

Ligand Substitution Reactions at Low-Valent Four-, Five-, and Six-Coordinate Transition-Metal Centers[†]

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Contents

I. Introduction	557
II. Ligand Substitution Pathways	557
III. Factors Influencing the Reactivity of Transition-Metal Complexes	558
IV. Complexes Based on M(CO) ₆	559
V. Complexes Based on M(CO) ₅ L	566
VI. Complexes Based on Bidentate M(CO) ₄ (L-L)	570
VII. Complexes Containing Olefin or Polyolefin Ligands	574
VIII. Complexes Based on M(CO) ₅	578
IX. Complexes Based on ML ₄	583
X. Nitrosyl, Cyclopentadienyl, and Allyl Complexes	585
XI. Acid- and Base-Catalyzed Substitution Reactions	587
XII. Ligand Migration Reactions and Reactions Proceeding via Free-Radical Intermediates	588
XIII. References	593

I. Introduction

The great expansion of synthetic organometallic chemistry has been accompanied to a lesser extent by an interest in the kinetics and mechanism of organometallic reactions. Among the most basic of these reactions are ligand substitution processes at low-valent transition-metal centers. The information obtained is useful not only in systematic organometallic synthesis, but is also quite relevant to the design and operation of homogeneous catalysts. In addition, such studies provide a basis for mechanistic studies in the increasingly important area of metal cluster chemistry. Such reactions differ significantly from classical coordination chemistry in that the low-valent metal is usually bound to π -acid ligands such as carbon monoxide, and since such reactions are studied in weakly polar or apolar media, solvent effects are much less marked.

Although several small reviews of various aspects of this area have appeared,^{1-4a,b} no comprehensive reviews have appeared since 1968.^{5,6} This article aims to provide coverage up to approximately the end of 1982. It is concerned primarily with thermal substitution reactions, although relevant photosubstitution results have been included.⁷ It is also limited to 18-electron complexes, as space does not permit a discussion of analogous reactions of d⁸ square-planar and d¹⁰ trigonal-planar 16-electron complexes.

II. Ligand Substitution Pathways

The characteristics of the primary D, I_d, I_a, and A substitution pathways have been described in both

[†]No reprints available.



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specialized⁸⁻¹⁰ and general^{11,12} texts. These are summarized in Schemes I-III for an octahedral ML₆ substrate.

A. D Mechanism

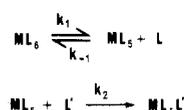
In Scheme I the rate law is

$$R = \frac{k_1 k_2 [\text{ML}_6][\text{L}']}{k_{-1} + k_2 [\text{L}']} \quad (1)$$

which reduces to

$$R = k_1 [\text{ML}_6] \quad (2)$$

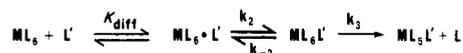
Scheme I



Scheme II



Scheme III



when $k_2[\text{L}'] \gg k_{-1}$. In practice, this last condition is satisfied for most reactions discussed in this article that proceed via a D pathway. The above rate law assumes rate-determining loss of L rather than rate-determining reaction of ML_5 with L' . The reaction proceeds via complete bond breaking to give an intermediate that is presumed to live long enough to show some discrimination between potential ligands. Detection of the intermediate provides the only unambiguous proof for the D pathway.

B. I_d and I_a Mechanisms

In Scheme II the rate law is

$$R = K_{\text{diff}}k_2[\text{ML}_5][\text{L}'] \quad (3)$$

This may be described as a diffusion-controlled cage combination which then proceeds via a transition state which can be represented as $[\text{L}_5\text{M} \cdots \text{L}, \text{L}']$ which positions the new ligand L' to enter the coordination sphere on departure of L. The I_d mechanism involves considerable extension, but not complete rupture, of the M-L bond while in the I_a pathway, interaction between M and L' is much more advanced in the transition state. The implicit assumption is made that k_2 is rate determining rather than K_{diff} .

C. A Mechanism

In Scheme III the rate law is

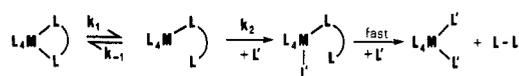
$$R = K_{\text{diff}}k_2[\text{ML}_5][\text{L}'] \quad (4)$$

The reaction proceeds via the formation of the intermediate $\text{ML}_6\text{L}'$ of increased coordination number, and the assumptions are made that k_2 is the rate-determining step rather than the initial diffusion or ligand loss from the intermediate (k_3). Rate laws do not differentiate between I_a or I_d and A mechanisms; the latter may be proved only by the detection of the intermediate of increased coordination number. True A mechanisms are not observed in reactions of 18-electron organometallic complexes (with the exception of reactions occurring at coordinated ligands), although this pathway is the common one observed for 16-electron square-planar complexes. The observed rate law has the form

$$R = k_a[\text{ML}_4] + k_a[\text{ML}_4][\text{L}'] \quad (5)$$

in which k_a may simply be viewed as a solvent-assisted associative pathway. Evidence indicates that reactions of 18-electron complexes that depend on $[\text{L}']$ are I_d in nature, although competing D and I_d pathways are often found.

Scheme IV



Activation parameters must be interpreted with caution since ΔH^* and ΔS^* extracted from the temperature dependence of the rate constant are a composite of those for all steps up to and including the rate-determining step. However, on the assumption that precursor equilibria are relatively fast, measured ΔH^* and ΔS^* values should reflect ΔH^* and ΔS^* values associated with the chemically significant activation step. Thus, large positive ΔH^* and ΔS^* values are highly suggestive of the D pathway, whereas smaller positive ΔH^* and negative ΔS^* values usually reflect more associative pathways. Few ΔV^* values have been measured for organometallic reactions.

For reactions involving the displacement of polydentate chelating ligands, the observed kinetic behavior may not resemble that to be expected for any of the above mechanisms, and a general "ring opening" pathway may be considered. In Scheme IV the rate law is

$$R = \frac{k_1k_2[\text{L}_4\text{M}(\text{L}-\text{L})][\text{L}']}{k_{-1} + k_2[\text{L}']} \quad (6)$$

Three different types of kinetic behavior may be displayed:

(1) If rechelation of the free end of the leaving group is less favored than displacement by entering group, then $k_2[\text{L}'] \gg k_{-1}$ and

$$R = k_1[\text{L}_4\text{M}(\text{L}-\text{L})] \quad (7)$$

(2) When both entering and leaving groups have similar properties, rechelation may be favored due to the high effective leaving-group concentration. Then, $k_{-1} \gg k_2[\text{L}']$ and

$$R = \frac{k_1k_2[\text{L}_4\text{M}(\text{L}-\text{L})]}{k_{-1}} \quad (8)$$

(3) Under conditions where $k_{-1} \approx k_2[\text{L}']$, plots of k_{obsd} against $[\text{L}']$ will be nonlinear, and represent the only case where a ring-opening pathway can be invoked from kinetic evidence alone. The above discussion covers only dissociative ring opening; more complicated examples involving a competing I_d initial step have been described.

Other more specialized pathways such as ligand migration, free-radical substitution, and catalyzed substitution will be discussed in separate sections.

III. Factors Influencing the Reactivity of Transition-Metal Complexes

A. Effective Atomic Number (EAN)

The main tenets of the EAN rule are contained in a review by Tolman.¹³

(1) Diamagnetic organometallic complexes of transition metals may exist in significant concentration at moderate temperature only if the metal valence shell contains 16 or 18 electrons.

(2) Organometallic reactions, including catalytic ones, proceed by elementary steps involving only species with 16 or 18 electrons.

Although originally empirical, the rule has been placed on a firmer theoretical basis that reflects the complete use of metal valence orbitals.¹⁴ The preparation of increasing numbers of stable 17-electron species may be noted, however, and such species have been implicated as intermediates in organometallic substitution reactions.

B. Coordination Number and Geometry

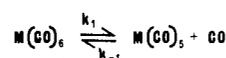
Different metals that share a common coordination number and geometry often exhibit similarities in reactivity, and recent theoretical studies primarily by Hoffman et al. provide an explanation.^{14,15} Thus, for an $M(CO)_n$ fragment, which may be either a stable molecule, a reaction intermediate, or a transition state, there will be $9 - n$ orbitals available to hold d electrons or to act as acceptor orbitals for the fragment. Most importantly, the spatial extent, hybridization, and energies of these orbitals are very sensitive to the geometric arrangement of the CO ligands.¹⁶ Similar arguments apply to other bonding fragments such as $CpM(CO)_n$ ($Cp = \text{cyclopentadienyl}$),¹⁶ or (polyene) M ,^{17a,b} and some of the fragments such as $M(CO)_3$, MCp , and $M(C_6H_6)$ may be termed isolobal, implying that the number, symmetry, extent in space, and energy of the frontier orbitals are similar.

It may be noted that there is unlikely to be any simple relationship between coordination number for 18-electron complexes and the nature of the substitution pathway followed. A simple d orbital only σ bonding angular overlap analysis¹² of structural preference energies for ML_6 , ML_5 , and ML_4 geometries shows that for a d^6 atom, the ML_6 geometry is strongly favored relative to either ML_5 or ML_4 . For a d^8 atom, the ML_5 trigonal bipyramid is favored relative to ML_6 or tetrahedral ML_4 , but a square-planar geometry is equally preferred (hence the large number of 16-electron square-planar d^8 complexes). For a d^{10} atom, there is no distinction in angular overlap terms between square-planar and tetrahedral ML_4 geometries although the latter will be preferred in terms of minimization of ligand-ligand repulsions. Indeed, it may be noted that in this simple treatment, tetrahedral ML_4 complexes are stable only because of $nd/(n + 1)p$ mixing; thus, some tendency towards facile ligand loss to give trigonal-planar ML_3 complexes may be expected, and large numbers of such derivatives are indeed known. Thus, decreasing coordination number cannot be equated with an increasing tendency towards associative substitution pathways.

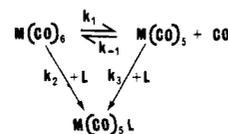
C. Transition State and Ground State

The relative importance of σ donation and π acceptance in metal-ligand bonds of π -acid ligands remains difficult to assess in ground-state structures, although molecular orbital calculations can give some idea of relative orbital populations. In any case, evidence suggests that reaction rates (and the activation parameters derived from them) may be more closely associated not with ground-state properties, but with geometrical and electronic changes in the intermediate or transition state of the reaction, something which can only be evaluated by calculation where an intermediate is not directly observable.

Scheme V



Scheme VI



The angular overlap model has successfully rationalized the observed rates of aqua substitution for the $M(H_2O)_6^{2+}$ series, assuming a dissociative mechanism proceeding through a square-pyramidal intermediate,¹⁸ and the model has also been applied to associative substitution at a square-planar d^8 center proceeding via a trigonal-bipyramidal intermediate.¹⁹ Application of the atomic orbital model suffers from a lack of a quantitative feel for the σ -donor capacities of π -acid ligands, but molecular orbital calculations have been reported on several systems, notably the Fenske-Hall results of Brown et al.²⁰ on cis labilization of CO in $Mn(CO)_5X$ derivatives (vide infra). Recent papers by Hoffman et al. also demonstrate the value of reaction pathway calculations in reactions other than substitution such as olefin activation²¹ and olefin metathesis.²²

Calculations should continue to provide qualitative and semiquantitative estimates of electronic contributions to activation barriers, to the exclusion of solvent or steric effects. The dependence on specific ground- and transition-state geometries, and the subtle interplay between σ - and π -ligand character indices, however, that generalizations must be treated with caution.

IV. Complexes Based on $M(CO)_6$

Of the hexacarbonyls, 17-electron $V(CO)_6$ is the most thermally labile, undergoing CO exchange at 25 °C with a half-life of several hours^{23a} and monosubstitution with PPh_3 at -70 °C over a period of 90 min.^{23b} The 18-electron species $V(CO)_6^-$ is inert to CO substitution even in molten PPh_3 .^{23c} Both $Mn(CO)_6^+$ and $Re(CO)_6^+$ show no measurable CO exchange at 60 °C over a period of days,²⁴ although an upper limit for CO dissociation from $Mn(CO)_6^+$ of $k_1 = 5.2 \times 10^{-7} \text{ s}^{-1}$ at 35 °C may be obtained from its substitution reaction with PPh_3 ;²⁵ the analogous value for dissociation from $Cr(CO)_6$ is ca. 10^{-12} s^{-1} .²⁶ The neutral carbonyls $M(CO)_6$ ($M = Cr, Mo, W$) undergo exchange in both the solution and gas phase (Table I),^{27a-c} the solvent effect on the activation parameters is negligible, in keeping with a D pathway of the type shown in Scheme V. It may be noted that the order of lability (as indicated by ΔG^*) $Mo > Cr > W$ is not mirrored in the measured mean thermochemical bond dissociation energies [W (176 kJ mol⁻¹) > Mo (150) > Cr (109) at 298 K].²⁸ A closer correlation exists between calculated M-C force constants which are in the order W (2.32 mdyn Å⁻¹) > Cr (2.10) > Mo (2.00).²⁹

Although initial work on substitution of $M(CO)_6$ by amines indicated a simple D mechanism,^{30a,b} later work has shown that a two-term rate law is applicable in reactions with amines,³¹ phosphines,^{32a,b} and even acetonitrile.³³

In Scheme VI the rate is given by

$$R = k_1[M(CO)_6] + k_2[M(CO)_6][L] \quad (9)$$

Table I. Activation Parameters for Reaction of $M(\text{CO})_6$ or $M(\text{CO})_5\text{L}$ Complexes with Group 5 Ligands ($M = \text{Cr}, \text{Mo}, \text{W}$)

reaction	ΔH_1^* , kJ mol ⁻¹	ΔS_1^* , J K ⁻¹ mol ⁻¹	ΔH_2^* , kJ mol ⁻¹	ΔS_2^* , J K ⁻¹ mol ⁻¹	ref
$M(\text{CO})_6 + * \text{CO}$					
M = Cr (gas phase)	161.9	77.4			27
M = Cr (decalin)	163.2				
M = Mo (gas phase)	126.4	-1.7			
M = Mo (decalin)	132.2				
M = W (gas phase)	166.5	46			
M = W (decalin)	169.9				
$M(\text{CO})_6 + \text{L} \rightarrow M(\text{CO})_5\text{L} + \text{CO}$					
M = Cr, L = PPh ₃	161.8	74			
M = Cr, L = PBu ₃	168.0	94	106.6	-61	32
M = Cr, L = MeCN			117.0	-29	33
M = Cr, L = 	158.4	66			30
M = Mo, L = PPh ₃	128.7	11			32
M = Mo, L = PBu ₃	132.5	28	90.7	-62	
M = Mo, L = PhCH ₂ NH ₂	150.4	80	113.7	-15	31
M = Mo, L = triazine	131.3	18			30
M = Mo, L = MeCN	123.7		107.0	-38	33
M = W, L = PPh ₃	165.5	49			32
M = W, L = PBu ₃	166.8	58	122.0	-29	
M = W, L = triazine	172.2	80			30
$\text{Cr}(\text{CO})_5[\text{C}(\text{OMe})\text{Me}] + \text{PR}_3 \rightarrow \text{cis-Cr}(\text{CO})_4[\text{C}(\text{OMe})\text{Me}](\text{PR}_3) + \text{Cr}(\text{CO})_5\text{PR}_3 + \text{Cr}(\text{CO})_4(\text{PR}_3)_2$					
L = PCy ₃	115.3	26			140
L = PPh ₃	114.9	15			
L = PPhEt ₂	114.9	15			
L = PET ₃	112.0	14	86.1	-53	
L = PBu ₃	108.7	3	83.2	-62	
$M(\text{CO})_5(\text{L-L}) \rightarrow M(\text{CO})_4(\text{L-L}) + \text{CO}$					
L-L = Ph ₂ P(CH ₂) ₂ PPh ₂ , M = Cr	135	27			153-155a
L-L = Ph ₂ P(CH ₂) ₂ PPh ₂ , M = Mo	120	14			
L-L = Ph ₂ P(CH ₂) ₂ PPh ₂ , M = W	155	40			
L-L = Me ₂ P(CH ₂) ₂ PMe ₂ , M = Cr	132	6			
L-L = Me ₂ P(CH ₂) ₂ PMe ₂ , M = Mo	118	-7			
L-L = Cy ₂ P(CH ₂) ₂ PCy ₂ , M = Cr	147	46			
L-L = Cy ₂ P(CH ₂) ₂ PCy ₂ , M = Mo	132	34			
L-L = Ph ₂ P(CH ₂) ₂ PPh ₂ , M = Cr	141	71			
$\text{W}(\text{CO})_5\text{CS} + \text{PPh}_3 \rightarrow \text{trans-W}(\text{CO})_4(\text{CS})\text{PPh}_3 + \text{CO}$	131.7	13	100.3	-50	156
$[\text{Cr}(\text{CO})_5(\text{CNEt}_2)]^+ + \text{PPh}_3 \rightarrow \text{trans-}[\text{Cr}(\text{CO})_4(\text{CNEt}_2)\text{PPh}_3]^+ + \text{CO}$	104	64			159
$\text{trans-Cr}(\text{CO})_4(\text{CNEt}_2) + \text{PPh}_3 \rightarrow \text{mer-Cr}(\text{CO})_3(\text{CNEt}_2)(\text{X})(\text{PPh}_3) + \text{CO}$					
X = Br	107	71			159
X = I	113	66			
$\text{cis-Ru}(\text{CO})_4(\text{SiCl}_3)_2 + * \text{CO}$	111.9	13			161-163

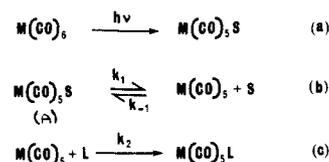
The activation parameters (Table I) are consistent with competing D and I_d pathways, and the similarity of ΔH_1^* and ΔS_1^* to those associated with CO exchange may be noted. There are two features associated with k_2 that are common to other systems:

(a) the dependence of k_2 on the basicity or polarizability of the ligand (as measured by ΔHNP)³⁴ for a given donor atom. Thus, phosphorus ligands may be placed in the order $\text{P}(\text{OPh})_3 < \text{PPh}_3 < \text{P}(\text{OCH}_2)_3\text{CET} < \text{P}(\text{OEt})_3 < \text{PBu}_3$ in terms of increasing k_2 ; on the basis of their k_2 values, amines and acetonitrile may be placed on a par with $\text{P}(\text{OCH}_2)_3\text{CET}$ and PPh_3 , respectively.

(b) the relative increasing importance of the k_2 pathway in the order $\text{Cr} \ll \text{Mo} \approx \text{W}$. This may be attributed both to the increase in covalent radius ($\text{Cr} < \text{Mo} \approx \text{W}$)³⁵ and to the related increase in effective nuclear charge ($\text{Cr} < \text{Mo} \ll \text{W}$). It is interesting that force constant calculations indicate a much stronger $\text{OC} \rightarrow \text{M} \sigma$ donation for W compared to Cr and Mo.

A similar monosubstitution can be achieved photochemically,³⁶ and both matrix-isolation and flash-photolytic results provide information about the nature of the $\text{M}(\text{CO})_5$ intermediate of the dissociative pathway.

Scheme VII

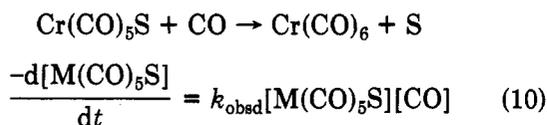


The reactions occurring can be represented by Scheme VII.

The initial photoproduct has not been detected but is presumed to be an excited state C_{4v} species. The C_{4v} nature of A has been amply demonstrated in both matrices and hydrocarbon glasses^{37a-g} but the great dependence of its visible spectrum on the matrix³⁸ indicates that it is best regarded as the solvated species shown, with the Ne derivative perhaps best approaching naked $\text{M}(\text{CO})_5$. Loss of solvent may be photoinitiated in the matrix, and the results³⁹ are consistent with a naked, undetected $\text{M}(\text{CO})_5$ intermediate of D_{3h} symmetry, although molecular orbital calculations indicate that the ground state for a d⁶ species is a square pyramid.^{15,40} Irradiation of $\text{M}(\text{CO})_6^-$ ($M = \text{V}, \text{Nb}, \text{Ta}$) in

rigid media at low temperature is also consistent with CO loss to yield isoelectronic $M(\text{CO})_5^-$ species of C_{4v} symmetry.^{37e,41a,b}

Flash photolysis studies are also in agreement with this scheme, yielding intermediates whose visible spectra are analogous to those produced in low temperature matrices or glasses.^{42a-d} λ_{max} values indicate a much weaker bonding of perfluoromethylcyclohexane^{42b} compared to cyclohexane,^{42a} and in agreement with this, measured recombination rates



show the perfluoroalkyl compound to be more reactive by a factor of 10^3 ($k_{\text{obsd}} = 3 \times 10^9$ and $3 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively). In both cases, in the absence of CO, decay occurs to an unknown species postulated to be either $\text{Cr}(\text{CO})_5\text{X}$ ($\text{X} = \text{oxygen}$) formed from scavenging^{42a} or $\text{Cr}_2(\text{CO})_{11}$, based on the dependence of the rate of decay on $[\text{Cr}(\text{CO})_6]$.^{42b} The quantum yield for photosubstitution of $\text{Cr}(\text{CO})_6$ by pyridine of 0.67⁴³ is also in agreement with the above Scheme VII.³⁹

In the presence of other donors (L), a study of the rate of decay of A with [L] yields values of k_1 and k_2/k_{-1} . Where $\text{M} = \text{W}$ and $\text{L} = 4\text{-acetylpyridine}$, $k_1 = 1.9 \times 10^6 \text{ s}^{-1}$ and $k_2/k_{-1} \approx 270$;^{42c} other less precise data on the reactivity of $\text{Cr}(\text{CO})_5\text{S}$ with various ligands yield k_1 values of similar magnitude⁴⁴ and comparable values are obtained for the $\text{Mo}(\text{CO})_3\text{L}_2\text{S}$ intermediate produced on flash photolysis of $\text{Mo}(\text{CO})_4\text{L}_2$ [$\text{L}_2 = \text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$ and $\text{H}_2\text{PC}_2\text{H}_4\text{PH}_2$].⁴⁵

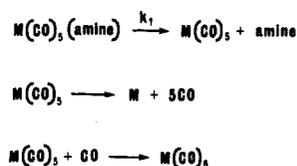
In normal thermal substitution reactions, equilibrium b is undetectable kinetically, assuming steady-state concentrations of $\text{M}(\text{CO})_5\text{S}$ and $\text{M}(\text{CO})_5$. However, provided that the trigonal-bipyramidal $\text{M}(\text{CO})_5$ intermediate has a reasonable lifetime, (b) provides a mechanism for intramolecular scrambling. The lifetime of $\text{M}(\text{CO})_5$ in (b) may be estimated as ca. 10^{-7} s ,⁴⁶ whereas NMR data on $\text{Fe}(\text{CO})_5$ indicate that the lifetime for axial \rightleftharpoons equatorial exchange has a maximum value of ca. 10^{-8} – 10^{-9} s .⁴⁷

It may be noted, however, that barriers to scrambling in substituted derivatives of $\text{M}(\text{CO})_5$ may be higher, and that the lifetime of $\text{M}(\text{CO})_5$ (and therefore the likelihood of its intramolecular scrambling) will be highly dependent on solvent, as on the basis of Scheme VII,

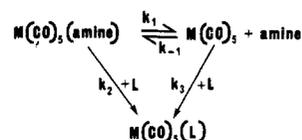
$$\tau = \frac{1}{k_2[\text{L}] + k_{-1}[\text{S}]}$$

Extrapolating to $[\text{L}] = 0$, it can be seen that $\tau \propto 1/k_{-1}$, and the lifetime would be expected to decrease with increasing solvent coordinating power, perhaps to a point where the intermediate will appear "experimentally" nonfluxional. Thus, reaction of *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})(\text{piperidine})$ with AsPh_3 in hexane yields a mixture of *cis*- and *trans*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})(\text{AsPh}_3)$ ⁴⁸ in which the distribution of ^{13}CO indicates a completely fluxional $\text{Mo}(\text{CO})_5$ intermediate. In contrast, *cis*- $[\text{W}(\text{CO})_4(^{13}\text{CO})\text{Cl}]^-$ reacts with Ag^+ in acetone in the presence of L (presumably via a $\text{W}(\text{CO})_5(\text{Me}_2\text{CO})$ solvate) to give exclusively *cis*- $\text{W}(\text{CO})_4(^{13}\text{CO})(\text{L})$ ($\text{L} = \text{PR}_3$, $\text{CNC}_6\text{H}_{11}$).⁴⁹ $\text{W}(\text{CO})_5(\text{Me}_2\text{CO})$ may be prepared photochemically⁵⁰ and undergoes dissociative acetone loss

Scheme VIII



Scheme IX



at rates which are orders of magnitude slower than those observed for solvent loss from $\text{W}(\text{CO})_5\text{S}$.^{42c}

$\text{M}(\text{CO})_5$ intermediates are also implicated in the thermal decomposition of $\text{M}(\text{CO})_5(\text{amine})$ complexes.

