



Inorganic and Organometallic Reaction Mechanisms

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INORGANIC AND ORGANOMETALLIC REACTION MECHANISMS

Jim D. Atwood

FUNDAMENTAL TRANSITION METAL ORGANOMETALLIC CHEMISTRY

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Preface

This book is designed for students who have had one semester of Inorganic Chemistry after General Chemistry, typically senior or graduate-level students. It may be used in its entirety for a one-semester course in reaction mechanisms or as a portion of a more general coverage of advanced inorganic chemistry. The book is thoroughly referenced to provide an introduction to the literature of each area of inorganic and organometallic reaction mechanisms. A unique feature is the coverage of both classic inorganic reaction mechanisms (substitution and electron transfer reactions of coordination complexes) and the newer area of organometallic reaction mechanisms (substitution, oxidative-addition, reductive-elimination, fluxional behavior, and homogeneous catalysis). The former material is covered briefly, with emphasis on the basic mechanisms and recent developments; the latter is discussed more thoroughly and is especially well referenced to the current literature.

Chapter One covers the concepts in chemical kinetics needed for a discussion of inorganic and organometallic reaction mechanisms but is not designed to be a thorough coverage of the field. Basic rate laws, kinetic terms, and kinetic techniques are discussed, with inorganic examples. *Chapter Two* describes the stereochemistry, reactivity effects, and mechanisms of substitution reactions on square planar complexes. *Chapter Three* provides similar coverage of substitution reactions of octahedral coordination complexes. *Chapter Four* covers organometallic substitution reactions in considerable detail. Metal carbonyl complexes, including metal alkyl complexes, metal hydrides, and metal nitrosyl complexes, are discussed. This chapter is extensively referenced and especially up-to-date. *Chapter Five* continues the organometallic coverage with oxidative-addition and reductive-elimination reactions. Stereochemistry and mechanisms are the primary features. Using the

background of Chapters Four and Five, *Chapter Six* goes into mechanisms of homogeneously catalyzed reactions. Hydrogenation, hydroformylation, acetaldehyde synthesis, hydrocyanation, olefin metathesis, polymerization, and methanol homologation are covered. *Chapter Seven* is an introduction to the large area of stereochemical nonrigidity. Coordination number isomerization, metal migration around a ring, and metal cluster fluxionality make up this chapter. *Chapter Eight* presents inorganic electron transfer through outer and inner sphere mechanisms.

This book is based on the lecture notes of the author for Chemistry 538, a graduate course in Kinetics and Mechanisms of Inorganic Reactions at the State University of New York at Buffalo. Gordon Harris used the manuscript in rough draft form for the same course and suggested many revisions based on his experience. I am also grateful to Gregory Geoffroy of Pennsylvania State University and William Jones of the University of Rochester, who reviewed the manuscript and made many helpful suggestions.

I would like to take this opportunity to acknowledge a number of other people who have aided in the preparation of this book: Mary Atwood, Ann Pierce, and Sue Slawatycki for their secretarial assistance; Jerry Keister, Melvyn Churchill, and Ken Takeuchi for proofreading and suggestions at the rough draft stage; and to the members of my research group over the three years of this project (Dave Sonnenberger, Mike Wovkulich, Ron Ruszczyk, Wayne Rees, Tom Janik, Brian Rappoli, Bih Huang, Martha Harris, Abdul Shojaie, and Karen Bernard) for help with proofreading and for keeping the research going without the full attention of the author.

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INORGANIC AND
ORGANOMETALLIC REACTION MECHANISMS

Chemical Kinetics

In this chapter we shall consider the aspects of kinetics that are required in later chapters to differentiate between mechanistic possibilities. This chapter is not designed to provide a comprehensive treatment of chemical kinetics (for a more detailed treatment refer to references 1–5 at the end of the chapter). Here we shall consider simple rate laws, reaction profiles, and the most commonly used techniques for data generation.

RATE LAWS

The **rate** of a chemical reaction is the rate of change of the concentration of a reactant or a product with time.

$$\text{rate} = \frac{-d[\text{reactant}]}{dt} = \frac{d[\text{product}]}{dt} \quad 1.1$$

The rate is usually given in terms of molarity per second (M/s). The **rate law** describes the rate of a reaction in terms of the concentrations of all species that affect the rate. For a simple reaction such as an isonitrile rearrangement,



the rate law is expressed as

$$\text{rate} = -k[\text{CH}_3\text{NC}] \quad 1.3$$

where k is the **rate constant**, which will be derived shortly. This reaction in which the rate depends linearly on the concentration of one reactant is

termed a **unimolecular** reaction. A reaction in which the rate depends linearly on the concentration of two reactants (equation 1.4) is a **bimolecular** or **second order reaction**.



$$\text{rate} = -k[\text{Br}][\text{H}_2] \quad 1.5$$

The rate law in general can be written

$$\text{rate} = -k \prod_i [\text{A}_i]^{\alpha_i} [\text{X}_j]^{\beta_j} \quad 1.6$$

where the A_i are reactants, k is the rate constant, and the X_j are any other species (catalysts) that affect the rate. The reaction order is defined as

$$\text{reaction order} = \sum_i \alpha_i \quad 1.7$$

Since the rate of a reaction has units of molarity per second, the units of a rate constant, k , depend on the reaction order. For a first order reaction, the rate constant has units of inverse seconds (s^{-1}). For a second order reaction, the units of the rate constant are $\text{M}^{-1}\text{s}^{-1}$.

INTEGRATED RATE EXPRESSIONS

First Order Reactions

Most reactions are either first order or are executed under conditions that approximate first order. For a first order reaction of this type,



$$\text{rate} = k[\text{A}] = \frac{-d[\text{A}]}{dt} \quad 1.9$$

which yields on rearrangement

$$\frac{-d[\text{A}]}{[\text{A}]} = k dt \quad 1.10$$

Integration from $t = 0$ (A_0) to $t = t$ (A_t) gives

$$-\ln [\text{A}_t] + \ln [\text{A}_0] = kt \quad 1.11$$

which is the equation of a straight line ($y = mx + b$) with $y = \ln [\text{A}_t]$, $X = t$ and $b = -\ln [\text{A}_0]$. Thus a plot of $\ln [\text{A}_t]$ versus time for a first order process produces a line with slope equal to the rate constant, k . This is shown in Figure

1.1. The units of k derived from the slope are s^{-1} . Examination of equation 1.11 reveals some other properties of first order reactions.

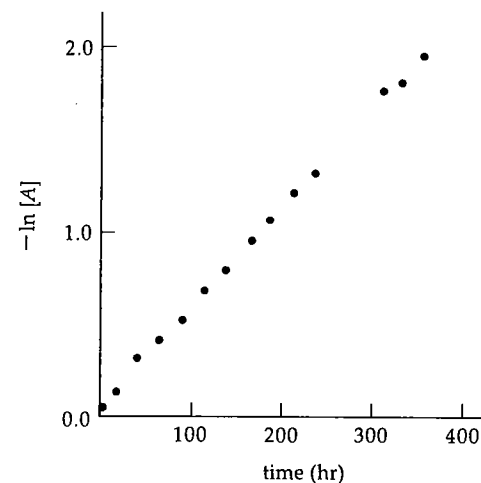


FIGURE 1.1. A plot of $-\ln [\text{A}_t]$ versus time for the reaction of *trans*- $\text{Cr}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$ with CO at 90°C . The reaction is followed by the decrease in the absorption of the starting complex at 1935 cm^{-1} . The rate constant derived from the slope is $1.49 \times 10^{-6}\text{ s}^{-1}$.

$$\ln \frac{[\text{A}_t]}{[\text{A}_0]} = -kt \quad 1.12$$

$$\frac{[\text{A}_t]}{[\text{A}_0]} = e^{-kt} \quad 1.13$$

$$[\text{A}_t] = [\text{A}_0]e^{-kt} \quad 1.14$$

Thus a plot of concentration of A varies exponentially with time. When the reaction is halfway to completion, $[\text{A}_t] = \frac{1}{2}[\text{A}_0]$, the time elapsed is termed the reaction half-life, $t_{1/2}$. Many first order reactions are described in terms of $t_{1/2}$.

$$\frac{[\text{A}_{t_{1/2}}]}{[\text{A}_0]} = e^{-kt_{1/2}} = 0.5 \quad 1.15$$

This indicates that

$$-kt_{1/2} = -0.693 \quad 1.16$$

or

$$t_{1/2} = \frac{0.693}{k} \quad 1.17$$

Note that the half-life is inversely related to the rate constant.

Reversible First Order Reactions

Some reactions, especially isotopic exchange reactions, are reversible under the reaction conditions.



The rate law for this reaction is

$$\text{rate} = -k_f[A] + k_r[P] \quad 1.19$$

At $t = 0$, $P_0 = 0$, and $[A_t] = [A_0]$. At any time

$$[P] = [A_0] - [A_t] \quad 1.20$$

Substituting equation 1.20 into equation 1.19 gives

$$\frac{-d[A]}{dt} = k_f[A_t] - k_r([A_0] - [A_t]) \quad 1.21$$

At equilibrium no net reaction occurs; thus

$$\frac{d[A]}{dt} = 0 \quad 1.22$$

Applying equation 1.22 and equation 1.20 to equation 1.19 gives

$$k_f[A_e] = k_r[P_e] = k_r([A_0] - [A_e]) \quad 1.23$$

or

$$[A_0] = \frac{k_f + k_r}{k_r} [A_e] \quad 1.24$$

Substitution of equation 1.24 into equation 1.21 leads to

$$\frac{-d[A]}{dt} = (k_f + k_r)[A] - (k_f + k_r)[A_e] \quad 1.25$$

Separation of the variables and integration leads to

$$\ln \left(\frac{[A_0] - [A_e]}{[A_t] - [A_e]} \right) = (k_f + k_r)t \quad 1.26$$

and a plot of $\ln ([A_t] - [A_e])$ versus time gives a straight line of slope $k_r + k_f$.

To define either k_r or k_f uniquely one must also evaluate the equilibrium constant, $K_{eq} = k_f/k_r$ to provide two equations in two unknowns. The most difficult problem in treating reversible first order reactions is accurately measuring $[A_e]$.

Second Order Reactions

The only type of second order reaction we need consider is a reaction that is first order in each of two reagents with a rate law

$$\text{rate} = k[A][B] \quad 1.27$$

This rate law can be integrated, but commonly the reaction is run with either A or B in large excess (for example, $[B_0] \gg [A_0]$). In this case [B] does not change significantly during the reaction.

$$\text{rate} = k[B][A] = (k[B])[A] = k_{obs}[A] \quad 1.28$$

These conditions ($[B_0] \gg [A_0]$) are referred to as **pseudo first order conditions** because the reaction may be treated as a first order reaction. A plot of $\ln [A]$ versus time yields a straight line of slope k_{obs} . The reaction must be investigated for several initial concentrations of B, always maintaining the large excess of B over A. This generates a series of k_{obs} for different $[B_0]$. Referring to equation 1.28, we have

$$k_{obs} = k[B] \quad 1.29$$

such that a plot of k_{obs} versus $[B]$ is linear with a slope of k . Such a plot is shown in Figure 1.2.⁶ It should be noted that the units of k_{obs} are s^{-1} while the units of k are $M^{-1}s^{-1}$ for a second order reaction.

Consecutive First Order Reactions

Often a ligand substitution reaction does not stop after one substitution, but continues to more highly substituted complexes. These are known as consecutive reactions. The plots of concentration of the substituted species as a function of time are rather distinctive; a sample plot is shown in Figure 1.3.⁷ The reactions can be represented in general as



and

$$\frac{-d[A]}{dt} = k_1[A], \quad \frac{d[B]}{dt} = k_1[A] - k_2[B], \quad \frac{d[C]}{dt} = k_2[B]$$

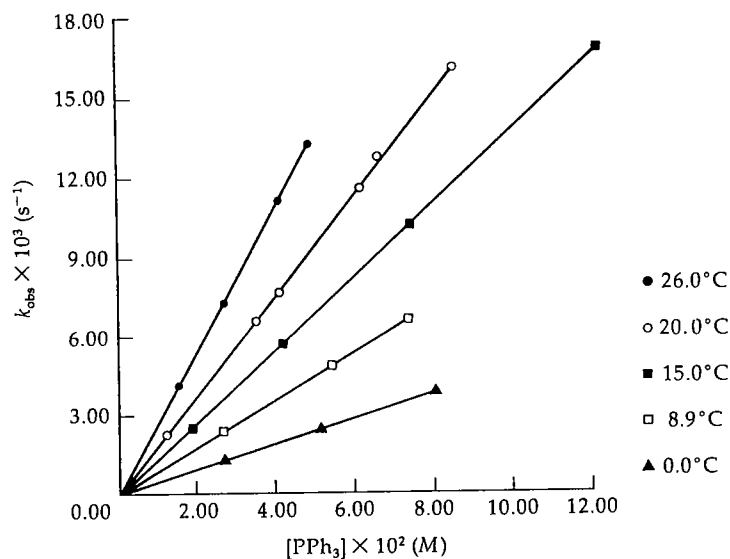


FIGURE 1.2. Plots of rate versus molar concentration of PPh_3 for substitution on $\text{V}(\text{CO})_6$ under pseudo first order conditions. Note the intersection at $k_{\text{obs}} = 20$. [Reprinted with permission from Q. Shi, T. G. Richmond, W. C. Troglor, and F. Basolo, *J. Am. Chem. Soc.* 104, 4032 (1982). Copyright 1982 American Chemical Society.]

Integrating, recognizing that at $t = 0$, $[A] = [A_0]$, $[B] = [C] = 0$, and that at any time $[A_0] = [A] + [B] + [C]$, yields

$$[A] = [A_0]e^{-k_1 t} \quad 1.32$$

$$[B] = \frac{[A_0]k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad 1.33$$

$$[C] = [A_0] \left[1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right] \quad 1.34$$

A simplifying assumption called the **steady state approximation** is often used for consecutive reactions. The assumption is that the $[B]$ is small and does not change very much during the reaction ($k_1 < k_2$):

$$\frac{d[B]}{dt} \approx 0 \quad 1.35$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \approx 0 \quad 1.36$$

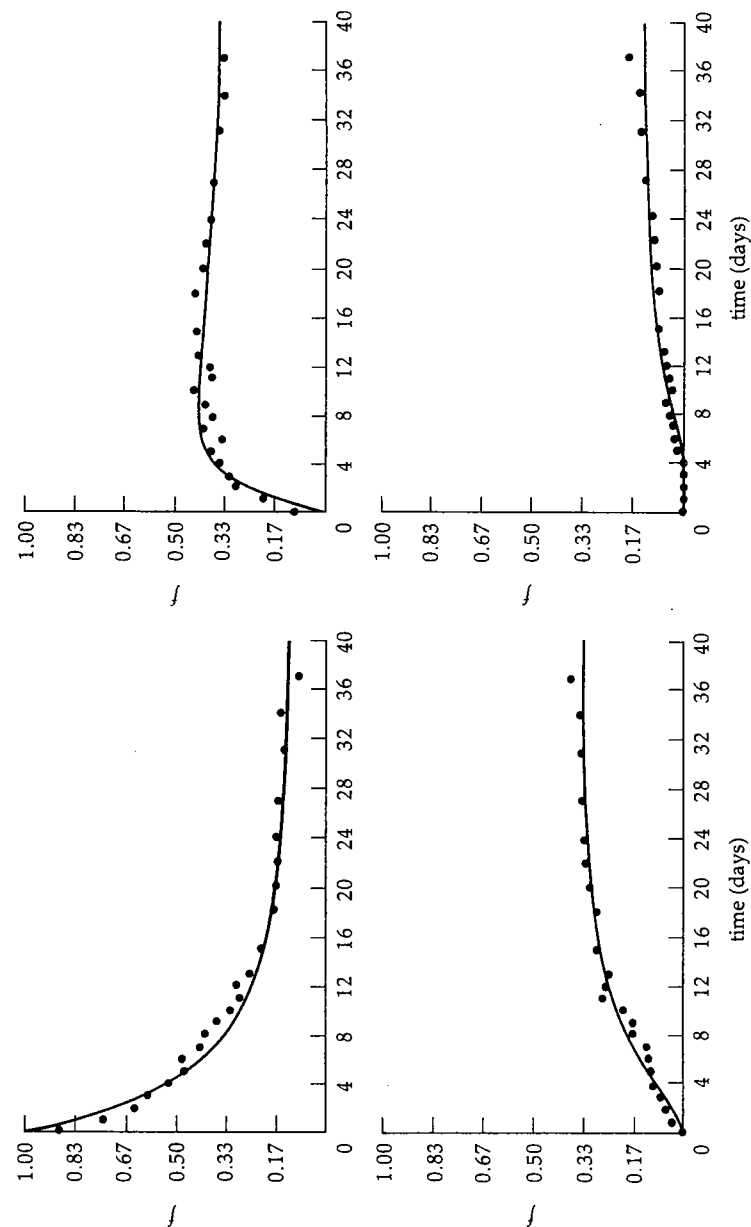


FIGURE 1.3. Plots for the enrichment of the position *cis* to Br in $\text{Mn}(\text{CO})_5\text{Br}$. The x axis is the fraction (f) of the molecules corresponding to 0, 1, 2, and 3 ^{13}CO molecules *cis* to Br. This is the pattern expected for consecutive formation of products.

$$[B] = \frac{k_1}{k_2} [A] = \frac{k_1}{k_2} A_0 e^{-kt} \quad 1.37$$

$$[C] = [A_0] - [A] - [B] \quad 1.38$$

$$= A_0 \left(1 - e^{-k_1 t} - \frac{k_1}{k_2} e^{-k_1 t} \right) \quad 1.39$$

$$\approx A_0 (1 - e^{-k_1 t}) \quad 1.40$$

As the reactions become more numerous, the analysis becomes more complicated. As long as each individual reaction is first order, a general treatment can be made.^{5,8} The treatment below is valid for any number of parallel or consecutive first order reactions. The differential equations can be represented as

$$\frac{dA_i}{dt} = -k_{i1}A_i - k_{i2}A_i - \cdots - k_{im}A_i + k_{1i}A_1 + k_{2i}A_2 + \cdots + k_{mi}A_m \quad 1.41$$

or

$$\frac{dA_i}{dt} = (-k_{i1} - k_{i2} - \cdots - k_{im}) A_i + k_{1i}A_1 + k_{2i}A_2 + \cdots + k_{mi}A_m \quad 1.42$$

where A_i is the concentration of species i ; k_{ij} is the rate constant for the reaction $A_i \rightarrow A_j$, and m is the number of species involved kinetically in the reaction. Equation 1.42 can be put into the form

$$\frac{dA_i}{dt} + \sum_{j=1}^m K_{ij} A_j = 0 \quad 1.43$$

where $K_{ij} = -k_{ji}$, except when $i = j$ and then $K_{ij} = \sum_{p=1}^m k_{ip}$ except for $p = i$.

We shall now assume a particular solution of the form usually observed,

$$A_i = B_i e^{-\lambda t} \quad 1.44$$

where A_i is the concentration of the species desired, B_i is a constant, and λ is a parameter that is yet to be determined. Substituting equation 1.44 into equation 1.43 gives

$$\lambda B_i e^{-\lambda t} + \sum_{j=1}^m K_{ij} B_j e^{-\lambda t} = 0 \quad 1.45$$

which simplifies to

$$\lambda B_i + \sum_{j=1}^m K_{ij} B_j = 0 \quad 1.46$$

and

$$\sum_{j=1}^m (K_{ij} - \delta_{ij} \lambda) B_j = 0 \text{ for } i = 1, 2, \dots, m \quad 1.47$$

where

$$\delta_{ij} = 1 \text{ if } i = j \text{ or } 0 \text{ if } i \neq j \quad 1.48$$

Equation 1.47 is the typical expression for the general eigenvalue (λ) – eigenvector (B) problem and can be solved by digital computer methods. For each λ , there is a set of relative values of B_j that are solutions of equation 1.47; we shall designate these B_{jr} . These particular solutions usually are not the solutions desired, but we can obtain a general solution as a linear combination of the particular solutions:

$$A_i = \sum_{r=1}^m B_{ir} Q_r e^{-\lambda_r t} \quad 1.49$$

where the Q_r s are the coefficients of the linear combinations and can be determined from the initial conditions.

A couple of examples serve to illustrate this analysis. For the simple example



of two consecutive reversible reactions, the secular equation is

$$\begin{vmatrix} k_{12} - \lambda & -k_{21} & 0 \\ -k_{12} & k_{21} + k_{23} - \lambda & -k_{32} \\ 0 & -k_{23} & k_{32} - \lambda \end{vmatrix} = 0 \quad 1.51$$

which can be readily solved. This analysis can be very useful in the analysis of data from isotope exchange reactions; $\text{Mn}(\text{CO})_5 \text{Br}$ reacting with ^{13}C CO serves as an example.⁷ If we assume that the intermediate generated by CO dissociation is rigid, the scheme shown in Figure 1.4 would give all possibilities, where k_c refers to dissociation *cis* to Br and k_t refers to dissociation *trans* to Br. Defining the A_i as shown in Figure 1.5, we can establish the K_{ij} in terms of k_c and k_t . Applying the initial conditions

$$A_1^0 = .945 A_0 \quad 1.52$$

$$A_2^0 = .011 A_0 \quad 1.53$$

$$A_4^0 = .044 A_0 \quad 1.54$$

$$A_3^0 = A_5^0 = A_6^0 = \cdots = A_7^0 = 0 \quad 1.55$$

[where A_i^0 is the initial concentration of A_i and A_0 is the concentration of $\text{Mn}(\text{CO})_5\text{Br}$] to equation 1.49 for $t = 0$ gives a set of twelve simultaneous linear equations, which can be solved for the Q_r . An isotopic exchange problem of this type is extremely difficult to solve without computer methods.

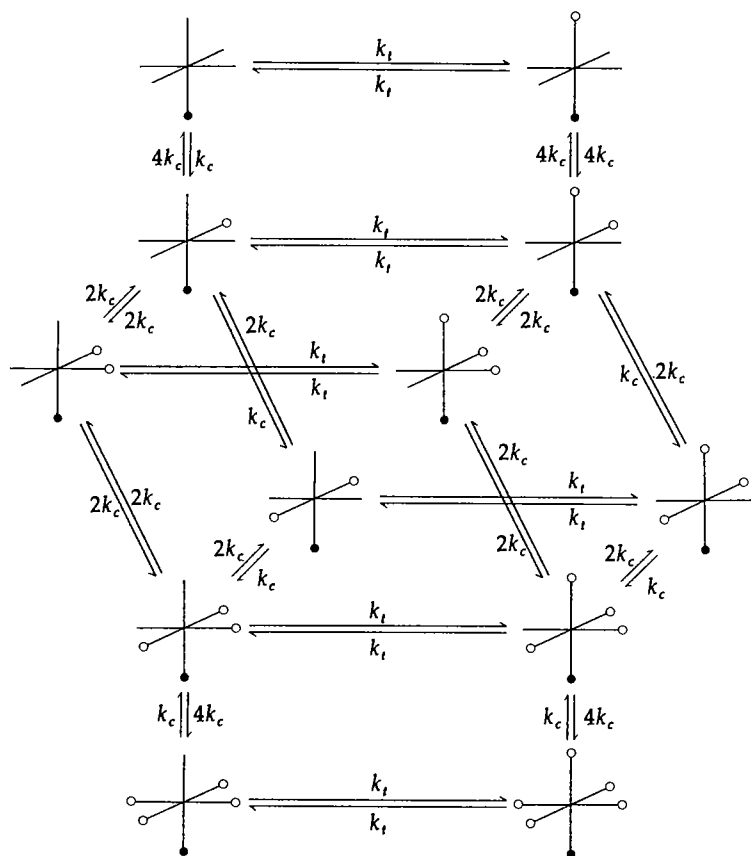


FIGURE 1.4. Scheme for isotopic exchange of ^{13}CO with $\text{Mn}(\text{CO})_5\text{Br}$ where k_c refers to dissociation of CO *cis* to Br and k_t refers to dissociation *trans* to Br.

Other Commonly Observed Rate Laws

Two other rate laws are often observed when inorganic reactions are run under pseudo first order conditions. For a number of inorganic reactions the plot of k_{obs} versus concentration of the entering ligand is linear but does not

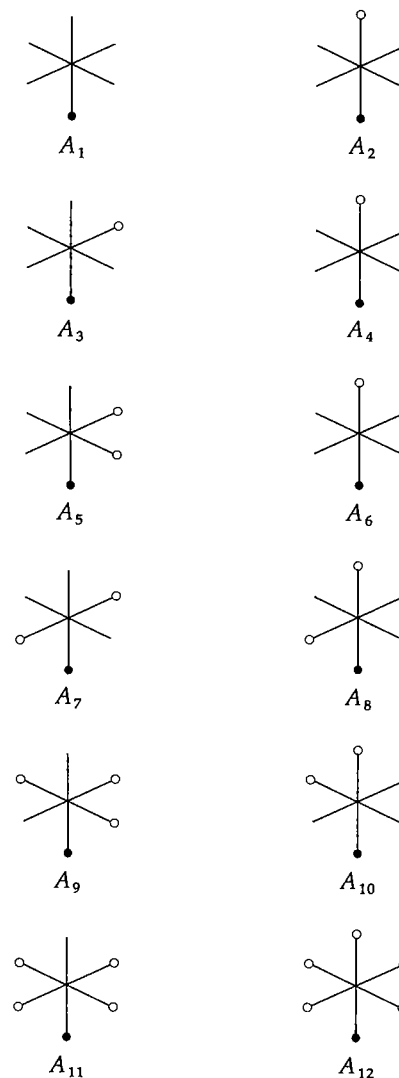


FIGURE 1.5. Definition of the A_i for isotopic labeling of $\text{Mn}(\text{CO})_5\text{Br}$.

intercept at $k_{\text{obs}} = 0$ for $[\text{L}] = 0$. A sample plot for substitution on $\text{Ir}_4(\text{CO})_{12}$ is shown in Figure 1.6 for three different entering ligands.⁹ Each ligand intercepts the y axis at a constant value of k_{obs} . This type plot is typical for the rate law

$$\text{rate} = k_1[\text{Ir}_4(\text{CO})_{12}] + k_2[\text{Ir}_4(\text{CO})_{12}][\text{L}]$$

This can be rearranged to

$$\text{rate} = (k_1 + k_2[\text{L}])[\text{Ir}_4(\text{CO})_{12}] \quad 1.57$$

$$= k_{\text{obs}}[\text{Ir}_4(\text{CO})_{12}] \quad 1.58$$

with

$$k_{\text{obs}} = k_1 + k_2[\text{L}] \quad 1.59$$

such that the plot of k_{obs} versus $[\text{L}]$ provides k_1 as the intercept and k_2 as the slope of the linear plot. This rate law indicates competing mechanisms, one ligand dependent and the other independent of $[\text{L}]$.

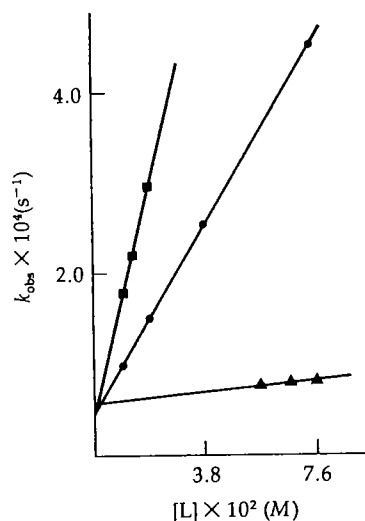


FIGURE 1.6. Plots of k_{obs} versus $[\text{L}]$ for the reaction of three different ligands with $\text{Ir}_4(\text{CO})_{12}$. The circles represent PPh_3 , the triangles, AsPh_3 , and the pluses represent P(OPh)_3 . The values of k_2 obtained from the slope are PPh_3 , $5.3 \times 10^{-3} \text{M}^{-1}\text{s}^{-1}$; AsPh_3 , $2.7 \times 10^{-4} \text{M}^{-1}\text{s}^{-1}$; and P(OPh)_3 , $1.3 \times 10^{-2} \text{M}^{-1}\text{s}^{-1}$. The value of k_1 obtained from the x -axis intercept is the same for each ligand, $6.0 \times 10^{-5} \text{s}^{-1}$. [Reprinted with permission from D. Sonnenberger and J. D. Atwood, *Inorg. Chem.* 20, 3243 (1981). Copyright 1981 American Chemical Society.]

If a reaction is composed of two steps, the first of which is a rapid preequilibrium,



the rate behavior is somewhat different. The rate of appearance of D is given by

$$\text{rate} = k_2[\text{C}] \quad \text{or} \quad k_{\text{obs}}([\text{A}] + [\text{C}]) \quad 1.61$$

Realizing that

$$\frac{[\text{C}]}{[\text{A}][\text{B}]} = K \quad 1.62$$

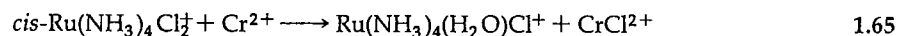
and substituting leads to

$$k_{\text{obs}} = \frac{k_2 K [\text{B}]}{1 + K [\text{B}]} \quad 1.63$$

or

$$\frac{-d\text{A}}{dt} = \frac{k_2 K [\text{A}][\text{B}]}{1 + K [\text{B}]} \quad 1.64$$

Under pseudo first order conditions with varying the initial concentrations of B , one obtains a plot of k_{obs} versus $[\text{B}]$. A sample plot is shown in Figure 1.7 for the electron transfer reaction



where $\text{A} = \text{cis-Ru}(\text{NH}_3)_4 \text{Cl}_2^+$ and $\text{B} = \text{Cr}^{2+}$.¹⁰ A rate law of the form in equation 1.64 is also observed in substitutions of classic coordination complexes.

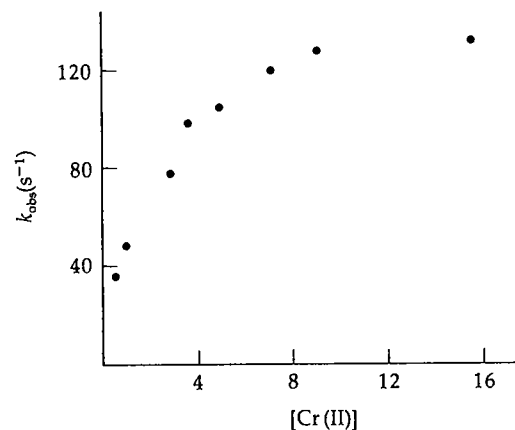


FIGURE 1.7. Plot of the observed rate constant versus concentration of $\text{Cr}(\text{II})$ in the reduction of $\text{cis-Ru}(\text{NH}_3)_4 \text{Cl}_2^+$. This shows the rate law of the form given in equation 1.64. [Reprinted with permission from W. G. Movius and R. G. Linck, *J. Am. Chem. Soc.* 92, 2677 (1970). Copyright 1970 American Chemical Society.]

For this rate law the dependence on $[B]$ varies between zero and one depending on the relative magnitude of the two terms in the denominator, $K[B]$ and 1. This rate law illustrates the care required to delineate a rate law fully since a partial investigation might be misleading.

ACTIVATION PARAMETERS

The rate law is very useful in assigning a mechanism for a reaction, but other data are also beneficial and activation parameters are usually essential. A reaction's activation parameters are derived from the temperature dependence of its rate constant. The relationship can be derived from absolute reaction rate theory,¹¹ but empirical relationships are more often used. The Arrhenius equation,

$$k = Ae^{-E_a/RT} \quad 1.66$$

where k is the rate constant for a reaction, A is a preexponential factor, E_a is the energy of activation, R is the gas constant, and T is the absolute temperature, was established a number of years ago.¹² A plot of $\ln k$ versus $1/T$

$$\ln k = -\frac{E_a}{RT} + \ln A \quad 1.67$$

gives a straight line of slope $-E_a/R$ and intercept of $\ln A$. Energies of activation are not currently cited very often; enthalpies and entropies of activation are more useful. The rate constant is related to the free energy of activation, $\Delta G^\ddagger$, by the equation

$$k = \frac{k'T}{h} e^{-\Delta G^\ddagger/RT} \quad 1.68$$

where k' is Boltzmann's constant and h is Planck's constant. Substituting

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \text{ gives}$$

$$k = \frac{k'T}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad 1.69$$

Rearranging and taking the logarithm gives

$$\ln \left(\frac{k}{T} \right) = \frac{-\Delta H^\ddagger}{RT} + \ln \left(\frac{k'}{h} \right) + \frac{\Delta S^\ddagger}{R} \quad 1.70$$

and a plot of $\ln(k/T)$ versus $(1/T)$ gives $\Delta H^\ddagger$ from the slope and $\Delta S^\ddagger$ from the intercept. This type of plot, which is called an Eyring plot, is shown in Figure 1.8.

The value of $\Delta H^\ddagger$ is not very informative regarding the mechanism. The

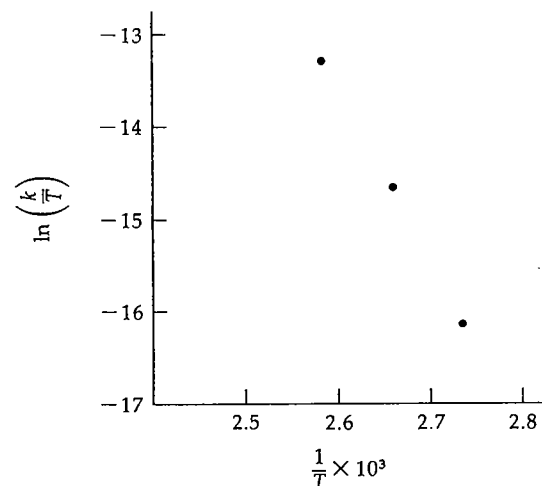


FIGURE 1.8. Plot of $\ln(k/T)$ versus $(1/T)$ giving the enthalpy of activation ($\Delta H^\ddagger$) and the entropy of activation ($\Delta S^\ddagger$) for reaction of $\text{Cr}(\text{CO})_4\text{PPh}_3(\text{P}(\text{OPh})_3)$ with CO . The values, $\Delta H^\ddagger = 36.6$ kcal/mole and $\Delta S^\ddagger = 24.4$ eu were obtained.

preted, although the value for associate reactions is usually smaller than for dissociative reactions. For dissociative reactions $\Delta H^\ddagger$ is used as a measure of the bond strength of the dissociating ligand. The entropy of activation is quite useful in determining the mechanism. Values of $\Delta S^\ddagger$ below -10 eu indicate an associative reaction, and values of greater than $+10$ eu indicate a dissociative reaction. One must be careful in interpreting the mechanism for reactions that have $\Delta S^\ddagger$ between these two limits because solvent reorganization may also contribute, especially for polar solvents and charged metal complexes.

Volume of Activation

The volume of activation is a supplement to the enthalpy and entropy of activation obtained by the variation of the rate constant with pressure:

$$\frac{d(\ln k)}{dP} = \frac{-\Delta V^\ddagger}{RT} \quad 1.71$$

The volume of activation, $\Delta V^\ddagger$, is a measure of the compressibility difference between the ground state and transition state. The $\Delta V^\ddagger$ changes with mechanism as $\Delta S^\ddagger$; a positive value indicates a dissociative mechanism, and a negative value indicates an associative mechanism. Unfortunately the volume of activation incorporates both the volume changes in the reactants and

has led to disagreement in the interpretation of volumes of activation in some cases.^{13,14}

Reaction Profiles

The energetics for a reaction are often described graphically with a reaction profile like those in Figure 1.9. The difference in energy between the reactants and the highest energy point (the transition state) is the activation energy. If there is a relative minimum in the reaction profile, then an intermediate exists and has a lifetime related to the depth of the relative minimum. Usually the data are insufficient to define all of the energy parameters in a reaction profile. Any process that accelerates a reaction must lower the activation barrier, either raising the energy of the ground state or decreasing the

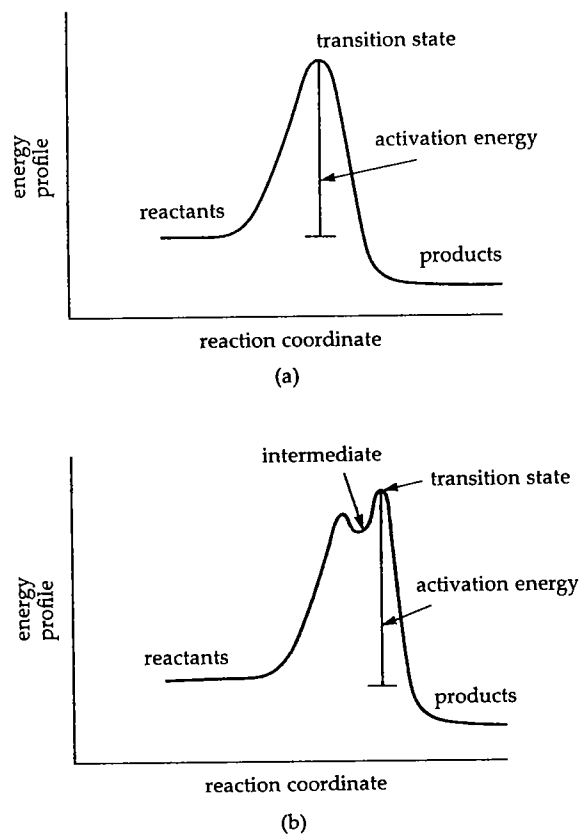


FIGURE 1.9. Reaction profiles illustrating the activation energy and the transition

energy of the transition state. Often kinetic results are interpreted in terms of only ground state changes, a practice that involves a confusion of kinetics and thermodynamics.

Microscopic Reversibility

According to the principle of microscopic reversibility, any molecular process and its reverse occur with equal rates at equilibrium.¹⁵ In mechanistic terms, microscopic reversibility means that the lowest energy path in the forward direction must also be the lowest energy path in the reverse direction. Thus if the mechanism in one direction is known, it is known in the other direction as well. The application is most straightforward for isotopic exchange of a ligand where the reverse process must be the same. This can be used to rule out certain mechanisms. For an isotopic exchange reaction it is also true that if there exists a preference for dissociation from a specific site, the entering ligand must show the same preference for that site (the low energy path in one direction must be the low energy path in the reverse direction). This has been applied to the interpretation of exchange of labeled CO on $\text{Mn}(\text{CO})_5\text{X}$.¹⁶ Another application is in reversible reactions such as the oxidative-addition and reductive-elimination of a molecule such as H_2 .

Linear Free-Energy Relationships

Although one must be careful to distinguish between kinetics and thermodynamics, it is often useful in determining the mechanism for reactions of related complexes to correlate kinetic parameters with thermodynamic ones. Such correlations are called linear free-energy relationships. A sample plot is shown in Figure 1.10 for $\text{Cr}(\text{CO})_5\text{L}$ where $\Delta G^\ddagger$ and ΔG are correlated.¹⁷ A

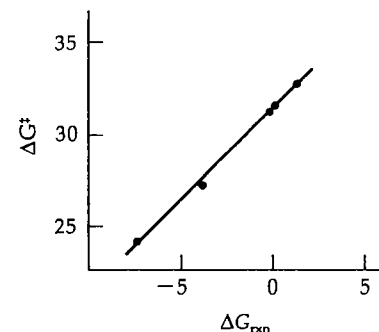


FIGURE 1.10. A linear free-energy plot of $\Delta G^\ddagger$ and ΔG_{rxn} for dissociation of L from $\text{Cr}(\text{CO})_5\text{L}$. [Reprinted with permission from M. J. Wovkulich and J. D. Atwood, *J.*

linear free-energy relationship with a slope of one is an indication that the differences in the complexes affect both the kinetic parameter (k or $\Delta G^\ddagger$) and the thermodynamic parameter (K or ΔG) in the same way — the difference in complexes has little effect on the transition state energy. Two examples serve to illustrate linear free-energy relationships. Reaction of $\text{Co}(\text{CO})_3\text{NO}$ with ligands leading to replacement of CO gives the relationship shown in Figure 1.11, where the rate is correlated with the basicity of the ligand towards a proton (the half-neutralization potential, ΔHNP).¹⁸ Several features are apparent from this relationship. Nitrogen donors of comparable basicity to phosphorus donors are considerably less reactive, but, within a series for the same donor atom, linear relationships exist. The slope of the line (2.5) indicates attack at the metal with bond formation in the transition state, consistent with the rate law, $\text{rate} = k[\text{Co}(\text{CO})_3\text{NO}][\text{L}]$. For substitution of CO on

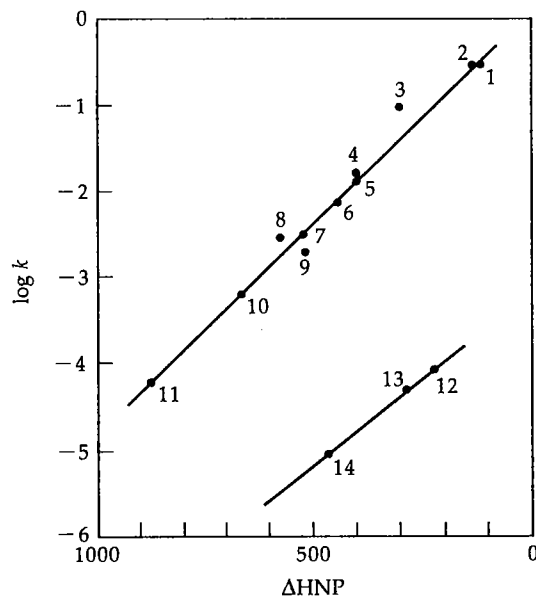


FIGURE 1.11. The linear free-energy relationships of the rate of reaction with the polarizability of the nucleophile for the reaction of $\text{CoNO}(\text{CO})_3$ with (1) $\text{P}(\text{C}_2\text{H}_5)_3$; (2) $\text{P}(\text{n-C}_4\text{H}_9)_3$; (3) $\text{P}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_2$; (4) $\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)$; (5) $\text{P}(\text{C}_6\text{H}_5)_2(\text{n-C}_4\text{H}_9)$; (6) $\text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3$; (7) $\text{P}(O\text{-n-C}_4\text{H}_9)_3$; (8) $\text{P}(\text{C}_6\text{H}_5)_3$; (9) $\text{P}(\text{OCH}_3)_3$; (10) $\text{P}(\text{OCH}_2)_3\text{CCH}_3$; (11) $\text{P}(\text{OC}_6\text{H}_5)_3$; (12) 4-picoline; (13) pyridine; (14) 3-chloropyridine. The ΔHNP measures basicity, which is believed to parallel polarizability for these compounds. [Reprinted with permission from E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.* 88, 3929 (1966). Copyright

$\text{Mo}(\text{CO})_4(\text{X-}o\text{-phen})$ with substituted orthophenanthrolines both a ligand-independent and a ligand-dependent step are seen.¹⁹ The free energy relationships for both steps as shown in Figure 1.12 are useful in assigning the mechanism.¹⁹ For the ligand-independent (k_1) step the rate increases with the ability of the *o*-phenanthroline to donate electron density, consistent with a dissociative reaction and stabilization of the transition state. For the ligand-dependent step the rate decreases with increasing ligand basicity, consistent with less nucleophilic attack for a complex with more electron density. A number of special linear free-energy relationships have been developed. Although these have been used primarily for organic reactions, there have been some applications to inorganic systems. The Hammett relationship correlates rates involving aromatic complexes with the nature and location of the substituents (*meta* and *para*) on the aromatic ring. These factors are measured as the Hammett constant σ .²⁰

$$\log \frac{k}{k_0} = \rho\sigma \quad 1.72$$

The rate constants k and k_0 are for the substituted and unsubstituted aromatic, respectively. The constant σ depends on the substituent and ρ depends on the reaction.

The Hammett constant has been effectively correlated with the rate of base hydrolysis for complexes of cobalt, $\text{Co}(\text{en})_2(\text{X-C}_6\text{H}_4\text{CO}_2)_2$, and with the oxidation potential of substituted ferrocene complexes.^{21,22} The Taft relationship, a modification of the Hammett relationship appropriate for aliphatic compounds and *ortho*-substituted aromatic species, has been applied to the base hydrolysis of alkyl carboxylate complexes of cobalt.²³ A few other specialized free energy relationships have also been used. We will discuss the Swain–Scott relationship in Chapter 2.

KINETIC TECHNIQUES

The fundamental problem in a kinetic experiment is to generate a series of concentrations of the species of interest at various times. Any technique that yields a measure of the concentration is appropriate. In the following section we shall consider a few of the most important techniques for obtaining kinetic data on inorganic systems.

Absorption Spectra

The most often used techniques involve measuring the absorption spectra in either infrared, visible, or ultraviolet spectral regions. Beer's law,

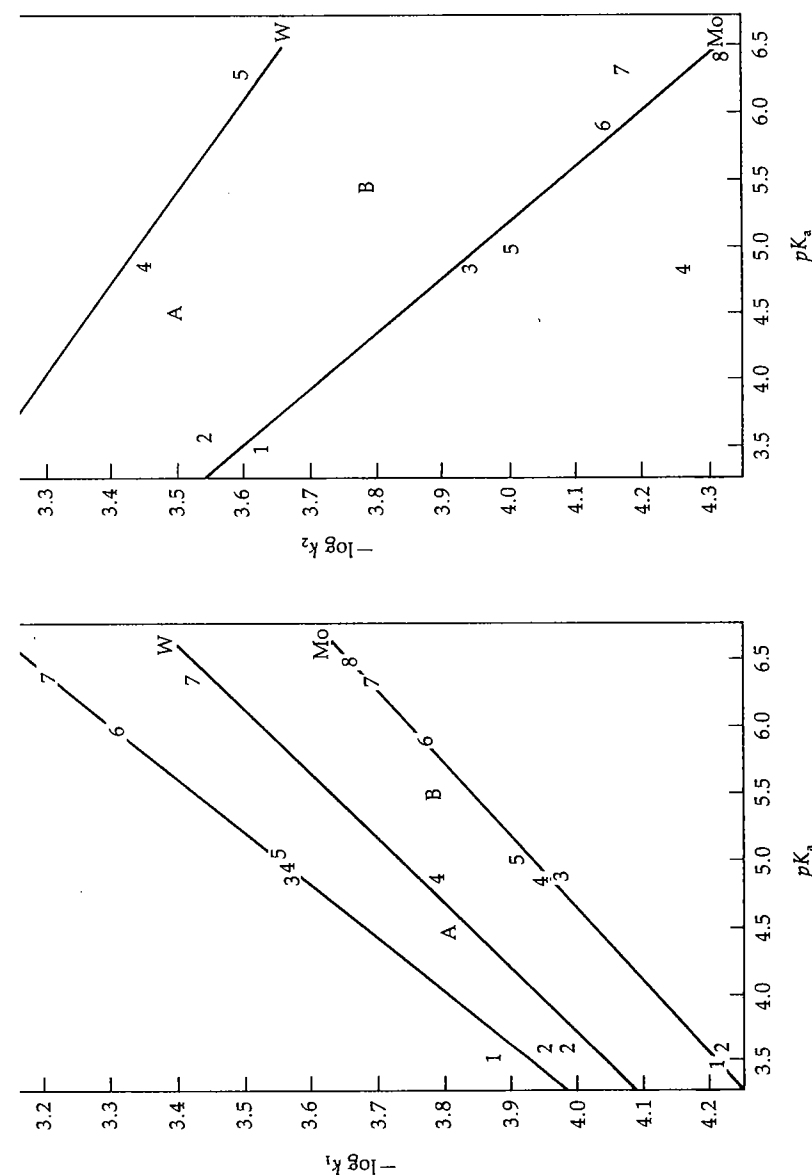


FIGURE 1.12. Linear free-energy plots for reactions of substituted orthophenanthroline complexes of the Group VI metals. Note that the ligand-independent and dependent steps depend on the pK_a in opposite ways. [Reprinted with permission from J. R. Graham and R. J. Angelici, *Inorg. Chem.* 6, 994 (1967). Copyright 1967 American Chemical Society.]

relates the concentration of a species directly to its optical absorbance, D . In equation 1.73 ϵ is the molar absorptivity and l is the path length in centimeters. Thus a measurement of the absorbance of a complex gives its concentration. Often a spectrophotometer measures the transmittance of light by a sample. The transmittance can be converted to absorbance by the equation

$$D = \log \frac{I_0}{I} \quad 1.74$$

where I_0 is the intensity of the incident light and I is the intensity of the transmitted light. These quantities are defined for an absorption spectrum in Figure 1.13. The area under an absorption curve should be used in quantitative studies; however for a single absorption that does not overlap other absorptions, the change in the absorption maximum is a useful approximation. A Beer's law plot of the quantity that is to be used versus the concentration of the absorbing species serves as a check on the procedure. Sample Beer's law plots are shown in Figure 1.14. The plot for $\text{trans-Cr(CO)}_4(\text{PBU}_3)_2$ shows deviations above $2.8 \times 10^{-4} \text{ M}$, and data collected at higher concentrations would be difficult to interpret.²⁴ The Beer's law plot serves as a check on any approximations made in the spectral analysis and on the behavior of the absorbing complex. Association or dissociation of the complex would lead to nonlinear Beer's law plots since the species formed would not have identical absorption properties and the extent of association or dissociation would vary with the concentration of the complex.

Ultraviolet and visible absorption spectra usually involve broad absorptions that overlap with other species present in solution. Although this sometimes makes interpretation of products more difficult, kinetic analysis can be done on overlapping absorption spectra. For the simple first order reaction

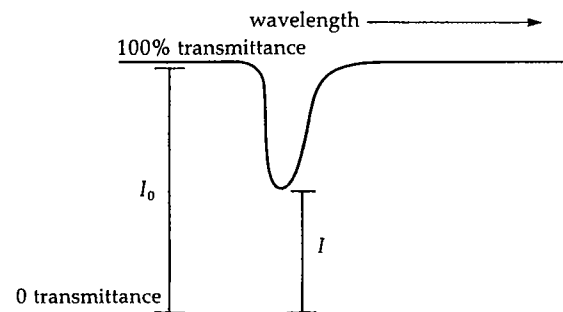


FIGURE 1.13. The definition of I_0 and I for a transmittance spectrum. The 100% transmittance is the base line for the spectrum.

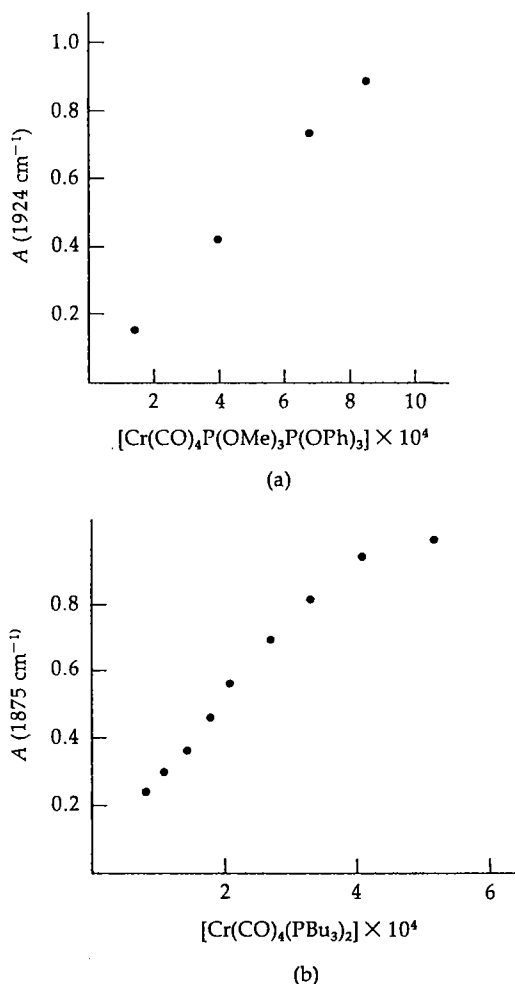


FIGURE 1.14. Beer's law plots of absorbance versus concentration for the most intense absorption of two chromium carbonyl complexes: (a) a normal linear Beer's law plot; (b) a similar complex showing deviation from linearity above $A = 0.7$. The ϵ value is $1.1 \times 10^3 \text{ M}^{-1}$ for $\text{Cr}(\text{CO})_4\text{P}(\text{OMe})_3\text{P}(\text{OPh})_3$ and 2.5×10^3 for $\text{Cr}(\text{CO})_4(\text{PBu}_3)_2$, ignoring data above $A = 0.7$.

the absorbance at any time is given by

$$D_t = \epsilon_A[A] + \epsilon_B[B]$$

and at completion by

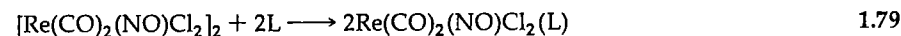
1.76

The term needed for kinetic analysis

$$\ln \frac{A_0}{A_t} = \ln \left(\frac{D_0 - D_\infty}{D_t - D_\infty} \right) = kt \quad 1.78$$

can be represented purely as absorbances. One should always keep in mind, however, that inability to completely assign the spectra from which kinetic data are obtained makes the data of limited utility.

