take up the cis position on the same metal because of steric interactions, as demonstrated by the PPh_3 substitution behavior of other maganese carbonyl compounds. On the other hand, since one metal center in the intermediate contains only 16 electrons, and the other 18, it should be readily possible for a CO group to migrate to the other metal, thus creating a vacancy at the second metal. This could occur via an intermediate two-electron, three-center bridging arrangement, or through a process in which a CO group acts transiently as a π-donor toward one metal while bonded in the usual manner to the first.[62] The overall substitution pattern of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ according to the proposed scheme is outlined in Scheme I.[63]

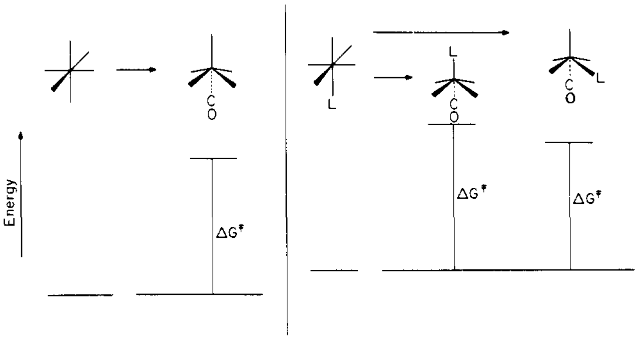
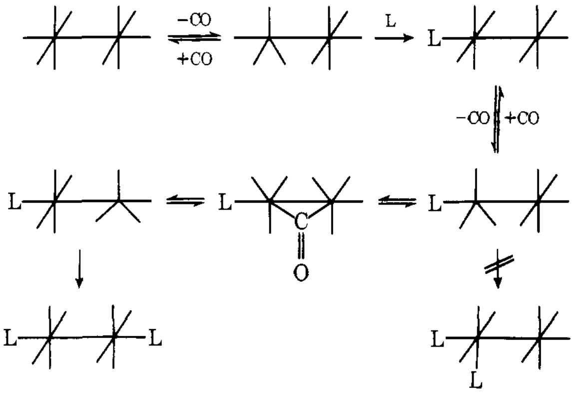


Figure 1. Schematic illustration of the cis-labilizing effect of the ligand L, according to the site preference model. The $\Delta G^{\ddagger}$ for cis CO dissociation from $M(CO)_5L$ is lower than for trans CO loss, or loss of CO from $M(CO)_6$, because L in a basal position lowers the energy of the transition state relative to the ground state more than CO in the same position.

Scheme I



The hypothesis that cis labilization is operative serves to explain the observed substitution behavior of $Ru_3(CO)_{12}$,[64,65] in which the metal is probably sufficiently close to octahedral for the present model to serve. It was observed in this case that substitution by PPh_3 leads only to the trisubstituted species, $Ru_3(CO)_9L_3$, with no sign of the mono- and disubstituted species along the way. The rate law is observed to be first order in carbonyl and zero order in ligand. The observations require that the successive first-order rate constants increase with increasing degree of substitution. These observations may be accounted for by invoking cis labilization, and assuming that migration of CO in the coordinatively unsaturated intermediate is facile. In support of the proposed mechanism, it is significant that the ligands for which the intermediate stages of substitution are observed are those for which a relatively small cis-labilizing effect is expected, e.g., $P(OPh)_3$.

The notion of cis labilization may serve also to explain the observed substitution patterns in $Os_4(CO)_{12}$.[66] In this case, formation of bridging CO groups as substitution proceeds adds an additional complication. It seems likely, however, that cis labilization of CO loss from the metal center containing the substituting ligand might still serve to account for the observed substitution pattern.

The operation of this mechanism to account for the relatively faster rates of successive substitutions requires a facile intramolecular CO migration. The failure of $Os_3(CO)_{12}$ to show the same characteristics as $Ru_3(CO)_{12}$[67] could be due to a less facile CO migration. In addition, the concept of cis labilization may not apply to systems in which the geometry at the metal center departs too greatly from octahedral, e.g., in $RCCo_3(CO)_9$.[68]

The labilizing properties of ligands could be of importance in determining the reactivities of metal complexes which act as catalysts, if there is a stage in the overall reaction process which is governed by ligand dissociation. There are no kinetics or equilibrium data available which speak to the matter at hand, but an example may serve to illustrate the point. Oxidative addition of H_2 to square planar, 16-electron metal centers leads to a six-coordinate, 18-electron species.[69] Loss of ligand by dissociation opens up a coordination position. Binding of an olefin may be followed by hydrogenation, or other chemistry of interest.

The catalytic effectiveness of a complex may be in some instances related to the rate of dissociation of a ligand from the six-coordinate complex which results from oxidative addition. This rate of ligand dissociation in turn, and even the particular ligand which dissociates, is determined by the identity and stereochemistry of the ligands bound to the metal. The labilizing properties of ligands on the metal are likely to be of importance in determining the rate at which the five-coordinate species is formed, and possibly also the steady-state concentration of this species.

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