In Scheme VIII a rate law of the form

$$\frac{-d[\text{M}(\text{CO})_5(\text{amine})]}{dt} = k_1[\text{M}(\text{CO})_5(\text{amine})] \quad (11)$$

is applicable.^{51,52} Enthalpies of activation (Table II) are consistently 40–60 kJ mol^{-1} lower than those for dissociation from $\text{M}(\text{CO})_6$, in agreement with the meager π -acceptor properties of the amines. There is generally a good correlation between decreasing k_1 and increasing amine basicity (as measured by $\text{p}K_a$) with the exception of unsaturated amines such as pyridine which are less labile than the $\text{p}K_a$ would indicate. While this has been attributed to back donation into ring π^* orbitals, crystal structure determinations on $\text{Cr}(\text{CO})_5(\text{py})$ and $\text{Cr}(\text{CO})_5(\text{piperidine})$ reveal identical Cr–N bond lengths, and a comparison of axial and equatorial Cr–CO bond lengths is consistent with virtually no π -acceptor capability in the ground state.⁵³ Enthalpies of activation for a given metal are very similar, however, and it is mainly the variation in ΔS^\ddagger that determines the overall variation in k_1 . Enthalpies of activation increase in the order $\text{W} \approx \text{Mo} < \text{Cr}$, in agreement with relative orbital size, but in contrast to the order for CO dissociation from $\text{M}(\text{CO})_6$. *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)(\text{amine})$ complexes decompose in the same way to give $\text{Mo}(\text{CO})_5(\text{PPh}_3)$, *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$, and decomposition products.⁵⁴ K_1 values indicate a labilization of amine compared to $\text{Mo}(\text{CO})_5(\text{amine})$, although there does not appear to be a simple relationship in terms of activation parameters. In the presence of other donors (L), $\text{M}(\text{CO})_5(\text{amine})$ complexes undergo exchange (Scheme IX) and exhibit a typical two-term rate law. K_1 values, and activation parameters associated with k_1 , are in agreement with decomposition studies (Table II), while k_2 can be associated with a competing I_d pathway and shows the usual dependence on ligand basicity ($\text{PBu}_3 > \text{P}(\text{OMe})_3 > \text{P}(\text{OCH}_2)_3\text{CEt} > \text{PPh}_3 > \text{P}(\text{OPh})_3 > \text{AsPh}_3$).^{55,58} In the presence of excess amine, competition ratios k_{-1}/k_3 can be determined for the reaction using $\text{Mo}(\text{CO})_5(\text{piperidine})$ ⁵⁵ and indicate (Table III) little discrimination of the $\text{Mo}(\text{CO})_5$ intermediate. Reaction of *cis*- $\text{Mo}(\text{CO})_4(\text{L}')(\text{piperidine})$ complexes [$\text{L}' = \text{PPh}_3$, $\text{P}(\text{OMe})_3$] with L to give *cis*- $\text{Mo}(\text{CO})_4(\text{L})(\text{L}')$ proceeds via a similar mechanism, although the k_2 term is observed only with the most basic ligands such as PBu_3 or $\text{P}(\text{OCH}_2)_3\text{CEt}$.^{54,59} Competition ratios (Table III) indicate

Table II. Activation Parameters for Reactions Involving Dissociation of Group 5 Ligands

reaction	ΔH_1^* , kJ mol ⁻¹	ΔS_1^* , J K ⁻¹ mol ⁻¹	ΔH_2^* , kJ mol ⁻¹	ΔS_2^* , J K ⁻¹ mol ⁻¹	ref
thermal decomposition					
Mo(CO) ₅ (piperidine)	98.7	22			51
Mo(CO) ₅ (piperidine)	96.6	-16			52
Cr(CO) ₅ (piperidine)	107.4	16			
Mo(CO) ₅ py	112.8	37			
Cr(CO) ₅ py	106.1	13			
Mo(CO) ₅ (cyclohexylamine)	96.6	-5			
Cr(CO) ₅ (cyclohexylamine)	115.7	50			
Cr(CO) ₅ (morpholine)	107.8	33			
Cr(CO) ₅ (morpholine)	94.0	-54			
Cr(CO) ₅ (3-picoline)	112.4	28			
Cr(CO) ₅ (aniline)	110.3	79			
Cr(CO) ₅ (pyrrole)	113.2	60			
Mo(CO) ₄ (PPh ₃)(piperidine)	108.2	57			54
Mo(CO) ₄ (PPh ₃)py	92.3	2			
substitution reactions					
Mo(CO) ₅ (amine) + PPh ₃ → Mo(CO) ₅ PPh ₃ + amine					
amine = quinuclidine	112.4	23	55.2	-158	55
amine = piperidine	107.8	12	68.9	-84	
amine = cyclohexylamine	102.4	9	66.5	-78	
W(CO) ₅ (aniline) + PPh ₃ → W(CO) ₅ PPh ₃ + aniline	92.4	-27	71.9	-76	58
<i>cis</i> -Mo(CO) ₄ (L)(piperidine) + CO → Mo(CO) ₅ L + piperidine					
L = P(OMe) ₃	122.9	58			59
L = PPh ₃	106.6	42			
Cr(CO) ₅ L + CO → Cr(CO) ₆ + L					
L = AsPh ₃	151.7	93			109
L = PPh ₃	151.7	131			
L = P(OPh) ₃	133.3	-8			
<i>trans</i> -M(CO) ₄ L ₂ + CO → M(CO) ₅ L + L					
M = Cr, L = P(OPh) ₃	157.1	78			110
M = Cr, L = PBU ₃	177.6	139			
M = Cr, L = P(OMe) ₃	181.0	107			
M = Mo, L = PPh ₃	95.7	-58			111
<i>cis</i> -Mo(CO) ₄ L ₂ + CO → Mo(CO) ₅ L + L					
L = P(O- <i>o</i> -tolyl) ₃	133.3	60			111
L = PPh ₃	124.0	59			
L = PPhCy ₂	126.2	91			
<i>cis</i> -Mo(CO) ₄ L ₂ + bpy → Mo(CO) ₄ bpy + 2L					
M = Mo, L = PPh ₃	109.5	25			112
M = Mo, L = AsPh ₃	112.0	41			
M = Mo, L = py	97.3	31			
M = W, L = py	97.0	-2			
<i>trans</i> -M(CO) ₄ L ₂ + bpy → M(CO) ₄ bpy + 2L					
M = Mo, L = PPh ₃	99.9	-33			113
M = W, L = PPh ₃	120.4	0			

Table III. Competition Ratios (k_{-1}/k_3) for Reaction of Mo(CO)₄(L)(pip)^a (L = CO, PPh₃) with Other Ligands L'

substrate	ligand	k_{-1}/k_3 ^b
Mo(CO) ₅ (pip)	P(OMe) ₃	0.74
	PPh ₃	0.85
	AsPh ₃	1.00
Mo(CO) ₄ (PPh ₃)(pip)	PPh ₃	0.68
	AsPh ₃	2.13
	SbPh ₃	0.90
	CO	3.24
	P(OCH ₂) ₃ CEt	0.42
	PBU ₃	1.47

^a pip, piperidine. ^b k_{-1}/k_3 refers to Scheme IX; data from ref 55.

a slightly more discriminating nature for the Mo(CO)₄PPh₃ intermediate. The substantially higher activation enthalpy for *cis*-Mo(CO)₄[P(OMe)₃](piperidine) may be noted, and the solid-state structure of this complex⁶⁰ and its Cr analogue⁵³ show a hydrogen-bond interaction between coordinated phosphite and piperidine. Indeed, substitution of Mo(CO)₅(piperidine) by PPh₃ proceeds faster by a factor of 100 in the presence of OPBu₃, with the evidence indicating that a 1:1 hy-

drogen-bonded adduct is responsible for assistance of the k_1 dissociative step:



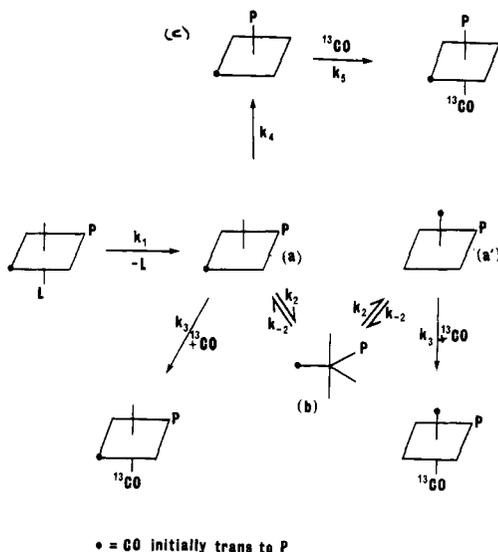
$$K_{\text{eq}} = 675 \text{ dm}^3 \text{ mol}^{-1} \text{ (M = Cr)}$$

$$K_{\text{eq}} = 633 \text{ dm}^3 \text{ mol}^{-1} \text{ (M = Mo)}$$

The enhanced rate of substitution in hydrogen-bonding solvents may also be interpreted in the same way, and in such solvents the pathway associated with k_2 is absent, indicating that a hydrogen-bond interaction between incoming ligand and metal complex may be the mode of interaction for the I_d pathway.^{61,62} There appears to be a general class of such base-catalyzed substitution reactions that will be discussed in detail in a separate section.

As has been mentioned previously, reaction of *cis*-Mo(CO)₄(¹³CO)(piperidine) with AsPh₃ indicates a completely fluxional Mo(CO)₅ intermediate.⁴⁸ Thermal substitution of *cis*-Mo(CO)₄(piperidine)L and *cis*-W(CO)₄(PPh₃)(piperidine) with ¹³CO yields only *cis*-Mo(CO)₄(¹³CO)(L) [L = PPh₃, P(OMe)₃] and *cis*-W-

Scheme X

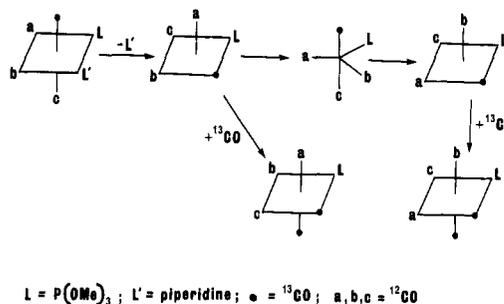


$(\text{CO})_4(^{13}\text{CO})(\text{PPh}_3)^{54,59a,b}$ (Scheme X) and highlights the problem of definition of fluxionality in these systems. The results may be interpreted in terms of the principle of microscopic reversibility most recently outlined by Dobson.⁶³

Thus, loss of L yields species (a) that undergoes geometrical relaxation to the lowest energy C_{2v} conformation (b) (vide infra; ref 20) which may by the principle of microscopic reversibility yield the equivalent species (a'). Thus, as drawn, the five-coordinate intermediate is fluxional, although only the *cis*- $(^{13}\text{CO})(\text{P})$ derivative is isolated. However, if ligand dissociation and geometrical relaxation (k_1, k_2) or $\text{tbp} \rightleftharpoons \text{spy}$ conversion and gain of ^{13}CO (k_{-2}, k_3) are regarded as concerted, then scrambling may simply be regarded as a consequence of the reaction pathway. In any case, the stereochemistry of the product will mirror the site of initial M-L bond breaking regardless of whether or not scrambling occurs. The principle applies rigorously only to isotopic exchange (L = CO); where L is not CO, the principle holds to the extent that the difference in free energies of combination of CO and L with (a/a') approaches 0. Measured values of $\Delta/\Delta G^*$ extracted from k_2/k_{-1} values such as those in Table III are in the range 0–9 kJ mol⁻¹, and seem too small to redirect the stereochemical path along that governed by k_4, k_5 . This process represents a genuine molecular rearrangement (although not strictly a fluxional process since (a) and (c) are not equivalent). Exceptions may arise where steric crowding at an octahedral edge or face would significantly increase the free energy of recombination via k_3 . Thus, *cis*- $\text{Mo}(\text{CO})_4[\text{P}(\text{OMe})_3](\text{piperidine})$ reacts with $\text{P}(\text{OMe})_3$ to give mainly *trans*- $\text{Mo}(\text{CO})_4[\text{P}(\text{OMe})_3]_2$ while *cis*- $\text{W}(\text{CO})_4(\text{PPh}_3)(\text{piperidine})$ reacts with PPh_3 to give a *cis/trans* mixture of $\text{W}(\text{CO})_4(\text{PPh}_3)_2$,^{59a,b} in contrast to their reactions with ^{13}CO .

Reaction of *cis*- $\text{Mo}(\text{CO})_4(\text{amine})_2$ complexes with ^{13}CO yields only *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})(\text{amine})$, while sequential reaction of *fac*- $\text{Mo}(\text{CO})_3(\text{py})_3$ with ^{13}CO yields only *fac*- $\text{Mo}(\text{CO})_3(^{13}\text{CO})_2(\text{py})$ ⁶⁴ and *fac*- $\text{Mo}(\text{CO})_3(^{13}\text{CO})[\text{P}(\text{OMe})_3](\text{piperidine})$ yields only *fac*- $\text{Mo}(\text{CO})_3(^{13}\text{CO})_2[\text{P}(\text{OMe})_3]$ on treatment with ^{13}CO .⁵⁹ Although these last results have been interpreted as implying nonfluxional intermediates, they may be interpreted in terms analogous to Scheme X in which the

Scheme XI



substitution process occurs via relaxation of an initially formed square-pyramidal intermediate to a trigonal-bipyramidal structure in which L is in the basal plane. Thus, as shown in Scheme XI for the reaction of *fac*- $\text{Mo}(\text{CO})_3(^{13}\text{CO})[\text{P}(\text{OMe})_3](\text{piperidine})$ with ^{13}CO , only *fac*- $\text{Mo}(\text{CO})_3(^{13}\text{CO})_2[\text{P}(\text{OMe})_3]$ is isolated, although the nonlabelled CO groups may undergo scrambling if the intermediate is fluxional. Finally, two points may be noted:

(a) In contrast to thermal substitution reactions, photolysis of $\text{M}(\text{CO})_5(\text{amine})$ complexes both in solution and low temperature matrices results in both amine and CO dissociation, depending on the wavelength used. Irradiation of *cis*- $\text{Mo}(\text{CO})_4(\text{amine})_2$ complexes also results predominantly in loss of amine.^{69,70} In common with thermal reactions, ^{13}CO is incorporated into positions *cis* to the amine.^{48,65-68}

Matrix photolysis of $\text{Mo}(\text{CO})_5\text{PCy}_3$ in methylcyclohexane results only in CO dissociation to yield two $\text{Mo}(\text{CO})_4(\text{PCy}_3)\text{S}$ intermediates resulting from both *cis* and *trans* loss of CO,⁷¹ although the ratio is solvent dependent since only *cis*- $\text{Mo}(\text{CO})_4(\text{PCy}_3)(\text{THF})$ is obtained on irradiation in THF.

(b) The carbonyl carbon also provides a point of attack for strongly nucleophilic reagents. Thus, $\text{W}(\text{CO})_6$ reacts with pseudohalides (OCN^- , SCN^- , CN^-) to give $[\text{W}(\text{CO})_5\text{X}]^-$ via perfect second-order kinetics:⁷²

$$\frac{-d[\text{W}(\text{CO})_6]}{dt} = k_2[\text{W}(\text{CO})_6][\text{X}^-]$$

Activation enthalpies (Table IV) are smaller and entropies more negative than those associated with the k_2 term of Table I, implying attack at a site other than the metal. The reactions of $\text{M}(\text{CO})_6$ with azide to give $[\text{M}(\text{CO})_5(\text{NCO})]^-$ ⁷³ and the reactions of $\text{M}(\text{CO})_6$ with MeLi ⁷⁴ and ClMgCH_2Ph ⁷⁵ to give $\text{M}(\text{CO})_5[\text{C}(\text{O})\text{Me}]^-$ and $\text{M}(\text{CO})_5[\text{C}(\text{O})\text{CH}_2\text{Ph}]^-$ are also second order and show characteristically lower activation enthalpies and more negative entropies. They also reveal a reactivity order ($\text{W} \gg \text{Mo} > \text{Cr}$) that is different from that associated with the k_2 term of Table I ($\text{Mo} > \text{Cr} \approx \text{W}$). The greater reactivity of the W complexes may be rationalized in terms of the force constant calculations mentioned previously,²⁹ which show a greater $\text{OC} \rightarrow \text{M}$ donation for W, thus rendering the carbon more susceptible to nucleophilic attack. $\text{M}(\text{CO})_5\text{L}$ complexes (L = phosphorus donor) also undergo attack by MeLi and PhCH_2MgCl to give *cis*- $[\text{M}(\text{CO})_4(\text{L})[\text{C}(\text{O})\text{R}]]^-$ species (R = Me, CH_2Ph) at rates that are less than the parent carbonyl and decrease as the cone angle of L increases.^{74,75} The reaction of $[\text{Mn}(\text{CO})_5\text{L}]^+$ with PhCH_2MgCl similarly yields *cis*- $[\text{Mn}(\text{CO})_4\text{C}(\text{O})\text{CH}_2\text{Ph}(\text{L})]$ (L = CO, Me_2PhP , PPh_3 , $\text{P}(\text{OPh})_3$), while unsurprisingly, $\text{V}(\text{CO})_6^-$

Table IV. Activation Parameters for Reactions Involving Attack at Coordinated Carbon

reaction	ΔH_2^* , kJ mol ⁻¹	ΔS_2^* , J K mol ⁻¹	ref
$W(CO)_6 + X^- \rightarrow W(CO)_5X^- + CO$			
X = NCS	66.9	-112	72
X = NCO	86.5	-54	
X = CN	91.1	-41	
$M(CO)_6 + N_3^- \rightarrow M(CO)_5NCO^- + N_2 + CO$			
M = Cr	76.1		73
M = Mo	63.9		
M = W	53.5		
$W(CO)_6 + ClMgCH_2Ph \rightarrow [W(CO)_5C(O)CH_2Ph]MgCl$	30.9	-159	75
$W(CO)_5PPh_3 + ClMgCH_2Ph \rightarrow cis-[W(CO)_4(PPh_3)C(O)CH_2Ph]MgCl$	25.8	-200	
$W(CO)_6 + Br^- \rightarrow W(CO)_5Br^- + CO$	110.8	-1	77
$(CO)_5CrC(OMe)Ph + RNH_2 \rightarrow (CO)_5CrC(NHR)Ph + MeOH$	-8 to -16		144a,b
$(CO)_5WCPH_2 + EtNCS \rightarrow (CO)_5W \leftarrow S = CPh_2$	40.0	-147	145
$(CO)_5MC(OMe)C_6H_4R + Et_2NC \equiv CMe \rightarrow (CO)_5MC(NEt_2)C(Me) = C(OMe)(C_6H_4R)$			
M = Cr, R = CF ₃	28.0	-145	146
M = Cr, R = H	33.5	-142	
M = W, R = CF ₃	25.1	-145	
M = W, R = Br	31.6	-132	
M = W, R = H	32.7	-134	
M = W, R = CH ₃	36.5	-130	
M = W, R = OCH ₃	39.4	-129	
$(CO)_5WC(SMe)_2 + PR_3 \rightarrow (CO)_5W \leftarrow S(Me)C(SMe) = PR_3$			
PR ₃ = PEt ₃	30.9	-129	
PR ₃ = PPhMe ₂	40.5	-132	
PR ₃ = PMePh ₂	41.8	-126	
PR ₃ = P(OMe) ₃	54.3	-119	
$W(CO)_5CS + X^- \rightarrow trans-W(CO)_4(CS)X^- + CO$	79.4	-33	156, 49
$W(CO)_5CS + RNH_2 \rightarrow W(CO)_5(CNR)$	29.2	-163	158

Table V. Structural Data and Cone Angles for M(CO)₅L and M(CO)₄L₂ Complexes

complex	d (M-P)	d (M-CO), trans	d (M-CO), cis	∠P-M-L	L cone angle ^e	ref
Cr(CO) ₅ PPh ₃	2.422	1.845	1.880	87.5, 94.3 ^a	145	99
				88.4, 96.2		
Cr(CO) ₅ P(OPh) ₃	2.309	1.861	1.896	87.6, 93.2 ^a	128	99
				90.6, 95.5		
Cr(CO) ₅ P(CH ₂ CH ₂ CN) ₃	2.364	1.876	1.891	89.2, 90.8 ^a	132	100
				88.7, 92.0		
Mo(CO) ₅ PPh ₃	2.560	1.995	2.046	87.4, 96.4 ^a	145	100
				87.6, 94.4		
Mo(CO) ₅ P(CH ₂ CH ₂ CN) ₃	2.506	2.008	2.044	89.5, 90.6 ^a	132	100
				88.8, 91.9		
Mo(CO) ₅ P(CH ₂) ₆ N ₃	2.479	2.034	2.007	89.6, 91.6 ^a	102	101
				89.5, 90.0		
W(CO) ₅ PBu-t ₃	2.686	1.98	2.02	94.8, 96.5 ^a	182	102
				90.2, 98.4		
W(CO) ₅ PMe ₃	2.516	2.00	2.01	88.1, 91.6 ^a	118	103
				88.1, 91.3		
<i>trans</i> -Cr(CO) ₄ [P(OPh) ₃] ₂	2.252		1.896	87.1, ^a	128	104
				90.8		
<i>cis</i> -Cr(CO) ₄ (PH ₃) ₂	2.349	1.847	1.914	89.8 ^b	87	105
<i>cis</i> -Mo(CO) ₄ (PPh ₃) ₂	2.58	1.972	2.040	104.6 ^b	145	106a
<i>cis</i> -Mo(CO) ₄ (PPh ₂ Me) ₂	2.55	1.979	2.027	92.5 ^b	136	106a
<i>cis</i> -Mo(CO) ₄ (PMe ₂ Ph) ₂	2.53	1.982	2.016	94.7 ^b	122	106a
Mo(CO) ₄ (diphos)	2.518	1.93	2.04	67.3 ^b	121	107
<i>cis</i> -Mo(CO) ₄ (PPh ₃)(PPhMe ₂)	2.562 ^c			97.7	122,	106b
	2.538 ^d				145	
<i>cis</i> -Mo(CO) ₄ (PMe ₃) ₂	2.522	1.971	2.032	97.5	118	106c
<i>cis</i> -Mo(CO) ₄ (PEt ₃) ₂	2.544	1.977	2.032	100.3	132	106c
<i>cis</i> -Mo(CO) ₄ (PBu ₃) ₂	2.546			99.3	132	106c

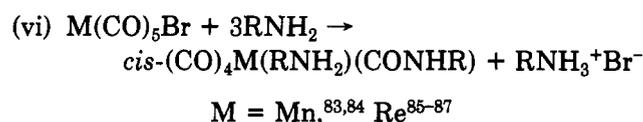
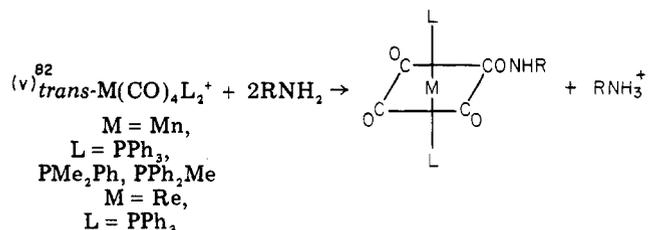
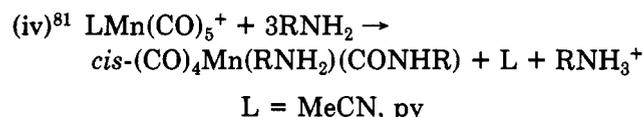
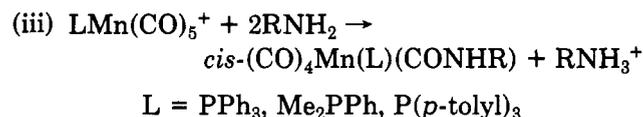
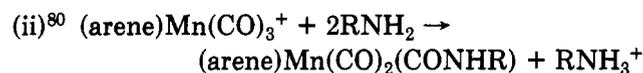
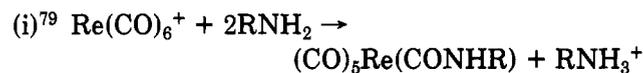
^a L = *cis*-CO. ^b L = PR₃. ^c L = PPh₃. ^d L = PMe₂Ph. ^e Cone angles taken from ref 108.

is unreactive towards Grignard reagents.⁷⁶

The reaction of halide with M(CO)₆ to give [M(CO)₅X]⁻ (X = Cl, Br, I) is more problematical. Although the Mo and W systems show perfect second-order kinetics, Cr(CO)₆ exhibits a two-term rate law of the type observed in reaction with group 5 ligands.⁷⁷ In addition, the order of reactivity (Mo > Cr > W) and the activation parameters more closely parallel reactions with phosphorus ligands. Thus, the ligand-dependent pathway observed here may reflect (wholly or in part)

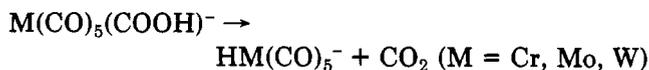
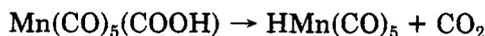
a genuine I₄ mechanism rather than attack at carbonyl carbon. The reaction of Cr(CO)₆ with N₃⁻ has been shown to have a ΔV^* of ca. 0 mL mol⁻¹, compared to values of -10 mL mol⁻¹ for the I₄ substitution of W(CO)₆ by PBu₃ and 15 mL mol⁻¹ for D substitution of Cr(CO)₆ by PPh₃.⁷⁸

In contrast to the chromium group, cationic manganese and rhenium complexes undergo reaction with primary and secondary amines to give products of attack at the carbonyl carbon:



The reactions in (vi) are thought to proceed via initial halide displacement to give [M(CO)₅(RNH₂)]Br. The third-row metal again shows a greater reactivity (Re > Mn), and the rate of reaction *v* decreases with increasing basicity of phosphine and increasing steric bulk of amine. The rate is proportional to [RNH₂]², and has been interpreted as a rate-determining attack of a hydrogen-bonded HRNH---NH₂R dimer on the carbonyl carbon. Reaction of *trans*-Mn(CO)₄L₂⁺ with OR⁻ similarly yields *mer*-(CO)₃MnL₂(COOR).⁸⁸

OH⁻ attack on M(CO)₆⁺ (M = Mn, Re),^{89,90} M(CO)₅L⁺ (M = Mn, Re; L = PMe₂Ph, py, MeCN),^{91,92} Mn(CO)₄(diphos)⁺,^{92,93} Fe(CO)₅,^{94a} and M(CO)₆⁺^{94b} to yield M-COOH intermediates has been postulated to account for the ¹⁸O exchange observed in the reactions of these carbonyls with H₂¹⁸O in basic solution. The order of rate of incorporation Mn(CO)₆⁺ > Mn(CO)₅L⁺ > Mn(CO)₄(diphos)⁺ or Cr(CO)₆ > Cr(CO)₅(phosphite) > Cr(CO)₅(phosphine) is consistent with the reduced electrophilic character of the carbonyl carbon. In Mn(CO)₅L⁺ and M(CO)₅L (M = Cr, Mo, W) complexes, stereospecific exchange at equatorial as opposed to axial positions is noted, consistent with C-O force constant calculations (equatorial 17.44 mdyn/Å; axial 17.43) which indicate a slightly greater positive charge on the carbon *cis* to L. Decarboxylation of the intermediates



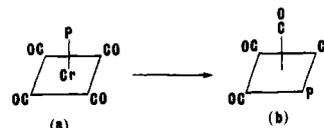
is competitive, and in the case of iron is sufficiently fast that a much smaller degree of ¹⁸O incorporation into Fe(CO)₅ is noted. Such M-COOH species have also been cited as intermediates in the water-gas shift reaction.⁹⁵⁻⁹⁸

TABLE VI. Relative Rates of Dissociation of L from Cr(CO)₄L₂ and Cr(CO)₅L Complexes^a

L	<i>k</i> _{bis} / <i>k</i> _{mono}
P(OMe) ₃	8.4
P(OPh) ₃	12.7
PPh ₃	5 × 10 ⁵
PBu ₃	1 × 10 ⁵

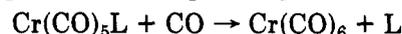
^a Data from ref 110.

Scheme XII

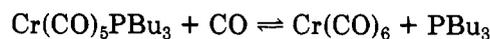


Ligand dissociation from M(CO)₅L and *cis*- and *trans*-M(CO)₄L₂ complexes where L is a non-nitrogen group 5 donor provides a good example of the difficulty in separating steric and electronic ground-state effects, and the difficulty in interpreting their importance relative to transition-state effects in substitution reactions. Thus, in the series Cr(CO)₅L (L = P(OPh)₃, P(CH₂CH₂CN)₃, PPh₃), the Cr-P bond lengths (Table V) increase (P(OPh)₃ < P(CH₂CH₂CN)₃ < PPh₃) as the donor/acceptor ratio increases (P(OPh)₃ < P(CH₂C-H₂CN)₃ < PPh₃), i.e., the shortest Cr-P bond is found for the strongest π-accepting ligand. Similar conclusions may be reached from a comparison of the structures of Mo(CO)₅PPh₃ and Mo(CO)₅P(CH₂CH₂CN)₃. However, the steric properties of the ligand also change within this series (as measured by the ligand cone angle), and it may be that the observed bond distances reflect an energy minimum which optimizes electronic overlap with minimum steric repulsions. Thus, a comparison of Mo(CO)₅PPh₃ with Mo(CO)₅P(CH₂)₆N₃ in which the two ligands are electronically similar but sterically quite different shows a substantial shortening of the Mo-P bond in the latter and a decrease in the angular distortions in the *cis*-Mo(CO)₄ plane. These effects are even more dramatically illustrated in a comparison of W(CO)₅PMe₃ and W(CO)₅PBu-*t*₃ in which the two ligands are electronically similar but differ in cone angle by ca. 65°.

The displacement of ligands by CO



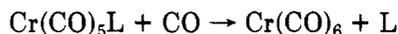
has been studied kinetically,¹⁰⁹ with the observed order of lability being AsPh₃ > PPh₃ > P(OPh)₃ > P(OMe)₃ > PBu₃; indeed, complete displacement of PBu₃ is not observed.



$$K_{\text{eq}} = 5.3 \times 10^{-5} \text{ at } 140^\circ \text{C}$$

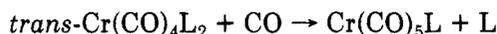
The other reaction rates are independent of [CO] and activation parameters are listed in Table II. Δ*H*^{*} values are lower than those associated with dissociation from M(CO)₆ but significantly greater than those associated with M(CO)₅(amine) dissociation. There is, however, no consistent correlation with ground-state properties such as Δ*H*_{NP} and cone angle, or various spectroscopic parameters. Indeed, the ordering of Δ*H*^{*} (PPh₃ > P(OPh)₃) may be contrasted with M-P bond lengths that are in the order PPh₃ > P(OPh)₃. The greater lability of PPh₃ is entirely due to the dramatic entropy difference.

As activation parameters are also known for the reaction of $\text{Cr}(\text{CO})_6$ with L, it is possible to obtain ΔG for the reaction



i.e., the difference in ground-state energies between $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_5\text{L}$. However, there is again no simple relationship between ΔG and the σ -donor or π -acceptor properties of L.

Ligand dissociation in the reaction



has also been studied¹¹⁰ and the lability order observed is $\text{AsPh}_3 > \text{PPh}_3 > \text{PBu}_3 > \text{P}(\text{OPh})_3 > \text{P}(\text{OMe})_3$. This is similar to the order previously observed with the exception of the position of PBu_3 . The higher ΔH^* value (Table II) for dissociation of $\text{P}(\text{OPh})_3$ from $\text{Cr}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$ compared to $\text{Cr}(\text{CO})_5\text{P}(\text{OPh})_3$ is consistent with the shortening of the Cr-P bond in the former; however, the much more positive ΔS^* term for dissociation from the bis complex means that $\text{P}(\text{OPh})_3$ is actually *more* labile compared to the mono complex. This is in fact true for all the complexes listed (Table VI). The lability ratio for the phosphite complexes may perhaps be interpreted solely in terms of transition-state effects, i.e., a rearrangement of initially formed intermediate (a) to the more stable (b) before coordination of CO (Scheme XII).

Indeed, reaction of *trans*- $\text{M}(\text{CO})_4(\text{PPh}_3)_2$ ($\text{M} = \text{Cr}, \text{Mo}$) with ^{13}CO yields only *cis*- $\text{M}(\text{CO})_4(^{13}\text{CO})(\text{PPh}_3)_2$.^{111a,b} The $k_{\text{bis}}/k_{\text{mono}}$ ratios for the phosphines are too large simply to attribute to such an effect, and may be due to a ground-state weakening of the M-P bond by coordination of *trans*- PR_3 ligands which are good σ donors but (unlike phosphites) poor π acceptors.

Ligand dissociation



has been studied kinetically;¹¹¹ here a much more obvious dependence of lability on steric hindrance (cone angle) is found, although electronic effects are also important as phosphite complexes are less labile than their phosphine analogues of similar cone angle. Crystal structures of *cis*- $\text{Mo}(\text{CO})_4\text{L}_2$ ($\text{L} = \text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{PPh}_3, \text{PMe}_3, \text{PEt}_3, \text{PBu}_3$) show (Table V) increasing P-M-P bond angles with increasing cone angle, results which are in agreement with the order of lability $\text{PMe}_2\text{Ph} \approx \text{PMePh}_2 \ll \text{PPh}_3$.