Infrared absorption spectra are limited primarily to ligands (CO, NO, NCR, CNR, etc.) that absorb in regions of the infrared uncluttered by common solvents, but infrared absorptions are usually not overlapping and provide for straightforward analysis. In Chapter 4 we shall see that infrared monitoring is commonly practiced for carbonyl compounds. An example using the nitrosyl absorption is illustrated here.²⁴



The chloride-bridged dimer has a ν_{NO} at 1803 cm^{-1} and the product has a ν_{NO} at 1780 cm^{-1} . Monitoring the decrease in the 1803 cm^{-1} absorption yields the kinetic plots shown in Figure 1.15.²⁴ The analysis is straightforward, giving

$$\text{rate} = k[\text{Re}_2(\text{CO})_4(\text{NO})_2\text{Cl}_4][\text{L}] \quad 1.80$$

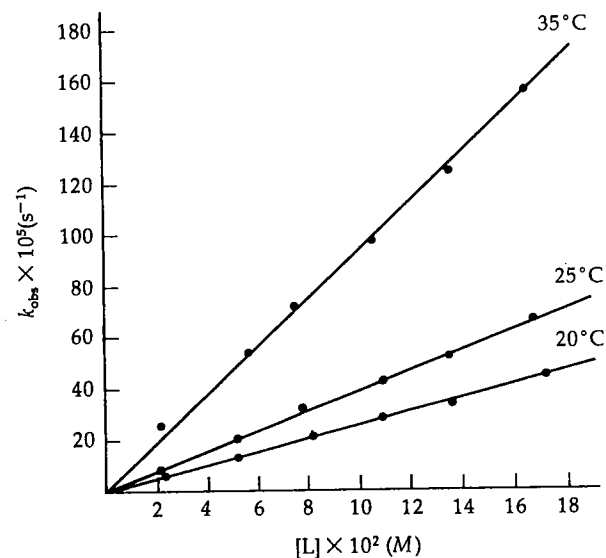


FIGURE 1.15. Kinetic results from the decrease in the absorbance of the nitrosyl (1803 cm^{-1}) of $\text{Re}_2(\text{CO})_4(\text{NO})_2\text{Cl}_4$ upon reaction with entering nucleophile. [Reprinted with permission from F. Zingales, A. Trovati, and P. Uguagliata,

The dependence on the concentration of the entering ligand suggests nucleophilic attack of L on the rhenium dimer.

Nuclear Magnetic Resonance

In contrast to the absorption spectra just considered, NMR provides data on the lifetime of systems that are at equilibrium. The time scale accessible for a typical NMR spectrum is $10^0 - 10^{-6}$ seconds, which covers a range of rates ($10^0 - 10^6 \text{ s}^{-1}$) that are not readily studied by other techniques.^{25,26} A system that undergoes exchange on a time scale appropriate for NMR investigation has changes in the NMR spectrum capable of providing rate data in the form of lifetimes τ_A which are the inverse of the rate constants.

$$\frac{-dA}{dt} = \frac{1}{\tau_A} [A], \quad k = \frac{1}{\tau_A} \quad 1.81$$

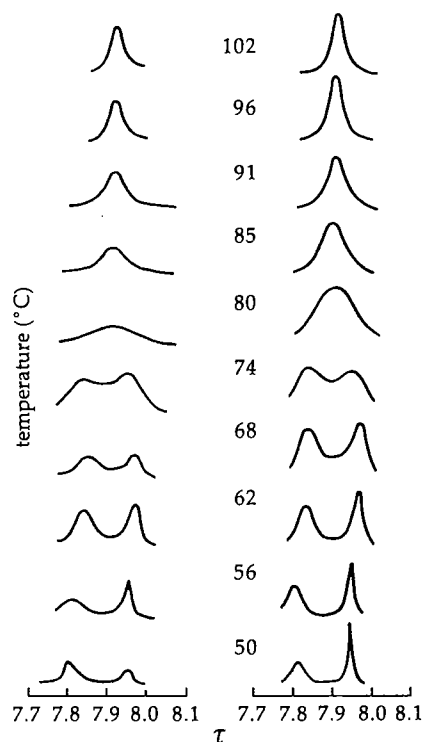


FIGURE 1.16. The proton NMR data for free and coordinated NH_3 from complexes with alkyl cobalt(III) complexes. This illustrates a two-site exchange. [Reprinted with permission from R. J. Guschl, R. Stewart and T. L. Brown, *Inorg.*

A typical set of spectra obtained at different temperatures is shown in Figure 1.16 for a two-site system (exchange occurs between two equivalent sites). The **fast-exchange** spectrum is the sharp single resonance seen at high temperature. It indicates that exchange is fast in comparison to the NMR time scale so that the environment for the proton is averaged. As the temperature is reduced the resonance begins to broaden in the near fast-exchange spectra. **Coalescence** is defined as the point just before the resonance splits into two resonances. When the two resonances are distinct but overlapping, the spectrum is said to be in the **intermediate-exchange** region. At lower temperature the two resonances are separate but broadened, and the spectrum is in the **slow-exchange** region. When no exchange is occurring, the two resonances are sharp, and the spectrum is at the **slow-exchange limit** or **stopped exchange**. Equations have been derived for the lifetime in the different regions of the spectra, such that a series of rate constants versus temperature are generated and activation parameters can be calculated. In general the preferred method for analysis of NMR data involves computer line-shape fitting, which has proven to be a powerful method, especially for fluxional molecules. The technique is illustrated in Figures 1.17 and 1.18 for $\text{H}_2\text{Fe}[\text{P}(\text{OEt})_3]_4$.²⁷ The observed spectra are shown in Figure 1.17 with the best calculated fit; other calculated possibilities are shown in Figure 1.18. This technique often provides the only way of differentiating mechanistic possibilities in fluxional molecules.

Gas Uptake

A number of the reactants of interest to inorganic chemists are gases, such as CO , H_2 and C_2H_4 . Reactions in which gases are given off or taken up can be monitored by studying the changing amount of gas over time. This is an especially important technique for homogeneously catalyzed reactions where a reactant is frequently gaseous. Since the reaction may be dependent on the pressure, a constant-pressure device is necessary. A typical model has been described (Figure 1.19).²⁸ The reaction of RuCl_2 with CO in dimethylacetamide was followed by gas uptake.²⁹



The plot of absorbed CO versus time is shown in Figure 1.20.²⁹ The CO uptake data were used to deduce $[\text{Ru}^{\text{II}}]$ by the relationship,

$$[\text{Ru}^{\text{II}}] + [\text{Ru}^{\text{II}}(\text{CO})] = [\text{Ru}^{\text{II}}]_0 \quad 1.83$$

giving

$$-d[\text{CO}] = d[\text{Ru}^{\text{II}}(\text{CO})] \quad 1.84$$

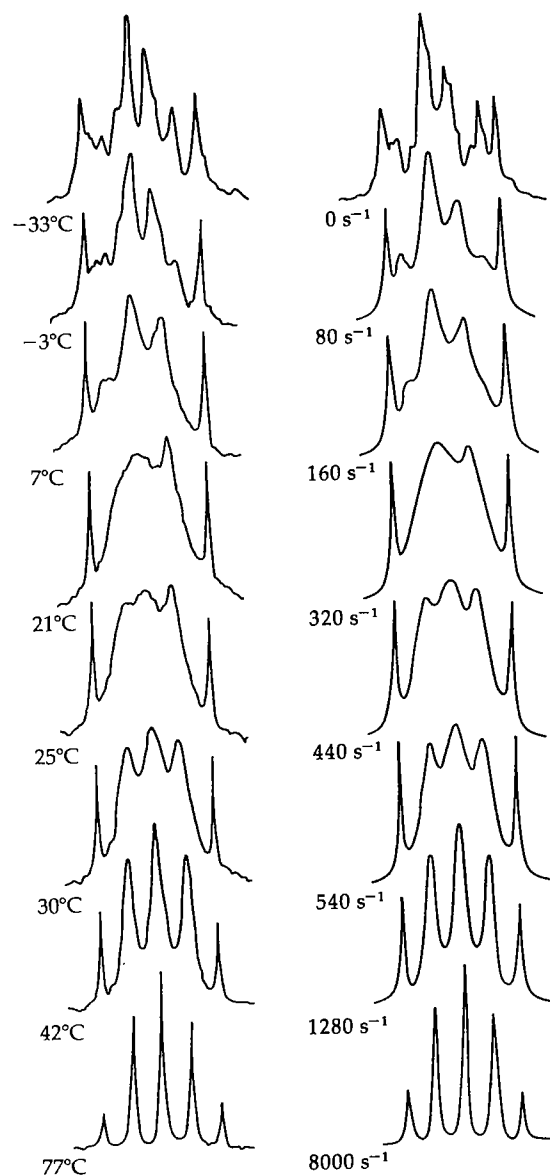


FIGURE 1.17. Calculated (best-fit) and observed 90 MHz proton NMR line shapes for $\text{H}_2\text{Fe}[\text{P}(\text{OEt})_3]_4$. [Reprinted with permission from J. P. Jesson and E. L. Muetterties, *Tetrahedron* 30, 232 (1974). Copyright 1974 Pergamon Press, Ltd.]

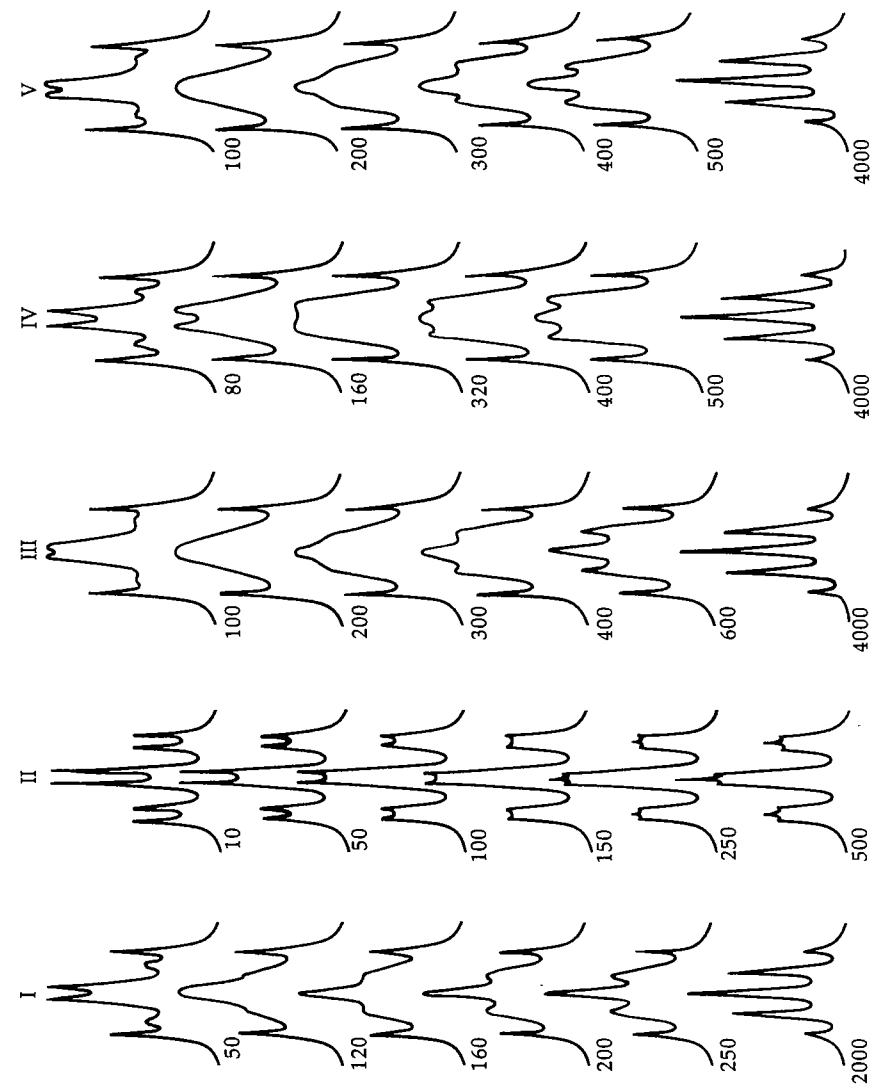


FIGURE 1.18. Line shapes calculated for different mechanistic possibilities in the fluxional behavior of $\text{H}_2\text{Fe}[\text{P}(\text{OEt})_3]_4$. [Reprinted with permission from J. P. Jesson and E. L. Muetterties, *J. Am. Chem. Soc.* 93, 4801 (1975). Copyright 1975 American Chemical Society.]

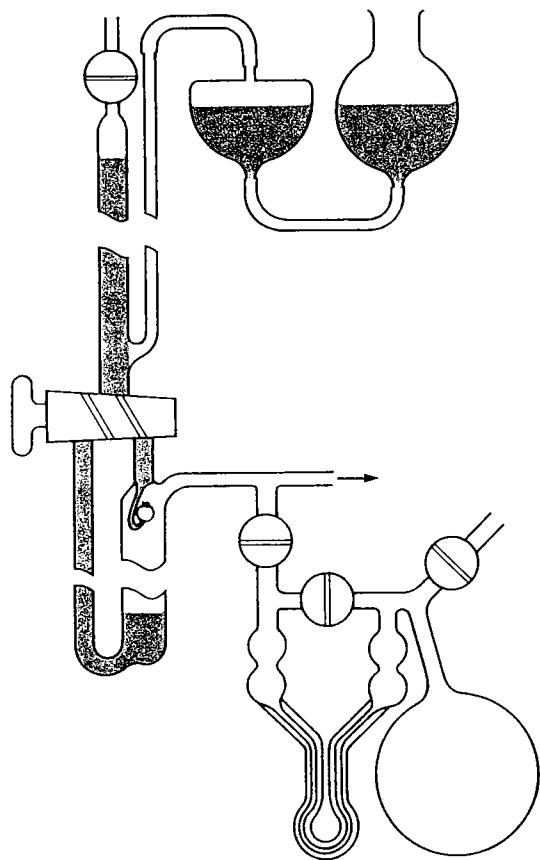


FIGURE 1.19. An apparatus for measuring the uptake of gases at constant pressure. [Reprinted with permission from J. E. Taylor, *J. Chem. Ed.* **42**, 618 (1965). Copyright 1965 Journal of Chemical Education.]

The value of k_1 was evaluated from plots such as shown in Figure 1.21.²⁹ Thus, once the concentration data were obtained the kinetic analysis was the same.

Stopped-Flow Techniques

Many reactions occur too rapidly for standard absorption spectroscopy. In the time required for sampling, the reaction would be complete. A simple technique that allows rapid reactions to be investigated is the stopped-flow

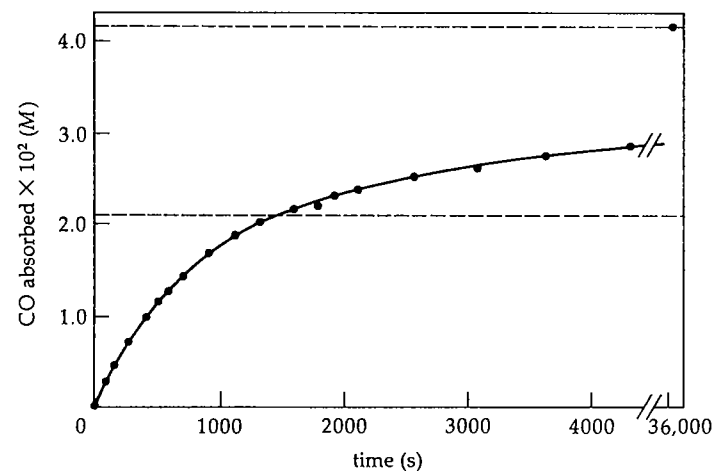


FIGURE 1.20. A plot of CO uptake versus time for reaction with Ru(II) chloride. [Reprinted with permission from B. C. Hui and B. R. James, *Can. J. Chem.* **48**, 3613 (1970). Copyright 1970 National Research Council of Canada.]

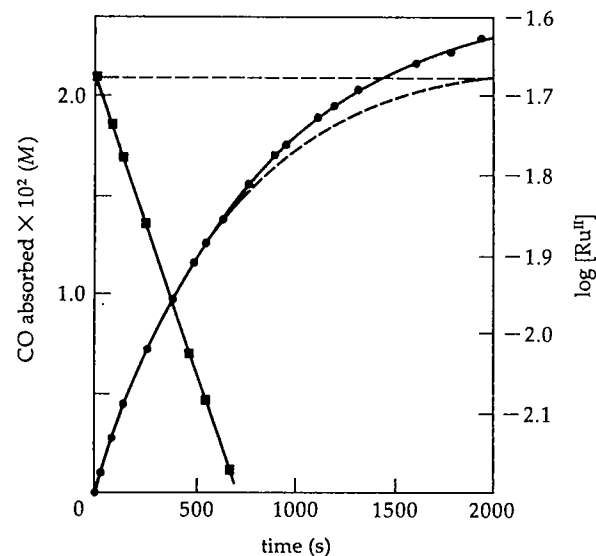


FIGURE 1.21. Kinetic plots to evaluate the rate constant from gas uptake experiments. The squares represent $\log [\text{Ru}^{\text{II}}]$ versus time. [Reprinted with permission from B. C. Hui and B. R. James, *Can. J. Chem.* **48**, 3613 (1970). Copyright 1970 National Research Council of Canada.]

technique. A schematic diagram of the apparatus is shown in Figure 1.22. The reactants are separately brought to a constant temperature, then mixed immediately prior to obtaining the spectra. The spectrometer is set on one wavenumber, and the absorbance versus time spectrum is recorded. The data are then analyzed in normal manner. The stopped-flow technique has been used primarily with ultraviolet-visible spectrophotometers, although some experiments have been done with infrared radiation.³⁰ Data for the reaction of $\text{Co}_2(\text{CO})_8$ with AsPh_3 are shown in Figure 1.23.³¹

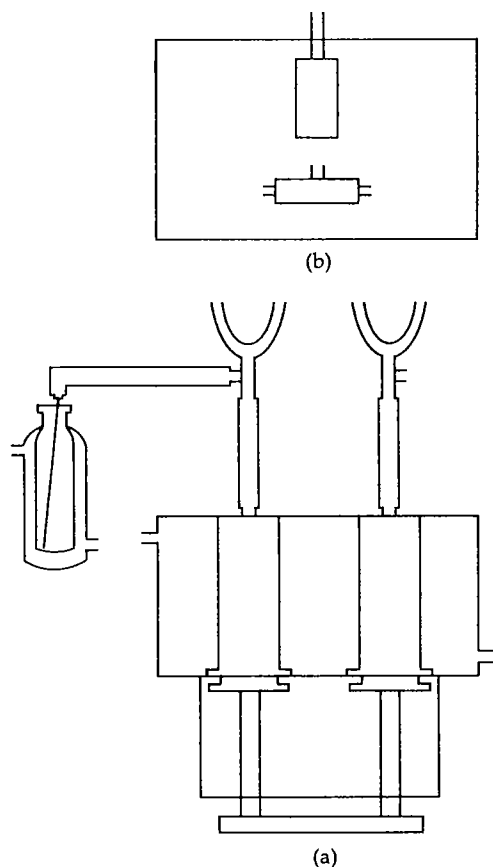


FIGURE 1.22. Schematic of a single stopped-flow apparatus. In (a), equilibrated solutions of the reactants are pulled into the syringes. The bar connecting the plungers of both syringes is pushed, and in (b) the two solutions pass through a mixer into a spectrophotometer, where the absorbance spectrum is recorded.

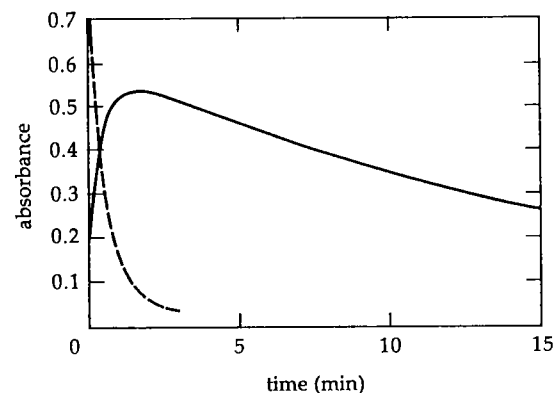
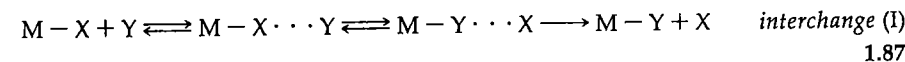
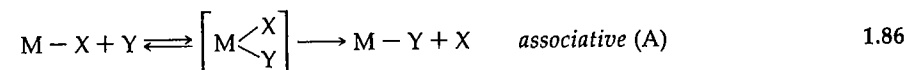
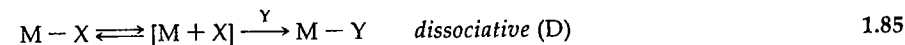


FIGURE 1.23. Typical absorbance plot obtained from a stopped-flow apparatus for reaction of $\text{Co}_2(\text{CO})_8$ with AsPh_3 . This plot shows the decrease in $\text{Co}_2(\text{CO})_8$ (dashed line, 2042 cm^{-1}) and the growth and slow decrease of $\text{Co}_2(\text{CO})_7\text{AsPh}_3$ (solid line, 1996 cm^{-1}). [Reprinted with permission from M. Absi-Halabi, J. D. Atwood, N. P. Forbus, and T. L. Brown, *J. Am. Chem. Soc.* 102, 6248 (1980). Copyright 1980 American Chemical Society.]

CLASSIFICATION OF MECHANISMS

A number of inorganic reactions can be classified according to simple mechanistic schemes.³² For many reactions the term **dissociative**, for a reaction that shows no dependence on the species reacting with the metal complex, or **associative**, for a reaction whose rate depends on the nature and the concentration of the species reacting, are sufficient. In some cases, however, a more precise distinction between mechanistic types is useful. The three basic mechanistic types are D(dissociative), A(associative), and I(interchange); each is illustrated below.



For a D mechanism an intermediate of reduced coordination number is formed; for an A mechanism an intermediate of increased coordination num-

ber is formed; and for an I mechanism no intermediate of altered coordination number is formed. Activation profiles for the D and A mechanisms are shown in Figure 1.24. The I mechanism is a concerted exchange of X and Y between the inner and outer coordination spheres of the metal. Interchange reactions may have a variety of transition states, but we shall distinguish two possibilities: I_a , in which the transition state displays substantial bonding of the metal to both the entering and leaving groups and in which there is some dependence of rate on the entering group; and I_d , in which the transition state has only very weak bonding to the entering and leaving groups in the transition state and there is a very slight dependence of the rate on the entering group. These are usually referred to as associative interchange (I_a) and dissociative interchange (I_d).

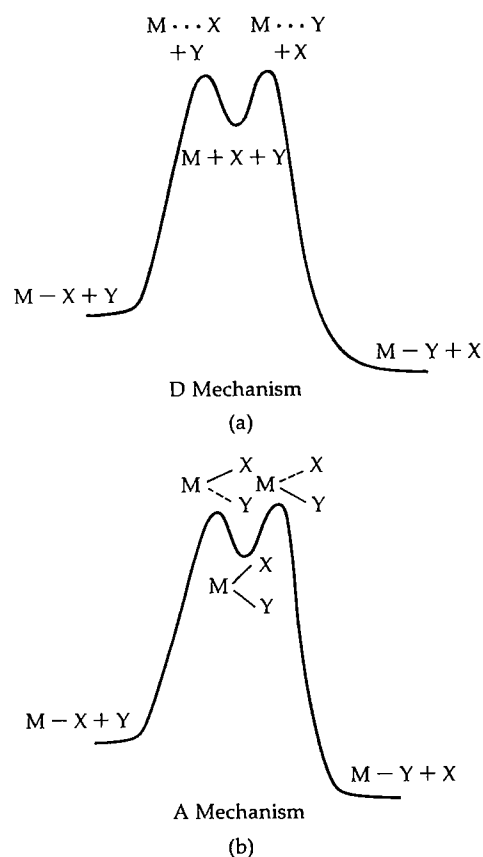


FIGURE 1.24. Energy profiles for (a) dissociative and (b) associative reactions.

The four possibilities can be separated as follows: If the rate shows a dependence on the entering group (nature and concentration) then it is either A or I_a ; if there is no dependence on the entering group then the mechanism is D or I_d . These two mechanisms, D and I_d , can be distinguished on the basis of whether an intermediate of reduced coordination number exists or not. This may be a difficult distinction to make since the primary difference is in the depth of the minimum in the energy profile (Figure 1.24). Most often competition experiments are accomplished to test the selectivity towards entering groups. Similar considerations can be used to differentiate I_a and A mechanisms.

REFERENCES

1. R. G. Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes* (Boston: Allyn and Bacon, 1974).
2. I. Amdur and G. G. Hammes, *Chemical Kinetics* (New York: Academic Press, 1966).
3. S. W. Benson, *The Foundation of Chemical Kinetics* (New York: McGraw-Hill, 1960).
4. W. C. Gardiner, Jr., *Rates and Mechanisms of Chemical Reactions* (New York: W. A. Benjamin, 1969).
5. A. A. Frost and R. G. Pearson, *Kinetics and Mechanisms* (New York: John Wiley, 1961).
6. Q. Shi, T. G. Richmond, W. C. Trogler, and F. Basolo, *J. Am. Chem. Soc.* **104**, 4032 (1982).
7. J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.* **98**, 3155 (1976).
8. F. A. Matsen and J. L. Franklin, *J. Am. Chem. Soc.* **72**, 3337 (1950).
9. D. Sonnenberger and J. D. Atwood, *Inorg. Chem.* **20**, 3243 (1981).
10. W. G. Movius and R. H. Linck, *J. Am. Chem. Soc.* **92**, 2677 (1970).
11. L. P. Hammett, *Physical Organic Chemistry*, 2nd ed. (New York: McGraw-Hill, 1970).
12. S. Arrhenius, *Z. Phys. Chem.* **4**, 226 (1889).
13. C. H. Langford, *Inorg. Chem.* **18**, 3288 (1979).
14. T. W. Saddle, *Inorg. Chem.* **19**, 3203 (1980).
15. R. L. Burwell, Jr. and R. G. Pearson, *J. Phys. Chem.* **70**, 300 (1966).
16. T. L. Brown, *Inorg. Chem.* **7**, 2673 (1968).
17. M. J. Wovkulich and J. D. Atwood, *J. Organomet. Chem.* **184**, 77 (1979).
18. E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.* **88**, 3929 (1966).
19. J. R. Graham and R. J. Angelici, *Inorg. Chem.* **6**, 992 (1967).
20. L. P. Hammett, *J. Am. Chem. Soc.* **59**, 96 (1937).
21. F. Aprile, V. Cagliotti, and G. Illuminati, *J. Inorg. Nucl. Chem.* **21**, 325 (1961).
22. W. F. Little, C. N. Reilley, J. D. Johnson, and A. P. Sanders, *J. Am. Chem. Soc.* **86**, 1382 (1964).
23. W. E. Jones and J. D. R. Thomas, *J. Chem. Soc. (A)*, 1481 (1966).
24. F. Zingales, A. Trovati, and P. Uguagliati, *Inorg. Chem.* **10**, 510 (1971).
25. K. Vrieze and P. W. N. M. van Leeuwen, *Prog. Inorg. Chem.* **14**, 1 (1971).
26. R. S. Drago, *Physical Methods in Chemistry* (Philadelphia: W. B. Saunders, 1977).
27. J. P. Jesson and E. L. Muetterties, *J. Am. Chem. Soc.* **93**, 4701 (1971).
28. J. E. Taylor, *J. Chem. Ed.* **42**, 618 (1965).
29. B. C. Hui and B. R. James, *Can. J. Chem.* **48**, 3613 (1970).
30. S. E. Rudolph, L. F. Charbonneau, and S. G. Smith, *J. Am. Chem. Soc.* **95**, 7083 (1973).

REFERENCES

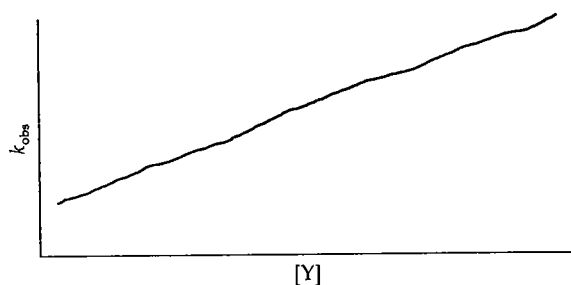
31. M. Absi Halabi, J. D. Atwood, N. P. Forbes, and T. L. Brown, *J. Am. Chem. Soc.* **102**, 6247 (1980).
32. C. H. Langford and H. B. Gray, *Ligand Substitution Processes* (New York: W. A. Benjamin, 1965).

PROBLEMS

- Derive the integrated rate equation for a reversible first order process.
- From the data below calculate E_a , $\Delta H^\ddagger$, and $\Delta S^\ddagger$.

$T(^{\circ}\text{C})$	$k(\text{s}^{-1})$
30.1	6.7×10^{-5}
40.2	3.3×10^{-4}
47.8	1.0×10^{-3}

- For the substitution reaction $\text{ML}_5\text{X} + \text{Y} \rightarrow \text{ML}_5\text{Y} + \text{X}$, which goes to completion, the rate was studied under conditions of excess ligand Y.
 - How can one determine the order of the reaction in ML_5X from a single kinetics run?
 - Assuming the reaction is first order in ML_5X , one obtains the following plot:



Write the general form of the rate law for substitution, and express the constant(s) in terms of the slope and/or intercept.

- The following data were obtained for the reaction $\text{Cr}(\text{CO})_4(\text{PPh}_3)_2 + \text{CO} \rightarrow \text{Cr}(\text{CO})_5\text{PPh}_3 + \text{PPh}_3$.

k	$T(^{\circ}\text{C})$
1.96×10^{-4}	50
4.29×10^{-4}	55
8.73×10^{-4}	60

Derive the enthalpy and entropy of activation ($\Delta H^\ddagger = 31.3$ kcal/mole, $\Delta S^\ddagger = 21.2$ eu). Calculate the rate constant for the reaction at 40°C and at 130°C . Which

PROBLEMS

- Given the following absorbance-versus-time data, calculate the rate constant for reaction of $\text{Cr}(\text{CO})_4(\text{P}(\text{OPh})_3)\text{AsPh}_3$ at 70°C :

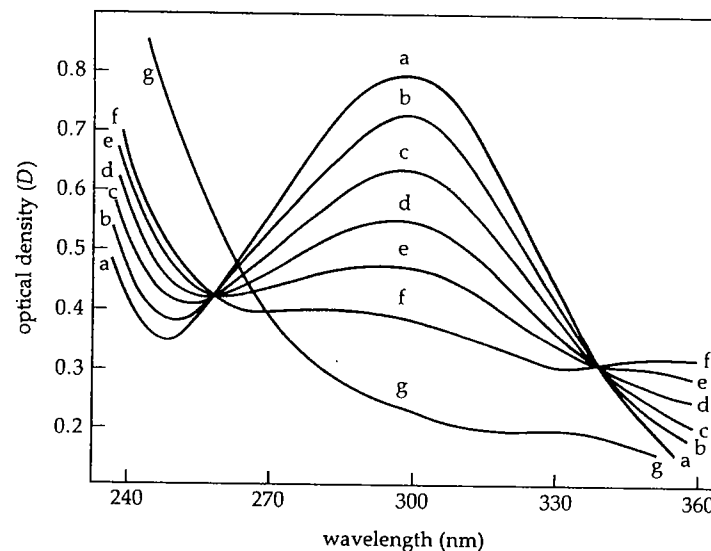
$A(1913\text{ cm}^{-1})$	time (min)
0.374	2
0.312	7
0.259	14
0.203	22
0.155	32
0.108	43
0.078	54
0.050	67

- Given the following data calculate all the rate parameters for the reaction of $(\eta^5\text{-C}_9\text{H}_7)\text{Mo}(\text{CO})_3\text{Br}$ with L in THF. [A. J. Hart-Davis, C. White, and R. H. Mawby, *Inorg. Chim. Acta* 4, 441 (1970).]

$T(^{\circ}\text{C})$	ligand	ligand concentration (M)	$10^4 k_{\text{obs}} (\text{s}^{-1})$
5.0	$\text{P}(\text{OMe})_3$	0.065	2.62
		0.149	4.22
		0.222	5.55
		0.286	6.64
		0.391	8.52
8.8	PPh_3	0.422	8.98
		0.046	3.25
		0.093	3.25
		0.140	3.40
		0.287	3.96
10.0	$\text{P}(\text{OMe})_3$	0.298	4.03
		0.094	6.61
		0.208	9.26
		0.248	11.2
		0.410	15.6
15.0	PPh_3	0.097	8.04
		0.146	8.45
		0.230	8.82
		0.299	9.08
		0.388	9.68
	$\text{P}(\text{n-Bu})_3$	0.094	16.3
		0.135	21.2

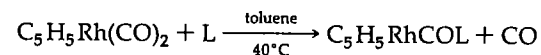
$T(^{\circ}\text{C})$	ligand	ligand concentration (M)	$10^4 k_{\text{obs}} (\text{s}^{-1})$
19.5	P(OPh) ₃	0.195	28.0
		0.248	32.3
		0.317	40.3
		0.105	7.87
		0.223	8.12
		0.296	8.22
	P(OMe) ₃	0.098	12.6
		0.133	14.0
		0.193	16.4
		0.231	17.7
		0.297	20.4
		0.099	20.6
20.0	PPh ₃	0.153	23.7
		0.192	26.4
		0.231	28.3
		0.300	33.0
		0.075	15.2
		0.152	15.8
25.7	PPh ₃	0.256	16.6
		0.366	16.7
		0.389	18.3
		0.041	34.9
		0.082	35.1
		0.216	37.4
		0.294	38.1

7. Given the absorption spectra below, calculate the rate constant for deoxygenation of $[(\text{NH}_3)_2\text{en}_2\text{Co}(\mu\text{-O}_2)\text{Co}(\text{NH}_3)_2\text{en}_2]^{4+}$.



Change in absorption spectra of $8 \times 10^{-5} \text{ M } [(\text{en})_2(\text{NH}_3)\text{Co}^{\text{III}}(\mu\text{-O}_2^-)\text{Co}^{\text{III}}(\text{NH}_3)(\text{en})_2]^{4+}$ in 0.01 M NaClO_4 solution at approximately 17°C (a) immediately after dissolution; (b) after 10 min; (c) after 20 min; (d) after 35 min; (e) after 55 min; (f) after 2 hr; (g) after 2 days. [Y. Sasaki, K. Z. Suzuki, A. Matsumoto, and K. Saito, *Inorg. Chem.* **21**, 1825 (1982).]

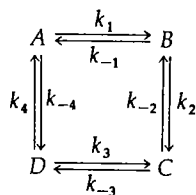
8. Given the following kinetic data for substitution on $\text{CpRh}(\text{CO})_2$, derive the rate law and suggest a mechanism for substitution:



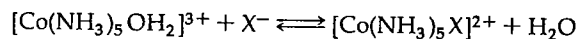
L	$[\text{C}_5\text{H}_5\text{Rh}(\text{CO})_2]$ (M)	[L] (M)	$10^5 k_{\text{obs}}$ (s^{-1})	$10^4 k$ ($\text{M}^{-1} \text{s}^{-1}$)
P(<i>n</i> -C ₄ H ₉) ₃	0.004	0.053	17.5	33
P(<i>n</i> -C ₄ H ₉) ₃	0.008	0.122	38.3	32 ^a
P(<i>n</i> -C ₄ H ₉) ₃	0.012	0.188	66	35
P(<i>n</i> -C ₄ H ₉) ₃	0.002	0.245	86	34
P(<i>n</i> -C ₄ H ₉) ₃	0.008	0.410	130	32 ^a
P(<i>n</i> -OC ₄ H ₉) ₃	0.0024	0.088	3.55	4.0
P(<i>n</i> -OC ₄ H ₉) ₃	0.0013	0.147	5.6	3.8
P(<i>n</i> -OC ₄ H ₉) ₃	0.0024	0.234	8.0	3.4
P(<i>n</i> -OC ₄ H ₉) ₃	0.0012	0.660	25.3	3.8

^a The reaction was followed by the rate of CO evolution. Other data were obtained by the infrared method.

9. Set up the differential equations and the secular equation for the scheme below.



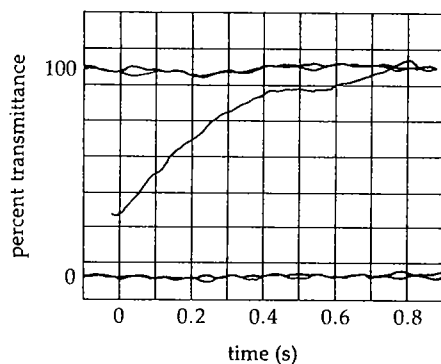
10. Given the data below for the reaction



where k_a is for the aquation, derive a linear free-energy relationship, and discuss the implications. [A. Haim, *Inorg. Chem.* 9, 426 (1970).]

X^{-1}	$k_a(\text{s}^{-1})$	$K_{\text{eq}}(\text{M}^{-1})$
NCS^-	4.1×10^{-10}	2.7×10^3
N_3^-	2.1×10^{-9}	8.3×10^2
F^-	8.6×10^{-8}	25
Cl^-	1.7×10^{-6}	1.11
Br^-	6.5×10^{-6}	0.35
NO_3^-	2.7×10^{-5}	0.08

11. Below is shown the plot of the infrared spectrum at 1658 cm^{-1} that resulted from a stopped-flow investigation of the reaction of a 0.02 M solution of a ketone with 0.24 M cyclopentylmagnesium bromide. Calculate the rate constant. [S. E. Rudolph, L. F. Charbonneau, and S. G. Smith, *J. Am. Chem. Soc.* 95, 7083 (1973).]

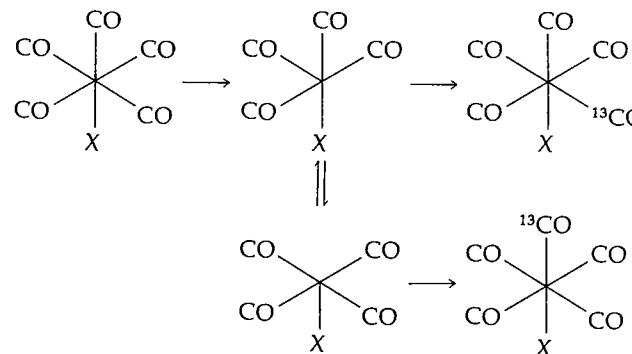


12. Given the data below for O_2 uptake by $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$, derive the form of the rate law. [P. B. Chock and J. Halpern, *J. Am. Chem. Soc.* 88, 3511 (1966).]

partial pressure

$\text{O}_2 (\text{mm})$	$k_{\text{obs}}(\text{s}^{-1})$
242	1.21×10^{-4}
371	1.93×10^{-4}
473	2.48×10^{-4}
630	3.25×10^{-4}

13. What is wrong with the scheme shown below for isotopic enrichment in $\text{Mn}(\text{CO})_5\text{X}$?

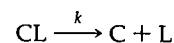


14. The competition ratio is the ratio of reaction rates for two separate species with one reactant. This is most often used to test the ability of an intermediate to discriminate between two possible reactants. Values of the competition ratio between the ligand L and piperidine for $\text{Mo}(\text{CO})_5$ are shown below.

L	competition ratio
$\text{P}(\text{OMe})_3$	0.74
PPh_3	0.85
AsPh_3	1.0

What information on the nature of the intermediate does this provide?

15. C. D. Falk and J. Halpern have studied the kinetic isotope effect in the reaction $\text{trans-Pt}(\text{PR}_3)_2\text{LCl} + \text{py} \rightarrow \text{Pt}(\text{PR}_3)_2\text{pyL}^+ + \text{Cl}^-$ L = H^- or D^- and found $k_{\text{H}}/k_{\text{D}} = 1.4$. The Pt-H stretching frequency is 2183 cm^{-1} in the ground state. Make some reasonable assumptions, and calculate the Pt-H stretching frequency in the transition state during substitution. [C. D. Falk and J. Halpern, *J. Amer. Chem. Soc.* 87, 3003 (1965).]
16. The $\Delta G^\ddagger$ values for the kinetic process involving rate-determining loss of ligand L from a complex CL,



are as follows:

L	$\Delta G^\ddagger$ (kcal/mole)
CH ₃ OH	13.0
CH ₃ CN	14.7
S(CH ₃) ₂	17.4
N(CH ₃) ₃	18.3
Ph ₃	18.5
Py	18.7
CH ₃ NC	20.1
P(OCH ₃) ₃	20.2
imidazole	21.1
P(<i>n</i> -C ₄ H ₉) ₃	23.5

Using these values and linear free-energy concepts, derive a set of ligand dissociation parameters δ_L . For the reaction $\text{CoNO}(\text{CO})_3 + \text{L} \rightarrow \text{CoNO}(\text{CO})_2\text{L} + \text{CO}$ the rate law is as follows:

$$\text{rate} = k_2[\text{Co}(\text{NO})(\text{CO})_3][\text{L}]$$

The rates at comparable conditions for some L are

ligand	$k(M^{-1} s^{-1})$
P(<i>n</i> -Bu) ₃	9.2×10^{-2}
P(OCH ₃) ₃	1.8×10^{-3}
Ph ₃	1.0×10^{-3}
Py	3.9×10^{-5}

Do these data correlate with the δ_L values derived above? Discuss the reasons for the observed relationship or the lack of it.

Ligand Substitution Reactions on Square Planar Complexes

Square planar complexes are often formed when the metal ion contains eight electrons in its *d*-orbitals as in complexes of Pt(II), Pd(II), Ni(II), Au(III), Rh(I), and Ir(I). Square planar complexes are invariably spin-paired (diamagnetic). Substitution reactions of square planar complexes of Rh(I) and Ir(I) are evidently rapid, but have not been studied extensively. Square planar complexes also undergo oxidative-addition reactions which are considered in Chapter 5. The most thoroughly studied substitution reactions are those of Pt(II) complexes, and we shall discuss these in some detail in this chapter. Reactions of complexes of Pd(II), Au(III), and Ni(II) will also be considered briefly. The first four references listed at the end of the chapter contain good general reviews of square planar substitution reactions.

SUBSTITUTION REACTIONS

The reaction that we are considering is substitution of one ligand for another on *trans*-Pt(T)(L)₂X, where X is the leaving group, T is the ligand *trans* to the leaving group and the Ls are ligands *cis* to the leaving group.



The substitution reaction proceeds with retention of the configuration at the metal as shown in Figure 2.1. Reactions 2.2 and 2.3 below show the stereochemistry of substitutions on square planar complexes.⁵

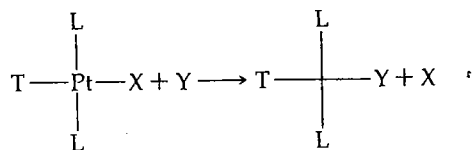
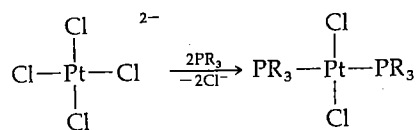
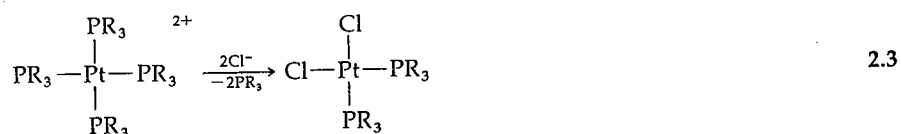
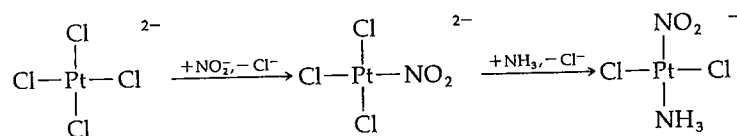
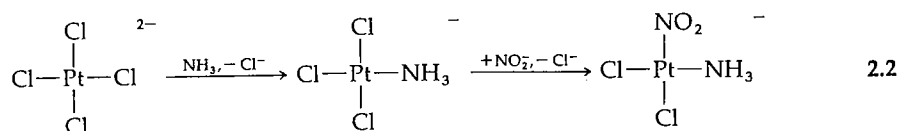
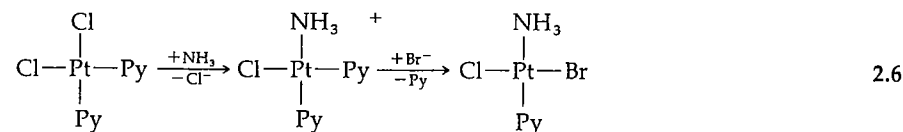
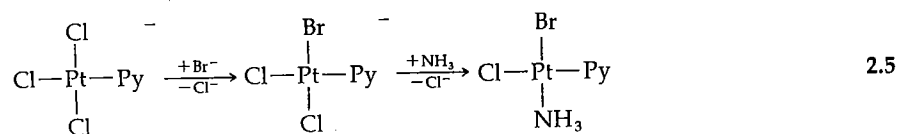
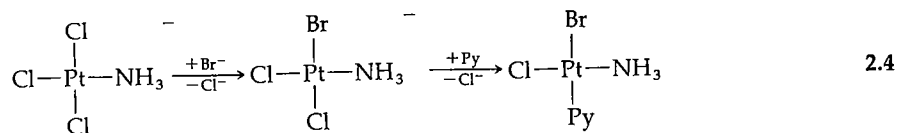


FIGURE 2.1. Substitution reactions of square planar complexes proceed with retention of stereochemistry.

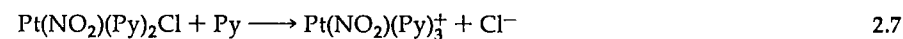


These reactions indicate that the order of addition of reagents can affect product geometry. The following substitution reactions show the preparation of the three isomers of $\text{Pt}(\text{Py})(\text{NH}_3)(\text{Cl})(\text{Br})$.

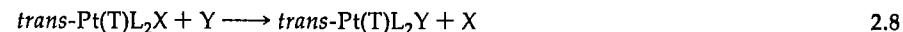


A combination of the effect of the *trans* ligand (*trans* effect) and the group that is being substituted (leaving-group effects) lead to the observed products in these reactions. Each of these is discussed later in this chapter.

Studies of the kinetics of the reaction show a dependence on the concentration of the entering ligand as shown in Table 2.1 and Figure 2.2 for the reaction of $\text{Pt}(\text{Py})_2(\text{NO}_2)\text{Cl}$ with pyridine (Py).



Under pseudo first order conditions, plots of $\ln [\text{metal complex}]$ versus time are linear with a slope of k_{obs} . Varying the initial concentration of the ligand (always under pseudo first order conditions) gives plots such as those shown in Figure 2.2 from which k_1 is derived as the intercept and k_2 as the slope. Thus the rate law for the reaction



has a ligand-independent and a ligand-dependent term. The ligand-dependent term (k_2) can be readily understood in terms of nucleophilic attack by the entering ligand. A square planar complex is coordinatively unsaturated and hence has a site for attack and an orbital available along the *z* axis. Addition of the two-electron ligand Y to the square planar species leads to a coordinatively saturated 18-electron intermediate. Data presented in a subsequent

TABLE 2.1

Dependence on $[\text{Py}]$ of the Rate of Substitution of Cl^- on $\text{Pt}(\text{NO}_2)(\text{Py})_2\text{Cl}$ in Nitromethane at 25°C .⁶

$[\text{Py}](\text{M})$	$k_{\text{obs}}(\times 10^3 \text{s}^{-1})$
0.02	0.703
0.05	0.832
0.10	1.35
0.20	1.86
0.30	2.20
0.40	2.96
0.50	3.60

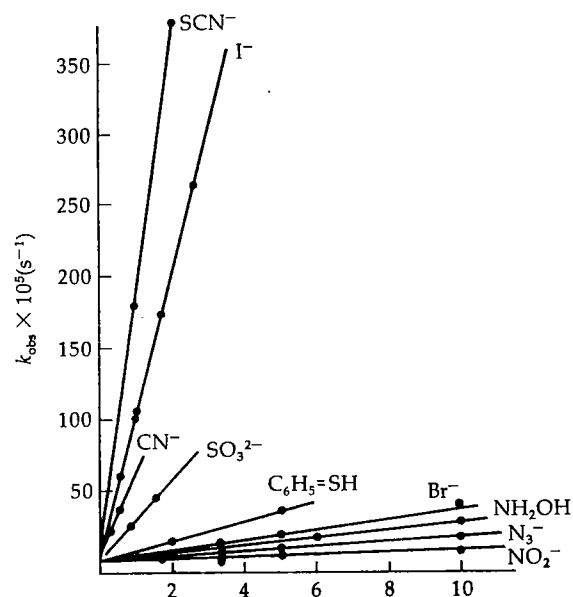


FIGURE 2.2. Rates of reaction of $\text{trans-[Pt(Py)}_2\text{Cl}_2\text{]}$ with various nucleophiles in methanol at 30°C. [Reprinted with permission from U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.* **87**, 241 (1965). Copyright 1965 American Chemical Society.]

section show the dependence of the rate of the substitution reaction on the nucleophilicity of the entering ligand.

The ligand-independent pathway could have several possible explanations; the one that is generally accepted involves attack of the solvent on the square planar complex. In this reaction the solvent becomes the entering nucleophile in the rate-determining step. The scheme showing both first and second order pathways is illustrated in Figure 2.3. The similarity of the two pathways is a strong feature in support of this mechanism, especially since the solvents often used, H_2O , CH_3OH , etc., have electron pairs and can be nucleophiles. The large excess in solvent concentration leads to the observed first order kinetics and makes up for the generally lower nucleophilicity of the solvent. That the first order step is not dissociation of a ligand but is dependent on the nature of the solvent is shown by the solvent dependence of the first order rate constant for reaction 2.7 (Table 2.2). This strong dependence of the first order rate constant on the nature of the solvent is consistent with direct nucleophilic attack by the solvent on the square planar complex. As we proceed, we shall find that all evidence supports this mechanism.

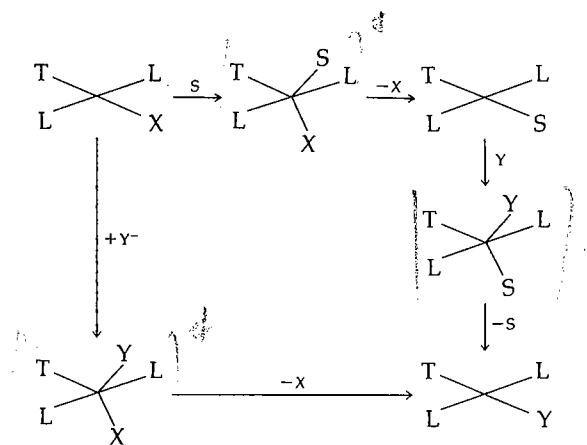


FIGURE 2.3. Associative mechanism for attack of ligand Y^- and of solvent S on a square planar complex.

TRANS EFFECT

The overriding consideration in studies of substitution reactions on Pt(II) was the effect on the rate of the ligand *trans* to the substitution site.⁵ The *trans* effect was recognized as early as about 1900 and played an important role in preparations of different isomers as shown in reactions 2.1–2.6.

The effect of a series of *trans* ligands on substitution of pyridine for chloride on $\text{trans-Pt(PEt}_3)_2\text{LCl}$ was determined.⁷

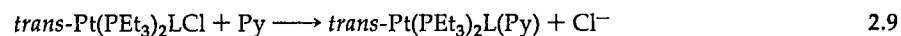


TABLE 2.2

Effect of Solvent on the Rate Constant for the First Order Step
 $\text{Pt(NO}_2\text{)(Py)}_2\text{Cl} + \text{Py} \longrightarrow \text{Pt(NO}_2\text{)(Py)}_3^+ + \text{Cl}^-$ at 30°C.⁶

solvent	$k_1(\times 10^4 \text{s}^{-1})$
dichloromethane	0.06
methanol	0.7
nitromethane	8.
acetone	3100 ^a

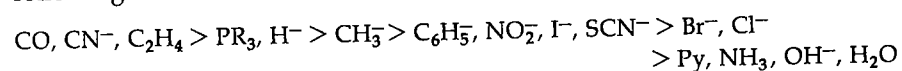
^aAt 20°.