Entropy effects (steric acceleration) are again important as PPhCy_2 is more labile than PPh_3 even though ΔH^* values (Table II) are in the order $\text{PPh}_3 < \text{PPhCy}_2$. The lower lability of PPh_3 in the mixed-ligand complex *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)(\text{PPhMe}_2)$ as compared to *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ is consistent with its crystal structure that shows less distortion of the P-M-P angle. It is of interest to note that reaction of CO with both *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)(\text{PPhMe}_2)$ and *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)(\text{PPhCy}_2)$ results in dissociation of PPh_3 to give $\text{Mo}(\text{CO})_5(\text{PPhMe}_2)$ and $\text{Mo}(\text{CO})_5(\text{PPhCy}_2)$, even though in the former PPh_3 is the ligand of largest cone angle, whereas in the latter it is the ligand of smallest cone angle. Incorporation of ^{13}CO is again stereospecific, yielding only *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{L}$ complexes.

It may be noted that PPh_3 is less labile in *trans*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ as opposed to the *cis* isomer, even though the ΔH^* values vary in the opposite direction.

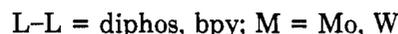
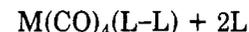
TABLE VII. Calculated CO Force Constants for $\text{Mn}(\text{CO})_5\text{X}$ Complexes^a

	$F(\text{CO}), \text{mdyn/\AA}$		$\nu_{\text{M-CO}}$ (equatorial), cm^{-1}
	axial	equatorial	
$\text{Mn}(\text{CO})_5\text{Cl}$	16.22	17.50	418
$\text{Mn}(\text{CO})_5\text{Br}$	16.26	17.41	422
$\text{Mn}(\text{CO})_5\text{I}$	16.30	17.28	427

^a Data from ref 12.

This is entirely due to the negative ΔS^* value for the *trans* isomer that implies a gross reorganization in the transition state of the type previously mentioned.

Similar observations have been made in the reactions



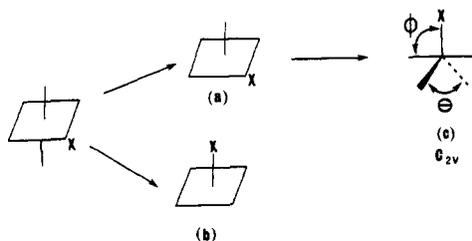
in which the rate-determining step is initial loss of L.^{112,113} The order of lability observed is $\text{PCl}_3 \gg \text{py} \gg \text{AsPh}_3 > \text{PPh}_3 > \text{SbPh}_3$. Again, the lower ΔH^* and negative ΔS^* values for *trans*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ may be noted.

V. Complexes Based on $\text{M}(\text{CO})_5\text{L}$

Complexes of the stoichiometry $\text{M}(\text{CO})_5\text{L}$ undergo further substitution and much effort has been devoted to an understanding of the site of M-CO bond breaking and the labilizing or nonlabilizing nature of L. Interpretations of observed kinetic trends have been based on both ground-state and transition-state arguments. Thus, in an $\text{M}(\text{CO})_5\text{L}$ complex where L is a poorer π acceptor than CO, a consideration of orbitals available leads to the conclusion¹¹⁴ that the extent of π bonding is expected to be about twice as great at a position *trans* to L as at a *cis* position [i.e., $F(\text{CO}_{\text{axial}}) < F(\text{CO}_{\text{equatorial}})$]. In addition, a "direct donation" mechanism may be operative in situations where L has lone pair orbitals, involving a "through space" interaction between the p_z substituent orbital and a linear combination of the π^* orbitals of the equatorial carbonyls. This direct donation should increase with increasing covalent radius of L and decreasing effective nuclear charge of L.^{115a-d} Calculated CO force constants (Table VII) for the $\text{Mn}(\text{CO})_5\text{X}$ series ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) agree with these conclusions.² The ordering of $F(\text{CO})$ indicates a greater lability of equatorial CO, while the order of $\nu_{\text{M-C}}$ is in agreement with the predicted order of direct donation, $\text{I}^- > \text{Br}^- > \text{Cl}^-$, and is reflected in the lability order observed (vide infra).

Such ground-state arguments, however, do not explain the relative inertness of $\text{Mn}(\text{CO})_6^+$, and indeed, molecular orbital calculations²⁰ show no obvious relationship between the ground-state electronic properties of $\text{Mn}(\text{CO})_5\text{Br}$ and $\text{Mn}(\text{CO})_6^+$ and the order of lability. A more generally applicable and satisfactory explanation is that based on arguments involving site preference in the five-coordinate $\text{M}(\text{CO})_4\text{L}$ transition state or intermediate. These arguments by Brown et al. have been presented both qualitatively²⁶ based on molecular orbital calculations of Hoffmann and others^{116,117a,b} of site preference in ML_5 fragments, and quantitatively²⁰ in the form of Fenske-Hall calculations of a comparison of relative activation energies in the loss of CO from both axial and equatorial positions of $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} =$

Scheme XIII



parent	intermediate	energy relative to parent (aeu)
Mn(CO) ₅ Br	a	1.20
	b	1.51
	c, $\theta = 98^\circ$, $\phi = 85^\circ$	0.92
Mn(CO) ₅ ⁺	a/b	1.19
	c, $\theta = 105^\circ$, $\phi = 90^\circ$ ^{a*}	1.10
Mn(CO) ₅ H	a	1.24
	b	1.28
	c, $\theta = 100^\circ$, $\phi = 90^\circ$ ^{a*}	1.12

^a Not maximized.

H, Br) with that from Mn(CO)₅⁺. Calculations were performed on the basis of Scheme XIII, evaluating relative energies of CO dissociation from either axial or equatorial positions to yield either cis-vacant (a) or trans-vacant (b) square-pyramidal intermediates, followed by a geometrical relaxation to the potential energy minimum (c), which calculations also show is thermally available *only* from the cis-vacant intermediate a.

From Scheme XIII it may be noted that (i) even without geometrical relaxation, cis loss of CO is preferred for Mn(CO)₅H and strongly preferred for Mn(CO)₅Br and (ii) without allowing geometrical relaxation to the minimum energy C_{2v} intermediate, the results indicate an approximately equal lability of Mn(CO)₅Br and Mn(CO)₅⁺. Only when relaxation is allowed, does Mn(CO)₅Br appear substantially more labile, and this may be directly traced to the π -donor capacity of Br involving overlap of a lone pair orbital with an appropriate empty metal orbital. The absence of such an orbital on hydrogen or CO means that little stabilization is achieved on geometrical relaxation. The approximately trigonal-bipyramidal nature of (c) may be noted, and it is of interest that matrix photolysis of Mn(CO)₅X (X = COMe, Me, H, Cl, Br, I) indicates a trigonal-bipyramidal geometry for the Mn(CO)₄X intermediates produced,^{118a-c} with X in an equatorial position.

The conclusions may be summarized as follows:

(i) Cis labilization and site preference in M(CO)₅L species will be greatest when L has potential π -donor character.

(ii) In the absence of π -donor character, site preference is much reduced, although cis-CO loss is still preferred. Increasing σ -donor strength increases the cis-labilizing ability, although the sensitivity to σ -donor character of L is much less marked than to its π -donor character. σ -Bonding ligands may thus be either weakly labilizing, nonlabilizing, or even inhibit cis-CO dissociation.

(iii) As a corollary, it follows that ligands which are stronger π acceptors than CO may preferentially labilize trans-CO loss.

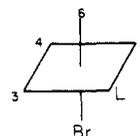
Thus, both Mn(CO)₅X and Re(CO)₅X (X = Cl, Br, I) undergo CO exchange in hydrocarbons at rates which

TABLE VIII. Activation Parameters for M(CO)₅X and M(CO)₄X₂ Complexes

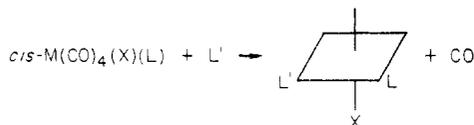
reaction	ΔH_1^* , kJ mol ⁻¹	ΔS_1^* , J K ⁻¹ mol ⁻¹	ref
Re(CO) ₅ X + *CO			
X = Cl (toluene)	122.1	44	120e
X = Br	131.7	59	
X = I	137.9	64	
X = Br (heptane)	122.9	43	
Mn(CO) ₅ X + AsPh ₃ → cis-Mn(CO) ₄ (X)(AsPh ₃) + CO			
X = Cl (CHCl ₃)	114.9	66	121a-d
X = Br	124.6	79	
X = I	134.6	87	
X = Br (nitrobenzene)	129		
Re(CO) ₅ X + PPh ₃ → cis-Re(CO) ₄ (X)(PPh ₃) + CO			
X = Cl (CCl ₄)	114.1	26	
X = Br	122.4	41	
X = I (<i>n</i> -octane)	132.9	54	
Re(CO) ₅ NCO + bpy → Re(CO) ₃ (bpy)(NCO) + CO	98.2	8	
XRe(CO) ₄ L + L' → XRe(CO) ₃ LL' + CO			
X = Cl, L = L' = py	117.0	63	124
X = Br, L = L' = py	121.2	59	
X = I, L = L' = py	122.2	42	
X = Cl, L = L' = PPh ₃	117.0	46	
X = Br, L = L' = PPh ₃	142.1	109	
Mn(CO) ₅ EPh ₃ + PPh ₃ → trans-Mn(CO) ₄ (EPh ₃)(PPh ₃) + CO			
E = Ge	164.7	67	136
E = Sn	173.1	62	
Br ₂ Fe(CO) ₄ + PPh ₃ → Br ₂ Fe(CO) ₃ PPh ₃	25.9	-181	164-166b

are independent of [CO] and faster by factors of 10–10² than the upper limit for CO dissociation from Mn(CO)₅⁺. Preferential cis labilization can be demonstrated, even though the five-coordinate intermediate is fluxional.^{24,119a-e} Similarly, M(CO)₅X (M = Mn, Re; X = Cl, Br, I, NCO) react with a variety of ligands (PPh₃, AsPh₃, SbPh₃, PPhCl₂, P(OBu)₃, P(OCH₂)₃CMe, P(OPh)₃) via first-order kinetics to yield exclusively cis-M(CO)₄(X)(L) complexes.^{119a,120a-d} In the Re system, activation parameters compare well with those observed for CO exchange (Table VIII), taking into account the known solvent dependence of the rate which decreases with increasing polarity of solvent.¹²¹ The general ordering of lability of NCO > Cl > Br > I and Mn > Re may be noted. The latter is reminiscent of the lower lability of W as compared to Cr, while the order of halide labilization is in agreement with the order of interaction of the halide orbitals with the metal in the ground-state molecule (Cl > Br > I) that is evident from photoelectron studies.¹²² Competition experiments indicate a poor discriminating nature for the M(CO)₄X intermediate.^{119a}

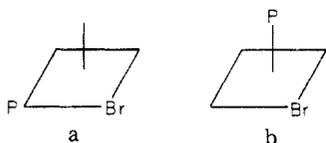
cis-M(CO)₄(Br)(L) complexes (L = py, PPh₃, P(OPh)₃; M = Mn, Re) also undergo ¹³CO exchange with the results indicating a fluxional BrMn(CO)₃L intermediate and preferential loss of CO from positions 3 and 5 cis to both Br and L.¹²³



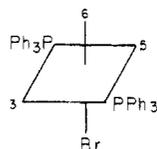
Similarly, reactions with other ligands L'



show the same order of cis-halide labilizing ability (Table VIII), and in terms of L, the labilizing order $py > PPh_3 > AsPh_3 > PBu_3 > P(OPh)_3 \approx SbPh_3 > P(OBu)_3$ is observed. In fact, ligands lower than PBu_3 in this series are less labilizing than CO in the $Mn(CO)_5X$ derivative.^{124,125} Although rates for the above reaction do not depend on $[L']$, they do depend on the nature of L' , with the rate constant decreasing as the steric hindrance of L' increases. This has been attributed to (i) competition of released CO for the five-coordinate intermediate in the case of severe steric hindrance or (ii) isomerization of the initial intermediate a to b.



This is necessarily a higher energy pathway, and indeed, $cis-BrMn(CO)_4(PPh_3)_2$ reacts most slowly with PPh_3 to give not the fac product above, but

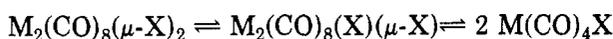


This complex also undergoes ^{13}CO exchange preferentially at the cis positions (3 and 5) via a fluxional intermediate.¹²³

It may also be noted that the halogen-bridged dimers $M_2(CO)_8(\mu-X)_2$ ($M = Mn, Re$) react with ligands via bridge splitting to give $cis-M(CO)_4(X)(L)$ complexes with the rate order $Cl > Br > I$.^{126,127} However, the rate law has the form

$$\frac{-d[M_2(CO)_8(\mu-X)_2]}{dt} = k_1[M_2(CO)_8(\mu-X)_2] + k_2[M_2(CO)_8(\mu-X)_2][L] \quad (12)$$

consistent with the preequilibria

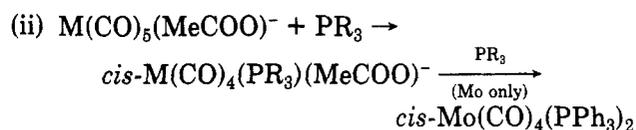
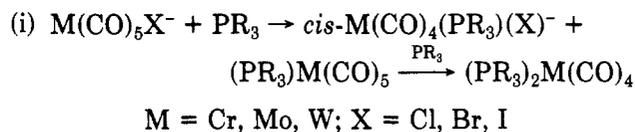


Even the reaction of X^- with $Mn(CO)_5X$ to give $cis-[Mn(CO)_4X_2]^-$ proceeds via a CO dissociative pathway,¹²⁸ in contrast to $Cr(CO)_6$. $M(CO)_5X$ ($M = Mn, Re$; $X = Cl, Br, I$) also react with CN^- to give $cis-[M(CO)_4(CN)_2]^-$; in all cases except $Mn(CO)_5Cl$, the reaction proceeds via initial formation of $[M(CO)_4(X)(CN)]^-$ followed by halide exchange to give $[M(CO)_4(CN)_2]^-$,^{129,130} and it may be noted that $Mn(CO)_5X$ derivatives undergo halogen exchange with $*X_2$ at rates which are independent of $[*X_2]$.¹³¹

Other ligands that may be classified as labilizing relative to CO include $X = NO_3^{132} > COCH_3^{133} > SO_2R$ ($R = Ph, Me$)^{134a,b} as judged by the rates of reaction of $Mn(CO)_5X$ with ligands, although no activation parameters are available. In addition, CO labilization by CH_3CN has been observed in $[(CH_3CN)Mn(CO)_5]^+$.^{25,81} CO appears less labile than in $Mn(CO)_6^+$ in the CO

exchange reaction of $Ph_3PAuMn(CO)_5^{135}$ and the reaction of $Ph_3EMn(CO)_5$ ($E = Ge, Sn$) with PPh_3^{136} for which activation parameters are available. These ligands are non- π -donors, and the isolation of the $trans-Mn(CO)_4(PPh_3)(EPh_3)$ product from the last reaction may perhaps be viewed in terms of the lower site preference of EPh_3 ligands for the basal position of the square pyramid, particularly in view of the substantial steric bulk of EPh_3 . The reactions of $HMn(CO)_5$ cannot be treated as characteristic in this context; however, $HRe(CO)_5$ is nonlabile to substitution by PBu_3^{137} under conditions where the halides are labile.

Similar conclusions can be drawn from the reactions of the chromium group. Thus, both $[W(CO)_5Cl]^{-49}$ and $[M(CO)_5(MeCOO)]^-$ ($M = Mo, W$)^{138a,b} undergo rapid exchange with ^{13}CO , in contrast to $M(CO)_6$. The halide and acetate ions also react with donors at similar rates^{138a,b,139}

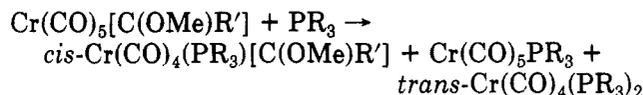


Kinetic studies¹³⁹ on the halide complexes show that the rate law

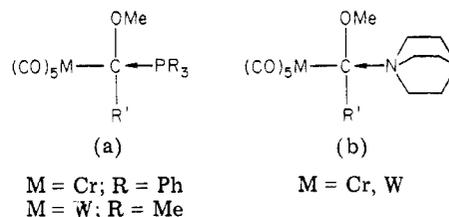
$$\frac{-d[M(CO)_5X^-]}{dt} = k_1[M(CO)_5X^-] + k_2[M(CO)_5X^-][L]$$

applies. The production of the $cis-M(CO)_4(L)(X)^-$ product may be associated with the k_1 dissociative pathway and exhibits the usual order of cis labilization $Cl > Br > I$ while the metal order $Mo > Cr \approx W$ is reminiscent of the dissociation order from $M(CO)_6$. The k_2 associative term may be linked with the production of the neutral $M(CO)_5L$ and $M(CO)_4L_2$ complexes, but the exact nature of the X^- displacement is not clear.

Reaction of $Cr(CO)_5[C(OMe)R']$ with PR_3 proceeds in a similar manner according to a two-term rate law.¹⁴⁰

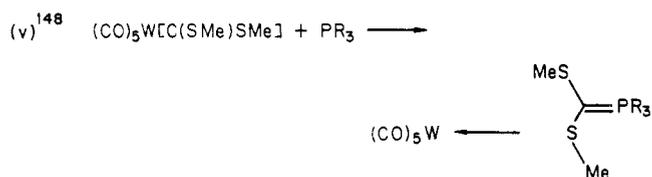
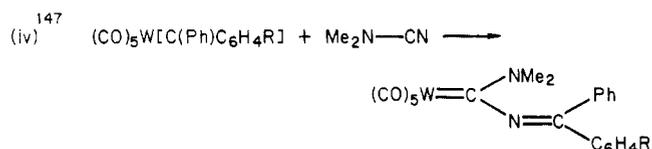
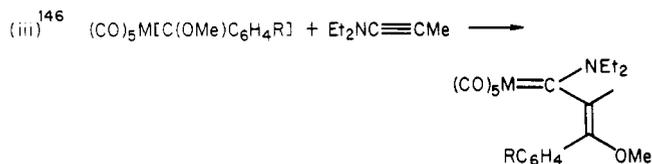
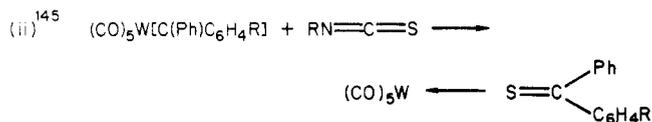
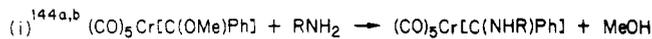


Again, k_1 may be associated with rate-determining CO dissociation and the activation parameters (Table I) show that carbene (in this case conjugated and therefore a potential π donor) may be regarded as a cis-labilizing ligand. However, the k_2 associative term may be directly linked to PR_3 attack at the carbene carbon to give the adduct a, which may be isolated and shown to de-



compose thermally not only to $M(CO)_5(PR_3)$ and $M-$

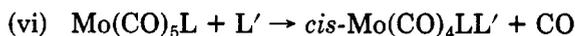
$(\text{CO})_4(\text{PR}_3)_2$, but also to *cis*- $\text{M}(\text{CO})_4(\text{PR}_3)[\text{C}(\text{OMe})\text{R}']$.^{141a,b,142} Activation parameters linked to k_2 are in agreement with an associative process. A similar adduct **b** may be isolated from reaction with hindered tertiary amines.¹⁴³ Reactions of a number of carbene species listed below have been characterized kinetically; with the exception of (i), all obey perfect second-order kinetics and activation parameters (Table IV) may be associated with rate-determining attack on the carbene carbon. In



(i), the rate is proportional to $[\text{RNH}_2]^2$, consistent with attack by a hydrogen-bonded $\text{RHNH}\cdots\text{NH}_2\text{R}$ dimer, in agreement with the negative ΔH^* for this reaction.

The greater susceptibility to attack ($\text{W} > \text{Cr}$) in reaction iii and the decreasing ΔH^* with increasing basicity of PR_3 in reaction v may be noted.

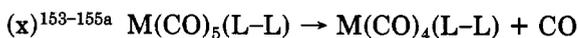
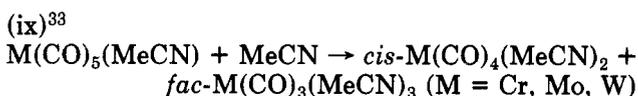
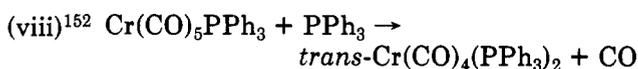
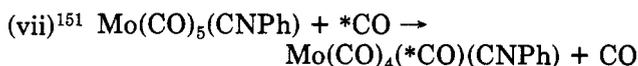
Group 5 donors, including MeCN , are also labilizing, with $\text{py} > \text{PPh}_3$ on the basis of rate constants reported for the reactions below. Isonitriles are essentially nonlabilizing.



$\text{L} = 4\text{-methylpyridine}; \text{L}' =$

4-picoline, 3,4-lutidine, 3-chloropyridine¹⁴⁹

$\text{L} = \text{PPh}_3, \text{P}(\text{OEt})_3, \text{CNC}_6\text{H}_{11}; \text{L}' = \text{PPh}_3$ ¹⁵⁰

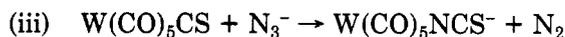
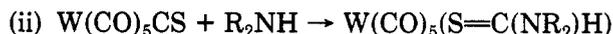


$\text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{L}-\text{L} = \text{bidentate phosphine}$

Note that in (viii), the *trans* isomer is isolated, although *cis* labilization occurs, and that reaction vi proceeds via a two-term rate law in which the k_2 term may be asso-

ciated with a competing I_d pathway. Activation enthalpies (Table I) for the chelation reactions of (x) are in the order $\text{W} > \text{Cr} > \text{Mo}$ usually associated with CO loss, but less than those associated with $\text{M}(\text{CO})_6$. It may, however, be noted that with bulky ligands such as PPh_3 , a steric contribution to the rate enhancement is likely, in addition to any electronic effect.¹⁰⁸

Finally, examples of *trans* labilization of CO in complexes containing strong π -accepting ligands have been reported. Thus, $\text{W}(\text{CO})_5\text{CS}$ undergoes ^{13}CO exchange to give almost exclusively *trans*- $\text{W}(\text{CO})_4(^{13}\text{CO})(\text{CS})$ and reacts with L via competing D and I_d pathways to give *trans*- $\text{W}(\text{CO})_4(\text{CS})(\text{L})$ ($\text{L} = \text{py}, \text{PPh}_3$), and with halide via a purely second-order process to give *trans*- $[\text{W}(\text{CO})_4(\text{CS})(\text{X})]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). ΔH^*_1 and ΔH^*_2 values for reaction with PPh_3 indicate a substantial *trans* labilization as compared to $\text{W}(\text{CO})_6$. While the *trans* product may be attributed to either a *cis* labilization followed by isomerization of a $\text{W}(\text{CO})_5\text{CS}$ intermediate, or to isomerization of an initially formed *cis*- $\text{W}(\text{CO})_4(\text{CS})(\text{L})$ complex, it is known that *trans*- $\text{W}(\text{CO})_4(^{13}\text{CO})(\text{CS})$ reacts with I^- to give exclusively *trans*- $[\text{W}(\text{CO})_4(\text{CS})\text{I}]^-$ and ^{13}CO .^{49,156} Matrix photolysis of $\text{M}(\text{CO})_5\text{CS}$ results in initial statistical loss of both axial and equatorial CO .^{157a,b} Products of attack at the CS carbon are also evident:

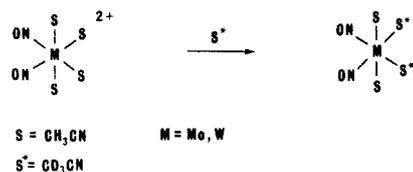


For reaction i, the dependence on $[\text{RNH}_2]^2$ and the low activation enthalpy are characteristic of attack by $\text{RHNH}\cdots\text{NH}_2\text{R}$. As expected, the use of *trans*- $\text{W}(\text{CO})_4(^{13}\text{CO})\text{CS}$ yields *trans*- $\text{W}(\text{CO})_4(^{13}\text{CO})(\text{CNR})$ and *trans*- $\text{W}(\text{CO})_4(^{13}\text{CO})(\text{NCS})^-$.^{49,158} The carbyne complex $\text{Cr}(\text{CO})_5(\text{CNET}_2)^+$ also undergoes stereospecific *trans* labilization to give *trans*- $\text{Cr}(\text{CO})_4(\text{CNET}_2)(\text{PPh}_3)^+$ under conditions where *cis*-*trans* isomerism is unlikely.¹⁵⁹ The neutral complexes *trans*- $\text{XCr}(\text{CO})_4(\text{CNET}_2)$ ($\text{X} = \text{Br}, \text{I}$) undergo substitution by PPh_3 to give *mer*- $\text{Cr}(\text{CO})_3(\text{X})(\text{PPh}_3)(\text{CNET}_2)$ with broadly similar activation parameters (perhaps indicating competition between *cis*-labilizing and *trans*-labilizing ligands). The activation parameters show the usual order of *cis* labilization, $\text{Br} > \text{I}$. In a similar way, *trans*- $\text{W}(\text{CO})_4(\text{CS})\text{I}^-$ undergoes exchange with ^{13}CO to give *mer*- $\text{W}(\text{CO})_3(\text{CS})(\text{I})(^{13}\text{CO})^-$.⁴⁹

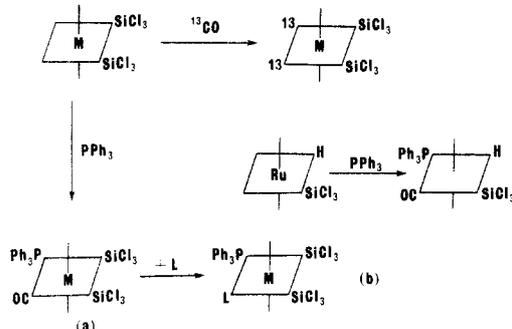
Trans labilization by NO is observed in the stereospecific exchange¹⁶⁰ shown in Scheme XIV. The order of lability is $\text{Mo} > \text{W}$, while it may be noted that *trans*- $\text{Cr}(\text{MeCN})_4(\text{NO})_2^{2+}$ does not undergo exchange. *Trans* labilization by the strongly π -accepting SiCl_3 may be noted in the stereospecific ^{13}CO incorporation into *cis*- $\text{Ru}(\text{CO})_4(\text{SiCl}_3)_2$ and the first-order reaction of *cis*- $\text{M}(\text{CO})_4(\text{SiCl}_3)_2$ and *cis*- $\text{Ru}(\text{CO})_4(\text{H})(\text{SiCl}_3)$ with PPh_3 to give the products shown in Scheme XV. The order of lability $\text{Ru} > \text{Fe} > \text{Os}$ is reminiscent of the chromium group ($\text{Mo} > \text{Cr} > \text{W}$). The remaining *trans*- CO is also labilized, with (a) reacting easily with ligands of small cone angle to yield (b). Bidentate ligands also react with *cis*- $\text{Ru}(\text{CO})_4(\text{SiCl}_3)_2$ to yield products of geometry (b).^{161-163b}

cis- $\text{Fe}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Br}, \text{I}$) reacts sequentially with group 5 ligands such as EPh_3 ($\text{E} = \text{P}, \text{As}, \text{Sb}$) to give

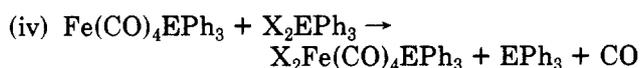
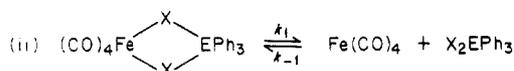
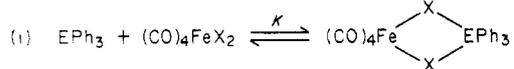
Scheme XIV



Scheme XV



$\text{Fe}(\text{CO})_3\text{X}_2\text{EPh}_3$ and $\text{Fe}(\text{CO})_2\text{X}_2(\text{EPh}_3)_2$ complexes.^{164-166b} The rate of initial monosubstitution is independent of both the nature and concentration of EPh_3 , yet has activation parameters consistent with associative character. This, and the inhibition by added X_2 , has been interpreted in terms of a rapid preequilibrium involving a bridging interaction with EPh_3 , followed by rate-determining generation of $\text{Fe}(\text{CO})_4$.¹⁶⁷



The much slower rates observed for $^*\text{CO}$ ¹⁶⁸⁻¹⁷⁰ and $^*\text{Br}_2$ ¹³¹ exchange may be attributed to their inability to assist X_2 dissociation via the bridging interaction shown. Indeed, the $^*\text{CO}$ exchange is dependent on $[\text{CO}]$, and the reaction may proceed via the $\text{Fe}(\text{CO})_5\text{I}_2$ intermediate which is evident from stopped-flow¹⁷¹ and spectroscopic^{172,173} studies of the reaction of $\text{Fe}(\text{CO})_5$ with I_2 .