TABLE 2.3

Effect of the *Trans* Ligand on Rate in Substitutions on *trans*-Pt(PEt₃)₂L(Cl).⁷ + R₇

L	$k_1(\text{s}^{-1})$	$k_2(\text{M}^{-1}\text{s}^{-1})$
PEt ₃	1.7×10^{-2}	3.8
H ⁻	1.8×10^{-2}	4.2
CH ₃ ⁻	1.7×10^{-4}	6.7×10^{-2}
C ₆ H ₅ ⁻	3.3×10^{-5}	1.6×10^{-2}
<i>p</i> -ClC ₆ H ₄ ⁻	3.3×10^{-5}	1.6×10^{-2}
<i>p</i> -CH ₃ OC ₆ H ₄ ⁻	2.8×10^{-5}	1.3×10^{-2}
Cl ⁻	1.0×10^{-6}	4.0×10^{-4}

(In many reactions the charge on the complex depends upon the nature of L as it does in reaction 2.9 above. In each case the platinum is in a +2 oxidation state and the charge on the complex is that required by standard charges on ligands.) The results for reaction 2.9 are given in Table 2.3.⁷ As the *trans* ligand changes through the series shown in going down the table, the rates of substitution decrease dramatically. Because within this series of complexes the only change is in the *trans* ligand, the 10⁴ difference in rate can be assigned to the *trans* effect. An important feature that supports the interpretation of the mechanism is that k_1 and k_2 are both affected in the same way by the change in *trans* ligand, indicating the mechanistic similarity of the two steps. From the data presented in Table 2.3, and many other reactions, the following *trans*-effect order has been developed:⁸



This order spans a factor of 10⁶ in rate and holds for all square planar platinum complexes thus far examined.

A rate enhancement can arise because of differences either in ground state or transition state energies. As shown in Figure 2.4 an increase in rate indicates either a ground state destabilization (increase in energy) or a transition state stabilization (decrease in energy). A ligand that exerts a strong *trans* effect weakens the bond to the *trans* ligand, stabilizes the transition state or affects both the ground and transition states.

Before discussing the origin of the *trans* effect, we must distinguish between the *trans* effect and the *trans* influence of a ligand. The *trans* effect is the effect of the ligand on the rate of substitution of the ligand that is

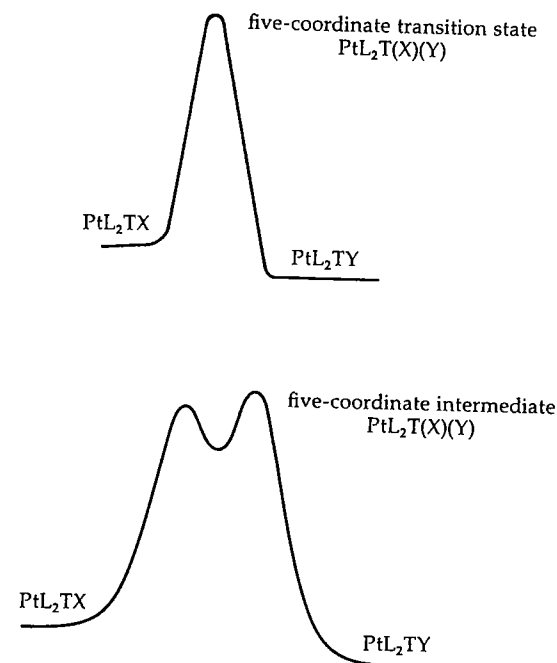


FIGURE 2.4. Plots of the reaction coordinate for square planar substitution reactions showing the difference between a five-coordinate transition state and a five-coordinate intermediate.

trans. The *trans* influence is the effect of the *trans* ligand on ground state properties such as bond lengths and infrared stretching frequencies. The difference is similar to the difference between kinetics and thermodynamics; thermodynamics concerns ground state measurements while kinetics concerns the difference in energy between the ground state and the transition state. Similarly, the *trans* influence provides information on the ground state influence of a *trans* ligand while the *trans* effect involves the effect of the *trans* ligand on both the ground state and the transition state. In the absence of transition state differences the *trans* effect order and the *trans* influence order would be similar. As we examine the reasons for the *trans* effect, differences in the *trans*-effect order and the *trans*-influence order will be ascribed to transition state energy differences.

A number of explanations have been offered for the *trans* effect. The best explanation considers both the sigma-donating and pi-acceptance capabilities of the ligand.^{1,3,9} The *trans* ligands in a square planar complex share a *p*-orbital as shown in Figure 2.5. A ligand that is a strong sigma-donor con-

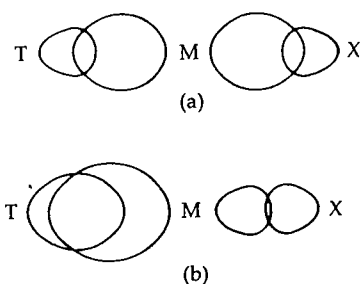
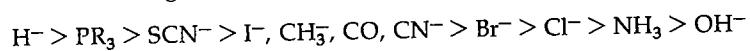
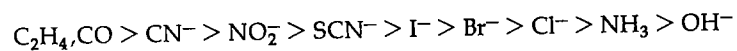


FIGURE 2.5. Schematic diagram showing the difference in M-X bond strengths for a weak (a) and a strong (b) sigma-donor ligand. In (b), the strong sigma donor weakens the bond to the *trans* ligand.

tributes more electron density to the shared p -orbital (p_x) and weakens the bond to the leaving group X. A graphical demonstration of this is shown in the lower part of Figure 2.5. In the five-coordinate intermediate the T group and X group do not directly share the same p -orbital, so that the effect of a strong sigma donor on the transition state is much smaller. Thus the effect of a sigma donor is primarily a ground state destabilization of the Pt-X bond. As primarily a ground state effect, the *trans* effect arising from sigma donation should parallel the order of *trans* influence. The expected order for the *trans* effect from sigma donation is as follows:



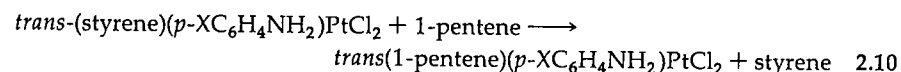
This order is similar to the general order of *trans*-effect ligands with some very notable exceptions (CO and CN^- are badly out of order). As we discussed above, discrepancies between the *trans*-effect order and the *trans*-influence order may be attributed to transition state effects. The ligands that have a substantially larger *trans* effect than would be predicted from their *trans* influence are ligands with pi-bonding capabilities. Thus a stabilization of the transition state by pi-accepting ligands is indicated. A ligand with pi-acceptance capabilities can remove electron density from the metal and thus stabilize the transition state. The order of pi-bonding ability of the ligands



accounts for the ligands that are not properly ordered by considering sigma donation only. The complete *trans*-effect order can be composed of the expected orders for sigma donation and pi acceptance and supports the idea of the *trans* effect arising from these different ligand capabilities.

One must be careful in applying general interpretations such as the *trans* effect. Clean separation of ground-state destabilization by

acceptor is impossible in some cases. Consider the electronic effect of *trans* ligands in several p -substituted aniline complexes for the following reaction.⁹



These reactions proceed very rapidly and show a dependence on the X group, as shown in Table 2.4. The rate of substitution decreases with increasing base strength of the *trans* aniline ligand, a difference opposite to that expected for the sigma *trans* effect. In this case, since an olefin (primarily a pi acceptor — see Chapter 4) is the ligand replaced, the Pt-olefin bond is strengthened by a stronger donor in the *trans* position, giving a rate dependence opposite to that expected from simple application of the interpretation in the preceding paragraph.

TABLE 2.4

The Effect of Changing Amine Basicity on Rate of Replacement of the *Trans* Ligand.⁹

X	$k(\text{M}^{-1}\text{s}^{-1})$	pK_a
Cl	9750	4.1
H	7030	4.63
CH_3	5000	5.08
OCH_3	3960	5.34

OTHER EFFECTS ON THE RATE

The *trans* group has a large and very significant effect on the rate of square planar substitution reactions, but other factors are also of importance. In this section we shall consider the effect of the *cis* ligand (steric effects), the effect of the leaving group, the effect of the entering nucleophile, and the effect of the solvent.

Cis Effect

The electronic effect of the *cis* ligands is relatively small.^{1,10} The reactions of $\text{cis-Pt}(\text{PEt}_3)_2\text{LCl}$ illustrate the magnitude expected.

TABLE 2.5

The Effect of L on the Rate of Reaction of *cis*-Pt(PEt₃)₂ClI with Py.

L	$k \times 10^2 (\text{s}^{-1})$
Cl ⁻	1.7
C ₆ H ₅ ⁻	3.8
CH ₃ ⁻	6.0

The data for this reaction (Table 2.5) can be compared to those in Table 2.3.⁷ For these ligands the *cis* effect is only a factor of 3 in rate while the *trans* effect is greater than two orders of magnitude.⁷ In general the *cis* effect is small and its order is variable unless steric factors are involved. Steric effects provide one of the best means of differentiating a dissociative mechanism from an associative one. For a dissociative reaction there is usually an increase in reaction rate with increasing steric interactions, a **steric acceleration**. For an associative reaction that involves an increased coordination number, increasing steric size decreases the rate of reaction. Data shown in Table 2.6 provide excellent confirmation of the associative nature of substitution reactions of Pt(II) complexes. Table 2.6 illustrates several features of interest. Increasing the size of the ligands dramatically slows the rate of substitution reactions.

TABLE 2.6

Steric Effects on the Rates of Square Planar Substitution Reactions at 25°C.^{1,7}

complex	$k_{\text{obs}} (\text{s}^{-1})$
<i>cis</i> -Pt(PEt ₃) ₂ ClI	
L = phenyl ^a	8.0×10^{-2}
L = <i>o</i> -tolyl ^a	2.0×10^{-4}
L = mesityl	1.0×10^{-6}
<i>trans</i> -Pt(PEt ₃) ₂ ClI	
L = phenyl	1.2×10^{-4}
L = <i>o</i> -tolyl	1.7×10^{-5}
L = mesityl	3.4×10^{-6}

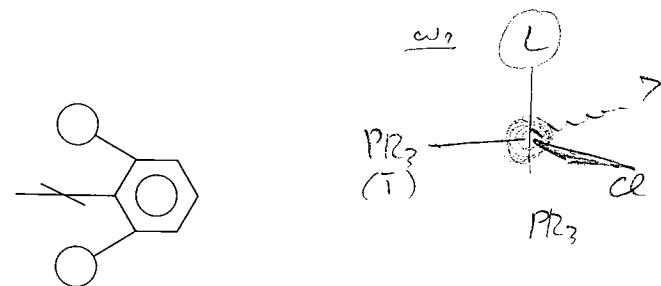
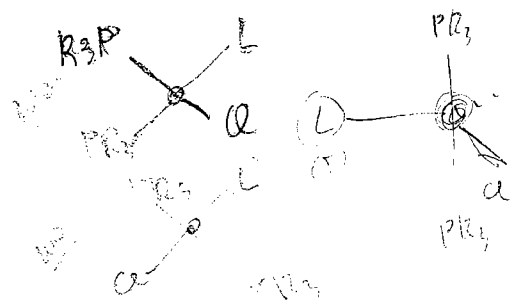
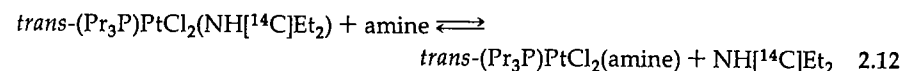


FIGURE 2.6. Geometry of aryl square planar complexes showing the *ortho* substituents blocking the site of attack.

The orientation of the aromatic ring of the aryl ligand is perpendicular to the plane of the molecule such that the substituents lie above and below the plane of the molecule and effectively block the site of attack (Figure 2.6). Changing the size of the *trans* ligand has less effect on the rate of substitution, as shown in Table 2.5. This can be understood by considering the trigonal bipyramidal intermediate formed. The *trans* group shares the equatorial plane and is away from the entering group and leaving group by an angle of 120°. The *cis* ligands occupy axial sites in the intermediate and interact with the entering and leaving groups at a 90° angle. Thus there is an increased effect on rate by steric interactions from the *cis* ligand. The importance of steric interactions is further shown by a comparison of the substitution reactions of Pt(dien)Cl⁺ and the tetraethyl substituted derivative, Pt(Et₄dien)Cl⁺ (dien = H₂NCH₂CH₂NHCH₂CH₂NH₂ and Et₄dien = Et₂NCH₂CH₂NHCH₂CH₂NEt₂; each is a tridentate ligand.) The Pt(dien)Cl⁺ undergoes substitution of Py for Cl⁻ at room temperature. The tetraethyl substituted derivative is so sterically hindered that reaction doesn't occur until 80°C and proceeds only by a first order reaction pathway that appears to be dissociative in nature.¹

Steric effects are further illustrated for a series of amine nucleophiles in the following reactions.¹¹



The plots in Figure 2.7 show the dramatic effect of the size of the incoming nucleophile.

Leaving-Group Effects

To investigate the effect of the leaving group (and other effects) on the rate of substitution reactions one must keep the *cis* and *trans* groups constant. The Pt(dien)X⁺ complexes have provided excellent information on leaving-

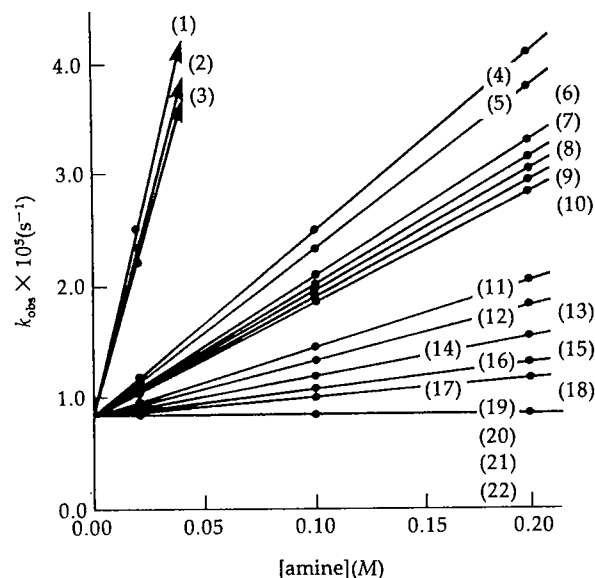


FIGURE 2.7. Reaction rates for $trans\text{-}(\text{Pr}_3\text{P})\text{PtCl}_2(\text{NH}_2\text{Et})^* + \text{amine}$ in methanol at 25° . Amine reagents (those marked with asterisk react to give new compounds): (1) 4-methylpyridine*; (2) 3-methylpyridine*; (3) pyridine; (4) methylamine; (5) aziridine*; (6) ethylamine; (7) isobutylamine*; (8) pyrrolidine*; (9) *n*-butylamine*; (10) ammonia; (11) isopropylamine*; (12) *s*-butylamine*; (13) 2-methylpyridine*; (14) piperidine; (15) dimethylamine; (16) 2,4,6-trimethylpyridine*; (17) *t*-butylamine*; (18) diethylamine; (19) di-isobutylamines*; (20) (21) di-isobutylamine*; (22) 2,4,6-trimethylpiperidine.* [Reprinted with permission from A. L. Odell and H. A. Raethel, *J. Chem. Soc. Chem. Comm.* 1323 (1968). Copyright 1968 Royal Society of Chemistry.]

group effects. The reaction of this complex with an entering nucleophile Y is shown in Figure 2.8. In dissociative reactions a large dependence on the nature of the leaving group can be expected since the bond from the metal to the leaving group is broken in the transition state. For associative reactions the effect of the leaving group depends on the extent of bond breaking in the transition state. Data for the following reaction



are presented in Table 2.7. The magnitude of the leaving-group effect shown in Table 2.7 indicates substantial bond breaking in the transition state. How much bond breaking exists in the transition state depends on the specific reaction. From volume of activation measurements it was concluded that

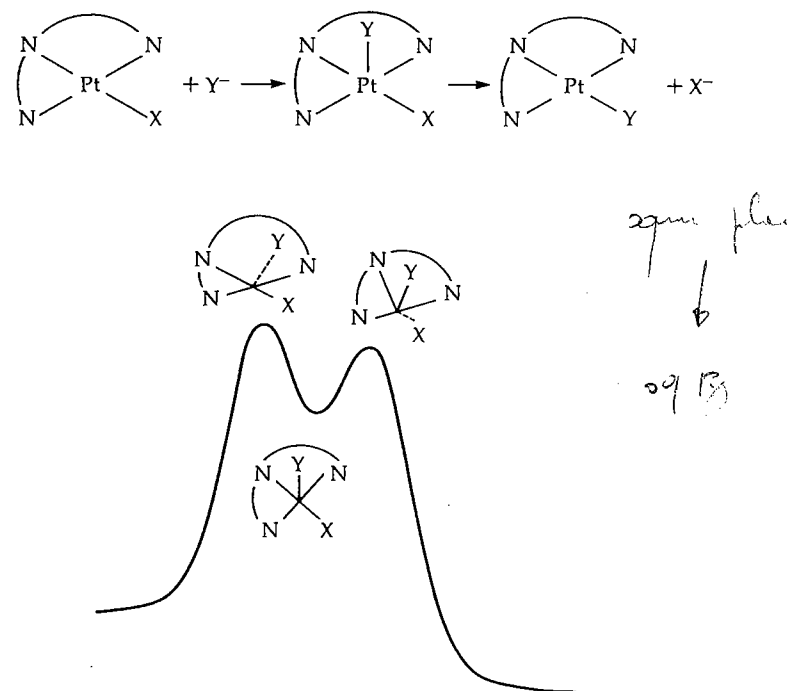
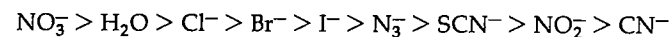


FIGURE 2.8. Reaction of $\text{Pt}(\text{dien})\text{X}$ with Y^- showing entering- and leaving-group effects.

replacement of Cl^- by Br^- on $trans\text{-Pt}(\text{PET}_3)_2\text{Cl}_2$ leads to a transition state with virtually no bond breaking of the $\text{Pt}\text{-Cl}$ bond.¹⁴ The order of leaving-group dependence for reaction 2.13



is almost the inverse of the *trans*-effect order. This reflects the fact that the *trans* effect depends on the strength of bonding (through either sigma or pi capability) and the more strongly bound ligands dissociate more slowly from the five-coordinate intermediate. In the section on activation parameters we shall obtain additional evidence on leaving-group effects.

Effect of the Entering Nucleophile

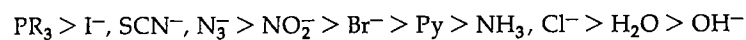
For a reaction that involves attack of the entering ligand we should certainly expect a dependence on the nucleophilicity of the entering ligand. To discuss the nucleophilicity of a ligand we must define the species that

TABLE 2.7

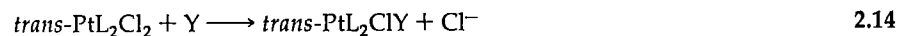
The Effect of the Leaving Group X on Rate of Substitution of Pt(dien)X⁺ with Py.^{12,13}

X	k_{obs}
NO ₃ ⁻	very fast
H ₂ O	1900
Cl ⁻	35
Br ⁻	23
I ⁻	10
N ₃ ⁻	0.8
SCN ⁻	0.3
NO ₂ ⁻	0.05
CN ⁻	0.02

interacts with the nucleophile. The order observed for Pt(II) substitution reactions¹⁻⁵



is certainly different than the order of basicity toward a proton. The **polarizability** or **softness** of a nucleophile is an important consideration. Soft nucleophiles prefer soft substrates and **hard (nonpolarizable)** ligands prefer hard substrates.¹⁵ The observation that larger donors are effective nucleophiles towards Pt(II) indicates that Pt(II) is a soft center. In general in describing the nature of a nucleophile one correlates the reactivity with other properties of the ligand. This type of correlation is a linear free-energy relationship (LFER). Data that have been collected for displacement of chloride from *trans*-PtL₂Cl₂,¹⁶⁻¹⁸



are presented in Table 2.8 and shown in Figure 2.9. The ligand dependence is clearly not on the basicity towards a proton. The parameter η_{Pt}° defined for each ligand is called the **nucleophilic reactivity constant** and is defined as follows:

$$\log \frac{k_{\text{Y}}}{k_{\text{S}}} = \eta_{\text{Pt}}^\circ \quad 2.15$$

where k_{Y} is the rate constant for reaction of an entering nucleophile Y with

TABLE 2.8

Effect of the Entering Nucleophile on Reaction at *trans*-PtL₂Cl₂.^a

Y	L = Py ^b	L = PEt ₃ ^c	η_{Pt}°
Cl ⁻	0.45	0.029	3.04
NH ₃	0.47	—	3.07
NO ₂ ⁻	0.68	0.027	3.22
N ₃ ⁻	1.55	0.2	3.58
Br ⁻	3.7	0.93	4.18
I ⁻	107	236	5.46
SCN ⁻	180	371	6.65
PPh ₃	249,000	—	8.93

^aEntries are 10³k in units of M⁻¹s⁻¹.

^bReference 16.

^cReferences 17 and 18.

Pt(Py)₂Cl₂ and k_{S} is the rate constant for attack by solvent (CH₃OH) on the complex.¹⁷ This constant measures the reactivity of a nucleophile towards platinum and is useful for correlation with other ligand properties. In addition plots of log k_{Y} for other Pt(II) complexes versus η_{Pt}° are observed to be linear (Figure 2.9). A LFER is given by

$$\log k_{\text{Y}} = s\eta_{\text{Pt}}^\circ + \log k_{\text{S}} \quad 2.16$$

and holds for a variety of different Pt(II) complexes and solvents. The constant s , called the **nucleophilic discrimination factor**, is a measure of the sensitivity of the metal center to the nucleophilicity of the entering ligand. A large value of s indicates that the rate is very sensitive to changes in nucleophilic character. Nucleophilic discrimination factors for several complexes are listed in Table 2.9.¹⁷ The comparison of the Pt(dien)X⁺ complexes (X = Br⁻, Cl⁻, H₂O) offers confirmation of an often-stated postulate: The complex that is most reactive (best leaving group) is least discriminating in its reactions (low value of s). This balance between reactivity and selectivity is a feature we shall return to in discussing catalytic reactions.

The order of the ligand nucleophilicities (Table 2.8) is similar to the *trans*-effect order. This can be understood in terms of the position of the Y group and the *trans* group in the transition state/intermediate. As shown in Figure 2.3, the entering nucleophile and *trans* ligand occupy approximately the same position and should have similar effects on the rate.

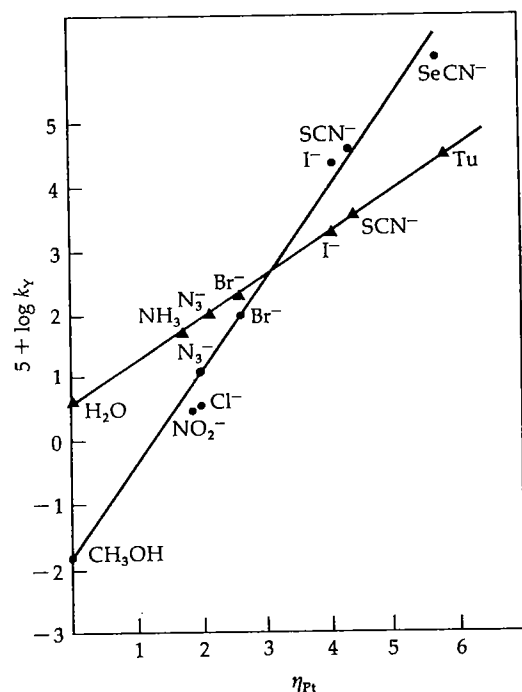
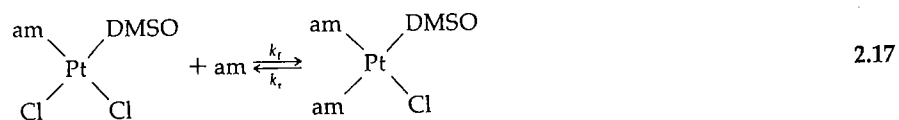


FIGURE 2.9. Correlation of the rates of reaction of Pt(II) complexes with the standard $\text{trans-[Pt(Py)}_2\text{Cl}_2]$ for different nucleophiles: ● = $\text{trans-[Pt(PEt}_3)_2\text{Cl}_2]$ in methanol at 30°; ▲ = $\text{[Pt(en)Cl}_2]$ in water at 35°. (Tu = thiourea, $s = \text{C(NH}_2)_2$.) [Reprinted with permission from U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.* 87, 241 (1965). Copyright 1965 American Chemical Society.]

The entering-group effects and leaving-group effects are closely related since both groups occupy equivalent positions in the intermediate. The magnitude of entering-group effects and leaving-group effects depends on the relative amounts of bond formation or bond weakening in the transition state. The similarity in the two is shown in Table 2.10 by the rate constants for the reaction¹⁹



In the reverse reaction, the *cis* complex is always formed because the *trans* complex has a much larger k_r than that of Cl^- . The small

TABLE 2.9

Nucleophilic Discrimination Factors for Pt(II) Complexes.¹⁷

complex	s
$\text{trans-Pt(PEt}_3)_2\text{Cl}_2$	1.43
$\text{trans-Pt(AsEt}_3)_2\text{Cl}_2$	1.25
$\text{trans-Pt(Py)}_2\text{Cl}_2$	1.0
$\text{trans-Pt(piper)}_2\text{Cl}_2$	0.91
Pt(en)Cl_2	0.64
Pt(dien)Br^+	0.75
Pt(dien)Cl^+	0.65
$\text{Pt(dien)H}_2\text{O}^{2+}$	0.44

cis effect that may exist for these complexes can be significant when basicity differences are minor, as they are for cyclopentylamine through cyclooctylamine.¹⁹

Solvent Effects

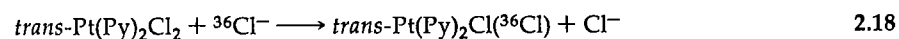
The rate law for square planar substitution includes a term that is independent of the entering nucleophile. This is ascribed to solvent attack; so it is not surprising that solvent effects are important in substitution reactions on

TABLE 2.10

Rate Constants Illustrating the Entering- and Leaving-Group Effects of a Series of Amines for Reaction 2.17.¹⁹

amine	k_f	k_r	pK_a
cyclopropylamine	4.82	14.8	8.66
cyclobutylamine	3.60	3.2	9.34
cyclopentylamine	1.96	1.22	9.95
cyclohexylamine	1.73	1.16	9.82
cycloheptylamine	1.38	1.37	9.99
cyclooctylamine	1.22	1.37	10.01

square planar complexes. Table 2.2 presents some pertinent data. Data for the chloride exchange reaction



are shown in Table 2.11.²⁰ Depending on the relative nucleophilicities of the solvent and of the entering ligand, the observed rate law may be dependent on or independent of the ligand. This is shown in Table 2.11 where the upper part of the table contains solvents of good coordinating ability, which react by a ligand-independent path, and the lower half of the table contains solvents of low coordination ability with the reactions proceeding purely by attack of the entering ligand on the square planar complex. For the solvents capable of coordinating to the metal, the rates show a direct dependence on the nucleophilicity of the solvent. For the poorly coordinating solvents, the larger rates occur in nonpolar solvents where the chloride would not be solvated and would be quite reactive.

TABLE 2.11

Effect of Solvent on the Chloride Exchange Reaction.²⁰

solvent	$k(10^{-5}\text{s}^{-1})$
DMSO	380
H ₂ O	3.5
EtOH	1.4
PrOH	0.4
solvent	$k(M^{-1}\text{s}^{-1})$
CCl ₄	10 ⁴
C ₆ H ₆	10 ²
<i>t</i> -BuOH	10 ⁻¹
Me ₂ C(O)	10 ⁻²
DMF	10 ⁻³

The extent of solvation in general is uncertain, but it has been determined for *cis*-Pt(PBu₃)₂Cl₂ in several solvents as shown in Table 2.12.²¹ The number *n* is the number of solvent molecules coordinated to the complex. These data support the concept of solvent attack through a five-coordinate intermediate for the first order step.

TABLE 2.12

Extent of Solvation of *cis*-Pt(PBu₃)₂Cl₂ in Several Solvents and Equilibrium Constants for Solvent Association.²¹

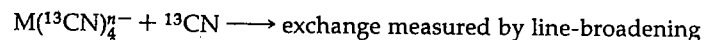
solvent	<i>n</i>	<i>K</i>
CH ₃ NO ₂	1.00	21.
CH ₃ CN	1.00	17.
(CH ₃ CH ₂) ₂ O	1.07	3.
CHCl ₃	0.99	0.3
CH ₃ OH	2.04	110.

ACTIVATION PARAMETERS

Activation parameters have been determined for a number of square planar substitution reactions. A few examples are shown in Table 2.13. These activation parameters are consistent with the mechanistic scheme we have developed. Especially significant are the uniformly negative entropies and volumes of activation. Negative values of both parameters indicate an associative reaction (see Chapter 1). The other significant feature is that the first and second order paths have very similar activation parameters, suggesting again a mechanistic similarity in both paths.

OTHER METAL CENTERS

Although most of the research on square planar substitution reactions has been of Pt(II) complexes, a few studies have been accomplished on Pd(II), Ni(II), Au(III), Rh(I), and Ir(I). A recent study of the CN⁻ exchange reactions for Pd(CN)₄²⁻, Pt(CN)₄²⁻, Ni(CN)₄²⁻ and Au(CN)₄⁻ by ¹³C NMR allows direct comparison of these metal centers.²⁴



The Ni(II) complex exchanged too rapidly for full analysis; the kinetic data for the other complexes are shown in Table 2.14.²⁴ As an entering ligand, CN⁻ is so strong that the rate law showed no *k*₁ term.

$$\text{rate} = k_2[\text{M}(\text{CN})_4^{2-}][\text{CN}^-]$$

TABLE 2.13

Activation Parameters for Square Planar Substitution Reactions.

reaction	solvent	$\Delta H^\ddagger$	k_1 $\Delta S^\ddagger$	$\Delta V^\ddagger$	$\Delta H^\ddagger$	k_2 $\Delta S^\ddagger$	$\Delta V^\ddagger$	reference
<i>trans</i> -Pt(Py) ₂ Cl(NO ₂) + Py	CH ₃ OH	—	—	—	12	-24	-9	6
<i>cis</i> -Pt(Py) ₂ Cl(NO ₂) + Py	CH ₃ OH	—	—	—	12	-32	-6	6
<i>trans</i> -Pt(PtEt ₃) ₂ Cl ₂ + Py	CH ₃ OH	—	—	—	14	-25	-14	6
<i>trans</i> -Pt(PtEt ₃) ₂ Cl ₂ + N ₃ ⁻	CH ₃ OH	—	—	—	15	-24	—	22
<i>trans</i> -Pt(PtEt ₃) ₂ Br ₂ + N ₃ ⁻	CH ₃ OH	—	—	—	13	-24	—	22
<i>trans</i> -Pt(PtEt ₃) ₂ I ₂ + N ₃ ⁻	CH ₃ OH	—	—	—	12	-16	—	22
<i>trans</i> -Pt(PtEt ₃) ₂ (2,4,6-Me ₃ C ₆ H ₂)Br + SC(NH ₂) ₂	CH ₃ OH	17	-20	-11	11	-33	-13	23
<i>cis</i> -Pt(PtEt ₃) ₂ (2,4,6-Me ₃ C ₆ H ₂)Br + I ⁻	CH ₃ OH	20	-14	-16	15	-29	-15	23
<i>cis</i> -Pt(PtEt ₃) ₂ (2,4,6-Me ₃ C ₆ H ₂)Br + SC(NH ₂) ₂	CH ₃ OH	19	-17	-17	14	-29	-13	23
Pt(dien)Cl ⁺ + SCN ⁻	H ₂ O	20	-18	—	10	-25	—	22
Pt(dien)Br ⁺ + SCN ⁻	H ₂ O	19	-17	—	9	-27	—	22
Pt(dien)I ⁺ + SCN ⁻	H ₂ O	—	—	—	10	-25	—	22
Pt(dien)N ₃ ⁺ + SCN ⁻	H ₂ O	—	—	—	14	-22	—	22
Au(dien)Cl ₂ ⁺ + Br ⁻	CH ₃ OH	—	—	—	13	-4	—	22

TABLE 2.14

Rate Constants and Activation Parameters for CN⁻ Exchange with M(CN)₄ⁿ⁻ at 24°C.

complex	$k_2(M^{-1}s^{-1})$	$\Delta H^\ddagger(kcal/mole)$	$\Delta S^\ddagger(eu)$
Ni(CN) ₄ ²⁻	$> 5 \times 10^5$	—	—
Pd(CN) ₄ ²⁻	120	4	-45
Pt(CN) ₄ ²⁻	26	6	-37
Au(CN) ₄ ⁻	3900	7	-24

The order of reactivity is Ni(II) > Au(III) > Pd(II) > Pt(II), but the difference between Pt(II) and Pd(II) and Au(III) is not as large as for other reactions.²⁴ These complexes will be examined in the following sections.

Pd(II) Complexes

Analogous Pd(II) complexes react approximately 10⁵ times faster than Pt(II) complexes. Data are presented in Tables 2.15 and 2.16. The greater reactivity of the Pd(II) complexes has previously been ascribed to a weaker Pd-X bond.* The overall mechanism appears to be of the same type with both

TABLE 2.15

Comparison of the Reactivity of Pd(II) and Pt(II) Complexes.

complex	k_{obs} , M = Pd(II)	k_{obs} , M = Pt(II)	reference
M(dien)Cl ⁺	fast	3.5×10^{-5}	20
M(dien)I ⁺	3.2×10^{-2a}	1.0×10^{-5}	20
M(dien)SCN ⁺	4.3×10^{-2a}	3.0×10^{-7}	20
M(dien)NO ₂ ⁺	3.3×10^{-2}	2.5×10^{-7}	20
<i>t</i> -M(PtEt ₃) ₂ ⁻ (<i>o</i> -tolyl)Cl	5.8×10^{-1}	6.7×10^{-6}	7

*It is generally considered that a higher effective nuclear charge leads to stronger metal ligand bonds (for ligands that do not accept electron density from the metal) as one proceeds from first to second to third row transition metals.

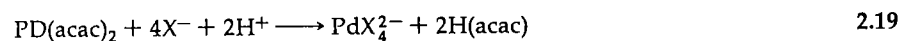
TABLE 2.16

Rate Constants for the Reaction of the Tetrahalides of Platinum and Palladium with Acetylacetonate.²⁵

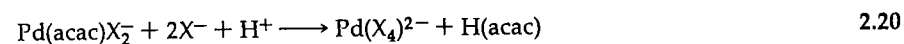
complex	$k_1(\text{s}^{-1})$	$k_2(\text{M}^{-1}\text{s}^{-1})$	$I(^{\circ}\text{C})$
PdCl_4^{2-}	71	2.2	25
PtCl_4^{2-}	1.2×10^{-2}	1.2×10^{-3}	55
PdBr_4^{2-}	210	1.9	25
PtBr_4^{2-}	3.0×10^{-1}	1.1×10^{-3}	55

a ligand-attack and a solvent-attack term, although the solvent-attack term appears to be more important for Pd(II) complexes than for Pt(II).²⁵

Substitution on $\text{Pd}(\text{acac})_2$ shows the similarity of entering-group effects for Pd(II) and Pt(II).²⁶



The rates for different X^- groups are shown in Table 2.17.²⁵ The mechanism suggested for the palladium dien complexes is very similar to that suggested for platinum dien complexes (Figure 2.8). A similar *trans* effect also appears operative in Pd(II) reactions from reactions of $\text{Pd}(\text{acac})\text{X}_2^-$.



In comparing the rate constants for the solvolysis path, the reaction for $\text{X} = \text{Br}^-$ was an order of magnitude more rapid than for $\text{X} = \text{Cl}^-$.²⁶

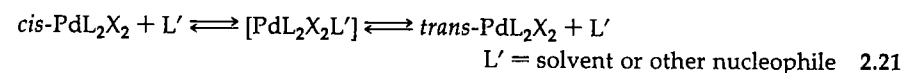
While *cis-trans* isomerization of Pt(II) complexes is a relatively slow

TABLE 2.17

Entering-Group Effects on the Rate of Substitution of $\text{Pd}(\text{acac})_2$.

X	$k(\times 10^2 \text{s}^{-1})$
OH^-	3.2
Cl^-	8.9
Br^-	32
I^-	fast
SCN^-	very fast

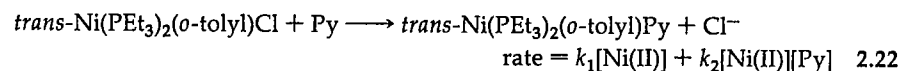
process, often requiring elevated temperatures, many palladium complexes establish a *cis-trans* equilibrium readily in solution. A series of complexes PdL_2X_2 have been investigated by NMR ($\text{L} = \text{PPh}_n\text{Me}_{3-n}$; $\text{X} = \text{Cl}^-$, N_3^- , CN^-).²⁷⁻²⁹ Equilibration was achieved in a few minutes at room temperature with the *cis* isomers generally thermodynamically more stable than the *trans* isomers. The mechanism apparently involves solvent attack on the palladium complex and is greatly catalyzed by the presence of a nucleophile.²⁷⁻²⁹



Square planar complexes of palladium show the same characteristics as platinum complexes in their substitution reactions: Substitutions are associative reactions, with attack either by solvent or by incoming nucleophile; and the *trans* ligand, the leaving group, the entering nucleophile, and the solvent all affect the rate of substitution. The significant difference between complexes of the two metals is that palladium complexes undergo substitution 10^5 times as fast as platinum complexes.

Ni(II) Complexes

Many Ni(II) complexes are octahedral. Those that are square planar react very rapidly; $\text{Ni}(\text{CN})_4^{2-}$ exchanges CN^- in seconds, a fact that is significant since $\text{Ni}(\text{CN})_5^{3-}$ is a known compound.³⁰ Reaction of *trans*- $\text{Ni}(\text{PET}_3)_2(\text{o-tolyl})\text{Cl}$ with pyridine showed a two-term rate law.⁶



The relative rates for the Ni(II), Pd(II), and Pt(II) complexes are 5×10^6 , 1×10^5 and 1 respectively.⁷ The most comprehensive data on Ni(II) square planar complexes is for a series of dithiolate ligands using stopped-flow techniques; they show entering-group, leaving-group, and *trans* effects similar to the Pt(II) complexes.³¹

Au(III) Complexes

Although Au(III) is isoelectronic with Pt(II), studies of Au(III) are much less common. The primary complication is the ease of reduction of Au(III) to Au(I) or Au(0). Table 2.18 shows the comparison of rates of Au(III) and Pt(II) complexes.³² The form of the rate law is the same as that for other square planar complexes although the solvent-attack term is less important. A plot of the observed pseudo first order rate constants versus concentration of bromide ion is shown in Figure 2.10. This can be compared to Figure 2.7, show-

TABLE 2.18

Comparison of the Rates of Substitution Reactions of Au(III) and Pt(II) Complexes.

reaction	$k_1(\text{s}^{-1})$	$k_2(\text{M}^{-1}\text{s}^{-1})$
$\text{AuCl}_4^- + \text{Cl}^-$	0.006	1.47
$\text{PtCl}_4^{2-} + \text{Cl}^-$	3.8×10^{-5}	0
$\text{Au}(\text{dien})\text{Cl}^{2+} + \text{Br}^-$	<0.5	154
$\text{Pt}(\text{dien})\text{Cl}^+ + \text{Br}^-$	8.0×10^{-5}	5.3×10^{-3}

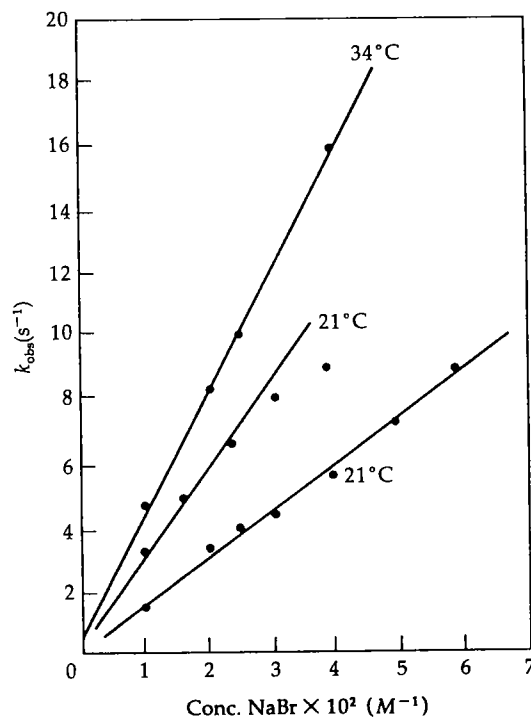


FIGURE 2.10. Dependence of k_{obs} on bromide ion concentration for the reaction of $[\text{Au}(\text{dien})\text{Cl}]^{2+}$ with this reagent. [Reprinted with permission from W. H. Baddley and F. Basolo, *Inorg. Chem.* 3, 1087 (1964). Copyright 1964 American Chemical Society.]

SUMMARY

smaller contribution to the rate for Au(III).³² Gold complexes react approximately 10^4 times as fast as isoelectronic Pt(II) complexes. This is attributable to the larger positive charge on Au(III), which favors formation of the electron-rich intermediate.

SUMMARY

Substitution reactions of square planar complexes proceed by nucleophilic attack of an incoming ligand on the square planar complex. The two-term rate law observed includes a term that is dependent on the incoming nucleophile

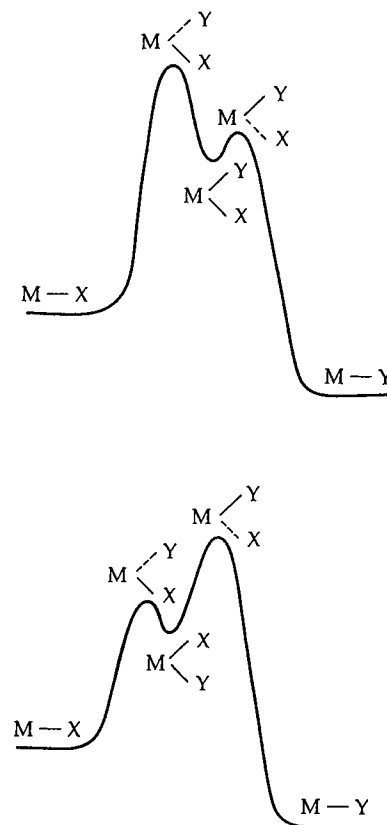


FIGURE 2.11. Diagrams of the reaction coordinate showing that for a specific reaction the dependence on entering and leaving groups may be more or less important.

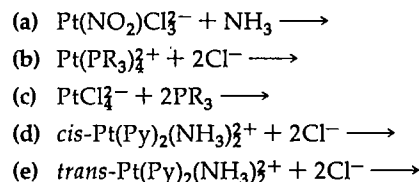
and a term that is independent of the incoming nucleophile. These terms correspond to attack on the complex by the entering ligand and the solvent, respectively. The rate of reaction shows a dependence on the ligand *trans* to the substitution site, on the leaving group, and on the entering nucleophile. The importance of these effects depends on the amount of bond formation or bond breaking in the transition state. One can consider the reaction as a double-humped potential curve as shown in Figure 2.11. These considerations were covered in a recent molecular orbital study.¹⁰ If the first maximum is the transition state, then bond formation is more important (a very sharp dependence on the entering nucleophile). If the second maximum is the transition state, then bond breaking is more important (leaving-group effects would be very large). Support for the energy profile shown in Figure 2.11, where the five-coordinate trigonal bipyramidal species is an intermediate, has come from studies showing that this intermediate exists for a sufficient time to undergo pseudorotation.^{33,34} All of the data on square planar substitution reactions are consistent with the mechanistic scheme shown in Figure 2.3.

REFERENCES

1. F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* (New York: John Wiley, 1968).
2. R. G. Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes* (Boston: Allyn and Bacon, 1974).
3. C. H. Langford and H. B. Gray, *Ligand Substitution Processes* (New York: W. A. Benjamin, 1965).
4. M. L. Tobe, *Inorganic Reaction Mechanisms* (London: Nelson, 1972).
5. F. Basolo and R. G. Pearson, *Prog. Inorg. Chem.* **4**, 381 (1964).
6. M. Kotowski, D. A. Palmer, and H. Kelm, *Inorg. Chem.* **18**, 2555 (1979).
7. F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.* 2207 (1961).
8. F. Basolo, *Adv. Chem. Ser.* **49**, 81 (1965).
9. S. S. Hupp and G. Dahlgren, *Inorg. Chem.* **15**, 2349 (1976).
10. J. K. Burdett, *Inorg. Chem.* **16**, 3013 (1977).
11. A. L. Odell and H. A. Raethel, *J. Chem. Soc. Chem. Comm.* 1323 (1968).
12. H. B. Gray and R. J. Olcott, *Inorg. Chem.* **1**, 481 (1962).
13. F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.* **82**, 4200 (1960).
14. T. Taylor and L. R. Hathaway, *Inorg. Chem.* **8**, 2135 (1969).
15. R. G. Pearson, *J. Am. Chem. Soc.* **85**, 3533 (1963).
16. R. G. Pearson, H. Sobel, and J. Songstad, *J. Am. Chem. Soc.* **90**, 319 (1968).
17. U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.* **87**, 241 (1965).
18. U. Belluco, M. Martelli, and A. Orio, *Inorg. Chem.* **5**, 582 (1966).
19. P. D. Braddock, R. Romeo, and M. L. Tobe, *Inorg. Chem.* **13**, 1170 (1974).
20. R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.* **82**, 787 (1960).
21. P. Haake and R. M. Pfeiffer, *Inorg. Chem.* **9**, 5243 (1970).
22. U. Belluco, R. Ettore, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.* **5**, 591 (1966).
23. R. van Eldik, D. A. Palmer, and H. Kelm, *Inorg. Chem.* **18**, 572 (1979).
24. J. J. Pesek and W. R. Mason, *Inorg. Chem.* **22**, 2958 (1983).
25. J. V. Rund, *Inorg. Chem.* **13**, 738 (1974).
26. R. G. Pearson and D. A. Johnson, *J. Am. Chem. Soc.* **86**, 3983 (1964).
27. D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.* **14**, 50 (1975).
28. A. W. Verstuyft and J. H. Nelson, *Inorg. Chem.* **14**, 1501 (1975).
29. A. W. Verstuyft, L. W. Cary, and J. H. Nelson, *Inorg. Chem.* **15**, 3161 (1976).
30. A. W. Adamson, J. P. Welker, and M. Volpe, *J. Am. Chem. Soc.* **72**, 4030 (1950).
31. R. G. Pearson and D. A. Sweigart, *Inorg. Chem.* **9**, 1167 (1970).
32. W. H. Baddley and F. Basolo, *Inorg. Chem.* **3**, 1087 (1964).
33. W. J. Louw, *Inorg. Chem.* **16**, 2147 (1977).
34. M. K. Cooper and J. M. Dounes, *J. Chem. Soc. Chem. Comm.* 381 (1981).

PROBLEMS

1. Predict the products of the following ligand substitution reactions:

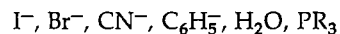


2. Design a two-step synthesis for *cis*- and *trans*- $\text{Pt}(\text{NO}_2)(\text{NH}_3)\text{Cl}_2^-$ beginning with PtCl_4^- .

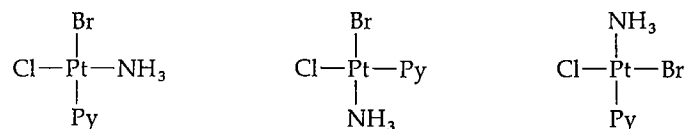
3. The following data have been obtained for reaction of a 0.0018 M solution of $\text{Pt}(\text{dien})\text{Cl}^+$ with Br^- . Derive k_1 and k_2 for this reaction. [H. B. Gray, *J. Am. Chem. Soc.* **84**, 1548 (1962).]

$[\text{Br}^-](M)$	$k_{\text{obs}}(\times 10^4 \text{s}^{-1})$
0.005	1.04
0.015	1.60
0.020	1.87
0.025	2.12

4. Arrange the following ligands in order of *trans*-labilizing power in square planar substitutions.



5. Present rational syntheses of the following three isomers:



6. How does each of the following affect the rate of a square planar substitution reaction?

- (a) changing *trans* ligand from H^- to Cl^-
 (b) changing leaving group from I^- to SCN^-
 (c) changing charge on the metal
 (d) making *cis* ligand larger
 (e) changing solvent from H_2O to $n\text{-C}_3\text{H}_7\text{OH}$
 (f) changing from $\text{Pd}(\text{II})$ to $\text{Ni}(\text{II})$

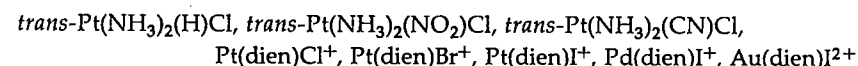
7. A number of $\text{Pt}(\text{II})$ complexes are effective anti-tumor agents. Among these are *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Pt}(\text{en})\text{Cl}_2$. Assuming that the binding to the protein requires two positions and that the Pt-protein complex should be stable, explain why

these complexes are reasonable choices for anti-tumor behavior. [B. Rosenberg, L. Van Camp, J. E. Trosco, and V. H. Mansour, *Nature* **222**, 385 (1969).]

8. There has been considerable discussion about the mechanism of *cis-trans* isomerization of square planar platinum(II) complexes, with both rate-determining dissociative and associative (solvent-attack) mechanisms suggested. Given the data below, decide between these possibilities for $\text{Pt}(\text{PEt}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Br}$ in CH_3OH . [R. van Eldik, D. A. Palmer, and H. Kelm, *Inorg. Chem.* **18**, 572 (1979).]

reaction	$k_1 \times 10^4$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
isomerization	1.90	20	-9.8
<i>cis</i> - $\text{Pt}(\text{PEt}_3)_2\text{RBr} + \text{I}^-$	1.86	18	-15

9. Arrange these complexes in order of increasing rate of substitution reactions:



10. Interpret the data below relating the intrinsic reactivity of a complex ($\log k_S$) with the nucleophilic discrimination factor s . [U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.* **87**, 241 (1965).]

complex	$\log k_S$	s
<i>trans</i> - $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$	-6.83	1.43
<i>trans</i> - $\text{Pt}(\text{AsEt}_3)_2\text{Cl}_2$	-5.75	1.25
<i>trans</i> - $\text{Pt}(\text{pip})_2\text{Cl}_2$	-4.56	0.91
$\text{Pt}(\text{en})\text{Cl}_2$	-4.33	0.64
$\text{Pt}(\text{dien})\text{Cl}^+$	-3.61	0.65

11. A competition study was carried out by reacting $\text{Pt}(\text{dien})\text{Br}^+$ with Y^- and OH^- in comparable concentrations, where $\text{Y}^- = \text{Cl}^-$, Br^- , and I^- . The initial product formed in each of these reactions is $\text{Pt}(\text{dien})\text{Y}^+$. No $\text{Pt}(\text{dien})\text{OH}^+$ is seen initially. $\text{Pt}(\text{dien})\text{Y}^+$ then converts to $\text{Pt}(\text{dien})\text{OH}^+$. (Dien is a tridentate amine.) What is the significance of the absence of $\text{Pt}(\text{dien})\text{OH}^+$ as the initial product? Write a plausible mechanistic scheme in which $\text{Pt}(\text{dien})\text{OH}^+$ would be an initial product. (Reference 3, p. 37.)

12. The complex $[\text{HPt}(\text{PEt}_3)_3]^+\text{BPh}_4^-$ was studied in acetone- d_6 in the presence of excess $\text{P}(\text{Et})_3$ using proton NMR at various temperatures. In the absence of added excess ligand the spectrum for the hydridic proton looks like this:



Addition of $\text{P}(\text{Et})_3$ causes the triplets to collapse. The collapsing of the spectrum is a function of the amount of added ligand. Explain the origin of the spectrum seen for the complex, and give a detailed mechanism to account for the effects of added $\text{P}(\text{Et})_3$.

Substitution Reactions of Octahedral Werner-Type Complexes

Complexes of transition metal ions (coordination complexes) were investigated extensively in the early 1900s to test bonding concepts. The data collected on the complexes confirmed Werner's theory of two types of valence, a primary valence representing the charge on the metal (oxidation state) and a secondary valence representing the ligands held tightly to the metal ion (coordination number).¹ For coordination number 6 the geometry postulated by Werner and confirmed by experiment is octahedral. Isomers played an important role in the original interpretation of coordination complexes. A general interpretation of possible isomers can be complicated, but if we allow only two different ligands, the possibilities can be readily constructed.^{2,3} Complex MA_5B has only one isomer, MA_4B_2 has two possibilities — *cis* and *trans* isomers — and MA_3B_3 has two possibilities — facial and meridional. These are shown in Figure 3.1. Optical isomers also exist, usually with bidentate ligands. Isomers have had considerable impact on the mechanistic interpretation of substitution reactions of Werner-type complexes.⁴⁻⁶

The presence of six-electron-donor ligands around the transition metal creates an octahedral electronic field, raising the energy of the *d*-orbitals by electron repulsion. The ligands lie along the *x*, *y* and *z* axes and have a larger effect on the orbitals that lie along the axes (d_{z^2} and $d_{x^2-y^2}$) than on the orbitals that lie between the axes (d_{xy} , d_{xz} , d_{yz}). This **crystal field splitting** is shown in Figure 3.2. The strength of the ligand field influences the magnitude of the splitting of the *d*-orbitals. From the electronic absorption spectra of a number of complexes a spectrochemical series has been developed. This series is a measure of the ability of the ligand to split the *d*-orbitals, a property we shall call *ligand strength*.^{2,5}

$\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{acetate} < \text{oxalate} < \text{H}_2\text{O} < \text{pyridine}$
 $\approx \text{NH}_3 < \text{en} < \text{bipy} \approx o\text{-phen} < \text{NO}_2^- < \text{CN}^-$

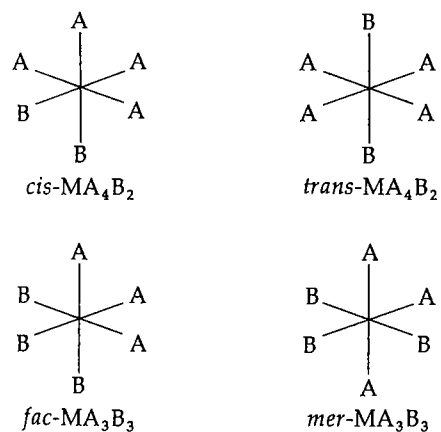
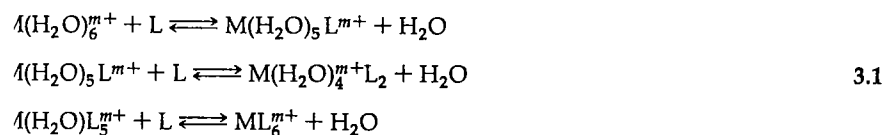


FIGURE 3.1. Possible stereoisomers of octahedral complexes containing only two different ligands.

As we shall see in a later section, both ligand strength and electronic configuration are important in determining reactivity of coordination complexes.

Most reactions of Werner-type complexes are studied in water, which may serve as a ligand for reactions:



The forward reactions are referred to as **formation** reactions or, if L is an anion, as **anation** reactions; the reverse reactions, in which water replaces a ligand, are called **aquation** reactions. The reactions in either direction are ligand substitutions and are pertinent for this chapter. The rate of substitution

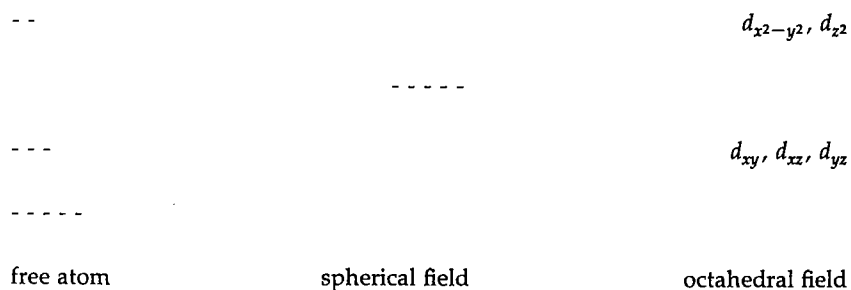


FIGURE 3.2. Splitting of the *d*-orbitals in an octahedral crystal field.

reactions on transition metals ranges from *diffusion controlled* to *no reaction* under ambient conditions. Complexes that react rapidly (half-life of a few seconds) are termed *labile*; those that react slowly (half-life of several minutes) are referred to as *inert*.

KINETICS

Depending on the specific reaction, a range of kinetic behavior can be seen for substitution reactions on octahedral transition metal complexes.⁴⁻⁶ The reactions cannot be as comprehensively defined as for substitutions on square planar complexes. The description that follows pertains to most reactions under neutral conditions. Under pseudo first order conditions, the rate is dependent on the concentration of the entering ligand at low ligand concentration and is independent of the concentration of L at high concentration of L. This behavior is consistent with the following two reactions and rate law derived from them.



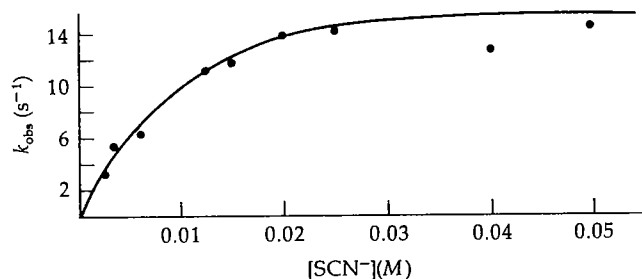
$$\text{rate} = \frac{k_1 k_2 [M-H_2O][L]}{k_{-1}[H_2O] + k_2[L]} \tag{3.4}$$

Since these reactions are studied in H_2O , the term $k_{-1}[H_2O]$ is a constant. Figure 3.3 shows typical plots of k_{obs} versus $[L]$.⁷ There is a dependence on the nature of L, a fact that is not surprising since reactions 3.2 and 3.3 can be considered a competition between H_2O and L for the intermediate M. The limiting rate constant (intercept) is the same for different L. The mechanism described by equations 3.2 and 3.3 is the dissociative or D mechanism. An I_d (interchange) mechanism (equations 3.5 and 3.6) can also lead to a rate law

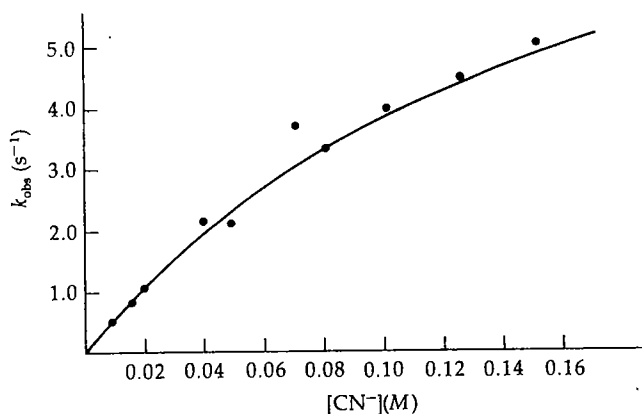


$$\text{rate} = \frac{kK[M-H_2O][L]}{1 + K[L]} \tag{3.7}$$

that is indistinguishable from that for the D mechanism. To simplify the interpretation of kinetic data, most reactions are examined at one of the limits,



(a)

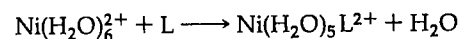


(b)

FIGURE 3.3. The observed rate constant as a function of [L] for (a) SCN^- and (b) CN^- in reaction with a Co(III) hematoporphyrin. [Reprinted with permission from E. B. Fleischer, S. Jacobs, and L. Mestichelli, *J. Am. Chem. Soc.* 90, 2527 (1968). Copyright 1968 American Chemical Society.]

where the reaction is expected to be first order (independent of ligand concentration) or second order (showing first order dependence on concentration of L). The metal complexes that have been studied in most detail are those of relatively inert first row metals, Cr(III), Co(III) and Ni(II).

Rate constants for the first order path are relatively independent of the nature of the incoming ligand as shown in Table 3.1 for the reactions



3.8

KINETICS

TABLE 3.1

Rate Constants for the Reaction of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ with Different Nucleophiles.⁸

L	$k \times (10^4 \text{ s}^{-1})^a$
SO_4^{2-}	1.5
CH_3COO^-	3
SCN^-	0.6
F^-	0.8
H_2O	3.0
NH_3	3
Py	3

^a Defined in equation 3.7.

The very small dependence evidenced by the data can be compared to that in associative reactions such as substitution on square planar complexes as shown in Table 2.8. There the ligand dependence of the rate constant spans four orders of magnitude. Second order rate constants for octahedral substitutions show a dependence on the nature of the incoming ligand as shown by the data in Table 3.2. The dependence on the nature of the ligand for the second order rate constant is not large enough to involve nucleophilic attack of L on the metal complex in an associative reaction (compare Table 2.8), but it is consistent with the ability of the ligand to compete with H_2O for the

TABLE 3.2

Second Order Rate Constants for Anation Reactions of Cobalimin [cobalt(III) corrinorid] with Different Ligands.⁹

L	$k(10^2 \text{ M}^{-1}\text{s}^{-1})$
SCN^-	23
I^-	14
Br^-	10
HSO_3^-	1.7

five-coordinate intermediate in a D mechanism or to interact with the complex in an I_d mechanism.

Substantial evidence can be cited in favor of a dissociative (either D or I_d) mechanism over an associative mechanism (A or I_a) in some reactions:^{4,5}

1. There is often little or no dependence on the entering ligand as discussed above.
2. An increase in charge on the complex decreases the rate of substitution. An increase in charge would be expected to accelerate an associative reaction with increased attraction for the incoming ligand and more facile acceptance of the negative charge build-up on the metal. A dissociative reaction would be slowed by an increase in charge since the dissociating ligand would be held more tightly. For example, the rate constant for substitution at $\text{Cr(en)}(\text{H}_2\text{O})_2\text{Cl}_2^+$ is $3.1 \times 10^{-5} \text{ s}^{-1}$ at 25°C and at $\text{Cr(en)}(\text{H}_2\text{O})_3\text{Cl}^{2+}$ is $3 \times 10^{-7} \text{ s}^{-1}$ at 25°C .¹⁰
3. Steric crowding increases the rate of substitution reactions. For associative reactions an increase in the crowding around the metal inhibits approach of the incoming ligand and would decrease the rate of reaction. Steric crowding would be relieved by dissociation to yield a five-coordinate intermediate and thus lead to an increase in the rate of dissociation. For example, Cl^- replacement on $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ occurs at a rate of $1.7 \times 10^{-6} \text{ s}^{-1}$ at 25°C while Cl^- removal from $\text{Co}(\text{NMeH}_2)_5\text{Cl}^{2+}$ occurs at a rate of 3.7×10^{-4} .¹¹
4. The rates for different leaving groups correlate with the bond strengths.¹²

TABLE 3.3

Rate and Equilibrium Constants for the Aquation Reaction of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$.¹²

X	$k(\text{s}^{-1})$	$K_{\text{eq}}(\text{M}^{-1})$
NCS^-	4.1×10^{-10}	3.7×10^{-4}
N_3^-	2.1×10^{-9}	1.2×10^{-3}
F^-	8.6×10^{-8}	0.040
Cl^-	1.7×10^{-6}	0.90
Br^-	6.5×10^{-6}	2.9
I^-	8.3×10^{-6}	8.3
NO_3^-	2.7×10^{-5}	12.

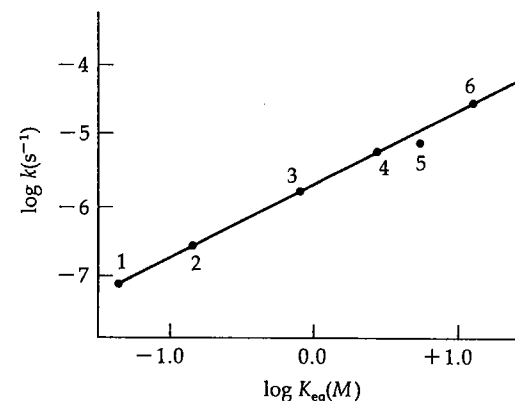


FIGURE 3.4. Linear free-energy relationship in the aquation of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ at 25°C . Points are designated: (1) $\text{X}^- = \text{F}^-$; (2) $\text{X}^- = \text{H}_2\text{PO}_4^-$; (3) $\text{X}^- = \text{Cl}^-$; (4) $\text{X}^- = \text{Br}^-$; (5) $\text{X}^- = \text{I}^-$; and (6) $\text{X}^- = \text{NO}_3^-$. [Reprinted with permission from C. H. Langford, *Inorg. Chem.* 4, 265 (1965). Copyright 1965 American Chemical Society.]

Data for the aquation reaction of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ are shown in Table 3.3 and Figure 3.4.

5. The activation parameters are consistent with a dissociative process. The activation parameters have been the focus of considerable discussion regarding the distinction between I_d and I_a mechanisms. As shown by the data in Table 3.4, the entropies and volumes of activation are near zero (between ± 10 , which, as discussed in Chapter 1, makes interpretation difficult), indicative of an interchange mechanism.

Early suggestions that transition metal complexes react by dissociative reactions are not supported by the majority of the activation data, although some examples of D mechanisms have been established (e.g., $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$).²⁰ The body of evidence for $\text{Co}(\text{III})$ complexes is consistent with I_d or D mechanisms. The situation for $\text{Cr}(\text{III})$ complexes is more complicated and perhaps more indicative of the situation for transition metal complexes in general. The kinetic parameters for the anation reactions of $\text{CrL}_5\text{H}_2\text{O}^{3+}$,



$\text{L} = \text{H}_2\text{O}, \text{NH}_3$

are shown in Table 3.5. The dependence on the entering ligand for $\text{L} = \text{H}_2\text{O}$ indicates an I_a mechanism, which is supported by volume of activation measurements on $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. This large dependence on the entering ligand for

TABLE 3.4

Activation Parameters for Substitution Reactions of Octahedral Coordination Complexes.

complex	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta V^\ddagger$	reference	product
$\text{Cr}(\text{H}_2\text{O})_5\text{NO}_2^{2+}$	19.8	9	—	13	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$
$\text{Cr}(\text{H}_2\text{O})_5\text{SO}_4^+$	26.5	-1	—	13	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$
$\text{Cr}(\text{H}_2\text{O})_5\text{N}_3^{2+}$	23.2	-8	—	13	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$
$\text{Cr}(\text{H}_2\text{O})_5\text{CN}^{2+}$	20.2	-6	—	13	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	30.3	9	—	14	$\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$
$\text{Cr}(\text{en})(\text{H}_2\text{O})_4^{3+}$	27.1	-3	—	15	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$
$\text{Mn}(\text{H}_2\text{O})_6^{2+}$	8.1	3	—	16	$\text{Mn}(\text{H}_2\text{O})_6^{2+}$
$\text{Fe}(\text{H}_2\text{O})_6^{2+}$	7.7	-3	—	16	$\text{Fe}(\text{H}_2\text{O})_6^{2+}$
$\text{Co}(\text{H}_2\text{O})_6^{2+}$	10.4	5	6-10	16,19	$\text{Co}(\text{H}_2\text{O})_6^{2+}$
$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	13.9	9	7	16,18	$\text{Ni}(\text{H}_2\text{O})_6^{2+}$
$\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	26.6	6.7	1.2	17	$\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$
$\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	24.6	0.8	-4.1	17	$\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$
$\text{Ir}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	28.1	2.7	-3.2	17	$\text{Ir}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	23.3	-6.8	-10.6	17	$\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	23.2	-3.8	-9.2	17	$\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$
$\text{Co}(\text{NH}_3)_5(\text{NCS})^{2+}$	30.1	-0.8	-4.0	17	$\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$
$\text{Co}(\text{NH}_3)_5(\text{NO}_3)^{2+}$	24.3	1.9	-6.3	17	$\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$
$\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$	33.2	13.1	16.8	17	$\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$

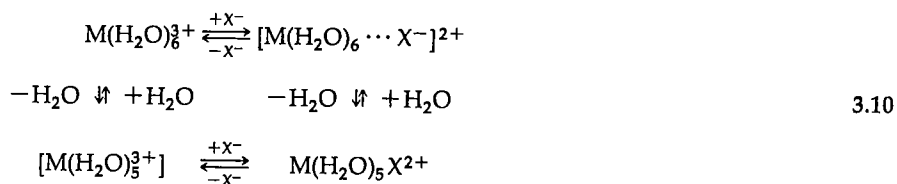
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$ may be contrasted to the very small dependence of the entering ligand in aquation of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$. The aquation of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ was thus suggested to be an I_d mechanism. The data in Table 3.5 indicate that the ligand environment may change the mechanism for substitution at a Cr(III) center. The greater electron density at the chromium in $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ than in $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ favors dissociative interchange over associative interchange. The volumes of activation for both $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ are negative. These observations have been explained in terms of a dissociative mechanism for entropies and volumes of activation that are near zero or even slightly negative,¹⁸ but active discussion persists on this question.¹⁹ The chemical evidence shown in Table 3.5 is relatively clear cut and provides evidence that I_a and I_d mechanisms are both operative in Cr(III) complexes. The substitution reactions of other Cr(III) complexes have been interpreted in terms of an I_d mechanism.²³

TABLE 3.5

Kinetic Parameters for the Aquation of $\text{CrL}_5\text{H}_2\text{O}^{3+}$ for $\text{L} = \text{H}_2\text{O}$ and NH_3 .^{21,22}

X	$k(10^8\text{M}^{-1}\text{s}^{-1})$	$\text{L} = \text{H}_2\text{O}$		$\text{L} = \text{NH}_3$	
		$\Delta H^\ddagger$	$\Delta S^\ddagger$	$k(10^4\text{M}^{-1}\text{s}^{-1})$	
NCS^-	180	25	1	4.2	
NO_3^-	73	26	1	—	
Cl^-	2.9	30	9	0.7	
Br^-	1.0	29	2	3.7	
I^-	0.08	31	6	—	
CF_3CO_2^-	—	—	—	1.4	

Thus considerable evidence supports a dissociative process for substitutions on octahedral coordination complexes. To differentiate between D and I_d mechanisms one needs to determine whether or not an intermediate of reduced coordination number (five-coordinate) exists in the reaction coordinate.²⁴ The two possibilities are shown in the following scheme:

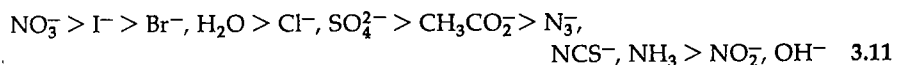


Outer sphere complexes such as $\text{M}(\text{H}_2\text{O})_6 \cdots \text{X}^-$ are well established by flow methods, temperature jump data, and ultrasonic absorption,²⁵⁻²⁷ but less evidence exists for five-coordinate intermediates. The question of whether these species are intermediates along the reaction coordinate is difficult to answer.^{28,29} Evidence for $\text{Co}(\text{NH}_3)_5^{3+}$ as an intermediate in the aquation of $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ was later questioned.^{28,30} There was no evidence for $\text{Cr}(\text{H}_2\text{O})_5^{3+}$ in the water exchange reaction but a good possibility for its formation in aquation of $\text{Cr}(\text{H}_2\text{O})_5\text{I}^{2+}$.²⁹

The diversity of transition metal coordination complexes makes unambiguous conclusions about their reactivity difficult. Most complexes apparently react by an I_d mechanism, although D and I_a mechanisms may also be possible for a given complex.

LEAVING-GROUP AND CHELATE EFFECTS

As expected for a reaction that proceeds by a dissociative mechanism, the rate is dependent on the nature of the leaving group. Data for aquation of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ are shown in Table 3.6.³¹ The order of leaving-group effects

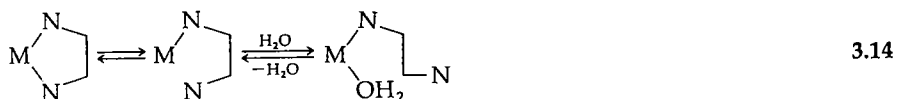


represents the order of complex stability as shown in Figure 3.4.¹² Thus the leaving-group order represents the bond-strength order for the ligands. The relationship between leaving-group effects and ligand strength is also shown by the similarity between the spectrochemical series and the leaving-group order.

Bidentate ligands are substituted more slowly than monodentate ligands, and complexes with chelate ligands are more stable than comparable complexes of monodentate ligands; this is termed the "chelate effect." Kinetics for substitution of bidentate ligands are presented for comparison to the monodentate analogues in Table 3.7.⁸ The chelate ligands are more slowly removed. Removing a bidentate ligand can be viewed as a two-step process:



A number of explanations have been offered for the chelate effect.^{4,5} The simplest is that, after dissociation of one end, there is a very high effective concentration near the metal of that end since the chelate is still bound to the metal. Thus the k_{-1} step is much larger for a chelate than for a related monodentate ligand. This simple explanation has been augmented by more detailed consideration for ethylenediamine and reaction 3.12 has been expanded to the following scheme:³¹



The initial bond breaking step is slower than for dissociation of a unidentate ligand because angular expansion of the chelate is required to lengthen the $\text{M}-\text{N}$ distance. This leads to a larger value of $\Delta H^\ddagger$ for chelate removal as commonly observed. The water would be prevented by steric interactions

TABLE 3.6

Rates of Aquation of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ at 25°C .

X	$k(\text{s}^{-1})$
NO_3^-	2.7×10^{-5}
I^-	8.3×10^{-6}
Br^-	6.3×10^{-6}
H_2O	5.8×10^{-6}
Cl^-	1.7×10^{-6}
SO_4^{2-}	1.2×10^{-6}
CH_3CO_2^-	1.2×10^{-7}
NH_3	10^{-10}
NCS^-	5×10^{-10}
N_3^-	2.1×10^{-9}
NO_2^-	slow
OH^-	slow

the metal as shown in the second step. Thus reversal of the bond breaking (first step) would be facile.

EFFECT OF THE METAL

Some metal complexes are labile regardless of the ligand environment while complexes of other metals are inert. This indication of influence of the metal center on reactivity is shown further by the rates of water exchange in the

TABLE 3.7

Chelate Effect on Reactions of Nickel Complexes.

complex	$k_1(\text{s}^{-1})$
$\text{Ni}(\text{Py})$	38.5
$\text{Ni}(\text{bipy})$	3.8×10^{-4}
$\text{Ni}(\text{NH}_3)$	5.8
$\text{Ni}(\text{en})$	0.27

TABLE 3.8

Rates of H₂O Exchange for Hexaaquo Metal Complexes.

metal	rate	electron configuration
Cr ²⁺	7×10^9	d^4
Mn ²⁺	3×10^7	d^5
Fe ²⁺	3×10^6	d^6
Co ²⁺	1×10^6	d^7
Ni ²⁺	3×10^4	d^8
Cu ²⁺	8×10^9	d^9
Fe ³⁺	3×10^3	d^5
Cr ³⁺	3×10^{-6}	d^3
Rh ³⁺	4×10^{-8}	d^6

hexaaquo complexes (Table 3.8).⁵ The rates vary enormously with the nature of the metal center. Some features can be readily understood in terms of the bonding of a ligand to the metal center. The bond involves an attraction of the pair of electrons on the ligand to the positive charge on the metal. An increase in the charge on the metal would lead to an increased attraction to the ligand and a decreased rate. Thus the 3+ ions dissociate H₂O more slowly than do 2+ ions. For the 2+ hexaaquo ions of the first row transition metals another explanation is required since the charge would steadily increase across the row and the rate clearly does not correlate with the increasing charge. One would anticipate that electrons in the e_g -orbitals directed toward the ligands would cause an extra destabilization of the metal-ligand bond. This concept has been semiquantitatively applied by considering **crystal field activation energies** (CFAE).⁵

A nonspherical ligand geometry splits the d -orbitals, stabilizing some orbitals and destabilizing others.^{2,3} The magnitude of the stabilization or destabilization, which is called the **crystal field stabilization energy** (CFSE), has been derived for several geometries. Since octahedral complexes react primarily by dissociative processes, we need consider CFSE only for octahedral and square pyramidal geometries.* The values for different d -electron configurations are given in Table 3.9.⁵ The CFAE is derived by subtracting the

* Trigonal bipyramidal geometry is also possible for the intermediate, but the results are similar to square pyramidal. In each case where there is a difference, square pyramidal is in better agreement with the experimental evidence.⁵

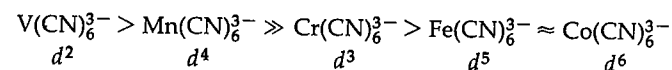
TABLE 3.9

Crystal Field Activation Energies for Substitution Reactions on Octahedral Coordination Complexes.

electron configuration	octahedral CFSE	square pyramidal CFSE	CFAE
d^0	0	0	0
d^1	4	4.6	-0.6
d^2	8	9.1	-1.1
d^3	12	10.0	2
d^4 (strong field)	16	14.6	1.4
d^4 (weak field)	6	9.1	-3.1
d^5 (strong field)	20	19.1	0.9
d^5 (weak field)	0	0	0
d^6 (strong field)	24	20.0	4
d^6 (weak field)	4	4.6	-0.6
d^7 (strong field)	18	19.1	-1.1
d^7 (weak field)	8	9.1	-1.1
d^8	12	10	2.0
d^9	6	9.1	-3.1
d^{10}	0	0	0

stabilization in the square pyramidal transition state from the stabilization for the octahedral ground state. For the hexaaquo complexes, which are weak field complexes, the correlation between CFAE and rate of H₂O exchange (Table 3.8) is quite good. It is necessary to realize that the contribution from CFAE is only one part of the total activation process and can only be applied for complexes with the same ligands and the same charge. From the CFAE values one would anticipate that the inert complexes would be of d^3 , d^8 and strong field d^6 configurations, i.e., Cr³⁺, Ni²⁺, Co³⁺. This is also the experimental observation.

Activation parameters for the tris-orthophenanthroline (*o*-phen) complexes are in the order expected from CFAE (Table 3.10).⁵ A series of strong field complexes, $M(CN)_6^{3-}$, have also been investigated.⁵ The reaction order is



which is very close to the order expected from CFAE values.

TABLE 3.10

Reactions of Strong Field Complexes.

complex	electrons	E_a (kcal/mole)
$\text{Mn}(o\text{-phen})_3^{2+}$	d^5	10.4
$\text{Fe}(o\text{-phen})_3^{2+}$	d^6	12.8
$\text{V}(o\text{-phen})_3^{2+}$	d^3	21.3
$\text{Ni}(o\text{-phen})_3^{2+}$	d^8	25.2

The crystal field activation model correctly predicts the reactivity of metal complexes in both weak field and strong field complexes. There are many approximations in the crystal field activation that may be questionable, but its utility in correlations with reactivity makes it a useful concept.

To summarize the effect of metal on reactivity:

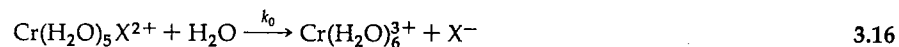
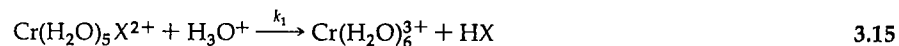
1. High oxidation state complexes are less reactive than low oxidation state transition metal complexes.
2. For analogous complexes the reactivity decreases going down a column.
3. A larger CFAE leads to slower reactions.

ACID AND BASE CATALYSIS

Substitution reactions on octahedral coordination complexes have been investigated mainly in aqueous solution, where the pH may vary. Thus it is important to understand the effect of acids and bases on substitution reactions. In general, acids and bases catalyze the substitution reactions of inert complexes.

Acid Catalysis

Substitution in the presence of acid can be considered



and the amount of rate acceleration can be seen by comparing k_1 (eq. 3.15) to k_0 (eq. 3.16) as is shown in Table 3.11.⁴ The mechanism of acid catalysis apparently is protonation of the leaving group,

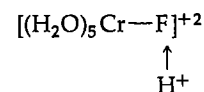


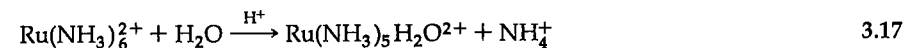
TABLE 3.11

Acid-Catalyzed Aquation Reactions of $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$.

X^-	k_0	k_1
N_3^-	2.6×10^{-8}	9.3×10^{-7}
F^-	6.2×10^{-10}	1.4×10^{-8}
CN^-	1.1×10^{-5}	5.9×10^{-4}
NH_3	no acceleration	

The protonation weakens the $\text{M}-\text{X}$ bond and facilitates X^- removal. Since coordinated NH_3 doesn't have an electron pair, NH_3 removal is usually not catalyzed by acid.

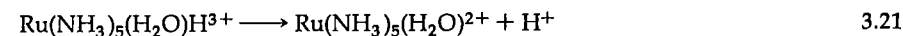
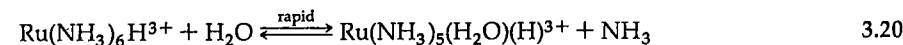
Aquation of $\text{Ru}(\text{NH}_3)_6^{2+}$ is acid-catalyzed.³³



The rate depends directly on the hydrogen ion concentration,

$$\text{rate} = k[\text{H}^+][\text{Ru}(\text{NH}_3)_6^{2+}] \quad 3.18$$

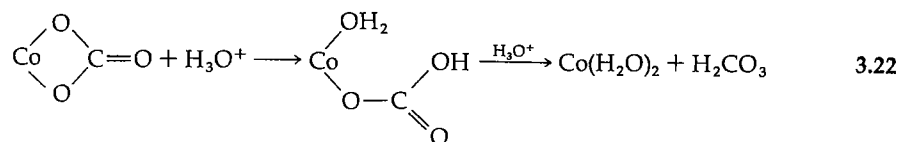
Since other hexamine complexes do not show an acceleration, this rate effect was ascribed to protonation of a t_{2g} pair of electrons on the metal as opposed to ligand protonation as described above. Thus the mechanism



accommodates a direct dependence of the rate on the hydrogen ion concentration. It was suggested that protonation of a filled t_{2g} -orbital is much more

likely for second and third row metals where the *d*-orbitals extend further into the coordination sphere.

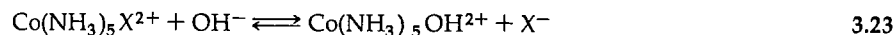
Acid-assisted dechelation (removal of a chelate) is the easiest way to remove a chelating ligand. As discussed earlier, chelate complexes are more stable primarily because of the large effective concentration of the chelating ligand. This effective concentration of the dissociated end of the chelate is eliminated by protonation of the free end as can be illustrated with the following carbonate complex:



Here protonation inhibits the re-formation of the oxygen-cobalt bond.

Base Catalysis

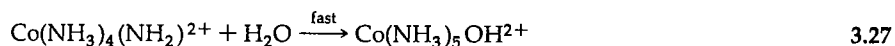
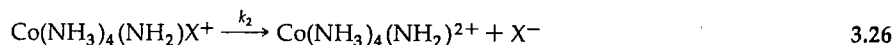
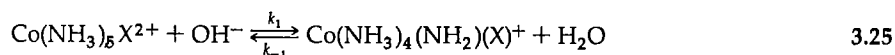
Presence of a base also facilitates substitution reactions.^{4,5} These reactions can be modeled by the replacement of a ligand by OH⁻.



The rate law for these reactions is different from that for other octahedral substitutions, showing a dependence on the concentration of the entering ligand:

$$\text{rate} = k[\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-] \quad 3.24$$

A number of mechanisms could lead to this rate law, but the accepted mechanism is the conjugate-base mechanism outlined below.^{4,5}

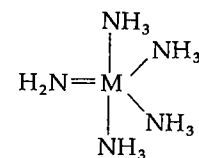


This scheme reduces to the rate law

$$\text{rate} = \frac{K_1 k_2 [\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-]}{1 + K_1 [\text{OH}^-]} \quad 3.28$$

where K_1 is the equilibrium constant for reaction 3.25. Equation 3.28 in turn reduces to the observed rate law if $K_1[\text{OH}^-]$ is much less than one. The key

feature of the conjugate-base mechanism is the labilization of dissociation by NH_2^- , presumably by stabilization of the transition state by the NH_2^- group.⁵



Consistent with the first step is the facile deuteration of the NH_3 ligands in the presence of D_2O . Evidence for the dissociative nature of the reaction comes from the observation that different nucleophiles react at similar rates, that steric acceleration is observed, and that the enthalpy of the transition state is independent of the nature of the leaving group.⁵

STEREOCHEMISTRY OF OCTAHEDRAL SUBSTITUTION REACTIONS

The stereochemical course of substitution reactions with octahedral complexes is not as easily generalized as that for square planar complexes.^{2,5,24} Dissociation of a ligand from an octahedron leads to a five-coordinate species. There is apparently very little energy difference between the two possibilities for five-coordinate complexes, trigonal bipyramidal and square pyramidal. (We shall consider this in more detail in Chapter 7.) Both geometries are suggested in different octahedral substitution reactions.⁵ A reaction that proceeds through a square pyramidal intermediate would lead to retention of stereochemistry; a reaction proceeding through a trigonal bipyramidal intermediate would lead to a mixture of stereoisomers. These alternatives are shown in Figure 3.5 for a *cis* isomer MA_2B_4 . In the absence of preferential sites for attack by the incoming ligand, stereochemical retention is an indication of a square pyramidal intermediate and loss of stereochemistry is evidence for a trigonal bipyramidal intermediate. Data for acid hydrolysis of *cis*- $\text{Co}(\text{en})_2(\text{A})(\text{X})$ are shown in Table 3.12 and those for *trans*- $\text{Co}(\text{en})_2(\text{A})(\text{X})$ in Table 3.13.⁵ The data in Tables 3.12 and 3.13 indicate several features that appear to be general. *Cis* complexes are more likely to proceed with complete stereochemical retention than are *trans* complexes, which often undergo stereochemical loss. Other metal complexes show similar stereochemical behavior—varying amounts of stereochemical retention depending on the specific complex. Often *cis* octahedral substitution reactions proceed with retention of configuration and *trans* complexes proceed with some loss, but in the absence of specific data for a given reaction predictions are unreliable.

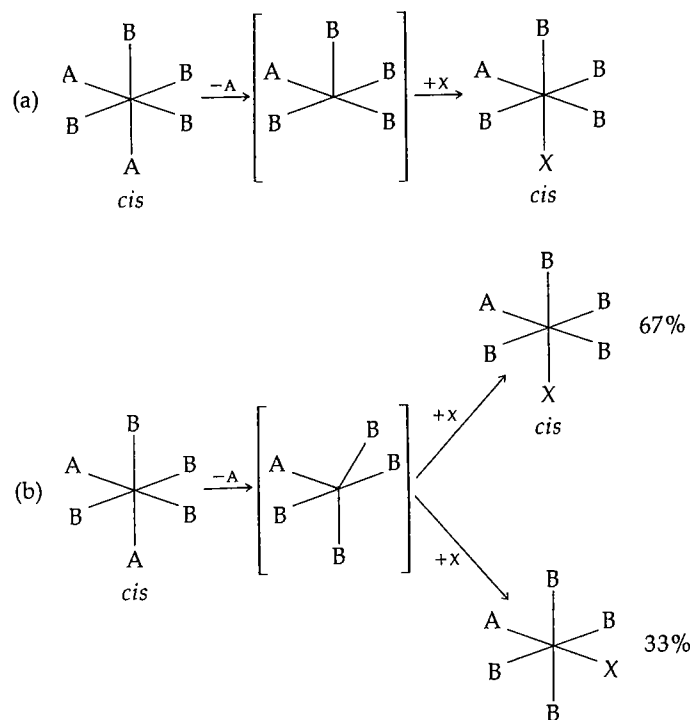


FIGURE 3.5. The possible stereochemistries for substitution reactions of octahedral Werner-type complexes depending on whether the intermediate is (a) square pyramidal or (b) trigonal bipyramidal.

TABLE 3.12

Stereochemical Course of the Reaction of *cis*-Co(en)₂(A)(X) with H₂O.

A	X	% <i>cis</i> in product
OH ⁻	Cl ⁻	100
Br ⁻	Cl ⁻	100
Cl ⁻	Cl ⁻	100
N ₃ ⁻	Cl ⁻	100
NCS ⁻	Cl ⁻	100
NO ₂ ⁻	Cl ⁻	100
Cl ⁻	Br ⁻	100

SUMMARY

TABLE 3.13

Stereochemical Course of the Reaction of *trans*-Co(en)₂(A)(X) with H₂O.

A	X	% <i>trans</i> in product
NO ₂ ⁻	Cl ⁻	100
NCS ⁻	Cl ⁻	30–50
Cl ⁻	Cl ⁻	65
OH ⁻	Cl ⁻	25
Cl ⁻	Br ⁻	80

SUMMARY

Although it is difficult to generalize for such a large group of complexes as the octahedral coordination complexes, the predominant mechanism of substitution reactions is dissociative or dissociative interchange. The dissociative mechanism persists even for acid- and base-catalyzed substitution reactions. Substitutional reactivity of octahedral Werner-type complexes depends on (1) the nature of the leaving group, with strongly binding ligands slower and with chelate ligands slower than monodentate ligands; (2) the charge on the metal center, the more highly charged metal undergoing substitution more slowly; (3) whether the metal is first, second, or third row, the reactivity decreasing in that order; and (4) the *d*-electron configuration of the metal.

REFERENCES

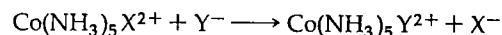
1. Several of Werner's papers have been translated and collected in G. B. Kauffman, *Classics in Coordination Chemistry* (New York: Dover, 1968).
2. K. F. Purcell and J. C. Kotz, *Inorganic Chemistry* (Philadelphia: W. B. Saunders, 1977).
3. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (New York: Interscience, 1972).
4. R. G. Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes* (Boston: Allyn and Bacon, 1974).
5. F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* (New York: John Wiley and Sons, 1967).
6. M. L. Tobe, *Inorganic Reaction Mechanisms* (London: Nelson, 1972).
7. E. B. Fleischer, S. Jacobs, and L. Mestichelli, *J. Am. Chem. Soc.* **90**, 227 (1968).
8. R. G. Wilkins, *Acc. Chem. Res.* **3**, 408 (1970).
9. D. Thusius, *J. Am. Chem. Soc.* **93**, 2629 (1971).
10. D. M. Tully-Smith, P. K. Kurimoto, D. A. House, and C. S. Garner, *Inorg. Chem.* **6**, 1524 (1967).
11. D. A. Buckingham, B. M. Foxman, and A. M. Sargenson, *Inorg. Chem.* **9**, 1790 (1970).
12. A. Haim, *Inorg. Chem.* **9**, 426 (1970).
13. Reference 4, p. 205.
14. J. H. Espenson, *Inorg. Chem.* **8**, 1554 (1969).
15. D. K. Lin and C. S. Garner, *J. Am. Chem. Soc.* **91**, 6637 (1969).
16. Reference 4, p. 222.
17. T. W. Swaddle, *Coord. Chem. Rev.* **14**, 217 (1974).
18. C. H. Langford, *Inorg. Chem.* **18**, 3288 (1979).
19. T. W. Swaddle, *Inorg. Chem.* **19**, 3203 (1980).
20. A. Haim and W. K. Wilmarth, *Inorg. Chem.* **1**, 573, 583 (1962).
21. D. Thusius, *Inorg. Chem.* **10**, 1106 (1971).
22. T. Ramasami and A. G. Sykes, *J. Chem. Soc. Chem. Comm.* 378 (1978).
23. S. T. D. Lo and D. W. Watte, *Aus. J. Chem.* **28**, 491, 501 (1975).
24. C. H. Langford and H. B. Gray, *Ligand Substitution Processes* (New York: W. A. Benjamin, 1965).
25. D. W. Carlyle and J. H. Espenson, *Inorg. Chem.* **8**, 575 (1969).
26. H. Brintzinger and G. G. Hammes, *Inorg. Chem.* **5**, 1286 (1966).
27. P. Hemmes and S. Petrucci, *J. Phys. Chem.* **72**, 3986 (1968).
28. R. G. Pearson and J. W. Moore, *Inorg. Chem.* **3**, 1334 (1964).
29. S. P. Ferraris and E. L. King, *J. Am. Chem. Soc.* **92**, 1215 (1970).
30. A. Haim and H. Taube, *Inorg. Chem.* **2**, 1199 (1963).

REFERENCES

31. D. W. Margerum, G. R. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, *Am. Chem. Soc. Monograph Series* **174**, 1 (1970).
32. P. C. Ford, J. K. Kuempel, and H. Taube, *Inorg. Chem.* **7**, 1976 (1968).

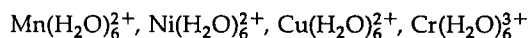
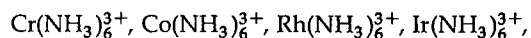
PROBLEMS

1. In the following reaction the rates of substitution at cobalt(III) are usually independent of the group Y^- :



The main exception is $Y = \text{OH}^-$, for which the rates are much faster than for other Y^- and for which there is a first order dependence on $[\text{OH}^-]$. Explain these observations in terms of mechanistic considerations.

2. Order the rates of substitution reactions for the following complexes:



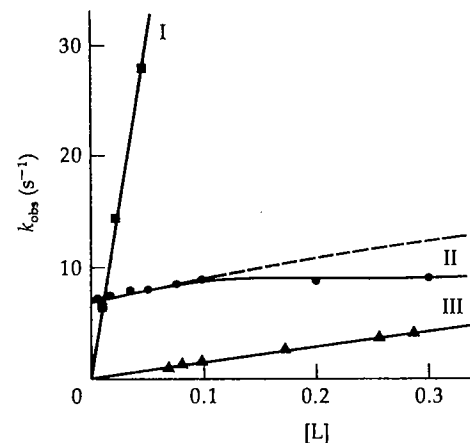
3. In associative reactions of octahedral complexes a pentagonal bipyramid is a possible intermediate. Given the data below, derive the order of reaction rates expected for the different electron configurations in an octahedral to pentagonal bipyramid reaction scheme.

	pentagonal bipyramid crystal field stabilization energies	
	strong field	weak field
d^0	0	0
d^1	5.28	5.28
d^2	10.56	10.56
d^3	7.74	7.74
d^4	13.02	4.93
d^5	18.30	0.0
d^6	15.48	5.28
d^7	12.66	10.56
d^8	7.74	7.74
d^9	4.93	4.93
d^{10}	0	0

4. There has been active discussion of the significance of the volumes of activation in mechanistic differentiation. Two points of view are presented in *Correspondences to Inorganic Chemistry*: (1) T. W. Swaddle, *Inorg. Chem.* **19**, 3205 (1980). (2) C. H. Langford, *Inorg. Chem.* **18**, 3288 (1979). Briefly summarize the main features of these arguments.

PROBLEMS

5. Substitution reactions are not always straightforward. Reactions of $\text{Ru}(\text{NH}_3)_4(\text{P}(\text{OEt})_3)(\text{H}_2\text{O})^{2+}$ with different entering ligands show the dependence below. Interpret these data.

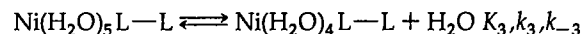
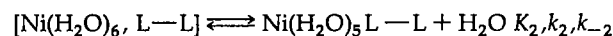
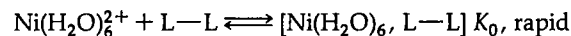


Dependence of k_{obs} on ligand concentration for the reaction of $\text{trans}[\text{Ru}(\text{NH}_3)_4\text{P}(\text{OEt})_3(\text{H}_2\text{O})]^{2+}$ with: (I) SO_3^{2-} , $\blacksquare$; (II) Me/Pyr^+ , $\bullet$; (III) imN , $\blacktriangle$. [Reprinted with permission from D. W. Franco and H. Taube, *Inorg. Chem.* **17**, 571 (1978). Copyright 1978 American Chemical Society.]

6. Base-hydrolysis data for $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ show very little dependence of the activation enthalpy on the leaving group X. Explain how these data are consistent with a dissociative mechanism. [D. A. House and H. K. J. Powell, *Inorg. Chem.* **10**, 1583 (1971).]

X	$\Delta H^\ddagger$
Cl^-	26.6
Br^-	27.0
I^-	27.2
NO_3^-	28.2

7. Given the following reactions describing chelate formation



derive the rate law for chelate formation, and discuss the step that is different for chelate ligands than for two monodentate ligands. [R. G. Wilkins, *Acc. Chem. Res.* **3**, 408 (1970).]

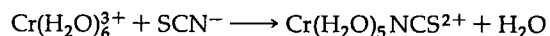
8. Decarboxylation reactions of *trans*-Rh(en)₂(X)(OCO₂) show a pH dependence as below at 25°C:

pH	$k_{\text{obs}} (\text{s}^{-1})$
0.30	0.48
0.60	0.51
1.30	0.51
2.00	0.55
3.25	0.58
3.90	0.58
4.88	0.59
5.68	0.54
6.00	0.44
6.33	0.36
6.45	0.31
6.75	0.22
6.88	0.17

Suggest a mechanism to explain this pH dependence. [R. van Eldik, D. A. Palmer, H. Kelm, and G. M. Harris, *Inorg. Chem.* **19**, 3679 (1980).]

9. The kinetic *trans* effect for acid hydrolysis of *trans*-Co(cyclam)ACl⁺ complexes was studied with various anions A and with Cl⁻ as the leaving group. Hammett-type substituent constants based on Cl⁻ = 0.0 were assigned from the observed kinetics: $\sigma(\text{Cl}^-) = 0.0$; $\sigma(\text{NCS}^-) = -3.00$; $\sigma(\text{OH}^-) = 4.04$. The first order rate constant for hydrolysis of the Co(cyclam)Cl₂⁺ complex is $3.5 \times 10^{-3} \text{ s}^{-1}$.
- Estimate the rate constants for the Co(cyclam)(NCS)Cl⁺ and the Co(cyclam)(OH)Cl⁺ complex.
 - Account for the differences in rates in terms of the electronic properties of the substituents.

10. In the reaction



the rate law is of the form

$$\frac{d[\text{CrNCS}^{2+}]}{dt} = [\text{Cr}^{3+}][\text{SCN}^-](k_1 + k_2/[\text{H}^+]) \text{ (waters omitted for convenience)}$$

- If conditions are sufficiently acid that only the first term in the rate law is important, does the form of the rate law require that the anation process proceed by an associative mechanism? Explain. (For example, if your answer

is no, show how a stoichiometric mechanism other than associative could lead to the observed rate law.)

- Account for the existence of the second term in the rate law.
- Using crystal field theory, explain how the crystal field activation energies would differ for dissociation of a ligand from a low spin Fe(II) compared with that of a high spin Fe(II) complex.
 - Using linear free-energy relationships and citing appropriate literature, present an argument in support of substitution of Co(NH₃)₅X⁺ complexes being dissociative in character.

Organometallic Substitution Reactions

Organometallic chemistry has enjoyed tremendous growth in the last twenty-five years. The use of organometallic complexes to model heterogeneous catalyst systems and as homogeneous catalysts themselves gave a practical reason for studying fascinating complexes that have very different properties than Werner-type complexes. The development of organometallic chemistry has followed that of many other areas of chemistry: First are synthetic studies, next structural studies, and then studies of reactivity. Most of the kinetic and mechanistic studies have occurred in the last ten to fifteen years, and many continue today.

Organometallic compounds are defined as complexes that contain a metal-carbon bond. The presence of the metal-carbon bond creates a number of very unusual properties for transition metal complexes: volatility (many complexes can be purified by sublimation), solubility in hydrocarbon solvents, and very low oxidation states for the metal (as low as -4). Two features of organometallic chemistry are especially important to our discussion of substitution reactions, ligand bonding and electron counting.

LIGAND BONDING

The nature of the low-oxidation state metal center requires ligands with different bonding properties than those commonly observed for Werner-type complexes. The bonding of carbon monoxide, illustrated in Figure 4.1, shows the dual bonding important to organometallic complexes. Electron density on carbon is donated to the metal, a sigma donation. There is also donation of

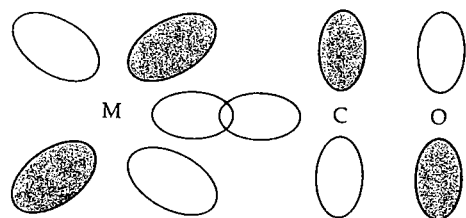


FIGURE 4.1. Bonding of CO to a transition metal, including both sigma donation and pi acceptance by CO.

electron density from the filled d -orbitals on the metal into the CO antibonding orbitals, pi back-bonding. Each of these types of bonding reinforces the other (sigma bonding increases the electron density on the metal, which enhances the pi back-bonding), creating a synergic interaction. The back-bonding into the CO antibonding orbital weakens the C-O bond, as shown by a lengthening of the C-O bond and a decrease in the infrared stretching frequencies of the carbonyls with respect to carbon monoxide. Synergic or dual binding is also observed for phosphorus bases and ethylene as shown in Figure 4.2. Phosphorus bases — phosphites, $P(OR)_3$, and phosphines, PR_3 — may utilize the d -orbitals to accept pi-electron density.* The sigma bonding of ethylene involves donation of the bonding electron density to the metal and back-bonding into the anti-bonding orbital. There has been much discussion in the literature about the relative amounts of pi- and sigma-bonding in a given ligand. A number of techniques including infrared spectroscopy,¹ carbon-13 and phosphorus-31 NMR,^{2,3} and reaction chemistry⁴ have been used

*The bonding of phosphorus ligands has been an area of active discussion for a number of years; the relative degrees of sigma donation and pi acceptance of electron density have been the focus of discussion. Recently it has been suggested that phosphines, PR_3 , do not accept electron density from a metal.⁵ For alkyl phosphines (PMe_3 , PEt_3 , PBu_3 , etc.) this may be correct. Certainly the predominant bonding is from the very strong electron donation. For these ligands the most accurate statement is that alkyl phosphines have a d -orbital that *may* accept electron density. For aryl phosphines such as PPh_3 , however, pi acceptance appears to be significant. The most straightforward evidence is from the Cr- PPh_3 bond lengths of *trans*-Cr(CO)₄L PPh_3 [L = PBu_3 , $P(OMe)_3$, $P(OPh)_3$, CO].⁶

ligand <i>trans</i>	Cr- PPh_3 bond length (Å)
PBu_3	2.345(3)
$P(OMe)_3$	2.362(2)
$P(OPh)_3$	2.393(1)
CO	2.422(1)

The shortening of the Cr- PPh_3 bond as the donor strength of the *trans* ligand increases is most easily accommodated in terms of pi acceptance by PPh_3 .

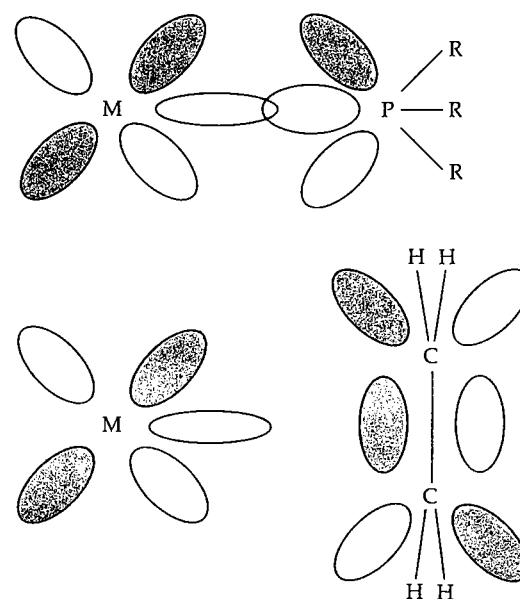
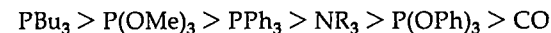


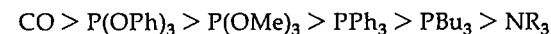
FIGURE 4.2. Bonding schemes for phosphines and ethylene in organometallic complexes.

to assess the binding capabilities. The following ordering is generally accepted for the common ligands in organometallic substitution reactions:

for sigma donation



and for pi acceptance



Any discussion of the electronic binding of these ligands is complicated by steric interactions of the rather bulky phosphine and phosphite ligands. The relative size of the ligands is as follows:⁷



Each of these ligand parameters is important in discussing reactivity of organometallic compounds. As we investigate reactions of organometallic complexes, we shall often refer to sigma-bonding ability, pi-accepting ability, or size of the ligand.

TABLE 4.1

Selected Binary Metal Carbonyls of the First Row and Their Electron Counts.

Cr(CO) ₆		Mn ₂ (CO) ₁₀		Fe(CO) ₅		Co ₂ (CO) ₈		Ni(CO) ₄	
Cr ⁰	6e ⁻	Mn ⁰	7e ⁻	Fe ⁰	8e ⁻	Co ⁰	9e ⁻	Ni ⁰	10e ⁻
6CO	12e ⁻	5CO	10e ⁻	5CO	10e ⁻	4CO	8e ⁻	4CO	8e ⁻
	18e ⁻	Mn-Mn bond	1e ⁻		18e ⁻	Co-Co bond	1e ⁻		18e ⁻
			18e ⁻				18e ⁻		

The majority of organometallic complexes have 18 electrons in the valence shell of the metal. The stable binary metal carbonyls shown in Table 4.1 form a nice series illustrating the importance of the 18-electron rule.⁸

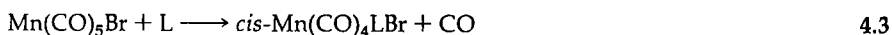
Electron counting is a very useful concept for predicting stable complexes. As we consider reactions of these complexes, the electron count in the starting complex and the intermediate will be useful in determining the reaction type. It has been proposed that organometallic reactions occur through a sequence of 16 and 18 electron intermediates.⁸ Although there are exceptions to this rule, it is quite valuable in discussing organometallic reactions.