Finally, care must be taken in interpreting mechanism from the stereochemistry of *isolated* $\text{M}(\text{CO})_4\text{L}_2$ and $\text{M}(\text{CO})_3\text{L}_3$ complexes, since *cis/trans* and *fac/mer* isomerism, respectively, are commonly observed features of such derivatives. Results on compounds of relevance to the preceding discussion are detailed in Table IX. The reactions may be divided into those which are intramolecular and those which appear to proceed via the dissociation of L on the basis of incorporation of CO or ligand exchange during the conditions required for isomerization. In the intramolecular cases, $\text{H}_2\text{Fe}[\text{PhP}(\text{OEt})_2]_4$ is unique in that NMR studies show that isomerization occurs via a process in which the hydrogens traverse the faces of an approximate tetrahedron of phosphorus atoms, and a crystal structure determination of the above complex reveals a ground-state structure that approximates to this.

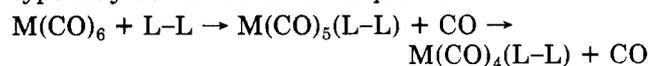
Other H_2ML_4 complexes [$\text{M} = \text{Fe}$, $\text{L} = \text{P}(\text{OEt})_3$, $\text{P}(\text{OPr-}i)_3$, $\text{P}(\text{OCH}_2)_3\text{CEt}$, $\text{PhP}(\text{OPr-}i)_2$, $\text{L}_2 = \text{diphos}$; $\text{M} = \text{Ru}$, $\text{L} = \text{P}(\text{OMe})_3$, PhMe_2P , PhEt_2P , Ph_2MeP , $\text{Ph}_2\text{P}(\text{OMe})$] undergo site exchange by the same mechanism, although only the *cis* isomer is detectable at equilibrium.¹⁷⁴⁻¹⁷⁷ The remainder of the intramolecular isomerizations are assumed to proceed via the trigonal-twist²⁰³ or related²⁰⁴⁻²⁰⁶ mechanisms. In addition, experiments on scrambling of ^{13}CO in *cis*- $\text{M}(\text{CO})_4(^{13}\text{CO})[\text{P}(\text{OMe})_3]$ ($\text{M} = \text{Cr}$, Mo , W) indicate that site exchange is also a feature of $\text{M}(\text{CO})_5\text{L}$ complexes (intramolecular for Cr and W, dissociative for Mo).^{94a,207}

The position of equilibrium (K_{eq}) in both intramolecular and dissociative isomerizations can be seen as a compromise between the electronically favored *cis*- $\text{M}(\text{CO})_4\text{L}_2$ isomer (particularly where L is a strong σ donor but weak π acceptor) and the sterically favored *trans* isomer. For systems in which both isomers are present at equilibrium, K_{eq} can be seen to depend predominantly on the steric interaction between the two ligands. A smaller dependence on the type of ligand and the metal center is also observed. Thus, $\text{MeCOMn}(\text{CO})_4\text{L}$ exists solely as the *cis* isomer when $\text{L} = \text{PEt}_3$ but in a 9:1 *cis/trans* ratio when $\text{L} = \text{P}(\text{OMe})_3$ even though PEt_3 has the larger cone angle.¹⁹⁴ This has been attributed to the greater π -acceptor capacity of $\text{P}(\text{OMe})_3$. In the $\text{M}(\text{CO})_4(\text{PBu}_3)_2$ series ($\text{M} = \text{Cr}$, Mo , W), the *cis/trans* ratio varies in the order $\text{Cr}(<.01) < \text{W}(.11) < \text{Mo}(.19)$.¹⁸⁶ Although the position of Cr is expected due to its smaller size, the differing ratios of the similarly sized Mo and W complexes perhaps reflects an electronic contribution to K_{eq} on the part of the metal. Similar steric influences are obvious in the *fac/mer* ratios adopted by $\text{XMn}(\text{CO})_3\text{L}_2$ complexes. It may be noted that formation of $\text{XMn}(\text{CO})_2\text{L}_3$ from $\text{XMn}(\text{CO})_3\text{L}_2$ may actually require initial isomerization. Thus, *fac*- $\text{BrMn}(\text{CO})_3[\text{P}(\text{OMe})_2\text{Ph}]_2$ undergoes reaction with $\text{P}(\text{OMe})_2\text{Ph}$ to give $\text{BrMn}(\text{CO})_2[\text{P}(\text{OMe})_2\text{Ph}]_3$ only after isomerization to the *mer* isomer.¹⁹⁸

Insufficient information exists to identify factors that determine the relative rates of intramolecular isomerization. In the $\text{M}(\text{CO})_4\text{L}_2$ series [$\text{M} = \text{Cr}$, Mo , W ; $\text{L} = \text{PR}_3$, $\text{P}(\text{OR})_3$], it may be noted that the rate of isomerization $\text{PR}_3 > \text{P}(\text{OR})_3$ parallels the rate of dissociation from the $\text{M}(\text{CO})_4\text{L}_2$ complex, although the relative rates in terms of metal ($\text{Cr} > \text{W} > \text{Mo}$) are not in the same order as the rate of dissociation ($\text{Mo} > \text{W}$). Finally, a dramatic influence of oxidation state on the rate of isomerization may be noted, with *cis*- $[\text{Mo}(\text{CO})_4(\text{PBu}_3)_2]^+$,^{208a} *cis*- $[\text{M}(\text{CO})_2(\text{P-P})_2]^+$ ($\text{M} = \text{Cr}$, Mo , W),^{208b} and *trans*- $[(\text{CO})_4\text{Mo}(\text{CN}(\text{Me})\text{CH}=\text{CHNMe})]^+$ ²⁰⁹ undergoing isomerization at rates that are orders of magnitude faster than their neutral analogues of Table IX.

VI. Complexes Based on Bidentate $\text{M}(\text{CO})_4(\text{L-L})$

In principle, formation of chelated complexes of this type may be viewed as the sequence



In practice, $\text{M}(\text{CO})_5(\text{L-L})$ complexes are not available by direct thermal substitution of $\text{M}(\text{CO})_6$, but have been isolated under milder conditions and the kinetics of the chelation step have been investigated. Thus, rates of

TABLE IX. Data for $cis\text{-M}(\text{CO})_4\text{L}_2 \rightleftharpoons trans\text{-M}(\text{CO})_4\text{L}_2$ and $mer\text{-M}(\text{CO})_3\text{L}_3 \rightleftharpoons fac\text{-M}(\text{CO})_3\text{L}_3$ Isomerizations

system	ΔH^* , kJ mol ⁻¹	ΔS^* , J K ⁻¹ mol ⁻¹	k , 10 ³ s ⁻¹ (temp)	K_{eq} , cis/trans	ref
A. Intramolecular					
$cis\text{-H}_2\text{Fe}[\text{PhP}(\text{OEt})_2]_4 \rightleftharpoons trans$	46.4	-37		1	174-177
$cis\text{-Cr}(\text{CO})_4[\text{C}(\text{OMe})\text{Me}]PR_3 \rightleftharpoons trans$					
$PR_3 = \text{PEt}_3$	88.6 ^{a,c}	-27		1.03	178-181
	94.1 ^{b,c}	-15			
	101.5 ^{a,d}	12		1.98	
	92.8 ^{b,d}	-10			
$PR_3 = \text{PCy}_3$	97.4 ^{a,c}	-6		0.32	
	107.4 ^{b,c}	16			
	96.6 ^{a,d}	-3		0.45	
	104.1 ^{b,d}				
$PR_3 = \text{P}(p\text{-tolyl})_3$				2.00 ^e	
$PR_3 = \text{PPh}_3$				4.58	
$PR_3 = \text{P}(p\text{-C}_6\text{H}_4\text{F})_3$				3.18	
$PR_3 = \text{P}(m\text{-C}_6\text{H}_4\text{F})_3$				3.30	
$PR_3 = \text{PPh}_2\text{Et}$				4.00	
$PR_3 = \text{PPhEt}_2$				3.33	
$PR_3 = \text{PEt}_3$				1.94	
$PR_3 = \text{PMe}_3$				2.98	
$PR_3 = \text{PBu}_3$				1.84	
$PR_3 = \text{P}(n\text{-C}_8\text{H}_{17})_3$				1.78	
$PR_3 = \text{PPr-}i_3$				0.59	
$cis\text{-Cr}(\text{CO})_4[\text{C}(\text{OR})\text{R}']\text{PPr}_3 \rightleftharpoons trans$					
$R = \text{Me}, R' = \text{Me}$				1.84	
$R = \text{Me}, R' = \text{Et}$				1.15	
$R = \text{Me}, R = \text{Pr-}i$				0.45	
$R = \text{Me}, R = \text{Ph}$				1.06	
$R = \text{Et}, R' = \text{Me}$				2.00	
$cis\text{-M}(\text{CO})_4[\text{C}(\text{OR})\text{R}']\text{PBu}_3 \rightleftharpoons trans$					
$M = \text{Cr}, R = \text{Me}, R' = \text{Me}$				1.84	
$M = \text{W}, R = \text{Me}, R' = \text{Me}$				11.5	
$M = \text{Cr}, R = \text{Me}, R' = \text{Ph}$				1.06	
$M = \text{W}, R = \text{Me}, R' = \text{Ph}$				4.18	
$trans\text{-}(\text{CO})_4\text{Mo}[\text{CN}(\text{R})(\text{CH}_2)_n\text{NR}]_2 \rightleftharpoons cis$					
$n = 2, 3, R = \text{Me}, \text{Et}$	ca. 70	ca. -70		<i>f</i>	182, 183
$trans\text{-}(\text{CO})_4\text{M}[\text{CN}(\text{Me})\text{CH}=\text{CHNMe}]_2 \rightleftharpoons cis$					
$M = \text{Cr}, \text{Mo}, \text{W}$				<i>f</i>	184, 185
$cis\text{-Cr}(\text{CO})_4(\text{PR}_3)_2 \rightleftharpoons trans$					
$PR_3 = \text{PBu}_3$				<0.01	186
$PR_3 = \text{P}(\text{OMe})_3$			10.5 (28)	0.20	
$cis\text{-Mo}(\text{CO})_4(\text{PR}_3)_2 \rightleftharpoons trans$					
$PR_3 = \text{PBu}_3$	102.4 ^a	-23		0.14	187
$PR_3 = \text{PEt}_3$	101.2 ^b				
$PR_3 = \text{PEt}_3$			2.02 (80)	0.19	
$PR_3 = \text{P}(\text{OMe})_3$			1.45 (93)	1.01	186
$cis\text{-W}(\text{CO})_4(\text{PR}_3)_2 \rightleftharpoons trans$					
$PR_3 = \text{PBu}_3$			3.45 (46)	0.11	186
$PR_3 = \text{P}(\text{OMe})_3$			2.81 (65)	0.98	
$PR_3 = \text{P}(\text{OPh})_3$			3.24 (94)	0.28	
$cis\text{-W}(\text{CO})_4(\text{PR}_3)(\text{PR}'_3) \rightleftharpoons trans$					
$PR_3 = \text{PPr-}i_3, PR'_3 = \text{PPh}_2\text{Pr-}i$				<0.05	188
$PR_3 = \text{PPr-}i_3, PR'_3 = \text{PPh}_3$				<0.05	
$PR_3 = \text{PPr-}i_3, PR'_3 = \text{P}(\text{NMe}_2)_3$				<0.05	
$PR_3 = \text{PPr-}i_3, PR'_3 = \text{P}(\text{OPr-}i)_3$				0.66	
$PR_3 = \text{PPr-}i_3, PR'_3 = \text{P}(\text{OPh})_3$				0.1	
$PR_3 = \text{PPh}_3, PR'_3 = \text{P}(\text{NMe}_2)_3$				<0.05	
$PR_3 = \text{PPh}_3, PR'_3 = \text{P}(\text{OPr-}i)_3$				2.5	
$PR_3 = \text{PPh}_3, PR'_3 = \text{P}(\text{OPh})_3$				0.5	
$PR_3 = \text{P}(\text{NMe}_2)_3, PR'_3 = \text{P}(\text{OPh})_3$				<0.05	
$cis\text{-W}(\text{CO})_4(^{13}\text{CO})(\text{CS}) \rightleftharpoons trans$	131.7 ^b	38		4.0	189
$cis\text{-W}(\text{CO})_4(\text{CS})(\text{L}) \rightleftharpoons trans$					
$L = \text{PR}_3, \text{P}(\text{OR})_3, \text{CNR}$				<4	
$cis\text{-M}(\text{CO})_4(\text{SiCl}_3)_2 \rightleftharpoons trans$					
$M = \text{Ru}$	104.1 ^a	-29		0.52	190
Fe				cis only	
Os				trans only	
$cis\text{-Os}(\text{CO})_4(\text{SiMe}_3)_2 \rightleftharpoons trans$	74.8 ^a	7		trans only	
$cis\text{-M}(\text{CO})_4\text{I}_2 \rightleftharpoons trans$					
$M = \text{Fe}, \text{Ru}$				<i>f</i>	191
$cis\text{-X}_2\text{Fe}(\text{CO})_2\text{L}_2 \rightleftharpoons trans$				<i>f</i>	192
B. Dissociative					
$cis\text{-MeCOMn}(\text{CO})_4\text{L} \rightleftharpoons trans$					
$L = \text{PPh}_3$			2.5 (30)	2.33	193
$L = \text{AsPh}_3$				9.0	194
$L = \text{SbPh}_3$				cis only	
$L = \text{PPh}_2\text{Me}$				cis only	

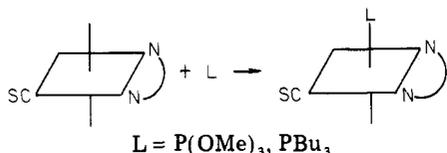
TABLE IX (Continued)

system	ΔH^* , kJ mol ⁻¹	ΔS^* , J K ⁻¹ mol ⁻¹	k , 10 ³ s ⁻¹ (temp)	K_{eq} , cis/trans	ref
L = P(OMe) ₃				9.0	
L = P(OPh) ₃				cis only	
L = P(OCH ₂) ₃ CMe				cis only	
<i>cis</i> -PhCH ₂ Mn(CO) ₄ L ⇌ <i>trans</i>					
L = PPh ₃				3.0	195
L = P(OPh) ₃				3.3	
<i>cis</i> -BrM(CO) ₄ L ⇌ <i>trans</i>					
M = Mn, Re, L = PPh ₃				cis only	120
<i>cis</i> -MeMn(CO) ₄ L ⇌ <i>trans</i>					
L = PR ₃ , P(OR) ₃				cis only	194
<i>cis</i> -Mo(CO) ₄ L ₂ ⇌ <i>trans</i>					
L = PPh ₃	98.6 ^a	-46		<i>trans</i> only	
L = P(OPh) ₃			0.364 (93)	0.31	186
<i>fac</i> -XMn(CO) ₃ L ₂ ⇌ <i>mer</i>					
X = Br, L = PPhCl ₂	110.4	13		<i>mer</i> only	197
X = Br, L = PBu ₃	115.8	16		<i>mer</i> only	
X = Br, L = P(OPh) ₃	121.2	38		<i>mer</i> only	
X = Br, L = P(OBu) ₃	132.9	60		<i>mer</i> only	
X = Br, L = PPh(OMe) ₂	130.8	79		<i>mer</i> only	198
X = Cl, L = PPh(OMe) ₂	125.4	74		<i>mer</i> only	
<i>fac</i> -BrMn(CO) ₃ (diphos) ⇌ <i>mer</i>				<i>fac</i> only	199
<i>fac</i> -MeCOMn(CO) ₃ L ₂ ⇌ <i>mer</i>					
L = PPh ₂ H, P(OCH ₂) ₃ CMe				<i>fac</i> only	200
L = Ph ₂ PMe, P(OPh) ₃ , PEt ₃ , PPhMe ₂ , P(OMe) ₃				<i>mer</i> only	
<i>fac</i> -MeCOMn(CO) ₃ (L-L) ⇌ <i>mer</i>					
L-L = Ph ₂ P(CH ₂) _n PPh ₂ , n = 1				19.0	201, 202
L-L = Ph ₂ P(CH ₂) _n PPh ₂ , n = 2, 3				<i>fac</i> only	
L-L = Ph ₂ PC(Me)HPPH ₂				3.0	
L-L = Ph ₂ C(Me) ₂ PPh ₂				<i>mer</i> only	
<i>fac</i> -MeMn(CO) ₃ (L-L) ⇌ <i>mer</i>					
L-L = PPh ₂ (CH ₂) _n PPh ₂ , n = 1, 2				<i>fac</i> only	
L-L = Ph ₂ PC(Me)HPPH ₂				<i>fac</i> only	

^a *cis* = *trans*. ^b *trans* = *cis*. ^c Methylcyclohexane. ^d Toluene. ^e Acetone. ^f No *trans* isomer present at equilibrium; *trans* isomer prepared by photochemical isomerization of *cis*.

Mo(CO)₃(diphos)L depending on the ligand used, proceed solely via rate-determining CO loss^{222,223} and ¹³CO-labelling experiments indicate only a partial fluxional character for the Mo(CO)₃(diphos) intermediate.²²⁴

Substitution reactions of W(CO)₃(phen)(CS)



may also be interpreted on the basis of Scheme XVII; a *cis* labilization of CO dissociation relative to W(CO)₆, W(CO)₅CS, and W(CO)₄(phen) may be noted.²²⁵

Substitution of L by an L-dissociative pathway



has been studied kinetically,²²⁶ rates (PBu₃ < P(OEt)₃ < P(OCH₂)₃CMe) and activation parameters (Table X) broadly parallel the trend observed for dissociation of L from Cr(CO)₅L, but with lower activation enthalpies due to the *cis*-labilizing effect of phen. Substitution of P(OPh)₃ in *fac*-M(CO)₃(phen)P(OPh)₃ by other ligands proceeds via the competing D and I_d pathways of Scheme XVII. In substitution of M(CO)₄(phen), the I_d pathway is observed only for Mo and W, but plays a diminished role compared to the substitution of M(CO)₄(phen); k_1 values increase as the basicity of the phen increases.²²⁷

For bidentate aliphatic nitrogen and sulfur ligands, complete displacement of L-L is usually observed. The

results have generally been interpreted on the basis of Scheme XVIII. Steady-state treatment of Scheme XVIII yields the rate law

$$\frac{-d[\text{S}]}{dt} = \frac{k_4\{(k_1k_3 + k_{-1}k_2)[\text{S}][\text{L}']\} + k_3k_2[\text{S}][\text{L}]^2}{k_{-1}(k_{-3} + k_{-2} + k_4) + k_3(k_{-2} + k_4)[\text{L}']} \quad (17)$$

where S is metal substrate complex.

The complexity of this expression means that rate constants and particularly derived activation parameters must be treated with caution. However, several points may be noted:

(a) For all reactions except the displacement of MeS(CH₂)₂SMe, curved plots of k_{obsd} against [L'] are observed, consistent with eq 17. Calculations show that an apparently linear plot of k_{obsd} against [L'] can be obtained with appropriate combinations of rate constants.²³³

(b) Assuming that $k_1 \gg k_2$, consideration of eq 17 shows that a plot of $1/k_{\text{obsd}}$ against $1/[\text{L}']$ should be linear. For different L', the intercepts of this plot should be constant if the reactions proceed solely by the D pathway (k_1) but different if the reactions proceed by both D and I_d pathways. Such linear plots are found for the examples in Scheme XVIII, with only the *t*-BuS(CH₂)₂SBu-*t* displacements giving a common intercept for different L'.

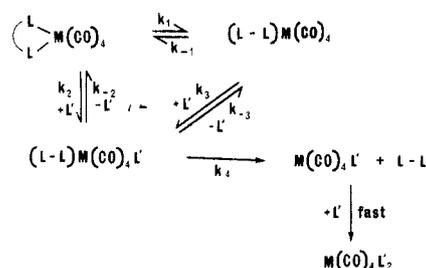
(c) The intermediates (η^2 -L-L)W(CO)₄P(OCH₂)₃CMe (L-L = Me₂N(CH₂)₃NMe₂ and *t*-BuS(CH₂)₃SBu-*t*) have been isolated and shown to react with L' at rates that are independent of [L'] to give the product.

(d) For both Me₂N(CH₂)_nNMe₂ and *t*-BuS(CH₂)_nSBu-*t* ($n = 2, 3$), the larger six-membered chelate

TABLE X. Activation Parameters for Reactions Involving $(\text{CO})_4\text{M}(\text{L}-\text{L})$ Complexes

reaction	ΔH_1^* , kJ mol ⁻¹	ΔS_1^* , J K ⁻¹ mol ⁻¹	ΔH_2^* , kJ mol ⁻¹	ΔS_2^* , J K ⁻¹ mol ⁻¹	ref
$(\text{CO})_4\text{Mo}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{NR}_2) + \text{CO} \rightarrow$ $(\text{CO})_5\text{Mo}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{NR}_2]$					
$n = 2, \text{R} = \text{Me}$	94.9	-132			209
$n = 3, \text{R} = \text{Me}$	89.8	10			
$n = 2, \text{R} = \text{Et}$	92.8	-3			
$(\text{CO})_4\text{Mo}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{C}_5\text{H}_4\text{N}] + \text{CO} \rightarrow$ $(\text{CO})_5\text{Mo}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{C}_5\text{H}_4\text{N}]$					
$n = 1$	83.6	-67			210
$n = 2$	89.5	-29			
$n = 3$	94.9	13			
$(\text{CO})_4\text{W}(\text{bpy}) + \text{PO}_3\text{C}_6\text{H}_5 \rightarrow$ $\text{fac}-(\text{CO})_3\text{W}(\text{bpy})(\text{PO}_3\text{C}_6\text{H}_5)$	141.7	52	93.2	-56	215
$(\text{CO})_4\text{Cr}(\text{phen}) + \text{C}^{18}\text{O}$	112.4	38			217
$(\text{CO})_4\text{M}(\text{phen}) + \text{P}(\text{OCH}_2)_3\text{CMe} \rightarrow$ $\text{fac}-(\text{CO})_3\text{M}(\text{phen})[\text{P}(\text{OCH}_2)_3\text{CMe}]$					
$\text{M} = \text{Cr}$	110.3	29			213
$\text{M} = \text{Mo}$	104.9	10	80.2	-71	
$\text{M} = \text{W}$	139.6	-44	98.6	-157	
$(\text{CO})_4\text{Mo}(\text{H}_2\text{PC}_2\text{H}_4\text{PH}_2) + \text{PBu}_3 \rightarrow$ $\text{fac}-(\text{CO})_3\text{Mo}(\text{H}_2\text{PC}_2\text{H}_4\text{PH}_2)(\text{PBu}_3)$	187.9	146	99.9	-49	220
$\text{fac}-(\text{CO})_3\text{Cr}(\text{phen})\text{L} + \text{CO} \rightarrow$ $(\text{CO})_4\text{Cr}(\text{phen}) + \text{L}$					
$\text{L} = \text{PBu}_3$	122.5	46			225
$\text{L} = \text{P}(\text{OEt})_3$	117.8	56			
$\text{L} = \text{P}(\text{OCH}_2)_3\text{CMe}$	91.5	-23			

Scheme XVIII



^a (i) ^{228,229} L-L = Me₂N(CH₂)₂NMe₂; M = Cr, W; L' = P(OMe)₃, P(OEt)₃, P(OCH₂)₃CMe, P(OPh)₃, PPh₃.
(ii) ^{223,224,230} L-L = Me₂N(CH₂)₃NMe₂; M = Cr, Mo, W; L' = P(OEt)₃, P(OPr-*i*)₃, P(OMe)₃, P(OCH₂)₃CMe, P(OPh)₃, PPh₃.
(iii) ^{223,231} L-L = MeS(CH₂)₂SMe; M = Cr, Mo; L' = P(OEt)₃, P(OMe)₃, P(OPh)₃.
(iv) ²³²⁻²³⁴ L-L = Bu-*t*-S(CH₂)₂SBu-*t*; M = Cr, Mo, W; L' = P(OEt)₃, P(OMe)₃, P(OPh)₃, PBu₃.
(v) ^{223,235} L-L = Bu-*t*-S(CH₂)₃SBu-*t*; M = W; L' = P(OEt)₃, P(OCH₂)₃CMe, PPh₃.

ring is more easily displaced than the five-membered ring. This agrees with the dechelation studies of M(CO)₄(N-P) complexes mentioned previously, and crystal structure determinations of W(CO)₄[*t*-BuS(CH₂)_nSBu-*t*] ($n = 2, 3$)²³⁶ reveal a greater potential for release of steric strain on opening of the six-membered ring.

(e) The site preference and fluxionality arguments presented in Scheme X may be applied to both the $(\eta^2\text{-L-L})\text{M}(\text{CO})_4$ and $\text{M}(\text{CO})_4\text{L}'$ intermediates of Scheme XVIII. Thus, the $\text{M}(\text{CO})_4\text{L}'_2$ products formed are of *cis* geometry, except where *cis-trans* isomerism occurs under the conditions of substitution, or where ligands L' of large cone angle are used where the *trans* isomer is formed directly from a five-coordinate intermediate. In the most extensive study, displacement of L-L from $\text{W}(\text{CO})_4(\text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2)$ yields a *cis/trans* mixture of $\text{W}(\text{CO})_4\text{L}'_2$ in which the decreasing *cis/trans* ratio [PPh₂Me > PPh₂Et > PPh₂Pr-*i* > PPh₂Bu-*t* > P(*p*-tolyl)₃ > P(*o*-tolyl)₃] is directly related to the increasing cone angle.²³⁷ In agreement with Scheme X,

fac-Mo(CO)₃(¹³CO)[Me₂N(CH₂)_nNMe₂] ($n = 2, 3$) reacts with SbPh₃ to give only *fac*-Mo(CO)₃(¹³CO)(SbPh₃)₂.²³⁸

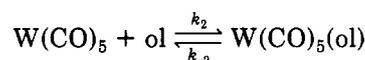
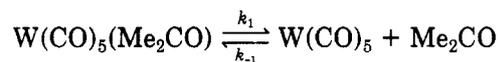
The displacement of L-L from Cr(CO)₄-(Ph₂AsC₂H₄AsPh₂) by P(OEt)₃²³⁹ may also be interpreted in terms of Scheme XVIII, and may be contrasted with the reaction of the diphos derivative which yields only products of carbonyl substitution.^{217,221}

VII. Complexes Containing Olefin or Polyolefin Ligands

Although olefins and polyolefins are much less nucleophilic than group 5 or group 6 ligands, an understanding of their substitution and exchange reactions is vital to an understanding of the mechanisms of catalytic transformations of olefins and polyolefins.

A. Monoolefin Complexes

Although (olefin)M(CO)₅ and related complexes have been prepared photochemically,^{240,241} they are not stable under the conditions required to effect thermal substitution of M(CO)₆. However, a kinetic study of their formation via displacement of acetone from W(CO)₅-(Me₂CO) has been reported.⁵⁰ The mechanism is D in nature, involving initial acetone dissociation:



$$K_{\text{eq}} = \frac{[\text{W}(\text{CO})_5(\text{ol})][\text{acetone}]}{[\text{W}(\text{CO})_5(\text{acetone})][\text{ol}]}$$

K_{eq} [1-hexene (>20) > 1-heptene (21.5) > 1-pentene (20.7) > *cis*-2-pentene (8.2) > *trans*-2-pentene (2.7) > 2-methyl-2-butene (0.9)] can be seen to decrease with increasing alkyl substitution (steric hindrance). The relative rates of substitution show some dependence also on the electronic character of the olefin (heptene

TABLE XI. Activation Parameters for Reactions Involving Octahedral Olefin and Polyolefin Complexes^a

reaction	ΔH_1^* , kJ mol ⁻¹	ΔS_1^* , J K ⁻¹ mol ⁻¹	ΔH_2^* , kJ mol ⁻¹	ΔS_2^* , J K ⁻¹ mol ⁻¹	ref
$cis-(CO)_4W(PEt_3)(DMF) + P(OPr-i)_3 \rightarrow$ $cis-(CO)_4W(PEt_3)[P(OPr-i)_3] + DMF$	109.0	38.9			241
$(cod)Mo(CO)_4 + 2L \rightarrow L_2Mo(CO)_4 + cod$					
$L_2 = bpy$	104.5	21	79.0	-46	243
$L_2 = diphos$	100.3	8	58.5	-105	
$L_2 = phen$	112.8	46	83.6	-13	
$L = PPh_3$	104.5	9	87.7	-13	
$L = AsPh_3$	104.5	9	71.0	-71	
$L = SbPh_3$	104.5	9	79.4	-4	
$L = py$	100.3	13	75.2	-50	
$L = PCl_2Ph$	100.3	13	83.6	-41	
$(nbd)Mo(CO)_4 + 2 P(OPh)_3 \rightarrow$ $(CO)_4Mo[P(OPh)_3]_2 + nbd$			36.8	-151	245
$(arene)Mo(CO)_3 + 3 PR_3 \rightarrow$ $fac-(CO)_3Mo(PR_3)_3 + arene$					
arene = toluene, R = Cl			66.9	-88	253-255
arene = <i>p</i> -xylene, R = OMe			62.7	-100	
arene = mesitylene, R = OMe			71.0	-84	
arene = mesitylene, R = OMe			72.3	-76	
$(arene)W(CO)_3 + 3 P(OMe)_3 \rightarrow$ $(CO)_3W[P(OMe)_3]_3 + arene$					
arene = mesitylene			79.4	-107	
arene = methyl benzoate			73.9	-102	
$(chpt)M(CO)_3 + 3 P(OMe)_3 \rightarrow$ $(CO)_3M[P(OMe)_3]_3 + chpt$					
M = Cr			68.9	-96	256
M = Mo			40.9	-117	
M = W			47.2	-113	
$(CO)_3Cr(R_3B_3N_3R'_3) + 3 P(OMe)_3 \rightarrow$ $(CO)_3Cr[P(OMe)_3]_3 + R_3B_3N_3R'_3$					
R = Me, R' = Me			24.9	-171	257
R = Et, R' = Me			22.6	-173	
R = Me, R' = Et			33.0	-158	
R = Et, R' = Et			42.6	-140	
R = Pr- <i>n</i> , R' = Me			20.1	-188	
R = Me, R' = Pr- <i>n</i>			48.0	-113	
R = Pr- <i>i</i> , R' = Me			47.6	-117	
$(chpt)M(CO)_3 + 3 RCN \rightarrow$ $fac-(CO)_3M(RCN)_3 + chpt$					
M = Cr, R = Me			90.2	-63	263
M = Mo, R = Me			47.2	-129	
M = W, R = Me			43.4	-179	
M = Cr, R = Ph			74.8	-109	
M = Mo, R = Ph			53.4	-109	
$(C_7H_7)M(CO)_3^+ + 3 MeCN \rightarrow$ $fac-(CO)_3M(MeCN)_3 + C_7H_7^+$					
M = Cr			101.2	-41	264
M = Mo			62.7	-125	
M = W			43.9	-167	
$(benzene)Cr(CO)_3 + *benzene$			105.8	-86	266-268
$Cp_2Ni + 4 P(OEt)_3 \rightarrow$ $Ni[P(OEt)_3]_4 + 2 Cp$			28.4	-225	265

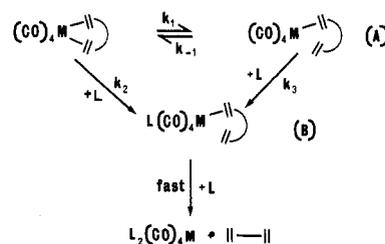
^a C₇H₇ = tropylium; nbd = norbornadiene; Cp = cyclopentadienyl; cod = 1,5-cyclooctadiene; chpt = 1,3,5-cycloheptatriene.