METAL CARBONYL SUBSTITUTION REACTIONS

Most studies of organometallic substitution reactions have been accomplished on transition metal carbonyl complexes. These complexes are readily prepared and purified, are stable, and have very characteristic infrared spectra that allow quantitative analysis. The reactions can be represented



where M is a transition metal and L is an entering ligand, usually a phosphine or phosphite. Two examples that were among the first to be investigated kinetically were Ni(CO)₄ and Mn(CO)₅Br.^{9,10}



The kinetic data in Table 4.2 indicate that the rate law is independent of the

TABLE 4.2

Kinetic Data for Reaction 4.3 at 30°C in CHCl₃.

L	[L](M)	k(10 ⁵ s ⁻¹)
PPh ₃	0.133	6.7
PPh ₃	0.344	6.8
AsPh ₃	0.132	6.6
SbPh ₃	0.135	6.6

concentration of L and first order in metal carbonyl complex. Plots of ln A versus time (A = absorbance of infrared stretching mode) were linear for several half-lives, confirming the first order behavior in metal complex.

$$\text{rate} = k_1[\text{Ni(CO)}_4]$$

The accepted mechanism involves rate-determining CO dissociation from the 18-electron complex to form a 16-electron intermediate,⁹



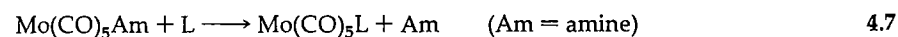
such that the substitution can be considered to be a two-step process. The second step (reaction 4.5) is much more rapid, occurring at a rate of 10⁶M⁻¹s⁻¹ in contrast to the first step (reaction 4.4), which occurs at a rate of 10⁻⁴s⁻¹.¹¹ The activation parameters were in agreement with a dissociative process that has a positive entropy of activation as shown in Table 4.3.^{9,12,13}

TABLE 4.3

Activation Parameters for the Reaction of Ni(CO)₄ with Nucleophiles.

L	ΔH [‡] (kcal/mole)	ΔS [‡] (eu)	k(10 ⁴ s ⁻¹) at 20°C
PPh ₃	24	13	50
C ¹⁸ O	24	14	52

Substitution of several metal carbonyl complexes shows a small dependence on the nature and concentration of the entering ligand.^{14,15}



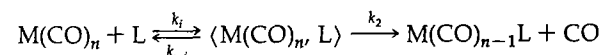
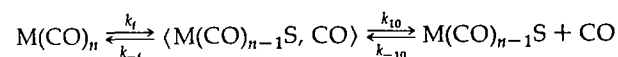
Under pseudo first order conditions, the rate law for these substitutions had two terms, as shown below for $\text{Cr}(\text{CO})_6$:

$$\text{rate} = k_1[\text{Cr}(\text{CO})_6] + k_2[\text{Cr}(\text{CO})_6][\text{L}]$$

The second order term was always much smaller than the first order term.^{14,15} It was originally suggested that this rate law indicated competing ligand attack on the metal and CO dissociation.¹⁴



An alternative mechanism that ascribes the second order term to dissociative interchange (I_d) has been suggested for the $\text{Mo}(\text{CO})_5\text{Am}$ system, which has a similar rate law.¹⁵ This mechanism is outlined as follows:¹⁵



Here S represents the solvent and the angular brackets enclose solvent-encased substrate and a species occupying a favorable site for exchange. These equations reduce to the observed rate law. This process seems much more reasonable than the concurrent formation of 16- and 20-electron intermediates that would be required in competing dissociative and associative steps. Thus the body of evidence for the simple metal carbonyls indicates CO dissociation is the mechanism of ligand substitution reactions.

Metal Effects on Reactivity

It has been recognized for a number of years that reactivity increases in the order "first row < second row > third row" for substitution reactions. The data in Table 4.4 show the effect for two homologous series.^{14,16} In each case described in Table 4.4 the reaction proceeds by dissociation of a ligand.

TABLE 4.4

Rate Constants for Substitution Reactions of $\text{M}(\text{CO})_6$ and $\text{M}[\text{P}(\text{OEt})_3]_4$.

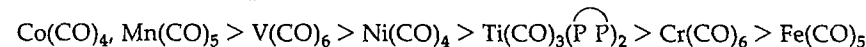
$\text{M}(\text{CO})_6$	k_{obs} at 130°C ^a	$\text{M}[\text{P}(\text{OEt})_3]_4$	k_{obs} at 40°C ^b
$\text{Cr}(\text{CO})_6$	1.4×10^{-4}	$\text{Ni}[\text{P}(\text{OEt})_3]_4$	3.7×10^{-6}
$\text{Mo}(\text{CO})_6$	2.0×10^{-3}	$\text{Pd}[\text{P}(\text{OEt})_3]_4$	1200
$\text{W}(\text{CO})_6$	4.0×10^{-6}	$\text{Pt}[\text{P}(\text{OEt})_3]_4$	0.3

^aReaction with PPh_3 . Values for Mo and W are estimated from other temperatures.

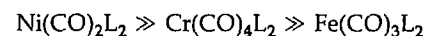
^bFor Ni the reaction was with cyclohexylisocyanide; for Pd and Pt the values were estimated from other temperatures for exchange reactions.

In general for organometallic substitution reactions the second row complex reacts most rapidly, but it is more difficult to generalize between first and third row complexes. The data illustrate this difficulty. For carbonyl complexes the third row complex usually reacts more slowly in dissociative reactions.

The effect of changing the metal across a row has not been thoroughly investigated, but the reactivity changes significantly. From qualitative, semi-quantitative, and quantitative data the following order of reactivity for the metal carbonyl complexes can be derived:



This order spans about ten orders of magnitude in rate and indicates a change in reactivity with the metal center that is large, comparable to that observed for Werner-type complexes. For the analogous compounds of chromium, iron, and nickel that have been quantitatively investigated, the order of reactivity is



with about 10^8 difference in rate between nickel and iron complexes. Data for different ligands are shown in Table 4.5.¹⁷ In each case the reactions proceed by first order kinetics and have been assigned to ligand dissociation. There are no data to suggest that the reactivity order shown in Table 4.5 arises predominantly from ground state energy differences.¹⁵ A possible explanation of the variation of the rate of substitution with the metal has been offered in terms of the crystal field activation energies (CFAE) for these substitution reactions.¹⁷ Crystal field activation energies have proven quite useful in interpreting the reactivity of classical coordination complexes as shown in Chap-

TABLE 4.5

Rate Constants for Ligand Dissociation from $\text{Cr}(\text{CO})_4\text{L}_2$, $\text{Fe}(\text{CO})_3\text{L}_2$, and $\text{Ni}(\text{CO})_2\text{L}_2$ at 25°C.

L	$\text{Cr}(\text{CO})_4\text{L}_2$	$\text{Fe}(\text{CO})_3\text{L}_2$	$\text{Ni}(\text{CO})_2\text{L}_2$
CO	1.9×10^{-12}	—	1.2×10^{-2}
$\text{P}(\text{O}i\text{Pr})_3$	4.6×10^{-11}	4.8×10^{-12}	1.0×10^{-7}
PPh_3	3.1×10^{-6}	5.0×10^{-11}	5.6×10^{-4}

ter 3. A primary uncertainty in applying crystal field activation energies is the geometry of the transition state. Values of the crystal field activation energy for substitution reactions of the first row mononuclear carbonyl complexes are shown in Table 4.6 for several possible geometries. Since $\text{Ni}(0)$ is d^{10} , there would be no CFAE. For chromium the predominant evidence is that the intermediate would be square pyramidal. Allowing the geometry of $\text{Fe}(\text{CO})_3\text{L}$ to be approximated as a tetrahedron gives an excellent inverse correlation of CFAE with reactivity. The geometry suggested by matrix isolation for $\text{Fe}(\text{CO})_4$ is a C_{2v} distorted tetrahedron.¹⁸ Replacement of one CO with

TABLE 4.6

Crystal Field Activation Energy for a Dissociation Mechanism in Organometallic Substitutions.

complex	system	ground state		transition state		CFAE
		geometry	CFSE ^a	geometry	CFSE ^a	
$\text{Ni}(\text{CO})_2\text{L}_2$	d^{10}	T_d	0	trigonal planar	0	0
$\text{Cr}(\text{CO})_4\text{L}_2$	d^6	O_h	-24	square pyramidal	-12	4
$\text{Fe}(\text{CO})_3\text{L}_2$	d^8	TBP	-14.6	tetrahedral	-4.6	10
				square planar	-25	-10

Handwritten notes:
 (2) PPh_3 Δ $\text{Cr}(\text{CO})_4\text{L}_2$ $\Rightarrow$ $\text{Ru}, \text{Os} \Rightarrow$
 $\text{Cr} \gg \text{Fe}$
 $\text{Ru} \ll \text{Os}$
 $\text{Os} \approx \text{Cr}$

^aAll values are given in D_q , a generalized measure of energy.

a more sterically demanding ligand should favor tetrahedral geometry. The observed dependence of rates of ligand substitution on the metal, $\text{Ni}(0) > \text{Cr}(0) > \text{Fe}(0)$, can be accounted for by the crystal field activation model.

For substitution reactions of the ruthenium and osmium complexes the d^8 16-electron transition state/intermediate should tend toward square planar and should be considerably more reactive than the analogous iron complexes. This is observed; while iron complexes, $\text{Fe}(\text{CO})_3\text{L}_2$, are much slower than the chromium complexes, analogous ruthenium complexes react more rapidly than molybdenum complexes, and osmium complexes react more rapidly than tungsten complexes.¹⁷

The similar effect of metal center on dissociation of different ligand types and the large difference in rate for different metal centers are like the corresponding observations for classical coordination complexes and suggest a general phenomenon such as crystal field stabilization energy. At this point there is insufficient data regarding metal effects on substitutional reactivity of organometallic complexes to properly test the hypothesis that crystal field activation energies are important in organometallic substitution reactions.

Solvent Effects

Unlike substitution reactions of Werner-type complexes, where solvent effects are quite important, metal carbonyl substitution reactions normally show very small solvent effects, usually a factor of 10 or less. This is understandable since a neutral complex dissociates a neutral ligand (CO) leading to a neutral intermediate, and solvation changes should be minimal during the course of the reaction. The rate constants for substitution on $\text{Mn}(\text{CO})_5\text{Br}$ in various solvents are shown in Table 4.7.¹⁰ The reactions are most rapid in

TABLE 4.7

Effect of Solvent on the Reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with AsPh_3 at 40.0°C.

solvent	$k(10^5\text{s}^{-1})$
cyclohexane	7.44
toluene	4.54
chloroform	3.29
acetone	1.79
nitrobenzene	1.08

hydrocarbon solvents. This observation was interpreted as an indication that the transition state is less polar than the ground state.¹⁰ An alternative explanation lies in the cohesive forces (solvent-solvent interactions) that can affect the reaction rate in a manner similar to the way external pressure affects reaction rate. The cohesive energy density (CED) is a measure of the internal pressure of the solvent. For nonpolar reactions the internal pressure influences reaction rates in the same direction as external pressure.¹⁹ For a metal carbonyl dissociative process a high internal pressure would thus slow the reaction rate. Table 4.8 includes the internal pressures of a few solvents compared to the reaction rates; the agreement is at least as good as with the dielectric constant.

TABLE 4.8

Comparison of Dielectric Constant and Cohesive Energy Density to Rate Constants for Solvent Effects.

solvent	dielectric constant ¹⁰	rate constant ¹⁰	CED ¹⁹
cyclohexane	1.99	7.44	2038
carbon tetrachloride	2.20	5.45	3034
toluene	2.34	4.54	3278
acetone	19.60	1.79	3853

Nature of the Intermediate

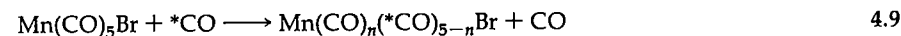
The process under consideration involves the loss of CO or other ligand from a metal center with 18 electrons in the valence shell orbitals of the metal. The 16-electron intermediate generated is of lower coordination number. Competition ratio studies have shown the 16-electron intermediate to be nondiscriminatory toward ligands of widely varying nucleophilicity.^{15,13,20} In these studies the concentration of the dissociating ligand is varied, and the change in rate of formation of product can be used to determine the preference the intermediate shows for one ligand over another. A value of 1 for the competition ratio indicates no preference. Studies of this sort have been carried out on $\text{Ni}(\text{CO})_3$ with CO and PPh_3 as competing ligands¹³; on $\text{Fe}(\text{CO})_4$ with CO and olefins competing²¹; on $\text{Mo}(\text{CO})_5$ with amines competing with phosphines²⁰; and on $\text{Mo}(\text{CO})_4\text{PPh}_3$ with amines competing

with phosphines and CO.¹⁵ In all of these cases the competition ratios range between 0.5 and 5 (close to 1) indicating that the unsaturated 16-electron intermediates are discrete and highly reactive, reacting with any nucleophile regardless of its nucleophilicity, with very low energy of activation.

Unfortunately, there is very little direct evidence regarding the rates of reaction of coordinatively unsaturated metal carbonyl intermediates with nucleophiles. The $\text{Cr}(\text{CO})_5$ complex, generated in a flash photolysis experiment, reacts with CO in solution with a bimolecular rate constant of $3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.¹¹ This is only about three orders of magnitude lower than the diffusion-controlled encounter rate. Thus, even if all the departure from the diffusion-controlled rate of collisions between $\text{Cr}(\text{CO})_5$ and CO were enthalpic in nature, a small activation energy is involved. The evidence therefore suggests that the intermediates in dissociation reactions of metal carbonyls that contain 16 electrons in the valence orbitals of the metal are reactive and that these intermediates combine with nucleophiles in reactions characterized by small energies of activation.

Stereochemistry of CO Dissociation

If a complex has nonequivalent CO groups, the stereochemistry of the dissociative process can be defined. This has prompted many studies of exchange reactions with $\text{Mn}(\text{CO})_5\text{Br}$.^{22,23} Substitution reactions always lead to *cis*- $\text{Mn}(\text{CO})_4\text{LBr}$,¹⁰ but substitution products do not necessarily provide information on the site of CO dissociation. In an *exchange* reaction the products must reflect the site of dissociation by the principle of microscopic reversibility (see discussion in Chapter 1). One would predict that the site of CO dissociation would be *cis* to the bromide in $\text{Mn}(\text{CO})_5\text{Br}$ since each *cis* CO (radial) is *trans* to CO and should not be as strongly pi bonded as the axial CO which is *trans* to Br. However, both the axial and equatorial positions were enriched when reacted with C^{18}O or C^{13}CO .²³



This rather surprising result was explained by recognizing that the 16-electron intermediate was five-coordinate and could equilibrate the *cis* and *trans* carbonyls. (Fluxional processes are considered in Chapter 7.) A fluxional five-coordinate intermediate would allow for enrichment in the axial position without dissociation of the axial CO.²³ Such a scheme is shown in Figure 4.3. A ${}^*\text{CO}$ that is already present in the radial position can rearrange to the axial position after dissociation of another CO. Thus enrichment in the axial position requires prior enrichment in the radial position. The time required for enrichment in the radial position would create an induction period for enrichment in the axial position, as is observed in Figure 4.4. Thus, the intermediate,

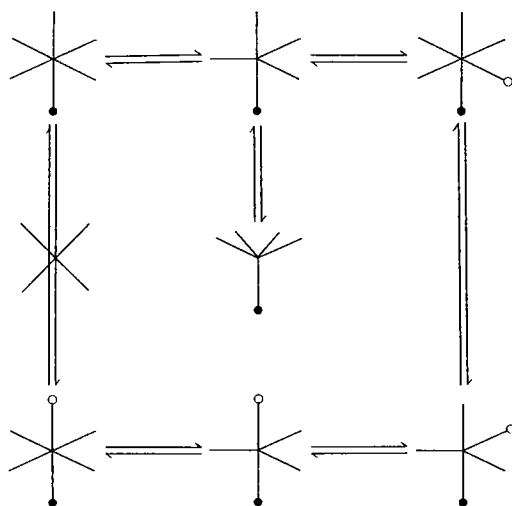


FIGURE 4.3. Mechanism for enrichment of the axial position in $\text{Mn}(\text{CO})_5\text{Br}$ involving a fluxional five-coordinate intermediate.

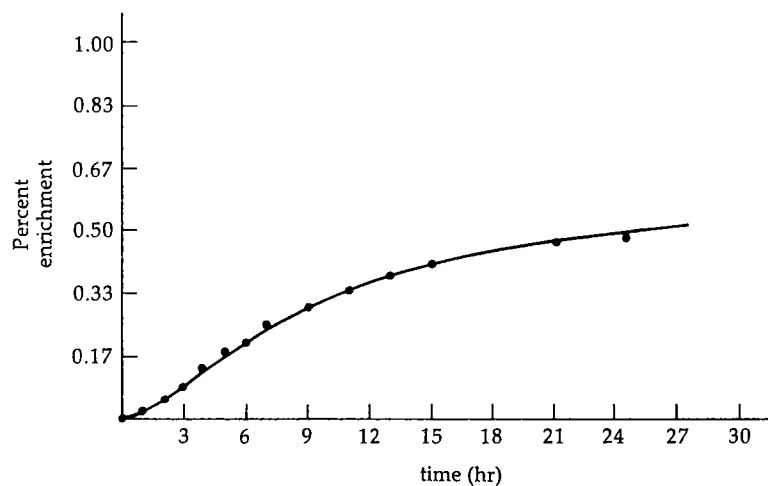


FIGURE 4.4. The induction period for enrichment of the axial position of $\text{Mn}(\text{CO})_5\text{Br}$ as fit by a mechanism involving a fluxional five-coordinate intermediate.

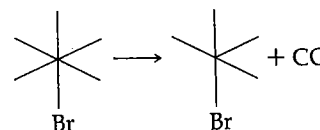
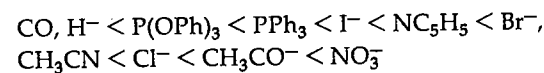


FIGURE 4.5. Stereospecific loss of CO *cis* to Br in $\text{Mn}(\text{CO})_5\text{Br}$.

$\text{Mn}(\text{CO})_4\text{Br}$, was shown to be fluxional (equilibrating the four carbonyl groups) during the lifetime of the intermediate.²³

In a further study of the stereochemistry of CO dissociation, it was shown that CO dissociates *cis* to both Br and L in *cis*- $\text{Mn}(\text{CO})_4\text{LBr}$, L = PPh_3 , $\text{P}(\text{OPh})_3$, or Py as shown in Figure 4.5.²⁴ The variation of rate with L as shown in Table 4.9 showed a *cis*-labilization of CO dissociation.²⁴ As shown in Table 4.10, *cis*-labilization also occurs for chromium complexes and spans several orders of magnitude.²⁵

The *cis*-labilization order



was derived from data for octahedral metal carbonyl complexes of groups VI and VII. For a given metal these ligands span eight orders of magnitude in dissociation rate for *cis* carbonyls and compare in magnitude with the *trans* effect seen in the substitution reactions of square planar complexes as discussed in Chapter 2.

The magnitude of the *cis*-labilization and the observed order of ligands invites a comparison with the much-studied *trans* effect in square planar substitutions. At first sight there would seem to be little basis for comparison, but in fact the two processes are remarkably opposite in character. Square

TABLE 4.9

Rate of CO Dissociation from the Position *cis* to Both L and Br in *cis*- $\text{M}(\text{CO})_4\text{LBr}$.²⁴

L	k for M = Mn, 23°C $\times 10^5(\text{s}^{-1})$	k for M = Re, 30°C $\times 10^7(\text{s}^{-1})$
CO	2.8	1.0
$\text{P}(\text{OPh})_3$	3.1	1.1
PPh_3	27.0	9.8
Py	—	72

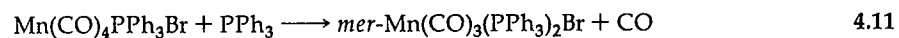
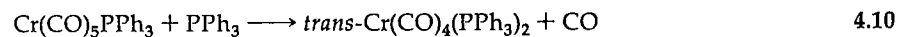
TABLE 4.10

First Order Rate Constants at 30°C for the Substitution Reactions of Chromium Carbonyl Complexes.

compound	$k_1(\text{s}^{-1})$
$\text{Cr}(\text{CO})_6$	1×10^{-12}
$\text{Cr}(\text{CO})_5\text{PR}_2\text{R}'$	1.5×10^{-10}
$\text{Cr}(\text{CO})_5\text{PPh}_3$	3.0×10^{-10}
$\text{Cr}(\text{CO})_5\text{C}(\text{OCH}_3)\text{CH}_3^-$	4×10^{-7}
$\text{Cr}(\text{CO})_5\text{I}^-$	$< 10^{-5}$
$\text{Cr}(\text{CO})_5\text{Br}^-$	2×10^{-5}
$\text{Cr}(\text{CO})_5\text{Cl}^-$	1.5×10^{-4}

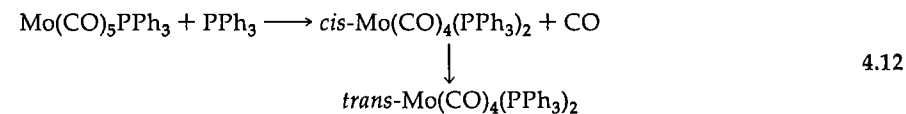
planar substitution occurs by an associative step to a five-coordinate 18-electron transition state, probably always of trigonal bipyramidal geometry. It is important to keep in mind that the *trans*-labilizing ligand in square planar substitution is in the trigonal plane in the trigonal bipyramidal transition state. In the process we are considering, we also have a five-coordinate transition state, but with 16 electrons, and the *cis*-labilizing ligand is probably located in the basal plane of a square pyramidal geometry. The order of *cis*-labilization is almost the opposite of the *trans*-effect order. As discussed in Chapter 2, a rate enhancement is the result of a reduction in activation energy, which can occur either by destabilization of the ground state or by stabilization of the transition state. There are no compelling reasons for believing that *cis*-labilization arises from ground state destabilization; crystal structure evidence shows a slight shortening of the *cis* M-CO bonds in many complexes. It has been postulated that the presence of the *cis*-labilizing ligand in the basal plane of a square pyramidal transition state lowers the energy. Calculations have shown that stabilization of the transition state is expected when CO is replaced by a labilizing ligand.²⁶

It is important to remember that the site of CO dissociation does not necessarily reflect the site of substitution. Two examples are shown below.



In both cases it has been shown that CO dissociation occurs from the *cis*-positions.²⁵ Steric interactions from the bulky phosphine make *cis* formation

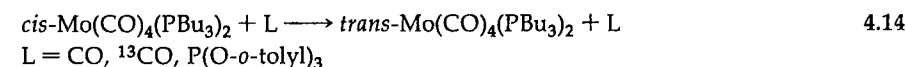
impossible for these first row metals. For larger metals (or smaller ligands) it is possible to form *cis* isomers.



Often the *cis* isomer rearranges to the *trans*, and some kinetic studies have been accomplished.²⁷⁻²⁹



For all of the ligands investigated, the reaction was first order in metal carbonyl complex although the suggested mechanism depends on the ligand. For $\text{L} = \text{PPh}_3$, dissociative loss of PPh_3 was believed to provide the mechanism for the isomerization. For $\text{L} = \text{PBu}_3$ and $\text{P}(\text{OMe})_3$ it was suggested that a trigonal (Bailar) twist (Figure 4.6) was operative. Two pieces of data were pertinent to the nondissociative nature of these isomerizations: (1) The activation entropies were slightly negative (~ -5 eu); and (2) when the isomerization was run in the presence of a nucleophile no substitution was observed.



The suggestion of a trigonal twist is an interesting postulate that could provide a mechanism for equilibration of axial and equatorial carbonyls in $\text{Mo}(\text{CO})_5\text{L}$. The twist should occur at least as rapidly for $\text{Mo}(\text{CO})_5\text{L}$ as for $\text{Mo}(\text{CO})_4\text{L}_2$ since the steric interactions would be less.

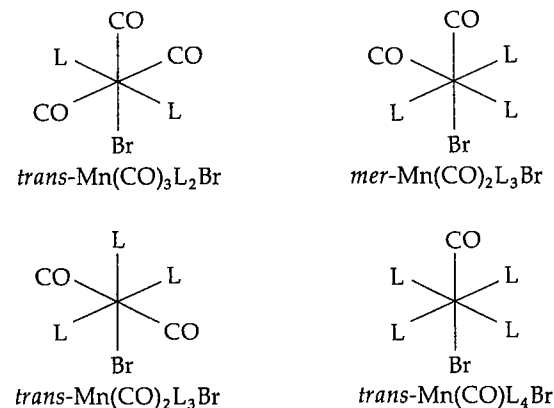


FIGURE 4.6. Substituted derivatives of manganese pentacarbonyl bromide.

TABLE 4.11

Complexes Prepared by Ligand Substitution on $\text{Mn}(\text{CO})_5\text{Br}$.^a

complex	L
<i>trans</i> - $\text{Mn}(\text{CO})_3\text{L}_2\text{Br}$	PPh_3 , P(OPh)_3 , AsPh_3
<i>mer</i> - $\text{Mn}(\text{CO})_2\text{L}_3\text{Br}$	PMe_2Ph , PMe_3 , $\text{P(OMe)}_2\text{Ph}$
<i>trans</i> - $\text{Mn}(\text{CO})_2\text{L}_3\text{Br}$	P(OMe)_3 , P(OEt)_3
<i>trans</i> - $\text{Mn}(\text{CO})\text{L}_4\text{Br}$	P(OMe)_3

^aThe geometries are shown in Figure 4.6.

The extent of substitution depends on the size of the substituting ligand. A series of substitutions on $\text{Mn}(\text{CO})_5\text{Br}$ have been studied for the effect of ligand size on the number of ligands that can be substituted and the geometry of substitution.³⁰ These data are shown in Table 4.11. The smaller ligands are able to substitute to a greater extent than the larger ones. Steric effects are certainly significant in complexes of this type. A crystal structure determination of *fac*- $\text{Cr}(\text{CO})_3(\text{PEt}_3)_3$ shows the effects on bond length and geometry, with lengthened Cr-P bonds and larger than 90° P-Cr-P angles.³¹

DISSOCIATION OF OTHER LIGANDS

There have been relatively few studies of dissociation of ligands other than CO from organometallic complexes. Because many of the ligands are large, one must analyze the data in terms of size as well as sigma and pi bonding ability. Indeed rates of L dissociation from NiL_4 correlate very nicely with ligand cone angles as shown in Table 4.12, suggesting a dominant role for steric effects in dissociation of L from NiL_4 .⁷



This is readily understandable because tetrasubstituted complexes should have very significant steric interactions. Steric interactions are also shown to be important in dissociations from *cis*- $\text{Mo}(\text{CO})_4\text{L}_2$ complexes as shown by the data in Table 4.13.³²

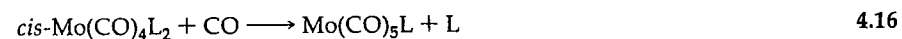


TABLE 4.12

Cone Angles for Common Ligands.

L	cone angle
PPh_3	145°
AsPh_3	142°
PBu_3	132°
P(OPh)_3	128°
P(OMe)_3	107°

The ordering of dissociation rates shows an effect on the size, but electronic effects must also be involved since phosphites of the same size as phosphines dissociate more slowly. It should not be overlooked that L dissociation from *cis*- $\text{Mo}(\text{CO})_4\text{L}_2$ leads to $\text{Mo}(\text{CO})_4\text{L}$ where the L group has a significant influence on the energy. The ordering observed in Table 4.13 is that expected for stabilization of the transition state by the ligand L. As suggested previously, it is very difficult to separate steric and electronic factors.

TABLE 4.13

Rates of Dissociation from *cis*- $\text{Mo}(\text{CO})_4\text{L}_2$ at 70°C in C_2Cl_4 .

L	cone angle	rate (s^{-1})
PMe_2Ph	122°	$<1.0 \times 10^{-6}$
PMePh_2	136°	1.3×10^{-5}
PPh_3	145°	3.2×10^{-3}
PPhCy_2	162°	6.4×10^{-2}
P(OPh)_3	128°	$<1.0 \times 10^{-5}$
$\text{P(O-}o\text{-tolyl)}_3$	141°	1.6×10^{-4}

A systematic investigation of ligand dissociation from chromium carbonyl complexes provided evidence regarding the electronic effects. The complexes $\text{Cr}(\text{CO})_5\text{L}$, *trans*- $\text{Cr}(\text{CO})_4\text{L}_2$ and *trans*- $\text{Cr}(\text{CO})_4\text{LL}'$ were investigated for their reaction with carbon monoxide.³³⁻³⁵



TABLE 4.14

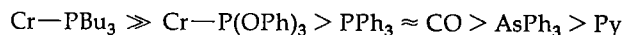
Rates and Activation Parameters for L Dissociation from $\text{Cr}(\text{CO})_5\text{L}$ at 130°C .

L	$k \times 10^6(\text{s}^{-1})$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
$\text{P}(\text{OMe})_3$	0.55	—	—
$\text{P}(\text{OPh})_3$	16.	32.	0
PPh_3	100	36.	12.
CO	130	40.	23.
AsPh_3	12000	36.	22.

The first order rate constants and activation parameters derived from those rate constants are shown in Table 4.14.³³ The substitution of ligands for CO on $\text{Cr}(\text{CO})_6$ has also been studied by kinetics. If the forward reaction is the microscopic reverse of the reverse reaction,



as it should be for simple, first order ligand dissociation, then we can apply the principle of microscopic reversibility to obtain relative ground state energies of the $\text{Cr}(\text{CO})_5\text{L}$ species. Microscopic reversibility mandates that the transition state for the forward reaction be the same as for the reverse. Since we know the activation energies for the reverse reaction [the difference in energy between $\text{Cr}(\text{CO})_6$ and the transition state] and the forward reaction [the difference in energy between $\text{Cr}(\text{CO})_5\text{L}$ and transition state], comparison of the activation energies gives the relative ground state energies of $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_5\text{L}$ for each L or ΔG for the reaction. The values for several different ligands are shown in Table 4.15.³³ The order of Cr-L bond stabilities in $\text{Cr}(\text{CO})_5\text{L}$ is



which indicates that the strength of bonding ability is more significant than whether the bonding is sigma or pi in nature.³³ The order of bond energies for Cr-L bonds where the ligand is bound to Cr(0) is remarkably similar to the order for *trans*- $\text{MePt}(\text{PMe}_2\text{Ph})_2\text{L}^+$ where the ligand is bound to Pt(II). A few values are shown in Table 4.16.³⁶ The similarity in M-L bond strengths for two metal centers as different as $\text{Cr}(\text{CO})_5$ and $\text{MePt}(\text{PMe}_2\text{Ph})_2^+$ suggests that this is a general order of bond strengths to organometallic centers.

A *trans* effect of octahedral metal carbonyl substitution reactions was observed in reactions of $\text{Cr}(\text{CO})_4\text{LL}'$ with CO.³⁵

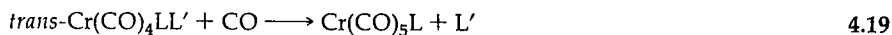


TABLE 4.15

Free Energy Changes for the Reaction $\text{Cr}(\text{CO})_5\text{L} + \text{CO} \longrightarrow \text{Cr}(\text{CO})_6 + \text{L}$ at 130°C .

L	$\Delta G_{\text{rxn}}(\text{kcal/mole})$
Py	-7.1
AsPh_3	-3.8
CO	0.0
PPh_3	0.1
$\text{P}(\text{OPh})_3$	1.5
PBu_3	8.1

The reactions progressed by L' dissociation showing first order kinetics and appropriate activation parameters. Two series of reactions indicate the effect of the *trans* ligand on the dissociation rate.³⁵ For L' = PPh_3 the complexes were prepared and reactions were investigated for L = PPh_3 , $\text{P}(\text{OPh})_3$, PBu_3 , $\text{P}(\text{OMe})_3$, and CO and for L' = $\text{P}(\text{OPh})_3$, L = $\text{P}(\text{OPh})_3$, PPh_3 , $\text{P}(\text{OMe})_3$, and CO. The results are shown in Table 4.17.³⁵ Thus the ordering of *trans* effect on dissociation of PPh_3 and of $\text{P}(\text{OPh})_3$ is identical:



This order is very similar to that expected for size, but it is difficult to visualize a significant steric interaction from *trans* ligands. Crystal structure determinations showed no correlation between the Cr- PPh_3 or Cr- $\text{P}(\text{OPh})_3$ bond lengths and rates of PPh_3 and $\text{P}(\text{OPh})_3$ dissociation from *trans*- $\text{Cr}(\text{CO})_4\text{LL}'$.³⁵

TABLE 4.16

Enthalpy Data for Formation Reactions of $\text{MePt}(\text{PMe}_2\text{Ph})_2\text{L}^+$.

L	$-\Delta H(\text{kcal/mole})$
Py	12.2
AsPh_3	12.8
PPh_3	19.5
$\text{P}(\text{OPh})_3$	21.4
PEt_3	24.3

TABLE 4.17

Effect of *trans* Ligand on Dissociation Rates of L' from Cr(CO)₄LL' at 130°C.

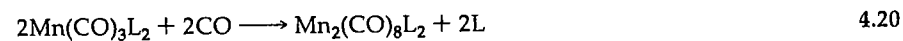
L	$k(s^{-1})L' = PPh_3$	$k(s^{-1})L' = P(OPh)_3$
PPh ₃	3.9	1.3×10^{-2}
PBu ₃	2.4×10^{-1}	
P(OPh) ₃	1.3×10^{-2}	4.0×10^{-4}
P(OMe) ₃	8.1×10^{-3}	1.8×10^{-4}
CO	1.0×10^{-4}	1.6×10^{-5}

Thus the rate acceleration by L from Cr(CO)₄LL' does not arise by a ground state destabilization, for that would be manifested as lengthening of Cr-L' bonds. Rather a transition state stabilization by L is indicated.

The similarity in the orders for phosphine and phosphite dissociation also strongly suggests a stabilization of the transition state. Dissociation of either ligand would lead to the same intermediate, Cr(CO)₄L. This *trans*-effect order on dissociation is similar to the *cis*-labilization order, which is also a transition state effect. The ligand in *cis*-labilization occupies a basal position in the transition state; for the *trans* effect it occupies an apical position. The stabilization of the transition state by the ligand apparently does not depend on the site the ligand occupies but reflects an ability to release electrons to the unsaturated 16-electron intermediate.³⁵ A stabilization of the 16-electron intermediate Cr(CO)₃(*o*-phenanthroline) by electron-releasing *o*-phenanthroline ligands was noted a number of years ago.³⁷ This simple concept is also applicable to *cis*-labilization of CO dissociation, to the *trans* effect noted for dissociation from Cr(CO)₄LL', and probably generally to organometallic substitution reactions that proceed through unsaturated intermediates.⁶ To completely understand the effect of a ligand on either stereochemistry or reactivity for a given reaction one must consider both ground and transition state effects. In *cis*-labilization the increased reactivity arises by stabilization of the 16-electron intermediate attributable to the presence of a donating ligand. The *cis* stereospecificity results from a stronger M-CO bond *trans* to the donor ligand (a ground state effect). A complete interpretation of substitution reactions of metal carbonyl complexes requires knowledge of site specificity, of steric effects in both the ground and transition states, and of the ground state bond energies; but the gross effects, especially in a series of complexes, can be accounted for in terms of a stabilization of the electron-deficient transition state by electron donating groups.

Complexes with 17 Electrons

Reports of the kinetics of substitution reactions of two carbonyl complexes containing 17 electrons at the metal, Mn(CO)₃L₂ (L = phosphine) and V(CO)₆ have appeared.^{38,39} The reaction of Mn(CO)₃L₂ with CO showed dependence on the concentration of CO in solution (Table 4.18).³⁸



Both the CO dependence and the more facile reaction with the smaller ligand strongly indicate associative mechanisms for their reactions. Similar results on V(CO)₆ (Figure 1.2) provide a further indication that 17-electron metal carbonyl complexes undergo substitution reactions by associative mechanisms involving nucleophilic attack of the entering ligand. One should be cautious in interpreting a class of compounds based on two examples, but the current data support associative mechanisms for 17-electron complexes—in contrast to the reactions of 18-electron complexes.

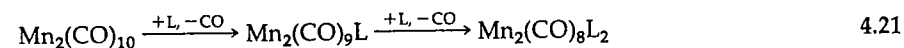
TABLE 4.18

Dependence upon [CO] of the Rate of L Replacement on Mn(CO)₃L₂.

L	[CO](10 ³ M)	$k_{obs}(s^{-1})$
P(<i>i</i> -Bu) ₃	1.7	5.2×10^{-4}
	2.5	7.9×10^{-4}
	5.0	1.6×10^{-3}
PBu ₃	5.0	2.0×10^{-1}

SUBSTITUTION ON METAL CARBONYL COMPLEXES CONTAINING METAL-METAL BONDS

A number of organometallic complexes form metal-metal bonds to achieve 18 electrons at each metal. Examples are Mn₂(CO)₁₀, Co₂(CO)₈, Cp₂Cr₂(CO)₆, Fe₃(CO)₁₂, and Co₄(CO)₁₂. Electron counting for these metal-metal bonded systems is shown in Figure 4.7. Substitution reactions on these complexes occur by replacement of a CO with an entering ligand.⁴⁰



$\text{Mn}_2(\text{CO})_{10}$		$\text{Co}_2(\text{CO})_8$		$\text{Cp}_2\text{Cr}_2(\text{CO})_6$	
$[\text{Mn}(\text{CO})_5]_2$		$[\text{Co}(\text{CO})_4]$		$[\text{CpCr}(\text{CO})_3]_2$	
Mn	$7e^-$	Co	$9e^-$	Cr ⁺	$5e^-$
5CO	$\frac{10e^-}{17e^-}$	4CO	$\frac{8e^-}{17e^-}$	Cp	$6e^-$
Mn—Mn	$\frac{1e^-}{18e^-}$	Co—Co	$\frac{1e^-}{18e^-}$	3CO	$\frac{6e^-}{17e^-}$
				Cr—Cr	$\frac{1e^-}{18e^-}$

$\text{Fe}_3(\text{CO})_{12}$		$\text{Co}_4(\text{CO})_{12}$	
$[\text{Fe}(\text{CO})_4]_3$		$[\text{Co}(\text{CO})_3]_4$	
Fe	$8e^-$	Co	$9e^-$
4CO	$\frac{8e^-}{16e^-}$	3CO	$\frac{6e^-}{15e^-}$
2Fe—Fe	$\frac{2e^-}{18e^-}$	3Co—Co	$\frac{3e^-}{18e^-}$

FIGURE 4.7. Electron counting of metal-metal bonded systems.

There are two features that are different for metal-metal bonded systems than for mononuclear complexes: possible substitution at different metals and the effect of the metal-metal bond on reactivity. In addition there are complexes that contain metals multiply bonded to each other. Reactions of these latter complexes are addition reactions, which will not be considered here.

Metal Carbonyl Dimers

The reactions that have been most often studied are those of the group VII dimers, $\text{Mn}_2(\text{CO})_{10}$, $\text{Tc}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, and $\text{MnRe}(\text{CO})_{10}$.⁴⁰⁻⁴³ These reactions may lead to either the mono- or bis-substituted complex depending on the dimer and the reaction conditions as shown in equation 4.21. The ligands are almost invariably substituted axially as shown in Figure 4.8. Kinetic studies on these dimers, summarized in Table 4.19, show the rate law

$$\text{rate} = (k_1 + k_2[\text{L}])[\text{M}_2(\text{CO})_{10}]$$

where the k_2 term is much smaller than the k_1 term. This rate law is identical to that seen for substitution at $\text{Cr}(\text{CO})_6$ and is best ascribed to a dissociative interchange mechanism.⁴³ Considerable controversy has existed over whether the mechanism involves CO dissociation^{40,43} or homolytic cleavage^{41,42} of the metal-metal bond. Each of these processes is shown in Figure

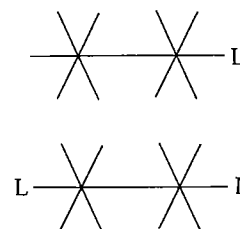


FIGURE 4.8. Structures of substituted derivatives of the decacarbonyl dimers.

4.9. This type of mechanistic question is difficult to resolve since each of the schemes could give rise to the rate law and kinetic evidence does not differentiate between CO dissociation and metal-metal bond cleavage. The ability to distinguish between the two metal centers in $\text{MnRe}(\text{CO})_{10}$ added mechanistic information that ruled out Mn-Re bond homolysis for substitutions on this complex. The observed products showed primarily the rhenium substituted isomer, $(\text{CO})_5\text{MnRe}(\text{CO})_4\text{L}$, with small amounts of the manganese substituted isomer, $\text{L}(\text{CO})_4\text{MnRe}(\text{CO})_5$.⁴³ As the reaction progressed, the bis-substituted product increased and the two mono products declined in

TABLE 4.19

Substitution Reactions on Group VII Carbonyl Dimers. Each Reaction Was First Order in Metal Carbonyl Dimer.⁴⁴

$\text{M}_2(\text{CO})_{10}$	L	product
$\text{Mn}_2(\text{CO})_{10}$	PPh_3 , $\text{P}(\text{OPh})_3$, etc.	$\text{Mn}_2(\text{CO})_9\text{L}$ and $\text{Mn}_2(\text{CO})_8\text{L}_2$
$\text{Mn}_2(\text{CO})_{10}$	PPh_3	$\text{Mn}_2(\text{CO})_9\text{PPh}_3$ and $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$
$\text{Re}_2(\text{CO})_{10}$	PPh_3	$\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$
$\text{Tc}_2(\text{CO})_{10}$	PPh_3	$\text{Tc}_2(\text{CO})_9\text{PPh}_3$ and $\text{Tc}_2(\text{CO})_8(\text{PPh}_3)_2$
$\text{MnRe}(\text{CO})_{10}$	PPh_3	$(\text{CO})_5\text{MnRe}(\text{CO})_4\text{PPh}_3$
$\text{MnRe}(\text{CO})_{10}$	PPh_3 , $\text{P}(\text{OPh})_3$, PBu_3	$(\text{CO})_5\text{MnRe}(\text{CO})_4\text{L}$ and $\text{MnRe}(\text{CO})_8\text{L}_2$

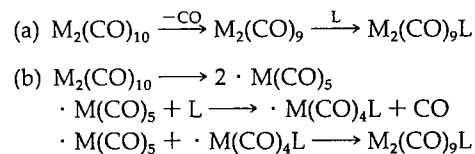
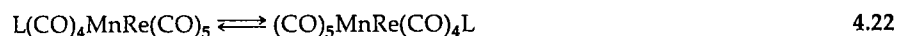
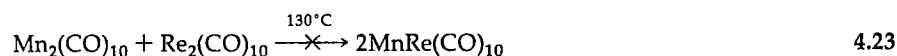


FIGURE 4.9. Two possible mechanisms for substitution on $\text{M}_2(\text{CO})_{10}$: (a) CO dissociation and (b) metal-metal homolysis.

concentration. The mechanism of metal-metal bond cleavage requires (1) that there be a selectivity for formation of Mn-Re bonds over Mn-Mn and Re-Re, an assumption for which there is no justification, and (2) that the manganese isomer rearrange to the rhenium isomer under the reaction conditions.^{43,44}



It has been shown that this isomerization does not occur. Thus substitution on $\text{MnRe}(\text{CO})_{10}$ does not occur by Mn-Re bond cleavage, and the CO dissociation pathway is most likely. Additional evidence that metal-metal bond homolysis is not the mechanism of substitution reactions is shown by reaction of $\text{Mn}_2(\text{CO})_{10}$ with $\text{Re}_2(\text{CO})_{10}$ at high temperature. Substitution reactions on $\text{Mn}_2(\text{CO})_{10}$ occur from 90 to 110°C and on $\text{Re}_2(\text{CO})_{10}$ from 130 to 150°C. When $\text{Mn}_2(\text{CO})_{10}$ is heated with $\text{Re}_2(\text{CO})_{10}$ under a variety of conditions at 130°C, no evidence was obtained for $\text{MnRe}(\text{CO})_{10}$ formation.^{44,45}



Heating these two dimers at 150°C under CO in a sealed tube showed no decomposition and no trace of $\text{MnRe}(\text{CO})_{10}$ in 48 hours.⁴⁵



These reactions show that under the most conservative interpretation both of these dimers cannot be undergoing metal-metal bond homolysis under substitution reaction conditions. The ultimate experiment to differentiate between metal-metal bond homolysis and other routes has recently been performed for $\text{Re}_2(\text{CO})_{10}$.⁴⁶ Two complexes with different rhenium isotopes were prepared ($^{185}\text{Re}_2(\text{CO})_{10}$ and $^{187}\text{Re}_2(\text{CO})_{10}$) for use in substitution and exchange reactions. No mixed isotopic species were observed after several half-lives under the reaction conditions, ruling out the metal-metal bond homolysis mechanism in thermal substitution and CO exchange reactions of $\text{Re}_2(\text{CO})_{10}$. The metal isotopes are not available for manganese, but similar reactions of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}_2(^{13}\text{CO})_{10}$ are fully consistent with CO disso-

ciation and inconsistent with metal-metal bond cleavage.⁴⁷ Thus definitive evidence has been presented to refute the suggestion that metal-metal bond homolysis is involved in ligand exchange or substitution reactions of the Group VII dimers.



As noted above, $\text{MnRe}(\text{CO})_{10}$ leads to predominantly the rhenium isomer, $(\text{CO})_5\text{MnRe}(\text{CO})_4\text{L}$. Comparing the reactivities of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ and analogous mononuclear complexes of manganese and rhenium, one would anticipate that CO dissociation from manganese would occur at a rate about one hundred times greater than from rhenium.⁴³ It has been suggested that CO dissociates from the manganese and that the intermediate/transition state contained a bridging CO such that the unsaturation at one metal center was shared by the other metal. The ligand would then attack at the most favorable site, which for steric reasons would be the rhenium. Such a scheme is shown in Figure 4.10.

The effect of substitution of one ligand for CO on the rate of substitution at the other metal has been investigated in only one study, the rate of L addition to $\text{Mn}_2(\text{CO})_9\text{L}$ (Table 4.20).⁴⁰ These rates, which were ascribed to CO dissociation, are very similar to the effects seen in *cis*-labilization of mononuclear complexes. This may be a long range effect, the phosphine on one metal center affecting the rate of dissociation at the second metal center, or the labilization by the phosphine may occur at the carbonyls *cis* to the phosphine at the same metal center. The unsaturation could be transferred from the substituted metal center to the unsubstituted one through a bridging CO in a scheme similar to that shown in Figure 4.10 for $\text{MnRe}(\text{CO})_{10}$.

TABLE 4.20

Variation with L of the Rate Constants for Further Substitution on $\text{Mn}_2(\text{CO})_9\text{L}$.

L	relative rate
PPh ₃	44
PBu ₃	12
P(OPh) ₃	1.5
CO	1

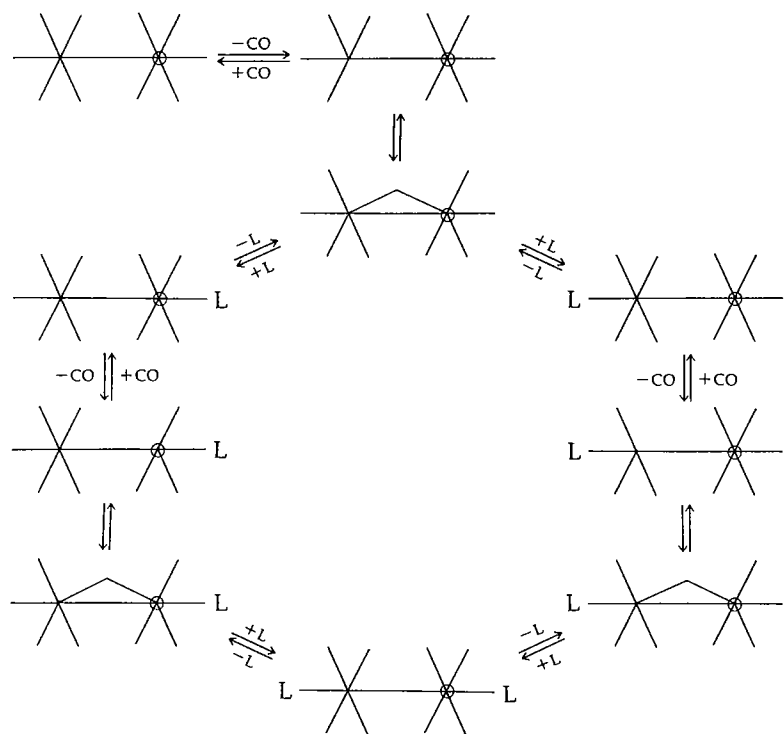
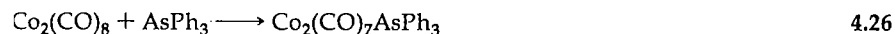


FIGURE 4.10. MnRe(CO)_{10} mechanism involving CO dissociation. The open circles represent rhenium atoms. [Reprinted with permission from D. Sonnenberger and J. D. Atwood, *J. Am. Chem. Soc.* **102**, 3484 (1980). Copyright 1980 American Chemical Society.]

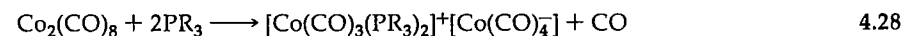
Substitution reactions of $\text{Co}_2(\text{CO})_8$ show more variation than the Group VII dimers. Reaction with ^{13}CO , AsPh_3 , and H_2 show a rate law that is independent of the concentration of the incoming nucleophile at temperatures from -15° to 30°C .⁴⁸



The activation parameters ($\Delta H^\ddagger = 22 \text{ kcal/rate}$ and $\Delta S^\ddagger = 10 \text{ eu}$) and the lack of dependence on the incoming ligand are consistent with CO dissociation.



The reaction with AsPh_3 leads to the disubstituted complex at a much slower rate, indicating that the ligand affects reactivity of $\text{Co}_2(\text{CO})_8$ differently than it does the Group VII metal carbonyl dimers. Substitution of $\text{Co}_2(\text{CO})_8$ by phosphines is quite different,



leading to ionic products at rates that are more rapid than CO dissociation and that depend on the concentration and the nucleophilicity of the entering ligand. In addition the apparent order with respect to $\text{Co}_2(\text{CO})_8$ varies within the range 1.0–1.5 depending on the reaction conditions. The kinetic data for substitution by PBu_3 at -15° are shown in Figure 4.11 with a 1.40 dependence on $[\text{Co}_2(\text{CO})_8]$. The reaction with PBu_3 was studied at -15 , -10 , 5 , and 10°C , and the order of the reaction in $\text{Co}_2(\text{CO})_8$ was found to be 1.40, 1.35, 1.20 and 1.0, respectively. A radical chain mechanism was suggested to account for these observations in the substitution of phosphine bases on $\text{Co}_2(\text{CO})_8$.⁴⁸

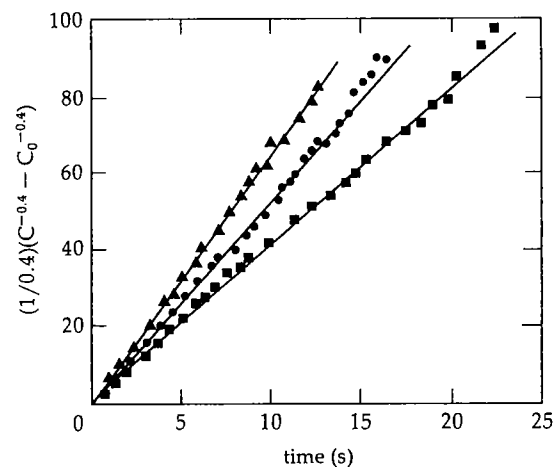
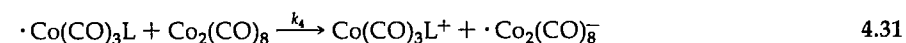
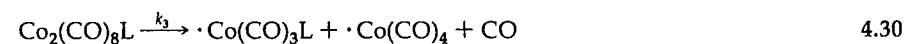


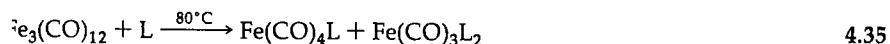
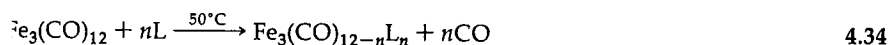
FIGURE 4.11. Pseudo 1.40-order plots for reaction of $\text{Co}_2(\text{CO})_8$ with PBu_3 at three different concentrations of PBu_3 .



Thus two distinct mechanisms exist for $\text{Co}_2(\text{CO})_8$ —for reaction with weak nucleophiles, a CO dissociative route and for reaction with strong nucleophiles, a radical chain pathway.

Transition Metal Clusters

Reactions of Lewis bases with metal clusters may yield either mononuclear or polynuclear products. Substitution reactions on $\text{Fe}_3(\text{CO})_{12}$ represent the features that may be seen. Reaction with L at 50°C leads to substituted metal clusters, but reaction at 80°C produces substituted mononuclear fragments.^{49,50}



The ruthenium and osmium analogues have less tendency to fragment, presumably because of the stronger metal-metal bonds.^{51,52}

In most metal clusters there are two possible sites for substitution, axial or equatorial, as shown for $\text{M}_3(\text{CO})_{12}$ and $\text{M}_4(\text{CO})_{12}$ in Figure 4.12. Substitution has been observed in both sites and often appears to be controlled by steric interactions. The first PPh_3 substituted onto $\text{Ir}_4(\text{CO})_{12}$ occupies an axial site.⁵³ When two PPh_3 ligands are substituted onto $\text{Ir}_4(\text{CO})_{12}$, one occupies an axial site and the second an equatorial site of a different basal iridium. Additional substitution on the bis-substituted complex leads to substitution at two

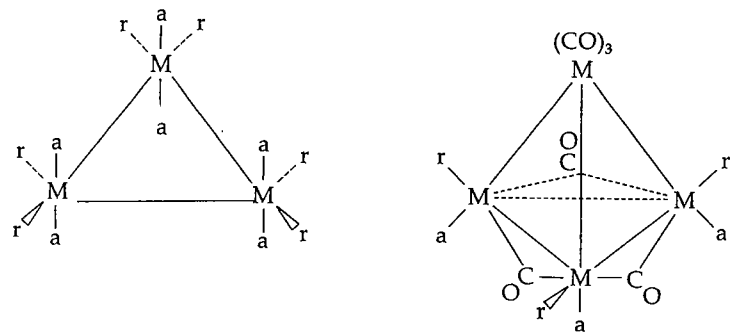


FIGURE 4.12. Axial (a) and radial (r) positions for $\text{M}_3(\text{CO})_{12}$ and $\text{M}_4(\text{CO})_{12}$.

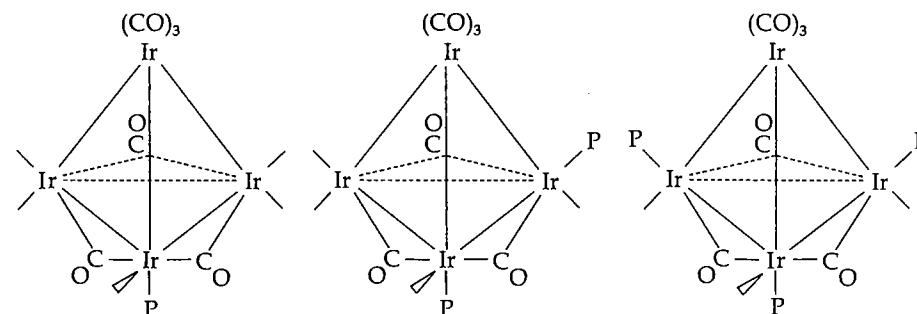


FIGURE 4.13. Substituted products of $\text{Ir}_4(\text{CO})_{12}$.

equatorial and one axial site. These substituted products are shown in Figure 4.13. Under the conditions for substitution reactions, metal cluster complexes are fluxional; that is, the three PPh_3 ligands are equivalent, and the nine carbonyl ligands are equivalent. (Fluxional processes are discussed in more detail in Chapter 7.)

Relatively few kinetic studies of metal clusters have been accomplished. Substitution on $\text{Ir}_4(\text{CO})_{12}$ has been the most thoroughly studied cluster reaction.⁵⁴⁻⁵⁷



The product observed depends on the reaction conditions and on the ligand L. The rate law observed has two terms:

$$\text{rate} = (k_1 + k_2[\text{L}])[\text{Ir}_4(\text{CO})_{12}] \quad 4.37$$

This rate law is of the same form as that seen for substitutions on other metal carbonyl complexes, but the relative values of the two terms are very different from those observed in other systems.⁵⁵ The ligand-dependent term predominates for ligands that are reasonably good nucleophiles, such as CNR , PBU_3 , PPh_3 , and P(OPh)_3 .^{55,58} As shown by the graph of $[\text{L}]$ versus k_{obs} in Figure 4.14, the value of k_1 is independent of the nature of L and can be ascribed to a CO dissociative pathway. The relative values of k_2 (Table 4.21) show a strong dependence on the nucleophilicity of the entering ligand, indicating nucleophilic attack on the metal complex. The site of attack is uncertain, although it has been argued that the accessible metal center (a third row metal with 100° angles between COs) is most likely.⁵⁵

As the tetrairidium cluster is substituted, some changes are noted.^{56,57} Substitution on $\text{Ir}_4(\text{CO})_{11}\text{L}$, for $\text{L} = \text{PPh}_3$, P(OPh)_3 , and AsPh_3 , occurs by a primarily ligand-independent mechanism, probably CO dissociation. For

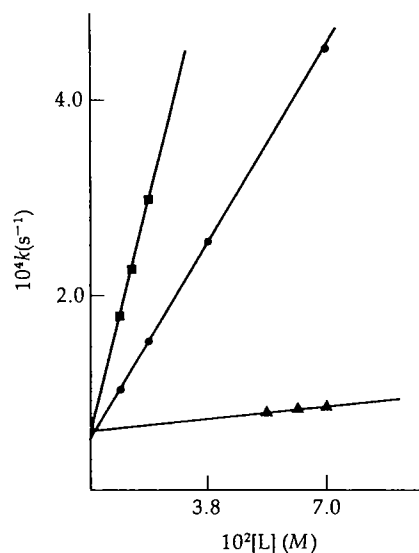


FIGURE 4.14. Plot of k_{obs} versus $[L]$ for a series of reactions with $\text{Ir}_4(\text{CO})_{12}$ at 109°C in chlorobenzene: $\circ$, $\text{P}(\text{C}_6\text{H}_5)_3$; Δ , $\text{As}(\text{C}_6\text{H}_5)_3$; $+$, $\text{P}(\text{OC}_6\text{H}_5)_3$. [Reprinted with permission from D. Sonnenberger and J. D. Atwood, *Inorg. Chem.* 20, 3243 (1981). Copyright 1981 American Chemical Society.]

more nucleophilic entering ligands (PBu_3 , $\text{CN-}t\text{-Bu}$) the ligand-dependent path still predominates.^{55,56,58} The CO dissociation rates from $\text{Ir}_4(\text{CO})_{11}\text{L}$ show the same trends with changes in L as mononuclear complexes and metal carbonyl dimers. The relative ordering is

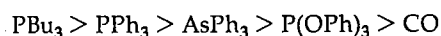


TABLE 4.21

Second Order Rate Constants for Substitution of $\text{Ir}_4(\text{CO})_{12}$ by L.⁵⁵

L	$k_2(10^5\text{M}^{-1}\text{s}^{-1})$
AsPh_3	27
PPh_3	530
P(OPh)_3	1300
PBu_3	too fast to measure

The same trends continue to the bis-substituted tetrairidium clusters, $\text{Ir}_4(\text{CO})_{10}\text{L}_2$, with a continued increase in rates of CO dissociation as shown in Table 4.22.^{56,57} An acceleration in rate with substitution is also seen in reactions of $\text{Ru}_3(\text{CO})_{12}$ with PPh_3 .⁵⁹

TABLE 4.22

Relative Reaction Rates for Substituted Derivatives of $\text{Ir}_4(\text{CO})_{12}$.

L	$\text{Ir}_4(\text{CO})_{10}\text{L}_2$	$\text{Ir}_4(\text{CO})_{11}\text{L}$
PBu_3	360	93
PPh_3	700	47
AsPh_3	700	34
P(OPh)_3	15	5.7
CO	0.7	0.7

The dependence on the ligands present on the metal cluster is very similar to that seen for mononuclear complexes both in order and magnitude. This suggests that the donor ability of the ligand is important in stabilizing the unsaturated metal cluster generated by ligand loss from the saturated cluster. It may also indicate dissociation from a substituted metal center, but the metal cluster may be capable of transmitting electronic effects between metal centers.

In metal clusters that are more highly substituted with phosphines, ligand steric effects may be significant. The rates of phosphine dissociation from $\text{Ir}_4(\text{CO})_8\text{L}_4$ show evidence of a steric effect.^{60,61}



L = PMe_3 , PEt_3 , PBu_3

Data for the substitution at 85°C are shown in Table 4.23. The steric interactions in $\text{Ir}_4(\text{CO})_8(\text{PMe}_3)_4$ are sufficient to cause an elongated Ir-Ir bond.⁶¹ A similar though smaller rate effect on CO dissociation from $\text{Ir}_4(\text{CO})_9\text{L}_3$ has also been attributed to steric interactions.⁶⁰ The rate of CO dissociation was investigated by ^{13}C exchange; the comparison of rate with ligand is shown in Table 4.24. Although the solvents are not the same for the two sets of data, it is interesting to note that there appears to be no significant increase in CO dissociation from $\text{Ir}_4(\text{CO})_{10}(\text{PBu}_3)_2$ ($k = 1.2 \times 10^{-3}$ at 80°C) to $\text{Ir}_4(\text{CO})_9(\text{PBu}_3)_3$ ($k = 1.3 \times 10^{-3}$ at 80°C). The lack of a significant enhance-

TABLE 4.23

A Comparison of the Cone Angle of the Ligand with the Rate Constant for Dissociation from $\text{Ir}_4(\text{CO})_8\text{L}_4$ at 85°C .

L	cone angle	$k(\text{s}^{-1})$
PMe_3	118	6.35×10^{-7}
PEt_3	132	2.09×10^{-3}
PBu_3	132	1.00×10^{-3}

rent in rate may indicate that the electronic effect does not continue to the third substitution and that steric interactions are not significantly different between the bis- and tris-substituted complexes.

Substitution reactions on metal clusters offer mechanistic possibilities unavailable for mononuclear complexes. The ligand may replace a metal-metal bond as is shown in the reaction of $\text{Cp}(\text{CO})_2\text{Mn}(\mu\text{-PPh})\text{Fe}_2(\text{CO})_8$ with Ph_3 (Figure 4.15).⁶² Reaction with a nucleophile leads to an adduct with no Mn-Fe bond. The reaction is reversible; dissociation of L leads to formation of the Mn-Fe bond. Despite this observation there appears to be no kinetic evidence for reversible metal-metal bond cleavage as an important step in metal cluster substitution reactions; only a few clusters have been studied, however.

Mixed metal clusters (clusters containing at least two different metals) have considerable potential for mechanistic investigations of metal cluster

TABLE 4.24

Rate Constants for CO Dissociation from $\text{Ir}_4(\text{CO})_9\text{L}_3$ at 80° .

L	cone angle	$k(10^3\text{s}^{-1})$
PMe_3	118	0.17
PEt_3	132	1.33
PBu_3	132	1.27
$\text{P}(i\text{-Pr})_3$	160	6.76

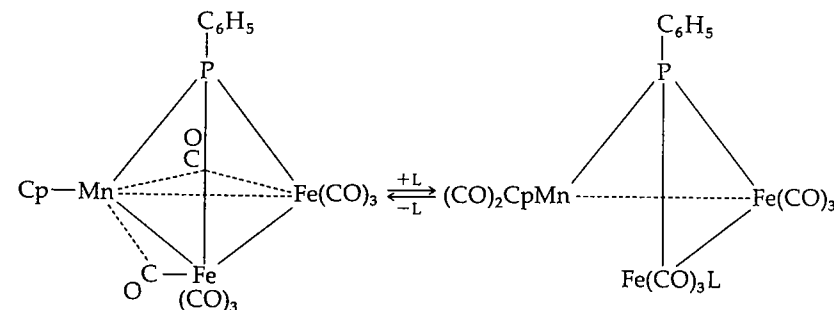
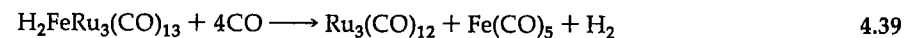


FIGURE 4.15. Reaction with a ligand ($\text{L} = \text{CO}, \text{PPh}_3$) leading to reversible metal-metal bond breaking.

reactions. Several reactions have been examined for the tetranuclear mixed metal clusters $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$.^{63,64}



Kinetics studies of this reaction show the rate law

$$\frac{-d[\text{H}_2\text{FeRu}_3(\text{CO})_{13}]}{dt} = (k_1 + k_2[\text{CO}])[\text{H}_2\text{FeRu}_3(\text{CO})_{13}] \quad 4.40$$

but the first order term is negligible. The plot of k_{obs} versus $[\text{CO}]$ is shown in Figure 4.16. The suggested mechanism involves association of CO with the

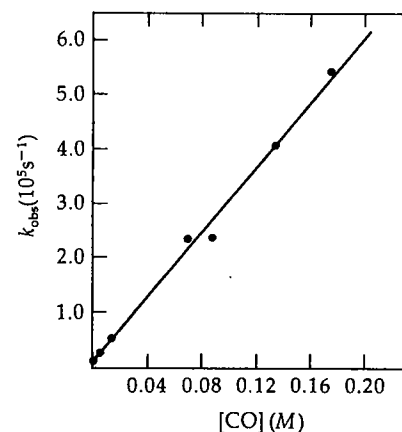


FIGURE 4.16. Plot of k_{obs} versus $[\text{CO}]$ for reaction of CO with $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ showing the linear dependence of rate on $[\text{CO}]$.

ntact cluster concomitant with cleavage of one metal-metal bond to give a butterfly cluster as an intermediate.⁶³ The activation parameters ($\Delta H^\ddagger = 20.0$ kcal/mole and $\Delta S^\ddagger = -25.4$ eu) are consistent with this mechanistic suggestion. Reaction of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ with phosphine and phosphite ligands leads to substituted derivatives of the tetranuclear cluster in moderate yields.⁶⁴ The reaction with PPh_3 occurs at lower temperatures than the reaction with CO, which leads to cluster break up, and with a rate law independent of $[\text{PPh}_3]$. A CO dissociative route has been suggested for this substitution reaction.⁶⁴ Substitution leads to two different isomers, both involving replacement of a CO on ruthenium, in varying quantities depending on the ligand size and basicity. It is rather surprising that the clusters thus far investigated show the same basic mechanistic features as mononuclear complexes. The primary reaction mode seen thus far is CO dissociation although large metals are susceptible to nucleophilic attack at the metal. As more clusters are prepared and more reactions are studied we may anticipate more divergence in the reactions of metal clusters from that of mononuclear complexes. An especially attractive area is in reactions of unsaturated metal clusters.

Unsaturated Metal Clusters

There has been intense interest in preparation of clusters that contain fewer electrons than those shown in Figure 4.7. One example that serves to illustrate the potential is $\text{H}_2\text{Os}_3(\text{CO})_{10}$ (Figure 4.17).⁶⁴ The compound is illustrated with a metal-metal double bond, but there is some contention about whether a double bond actually exists. The reactivity is certainly consistent with unsaturation in this tri-osmium cluster.⁶⁴



These reactions occur readily at room temperature in contrast to reactions of $\text{Os}_3(\text{CO})_{12}$, which require elevated temperatures. Although kinetic studies have not been accomplished, it seems likely that these reactions occur by attack of L on the cluster and would show second order behavior.

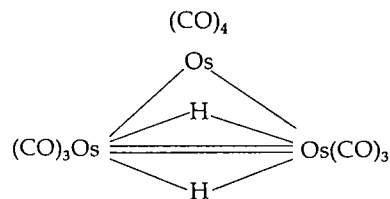
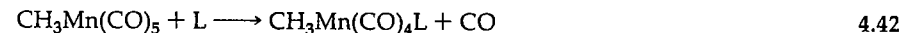


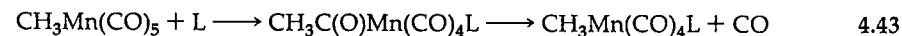
FIGURE 4.17. Unsaturation in $\text{H}_2\text{Os}_3(\text{CO})_{10}$.

LIGAND SUBSTITUTION REACTIONS ON ALKYL COMPLEXES

Alkyl complexes undergo ligand substitution processes



similar in stoichiometry to other substitution reactions. An important difference is that in many reactions of this type an acyl intermediate is observed.



Reactions of this type are termed CO insertion or alkyl migration since the net reaction in forming the acyl intermediate is cleavage of the $\text{CH}_3\text{-Mn}$ bond and formation of a methyl carbon bond as shown in Figure 4.18. These reactions are very important in several catalytic reactions, such as hydroformylation, methanol carbonylation, and homogeneous CO reduction.

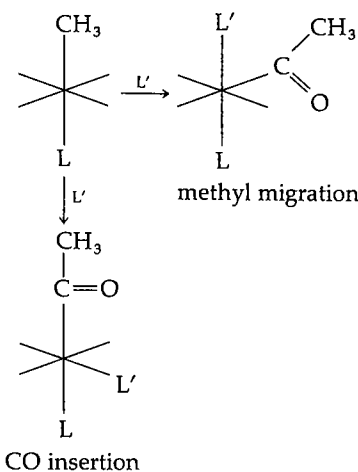


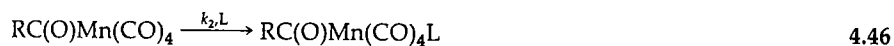
FIGURE 4.18. Product difference for methyl migration and carbon monoxide insertion.

Kinetics and Rate Law

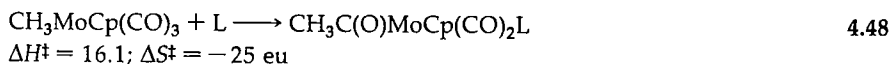
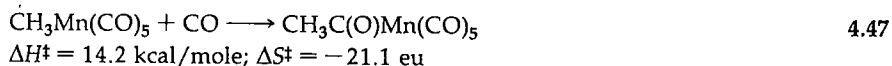
Most of the studies of kinetics of substitutions of alkyl complexes have involved $\text{RMn}(\text{CO})_5$. The rate is dependent on the concentration of the metal complex and on the entering ligand.^{65,66} The rate law that best accommodates the observations is

$$\text{rate} = \frac{k_1 k_2 [\text{L}][\text{RMn}(\text{CO})_5]}{k_{-1} + k_2 [\text{L}]} \quad 4.44$$

The mechanism most consistent with this rate law involves a rapid preequilibrium,



followed by reaction of the 16-electron acyl intermediate with L.⁶⁶ The characteristics of this type of rate law, as discussed earlier, are independence of the rate from ligand concentration at high ligand concentration ($k_2[\text{L}] \gg k_{-1}$) and linear dependence of rate on the ligand concentration at low concentration of ligand. A plot of k_{obs} versus $[\text{L}]$ is shown in Figure 4.19. The activation parameters observed for these reactions



are consistent with the mechanism suggested in equations 4.45 and 4.46.^{65,66}

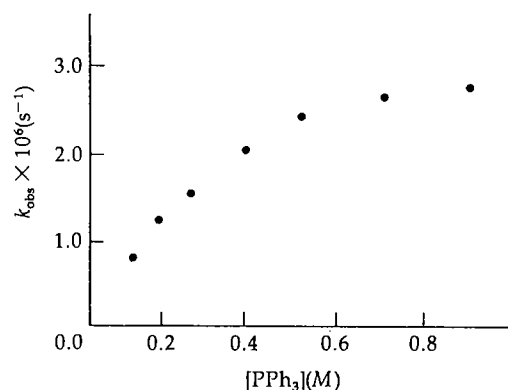
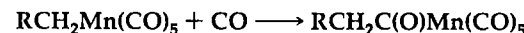


FIGURE 4.19. Dependence on $[\text{PPh}_3]$ of the rate of substitution for the reaction with $\text{CH}_3\text{FeCp(CO)}_2$.⁵¹

The rate of carbonylation on the alkyl group has been shown to depend on the electron-withdrawing ability of the R group.⁶⁷ The results of the carbonylation of substituted methylmanganese pentacarbonyl complexes are shown in Table 4.25. The presence of an electron-withdrawing R group dramatically slows the rate, most likely by affecting the preequilibrium

TABLE 4.25

Rates of Carbonylation for a Series of Substituted Methylmanganese Pentacarbonyl Complexes at 30°C in β, β' -Diethoxydiethyl Ether.



R	$\sigma^*(\text{RCH}_2)^a$	$10^5 k(\text{M}^{-1}\text{s}^{-1})$
C_2H_5	-0.115	14000
CH_3	-0.10	12000
cyclo- C_6H_{11}	-0.06	2500
H	0.00	1200
CH_3O	0.52	25
C_6H_5	0.22	12
HOC(O)	1.05	<5

$\rho^* = -8.7$

^aTaft parameter.

Solvent Effect

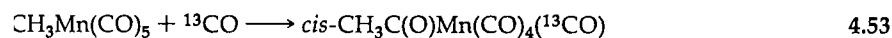
The formation of a 16-electron intermediate in a preequilibrium would allow the binding of solvent and suggest a large solvent effect. This is observed in reactions of alkyl complexes. Coordinating solvents accelerate the reaction as shown in Table 4.26 for $\text{CH}_3\text{Mn(CO)}_5$ and $\text{CH}_3\text{MoCp(CO)}_3$. This dependence on the solvent is consistent with coordination of the solvent to

TABLE 4.26

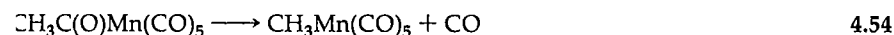
Solvent Effect on the Methyl Migration Reaction.⁶⁵⁻⁶⁷

$\text{CH}_3\text{Mn(CO)}_5$			$\text{CH}_3\text{MoCp(CO)}_3$	
solvent	K_{eq}	relative rate	solvent	relative rate
mesitylene	220	1	toluene	1
(<i>n</i> -Bu) ₂ O	120	2	THF	10
<i>n</i> -octyl chloride	200	4	nitromethane	70
DMF	3000	50	DMF	8000

As discussed previously, the stereochemistry of substitution reactions does not necessarily provide information on the stereochemistry of the intermediates. In this case, however, the formation of a kinetically stable product, *cis*-CH₃C(O)Mn(CO)₄L, indicates that the substitution reaction probably does provide stereochemical information. This is confirmed by carbonylation with ¹³CO, which leads exclusively to *cis*-CH₃C(O)Mn(CO)₄(¹³CO).

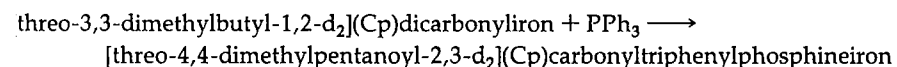
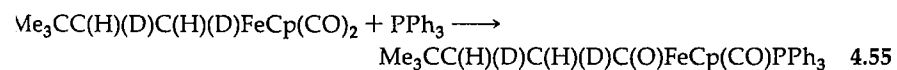


The fact that the labeled CO does not appear in the acyl confirms that the initial preequilibrium step (equation 4.45) does occur and that the CO does not insert directly into the CH₃-Mn bond. A more difficult question to answer concerned whether the methyl group migrates to a CO or whether a CO inserts into the CH₃-Mn bond. These processes are termed **methyl migration** and **CO insertion**, respectively. The distinction between these two is based on which group is moving in formation of the 16-electron acyl intermediate. This question was addressed for the manganese complex by a consideration of the decarbonylation of labeled CH₃C(O)Mn(CO)₅ complexes.⁷²



Because this reaction is the microscopic reverse of the carbonylation, determining which group moves for the decarbonylation also proves which group moves in the carbonylation—i.e., whether the reaction is a methyl migration or CO insertion. Figure 4.20 shows the results expected for both methyl migration and CO insertion. The observed distribution of *cis* to *trans* product was 2 : 1, in agreement with methyl migration.⁷²

Reaction of optically active alkyl groups shows that the carbonylation proceeds with retention of configuration at the carbon.⁷³



This suggests that the C-Fe bond remains as the C-C bond forms, as shown in the following scheme:



but doesn't help determine whether the alkyl group migrates or the carbonyl inserts. That the C-Fe bond remains while the C-C bond forms is consistent with the results of an extended Hückel calculation of the reaction coordinate

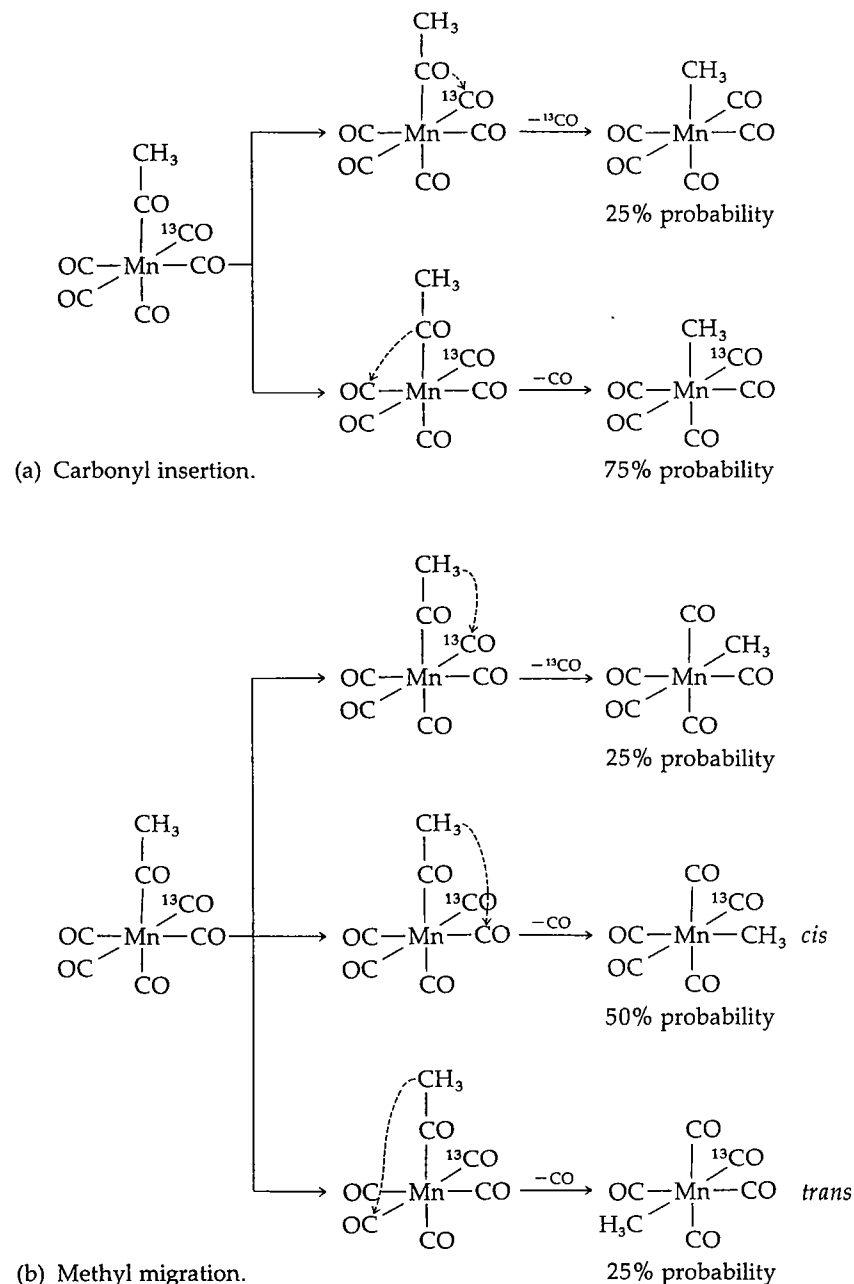


FIGURE 4.20. Decarbonylation of CH₃C(O)Mn(CO)₅ illustrating the differences in (a) carbonyl insertion and (b) methyl migration. [Reprinted with permission from K. Noack and F. Calderazzo, *J. Organomet. Chem.* 10, 101 (1967). Copyright 1967 Elsevier Sequoia S. A.]

for migration of CH_3 in $\text{CH}_3\text{Mn}(\text{CO})_5$.⁷⁴ It has been suggested that the transition state for the methyl migration corresponds to the methyl bonded to both the metal and to CO as shown in Figure 4.21.

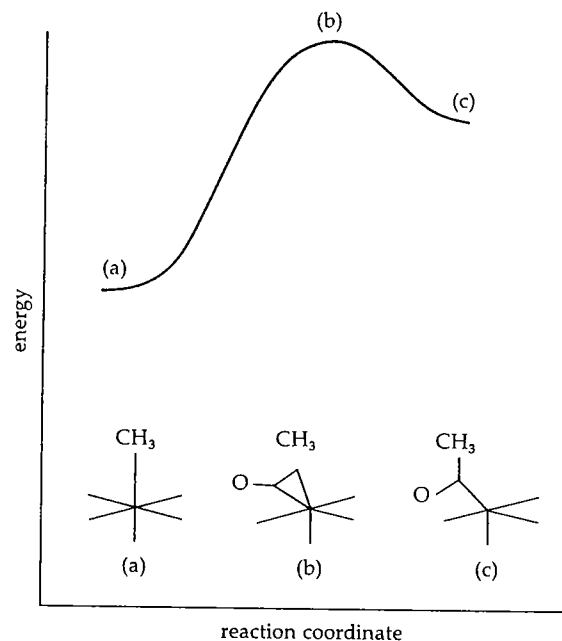


FIGURE 4.21. Energy profile calculated for methyl migration on $\text{CH}_3\text{Mn}(\text{CO})_5$.

Nature of the Intermediate

Several studies have attempted to identify the 16-electron acyl intermediate, especially that for manganese. Photochemical generation of the intermediate by CO dissociation from $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_5$ in an inert matrix at low temperature showed the geometry to be trigonal bipyramidal with the acyl in the equatorial plane.⁷⁵ Significant amounts of $\text{CH}_3\text{Mn}(\text{CO})_5$ also formed, suggesting a very low activation energy for methyl migration from the 16-electron acyl intermediate. Careful consideration of the labeling ratios in $\text{CH}_3\text{Mn}(\text{CO})_5$ by ^{13}C NMR led to the conclusion that the geometry was square pyramidal with the acyl in the equatorial plane.⁷⁶ Figure 4.22 shows these possibilities.⁶⁰ The two results may be rationalized by realizing that the ^{13}C NMR study was done in THF/acetone mixtures where a solvent may occupy the empty coordination site, preventing relaxation of the square pyra-

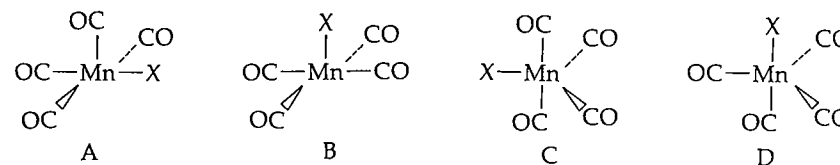
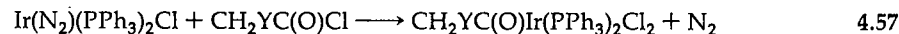


FIGURE 4.22. Possible intermediates in the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$. On the basis of ^{13}C NMR investigations of the reaction intermediate A ($\text{X} = \text{C}(\text{O})\text{CH}_3$) was suggested.

mid. In neither the matrix isolation nor the ^{13}C NMR was there any evidence for an η^2 -acyl as has been observed for early transition metal complexes.

A stable "intermediate" was formed by oxidative-addition of various substituted phenylacetyl chlorides to *trans*-chlorobis(triphenylphosphine) dinitrogeniridium.⁷⁷



These five-coordinate iridium acyls could be isolated and characterized, and the kinetics of the rearrangement to the six-coordinate benzyl complex investigated.



$\text{L} = \text{PPh}_3$; $\text{Y} = \text{C}_6\text{H}_5$, C_6F_5 , etc.

As expected, the presence of a ligand that could occupy the sixth coordination position inhibits the reaction. As shown in Table 4.29, the presence of electron-releasing substituents on the benzyl group promotes migration, and electron-withdrawing substituents retard the migration.⁷⁷

Many of the features of alkyl migration that we have discussed are incorporated into a study of the decarbonylation of ^{13}C -labeled *cis*-acetylbenzoyltetracarbonylrhenate(I) complexes.⁷⁸

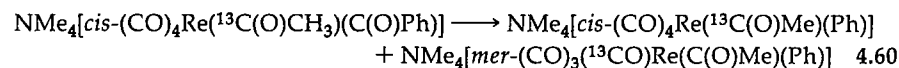
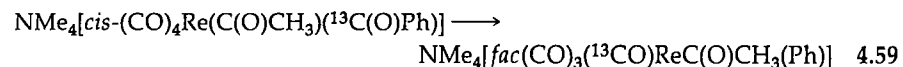


TABLE 4.29

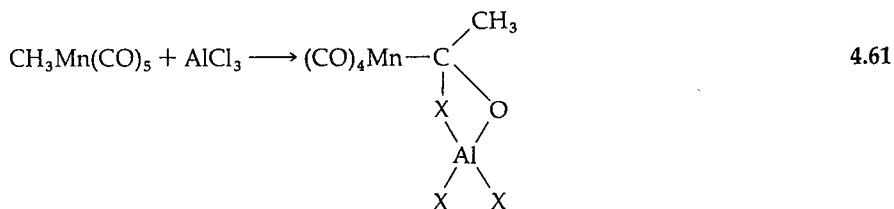
Rate Constants for the Rearrangement of Phenylacetyl, $\text{CH}_2\text{YC(O)Ir(PPh}_3)_2\text{Cl}_2$, Complexes to Benzyl (Carbonyl) Complexes in Benzene at 30°C.

Y	$k \times 10^4$
C_6H_5	7.09
$p\text{-CH}_3\text{OC}_6\text{H}_4$	9.19
$p\text{-CH}_3\text{C}_6\text{H}_4$	8.35
$p\text{-O}_2\text{NC}_6\text{H}_4$	3.90
C_6F_5	0.68 ^a

^aAt 40°C.

The scheme that was used to explain the labeling of these reactions is shown in Figure 4.23.⁷⁸ This detailed scheme is composed of three primary steps, methyl group migration, phenyl group rearrangement and fluxional behavior of the five-coordinate intermediate. The methyl group migration occurs relatively rapidly; phenyl migration and five-coordinate rearrangement occur at comparable (slower) rates. This scheme includes several aspects that we have discussed. Note that in each case the alkyl group migrates to a position *cis*, that CO dissociation occurs *cis* to both the acetyl and the benzoyl groups, that the equilibration of CO in the five-coordinate intermediate leads to all three possible products.⁷⁸

Alkyl migration (CO insertion) is catalyzed by the presence of Lewis acids such as AlCl_3 .⁷⁹ Cyclic products can be formed as shown in reaction 4.61.



The effects of several Lewis acids are shown in Table 4.30.⁶⁹ As shown by the data in Table 4.30, a Lewis acid can accelerate the methyl migration by a factor of 10^8 . By coordinating to the oxygen of a CO, the Lewis acid weakens

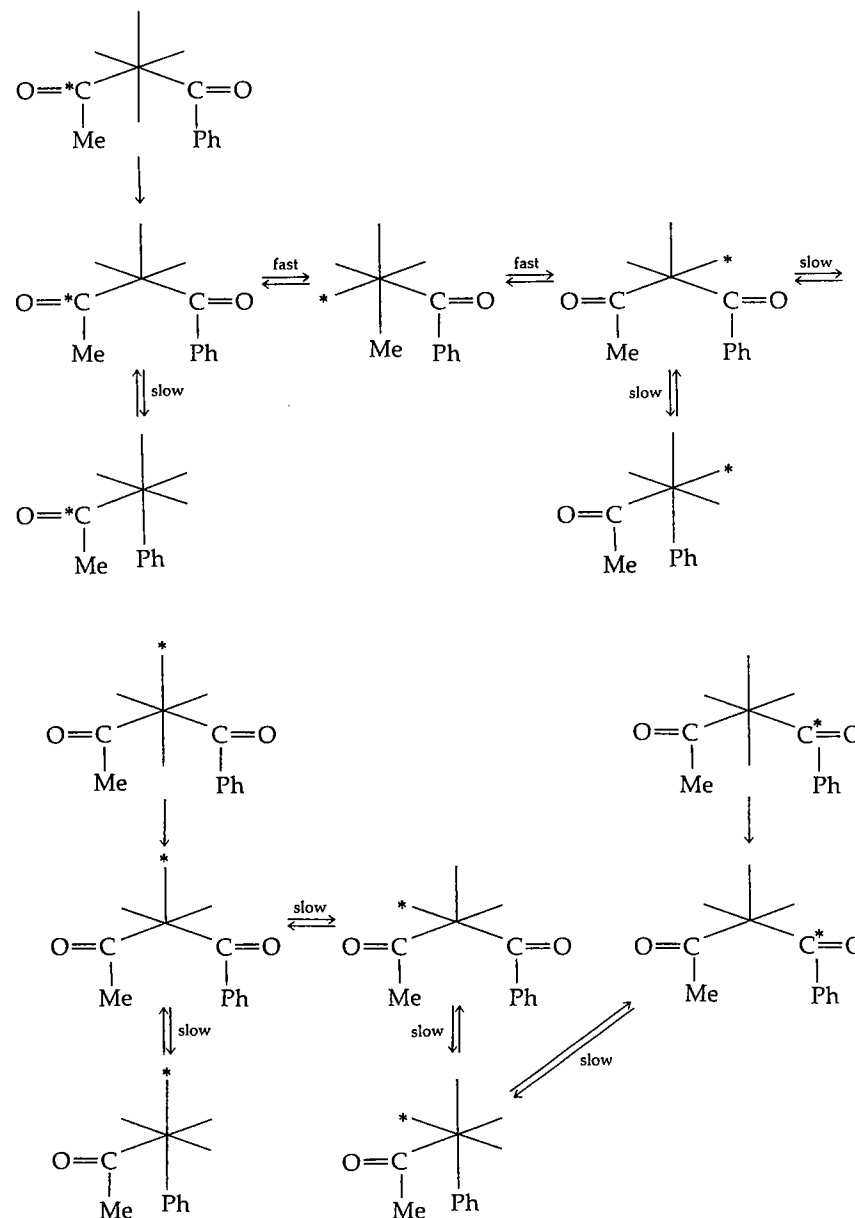


FIGURE 4.23. Scheme proposed to explain the isotopic labeling in decarbonylations of $\text{Re(C(O)Me)(C(O)Ph)(CO)}_4^-$. In each case the central metal is rhodium, and the vacant coordination sites are CO.

the C-O bond and lowers the activation energy for the migration. Such a mechanism is shown below.⁷⁹

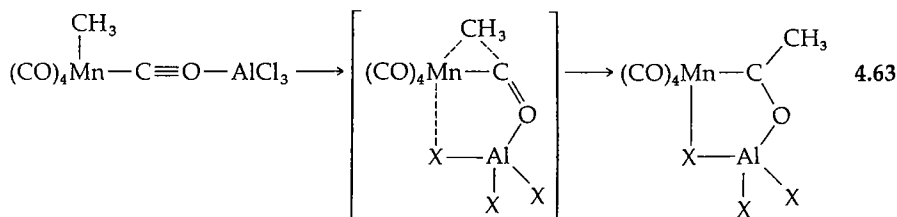
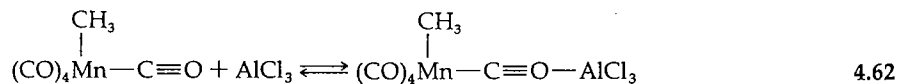


TABLE 4.30

Kinetic Data for Reactions Similar to Reaction 4.61.⁶⁹

Lewis acid	$k_{\text{obs}}(\text{s}^{-1})$
none	2×10^{-6}
AlClEt_2	0.37
AlCl_2Et	10.
AlCl_3	170

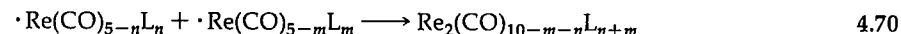
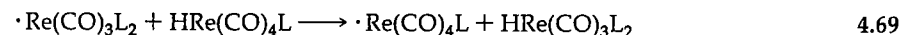
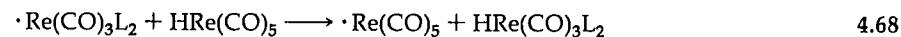
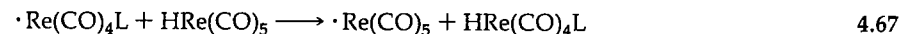
To summarize the results on substitution at alkyl complexes:

1. A preequilibrium exists between the 18-electron alkyl carbonyl complex and a 16-electron acyl, which probably is solvent coordinated.
2. The rate of migration depends on the electron-withdrawing ability of the alkyl group, more electron-withdrawing groups reacting more slowly.
3. More nucleophilic entering ligands speed the reaction.
4. The reaction proceeds by methyl migration as the carbanion.
5. The migration may be catalyzed by Lewis acids.

HYDRIDE COMPLEXES

Hydride complexes are important in many reactions catalyzed by organometallic complexes, yet the understanding of substitution reactions of hydrides

oxygen, and therefore difficult to study quantitatively. Another difficulty is that the presence of trace impurities leads to rapid reactions by **radical chain mechanisms**. Most hydride complexes have been observed to undergo facile ligand substitution reactions, probably by radical reactions like those studied for $\text{HRe}(\text{CO})_5$.^{80,81} Under rigorously pure conditions, with the exclusion of light, $\text{HRe}(\text{CO})_5$ showed no reaction with PBu_3 in 60 days at 25°C .⁸⁰ When such care was not taken, the reaction yielded $\text{HRe}(\text{CO})_4\text{PBu}_3$ and $\text{HRe}(\text{CO})_3(\text{PBu}_3)_2$ at variable rates. The following sequence of reactions was proposed to explain the radical reactions:



Thus the substitution reaction is catalyzed by trace impurities ($\text{R}\cdot$) which initiate a self-perpetuating chain mechanism for substitution. Reaction 4.70 is a chain termination step. The most recent evidence suggests that radical substitution reactions such as those in equations 4.65 and 4.66 occur by an associative mechanism.^{38,39} Regardless of this mechanism, it is clear that, once generated, 17-electron complexes undergo rapid ligand scrambling. A primary piece of evidence for the radical chain mechanism was that photolysis of catalytic amounts of $\text{Re}_2(\text{CO})_{10}$ under conditions known to cause metal-metal bond cleavage initiates the radical chain process.⁸⁰

Metal hydride complexes might also undergo substitution by dissociative, associative, or hydride migration processes. Very few studies have been accomplished under conditions that clearly rule out radical mechanisms. The reactions of $\text{HMn}(\text{CO})_5$ with L ($\text{L} = {}^{13}\text{CO}$, AsPh_3 , PPh_3 , and PBu_3) have been investigated showing dependence of the rate on the nature and concentration of the entering ligand.⁸² The rates for different ligands are shown in Table 4.31.⁸² These reactions clearly did not involve a CO dissociative route and were interpreted in terms of a hydride migration mechanism that has often been postulated in reactions of metal hydrides.



TABLE 4.31

Variation in the Rate of Substitution on HMn(CO)_5 with $\text{L} = {}^{13}\text{CO}$, AsPh_3 , PPh_3 , and PBu_3 at 20°C .⁸²

L	rate ($M^{-1}s^{-1}$)
${}^{13}\text{CO}^a$	1.2×10^{-3}
AsPh_3^b	3×10^{-4}
PPh_3	1.4×10^{-2}
PBu_3	fast

^aAt 26°C .

^bAt 28°C .

The dependence on the nature of the entering ligand is considerably greater than that observed for alkyl migration (Table 4.28). Nucleophilic attack must be much more important for the hydride complexes. Thus the hydride migration would not be a rapid preequilibrium, and would only occur as a result of the nucleophilic attack. At this point there is no evidence favoring hydride migration over direct nucleophilic attack on the complex in substitution reactions of HMn(CO)_5 .

The very rapid substitution reactions of hydride complexes $\text{H}_2\text{Fe(CO)}_4$ and $\text{H}_2\text{Ru(CO)}_4$ at -70°C were interpreted in terms of hydride migration.⁸³ Since these complexes also undergo facile thermal decomposition, it has been suggested that a weak M-H bond may be a requirement for both reactions.⁸³ A weak M-H bond may also facilitate radical mechanisms, and at this point there are no data that allow an unambiguous mechanistic interpretation of metal hydride substitution reactions that are not initiated by radical (17-electron) species. Much more research on reactions of metal hydride complexes is required before the mechanisms of this very important class of complexes are understood.

NITROSYL AND ALLYL COMPLEXES

The nitrosyl ligand, NO, and the allyl ligand, $\text{CH}_2=\text{CH}-\text{CH}_2$, may function as either three-electron or one-electron donors to a metal, and it is this feature that dominates their substitution reactions. The different types of

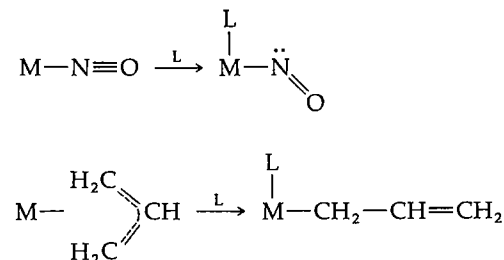
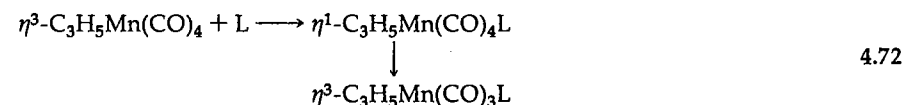


FIGURE 4.24. Modes of rearrangement for the nitrosyl and allyl groups to accommodate an entering two-electron nucleophile.

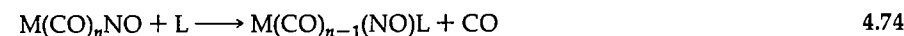
binding are shown in Figure 4.24 for NO and C_3H_5 . This capability allows associative reactions to occur through 18-electron intermediates.



Substitution reactions of nitrosyl complexes $\text{Mn(CO)}_4\text{NO}$ and $\text{Co(CO)}_3\text{NO}$ show a rate law consistent with attack of the ligand in an associative reaction.^{84,85}

$$\text{rate} = k[\text{Metal nitrosyl}][\text{L}] \quad 4.73$$

The activation parameters as shown in Table 4.32 are also consistent with the associative nature of the substitution reaction.^{84,85} The negative entropies of activation are indicative of an associative process. The dependence on the entering ligand (Table 4.33) shows the nucleophilic nature of the attack.



The ordering

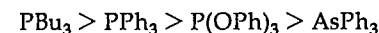


TABLE 4.32

Activation Parameters for Substitution of Nitrosyl Complexes.^{84,85}

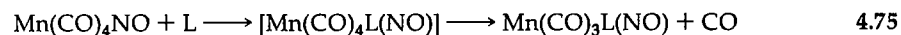
complex	$\Delta H^\ddagger$ (kcal/mole)	$\Delta S^\ddagger$ (eu)
$\text{Mn(CO)}_4\text{NO}$	19	-11
$\text{Co(CO)}_3\text{NO}$	21	-13

TABLE 4.33

Dependence of the Rate for Substitution of Nitrosyl Complexes on the Entering Ligand for Equation 4.74.

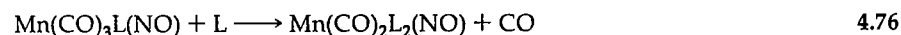
L	M = Co, $n = 3$	M = Mn, $n = 4$
AsPh ₃	.002	0.015
P(OPh) ₃	0.03	0.08
PPh ₃	1	1
PBu ₃	90	40

is in agreement with the nucleophilicities of these ligands. The data are all consistent with the sequence



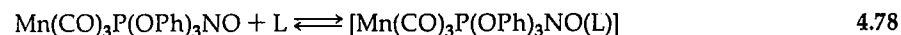
in which the nitrosyl changes from a three-electron donor in the beginning and final complexes to a one-electron donor (bent configuration) in the intermediate. Each of the complexes in equation 4.75 contains 18 electrons at the metal.

Further substitution on $\text{Mn}(\text{CO})_3\text{L}(\text{NO})$ shows a two term rate law,⁸⁴



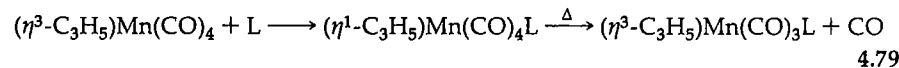
$$\text{rate} = (k_1 + k_2[\text{L}])[\text{Mn}(\text{CO})_3\text{L}(\text{NO})] \quad 4.77$$

for $\text{L} = \text{PPh}_3$, PBu_3 and P(OPh)_3 . It has been suggested that the presence of the bulky phosphorus ligand inhibits further attack. However, phosphorus ligand exchange on $\text{Mn}(\text{CO})_3\text{P(OPh)}_3\text{NO}$ by PBu_3 or PPh_3 occurs via a ligand-dependent pathway at a lower temperature than the further substitution for CO. It would seem most likely that the ligand attacks the complex in an associative step.

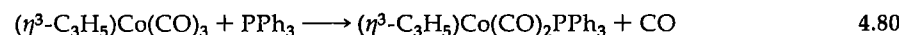


Bis-substituted six-coordinate complexes often undergo relatively rapid phosphine or phosphite dissociation.³³⁻³⁵ For phosphorus ligand exchange the phosphite would dissociate from the six-coordinate intermediate. For further substitution, CO dissociation would require higher temperatures, and the ligand attack would be a rapid preequilibrium. The rate law for this process would show two terms as observed. Substitution of other nitrosyl complexes has also shown a two term rate law, and a similar mechanism may be operative for those complexes.^{86,87}

Allyl complexes have the potential to react as the nitrosyl complexes. Reactions of $(\eta^3\text{-C}_3\text{H}_5)\text{Mn}(\text{CO})_4$ with a ligand leads to $(\eta^1\text{-C}_3\text{H}_5)\text{Mn}(\text{CO})_4\text{L}$, which could be viewed as the intermediate.

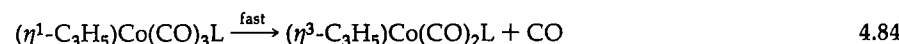
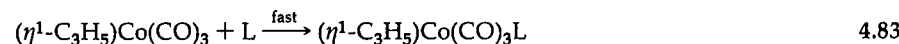
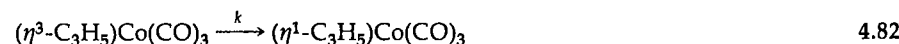


Although the kinetics of this substitution reaction have not been investigated, the mechanism is obvious and similar to that suggested for the analogous nitrosyl complex, $\text{Mn}(\text{CO})_4(\text{NO})$. Very few kinetic studies have been accomplished that allow an unambiguous interpretation of the data. Reaction of $(\eta^3\text{-C}_3\text{H}_5)\text{Co}(\text{CO})_3$ with PPh_3 under pseudo first order conditions showed a rate law



$$\text{rate} = k[(\eta^3\text{-C}_3\text{H}_5)\text{Co}(\text{CO})_3] \quad 4.81$$

which is independent of the concentration of PPh_3 .⁸⁸ This was interpreted as a CO dissociative process although a rate-determining $\eta^3\text{-C}_3\text{H}_5 \rightarrow \eta^1\text{-C}_3\text{H}_5$ rearrangement would also be consistent. It is important to emphasize that for the observed rate law the $\eta^3\text{-allyl} \rightleftharpoons \eta^1\text{-allyl}$ cannot be a rapid preequilibrium. The sequence would have to be as follows:



One could consider the first step to be rate-determining dissociation of the olefin. Although this scheme would be consistent with the binding capability of the allyl group, it is no more reasonable than the CO dissociative process. Changing the substituent in the two position to either electron-withdrawing (Br, Cl, Ph) or electron-releasing (CH_3) groups increases the rate of reaction, a change not readily explained in terms of either CO dissociation or $\eta^3 \rightarrow \eta^1$ allyl interconversion.⁸⁸ Further kinetic studies of substitutions on allyl complexes will be required to understand the details of the reaction.