> hexene > *cis*-2-pentene > pentene > *trans*-2-pentene > 2-methyl-2-butene), implying that the steric effect of the olefin is not fully developed in the transition state. Displacement of olefin



also proceeds via a dissociative pathway, in keeping with the activation parameters (Table XI). The lability of C₂H₄ in the series C₂H₄ > dimethyl maleate > dimethyl fumarate >> maleic anhydride is consistent with the increased π back donation to those olefins with electron-withdrawing substituents. The order of olefin lability in terms of PR₃ [PPr-*i*₃ > PPh₃ > PPhPr-*i*₂ > PPh₂Pr-*i* > PEt₃] can be seen to be dependent on ligand cone angle. A typical order of lability in terms of metal (Mo >> Cr > W) is found.²⁴²

Scheme XIX



B. Polyene and Arene Complexes

Displacement of diene by group 5 ligands from (diene)M(CO)₄ complexes can be treated in terms of a simplified version of the ring opening pathway previously outlined.

Application of the steady-state approximation to (A) and (B) in Scheme XIX yields the rate equation

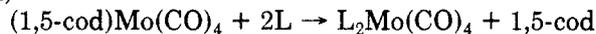
$$\frac{-d[S]}{dt} = \frac{k_1 k_3 [S][L]}{k_{-1} + k_3 [L]} + k_2 [S][L] \quad (18)$$

If $k_3 [L] \gg k_{-1}$, this reduces to

$$k_{\text{obsd}} = k_1 + k_2 [L] \quad (19)$$

and indeed, plots of k_{obsd} against $[L]$ for all the systems noted below are linear with reactions i and iii having non-zero intercepts.

(i)^{243,244}

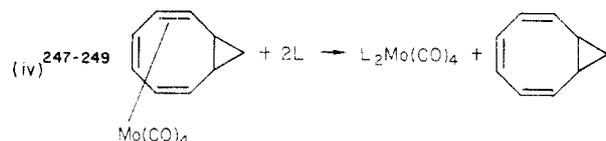


$2\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{py}, \text{PCl}_2\text{Ph}, \text{PCl}_3,$
picoline, PBu_3 ; $\text{L}_2 = \text{bpy}, \text{diphos}, \text{phen}$

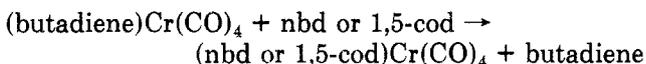
(ii)²⁴⁵ $(\text{nb})\text{M}(\text{CO})_4 + 2\text{L} \rightarrow \text{L}_2\text{M}(\text{CO})_4 + \text{nb}$

$\text{nb} = \text{norbornadiene}; \text{M} = \text{Cr}, \text{Mo}, \text{W}; 2\text{L} =$
 $\text{PBu}_3, \text{P}(\text{OMe})_3, \text{P}(\text{OPh})_3$

(iii)²⁴⁶ $(\text{butadiene})\text{Cr}(\text{CO})_4 + 2\text{P}(\text{OMe})_3 \rightarrow$
 $[\text{P}(\text{OMe})_3]_2\text{Cr}(\text{CO})_4 + \text{butadiene}$



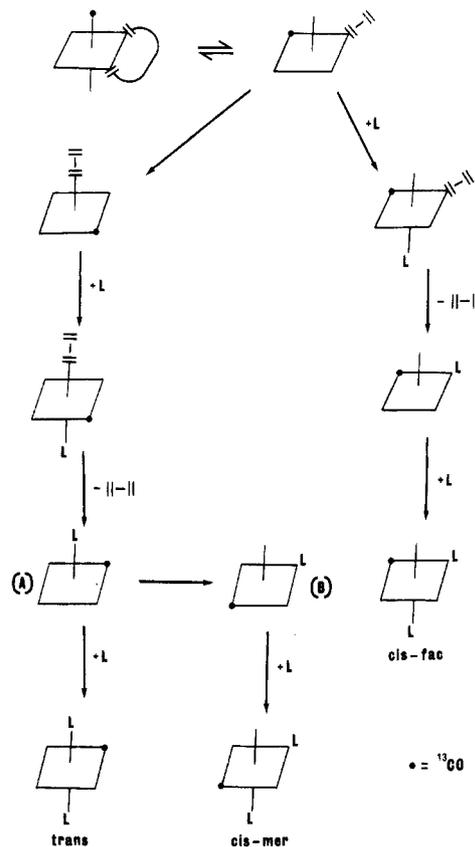
Activation parameters (Table XI) associated with k_1 and k_2 are consistent with competing D and I_d pathways, and in both (ii) and (iii), linear plots of $\log k_2$ against ΔHNP are obtained. The greater lability of the 1,3-diene in (iii) may be noted, and the preference in molecular orbital terms of a $\text{Cr}(\text{CO})_4$ fragment for a nonconjugated rather than a conjugated diene has been discussed.¹⁵ Indeed, $(\text{butadiene})\text{Cr}(\text{CO})_4$ undergoes olefin exchange



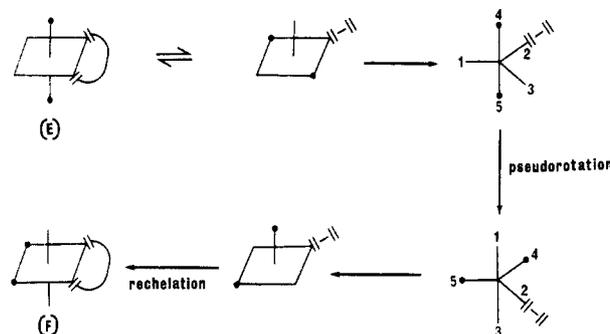
via a purely D pathway, reflecting the lower nucleophilicity of diene as an entering ligand.²⁴⁶

The $\text{L}_2\text{M}(\text{CO})_4$ complex initially formed is of *cis* geometry, with the exception of reaction iv in which use of $\text{P}(\text{OMe})_3$ yields a *cis/trans* mixture of $\text{Mo}(\text{CO})_4[\text{P}(\text{OMe})_3]_2$ under conditions where *cis-trans* isomerization does not occur. Labelling experiments are illuminating; thus, reaction using the *fac*-(diene) $\text{Mo}(\text{CO})_3(^{13}\text{CO})$ complex yields exclusively *fac*- $\text{Mo}(\text{CO})_3(^{13}\text{CO})\text{L}_2$ where $\text{L} = \text{PPh}_3, \text{SbPh}_3, \text{ or } \text{P}(\text{OPh})_3$, but where $\text{L} = \text{P}(\text{OMe})_3$, the *cis* isomer formed is a *fac/mer* mixture. The results can be interpreted in terms of Scheme XX. Thus, isolation of the *cis*- $\text{M}(\text{CO})_4\text{L}_2$ isomer only requires formation of *fac*- $\text{M}(\text{CO})_3(^{13}\text{CO})\text{L}_2$ only, whereas formation of *trans*- $\text{M}(\text{CO})_4\text{L}_2$ (which requires formation of the higher energy intermediate with the η^2 -diene in the axial position of a square pyramid) must be accompanied by formation of the *mer*- $\text{M}(\text{CO})_3(^{13}\text{CO})\text{L}_2$ *cis* isomer due to the rearrangement of (A) to the more stable form (B) with L in an equatorial position. Also consistent with this scheme is the isolation of *cis/trans* mixtures of $\text{Mo}(\text{CO})_4(^{13}\text{CO})_2$ from the reaction of $(\text{nb})\text{M}(\text{CO})_4$ ($\text{M} = \text{Cr}, \text{Mo}$)^{217,250} or the diene complex of iv²⁴⁸ with ^{13}CO .

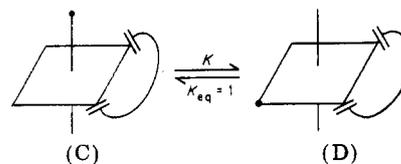
Scheme XX



Scheme XXI

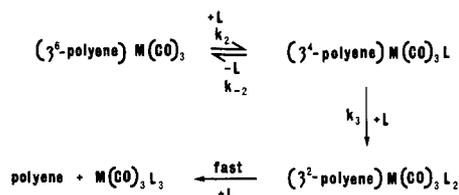


Ring opening may also provide the initial step leading to site exchange in these derivatives. Thus, the monolabelled complex (C) undergoes scrambling of the label on heating to give D:



The similarity of the activation enthalpies to those associated with the k_1 term of Scheme XIX may be noted. Similarly, the conversion of the dilabelled species (E) into *only* (F) on heating can be accounted for by initial ring opening followed by pseudorotation of the five-coordinate intermediate (Scheme XXI). A simple trigonal twist mechanism does not give this result. Although unambiguously proved only for the above example,²⁵¹ this scheme offers an alternative to the trigonal twist in other chelated systems. Consistent

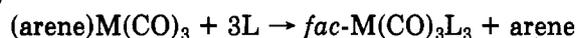
Scheme XXII



with the greater lability of the conjugated diene, (butadiene)Cr(CO)₄ undergoes site exchange ($\Delta G^\ddagger = 42.6 \text{ kJ mol}^{-1}$) on the NMR time scale, whereas (1,5-cod)-Cr(CO)₄ is static.²⁵²

Displacement of trienes and arenes to give *fac*-M(CO)₃L₃ complexes has also been investigated:

(i)²⁵³⁻²⁵⁵

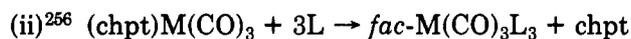


M = Mo; L = P(OMe)₃, PBu₃, PCl₂Ph, PCl₃;

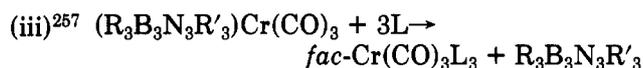
arene = benzene, toluene, *o*-, *m*- and *p*-xylene, mesitylene, tetramethylbenzene, hexamethylbenzene, *N,N*-dimethylaniline

M = W; L = P(OMe)₃; arene =

benzene, toluene, mesitylene, anisole, *N,N*-dimethylaniline, methyl benzoate



chpt = 1,3,5-cycloheptatriene; M = Cr, Mo, W



L = P(OEt)₃, P(OMe)₃, P(OPh)₃

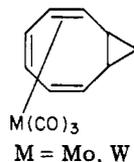
All reactions show a simple second-order rate law, and activation parameters are consistent with an I_d pathway as outlined in Scheme XXII. Steady-state treatment of Scheme XXII yields the expression

$$k_{\text{obsd}} = \frac{k_2 k_3 [\text{L}]^2}{k_{-2} + k_3 [\text{L}]} \quad (20)$$

which if $k_3 [\text{L}] \gg k_{-2}$, reduces to

$$k_{\text{obsd}} = k_2 [\text{L}] \quad (21)$$

Indeed, (η^6 -cyclooctatetraene)- and (η^6 -cyclooctatriene)Mo(CO)₃ react with CO to give isolable (η^4 -1,5-diene)Mo(CO)₄ complexes,²⁵⁸ while



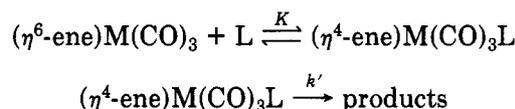
reacts with both CO and P(OPh)₃ to give (η^4 -1,5-diene)Mo(CO)₄ and (η^4 -1,5-diene)Mo(CO)₃P(OPh)₃ complexes, respectively.^{247,259,260}

Within the arene series, the lability (primarily enthalpy controlled) decreases with increasing alkyl substitution, and parallels the trend in ground-state bond enthalpy contributions [Cr-C₆H₆ (177 kJ mol⁻¹) ≈ Cr-C₆H₅Me (173) < Cr-C₆H₃Me₃ (191) < Cr-C₆Me₃ (230)].^{261a} Although containing electron-withdrawing substituents, the greater lability of anisole and *N,N*-dimethylaniline may be partially attributable to their

ability to stabilize the η^4 -coordinated intermediate by resonance. Within the borazine series, it may be noted that the rate is much more sensitive to nitrogen substituent than boron, and spectroscopic results show that the nitrogens mainly determine the donor characteristics of borazines. The ordering of ligand lability in the series (arene)Cr(CO)₃ < (chpt)Cr(CO)₃ < (borazine)-Cr(CO)₃ is also consistent with the trend in bond enthalpy contributions Cr-C₆H₆ (177 kJ mol⁻¹) > Cr-chpt (150) > Cr-B₃N₃Et₆ (104). The order of lability in terms of metal (Mo ≫ Cr ≈ W) is not reflected in bond enthalpy contributions which are in the order W-C₆H₃Me₃ (334 kJ mol⁻¹) > Mo (279) > Cr (191),^{261b} a feature that is also common to the hexacarbonyls.

Kinetic studies give no information about steps subsequent to the rate-determining step, and some caution must be exercised in interpretation of eq 21, since such a rate law may result if the initial reaction of Scheme XXII is regarded as a rapid preequilibrium. Two cases may be envisaged:

(i) a rapid preequilibrium followed by a D pathway to the product

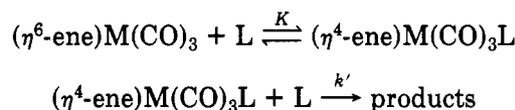


for which

$$k_{\text{obsd}} = \frac{k'K[\text{L}]}{1 + K[\text{L}]} \quad (22)$$

Thus, at low [L], a first-order dependence on [L] may be found.

(ii) a rapid preequilibrium followed by I_d formation of products



for which

$$k_{\text{obsd}} = \frac{k'K[\text{L}]^2}{1 + K[\text{L}]} \quad (23)$$

Thus, at low [L], a second-order dependence on [L] may be found. Indeed, displacement of triene from (chpt)M(CO)₃ (M = Cr, Mo, W) by MeCN and from (chpt)Mo(CO)₃ by PhCN to give *fac*-M(CO)₃(RCN)₃ proceed by such a rate law

$$-\frac{d[\text{S}]}{dt} = k_{\text{obsd}}[\text{S}][\text{L}]^2 \quad (24)$$

However, the results indicate a *K* value of ≫ 2 mol⁻¹ dm³, implying that the (η^4 -ene)M(CO)₃L intermediate of Scheme XXII predominates, yet none is observed spectroscopically. The second-order dependence on [L] seems best explained by assuming that $k_3[\text{RCN}] \ll k_{-2}$ in eq 20, in which case

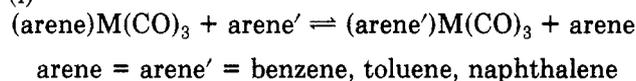
$$k_{\text{obsd}} = \frac{k_2 k_3 [\text{RCN}]^2}{k_{-2}} \quad (25)$$

This assumption is not inconsistent with the lower nucleophilicity of RCN as compared to P(OR)₃.^{262,263} Displacement of C₇H₇⁺ from (C₇H₇)M(CO)₃⁺ by

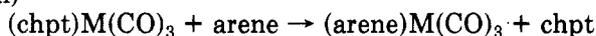
MeCN²⁶⁴ and of chpt from (chpt)Cr(CO)₃ by PhCN²⁶³ proceed via the simple second-order rate eq 21. The reaction of Cp₂Ni with P(OEt)₃ to give Ni[P(OEt)₃]₄ proceeds via a rate law of type 24, and may represent a genuine case of a rapid preequilibrium.²⁶⁵

Arene exchange reactions of the types

(i)²⁶⁶⁻²⁶⁸



(ii)²⁶⁶⁻²⁶⁸



have been characterized kinetically in hydrocarbon solvents. Reactions i and ii involving the more weakly coordinated naphthalene and chpt ligands proceed via a two-term rate law of the type

$$\frac{-d[\text{S}]}{dt} = k_1[\text{S}] + k_2[\text{S}][\text{arene}] \quad (26)$$

consistent with competing D and I_d pathways, although the [arene] dependent term makes only a small contribution to the overall rates. The exchange reactions of the more strongly bound ligands listed in (i) obey the unusual rate law

$$\frac{-d[\text{S}]}{dt} = k_1[\text{S}]^2 + k_2[\text{S}][\text{arene}'] \quad (27)$$

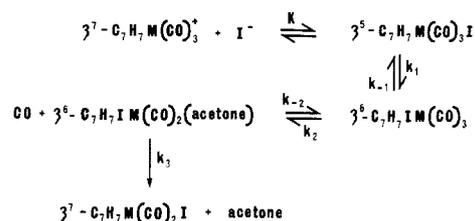
The dependence on [S]² has been attributed to an initial thermal decomposition to give CO which then reacts with substrate to give a (η⁴-arene)M(CO)₄ intermediate that undergoes arene exchange. The lability of the leaving ligand (naphthalene > chpt > benzene) again agrees with the trend in metal-ligand bond enthalpy contributions, although the order in terms of metal (Mo > W > Cr) again does not.

In solvents of greater polarity such as cyclohexanone or THF, arene exchange proceeds at faster rates that are essentially independent of the concentration or nature of the entering arene, but dependent as before on the leaving arene. Entropies of activation are strongly suggestive of an I_d mechanism involving solvent participation.²⁶⁹⁻²⁷²

The substitution of Mo(CO)₆ by nbd to give (nbd)-Mo(CO)₄ and by arenes and chpt to give (arene)Mo(CO)₃ and (chpt)Mo(CO)₃, respectively, also obeys a two-term rate law of type 26, with the k₂ term again making only a minor contribution. K₁ values are significantly smaller than the k₁ value associated with phosphine substitution, and also depend on the nature of the incoming ligand; these results imply a competition of released CO with the incoming polyene. Relative rates of substitution by arenes increase in the order C₆H₅F < C₆H₆ < C₆H₅Me < C₆H₄Me₂ < C₆Me₆; however, the relative rates of substitution chpt > benzene may be contrasted with the ease of displacement (chpt > benzene) mentioned previously, and may reflect the greater loss of resonance energy associated with formation of the (η²-benzene)Mo(CO)₅ intermediate in the rate-determining step.²⁷³⁻²⁷⁶

The relevance of these exchange studies to catalytic reactions involving M(CO)₆ may be noted. Thus, M(CO)₆ (M = Cr, Mo, W) photocatalyze the hydrogenation, isomerization,^{277a-g} and hydrosilylation²⁷⁸ of 1,3-dienes and the dimerization of nbd.²⁷⁹ These reactions

Scheme XXIII

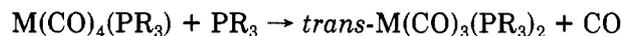


proceed via formation of the (η⁴-diene)M(CO)₄ complex, and the ability of (arene)Cr(CO)₃^{280a,b} and fac-Cr(CO)₃(MeCN)₃²⁸¹ complexes to thermally catalyze the same reaction (albeit at higher temperatures) is also consistent with polyolefin exchange. Photoassisted isomerization of monoolefins by M(CO)₆ proceeds via initial formation of M(CO)₅(olefin) complexes.^{282a,b}

Products other than those resulting from polyene displacement have been reported. Thus, (C₇H₇)M(CO)₃⁺ (M = Cr, Mo, W) reacts with a variety of halides and pseudohalides to give (C₇H₇)M(CO)₂X complexes.²⁸³ A stopped flow NMR study of the reaction with I⁻ in acetone reveals the surprising series of steps shown in Scheme XXIII.²⁸⁴ Rapid attack at the metal is followed by rate-determining transfer from metal to the ring, followed by acetone substitution and final transfer of iodide back to the metal. Reaction of softer nucleophiles such as phosphines, phosphites, and acetylacetonate with (C₇H₇)M(CO)₃⁺ results in nucleophilic addition to the ring, and kinetic studies indicate no direct metal involvement in the reaction.²⁸⁵⁻²⁸⁹

VIII. Complexes Based on M(CO)₅

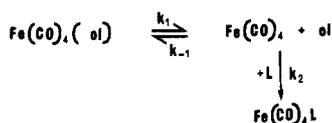
Although the thermal substitution of Fe(CO)₅ has been reported at temperatures as low as 60 °C,²⁹⁰ experiments with carefully purified Fe(CO)₅ show that it does not undergo substitution below 90 °C, at which temperature, slow decomposition occurs to give impurities which catalyze the substitution.²⁹¹ However, Ru(CO)₅ is more labile, undergoing substitution with PPh₃ by a D mechanism (Table XII).²⁹² Reactions must be conducted under an atmosphere of CO, since in the absence of CO, trimerization of the Ru(CO)₄ intermediate to Ru₃(CO)₁₂ occurs. The trend in lability Ru > Fe parallels the group 6 trend Mo > Cr, and across the transition series, the trend in CO lability Mo < Ru < Pd may be noted, with Pd(CO)₄ being detected only in low temperature matrices.²⁹³ A direct comparison of Fe and Ru can be obtained from the substitution reactions



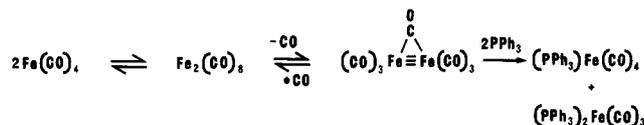
which also proceed via a CO-dissociative pathway (Table XII). The lower ΔH* for Ru and the essentially nonlabilizing nature of PR₃ may be noted. The rate constant in terms of PR₃ (PPh₃ > PPh₂Me > PBu₃) follows the order of decreasing cone angle, indicating a steric acceleration in the reaction.^{291,294,295}

Reactions involving Fe(CO)₄ intermediates have been characterized involving dissociative loss of the more

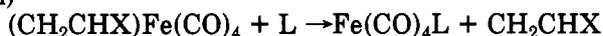
Scheme XXIV



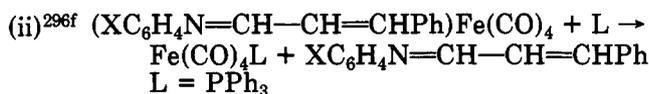
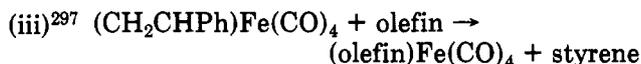
Scheme XXV



weakly bound olefin ligand in (olefin)Fe(CO)₄ complexes:

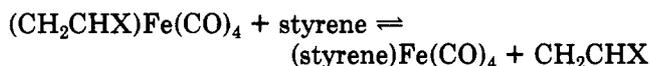
(i)^{296a-e}L = CO, AsPh₃, SbPh₃, PPh₃, py; X =

OEt, Bu, Ph, Cl, Br

L = PPh₃

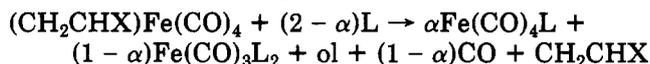
olefin = cycloheptene, cyclooctene, methyl acrylate

For reactions i and iii in the presence of excess styrene, k_2/k_{-1} values may be obtained that are in the order py > PPh₃ > AsPh₃ > SbPh₃ > CO ≈ methyl acrylate, in agreement with the relative nucleophilicities of the various ligands. The range of values spanned (1.0 for methylacrylate to 8.9 for py) indicates a more discriminating nature for Fe(CO)₄ as compared to M(CO)₅ (M = Cr, Mo, W). Equilibrium constants for the olefin exchange reaction



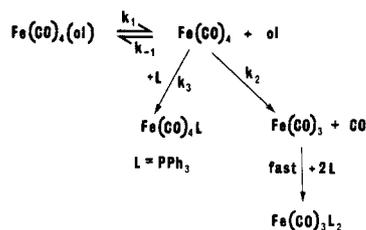
can be obtained directly ((X, K_{eq}) OEt, 6.7; Bu, 0.62; Ph, 1.00; CN, 9.2×10^{-2} ; CO₂Me, 8.7×10^{-3}). The presence of the conjugative electron-withdrawing groups especially lowers the energy of the π* olefinic orbital, thus increasing the amount of back donation. The importance of this is also evident in the order of olefin lability in reaction i (L = CO) [OEt ≈ Bu > Ph >> CN ≈ CO₂Me] which is primarily enthalpy controlled. In the absence of excess olefin or L, trimerization of Fe(CO)₄ to give Fe₃(CO)₁₂ occurs.^{297,298} Olefin, rather than CO, dissociation is also consistent with ground-state bond enthalpy contributions that are in the order Fe-C₂H₄ (96.7 kJ mol⁻¹) < Fe-CO (116.3).²⁹⁹

The reaction of (CH₂CHX)Fe(CO)₄ with PPh₃ is unusual in that the disubstituted complex Fe(CO)₃(PPh₃)₂ is also isolated under conditions where Fe(CO)₄PPh₃ is known not to undergo thermal substitution:

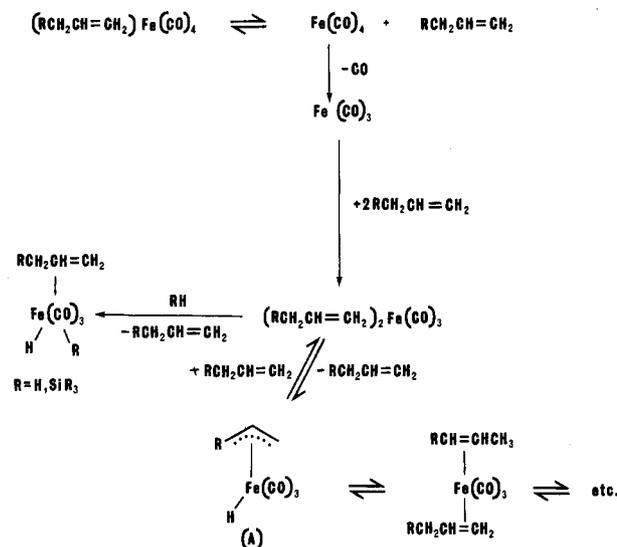


The value of α is essentially independent of X. Other reactions in which Fe(CO)₄ is probably generated, namely the thermal^{300a,b} and photochemical³⁰¹ reaction of Fe(CO)₅ and the reactions of Fe₂(CO)₉³⁰² and Fe₃(CO)₁₂^{303a,b} with PPh₃, also yield mixtures of mono- and

Scheme XXVI



Scheme XXVII

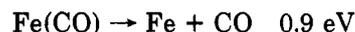


disubstituted products. This had been attributed mechanistically to either

(i) the presence of two reactive forms of Fe(CO)₄ in solution, one of which reacts with PPh₃ to give the disubstituted product. Matrix photolysis^{304a-e} of Fe(CO)₅ in certain matrices (Ar, CH₄) is known to yield a mixture of "naked" C_{2v} Fe(CO)₄ and a C_{2v} solvated Fe(CO)₄S species, in contrast to M(CO)₆ where only the M(CO)₅S species is observed. Although α is solvent dependent, there is no consistent variation of α with solvent coordinating power.

(ii) dimerization of Fe(CO)₄ followed by CO loss and reaction with PPh₃ (Scheme XXV). Annealing of matrices containing Fe(CO)₄ indeed yields Fe₂(CO)₈ in both bridged and nonbridged forms.