The capability of a ligand to coordinate with variable numbers of electrons may be important in reactions of organic ligands such as butadienes, cyclopentadienyls and aromatic complexes. The possible bonding modes are shown in Figure 4.25. Very few kinetic studies have been reported on complexes of this type. Substitution reactions on $(\eta^5\text{-indenyl})\text{tricarbonylmolybdenum}$ halides showed a rate law of the type

$$\text{rate} = (k_1 + k_2[\text{L}])(\eta^5\text{-C}_9\text{H}_7)\text{Mo}(\text{CO})_3\text{X} \quad 4.85$$

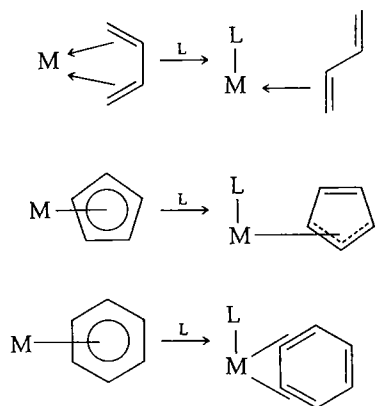


FIGURE 4.25. Possible modes of rearrangement for diene, cyclopentadiene, and arene complexes to accommodate an entering nucleophile.

and the second order path was ascribed to an η^5 -indenyl $\rightarrow$ η^3 -indenyl conversion (cyclopentadienyl $\rightarrow$ allyl).⁸⁹ The generality of this mechanism is uncertain. Reaction of $\text{CpRh}(\text{CO})_2$ with nucleophiles occurs by a second order mechanism.⁹⁰



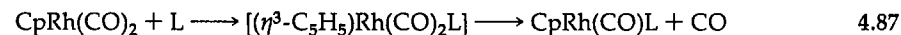
Data for different ligands as shown in Table 4.34 indicate the dependence on the nature of the entering nucleophile. The rate law is consistent with direct nucleophilic attack on the complex. This is most readily accomplished by

TABLE 4.34

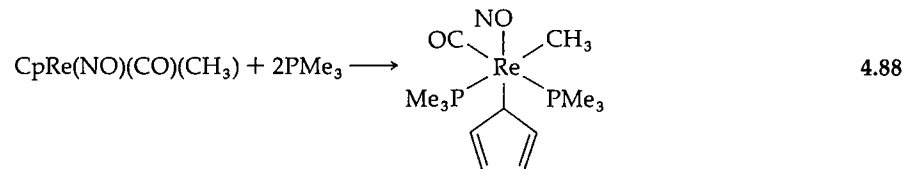
Rate Constants for Reaction 4.86 at 40°C, Showing the Dependence on the Nature of L.⁹⁰

L	$k(\text{M}^{-1}\text{s}^{-1})$
Py	very slow
AsPh ₃	very slow
P(OPh) ₃	7.3×10^{-5}
PPh ₃	2.9×10^{-4}
P(OBu) ₃	5.6×10^{-4}
PBu ₃	4.3×10^{-3}

attack leading to an $(\eta^3\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2\text{L}$:

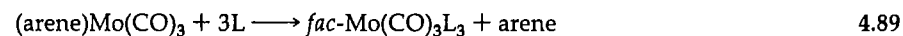


Synthetic evidence for reduced coordination by a cyclopentadienyl has been provided in the reaction of PMe_3 with $\text{CpRe}(\text{NO})(\text{CO})\text{CH}_3$.⁹¹

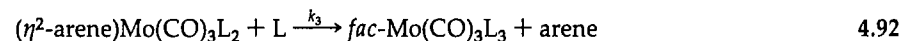
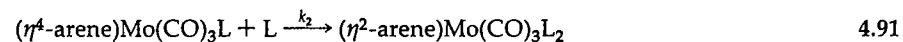
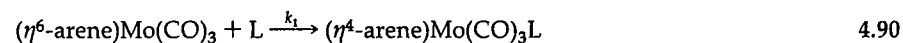


In this reaction the $\eta^5\text{-C}_5\text{H}_5$ group rearranges to an $\eta^1\text{-C}_5\text{H}_5$. This is especially interesting since the molecule has two other means of accommodating an incoming nucleophile — methyl migration to an acyl and changing the nitrosyl from a three-electron donor to a one-electron donor. If it is easier for a cyclopentadienyl to rearrange to $\eta^3\text{-C}_5\text{H}_5$ or $\eta^1\text{-C}_5\text{H}_5$ than for methyl migration or nitrosyl rearrangement to occur, then this may be a very common mode of reaction.

Displacement of arene ligands from organometallic complexes also occurs by a ligand-dependent path.⁹²



The reaction is first order in arene complex and first order in entering nucleophile, dependent on the nucleophilicity of the ligand L, and leads specifically to the facial isomer.⁹² The most reasonable mechanism, as shown below, involves reduced coordination by the arene from a six-electron donor, to a four-electron donor, to a two-electron donor before loss of arene from the complex.



The rate-determining step would be k_1 , which accounts for the rate dependences. The facial stereochemistry requires that the arene remain coordinated through the final addition of L. Arene ligand exchange may also proceed through similar steps where the entering ligand is another arene.⁹³

Many types of ligands that have variable bonding capabilities undergo substitution reactions by nucleophilic attack on the metal complex. In each case the intermediate contains 18 electrons. At this point there is no evidence

for 20-electron intermediates in organometallic reactions that occur by nucleophilic attack.

SUMMARY

Ligand substitutions on organometallic complexes occur by CO dissociation (either D or I_d) unless special features of the ligands allow associative steps. Ligands that have this capability are CH₃ and H, which can undergo migrations; NO and allyls, which can function as either three-electron donors or one-electron donors; and possibly other ligands that can readily assume variable coordination modes such as $\eta^5\text{-C}_5\text{H}_5 \rightarrow \eta^3\text{-C}_5\text{H}_5$ conversions.

REFERENCES

1. F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.* **84**, 4432 (1962).
2. S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Am. Chem. Soc.* **89**, 5573 (1967).
3. G. M. Bodner, *Inorg. Chem.* **14**, 2694 (1975).
4. M. J. Wovkulich and J. D. Atwood, *J. Organomet. Chem.* **184**, 77 (1980).
5. J. P. Collman and L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry* (Mill Valley, CA: University Science Books, 1980.)
6. J. D. Atwood, M. J. Wovkulich, and D. C. Sonnenberger, *Acc. Chem. Res.* **16**, 350 (1983).
7. C. A. Tolman, *J. Am. Chem. Soc.* **92**, 2956 (1970).
8. C. A. Tolman, *Chem. Soc. Rev.* **1**, 337 (1972).
9. J. P. Day, F. Basolo, R. G. Pearson, L. F. Kangas, and P. M. Henry, *J. Am. Chem. Soc.* **90**, 1925 (1968).
10. R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.* **84**, 2495 (1962).
11. J. M. Kelley, H. Herman, and E. K. Von Gustorf, *J. Chem. Soc. Chem. Comm.* 105 (1973).
12. F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.* **83**, 520 (1961).
13. J. P. Day, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.* **90**, 6927 (1968).
14. J. R. Graham and R. J. Angelici, *Inorg. Chem.* **6**, 2082 (1967).
15. W. D. Covey and T. L. Brown, *Inorg. Chem.* **12**, 2820 (1973).
16. M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.* **8**, 795 (1969).
17. S. P. Modi and J. D. Atwood, *Inorg. Chem.* **22**, 26 (1983).
18. M. Poliakoff and J. J. Turner, *J. Chem. Soc. Dalton Trans.* 2276 (1974).
19. M. R. J. Dack, *J. Chem. Ed.* **51**, 231 (1974).
20. C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.* **12**, 1286 (1973).
21. G. Cardaci and V. Narciso, *J. Chem. Soc. Chem. Comm.* 2289 (1972).
22. A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.* **83**, 525 (1961).
23. J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.* **97**, 3380 (1975).
24. J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.* **98**, 3155 (1976).
25. J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.* **98**, 3160 (1976).
26. D. L. Lichtenberger and T. L. Brown, *J. Am. Chem. Soc.* **100**, 366 (1978).
27. D. J. Darensbourg and M. A. Murphy, *J. Am. Chem. Soc.* **100**, 463 (1978).
28. D. J. Darensbourg, *Inorg. Chem.* **18**, 14 (1979).
29. D. J. Darensbourg and R. L. Kump, *Inorg. Chem.* **17**, 2680 (1978).
30. R. H. Reimann and E. Singleton, *J. Chem. Soc. Dalton Trans.* 841 (1973).
31. A. Holladay, M. R. Churchill, A. Wong, and J. D. Atwood, *Inorg. Chem.* **19**, 2195 (1980).
32. D. J. Darensbourg and A. H. Graves, *Inorg. Chem.* **18**, 1257 (1979).
33. M. J. Wovkulich and J. D. Atwood, *J. Organomet. Chem.* **184**, 77 (1980).

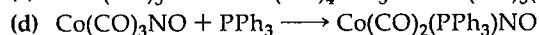
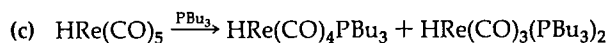
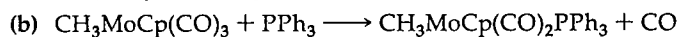
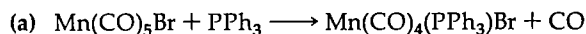
34. M. J. Wovkulich, S. J. Feinberg, and J. D. Atwood, *Inorg. Chem.* **19**, 2608 (1980).
35. M. J. Wovkulich and J. D. Atwood, *Organometallics* **1**, 1316 (1982).
36. L. E. Manzer and C. A. Tolman, *J. Am. Chem. Soc.* **97**, 1955 (1975).
37. R. J. Angelici, S. E. Jacobson, and C. M. Ingemanson, *Inorg. Chem.* **7**, 2466 (1968).
38. S. B. McCullen, H. W. Walker, and T. L. Brown, *J. Am. Chem. Soc.* **104**, 4007 (1982).
39. Q.-Z. Shi, T. G. Richmond, W. C. Trogler, and F. Basolo, *J. Am. Chem. Soc.* **104**, 4032 (1982).
40. H. Wawersik and F. Basolo, *Inorg. Chim. Acta* **3**, 113 (1969).
41. L. I. B. Haines, D. Hopgood, and A. J. Poë, *J. Chem. Soc. A*, 421 (1968).
42. L. I. B. Haines and A. J. Poë, *J. Chem. Soc. A*, 2826 (1969).
43. D. Sonnenberger and J. D. Atwood, *J. Am. Chem. Soc.* **102**, 3484 (1980).
44. J. D. Atwood, *Inorg. Chem.* **20**, 4031 (1981).
45. S. Schmidt, F. Basolo, and W. Trogler, *Inorg. Chem.* **21**, 1699 (1982).
46. A. M. Stolzenberg and E. L. Muetterties, *J. Am. Chem. Soc.* **105**, 822 (1983).
47. N. J. Coville, A. M. Stolzenberg, and E. L. Muetterties, *J. Am. Chem. Soc.* **105**, 2499 (1983).
48. M. Absi-Halabi, J. D. Atwood, N. P. Forbes, and T. L. Brown, *J. Am. Chem. Soc.* **102**, 6248 (1980).
49. S. M. Grant and A. R. Manning, *Inorg. Chim. Acta* **31**, 41 (1978).
50. A. F. Clifford and A. K. Mukerjee, *Inorg. Chem.* **2**, 151 (1963).
51. J. P. Candlin and A. C. Shortland, *J. Organomet. Chem.* **16**, 289 (1969).
52. S. M. Grant and A. R. Manning, *Inorg. Chim. Acta* **31**, 41 (1978).
53. G. F. Stuntz and J. R. Shapley, *J. Am. Chem. Soc.* **99**, 607 (1977).
54. K. J. Karel and J. R. Norton, *J. Am. Chem. Soc.* **96**, 6812 (1974).
55. D. Sonnenberger and J. D. Atwood, *Inorg. Chem.* **20**, 3243 (1981).
56. D. Sonnenberger and J. D. Atwood, *J. Am. Chem. Soc.* **104**, 2113 (1982).
57. D. Sonnenberger and J. D. Atwood, *Organometallics* **1**, 694 (1982).
58. G. F. Stuntz and J. R. Shapley, *J. Organomet. Chem.* **213**, 389 (1981).
59. S. K. Malik and A. Poë, *Inorg. Chem.* **17**, 1484 (1978).
60. D. J. Darensbourg and B. J. Baldwin-Zuschke, *J. Am. Chem. Soc.* **104**, 3906 (1981).
61. D. J. Darensbourg and B. J. Baldwin-Zuschke, *Inorg. Chem.* **20**, 3846 (1981).
62. G. Huttner, J. Schneider, H. D. Muller, G. Mohr, J. van Seyer, and L. Wohlfahrt, *Angew. Chem. Int. Ed. Engl.* **18**, 76 (1979).
63. (a) J. R. Fox, W. L. Gladfelter, and G. L. Geoffroy, *Inorg. Chem.* **19**, 2574 (1980).
(b) J. R. Fox, W. L. Gladfelter, T. G. Wood, J. A. Smegal, T. K. Foreman, G. L. Geoffroy, I. Tavanaiepour, V. W. Day, and C. S. Day, *Inorg. Chem.* **20**, 3214 (1981).
64. J. B. Keister and J. R. Shapley, *J. Am. Chem. Soc.* **98**, 1056 (1976).
65. F. Calderazzo and F. A. Cotton, *Inorg. Chem.* **1**, 30 (1962).
66. I. S. Butler, F. Basolo, and R. G. Pearson, *Inorg. Chem.* **6**, 2074 (1967).
67. J. N. Cawse, R. A. Fiato, and R. L. Pruett, *J. Organomet. Chem.* **172**, 405 (1979).

68. K. Nicholas, S. Raghu, and M. Rosenblum, *J. Organomet. Chem.* **78**, 133 (1974).
69. J. P. Bibler and A. Wojcicki, *Inorg. Chem.* **5**, 889 (1966).
70. M. J. Wax and R. G. Bergman, *J. Am. Chem. Soc.* **103**, 7028 (1981).
71. C. S. Kraihanzel and P. K. Maples, *Inorg. Chem.* **7**, 1806 (1968).
72. K. Noack and F. Calderazzo, *J. Organomet. Chem.* **10**, 101 (1967).
73. G. M. Whitesides and D. J. Boschetto, *J. Am. Chem. Soc.* **91**, 4313 (1969).
74. H. Berke and R. Hoffmann, *J. Am. Chem. Soc.* **100**, 7224 (1978).
75. T. M. McHugh and A. J. Rest, *J. Chem. Soc. Dalton Trans.* 2323 (1980).
76. T. C. Flood, J. E. Jensen, and J. A. Statler, *J. Am. Chem. Soc.* **103**, 4411 (1981).
77. M. Kubota, D. M. Blake, and S. A. Smith, *Inorg. Chem.* **10**, 1430 (1971).
78. C. P. Casey and L. M. Baltusis, *J. Am. Chem. Soc.* **104**, 6347 (1982).
79. T. G. Richmond, F. Basolo, and D. F. Shriver, *Inorg. Chem.* **21**, 1272 (1982).
80. B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.* **99**, 2527 (1977).
81. N. W. Hoffman and T. L. Brown, *Inorg. Chem.* **17**, 613 (1978).
82. B. H. Byers and T. L. Brown, *J. Organomet. Chem.* **127**, 181 (1977).
83. R. G. Pearson, H. W. Walker, H. Mauermann, and P. C. Ford, *Inorg. Chem.* **20**, 2741 (1981).
84. H. Wawersik and F. Basolo, *J. Am. Chem. Soc.* **89**, 4626 (1967).
85. E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.* **88**, 3929 (1966).
86. G. Innorta, G. Reichenbach, and A. Foffani, *J. Organomet. Chem.* **22**, 731 (1970).
87. G. Cardaci and S. M. Murgia, *Inorg. Chim. Acta* **6**, 222 (1972).
88. R. F. Heck, *J. Am. Chem. Soc.* **85**, 651 (1963).
89. A. J. Hart-Davis, C. White, and R. J. Mawby, *Inorg. Chim. Acta* **4**, 441 (1970).
90. H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.* **88**, 1657 (1966).
91. C. P. Casey and W. D. Jones, *J. Am. Chem. Soc.* **102**, 6156 (1980).
92. F. Zingales, A. Chiesa, and F. Basolo, *J. Am. Chem. Soc.* **88**, 2707 (1966).
93. W. Strohmeier and R. Müller, *Z. Phys. Chem.* **40**, 85 (1964).

PROBLEMS

1. Show that the following are 18-electron complexes: $\text{W}(\text{CO})_6$; $\text{HFe}(\text{CO})_4^-$; $\text{CH}_3\text{Co}(\text{CO})_3\text{PPh}_3$; $\text{Ru}_3(\text{CO})_{12}$; $\text{Mn}(\text{CO})_4\text{NO}$; $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$; $(\eta^5\text{-C}_5\text{H}_5)\text{-Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$.

2. Show the electron count for the starting material, intermediates, and products of the following organometallic substitution reactions:



3. Discuss in terms of ligand bonding the infrared data for *trans*- $\text{Cr}(\text{CO})_4\text{L}_2$ complexes as shown below:

L	$\nu(\text{cm}^{-1})$
$\text{P}(\text{OPh})_3$	1935
$\text{P}(\text{OMe})_3$	1916
PPh_3	1884
PBu_3	1873

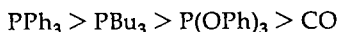
4. Why are the solvent effects for organometallic substitution reactions, which proceed by ligand dissociation (Table 4.7), so small in comparison to the solvent effects for ligand dissociation in Werner-type inorganic complexes?

5. What information does the competition ratio give regarding energy profiles?

6. Rates of decarbonylation of $\text{RC}(\text{O})\text{Mn}(\text{CO})_5$, which proceeds by rate-determining CO dissociation, are shown below as a function of R. Explain these observations. [J. N. Cawse, R. A. Fiato, and R. L. Pruett, *J. Organomet. Chem.* **172**, 405 (1979).]

R	$10^5k(\text{s}^{-1})$
CF_3	2.8
CH_3OCH_2	58
$\text{C}_6\text{H}_5\text{CH}_2$	160
CH_3	250

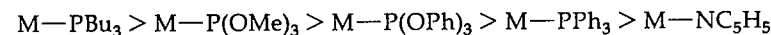
7. Explain the following order of ligand effects as observed for the further substitution of $\text{Mn}_2(\text{CO})_9\text{L}$:



PROBLEMS

8. Suggest a reason other than steric effects why phosphines cannot substitute as extensively as phosphites on metal carbonyl complexes. (Consider the infrared frequencies of *fac*- $\text{Cr}(\text{CO})_3(\text{PEt}_3)_3$, 1920(s), 1820(s) cm^{-1}).

9. The general order of ligand bond strengths to organometallic centers is as follows:



Contrast this order to trends for sigma donation, pi acceptance, and size. Offer an explanation for the observed order of bond strength.

10. Explain in some detail the data presented in Table 4.10.

11. Explain the observation that $\text{Mn}_2(\text{CO})_9\text{PPh}_3$ and $\text{Re}_2(\text{CO})_9\text{PPh}_3$ are not observed but $\text{MnRe}(\text{CO})_9\text{PPh}_3$ is observed as intermediate in substitution reactions. [D. Sonnenberger and J. D. Atwood, *J. Am. Chem. Soc.* **102**, 3484 (1980).]

12. The order of reactivity for trinuclear metal clusters, $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) is $\text{Fe} > \text{Ru} > \text{Os}$, a different order than that for mononuclear complexes. At this point the reason for this reversal is unknown. Suggest at least one possible reason.

13. Show that the rate law for $\text{CH}_3\text{Mn}(\text{CO})_5$ is that given as derived from reactions 4.45 and 4.46.

14. Draw an energy profile for the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with CO.

15. Predict the effect that a ligand (PR_3) will have on an alkyl migration. (How will replacing a CO with PR_3 affect the energy profile from problem 4.14?)

16. How does the presence of a Lewis acid affect the energy profile in problem 4.14?

17. Most catalytic reactions of transition metal hydride complexes are suggested to occur by ligand dissociation. Can you rationalize these postulates in terms of the observed stoichiometric reactions of transition metal hydrides?

18. $\text{Mn}(\text{CO})_4\text{NO}$ and $\text{Co}(\text{CO})_3\text{NO}$ react by associative mechanisms. Can you justify their relative reactivity by consideration of crystal field activation energies? (Refer to Table 3.9.)

19. Reactions of a number of complexes of bidentate ligands such as $(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)\text{Cr}(\text{CO})_4$ occur by ligand-dependent pathways. Suggest a scheme that conforms to the $18e^- \rightarrow 16e^- \rightarrow 18e^-$ transition and show how the ligand dependency arises. [G. R. Dobson, *Acc. Chem. Res.* **9**, 300 (1976).]

20. Based on the scheme from problem 4.19 and your knowledge of metal ligand bond strengths, suggest the initial (mild-condition) product of the reaction of $\text{Cr}(\text{CO})_4(\text{P}^*\text{N})$ where P^*N is a bidentate ligand with a phosphorus and a nitrogen donor atom. [W. J. Knebel and R. J. Angelici, *Inorg. Chem.* **13**, 627 (1974).]

Oxidative-Addition and Reductive-Elimination

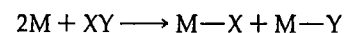
Oxidative-addition and reductive-elimination are reactions often used in synthesis and are involved in most mechanistic schemes proposed for homogeneously catalyzed reactions. Oxidative-addition reactions lead to an expansion of the coordination number of a metal with concomitant increase of the formal oxidation state. Reductive-elimination reactions are the reverse of oxidative-additions, leading to a decrease in the coordination number of the metal and in the formal oxidation state of the metal. Although in many cases the oxidative-addition and reductive-elimination reactions are the microscopic reverse of each other and mechanistic information for one may pertain to the other, studies have typically focused on the reactions separately. For this reason we shall consider the reactions separately until the concluding section.

OXIDATIVE-ADDITION

Oxidative-addition has been observed at a number of metal centers, often with different mechanisms.¹⁻⁵ The reaction can, in general, be represented as in equation 5.1 below,



or



where M represents a metal complex and XY is a compound such as hydro-

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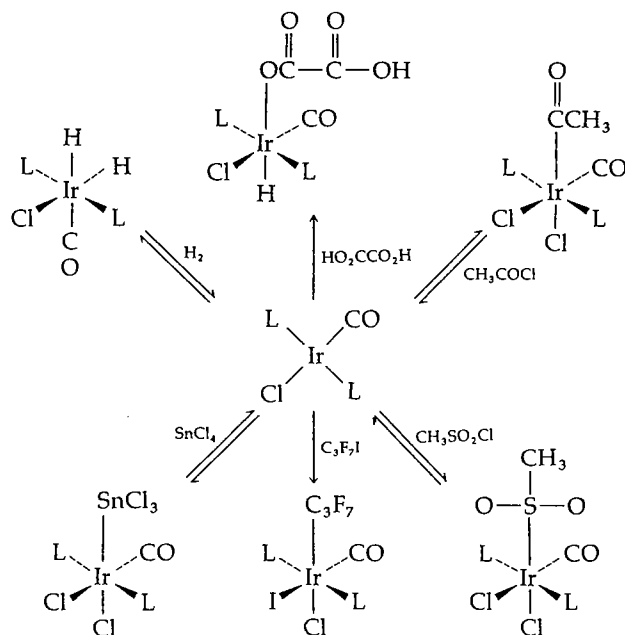
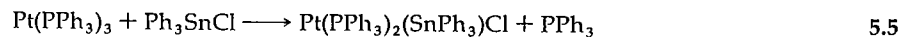
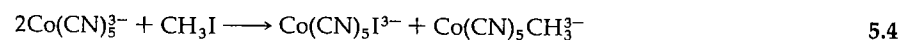
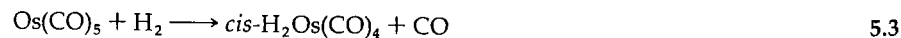
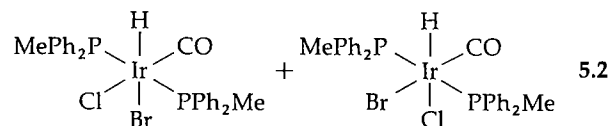
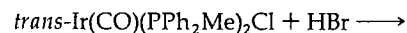


FIGURE 5.1. Oxidative-addition reactions. [Reprinted with permission from J. P. Collman, *Acc. Chem. Res.* 1, 136 (1968). Copyright 1968 American Chemical Society.]

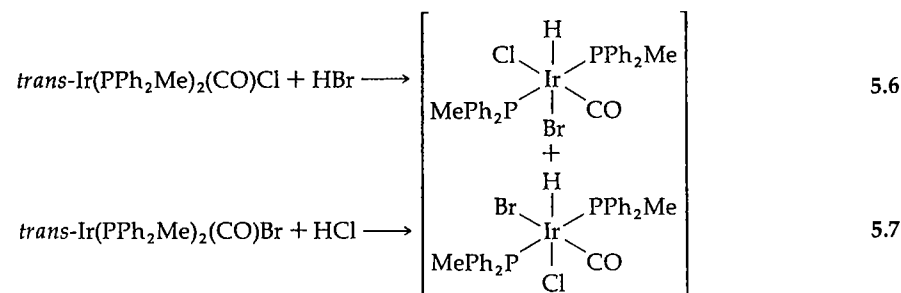
gen, halogen, alkyl halide or metal halide. The mechanism depends on both the metal complex and the adding group.³ Several examples are shown below and in Figure 5.1.



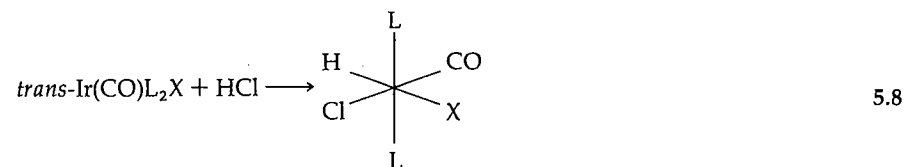
In reaction 5.2 the square planar iridium(I) complex is transformed into an octahedral iridium(III) complex by oxidative-addition of HBr. Oxidative-addition of H₂ to Os(CO)₅ in reaction 5.3 converts the trigonal bipyramidal osmium(0) complex into a hexacoordinate Os(II) complex. Reaction 5.4 is an

example of addition to two metal centers, where each is changed to an octahedral cobalt(III) complex.² In reaction 5.5 a three-coordinate platinum(0) complex is converted to a square planar Pt(II) complex. These examples indicate the generality of the oxidative-addition reaction. Most of the detailed studies have been accomplished on square planar complexes such as those shown in equation 5.2 and Figure 5.1.

The stereochemistry of addition is specific, only one of the possible isomers being formed in most cases.^{3,6} Addition of hydrogen to square planar complexes leads to *cis* distribution of the hydrogen atoms in the octahedral product. Addition to Ir(CO)(PPh₃)₂Cl is shown in Figure 5.1. Oxidative-addition of polar molecules to square planar complexes usually occurs *trans* as shown in Figure 5.1 and reaction 5.2.⁶ In a few cases mixtures of isomers are observed. The reaction of HBr with Ir(PPh₂Me)₂(CO)Cl (equation 5.2) is one example; here both *cis* and *trans* isomers are formed. The reaction of HCl with Ir(PPh₂Me)₂(CO)Br produced the same mixture of products.³



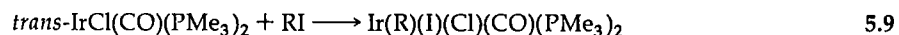
The same product ratio from two different routes suggests that an equilibrium is attained between the two octahedral isomers leading to an equilibrium distribution. Thus the addition may be stereospecific (lead to a specific isomer) although a mixture is observed.³ A solvent dependence of the stereochemical course of oxidative-addition of hydrogen halides to *trans*-IrL₂(CO)X (L = phosphine) has been observed.⁷ In methanol, water, or acetonitrile mixtures of isomers are obtained (as in reactions 5.6 and 5.7); in benzene or chloroform the addition leads exclusively to the *cis* isomer.



In polar solvents free halide may be present to exchange with the square planar complex *trans*-Ir(CO)L₂X or with the six-coordinate complex IrL₂(CO)X₂(H).⁷

Oxidative-additions to five-coordinate 18-electron complexes differ in some respects from the square planar examples above. The reaction is accompanied by ligand loss such that the product of the addition has 18 electrons. The reaction leads to a *cis* stereochemistry, even for addition of polar molecules such as CH_3I and HCl .³

Enthalpy changes for oxidative-addition to Ir(I) have been evaluated by calorimetric methods (Table 5.1).⁸



$\text{R} = \text{I, H, CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, \text{etc.}$

TABLE 5.1

Enthalpy Changes for Oxidative-Addition of RI to $\text{Trans-IrCl(CO)(PMe}_3)_2$ in 1,2-dichloroethane.

RI	ΔH
I_2	$-185. \pm 7.$
HI	$-160. \pm 3.$
MeI	$-117. \pm 7.$
EtI	$-110. \pm 3.$
PrI	$-103. \pm 4.$
$i\text{-PrI}$	$-88. \pm 10.$
$\text{C}_6\text{H}_5\text{CH}_2\text{I}$	$-95. \pm 7.$
$\text{CH}_3\text{C(O)I}$	$-125. \pm 4.$
$\text{C}_6\text{H}_5\text{C(O)I}$	$-121. \pm 3.$

The enthalpy changes listed have a number of implications for bonding and reactions, but for the purposes of our discussion the stronger bond of R to Ir leads to a larger enthalpy for the reaction.⁸ In the reaction with iridium each addition has a favorable enthalpy.

Kinetic Studies

Many kinetic studies have been accomplished on Ir(I) complexes, trans-IrX(CO)L_2 .⁹ The oxidative-addition reactions generally exhibit second order kinetics, their rates dependent on the concentration of the metal complex and on the adding molecule.

$$\text{rate} = k[\text{Ir}][\text{YZ}] \quad 5.10$$

TABLE 5.2

Rates and Activation Parameters for Reaction of $\text{IrX(CO)(PPh}_3)_2$ with H_2 or CH_3I at 30°C in Benzene.⁹

X	YZ	$k(\text{M}^{-1}\text{s}^{-1})$	$\Delta H^\ddagger(\text{kcal/mole})$	$\Delta S^\ddagger(\text{eu})$
Cl	H_2	0.93	10.8	-23
Br	H_2	14.3	12.0	-14
I	H_2	$>10^2$	—	—
Cl	CH_3I	3.9×10^{-3}	5.6	-51
Br	CH_3I	1.8×10^{-3}	7.6	-46
I	CH_3I	1.05×10^{-3}	8.8	-43

Data collected for $\text{IrX(CO)(PPh}_3)_2$ show the dependence of X and YZ (Table 5.2).⁹ The rate of oxidative-addition depends on the X group to a small extent and to the adding molecule quite significantly.⁹ The data in Table 5.2 indicate basic differences for oxidative-addition of H_2 and CH_3I to $\text{IrX(CO)(PPh}_3)_2$. For H_2 the reactivity changes with X as $\text{Cl} < \text{Br} < \text{I}$, but for CH_3I the order of reactivity is reversed.⁹ This difference is shown in both rates and activation parameters. For H_2 addition the enthalpy and entropy of activation are larger than for CH_3I . In both cases the negative entropies of activation are consistent with the second order nature of the reaction. The dependence of the oxidative-addition on the phosphine ligand has been examined. The results are shown in Tables 5.3 and 5.4.¹⁰ The rate of addition of CH_3I is shown to be

TABLE 5.3

Reaction of IrCl(CO)L_2 with CH_3I at 25°C .

L	$k(\text{M}^{-1}\text{s}^{-1})$	$\Delta H^\ddagger(\text{kcal/mole})$	$\Delta S^\ddagger(\text{eu})$
PPh_3	$3.3 \pm 0.1 \times 10^{-3}$	7.0	-47
PEtPh_2	$1.2 \pm 0.1 \times 10^{-2}$	9.8	-34
PEt_2Ph	$1.4 \pm 0.1 \times 10^{-2}$	9.9	-34
$\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3$	$3.3 \pm 0.2 \times 10^{-2}$	13.8	-20
$\text{P}(p\text{-C}_6\text{H}_5\text{F})_3$	$1.5 \pm 0.2 \times 10^{-4}$	17.0	-20
$\text{P}(p\text{-C}_6\text{H}_5\text{Cl})_3$	$3.7 \pm 0.1 \times 10^{-5}$	14.9	-28

TABLE 5.4

Second Order Rate Constants for Reaction of *Trans*-IrCl(CO)[P(*p*-C₆H₄Y)₃]₂ with H₂ at 30°C.

Y	$k(\times 10 M^{-1}s^{-1})$	$\Delta H^\ddagger(\text{kcal/mole})$	$\Delta S^\ddagger(\text{eu})$
OCH ₃	6.6	6.0	-39
CH ₃	5.3	4.3	-45
H	9.3	10.8	-23
F	2.5	11.6	-22
Cl	1.6	9.8	-28

quite dependent on the ligand environment at the metal center, but the rate of hydrogen addition is relatively insensitive to the ligand environment. For CH₃I addition the rate is enhanced by electron-donating ligands. The electron donation would increase the nucleophilicity of the iridium. Thus the importance of the nucleophilicity of the metal center is indicated for oxidative-addition of CH₃I. Steric effects may also be important, but they are difficult to separate from electronic effects. Plotting log *k* against the Ham-

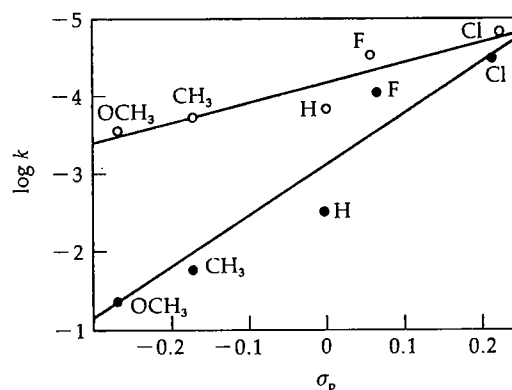
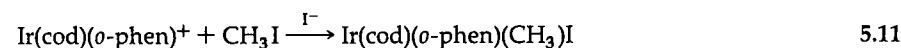


FIGURE 5.2. Plots of the rate constant for oxidative-addition of CH₃I (solid circle) and C₆H₅CH₂Cl (open circles) versus the basicity of the metal as measured by the Hammett constants for the substituents on the phosphines of *trans*-IrCl(CO)[P(*p*-C₆H₄Y)₃]₂. [Reprinted with permission from R. Ugo, A. Pasini, A. Fusi, and S. Cenini, *J. Am. Chem. Soc.* **94**, 7364 (1972). Copyright 1972 American Chemical Society.]

mett constant for the *para* substituents of the phosphine gives a straight line showing a direct relation between the basicity of the metal and the rate of reaction (Figure 5.2).¹⁰ The effect of both size and basicity of the ligand on oxidative-additions at IrL₂Cl(CO) for L = PMe₂Ph, PMe₂(*o*-MeOC₆H₄), PMe₂(*p*-MeOC₆H₄), P(*t*-Bu)Me₂, P(*t*-Bu)Et₂, and P(*t*-Bu)₂Me shows that increasing the basicity of the ligand increases the rate of reaction.¹¹ Increasing the size of the ligand greatly reduces the tendency for oxidative-addition.¹²

The effect of added iodide on the addition of CH₃I to the iridium complex [Ir(cod)(*o*-phen)]Cl was investigated.¹³



Catalytic amounts of I⁻ increase the rate of reaction. This is shown in Figure 5.3 for different concentrations of iodide. These data could be fit to the rate law

$$\text{rate} = \left(\frac{k_1 + k_2 K_s [\text{I}^-]}{1 + K_s [\text{I}^-]} \right) [\text{CH}_3\text{I}] [\text{Ir(cod)(o-phen)}^+] \quad 5.12$$

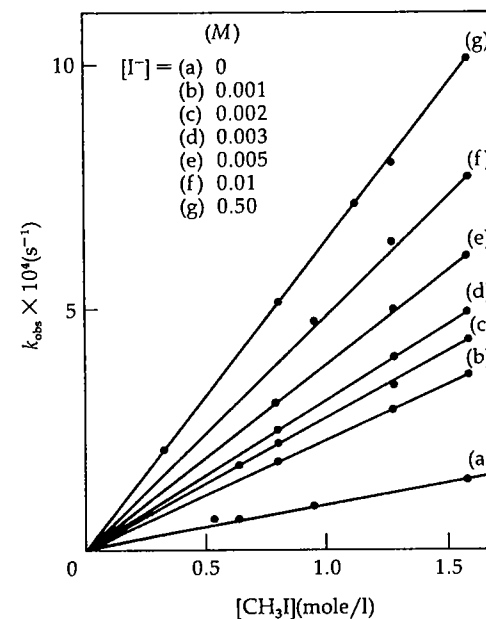


FIGURE 5.3. The effect of added I⁻ on the rate of CH₃I addition to (cod)Ir(*o*-phenanthroline)⁺. [Reprinted with permission from D. J. A. de Waal, T. I. A. Gerber, and W. J. Louw, *Inorg. Chem.* **21**, 1260 (1982). Copyright 1982 American Chemical Society.]

where the constants are defined in Figure 5.4.¹³ This rate law is consistent with two separate mechanisms—electrophilic attack by the methyl group followed by coordination of the iodide, or coordination of the iodide followed by methylation. The catalysis of addition by free iodide occurs by coordination of iodide to the iridium.¹³

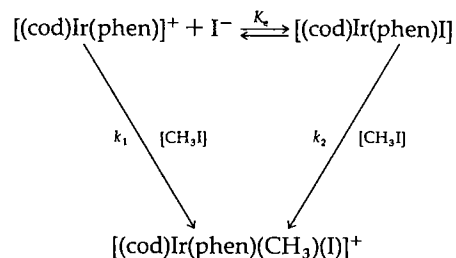
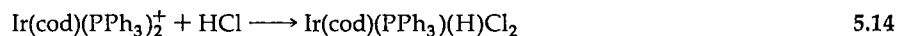


FIGURE 5.4. A scheme that explains the dependence of the rate of oxidative-addition on added I^- .

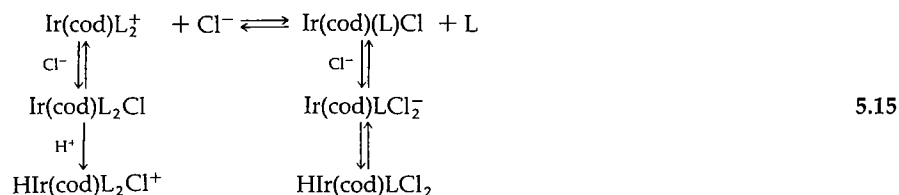
Initial attack by chloride on $\text{Ir}(\text{cod})\text{L}_2^+$ has also been suggested in oxidative-addition of HCl .¹⁴



$\text{L} = \text{PMe}_2\text{Ph}, \text{PEtPh}_2$



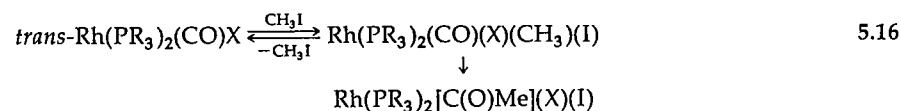
The rates of these reactions are independent of added $[\text{H}^+]$ but dependent on $[\text{Cl}^-]$. A mechanism involving initial attack of Cl^- on the complex has been suggested to account for the rate dependences and the different products.



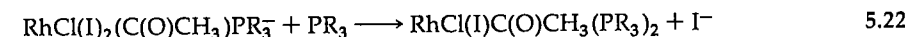
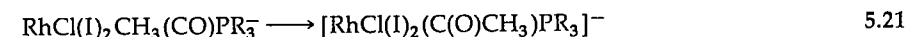
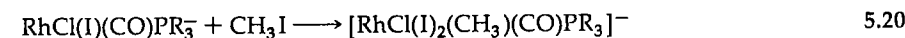
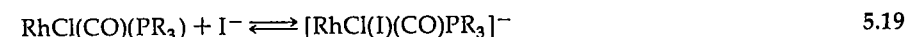
The hydride is *trans* to the chloride in the products.

The addition of free halide to square planar complexes is the expected first step in ligand substitution reactions, which occur very rapidly for $\text{Ir}(\text{I})$.¹⁴ The role of such a halide addition in oxidative-addition reactions is evidently to increase the nucleophilicity of the metal complex for subsequent protonation or methyl addition.

Reactions of the rhodium complex *trans*- $\text{Rh}(\text{PR}_3)_2(\text{CO})\text{X}$ with alkyl halides don't stop at the alkyl but continue to the acyl complex.¹⁵



The kinetics of both steps were evaluated, but our primary interest is in the first step.¹⁵ Values for the rates and equilibrium constants are shown in Table 5.5. The reversibility of the rhodium reaction indicates that the reaction is not as energetically favorable as that of iridium analogues. The rate of addition to $\text{Rh}(\text{I})$ is more strongly affected by the nature of the phosphine than that to iridium as seen by comparison of the data in Tables 5.4 and 5.5. For these rhodium complexes the addition reaction was autocatalytic; the formation of the acetyl product speeded the reaction.¹⁵ Oxidative-addition of $\text{C}_2\text{H}_5\text{I}$ or $\text{C}_4\text{H}_9\text{I}$ did not occur. An alternative proposal for the preparation of the acyl product has been offered.¹⁶



The primary evidence for the mechanism was an improvement in the fit of the complicated kinetic data.¹⁶

TABLE 5.5

Rate and Equilibrium Constants for the Addition of CH_3I to *Trans*- $\text{Rh}(\text{PR}_3)_2(\text{CO})\text{Cl}$ at 25°C .

R	$k_1 (\times 10^4 \text{s}^{-1})$	K_{eq}
Ph	5.5	0.93
<i>p</i> -MeOC ₆ H ₄	44.3	6.1
<i>p</i> -FC ₆ H ₄	1.2	0.82

Mechanisms

No single mechanism holds for all oxidative-addition reactions. Three different mechanisms (concerted addition, nucleophilic attack, and free radical) have been observed depending on the reactants and the conditions for the reaction. The data pertinent to each mechanism are considered separately.

Concerted addition is the suggested mechanism for addition of H_2 , an addition that invariably occurs *cis*. Concerted addition of H_2 can be viewed as a donation of the bonding electron density of the hydrogen molecule to the metal, a simultaneous formation of two M-H bonds while the H-H bond weakens (Figure 5.5). This mechanism is consistent with the observed kinetics, activation parameters, and stereochemistry of addition. Both the small deuterium isotope effect ($k_H/k_D = 1.22$) and calculations indicate that only a little hydrogen bond weakening occurs in the transition state.^{17,18} Only the most reactive complexes form stable adducts by oxidative-addition of hydrogen. Usually the addition of H_2 is rapid and reversible, is favored by donor ligands, is greater for iridium complexes than for rhodium analogues, and has a reactivity order $I^- > Br^- > Cl^-$.

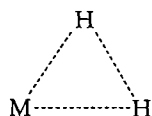


FIGURE 5.5. Concerted addition of H_2 to a square planar metal M.

Evidence for nucleophilic attack by the metal arises from studies of the oxidative-addition of alkyl halides, although not all oxidative-additions of alkyl halides proceed by nucleophilic attack. The definitive evidence comes from the inversion of configuration at the carbon attached to the metal.⁵ Inversion has been demonstrated for addition of alkyl halides to a number of complexes; several examples are shown in Figure 5.6.⁵ Utilization of a sequence of reactions in which the stereochemistry was known for every reaction except the oxidative-addition led to the definition of stereochemistry at the carbon in additions to palladium. The oxidative-addition of a benzyl halide, $Ph(R)HCX$, to PdL_3 or PdL_4 was followed by carbonylation to the acyl (which, as discussed in Chapter 4, proceeds by retention of configuration) and decomposition by CH_3OH to the ester (which occurs with retention of configuration).⁵ Since the absolute configuration and the purity of the alkyl halides and the ester products could be determined from their optical rotations, the stereochemistry of the oxidative-addition reaction could be determined. The reactions are shown in Figure 5.7 and Table 5.6.⁵ These oxida-

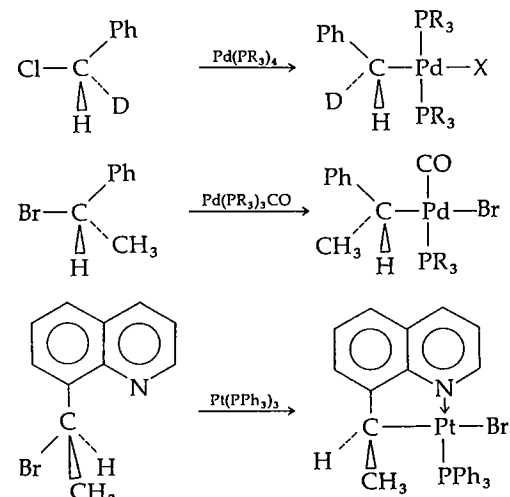


FIGURE 5.6. Examples of oxidative-addition that proceed with inversion of configuration at carbon.

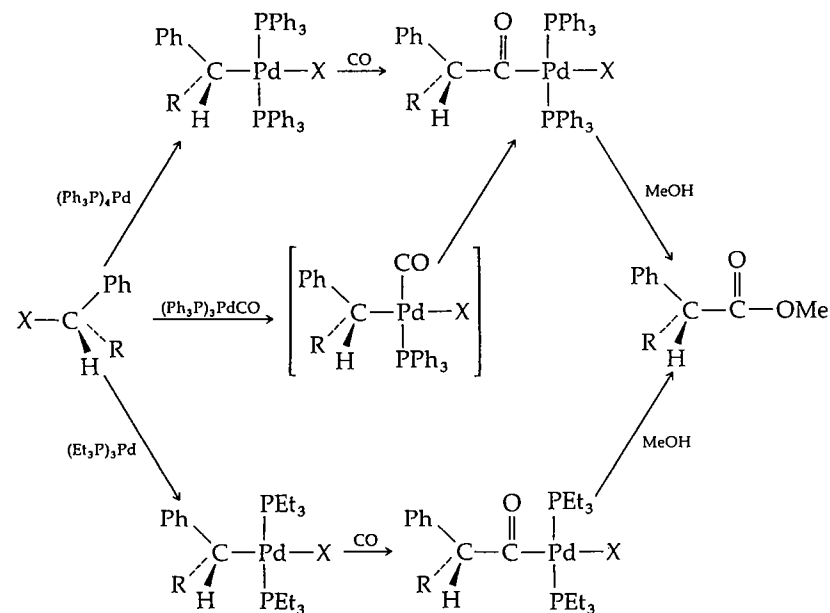


FIGURE 5.7. Scheme used to determine the stereochemistry at carbon for oxidative-addition to palladium complexes. [Reprinted with permission from J. K. Stille and K. S. Y. Lau, *Acct. Chem. Res.* 10, 434 (1977). Copyright 1977 American Chemical Society.]

TABLE 5.6

Stereochemistry for the Oxidative-Addition of Benzyl Halides, Ph(R)HCX, to Pd(0) Complexes.

Pd(0) complex	R	X	net inversion	relative rate
Pd(PEt ₃) ₃	D	Br	30	10 ³
	D	Cl	72	5 × 10 ²
Pd(PPh ₃) ₄	D	Cl	74	3
Pd(PPh ₃) ₄ ^a	D	Cl	100	
Pd(CO)(PPh ₃) ₃	D	Cl	100	2
Pd(PPh ₃) ₄	CH ₃	Br	90	1.5
Pd(PPh ₃) ₃ (CO)	CH ₃	Br	90	1
Pd(PPh ₃) ₄	CF ₃	Cl	<10	very slow

^a Under CO.

tive-additions proceed with predominant inversion of configuration, in some cases with 100% net inversion.⁵ This is consistent with S_N² (nucleophilic) attack at the carbon by the metal, with inversion just as observed in organic reactions that occur by nucleophilic attack at carbon. The reactivity towards RX is also consistent with nucleophilic attack.

R = CH₃ > CH₃CH₂ > secondary > cyclohexyl > adamantyl

X = I > tosylate ≈ Br > Cl

This order was determined for the reaction of the rhodium complex shown in Figure 5.8.^{19,20} The transition state for nucleophilic attack is shown in Figure 5.9. The reactions presumably go through an ionic complex, [RM]⁺X⁻, which

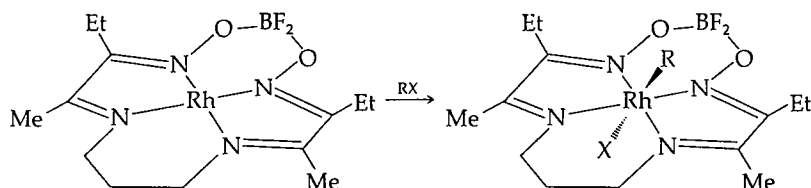


FIGURE 5.8. Reaction used to determine the dependence of rate on the nucleophilicity of R. [Reprinted with permission from J. K. Stille and K. S. Y. Lau, *Acct. Chem. Res.* 10, 438 (1977). Copyright 1977 American Chemical Society.]

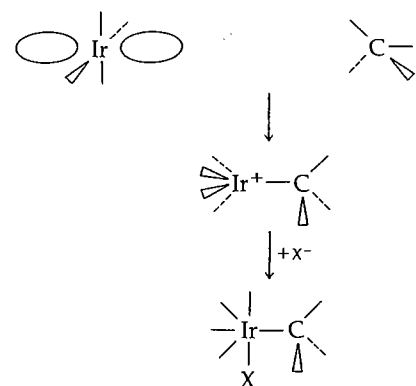


FIGURE 5.9. Nucleophilic attack on carbon by an iridium complex.

can be isolated in some cases before the final product formation. The product is often of *trans* stereochemistry, but it may be *cis*.

Alkyl halides that do not readily undergo nucleophilic attack often add to a metal by radical mechanisms.²¹⁻²⁵ The characteristics associated with a radical mechanism are loss of stereochemistry, nonreproducible rates, inhibition by radical inhibitors, and acceleration by O₂ or light. Radical reactions have been observed in a number of cases. Reactions of IrCl(CO)(PMe₃)₂ showed radical characteristics and the following scheme involving a radical chain process has been suggested:^{18,19}



Reactions of methyl, benzyl, allyl halides, and α-haloethers showed no indications of radical behavior, but other saturated alkyl halides, vinyl and aryl halides, and α-haloesters showed characteristics consistent with a radical chain pathway in reaction with IrCl(CO)(PMe₃)₂.²²⁻²⁴ The phosphine ligand is very important in radical reactions as shown in Table 5.7.²⁴ A *non-chain* radical mechanism was proposed for addition of alkyl halides to Pt(PPh₃)₂. The first step was abstraction of the halide from RX.^{26,27}



The mechanism outlined in equations 5.25 and 5.26 was based on spin trapping experiments and the observation of Pt(PPh₃)₂X₂ in solvents where hydrogen abstraction by R· can occur.^{26,27} A mechanism to accommodate both nucleophilic attack and radical paths was proposed for oxidative-addi-

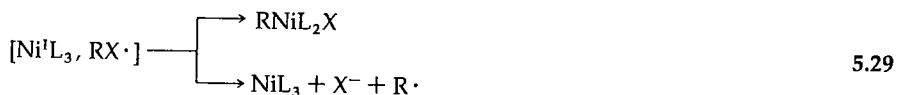
TABLE 5.7

Effect of Phosphine Ligands on Reactions of Alkyl Halides with $\text{IrCl}(\text{CO})\text{L}_2$.

L	radical reaction (% of reaction) ^a	nucleophilic attack ($M^{-1}s^{-1}$) ^b
PMe_3	100 (<30 min)	5.0×10^{-2}
PMe_2Ph	100 (5 hr)	1.6×10^{-2}
PMePh_2	10 (1 week)	3.5×10^{-3}

^a $\text{RX} = \text{PhCHFCH}_2\text{Br}$.^b $\text{RX} = \text{MeI}$.

tion to NiL_4 ($\text{L} = \text{phosphine}$).²¹ This oxidative-addition to $\text{Ni}(0)$ led to the $\text{Ni}(\text{II})$ complex, RNiL_2X , and to the paramagnetic $\text{Ni}(\text{I})$ complex, XNiL_3 , in varying yields. The following scheme was suggested:²¹



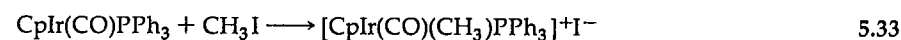
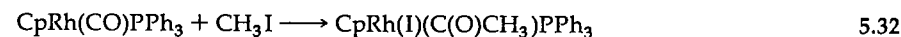
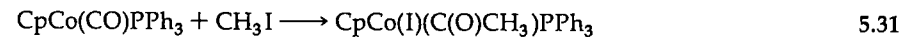
$\text{R} = \text{aryl}$; $\text{L} = \text{PEt}_3, \text{PPh}_3$

A key feature is the electron transfer from the nickel complex to the alkyl halide, forming a radical pair.