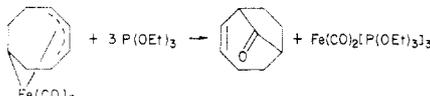
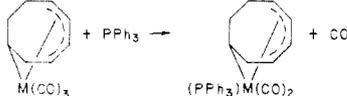
(iii) dissociation of CO from Fe(CO)₄ which is competitive with capture of Fe(CO)₄ by PPh₃ (Scheme XXVI). Indeed, the dependence of rate on P_{CO} and [PPh₃] are in agreement with this postulate, as are combined electron affinity and appearance potential measurements^{305,306} that allow estimation of enthalpies for the stepwise losses



and show the extreme lability associated with Fe(CO)₄.

Scheme XXVI is also relevant to the ability of iron-group carbonyls to catalytically isomerize olefins. Thus, a variety of terminal olefins CH₂=CH(CH₂)_nCH₃ (n = 2,3,5,9,10) are thermally isomerized to isomeric mixtures

TABLE XII. Activation Parameters for Reactions Involving Pentacoordinate Complexes^a

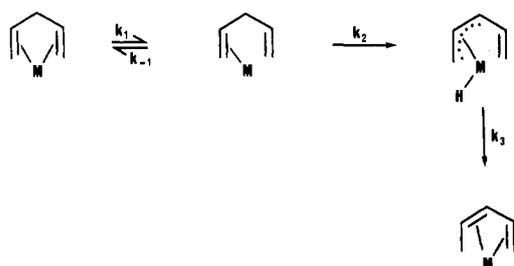
reaction	ΔH_1^* , kJ mol ⁻¹	ΔS_1^* , J K ⁻¹ mol ⁻¹	ΔH_2^* , kJ mol ⁻¹	ΔS_2^* , J K ⁻¹ mol ⁻¹	ref
Ru(CO) ₅ + PPh ₃ → Ru(CO) ₄ PPh ₃ + CO	115.5	64			292
Ru(CO) ₄ PR ₃ + PR ₃ → <i>trans</i> -Ru(CO) ₃ (PR ₃) ₂ + CO					
R = Ph	124.0	59			294,295
R ₃ = MePh ₂	132.0	77			
Fe(CO) ₅ PPh ₃ + PPh ₃ → <i>trans</i> -Fe(CO) ₃ (PPh ₃) ₂	178.0	77			291
(CO) ₄ Fe(styrene) + L → (CO) ₄ FeL + styrene					
L = PPh ₃	136.6	108			296a-c
L = AsPh ₃	127.1	88			
L = SbPh ₃	123.3	67			
L = py	123.7	71			
L = CO	121.2	54			
(CO) ₄ Fe(CH ₂ CHX) + CO → Fe(CO) ₅ + CH ₂ CHX					
X = Ph	102.8	54			
X = OEt	99.0	-79			
X = Bu	103.2	-4			
X = CN	112.9	4			
X = CO ₂ Me	112.9				
(1,4-chpd)Fe(CO)(chd) → (1,3-chpd)Fe(CO)(chd)	104.9	13			323
(1,5-cod)Fe(CO) ₃ → (1,3-cod)Fe(CO) ₃	112.9	7			322
(cot)Fe(CO) ₃ + 2 L → <i>trans</i> -Fe(CO) ₃ L ₂ + cot					
L = PPh ₃			47.7	-159	332
L ₂ = diphos			59.8	-126	
(1,4-chpd)Fe(CO)(chd) + 2 PPh ₃ → (chd)Fe(CO)(PPh ₃) ₂ + 1,4-chpd			84.8	-12	323
(1,3-cod)Fe(CO) ₃ + 2 PPh ₃ → <i>trans</i> -Fe(CO) ₃ (PPh ₃) ₂ + 1,3-cod			86.8	-33	333
			86.8	-33	333
			57.2	-113	334
					
M = Fe	122.0	64			334
M = Ru	110.8	59			
(chd)Fe(CO) ₃ + PPh ₃ → (chd)Fe(CO) ₂ PPh ₃ + CO	175.9	70			333
<i>trans</i> -(CO) ₃ Fe[C(OEt)R]PPh ₃ + L → <i>trans</i> -(CO) ₃ Fe[C(OEt)R]L + PPh ₃					
L = PBu ₃ , R = Ph	115.3	44			335
L = PBu ₃ , R = Me	121.2	45			
Rh[P(OMe) ₃] ₃ ⁺ (intermolecular exchange)	66.4	30			340
MeCOCo(CO) ₄ + L → MeCOCo(CO) ₃ L + CO					
L = PPh ₃	86.9	14			341a,b
L = P(OCH ₂) ₃ CPr	85.7	-1			
MeCOCo(CO) ₃ L + L → MeCo(CO) ₂ L ₂ + CO					
L = P(OCH ₂) ₃ CPr	104.1	14			

^a chd = 1,3-cyclohexadiene; chpd = 1,3-cycloheptadiene; cod = 1,5-cyclooctadiene; cot = cyclooctatetraene.

of internal olefins by using catalysts such as Fe(CO)₅,^{307a-f} Fe₃(CO)₁₂,^{307a,d} Ru₃(CO)₁₂,^{307g} Fe₂(CO)₉,^{307a,d} M(CO)₂(PPh₃)₃,^{307h} and (styrene)Fe(CO)₄.³⁰⁷ⁱ Where equilibrium is attained, the ratio of olefin isomers reflects their thermodynamic order of stability.^{307a,i} Deuterium labeling and other studies^{308a-h} show that the species directly responsible for isomerization is most likely the π -allyl hydride intermediate (A) of Scheme XXVII, although the lack of a deuterium isotope effect^{308a} shows that neither oxidative addition or re-

ductive elimination are rate determining. The conditions required for use of the catalysts suggest that (olefin)M(CO)₄ or (olefin)M(CO)₂(PPh₃)₂ complexes are initially formed;³⁰⁹ however, these complexes are unlikely to be the direct precursor of (A) since in the absence of excess olefin, (olefin)Fe(CO)₄ complexes are known to decompose to give Fe₃(CO)₁₂ and unisomerized olefin.^{297,298,311a,b} The most likely direct precursor is the (olefin)₂Fe(CO)₃ complex shown in Scheme XXVII. (Olefin)₂M(CO)₃ complexes (M = Fe, Ru) of

Scheme XXVIII



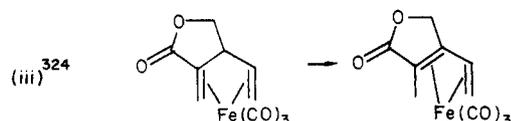
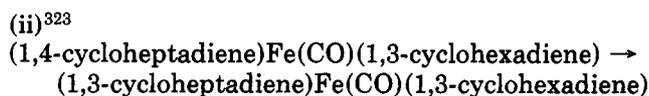
nonisomerizable olefins such as methyl acrylate have been prepared, and show considerable lability of one of the complexed olefins.^{312a-c}

$\text{Fe}(\text{CO})_5$,^{313a-d} $\text{Ru}_3(\text{CO})_{12}$,³¹⁴ and the mixed-ligand series $\text{Fe}(\text{CO})_x(\text{PF}_3)_{5-x}$ ($x = 1-4$)³¹⁵ also photocatalyze olefin isomerization. Here, the precursor (olefin) $_2\text{M}(\text{CO})_3$ complexes may be produced also by further photochemical substitution of initially formed (olefin) $\text{M}(\text{CO})_4$ complexes^{312a-c} or as primary photoproducts. Matrix photolysis of $\text{Fe}(\text{CO})_5$ is known to produce amounts of $\text{Fe}(\text{CO})_3$,^{302d} and $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ has been identified as a primary photoproduct of the substitution of $\text{Fe}(\text{CO})_5$.^{313a}

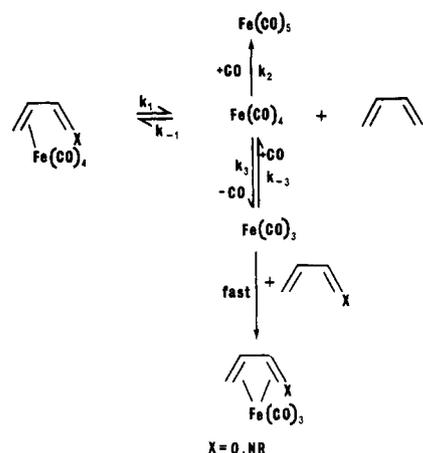
$\text{Fe}(\text{CO})_5$ ^{316a,b} and (dimethyl fumarate) $\text{Fe}(\text{CO})_4$ ^{316c} thermally catalyze the hydrogenation of olefins, and $\text{Fe}(\text{CO})_5$ photolytically catalyzes the hydrogenation^{313a} and hydrosilylation³¹⁷ of olefins, reactions that may be assumed to proceed via an (H)(R) $\text{Fe}(\text{CO})_3$ (olefin) intermediate (R = H, SiR₃) (Scheme XXVII) that undergoes the usual insertion and reductive elimination reactions. $\text{Fe}(\text{CO})_2(\text{PPh}_3)_3$ reacts with H_2 to give stable *cis*- $\text{H}_2\text{Fe}(\text{CO})_2(\text{PPh}_3)_2$, which also acts as a hydrogenation catalyst.^{307h}

The hydride $\text{H}_2\text{Fe}(\text{CO})_4$ also catalyzes olefin isomerization^{318a,b} and while it has been proposed to decompose to give $\text{Fe}(\text{CO})_3$ as an intermediate,³¹⁹ its catalytic activity may better be ascribed to an M-H addition-elimination or free-radical mechanism.

The preference of iron-group elements for coordination to conjugated rather than nonconjugated dienes is well established, and indeed, iron group carbonyls [$\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$, and $\text{Ru}_3(\text{CO})_{12}$] thermally catalyze the isomerization of acyclic^{320a,b,d} and cyclic^{320a,c,d,f,g} 1,5- and 1,4-dienes to 1,3-dienes, with the (η^4 -1,3-diene) $\text{Fe}(\text{CO})_3$ complex itself being isolated under conditions where it is thermally stable. Indeed, preparations of the most synthetically useful of these complexes, those based on (cyclohexadiene) $\text{Fe}(\text{CO})_3$,³²¹ conventionally use reaction of $\text{Fe}(\text{CO})_5$ with substituted 1,4-cyclohexadienes that are readily available from Birch reduction of aromatics. Coordinated η^4 -1,5- and -1,4-dienes have been isolated under milder conditions, and are known to isomerize intramolecularly to the η^4 -1,3-diene complexes (Table XII).

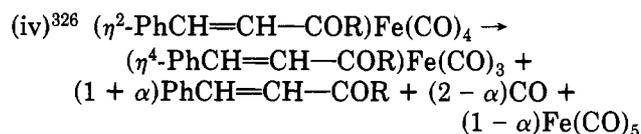
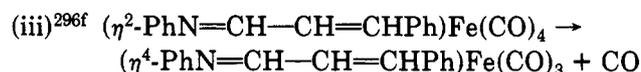
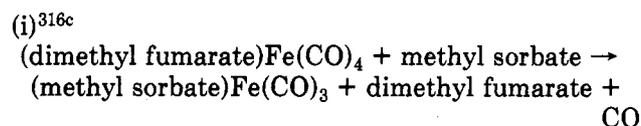


Scheme XXIX



The results are most consistent with the allyl hydride mechanism of Scheme XXVIII in which dechelation of the diene, rather than oxidative addition is rate determining. While such a mechanism involving an additional diene exchange step may be invoked to explain the catalytic isomerizations observed, evidence indicates that at least part of the isomerization follows the pathway of Scheme XXVII in which the diene is coordinated only in a η^2 fashion.^{308g} Scheme XXVIII may also be invoked to explain the observed substituent migration in thermolyses of (diene) $\text{Fe}(\text{CO})_3$ complexes.^{325a,b}

The formation of (diene) $\text{Fe}(\text{CO})_3$ complexes most probably involves the intermediacy of the (η^2 -diene)- $\text{Fe}(\text{CO})_4$ derivative, and the η^2 to η^4 conversion has been studied kinetically.



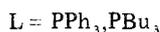
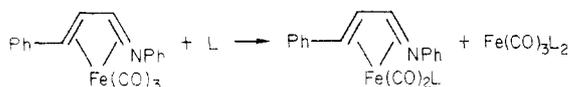
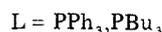
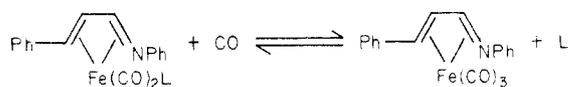
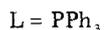
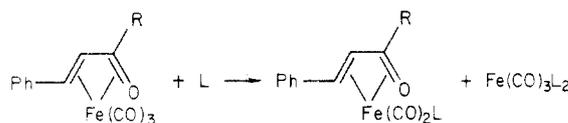
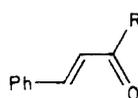
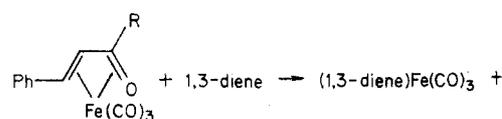
Like other reactions of (olefin) $\text{Fe}(\text{CO})_4$ complexes, these proceed via initial rate-determining olefin dissociation to give $\text{Fe}(\text{CO})_4$ (Scheme XXIX); the dependence of reaction ii on P_{CO} is again consistent with dissociation of $\text{Fe}(\text{CO})_4$ to $\text{Fe}(\text{CO})_3$. Reaction i presumably proceeds via initial olefin exchange of the type previously described.

Both (η^4 -diene) $\text{Fe}(\text{CO})_3$ and (η^4 -heterodiene) $\text{Fe}(\text{CO})_3$ complexes undergo reactions with group 5 ligands in which the diene or heterodiene ligand is displaced. Comparisons with other $\text{Fe}(\text{CO})_4\text{L}$ or $\text{Fe}(\text{CO})_3\text{L}_2$ systems must be treated with caution, since both (diene)- and (heterodiene) $\text{Fe}(\text{CO})_3$ complexes adopt square-pyramidal structures with the diene in the basal plane, rather than trigonal-bipyramidal geometries. Hetero-

TABLE XIII. Activation Parameters for Reactions of ML_4 Complexes

reaction	ΔH_1^* , kJ mol ⁻¹	ΔS_1^* , J K ⁻¹ mol ⁻¹	ref
$Ni(CO)_4 + L \rightarrow$			
$Ni(CO)_3L + CO$			
L = PPh ₃ (toluene)	93.2	35	343a
L = PPh ₃ (hexane)	101.2	56	
L = PPh ₃ (toluene)	85.2	8	343b
L = P(OCH ₂) ₃ CMe (toluene)	91.9	30	
$Ni(CO)_4 + *CO$	100.3	55	343d
$Ni[P(OEt)_3]_4 + CyNC \rightarrow$			
$Ni[P(OEt)_3]_3CyNC + P(OEt)_3$			
benzene	109.5	8	352
hexane	134.2	79	
$M(PF_3)_4 + CyNC \rightarrow$			
$M(PF_3)_3CyNC + PF_3$			
M = Ni (heptane)	121.2	59	358
M = Ni (toluene)	117.0	46	
M = Pt (hexane)	100.3	75	
M = Pt (toluene)	96.0	50	
$Ni(CO)_2L_2 + PBu_3 \rightarrow$			
$Ni(CO)_2(L)(PBu_3) + L$			
L = P(CH ₂ CH ₂ CN) ₃	106.5	44	346

diene complexes are the most labile, and several reactions have been investigated kinetically.

(i) ³²⁷(ii) ³²⁸(iii) ³²⁹(iv) ²⁹⁷

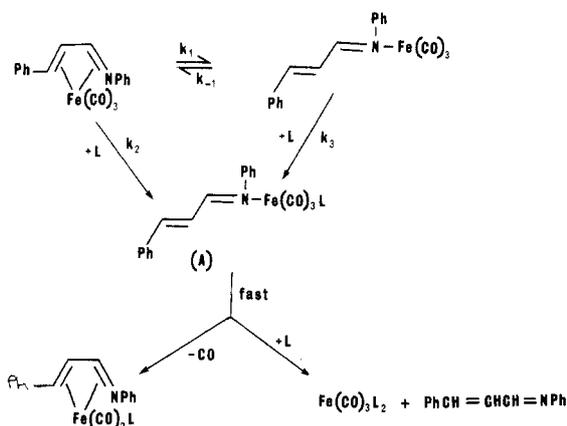
The results show that the reactions can be described by Scheme XXXA and B involving ring-opening mechanisms whose initial steps are competing D and I_d dechelation of the olefinic bond in (i) and (ii) and the π -ketonic bond in (iii) and (iv). The η^2 intermediates (A and A') may be observed spectroscopically³³⁰ and may be isolated in some cases.^{331a,b} Steady-state treatment of (A/A') yields the rate law

$$k_{\text{obsd}} = \frac{k_1 k_3 [\text{L}]}{k_{-1} + k_3 [\text{L}]} + k_2 [\text{L}] \quad (28)$$

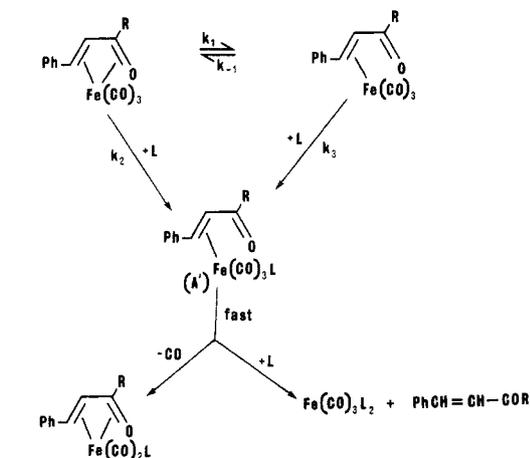
and in agreement with this, curved, nonlimiting plots

Scheme XXX

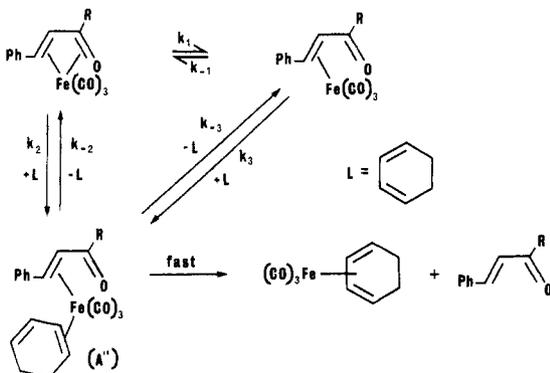
A



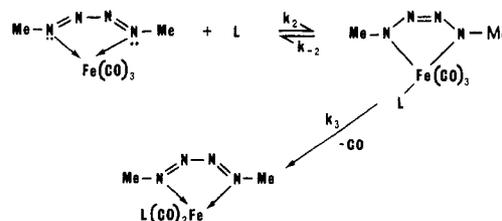
B



C

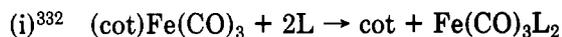


Scheme XXXI

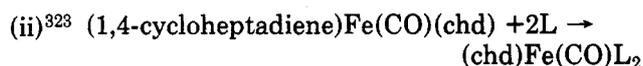


of k_{obsd} against $[\text{L}]$ are found. Reaction ii may be seen to be the reverse of (i), and although it reaches equilibrium, the path to equilibrium proceeds via Scheme XXXA with $k_2 = 0$ due to the low nucleophilicity of CO. The synthetically important olefin exchange reaction (iv) has been shown to proceed via the slightly more complicated Scheme XXXC involving reversible D and I_d formation of intermediate (A').

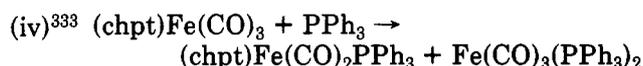
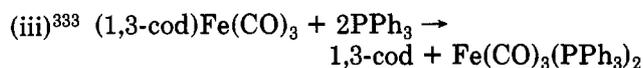
(Diene)Fe(CO)₃ complexes are much less labile than these heterodiene derivatives, although several examples have been characterized kinetically.



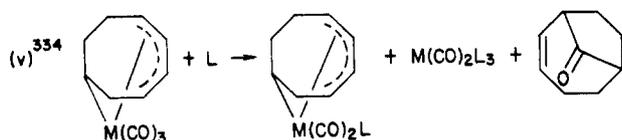
cot = cyclooctatetraene, L = PPh₃, PPh₂Et, PBu₃, L₂ = diphos



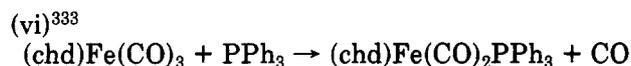
chd = 1,3-cyclohexadiene, L = PPh₃, CO



chpt = cycloheptatriene



M = Fe, Ru; L = PP₁, P(OR)₃, PR₃

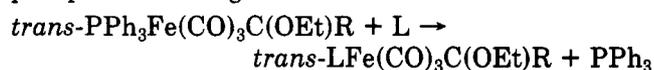


For reactions in which π -ligand displacement is observed, the lower lability of the diene is reflected in the pure second-order nature of the rate law

$$k_{\text{obsd}} = k_2[\text{L}] \quad (29)$$

and in the associated activation parameters (Table XII), which are consistent with an I₃ ring-opening mechanism. The order of diene lability (which is primarily enthalpy controlled) is cot > 1,3-cod > chpt >> chd; this order seems most closely related to the relief of steric strain in the diene on proceeding to the presumed (η^2 -diene)Fe(CO)₃L intermediate. The diene-Fe bond enthalpy contribution has been estimated as 184 kJ mol⁻¹ which is approximately twice that of the C₂H₄-Fe bond (96.7).²⁹⁹ A comparison with the Fe-CO bond enthalpy contribution (116.3 kJ mol⁻¹) thus shows that diene displacement is not unexpected, although caution must be used because of the I_d nature of the substitution. Indeed, in reactions iv and v, CO displacement is competitive, while in (vi), it is the sole reaction observed. These products are formed by rate-determining dissociative loss of CO (Table XII); the low ΔH^* for (v) may be ascribed to the labilizing effect of the trans M-C σ bond; the ΔH^* value for (vi), however, indicates an essentially nonlabilizing nature for the diene.

Little other information is available on the labilizing nature of ligands in five-coordinate systems. The phosphine exchange reaction

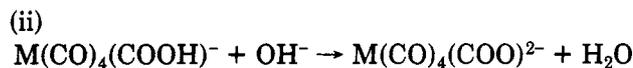


L = PBu₃, P(OPh)₃, PCy₃

which proceeds via rate-determining loss of PPh₃ (Table XII) indicates a trans-labilizing character for the carbene ligand.³³⁵ One interesting reaction is that of the tetraazabutadiene complex of Scheme XXXI.³³⁶ Although resulting in carbonyl substitution, it proceeds with second-order kinetics and activation parameters

(Table XII). This has been attributed to the ability of the ligand to transform easily without bond breaking from a η^4 to a η^2 coordination in the rate-determining step.

Although Fe(CO)₅ is known to react with I⁻ to give Fe(CO)₄I⁻,³³⁷ the only reaction with anionic nucleophiles that has been investigated kinetically^{338a,b} is that with OH⁻ mentioned previously.

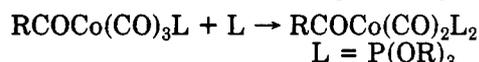
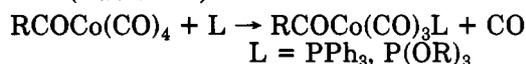


M = Fe, Ru, Os

The linear dependence of rate on [OH⁻] and [OMe⁻] in reactions involving Fe(CO)₅ clearly demonstrates the rate-determining nature of the nucleophilic attack, and the ordering of reactivity Os > Ru >> Fe is reminiscent of the reactivity order observed on reaction of M(CO)₆ with MeLi.

Investigations of other ML₅ systems are relatively rare. The complexes Co(CNR)_{5-x}(PR₃)_x⁺ (x = 0,1,2) undergo intermolecular exchange by a dissociative process with the rate increasing in the order x = 2 < 1 < 0.³³⁹ Rh[P(OMe)₃]₅⁺ similarly undergoes intermolecular exchange with activation parameters (Table XII) that are consistent with a D mechanism.³⁴⁰

Of the substitution reactions of the complex XCo(CO)₄ [X = H, R, COR, ER₃ (E = Si, Ge, Sn)] that have been studied kinetically, only the acyl complexes undergo substitution unambiguously by a D mechanism^{341a,b} (Table XII).



Rates of both reactions are independent of [L], and a comparison of ΔH^* values again shows the essentially nonlabilizing nature of the P(OR)₃ ligand. Rates increase with the size of R, indicating a steric acceleration in the reaction, and the ordering R = Ph > Me > CF₃ is consistent with π -donor labilization of the type described for MeCOMn(CO)₅. The rate of *CO exchange in MeCOC(CO)₄ is in agreement with the rates of the substitution reactions.³⁴²

Finally, it may be noted that (unlike six-coordinate systems), mechanistic conclusions based on product stereochemistry are meaningless in five-coordinate complexes because of the low barriers to intramolecular exchange in both square-pyramidal and trigonal-bipyramidal geometries.

IX. Complexes Based on ML₄

Ni(CO)₄ thermally undergoes both mono- and di-substitution:

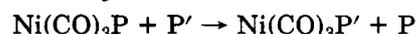
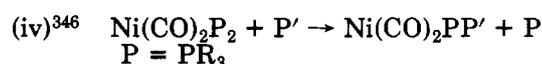
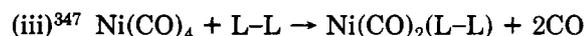
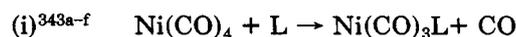
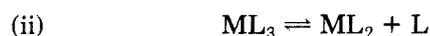
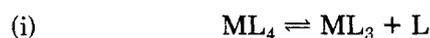


TABLE XIV. Parameters for Dissociation of MP_n Complexes ($M = Ni, Pt, Pd; n = 2-4$)

	detectable values n		K_d , M^{-1}	ΔH^\ominus , $kJ\ mol^{-1}$	ΔS^\ominus , $J\ K^{-1}\ mol^{-1}$	ref			
	soln	solid							
(a) $NiP_4 \rightleftharpoons NiP_3 + P$									
P = P(OEt) ₃	4	4	$< 10^{-10}$			348-350			
P = P(O- <i>p</i> -tolyl) ₃	4, 3	4	6×10^{-10}	97.4	146				
P = P(O- <i>p</i> -C ₆ H ₄ Cl) ₃	4, 3	4	2×10^{-10}	88	109				
P = P(OPr- <i>i</i>) ₃	4, 3	4	2.7×10^{-5}	98.2	109				
P = P(OMe)Ph ₂	4, 3	4	$< 4 \times 10^{-5}$						
P = P(O- <i>p</i> -Cl- <i>o</i> -tolyl) ₃	4, 3	4	0.7×10^{-2}	52	134				
P = P(O- <i>p</i> -Me- <i>o</i> -tolyl) ₃	4, 3	4	3.1×10^{-2}	52	137				
P = P(O- <i>o</i> -tolyl) ₃	4, 3	4, 3	4×10^{-2}	54	154				
P = dmpe(P ₂)	4	4	$< 10^{-10}$						
P = PMe ₃	4	4	$< 10^{-9}$						
P = PEt ₃	4, 3	4	1.2×10^{-2}	67	188				
P = PMePh ₂	4, 3	4	5.0×10^{-2}						
P = PPh ₃	3	4, 3	> 10			351			
	detectable values n		ΔH^\ominus , $kJ\ mol^{-1}$	ΔS^\ominus , $J\ K^{-1}\ mol^{-1}$	ΔH_1^* , $kJ\ mol^{-1}$	ΔS_1^* , $J\ K^{-1}\ mol^{-1}$	ΔH_2^* , $kJ\ mol^{-1}$	ΔS_2^* , $J\ K^{-1}\ mol^{-1}$	ref
	soln	solid							
(b) $PtP_4 \rightleftharpoons PtP_3 + P$									
P = P(OEt) ₃	4	4			115	112			352, 353
P = PMe ₃	4	4			57.6	-28			
P = PMe ₂ Ph	4	4			59.9	-18			
P = PMePh ₂	4, 3	4	63.1	115	65.2	26	2.1	-88	
P = PEt ₃	4, 3	4, 3	63.5	226	67.7	96	3.8	-131	
P = PBu ₃	4, 3	4, 3	70.2	264	71.0	96	0.6	-167	
P = PPh ₃	3	4, 3							354, 355
(c) $PtP_3 \rightleftharpoons PtP_2 + P$									
P = P(CH ₂ Ph) ₃	3	3			63.5	-14			353, 356
P = PCy ₃	3, 2	3, 2	54.7	202			10.6	-116	
P = PPr- <i>i</i> ₃	3, 2	3, 2	42.2	169			15.8	-135	
P = PBu- <i>t</i> ₂ Ph	2	2					50.5	-122	
(d) $PdP_4 \rightleftharpoons PdP_3 + P$									
P = P(OEt) ₃	4	4			93.6	92			352
P = PMe ₃	4	4			73.6	61			356, 357
P = PMe ₂ Ph	4	4			88.1	104			
P = PEt ₃	4, 3								
P = PBu ₃	4, 3								
P = PPh ₃	3								
P = P(CH ₂ Ph) ₃	3	3			93.6	102			
P = PPr- <i>i</i> ₃	3, 2								
P = PCy ₃	3, 2								
P = PBu- <i>t</i> ₂ Ph	2	2					32.6	-168	

Activation parameters, together with the results of *CO exchange experiments and thermal decomposition studies,³⁴⁴ demonstrate conclusively the D nature of the substitution involving rate-determining CO dissociation. The ΔH^\ominus values may be seen to be less than the mean thermochemical Ni-CO bond dissociation energy of 146 $kJ\ mol^{-1}$.³⁴⁵ The disubstitution step ii and the reaction iii with chelating ligands also proceed by D pathways, as do the phosphine exchange reactions in (iv) (Table XIII). Rates of *CO exchange are in the order $Ni(CO)_4 > Ni(CO)_3L > Ni(CO)_2L_2$,^{343e} in keeping with the non-labilizing nature of phosphine ligands.

Although $Pd(CO)_4$ and $Pt(CO)_4$ are unstable under normal conditions, comparisons of the three metals may be obtained from the ML_4 series [$L = PR_3, P(OR)_3$]; relevant data are collected in Table XIV. Extensive dissociation is observed in many cases, a feature of obvious importance in the catalytic activity of complexes of this type:



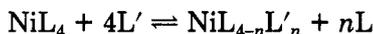
In the case of nickel, dissociation to ML_3 only is observed; a comparison of ΔG^\ominus for $Pt(PEt_3)_4$ and $Ni(PEt_3)_4$ indicates a greater dissociation of the platinum

complex, and indeed, PtL_2 complexes may be observed and isolated, although no further dissociation of PtL_2 is detectable. Equilibria in the palladium series closely parallel those of the platinum series, although ΔH^\ominus and ΔS^\ominus values (Table XIV) are not usually available due to the faster rates of exchange of free and complexed phosphine.

For phosphines, increasing dissociation to ML_3 and ML_2 may be seen to be primarily a function of steric size (cone angle), while data on the nickel phosphite series show the same dependence of K_d on the cone angle of the phosphite. The influence of the cone angle on ΔH^\ominus and ΔS^\ominus is, however, rather subtle. Comparison of values for the complexes $Pt(PR_3)_4$ ($PR_3 = PMePh_2, PEt_3, PBu_3$) shows that the increasing degree of dissociation is primarily entropy controlled, and only in cases of ligands that create severe steric congestion (significant nonbonded ligand-ligand interaction) is there a dramatic lowering of ΔH . Similar behavior is seen in the nickel phosphite series, although entropy changes are somewhat masked by the larger ΔH^\ominus values.

Electronic effects are, however, evident in a comparison of phosphine and phosphite complexes of similar cone angle. Thus, $Ni(PPh_3)_4$ is completely dissociated at room temperature, whereas $Ni[P(O-*o*-tolyl)]_4$ has a K_d value of $4 \times 10^{-2}\ mol\ dm^{-3}$. This has been

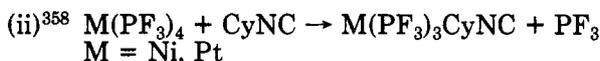
attributed to the greater π -acceptor character of the phosphite which is thus able to better stabilize the 4-coordinate electron-rich center. Similar conclusions are reached from studies of the exchange reaction



When L is the good π -acceptor phosphite $\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OMe})_3$, the extent of substitution in terms of L' , $\text{PBu}_3 > \text{PPH}_3 > \text{P}(\text{O}-o\text{-tolyl})_3$, roughly parallels the increasing cone angle of L' . In contrast, when L is the poor π acceptor PMe_3 , the order is reversed, with the best π acceptor $[\text{P}(\text{O}-o\text{-tolyl})_3]$ giving the greatest degree of substitution.³⁵⁰

Exchange between free and complexed ligand in the MP_4 series proceeds exclusively by a D mechanism. The slower exchange of phosphites as compared to phosphines is primarily an enthalpy-controlled process. Within both the Ni-phosphite and Pt/Pd-phosphine series, the rates of exchange increase as the cone angle of the ligand increases, consistent with a steric acceleration in the reaction. Activation parameters for the $\text{Pt}(\text{PR}_3)_4$ series (Table XIV) indicate that this is primarily entropy controlled. Rates of exchange vary in the order $\text{Pd} > \text{Pt} \approx \text{Ni}$. The greater lability of the second-row element is not unexpected; however, activation parameters show, quite surprisingly, that (at least as far as Pt and Pd are concerned) this is also entropy controlled, since in fact $\Delta H^*(\text{Pd}) > \Delta H^*(\text{Pt})$. It may be noted, however, that a comparison of parameters for $\text{M}[\text{P}(\text{OEt})_3]_4$ ($\text{M} = \text{Pd}, \text{Pt}$) indicates that ΔH^* is controlling here. Exchange at $\text{Pt}(\text{PR}_3)_3$ complexes occurs by competing dissociative and associative pathways, while exchange at $\text{Pt}(\text{PR}_3)_2$ complexes is purely associative, as indicated by the activation parameters in Table XIV.

Kinetic studies of the substitution reactions below agree with these exchange studies.



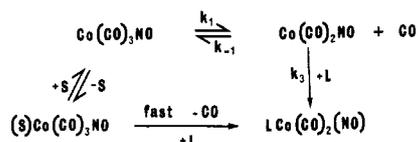
Reactions are independent of $[\text{CyNC}]$, with the order of lability $\text{Ni} < \text{Pt}$ in reaction ii being enthalpy controlled. Rates for (i) increase in the order $\text{P}(\text{OCH}_2)_3\text{Pr} \ll \text{P}(\text{OMe})_3 < \text{P}(\text{OEt})_3 < \text{P}(\text{OPh})_3$, again consistent with steric acceleration in the reaction.

X. Nitrosyl, Cyclopentadienyl, and Allyl Complexes

Complexes containing these ligands are grouped together because, in principle, by transformation from $3e^- \rightarrow 1e^-$ donor (NO, allyl) or $5e^- \rightarrow 3e^- \rightarrow 1e^-$ donor (cyclopentadienyl), these ligands offer low-energy associative pathways for substitution, even though they may not be displaced themselves (in contrast to the polyolefin ligands discussed previously).

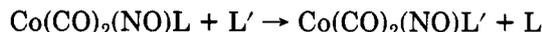
Reactions of the nitrosyl complexes $\text{Mn}(\text{CO})_4\text{NO}$, $\text{Co}(\text{CO})_3\text{NO}$, and $\text{Fe}(\text{CO})_2(\text{NO})_2$ with group 5 ligands have been studied extensively³⁵⁹⁻³⁶⁴ and the results may be encompassed within the mechanism shown in Scheme XXXII for $\text{Co}(\text{CO})_3\text{NO}$. In noncoordinating solvents such as cyclohexane, benzene, toluene, and nitromethane, the mechanism may be viewed as com-

Scheme XXXII



peting dissociative and associative pathways, although only for poorly basic ligands such as AsPh_3 does the dissociative pathway make a significant contribution to the overall rate. For reactions of $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Fe}(\text{CO})_2(\text{NO})_2$ in coordinating solvents such as THF, acetonitrile, or dimethyl sulfoxide, a much greater dissociative contribution is apparent from the observed rate law; activation parameters, however (Table XV), show that this is more properly regarded as the solvent-assisted substitution shown in Scheme XXXII. Values of k_2 show the usual dependence on ΔHNP . *CO exchange³⁶⁵ with $\text{Co}(\text{CO})_3\text{NO}$ proceeds at rates that are independent of P_{CO} and which agree with k_1 values obtained from the substitution reactions. Surprisingly, however, both $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Fe}(\text{CO})_2(\text{NO})_2$ undergo exchange with *NO at rates that are linear with P_{NO} with ΔH^* values much less than those that are linked with associative CO substitution.³⁶⁶

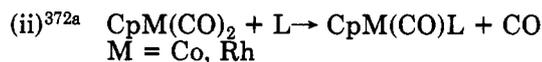
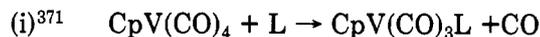
Both $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Fe}(\text{CO})_2(\text{NO})_2$ react with bidentate ligands via rate-determining associative CO loss to give $\text{Fe}(\text{NO})_2(\text{L}-\text{L})$ and $\text{Co}(\text{CO})(\text{NO})(\text{L}-\text{L})$ complexes,³⁴⁷ and the conversion of the monosubstituted $\text{Co}(\text{CO})_2(\text{NO})\text{L}$, $\text{Fe}(\text{CO})(\text{NO})_2\text{L}$ and $\text{Mn}(\text{CO})_3(\text{NO})\text{L}$ complexes into the disubstituted derivative on further reaction with L has also been studied kinetically.^{359,367,368} Competing dissociative and associative pathways are again observed, with the overall rates being slower than those of the initial monosubstitution. The ligand exchange reaction



proceeds via an associative pathway.³⁶⁹ Within the constraints of steric hindrance, reactions proceed fastest in cases where L is a good π acceptor, and thus able to better stabilize the presumed five-coordinate intermediate.

The predominance of the associative pathway has been attributed to the ease of the $3e^- \rightarrow 1e^-$ transformation. Indeed, matrix photolysis^{370a-d} of $\text{Mn}(\text{CO})_4\text{NO}$, $\text{Mn}(\text{CO})(\text{NO})_3$, and $\text{CpV}(\text{CO})(\text{NO})_2$ yields [in addition to $\text{Mn}(\text{CO})_3\text{NO}$ and $\text{Mn}(\text{NO})_3$] the species $\text{Mn}(\text{CO})_4(\text{NO}^\#)$, $\text{Mn}(\text{CO})(\text{NO})_2(\text{NO}^\#)$, and $\text{CpV}(\text{CO})(\text{NO})(\text{NO}^\#)$ in which infrared studies indicate a $1e^-$ -donor character for $\text{NO}^\#$. Quantum yields for photolytic substitution of $\text{Mn}(\text{CO})_4\text{NO}$ are in agreement with this hypothesis.^{370e} $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Fe}(\text{CO})_2(\text{NO})_2$ yield only products of CO loss on matrix photolysis.^{370f,g}

Carbonyl substitution in the cyclopentadienyl systems



has been studied kinetically. Reaction i is independent of $[\text{L}]$ and proceeds with typical dissociative activation parameters. Reaction ii, however, shows a linear dependence on $[\text{L}]$ with typical associative parameters, consistent with a η^5 to η^3 transformation in the rate-

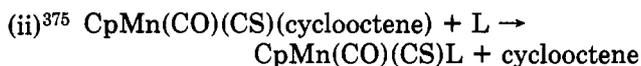
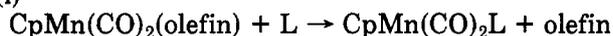
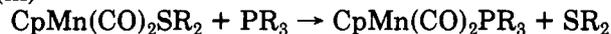
TABLE XV. Activation Parameters for Nitrosyl, Cyclopentadienyl, and Allyl Complexes

reaction	ΔH_1^* , kJ mol ⁻¹	ΔS_1^* , J K ⁻¹ mol ⁻¹	ΔH_2^* , kJ mol ⁻¹	ΔS_2^* , J K ⁻¹ mol ⁻¹	ref
Mn(CO) ₄ NO + L → LMn(CO) ₃ NO + CO L = PPh ₃			79.4	-46	359
Co(CO) ₃ NO ⁺ + L → LCo(CO) ₂ NO + CO L = PPh ₃ ,Et			62.7	-79	341b
L = PPh ₃			62.7	-100	360
L = P(OPh) ₃			79.4	-58	
L = PPh ₃ Cl			71.0	-79	
L = AsPh ₃ (toluene)	122.8	25	77.7	-100	361
L = AsPh ₃ (benzene)	129.9	59	71.0	-117	362
L = AsPh ₃ (C ₆ H ₁₂)	125.4	29	78.2	-100	
L = AsPh ₃ (CH ₃ NO ₂)	142.1	92	58.5	-150	
L = AsPh ₃ (THF)	103.2	-17	83.6	-67	
L = AsPh ₃ (CH ₃ CN)	75.2	-96			
L = AsPh ₃ (Me ₂ SO)	87.7	-42			
LCo(CO) ₂ NO + PBu ₃ → Co(CO) ₂ (NO)PBu ₃ + L L = P(OCH ₂) ₃ CMe			50.1	-125	369
L = P(OMe) ₃			50.1	-142	
Co(CO) ₃ NO + *NO			40.5	-209	366
Fe(CO) ₂ (NO) ₂ + *NO			34.6	-209	
Fe(CO) ₂ (NO) ₂ + L → Fe(CO)(NO) ₂ L + CO L = PPh ₃			66.9	-84	364
L = P(OPh) ₃			91.9	-30	365
L = AsPh ₃			100.3	-4	
CpV(CO) ₄ + L → CpV(CO) ₃ L + CO L = PBu ₃	230.3	150			371
CpRh(CO) ₂ + L → CpRh(CO)L + CO L = PPhEt ₂			62.7	-84	372
L = P(OBu) ₃			75.2	-67	
CpMn(CO) ₂ SR ₂ + PR ₃ → CpMn(CO) ₂ PR ₃ + SR ₂ R ₂ S = tetrahydrothiophene	154	92			376
R = Me	146	75			
R = Et	146	79			
R = Bu	150	92			
R = <i>n</i> -propyl	146	79			
R = benzyl	133	54			
R = Ph	133	79			
CpMn(CO) ₂ (ol) + PR ₃ → CpMn(CO) ₂ PR ₃ + ol ol = C ₂ H ₄	144.1	79			373
ol = cyclooctene	145.8	120			
ol = propylene	141.2	115			
ol = cyclopentene	140.0	115			
ol = 1-pentene	138.7	102			
ol = cycloheptene	135.0	49			
(allyl)Co(CO) ₃ + L → (allyl)Co(CO) ₂ L + CO L = P(OCH ₂) ₃ Pr	99.1	9			341b
L = PPh ₃	95.3	30			343c
(allyl)Co(CO) ₂ L + L → (allyl)Co(CO)L ₂ + CO L = P(OCH ₂) ₃ Pr	112.9	28			
(η^3 -C ₃ H ₄ X)Fe(CO) ₂ NO + L → (η^3 -C ₃ H ₄ X)Fe(CO)(NO)L + CO X = H, L = P(OEt) ₃			58.5	-117	382a-c
X = H, L = PPh ₃			64.8	-129	
X = H, L = PBu ₃			27.5	-221	
X = H, L = P(OCH ₂) ₃ CEt			88.6	-21	
X = 2-Me, L = P(OEt) ₃			56.8	-137	
X = 2-Me, L = PPh ₃	143.8	79	71.0	-125	
X = 1-Ph, L = P(OEt) ₃			48.4	-133	
(η^3 -C ₃ H ₄ X)Fe(CO) ₂ NO + L → (η^1 -C ₃ H ₄ X)Fe(CO) ₂ (NO)L X = 2-Cl, L = PPh ₃			56.8	-134	
X = 2-Cl, L = PPh ₂ Et			18.8	-230	
X = 2-Cl, L = P(OEt) ₃			52.2	-113	
X = 1-Cl, L = PPh ₃			30.1	-217	
X = 1-Cl, L = PPh ₂ Et			44.7	-146	
X = 2-Br, L = P(OEt) ₃			54.8	-113	

TABLE XV (Continued)

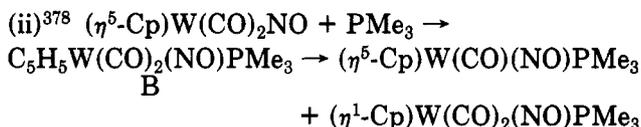
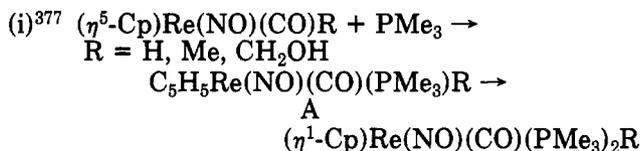
reaction	ΔH_1^* , kJ mol ⁻¹	ΔS_1^* , J K ⁻¹ mol ⁻¹	ΔH_2^* , kJ mol ⁻¹	ΔS_2^* , J K ⁻¹ mol ⁻¹	ref
$(\eta^1\text{-C}_3\text{H}_4\text{X})\text{Fe}(\text{CO})_2(\text{NO})\text{L} \rightarrow$ $(\eta^3\text{-C}_3\text{H}_4\text{X})\text{Fe}(\text{CO})(\text{NO})\text{L} + \text{CO}$					
L = P(OEt) ₃ , X = 2-Cl	83.2	-63			
L = P(OEt) ₃ , X = 1-Cl	79.8	-58			
L = P(OEt) ₃ , X = 2-Br	74.0	-88			
X = 1-CN	81.9	-38			
$\text{Cp}'\text{Mo}(\text{CO})_2\text{Cl} + \text{PPh}_3 \rightarrow$ $\text{Cp}'\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Cl} + \text{CO}$					
Cp' = C ₅ H ₅	113.0	36			
Cp' = tetrahydroindenyl	111.5	41			429a
$\text{Cp}'\text{Ru}(\text{CO})_2\text{Br} + \text{PBu}_3 \rightarrow$ $\text{Cp}'\text{Ru}(\text{CO})(\text{PBu}_3)\text{Br} + \text{CO}$					
Cp' = C ₅ H ₅	155.9	67			427
Cp' = C ₅ Me ₅	132.0	27			

determining step. Indeed, matrix photolysis of CpFe(CO)₂Me at high dilution has been shown to result in a η^5 to η^3 change in coordination of the cyclopentadienyl ligand.^{370h} Interestingly, however, CpCo(PPh₃)₂ reacts with PMe₃ to give CpCo(PPh₃)(PMe₃) by a rate-determining dissociative loss of PPh₃.^{372b} The isoelectronic CpMn(CO)₃ and CpMn(CO)₂CS complexes are, unfortunately, inert to carbonyl substitution.^{373,374} While kinetic studies of the reactions below have been reported, these proceed exclusively via rate-determining dissociation of the weakly bound olefin or sulfide ligand.

(i)^{373,374}(iii)³⁷⁶

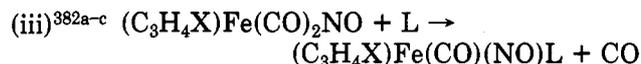
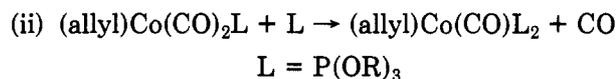
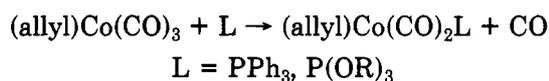
Rates for reaction i increase with increasing electron-donating character of the olefin substituent, whereas reaction iii shows the characteristic increase in rate with increasing size of R.

Interesting reactions of mixed nitrosyl-cyclopentadienyl complexes have been reported.



The η^1 -complex of (i) may be isolated and characterized by crystallography, whereas the η^1 -species of (ii) may be observed by NMR at low temperature and decomposes on warming to yield the product of carbonyl substitution. Both reaction rates are linear with [PMe₃] and are thought to proceed via intermediates A and B; neither can be observed spectroscopically, and assignment as containing either a 1e⁻ NO or a η^3 -Cp ligand is not possible. The isoelectronic cationic species CpMn(CO)₂NO⁺,³⁷⁹ CpMn(CO)(CS)(NO)⁺,³⁸⁰ and CpM(CO)(NO)₂⁺³⁸¹ (M = Mo, W) undergo facile carbonyl substitution compared to CpMn(CO)₃ on reaction with PR₃, although this may be ascribed to the labilizing effect of NO.

The $\eta^3 \rightarrow \eta^1$ -allyl transformation is a well-established pathway for syn \rightleftharpoons anti exchange in allyl complexes, and is also an important factor in their considerable catalytic activity. Three systems have been the subject of kinetic study.

(i)^{341b,343c}

Both mono- and disubstitution of (allyl)Co(CO)₃ are independent of [L], and in conjunction with activation parameters (Table XV), indicate a rate-determining CO dissociation. While the isoelectronic (allyl)Mn(CO)₄ is known to undergo mono- and disubstitution,^{383a,b} no kinetic studies have been reported.

In contrast, the mixed allyl-nitrosyl complexes of (iii) undergo substitution by PR₃ and P(OR)₃ at rates that depend linearly on [L] (with the exception of the 2-Me complex for which competing dissociative and associative pathways are evident). For the strongly electron-withdrawing substituents (X = CN, Cl, Br), the intermediates have been isolated and shown to be (η^1 -C₃H₄X)Fe(CO)₂(NO)L complexes, which then undergo a first-order internal chelation. The similarity of the dependence of the rate on the nature of L indicates that reactions of the aryl- and alkyl-substituted derivatives proceed in the same way, although intermediates cannot be isolated. Simple plots of log *k* against $\Delta H_{\text{N.P.}}$ are not obtained here; steric bulk of the ligand is much more significant due to the spatial requirements of the allyl ligand.

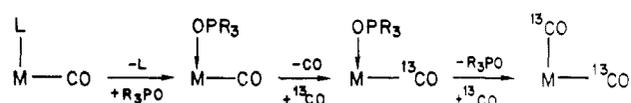
XI. Acid- and Base-Catalyzed Substitution Reactions

Many carbonyl substitution or exchange reactions proceed at enhanced rates in the presence of stoichiometric, or, more usually, catalytic amounts of acids or bases (taking these terms in their broadest context).

A. Base-Catalyzed Substitution

In general, the key step in reactions of this kind involve either intermediate metal coordination of a catalyst molecule that is strongly cis labilizing or trans-

Scheme XXXIII

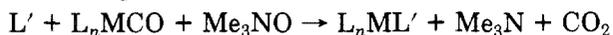


formation of one carbonyl ligand into a strongly cis-labilizing moiety by base attack at the carbonyl carbon.

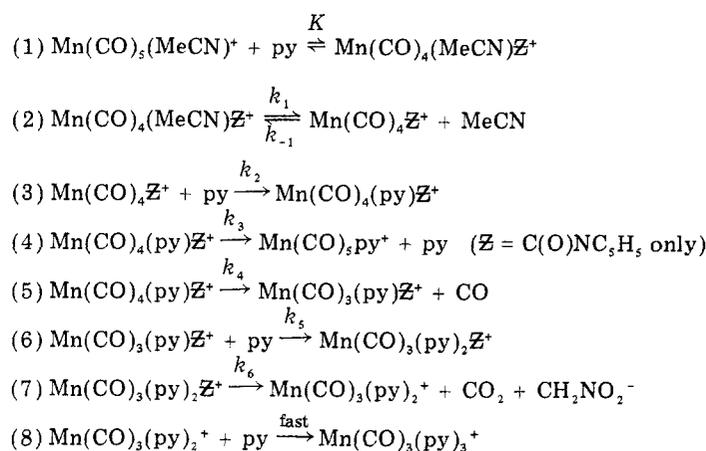
As an example of the first case, reaction of (η^6 -chpt)Cr(CO)₃, (py)Cr(CO)₅, (piperidine)M(CO)₅ (M = Mo, W), (piperidine)₂M(CO)₄, or (py)₃M(CO)₃ with ¹³CO in the presence of Bu₃PO all yield essentially 100% labelled M(¹³CO)₆, and (py)Fe(CO)₄ similarly yields approximately 70% enriched Fe(¹³CO)₅.^{384a,b} In the case of (η^6 -chpt)Cr(CO)₃, the reaction intermediate may be identified as Cr(CO)₃(Bu₃PO)₃ formed by triene displacement, which is converted to Cr(¹³CO)₆. The enhanced exchange of the carbonyls is attributed to the highly labilizing nature of the oxygen-bonded phosphine oxide ligand, and the general process may be viewed in terms of Scheme XXXIII. The reaction requires the presence of one easily displaced ligand L, as M(CO)₆ or Fe(CO)₅ do not exchange themselves in the presence of Bu₃PO. In the cases where L is an aliphatic amine, displacement of the amine is also accelerated by hydrogen-bonded adduct formation with Bu₃PO,^{61,62} and in the presence of phosphines rather than ¹³CO, only the (PR₃)M(CO)₅ complex is isolated due to preferential coordination of the M(CO)₅ intermediate by PR₃ rather than R₃PO.

Nucleophilic attack at the carbonyl carbon to yield stable products has already been noted, and such an interaction may also be responsible for the base-catalyzed substitutional lability of several metal complexes. For example, [Mn(CO)₅(MeCN)]⁺ reacts with py in acetonitrile or nitromethane to give [Mn(CO)₅py]⁺ and [Mn(CO)₃(py)₃]⁺, respectively,^{385a-c} at rates that far exceed those for substitution by PPh₃ in acetonitrile or exchange with CD₃CN. In acetonitrile, this is attributed to initial attack of pyridine at the carbonyl carbon to yield an [Mn(CO)₄(MeCN)Z]⁺ intermediate (Scheme XXXIV) in which the substitutional lability is enhanced by the strongly cis-labilizing nature of Z. Kinetic results indicate that the py ligand of the product [Mn(CO)₅(py)]⁺ is that which initially attacks the carbonyl carbon; thus, steps 3 and 4 of Scheme XXXIV may in fact be coincident. Reaction in nitromethane is thought to proceed via a similar mechanism involving not py attack, but attack by CH₂NO₂⁻ generated from the solvent [i.e., Z = C(O)ONOC₂H₅⁻]. Here, labilization not only of MeCN but also of the carbonyls as well to give [Mn(CO)₃(py)₃]⁺ is observed. Activation parameters ($\Delta H^* = 81.2 \text{ kJ mol}^{-1}$, $\Delta S^* = -26 \text{ J K}^{-1} \text{ mol}^{-1}$ in nitromethane; $\Delta H^* = 50.5$, $\Delta S^* = -136$ in acetonitrile) are consistent with a rate-determining step (2) but including a component associated with the preequilibrium (1); these values may be contrasted with activation parameters for [Mn(CO)₅(MeCN)]⁺/CD₃CN exchange ($\Delta H^* = 116 \text{ kJ mol}^{-1}$, $\Delta S^* = 23 \text{ J K}^{-1} \text{ mol}^{-1}$) which is dissociative in character.

The oxidation of coordinated CO to CO₂ in step 7 of Scheme XXXIV may be noted. One reagent which has generally been used to effect stoichiometric carbonyl substitution in Fe(CO)₅ and M(CO)₆ is Me₃NO^{386a-d} for which the general reaction



Scheme XXXIV



may be written. This reaction may also be viewed as proceeding via nucleophilic attack at carbonyl carbon followed by elimination and trapping of the L_nM intermediate.

Substitution of Fe(CO)₅ by primary and secondary saturated amines may also proceed via a similar mechanism. Initial adduct formation (2:1 for pyrrolidine, 3:1 for piperidine) may be demonstrated unambiguously.^{387a-c} The stoichiometry is reminiscent of the second-order dependence on [RNH₂] of reactions involving attack of RNH₂ at carbonyl carbon mentioned previously, and analogous structures may be described for these iron complexes. The substitution of Fe(CO)₂(NO)₂ is also catalyzed by the addition of amine.³⁶⁴

B. Acid-Catalyzed Substitution

Acid-catalyzed substitution has been less extensively studied. Protonation of Fe(CO)₅ to give HFe(CO)₅⁺ results in an enhanced lability towards CO exchange.³⁸⁸ This may, however, be associated with a low-energy ligand migration pathway involving the Fe-H bond (vide infra).

Recently, it has been found that a variety of transition-metal salts (Rh^I, Co^{II}, Ni^{II}, Ru^{II}) catalyze the substitution of Fe(CO)₅ and M(CO)₆ and other complexes by phosphine, phosphite, and isonitrile ligands. The reactions are not radical initiated, and perhaps the most likely mode of carbonyl activation involves an initial L_nM-CO---M^{II} isocarbonyl interaction.^{389a-f} In contrast, catalytic substitution using metal oxides or oxide-supported metals does appear to proceed via free-radical intermediates.^{390a-c}

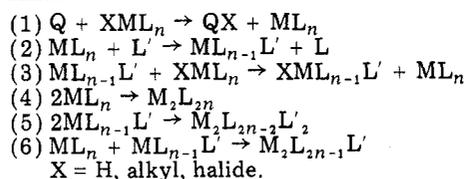
XII. Ligand Migration Reactions and Reactions Proceeding via Free-Radical Intermediates

There is increasing evidence that some stoichiometric substitution reactions proceed via the intermediacy of free radicals in which the high substitutional lability of the radical and the chain nature of the mechanism are the important features in determining the high rates of substitution observed.^{391a,b}

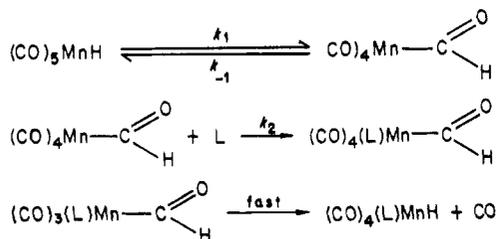
A. Metal Hydride, Alkyl, and Halide Complexes

Studies on many complexes of this type show that the free-radical contribution to substitution may be represented by Scheme XXXV. Reaction 1 represents initiation that may occur via adventitious impurities or

Scheme XXXV



Scheme XXXVI



added initiator [usually a small amount of M_2L_{2n} followed by photolysis]. It may be noted that the free-radical pathway is frequently in competition with normal D or I_d substitution, and may be reduced or eliminated by rigorous purification of materials and exclusion of light. Reactions 2 and 3 represent radical substitution and chain propagation, respectively, while reactions 4–6 represent possible chain-termination steps. Scheme XXXV describes only monosubstitution; the disubstituted products also formed in several cases may be accounted for by a similar mechanism.

1. Metal Hydrides and Alkyls

Radical pathways have been established unambiguously for substitution of $\text{HM}(\text{CO})_5$ ($\text{M} = \text{Mn, Re}$),^{392a-d} $\text{HM}(\text{CO})_3\text{Cp}$ ($\text{M} = \text{Mo, W}$),^{393a} and $\text{HOs}(\text{CO})_4\text{Me}$ ^{393b} by phosphines and phosphites. Such a pathway seems a possibility for the rapid substitution of $\text{HCo}(\text{CO})_4$,^{341a} and the kinetics of the thermal decomposition of $\text{HCo}(\text{CO})_4$ to give H_2 and $\text{Co}_2(\text{CO})_8$ may be explained on the basis of initial generation of $\text{Co}(\text{CO})_4$ radicals via a reaction of type 1.³⁹⁴

In the case of $\text{HMn}(\text{CO})_5$, the non-radical pathway has been clearly defined.^{392c,d} Neither the rate law

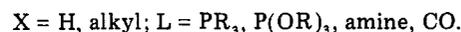
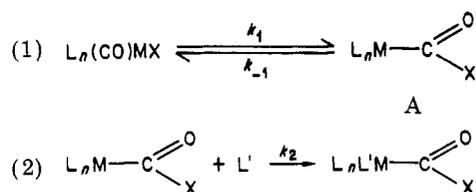
$$\frac{-d[\text{HMn}(\text{CO})_5]}{dt} = k_{\text{obsd}}[\text{HMn}(\text{CO})_5][\text{PR}_3]$$

nor the results of ^{13}CO exchange experiments are consistent with a simple cis labilization of CO as described for other $\text{XMn}(\text{CO})_5$ complexes, and the hydride migration pathway of Scheme XXXVI provides the best alternative. Hoffmann et al.³⁹⁵ have recently provided a detailed theoretical analysis of this ligand migration pathway, and it is of interest to compare their results with experiment.

a. Kinetics and Mechanism. The conventionally accepted mechanism for ligand migration is shown in Scheme XXXVII. Labelling experiments are in agreement, showing no incorporation of $^*\text{CO}$ into the acyl group in the reactions of ^{13}CO or ^{14}CO with $(\text{CO})_5\text{MnMe}$ to give $(\text{CO})_4(^*\text{CO})\text{Mn}(\text{COMe})$ ^{396a,b} or the reaction of $(\text{PPh}_3)(\text{CO})_3\text{CoCH}_2\text{Ph}$ with ^{13}CO to give $(\text{PPh}_3)(\text{CO})_2(^{13}\text{CO})\text{CoCOCH}_2\text{Ph}$.³⁹⁷

Hoffmann's calculations are based on an estimation of the activation energy for reaction 1 of Scheme XXXVII for $(\text{CO})_5\text{MnX}$ species. It is found that intermediate A is only slightly lower in energy than the

Scheme XXXVII



transition state and differs only in the degree of distortion of the square pyramid. This indicates a significant contribution from the k_{-1} step, and assuming that $k_{-1} \gg k_2[\text{L}]$, a steady-state treatment of Scheme XXXVII yields

$$k_{\text{obsd}} = \frac{k_1 k_2 [\text{L}]}{k_{-1}}$$

A linear dependence on $[\text{PR}_3]$ has already been noted in the substitution of $(\text{CO})_5\text{MnH}$ in hexane,^{392c} and the reactions of $(\text{CO})_5\text{MnR}$,^{398a-c} $\text{Cp}(\text{CO})_2\text{FeR}$,^{399a-c} and $\text{Cp}(\text{CO})_3\text{MoR}$ ^{399b,400a-e} with various ligands to give $(\text{CO})_4(\text{L})\text{MnCOR}$, $\text{Cp}(\text{CO})(\text{L})\text{FeCOR}$, and $\text{Cp}(\text{CO})_2(\text{L})\text{MoCOR}$ complexes, generally in noncoordinating solvents, exhibit a similar dependence on $[\text{L}]$.

Steady-state treatment of Scheme XXXVII assuming $k_2[\text{L}] \gg k_{-1}$ yields

$$k_{\text{obsd}} = k_1$$

and migration reactions that are independent of $[\text{L}]$ in relatively noncoordinating solvents have been reported.^{400f} One may also note that the cis migration described in Scheme XXXVII does not necessarily imply a cis geometry for the product in octahedral systems. While the $(\text{CO})_4(\text{L})\text{MnCOR}$ complexes formed are invariably of cis geometry, reaction of $[(\text{diars})\text{Fe}(\text{CO})_3\text{Me}]^+$ with ligands or ^{13}CO yields $[(\text{diars})\text{Fe}(\text{CO})_2(\text{L})\text{COMe}]^+$ in which L is trans to the acetyl group.^{400f} The geometry of the product reflects the site preference of the COR ligand in the square-pyramidal intermediate. In cases where σ -donor character is most important, preferential occupation of the axial position is observed, whereas π interaction is maximized in a basal position.^{116,117a} The π interaction is also greatly sensitive to the degree of distortion of the square pyramid, and general predictions do not seem possible. In any case, the difference in energy of the axial vs. basal coordination will be small relative to the activation energy for the initial cis migration.

Both the rate and rate law for the above ligand migrations are markedly dependent on solvent. As the coordinating power of the solvent increases, the rate increases and the rate law gradually changes from first order in $[\text{L}]$ in noncoordinating solvents to one that is independent of $[\text{L}]$ in strongly coordinating solvents. These observations seem best interpreted in terms of an increasingly dominant catalysis by the solvent of the migration step 1 of Scheme XXXVII by some means other than solvent-metal coordination (possibly adduct formation at the carbonyl carbon). Calculations show no lowering of the activation energy by solvent-metal coordination in the transition state, and increasingly strong coordination of intermediate A by solvent should result in slower rates of product formation.

b. Effect of X. Calculations on $(\text{CO})_5\text{MnR}$ show a decreasing activation energy for reaction 1 of Scheme

XXXVII in the order Me (83.6 kJ mol⁻¹) > Et (64.9) > Pr (62.8), which is attributable in part to the decreasing electronegativity of R and in part to the increasing delocalization of the carbon coefficient of the σ -bonded carbon. In general, the activation energy decreases with decreasing electronegativity of X, with the important exception of hydrogen which has a lower activation energy of 68.8 kJ mol⁻¹ than Me due to a compensating stabilization of the orbital which develops into the C-H bond and which is absent where X = Me. One may note the contrast in the ordering of activation energies (Me > H) with ground-state bond dissociation enthalpies which are in the order Me-Mn(CO)₅ (116.9 or 129.2 kJ mol⁻¹)⁴⁰¹ < H-Mn(CO)₅ (267 kJ mol⁻¹).⁴⁰²

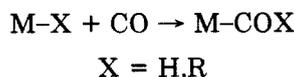
Experiment indeed shows an increasing rate of ligand migration for (CO)₅MnR complexes in the order CF₃ < Me < Et < Pr⁴⁰³ and a similar ordering is found for Cp(CO)₂FeR^{399a} and Cp(CO)₃MoR^{400a} complexes. The ordering of the second-order rate constants for ligand migration in hexane of HMn(CO)₅ with PBu₃ (1.2 × 10⁻³ dm³ mol⁻¹ s⁻¹)^{392c} and MeMn(CO)₅ with cyclohexylamine (2.70 × 10⁻⁵)^{398a} is also consistent with the above calculations.

Ligand migration studies on the benzyl complexes Cp(CO)₂FeCH₂C₆H₄X^{399c} and Cp(CO)₃MoCH₂C₆H₄X^{400d,e} also show the importance of steric acceleration in the reaction, particularly where X is a bulky ortho substituent.

c. Effect of Metal and Metal Geometry. Calculations show a higher barrier for ligand migration in MeRe(CO)₅ (140 kJ mol⁻¹) as compared to MeMn(CO)₅ (83.6), and indeed, both MeRe(CO)₅ and HRe(CO)₅ are unreactive under conditions where the Mn analogues yield products of ligand migration.^{392,399} A similar ordering of reactivity (Fe > Ru > Os) is observed in the ligand migration reactions of Cp(CO)₂MR (M = Fe, Ru)⁴⁰³ and the substitution reactions of H₂M(CO)₄ (M = Fe, Ru, Os).⁴⁰⁴

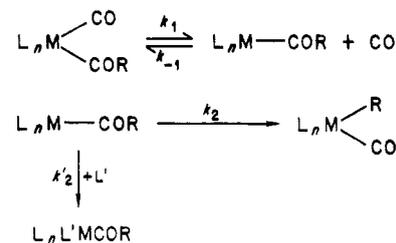
Calculations on MeCo(CO)₄ show that the barrier to ligand migration is effectively that of pseudorotation to bring the methyl from its ground-state axial position⁴⁰⁵ to an equatorial position in the trigonal bipyramid. This is calculated to be 51.3 kJ mol⁻¹ and may be compared with an experimentally measured value for intramolecular exchange in CF₃Co(CO)₄ of 49.4 kJ mol⁻¹.⁴⁰⁶ Indeed, RCo(CO)₄ complexes exhibit a very facile ligand migration on reaction with CO to give RCOC(CO)₄ or with L to give RCOC(CO)₃L complexes.^{407a-e}

The intermediacy of formyl complexes in the substitution of metal hydrides requires that the decarbonylation step (3) in Scheme XXXVI be facile, and some comment on the kinetic and thermodynamic stability of formyl as opposed to acyl complexes is in order. Since C-H and C-C bonds differ in energy by only 25 kJ mol⁻¹, ΔG for the reaction



will be determined primarily by a comparison of M-H with M-C bond strengths. These indicate that formyl-metal complexes are indeed less thermodynamically stable than acyl complexes with respect to the above reaction, and only recently has the first example of a reversible migration of hydrogen to CO been ob-

Scheme XXXVIII

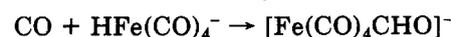


served.⁴⁰⁸ However, only small amounts of formyl complexes are required to function as intermediates, and factors that influence the *rate* of decarbonylation would seem to be more important. Kinetic and labelling studies of the decarbonylation of acyl complexes show that the reaction proceeds via the reverse of Scheme XXXVII, i.e., a rate-determining loss of terminal CO followed by a rapid ligand migration to generate the metal alkyl or combination with L' to give the substituted acyl (Scheme XXXVIII). Thus, rates of substitution of RCOMn(CO)₅ complexes parallel those of decarbonylation,^{409a,b} while the orderings of the rates of decarbonylation MeCOC(CO)₄ >> MeCOMn(CO)₅^{341a} and MeCOMn(CO)₅ >> MeCOCRe(CO)₅⁴⁰³ parallel those of the initial methyl migration, as required by the principle of microscopic reversibility. Also in agreement, substitution of MeCOMn(CO)₅ is essentially solvent independent,⁴¹⁰ and reaction of Me¹³COMn(CO)₅ with PPh₃ yields exclusively Me¹³COMn(CO)₄PPh₃.^{411a} Similarly, decarbonylation of CpFe(CO)₂¹³COMe proceeds to give only CpFe(CO)₂(¹³CO)Me.^{411b} Labelling studies on the decarbonylation of *cis*-[(CO)₄Re(COMe)(COPh)]⁻ to [(CO)₄Re(COMe)Ph]⁻ are also consistent with rate-determining terminal CO loss,^{411c} and additionally indicate some fluxional character for the five-coordinate intermediate so produced.

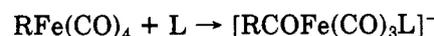
If decarbonylation of formyl complexes proceeds via the same pathway, then the principle of microscopic reversibility would indeed indicate a lower activation energy for CO loss compared to the acyl complex, based on the calculations of Hoffmann. Of the studies of decarbonylation of formyl complexes which have been reported, the reaction



has been the best characterized.⁴¹² It proceeds at room temperature or below, depending on the cation (Li⁺ > Ne⁺ > K⁺ > PPN⁺), and is thought to occur via rate-determining terminal CO loss. The order in terms of cation may be linked to its strength of binding to the formyl oxygen—the greater the binding, the greater the lability of the terminal carbonyls. The reverse reaction



has not been reported.⁴¹³ However, the related alkyl migration reaction

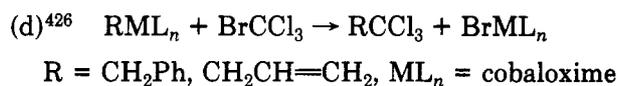
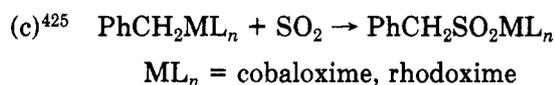
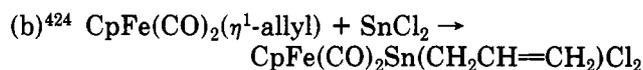
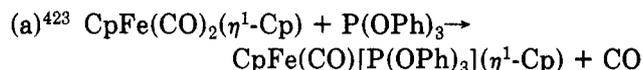


does exhibit the expected linear dependence of rate on [L].⁴¹⁴ The dependence of rate on cation (Li⁺ > Na⁺ > PPN⁺) is also consistent with a cationic catalysis of the migration step, and the cation---OC-Fe interaction is quite evident from crystallographic and infrared studies.^{415a-e} Other decarbonylation reactions of formyl complexes are less well characterized; pathways other

than ligand migration are evident, primarily those involving transfer of hydrogen as hydride.⁴¹⁶

Although free radicals have not been implicated in the thermal reactions of *saturated* alkyl complexes, there is some evidence that M-R homolysis is competitive with CO dissociation in the ultraviolet photolysis of species such as CpFe(CO)₂R,^{417a-d} CpM(CO)₃R (M = Cr, Mo, W),^{417a,418a-e} RMn(CO)₅,⁴¹⁹ and R₃SiCo(CO)₄.^{420a,b} Photolysis of HCo(CO)₄^{421a,b} and HMn(CO)₅^{422a,b} also results in competitive CO loss and M-H bond homolysis.

Free radicals have been implicated in the thermal reactions of *unsaturated* metal alkyl complexes, as noted below:



In general, the reactions may be viewed as occurring by the initiation step (1) of Scheme XXXV where X is R and Q is either adventitious or deliberately added.

2. Metal Halide Complexes

Free-radical pathways have been established for the substitution of CpW(CO)₃Br^{391a} and CpRu(CO)₂Br and its pentamethyl analogue.⁴²⁷ The initiation may again be viewed as reaction 1 of Scheme XXXV where X = Br. The non-radical pathway for the ruthenium complexes has also been defined under rigorous conditions as a normal D pathway, and this is the pathway adopted by the related complexes CpFe(CO)₂I⁴²⁸ and CpMo(CO)₃Cl.^{429a-c} One exception appears to be (η⁵-indenyl)Mo(CO)₃Cl^{429c} which exhibits a ligand-dependent term in its rate law; this has been attributed to a slippage of the indenyl ligand to a η³ coordination in the intermediate or transition state. Activation parameters are given in Table XV.

There is some evidence that homolysis or heterolysis of M-halide bonds is competitive with CO loss in the ultraviolet photolysis of M(CO)₅X complexes (M = Mn, Re; X = Cl, Br).⁴³⁰

3. Metal-Metal Bonded Complexes

There is currently a great deal of interest in the role of radical intermediates in the thermal substitution reactions of metal-metal dimers, and, by extension, metal cluster complexes.^{391a} A detailed discussion is, however, beyond the scope of this review.

B. Structure and Reactivity of Radicals

Matrix photolysis of HMn(CO)₅ (M = Mn, Re) yields M(CO)₅ radicals; the Mn analogue has a C_{4v} structure with an axial radial angle of 96°. ⁴²² Matrix photolysis of Co(CO)₄NO⁴³¹ or low-temperature cocondensation experiments^{432a,b} yield M(CO)₄ radicals (M = Co, Rh, Ir); the Co analogue has a C_{3v} geometry with an axial

radical angle of approximately 100°.

Neutral ML_n radicals can commonly be generated for chemical study by ultraviolet irradiation into a transition characterized as σ → σ* of the metal-metal bond of the M₂L_{2n} dimer.⁴³³ Thus, the results of matrix and flash photolysis, spin trapping and chemical trapping [primarily by reaction with halogenated hydrocarbons to give XML_n], quantum yield and synthetic measurements show clearly that such radicals are formed from the photolysis of M₂(CO)₁₀ (M = Mn, Re),^{434a-m} Mn-Re(CO)₁₀,^{434a} substituted derivatives of Mn₂(CO)₁₀,^{434e,f} Cp₂M₂(CO)₄ (M = Fe, Ru),^{434f,435a-d} Cp₂M₂(CO)₆ (M = Cr, Mo, W),^{434f,435d,436a-d} the mixed-metal dimers (CO)₅M'-M(CO)₃Cp (M' = Mn, Re; M = Mo, W),⁴³⁷ and Co₂(CO)₈ and its substituted derivatives.^{431,434f}

Only in two instances have competing processes been identified:

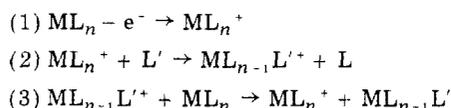
(i) Flash photolysis of Cp₂M₂(CO)₆ yields, in addition to CpMo(CO)₃, a longer lived intermediate^{436b,d} that has been assigned a Cp(CO)₂Mo-(C=O)-Mo(CO)₃Cp structure containing one coordinatively unsaturated Mo atom. Careful wavelength studies show that it is this intermediate which is responsible for formation of Cp₂Mo₂(CO)₅L and the disproportionation products [CpMo(CO)₂L₂][CpMo(CO)₃] derived from this by further photolysis. The disproportionation products CpMo(CO)₃X and CpMo(CO)₃⁻ isolated from photolysis of Cp₂Mo₂(CO)₆ and X⁻ may also be derived from this same intermediate.⁴⁴² An additional intermediate observed in the flash photolysis of Cp₂Fe₂(CO)₄^{435c} may be assigned an analogous structure, and may be trapped as Cp(CO)₂Fe-(C=O)-Fe(CO)(L)Cp at low temperature [L = P(OPr-i)₃].⁴⁴³

(ii) Photolysis of Mn₂(CO)₁₀ also yields a second intermediate; while it may be assigned a related (C₃)₅Mn-(C=O)-Mn(CO)₄ structure,⁴⁴⁴ flash photolytic and synthetic studies indicate that it is best regarded as 15-electron Mn(CO)₄ derived from Mn(CO)₅ by CO loss. This does not imply a facile dissociative loss of CO from thermally generated Mn(CO)₅. Molecular beam studies⁴⁴⁵ show that the energy of the photon required for homolysis (398 kJ mol⁻¹) is much higher than the sum of the energies required for Mn-Mn cleavage (92 kJ mol⁻¹) and excess kinetic energy (63 kJ mol⁻¹). The remaining energy is greater than the Mn-CO bond energy (84 kJ mol⁻¹), and thus CO loss probably occurs from a vibrationally excited Mn(CO)₅ radical. In the case of Re₂(CO)₁₀ where both Re-Re (214 kJ mol⁻¹) and Re-CO (164 kJ mol⁻¹) bond energies are higher, CO loss from Re(CO)₅ is not observed.

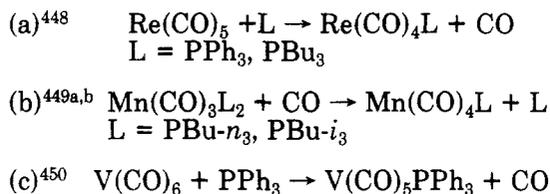
The rates of recombination for CpFe(CO)₂, CpM(CO)₃, and M(CO)₅ measured from flash photolysis (1-5 × 10⁹ dm³ mol⁻¹ s⁻¹) are in agreement with those obtained for M(CO)₅ radicals from pulse radiolysis studies^{446a,b} and indicate an essentially diffusion-controlled process. Rates of bimolecular reaction with CCl₄ are less rapid (10⁴-10⁷ dm³ mol⁻¹ s⁻¹) and indicate an ordering of reactivity Re(CO)₅ > Mn(CO)₅ > CpW(CO)₃.^{446b,436c} A more complete ordering of radical reactivity in this respect has been obtained from photochemical cross-coupling experiments (Re(CO)₅ > Mn(CO)₅ > CpW(CO)₃ > CpMo(CO)₃ > CpFe(CO)₂ > Co(CO)₄).⁴⁴⁷

The efficient operation of Scheme XXXV requires that the radical substitution reaction (3) be rapid. From

Scheme XXXIX



the few reactions reported below on which kinetic information is available, it would appear that this most likely involves a low-energy associative pathway:



Reaction a has been studied indirectly by competition experiments. The $\text{Mn}(\text{CO})_3\text{L}_2$ radicals of (b) are formed from extended photolysis of $\text{Mn}_2(\text{CO})_8\text{L}_2$ and are stable with respect to dimerization because of the steric bulk of L; the product $\text{Mn}(\text{CO})_4\text{L}$ radicals do, however, undergo dimerization to give $\text{Mn}_2(\text{CO})_8\text{L}_2$ as the isolated product.⁴⁵¹ All the reactions exhibit a perfect first-order dependence of rate on the concentration of entering ligand, and activation parameters for $\text{V}(\text{CO})_6$ ($\Delta H^* = 41.8 \text{ kJ mol}^{-1}$, $\Delta S^* = -116 \text{ J K}^{-1} \text{ mol}^{-1}$) are consistent with an associative process which is 10^{10} faster than the I_d component of the substitution of $\text{Cr}(\text{CO})_6$. Nucleophilic attack at the stereochemically active half-filled orbital of $\text{Re}(\text{CO})_5$ or $\text{Mn}(\text{CO})_3\text{L}_2$ provides a reasonable pathway; for $\text{V}(\text{CO})_6$, the hole in the bonding t_{2g} orbital set permits nucleophilic attack at a triangular face of the octahedron.

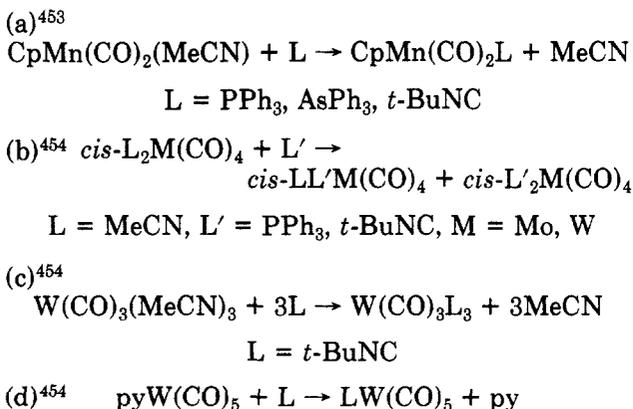
With the increasing availability of 17-electron complexes stable enough for kinetic investigation,⁴⁵² a greater understanding of the factors affecting radical lability seems likely.

C. Substitution by Oxidation-Reduction Catalysis

Catalytic substitution of 18-electron complexes containing only π -acid ligands may be initiated by either chemical or electrochemical oxidation or reduction.

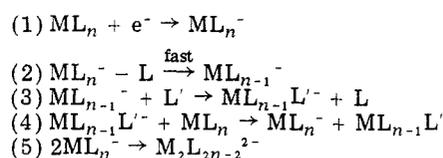
1. Oxidation

Catalytic substitution initiated by oxidation has been reported for the reactions below:

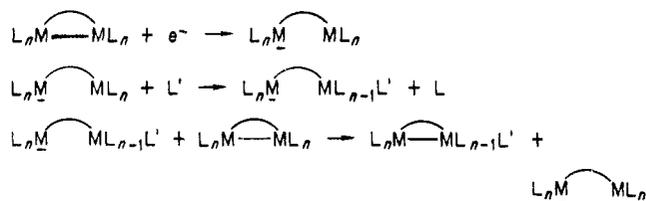


Oxidation of only a few percent of the starting material is required to initiate substitution, and the results are

Scheme XL



Scheme XLI



best interpreted in terms of the radical chain pathway of Scheme XXXIX. With the exception of the initiation step, the similarity to Scheme XXXV may be noted; particularly, a rapid substitution of the cation radical is seen to be necessary. The possibility of catalytic substitution by oxidation emphasizes the need for rigorous exclusion of air and other oxidizing impurities in kinetic studies of 18-electron complexes.

The radicals $\text{Cr}(\text{CO})_6^+$, $\text{Fe}(\text{CO})_5^+$, $\text{Ni}(\text{CO})_4^+$, $\text{CpMn}(\text{CO})_3^+$, and $\text{CpFe}(\text{CO})_2(\text{COR})^+$ may be generated in solvents such as acetonitrile or trifluoroacetic acid,^{455a-d} and have lifetimes ranging from less than a second to several minutes at room temperature. The order of stability ($\text{Cr} > \text{Fe} > \text{Ni}$) parallels that of the neutral radicals ($\text{Mn} > \text{Co}$).

2. Reduction

It has recently been shown that the monosubstitution of $\text{Fe}(\text{CO})_5$ ⁴⁵⁶ and $\text{M}(\text{CO})_6$ ⁴⁵⁷ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) may be effected by catalytic electrochemical reduction; the results seem most consistent with Scheme XL. Electron addition is followed by rapid ligand loss^{455e} to give the 17-electron radical anion of (2), which is assumed to undergo rapid substitution and chain propagation. Unfortunately, chain termination by dimerization is competitive, and although good yields of the $\text{M}(\text{CO})_5\text{L}$ complexes are obtained (50–90%), yields of $\text{Fe}(\text{CO})_4\text{L}$ are low (10%) due to competitive formation of $\text{Fe}_2(\text{CO})_8^{2-}$. Indeed, reduction of $\text{Fe}(\text{CO})_5$ or $\text{M}(\text{CO})_6$ in the absence of L yields only $\text{Fe}_2(\text{CO})_8^{2-}$ or $\text{Cr}_2(\text{CO})_{10}^{2-}$ as detectable species.^{458a-c} Reduction of (maleic anhydride) $\text{Fe}(\text{CO})_4$ does, however, yield detectable concentrations of (maleic anhydride) $\text{Fe}(\text{CO})_3^-$, which is labile towards substitution.^{459a} The anion radicals $\text{Cr}(\text{CO})_5^-$, $\text{Fe}(\text{CO})_4^-$, and $\text{Ni}(\text{CO})_3^-$ have been characterized by matrix techniques, however,^{459b-d} and have the C_{4v} , C_{3v} , and D_{3h} symmetries of their isoelectronic neutral analogues $\text{Mn}(\text{CO})_5$, $\text{Co}(\text{CO})_4$, and $\text{Cu}(\text{CO})_3$. Very recently, it has been shown that (diazadiene) $\text{M}(\text{CO})_4$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) undergo both catalytic reductive and oxidative substitution.⁴⁶⁰

One interesting development concerns the catalytic reductive substitution of metal cluster complexes such as $\text{Co}_2(\text{CO})_8(\mu\text{-C}_2\text{Ph}_2)$ ⁴⁵⁶ and related complexes⁴⁶¹ and $\text{Ru}_3(\text{CO})_{12}$.^{462a-c} The reactions most likely proceed via electron addition to the $\sigma^* \text{M-M}$ orbital to generate a formally 17-electron center that undergoes rapid substitution and electron transfer (Scheme XLI). Anion radicals such as $\text{Mn}_2(\text{CO})_{10}^-$, $\text{Mn}_2(\text{CO})_8(\text{PR}_3)_2^-$, and

$\text{Co}_2(\text{CO})_6(\text{PR}_3)_2^-$ have been detected by ESR,^{463a-d} and have been postulated as intermediates in both thermal^{464a,b} and photochemical^{434b} substitution reactions of metal-metal dimers.

Redox catalysis is currently an area of active interest, and more information is needed especially on the lability of the charged radicals and on the nature of the electron-transfer process.

D. Relevance to Catalytic Organic Reactions⁴⁶⁵

CIDNP studies show clearly that the hydrogenation of α -methylstyrene by $\text{HMn}(\text{CO})_5$ proceeds via the intermediacy of $\text{Mn}(\text{CO})_5$ and PhCMe_2 radicals,⁴⁶⁶ while the stoichiometric hydrogenation of anthracene by $\text{HCo}(\text{CO})_4$ ⁴⁶⁷ and of cyclopropenes^{468a} and 1,1-diphenylethene^{468b} by $\text{HCo}(\text{CO})_4$ and $\text{HMn}(\text{CO})_5$ and the hydroformylation of 3,3-dimethyl-1,2-diphenylcyclopropene^{468c} also proceed via initial hydrogen-atom transfer. A rate-determining transfer of hydrogen from metal to CO has also been suggested for the homogeneously catalyzed hydrogenation of CO to methanol.⁴⁰²

Although more experimental evidence is not available, it seems likely that radicals may be implicated in other catalytic reactions involving olefin isomerization and hydrogenation, and hydroformylation.

XIII. References

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