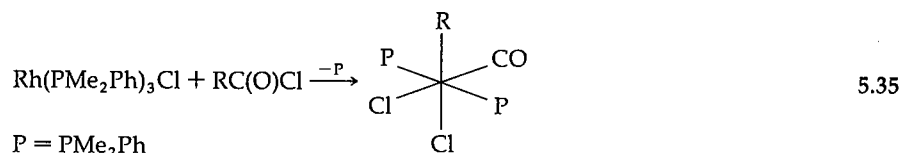
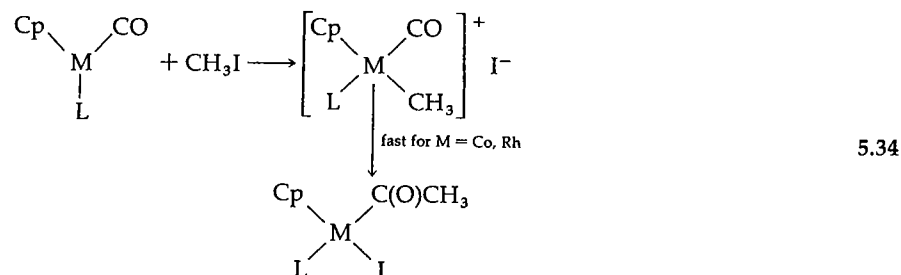
Our examples thus far have encompassed only square planar $\text{M}(\text{I})$ complexes ($\text{M} = \text{Rh}$ and Ir) and $\text{M}(0)$ complexes of nickel, palladium, and platinum. In this section we shall examine other examples that reemphasize the mechanistic features. Oxidative-additions of a number of organic halides to Cp_2ZrL_2 ($\text{L} = \text{PMe}_2\text{Ph}$ or PMePh_2) were shown to proceed by a radical chain process.^{28,29}



The mechanistic interpretation was based on characterization of the products and on an ESR investigation during the course of the reaction, which allowed the intermediate $\text{Cp}_2\text{Zr}^{\text{III}}\text{X}(\text{PPh}_2\text{Me})$, a metal centered radical, to be identified.^{28,29} Oxidative-addition to the complexes, $\text{CpML}(\text{CO})$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) were investigated. Depending on the metal, different products are observed.³⁰



Each reaction is oxidative-addition to an 18-electron complex, and the product in each case contains 18 electrons. The reaction is first order in CH_3I and metal complex $\text{CpML}(\text{CO})$ and is dependent on the nature of L , as shown in Figure 5.10.³⁰ These reactions proceed by nucleophilic attack to the intermediate, $[\text{CpM}(\text{CO})(\text{CH}_3)\text{L}]^+\text{I}^-$, which for $\text{M} = \text{Ir}$ is the stable product. For $\text{M} = \text{Co}$ and Rh , methyl migration to the CO opens a coordination site for the iodide.

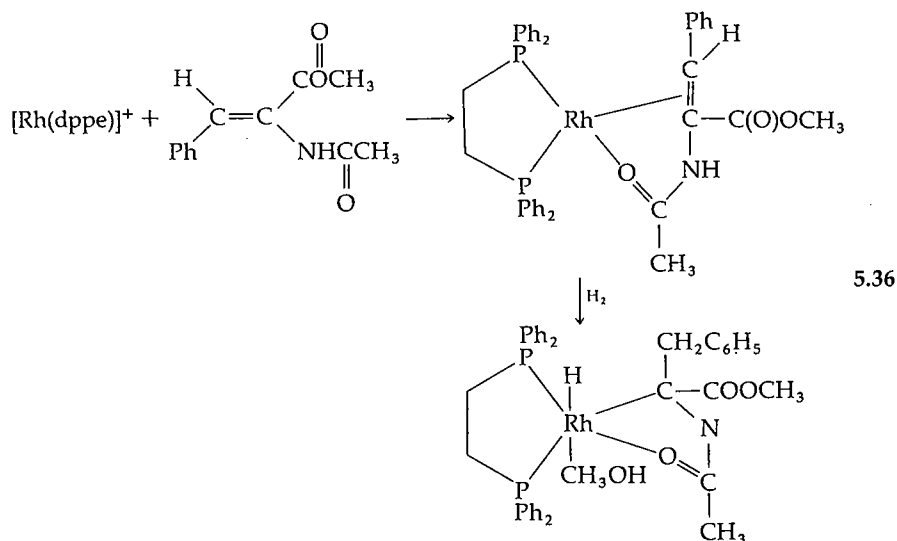


The phosphine ligand dependence as shown in Figure 5.10 represents the steric hindrance by bulky ligands to the expansion of the coordination sphere. Oxidative-addition to $\text{CpML}(\text{CO})$ was followed by acyl formation (reaction 5.34); oxidative-addition may also be followed by a decarbonylation as shown for the rhodium complex $\text{Rh}(\text{PMe}_2\text{Ph})_3\text{Cl}$.³¹

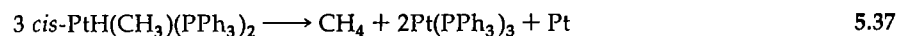
REDUCTIVE-ELIMINATION

Reductive-elimination has not been studied as thoroughly as oxidative-addition. A number of complexes undergo oxidative-addition leading to stable complexes, but only a few reductive-elimination reactions proceed from

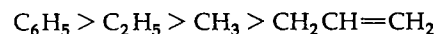
stable starting materials to stable products.^{32,33} Thus there are few systems in which reductive-elimination can be studied. Reductive-elimination is equally as important in catalytic cycles as oxidative-addition although the reductive-elimination reactions appear to be very rapid in most catalytic cycles. In only one case has an alkyl hydride been isolated from a catalytic cycle.³⁴



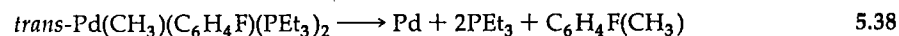
The product was characterized at low temperature by spectroscopic measurements. At room temperature the reductive-elimination occurred too rapidly for the alkyl hydride to be observed.³⁴ This is often the case as shown for elimination of CH_4 from $\text{cis-PtH}(\text{CH}_3)(\text{PPh}_3)_2$, which could be prepared at low temperature but reductively eliminated CH_4 at -25°C .³⁵



The use of other alkyl complexes showed the following qualitative order of reactivity:³⁵



Reductive-elimination of fluorotoluene from the fluorophenyl methyl palladium complexes has been observed.³⁶



This reaction was investigated for both *meta*- and *para*-fluorobenzenes and appeared to involve a *cis-trans* isomerization prior to the reductive-elimina-

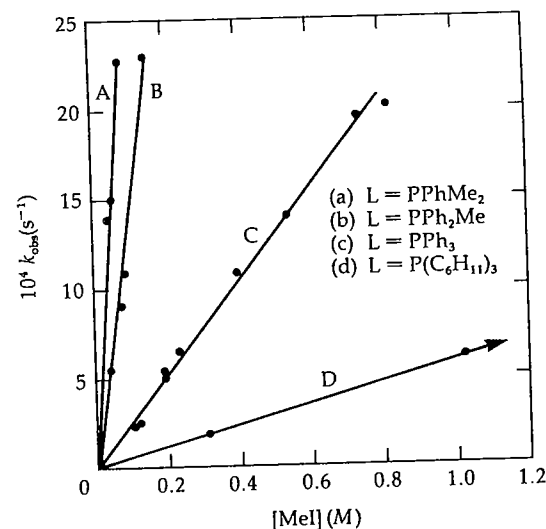
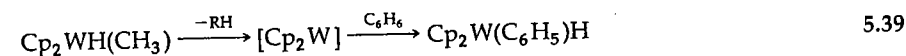
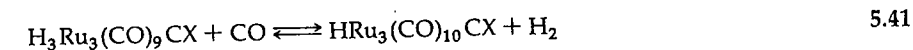
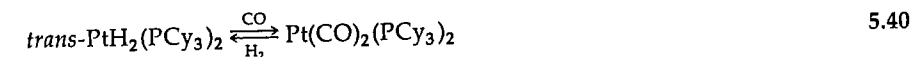


FIGURE 5.10. The dependence of the rate of CH_3I addition on the size of the phosphine ligand on $\text{CpCo}(\text{CO})\text{L}$. [Reprinted with permission from A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.* 9, 2658 (1970). Copyright 1970 American Chemical Society.]

tion.³⁴ A set of complexes that have some potential for mechanistic investigations are $\text{Cp}_2\text{WR}(\text{H})$, which are stable at ambient conditions but reductively eliminate RH on warming to 70°C .³⁷



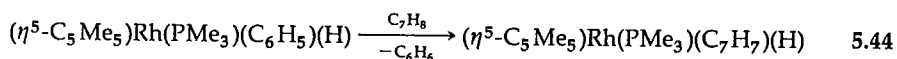
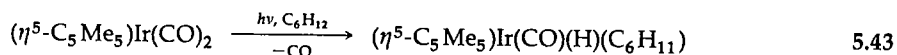
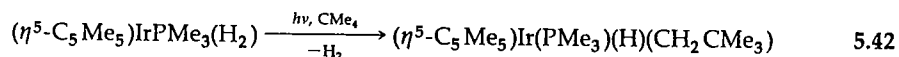
Since several complexes can be prepared, the relative reactivities could be investigated. Reductive-elimination can be induced by the addition of a nucleophile, sometimes a very weak nucleophile. The following examples show both mononuclear and cluster examples in which the elimination is reversible.^{38,39}



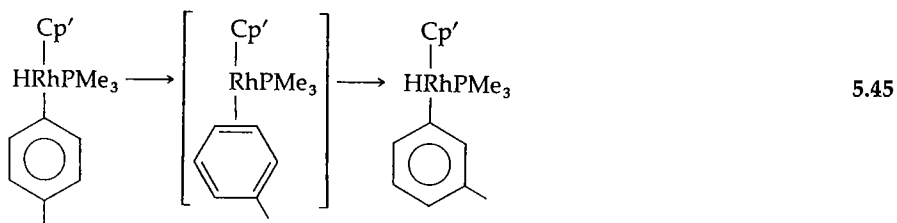
In both examples the hydride complex is thermally stable toward reductive-elimination, but the presence of CO induces the elimination. The ability of such a weak nucleophile as CO to induce reductive-elimination and the facile

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addition to and elimination from Cp_2W may indicate that these reductive-eliminations proceed through a preequilibrium in which the metal complex and RH are distinct but held together, perhaps by the solvent cage or by interaction of a C-H or H-H bond with the metal. This would account for the elimination induced by CO and would also be consistent with reaction 5.39. This interpretation of the reductive-elimination of R-H requires that addition of a R-H bond to an electron-deficient metal complex occur readily. Such activation of C-H bonds has been the subject of considerable investigation that has recently come to fruition.⁴⁰⁻⁴³ Activation of C-H bonds has been successful in several different systems. The 16-electron species $(\eta^5\text{-C}_5\text{Me}_5)\text{ML}$ ($\text{M} = \text{Rh}, \text{Ir}; \text{L} = \text{CO}, \text{PMe}_3$) add saturated C-H bonds as shown below.⁴¹⁻⁴³

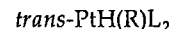
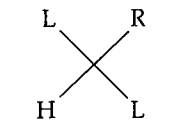


Isomerization studies on $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(\text{C}_7\text{H}_7)(\text{H})$ indicate that the site of attachment of the aryl group may change without loss of the arene from the coordination sphere.⁴³

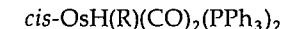
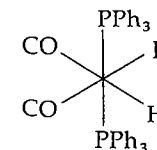


It has been suggested that facile oxidative-addition and reductive-elimination of arene C-H bonds occur in the rhodium system (equations 5.44 and 5.45) at low temperature while higher temperatures are required to remove the arene from the coordination sphere.⁴³ The ready activation of C-H bonds when an unsaturated metal center is available is consistent with a preequilibrium as suggested for reactions 5.40 and 5.41.

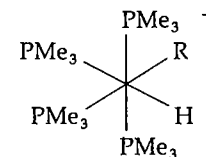
Reductive-elimination is usually very rapid in catalytic cycles. It has been observed stoichiometrically as in the examples above, but a number of complexes have been prepared that do not undergo reductive-elimination. A few examples are shown below.⁴⁴⁻⁴⁶



$\text{R} = \text{Ph}, \text{Me}; \text{L} = \text{phosphine}$



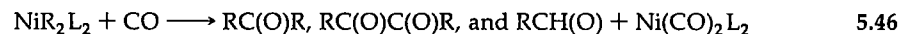
$\text{R} = \text{CH}_3\text{C(O)}, \text{CH}_3, \text{CH}_2\text{OH}$



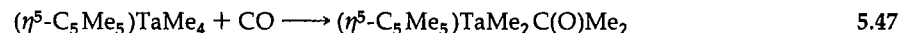
$\text{R} = \text{CH(O)}, \text{C(O)OCH}_3, \text{CH}_3, \text{CH}_2\text{OH}$

The question of why one complex readily reductively eliminates while another doesn't has not been fully answered.

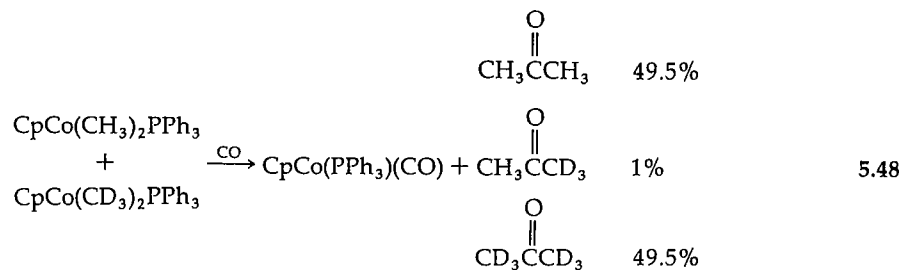
Several polyalkyl complexes that do not eliminate alkanes *do* eliminate ketones in the presence of CO. The nickel complexes NiR_2L_2 have been investigated extensively.⁴⁷



The exact products depend on the temperature, the nature of L, and the R group.⁴⁷ Coordinated acetone is also formed by carbonylation of $(\eta^5\text{-C}_5\text{Me}_5)\text{TaMe}_4$.⁴⁸

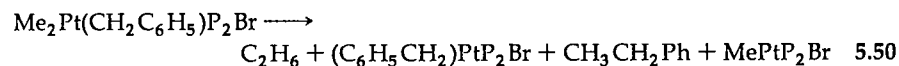
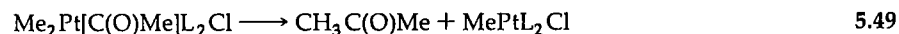


Further reaction of the coordinated acetone was observed, but it is apparently not related to the question of why $\text{CH}_3\text{C(O)CH}_3$ can form the carbon-carbon bond when CH_3CH_3 cannot. The elimination of acetone has also been observed when $\text{CpCo(Me)}_2\text{PPh}_3$ reacts with CO.⁴⁹



That this reaction is intramolecular (occurring on one metal center) is shown by the use of a 1 : 1 mixture of $\text{CpCo}(\text{CH}_3)_2\text{PPh}_3$ and $\text{CpCo}(\text{CD}_3)_2\text{PPh}_3$.⁴⁹

Studies of the pyrolysis of $\text{R}_2\text{R}'\text{PtL}_2\text{X}$ complexes (L = phosphine and X = halogen) have shown that acetone is eliminated in preference to ethane,



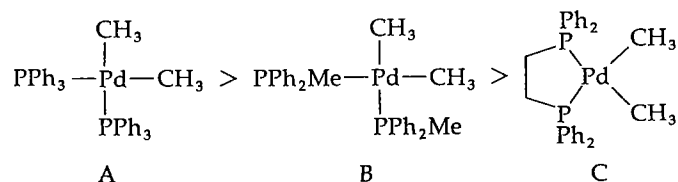
that ethane is slightly preferred over ethylbenzene, that toluene is eliminated in preference to biphenyl,



and that ethane is eliminated in preference to CH_3CF_3 ($\text{L} = \text{AsMe}_2\text{Ph}$, $\text{P} = \text{PMe}_2\text{Ph}$, $\text{Y} = \text{CNC}_6\text{H}_4\text{CH}_3$).⁵⁰⁻⁵² The nature of the pyrolysis prevents an assessment of whether kinetic or thermodynamic factors are responsible for these selectivities.

Mechanistic Investigations

Reductive-elimination was studied from the series of dimethyl palladium compounds shown in Figure 5.11.⁵³ The rate of reductive-elimination was evaluated by the disappearance of the $\text{Pd}-\text{CH}_3$ NMR resonance. The data shown in Figure 5.12 indicate that these reactions were first order in dimethyl palladium. Only *cis* complexes could undergo reductive-elimination directly; elimination of ethane from *trans* complexes was preceded by isomerization.⁵³ A polar solvent aided the reductive-elimination by stabilizing the *cis* complex, by aiding the isomerization of a *trans* complex, and by stabilizing the reduced coordination species that is formed. The rates of reductive-elimination of ethane from the three complexes shown below parallel the rates of dissociation of the phosphine.



The quantitative data are shown in Table 5.8.⁵³ The electronic and steric interactions should be very similar in B and C, but C is stabilized by the chelate effect. The presence of added phosphine inhibits the reductive-elimination

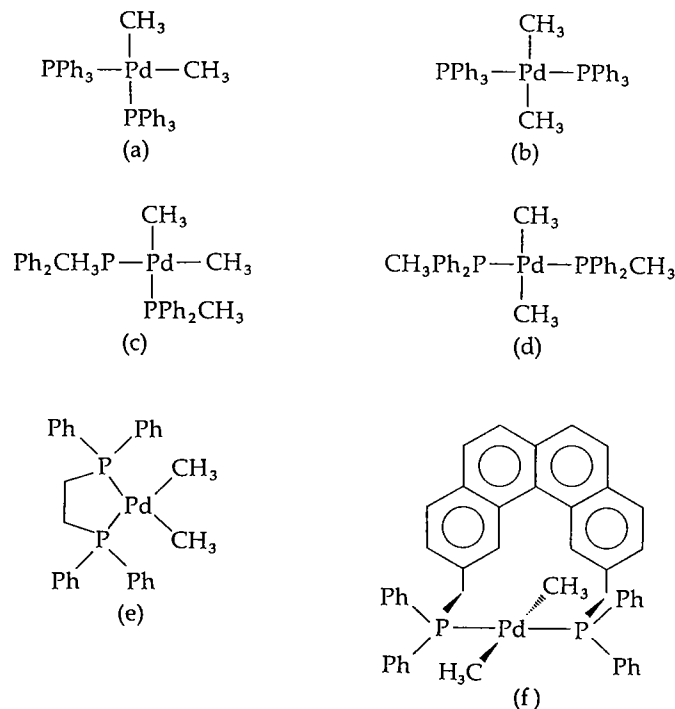
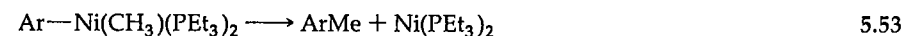


FIGURE 5.11. Dimethyl palladium complexes that were investigated for reductive-elimination. [Reprinted with permission from A. Gillie and J. K. Stille, *J. Am. Chem. Soc.* 102, 4933 (1980). Copyright 1980 American Chemical Society.]

nation from A and B. Thus phosphine dissociation appears to be important to the rate of reductive-elimination. A coordination site is not necessary for reductive-elimination, but evidently the phosphines, which are good sigma donors and enhance oxidative addition, inhibit the reductive-elimination. The complex in which the methyl groups are constrained *trans* (Figure 5.11f) does not undergo reductive-elimination at 100°C. These organopalladium complexes undergo reductive-elimination with retention of configuration at the carbon, suggesting a concerted process for the carbon-carbon bond forming step.⁵⁴

Investigations of the reductive-elimination of methylarenes from nickel complexes show evidence for two mechanisms, a concerted process and a radical chain process.⁵⁵



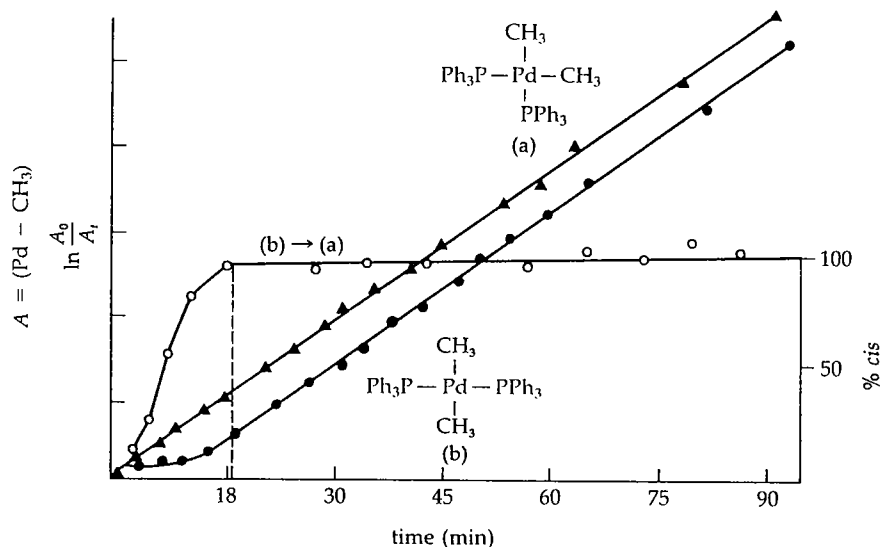


FIGURE 5.12. Reductive-elimination of ethane from dimethyl palladium complexes. [Reprinted with permission from A. Gillie and J. K. Stille, *J. Am. Chem. Soc.* 102, 4933 (1980). Copyright 1980 American Chemical Society.]

The reaction was first order in nickel complex and showed an inverse dependence on the concentration of PEt_3 .⁵⁵ These data, which are shown in Figure 5.13, suggest a concerted elimination from $\text{Ni}(\text{Ar})(\text{CH}_3)\text{PEt}_3$. In the presence of an arylhalide the kinetic behavior showed an induction period (Figure 5.14) and aryl group scrambling suggestive of a radical chain mechanism. Inhibition of the reaction was seen by radical inhibitors such as duroquinone.

TABLE 5.8

Rates of Ethane Elimination from *Cis* Palladium Complexes at 60°C.

complex	$k(\text{s}^{-1})$
A	1.04×10^{-3}
B	8.33×10^{-5}
C ^a	4.78×10^{-7}

^a At 80°C.

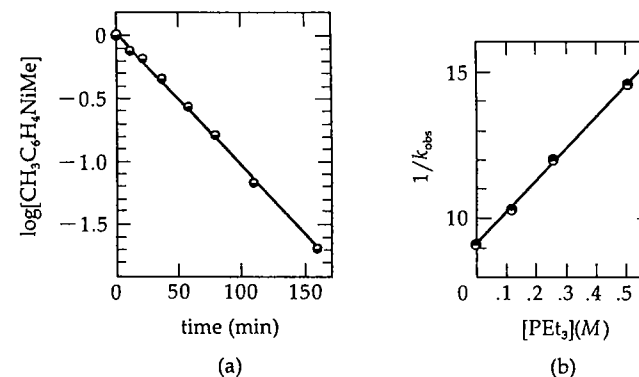
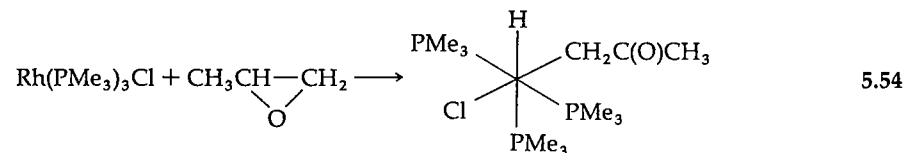


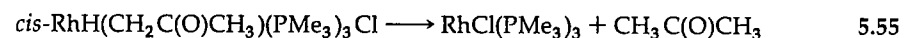
FIGURE 5.13. Rate data for the disappearance of *o*-tolyl methyl nickel(II) illustrating (a) the first order nature of the reaction, and (b) the inverse dependence of rate on phosphine concentration. [Reprinted with permission from G. Smith and J. K. Kochi, *J. Organomet. Chem.* 198, 199 (1980). Copyright 1980 Elsevier Sequoia S. A.]

Thus different mechanisms may be seen for reductive-elimination depending on the conditions, much as for oxidative-addition.

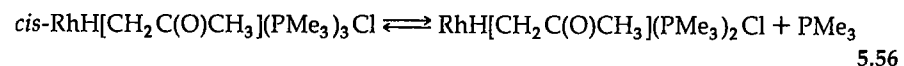
Reductive-elimination of alkanes from hydrido-alkyl complexes has not often been investigated because stereospecific synthetic procedures are not available for many of the needed complexes. The reaction of $\text{Rh}(\text{PMe}_3)_3\text{Cl}$ with propylene oxide led to one example.⁵⁶



The stereochemistry was assigned from the ^1H and ^{31}P NMR spectra. Reductive-elimination of acetone showed first order kinetics with $\Delta H^\ddagger = 25.0$ kcal/mole and $\Delta S^\ddagger = 5.3$ eu.⁵⁶



The presence of PMe_3 inhibits the reaction. Mixtures of *cis*- $\text{RhH}(\text{CH}_2\text{C}(\text{O})\text{CH}_3)(\text{PMe}_3)_3\text{Cl}$ and *cis*- $\text{RhD}(\text{CD}_2\text{C}(\text{O})\text{CD}_3)(\text{PMe}_3)_3\text{Cl}$ led to only $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ and $\text{CD}_3\text{C}(\text{O})\text{CD}_3$ showing that the elimination was intramolecular.⁵⁶ The following scheme was suggested:



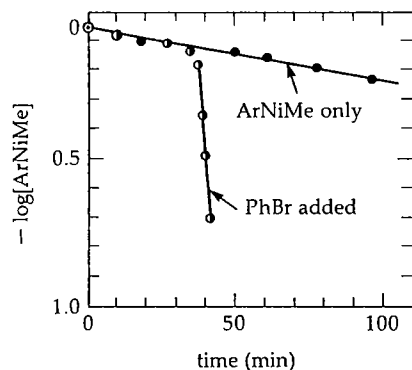
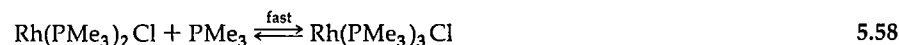
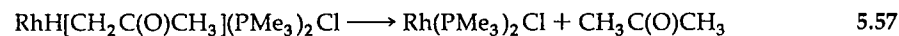


FIGURE 5.14. Graph illustrating the induction period required upon addition of C_6H_5Br . [Reprinted with permission from G. Smith and J. K. Kochi, *J. Organomet. Chem.* 198, 199 (1980). Copyright 1980 Elsevier Sequoia S. A.]

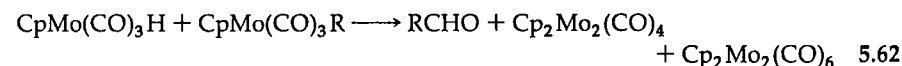
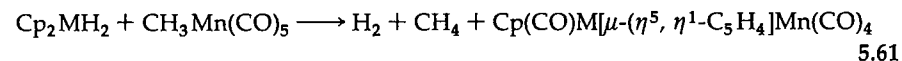


The requirement for dissociation of PMe_3 is similar to the eliminations observed from palladium.

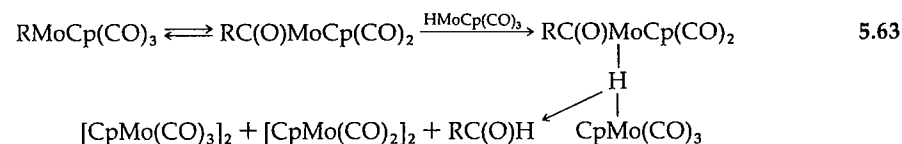
In a number of cases binuclear reductive-elimination, in which two metal centers participate in the reaction, has been observed. The decomposition of hydrido carbonyls is an example of this type of reductive-elimination.^{57,58}



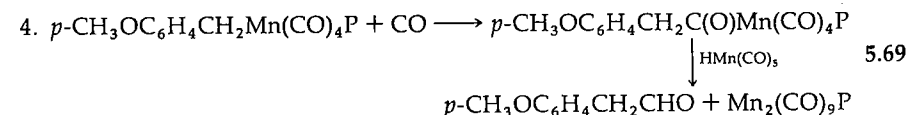
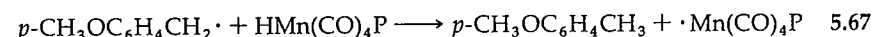
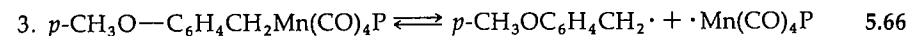
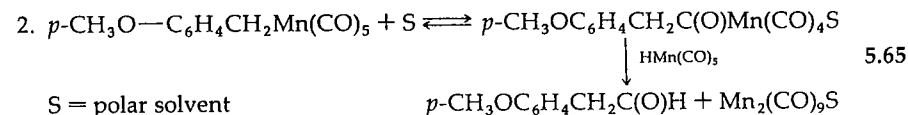
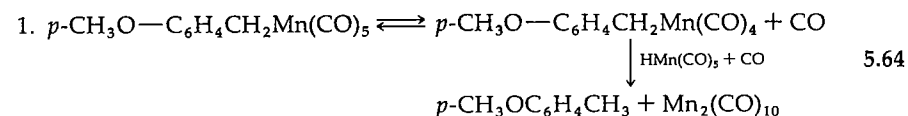
In other cases binuclear reductive-elimination of alkanes has been observed.^{59,60}



The mechanism for the latter reaction was suggested to be



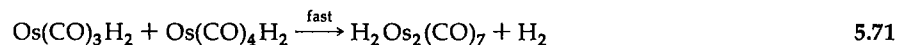
The sequence is an alkyl migration that opens a coordination site for the bridging hydride, reductive-elimination of aldehyde, and the combination of metal carbonyl fragments to give the products, which have a metal single and triple bond, $Cp_2Mo_2(CO)_6$ and $Cp_2Mo_2(CO)_4$. This reaction bears some similarity to hydroformylation, which we shall discuss in the next chapter. The reaction of $cis-RMn(CO)_4L$ and $cis-HMn(CO)_4L$, where R = benzoyl derivatives and $L = CO$ or $P(p-CH_3OC_6H_4)_3$, has been investigated.⁶¹ Four distinct pathways have been identified for this binuclear reductive-elimination:



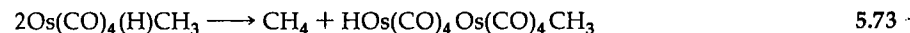
The relatively minor changes involved in the completely different mechanisms for binuclear reductive-eliminations from these manganese systems suggest that great care must be exercised in interpreting and generalizing from a specific set of experiments.

The binuclear reductive-elimination reactions considered in the paragraph above were obviously binuclear since the two groups that reductively eliminate are on different metal centers. A fascinating set of experiments on $cis-Os(CO)_4RR'$ have shown that formation of RR' also occurs by binuclear elimination.⁶² For $R = R' = CH_3$ the elimination does not occur; above $160^\circ C$ decomposition to CH_4 , $(CH_3)_2C(O)$, and unidentified osmium complexes is observed. For $R = R' = H$ the elimination to H_2 and $H_2Os_2(CO)_8$, which occurs at $126^\circ C$, was indicated as a binuclear reaction with the following mechanistic scheme:⁶²

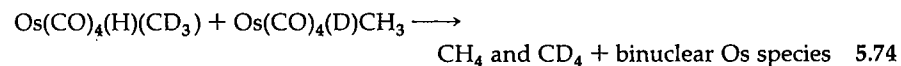
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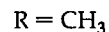
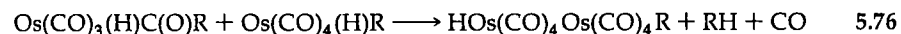
Elimination of methane from $\text{Os}(\text{CO})_4(\text{H})\text{CH}_3$ is more facile, occurring at 49°C .



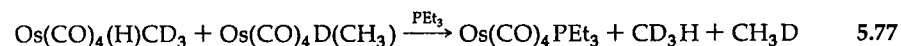
Labeling experiments confirmed the binuclear nature of the reaction.⁶²



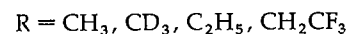
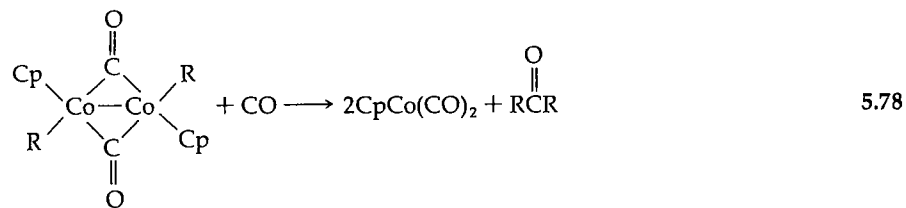
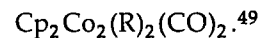
Since no scrambling of label in methane occurs under the reaction conditions, the products CH_4 and CD_4 could only arise from binuclear elimination. An initial methyl migration was suggested to open a coordination site.



It has been suggested that in order for dinuclear elimination to occur one of the eliminating groups must be a hydride and the other complex must be able to open a coordination site for a bridging hydride. In the presence of an entering nucleophile such as PEt_3 , the elimination of CH_4 is mononuclear.⁶²

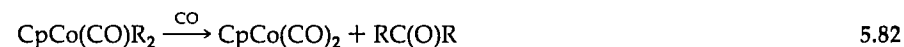
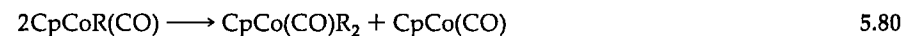


Elimination from a dimeric complex has been examined on



Use of a 1 : 1 mixture of $\text{Cp}_2\text{Co}_2(\text{Me})_2(\text{CO})_2$ and $\text{Cp}_2\text{Co}_2(\text{Et})_2(\text{CO})_2$ in reac-

tion with CO led to a statistical distribution of $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, $\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5$, and $\text{C}_2\text{H}_5\text{C}(\text{O})\text{C}_2\text{H}_5$, showing intermolecular reductive-elimination.⁴⁹ The following scheme was suggested for reductive-elimination of ketone from these dimeric complexes:

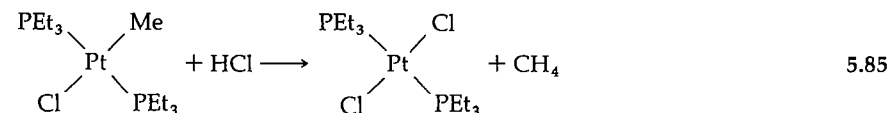
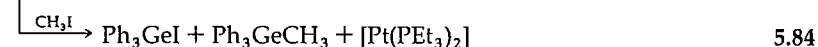
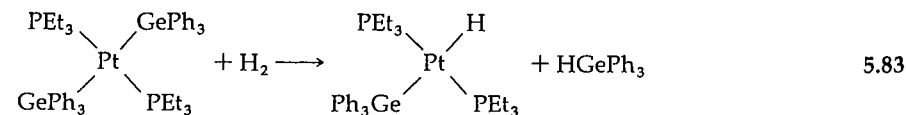


The monomeric unit, $\text{CpCoR}(\text{CO})$, also reacted with CO to give the acyl, $\text{CpCoC}(\text{O})\text{R}(\text{CO})$, which could dimerize to *cis* and *trans* $\text{Cp}_2\text{Co}_2(\text{CO})_2[\text{C}(\text{O})\text{R}]_2$ or could react with $\text{CpCoR}(\text{CO})$ to give ketone.⁴⁹ In this case, although the reaction begins with a dimer, the first step is break down to monomer with methyl transfer followed by reductive-elimination from a single metal center.

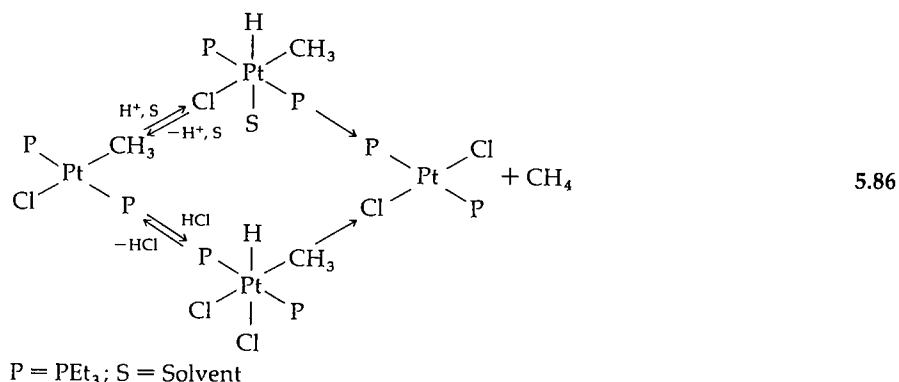
We have seen that reductive-elimination, like oxidative-addition, can occur via several mechanisms as expected from microscopic reversibility. The specific circumstances (solvent, reactants, additives, and so on) determine which mechanism functions in an elimination. Substantially more information is required for a complete understanding of reductive-elimination.

OXIDATIVE-ADDITION AND REDUCTIVE-ELIMINATION

In many cases reductive-elimination and oxidative-addition occur in concert. Examples are shown below.^{63,64}

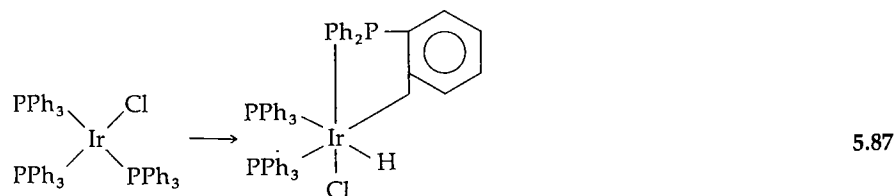


The kinetics of reaction 5.85 have been investigated, and the following mechanism suggested:



The oxidative-addition of H^+ (which is considered as a hydride when attached to the metal) is followed by reductive-elimination of methane.

Orthometallation is another example of an oxidative-addition that may be followed by reductive-elimination. Orthometallation can be considered as the oxidative-addition of an aryl C-H bond on a coordinated ligand to a 16-electron metal complex.



The reversibility of orthometallation was shown in reactions of $\text{HCo}(\text{N}_2)(\text{PPh}_3)_3$ with deuterium where 19 hydrogens per mole of cobalt were exchanged.⁶⁵ It was shown that the incorporation into the aryl groups occurred exclusively in the *ortho* position, and the scheme shown in Figure 5.15 was indicated.⁶⁵

The oxidative-addition and reductive-elimination of hydrogen on tri-ruthenium clusters has been reported.³⁹ This reaction is interesting because the hydrogen atoms are located on different metal atoms. The reaction is shown below:

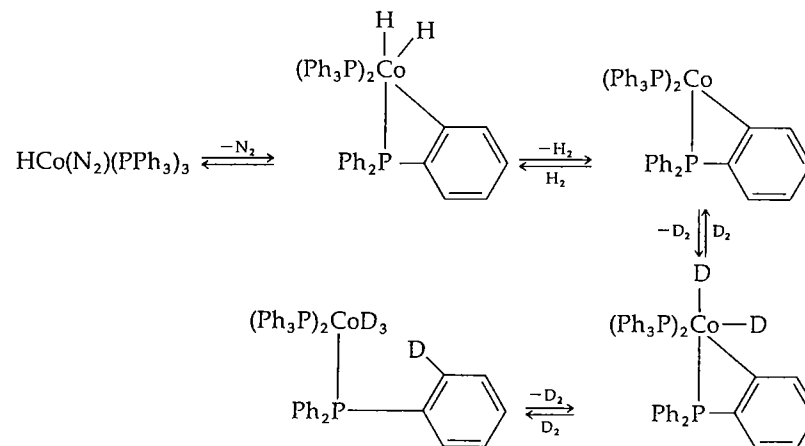
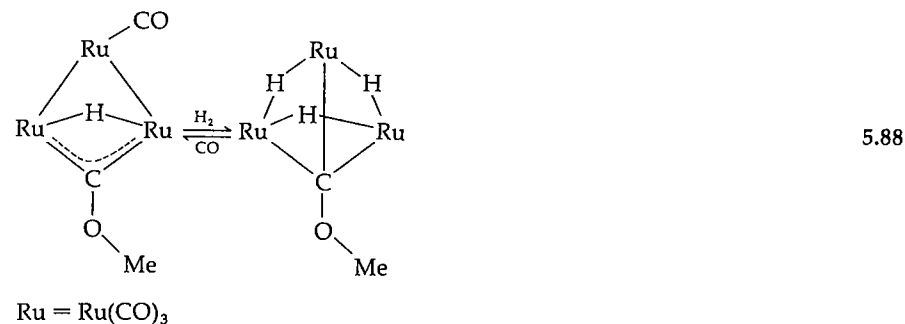
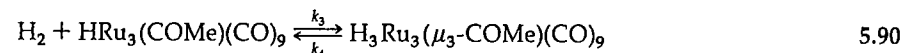
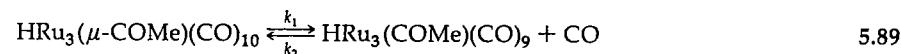


FIGURE 5.15. The oxidative-addition and reductive-eliminations via orthometallation that leads to incorporation of 19 deuteriums per mole of $\text{HCo}(\text{N}_2)(\text{PPh}_3)_3$.⁶⁵



The equilibrium constant for this reaction was 2.6. The reductive-elimination of hydrogen occurred with activation parameters $\Delta H^\ddagger = 31.0$ kcal/mole and $\Delta S^\ddagger = 8$ eu and with kinetic isotope effect (1.4) similar to that in reductive-elimination from mononuclear dihydrides. It has been suggested from this data that the reductive-elimination of H_2 from $\text{H}_3\text{Ru}_3(\mu_3\text{-COMe})(\text{CO})_9$ occurred from a single ruthenium center following a rearrangement of this fluxional molecule (see Chapter 7). The reactions were described by the following mechanism,



with both oxidative-addition and reductive-elimination occurring through a three-center transition state at a single ruthenium atom.³⁹

CONCLUSION

Oxidative-addition and reductive-elimination may proceed by different mechanisms. For reactions involving alkyl complexes, retention of stereochemistry is indicative of nucleophilic attack, and loss of stereochemistry indicates radical mechanisms. It is difficult to predict the mechanism in the absence of data for a given reaction. Oxidative-addition may lead to either *cis* or *trans* products depending on the adding molecule and the metal complex; H₂ addition always occurs *cis*. Reductive-elimination from one metal center evidently requires a *cis* geometry but may also occur from two metal centers in a binuclear process. Both oxidative-addition and reductive-elimination are very important in homogeneous catalysis, which is discussed in Chapter 6.

REFERENCES

1. L. Vaska, *Acc. Chem. Res.* **1**, 335 (1968).
2. J. Halpern, *Acc. Chem. Res.* **3**, 386 (1970).
3. J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.* **7**, 53 (1968).
4. J. P. Collman, *Acc. Chem. Res.* **1**, 136 (1968).
5. J. K. Stille and K. S. Y. Lau, *Acc. Chem. Res.* **10**, 434 (1977).
6. J. P. Collman and C. T. Sears, Jr., *Inorg. Chem.* **7**, 27 (1968).
7. D. M. Blake and M. Kubota, *Inorg. Chem.* **9**, 989 (1970).
8. G. Yoneda and D. M. Blake, *Inorg. Chem.* **20**, 67 (1981).
9. P. B. Chock and J. Halpern, *J. Am. Chem. Soc.* **88**, 3511 (1966).
10. R. Ugo, A. Pasini, A. Fusi, and S. Cenini, *J. Am. Chem. Soc.* **94**, 7364 (1972).
11. E. M. Miller and B. L. Shaw, *J. Chem. Soc. Dalton* **480** (1974).
12. B. L. Shaw and R. E. Stainbank, *J. Chem. Soc. Dalton* **223** (1972).
13. D. J. A. de Waal, T. I. A. Gerber, and W. J. Louw, *Inorg. Chem.* **21**, 1259 (1982).
14. T. V. Ashworth, J. E. Singleton, D. J. A. de Waal, W. J. Louw, E. Singleton, and E. van der Stok, *J. Chem. Soc. Dalton* **340** (1978).
15. J. C. Douek and G. Wilkinson, *J. Chem. Soc. (A)*, 2604 (1969).
16. S. Fraks, F. R. Hartley, and J. R. Chipperfield, *Inorg. Chem.* **20**, 3238 (1981).
17. J. Chatt and J. M. Davidson, *J. Chem. Soc.* **843** (1965).
18. K. Kitaura, S. Ohara, and K. Morokuma, *J. Am. Chem. Soc.* **103**, 2891 (1981).
19. J. P. Collman and M. R. MacLaury, *J. Am. Chem. Soc.* **96**, 3019 (1974).
20. J. P. Collman, D. W. Murphy, and G. Dolcetti, *J. Am. Chem. Soc.* **95**, 2687 (1973).
21. T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.* **101**, 6319 (1979).
22. J. A. Labinger and J. A. Osborn, *Inorg. Chem.* **19**, 3230 (1980).
23. J. A. Osborn in *Organotransition Metal Chemistry*, Y. Ishii and M. Tsutsui, eds. (New York: Plenum, 1975) p. 65–80.
24. J. A. Labinger, J. A. Osborn, and N. J. Coville, *Inorg. Chem.* **19**, 3236 (1980).
25. T. L. Hall, M. F. Lappert, and P. W. Lednor, *J. Chem. Soc. Dalton* **1448** (1980).
26. A. V. Kramer, J. A. Labinger, J. S. Bradley, J. A. Osborn, *J. Am. Chem. Soc.* **96**, 7145 (1974).
27. A. V. Kramer and J. A. Osborn, *J. Am. Chem. Soc.* **96**, 7832 (1974).
28. G. M. Williams, K. I. Gell, and J. Schwartz, *J. Am. Chem. Soc.* **102**, 3660 (1980).
29. G. M. Williams and J. Schwartz, *J. Am. Chem. Soc.* **104**, 1122 (1982).
30. A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.* **9**, 2658 (1970).
31. M. A. Bennett, J. C. Jeffery, and G. B. Robertson, *Inorg. Chem.* **20**, 323 (1981).
32. A. C. Balazs, K. H. Johnson, and G. M. Whitesides, *Inorg. Chem.* **21**, 2162 (1982).
33. K. Tatsumi, R. Hoffmann, A. Yamamoto, and J. K. Stille, *Bull. Chem. Soc. Japan* **54**, 1857 (1981).
34. A. S. C. Chan and J. Halpern, *J. Am. Chem. Soc.* **102**, 838 (1980).
35. L. Abis, A. Sen, and J. Halpern, *J. Am. Chem. Soc.* **100**, 2915 (1978).

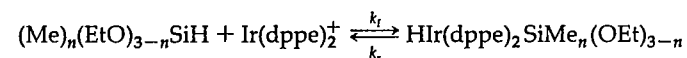
36. G. W. Parshall, *J. Am. Chem. Soc.* **96**, 2360 (1974).
37. N. J. Cooper, M. L. H. Green, and R. Mahtab, *J. Chem. Soc. Dalton* 1557 (1979).
38. G. K. Anderson, H. C. Clark, and J. A. Davies, *Organometallics* **1**, 550 (1982).
39. L. M. Bavaro, P. Montangero, and J. B. Keister, *J. Am. Chem. Soc.* **105**, 4977 (1983).
40. R. H. Crabtree, P. C. Demou, D. Eden, J. M. Miheleic, C. A. Parnell, J. M. Quirk, and G. E. Morris, *J. Am. Chem. Soc.* **104**, 6994 (1982).
41. A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.* **104**, 352 (1982).
42. J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.* **104**, 3723 (1982).
43. W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.* **104**, 4240 (1982).
44. D. P. Arnold and M. A. Bennett, *J. Organomet. Chem.* **199**, C17 (1980).
45. C. E. L. Headford and W. R. Roper, *J. Organomet. Chem.* **198**, C7 (1980).
46. D. L. Thorn, *Organometallics*, **1**, 197 (1982).
47. T. Yamamoto, T. Kohara, and A. Yamamoto, *Bull. Chem. Soc.* **54**, 2161 (1981).
48. C. D. Wood and R. R. Schrock, *J. Am. Chem. Soc.* **101**, 5421 (1979).
49. R. G. Bergman, *Acc. Chem. Res.* **13**, 113 (1980).
50. J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. (A)* 2969 (1969).
51. M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J. Chem. Soc. Dalton* 1613 (1974).
52. T. G. Appleton, H. C. Clark, and L. E. Manzer, *J. Organomet. Chem.* **65**, 275 (1974).
53. A. Gillie and J. K. Stille, *J. Am. Chem. Soc.* **102**, 4933 (1980).
54. M. K. Loar and J. K. Stille, *J. Am. Chem. Soc.* **103**, 4174 (1981).
55. G. Smith and J. K. Kochi, *J. Organomet. Chem.* **198**, 199 (1980).
56. D. Milstein, *J. Am. Chem. Soc.* **104**, 5226 (1982).
57. H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.* **75**, 2717 (1953).
58. J. J. Eisch and R. B. King, *Organometallic Syntheses*, **1** (New York: Academic Press, 1965) p. 158.
59. R. J. Hoxmeier, J. R. Blickensderfer, and H. D. Kaesz, *Inorg. Chem.* **18**, 3453 (1979).
60. W. D. Jones and R. G. Bergman, *J. Am. Chem. Soc.* **101**, 5447 (1979).
61. M. J. Nappa, R. Santi, S. P. Diefenbach, and J. Halpern, *J. Am. Chem. Soc.* **104**, 619 (1982).
62. J. R. Norton, *Acc. Chem. Res.* **12**, 139 (1979).
63. R. J. Cross and F. Glockling, *J. Chem. Soc.* 5422 (1965).
64. U. Belluco, M. Giustiniani, and M. Graziani, *J. Am. Chem. Soc.* **89**, 6494 (1967).
65. G. W. Parshall, *J. Am. Chem. Soc.* **90**, 1669 (1968).

PROBLEMS

1. Identify which of the following are oxidative-addition and reductive-elimination reactions.

- (a) $2\text{HCo}(\text{CO})_3\text{PPh}_3 \longrightarrow \text{Co}_2(\text{CO})_6(\text{PPh}_3)_2 + \text{H}_2$
- (b) $\text{CH}_3\text{Mn}(\text{CO})_5 + \text{PMe}_3 \longrightarrow \text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_4\text{PMe}_3$
- (c) $\text{HCo}(\text{N}_2)(\text{PPh}_3)_3 + \text{C}_2\text{H}_4 \longrightarrow \text{HCo}(\text{C}_2\text{H}_4)(\text{PPh}_3)_3 + \text{N}_2$
- (d) $\text{HCo}(\text{N}_2)(\text{PPh}_3)_3 + \text{H}_2 \longrightarrow \text{H}_3\text{Co}(\text{PPh}_3)_3 + \text{N}_2$
- (e) $2\text{Co}(\text{CN})_5^{3-} + \text{CH}_3\text{I} \longrightarrow \text{CH}_3\text{Co}(\text{CN})_5^{3-} + \text{Co}(\text{CN})_5\text{I}^{3-}$
- (f) $\text{trans-HPt}(\text{PMe}_3)_2\text{Cl} + \text{CH}_3\text{I} \longrightarrow \text{trans-Pt}(\text{PMe}_3)_2(\text{I})(\text{Cl}) + \text{CH}_4$

2. The following reaction has been investigated in each direction:



Interpret the activation parameter data shown below.

n	$\Delta H_f^\ddagger(\text{kcal/mol})$	$\Delta S_f^\ddagger(\text{eu})$	$\Delta H_r^\ddagger(\text{kcal/mol})$	$\Delta S_r^\ddagger(\text{eu})$
0	5.56	-47.3	25.3	8.2
1	5.62	-46.5	22.7	1.2
2	5.59	-48.2	19.2	0.1

3. Given the following data, determine the rate law for oxidative-addition of $\text{C}_6\text{H}_5\text{CH}_2\text{I}$ to $\text{CpRh}(\text{CO})\text{PPh}_3$:

$[\text{C}_6\text{H}_5\text{CH}_2\text{I}][\text{M}]$	$10^4 k_{\text{obs}}(\text{s}^{-1})$
0.166	7.37
0.237	10.7
0.402	16.0

[A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.* **10**, 1653 (1971).]

4. The dependence on the halide is as follows



for $\text{C}_6\text{H}_5\text{CH}_2\text{X}$ in the reaction of problem 3. Interpret these observations in terms of the mechanism.

5. Since oxidation number is a formalism that may or may not have any relationship to reality, there has been some discussion as to whether additions are oxidative in

character. Discuss the significance of the following data for addition to $\text{Ir}(o\text{-phen})(\text{cod})^+$:

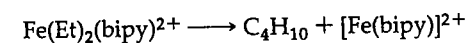
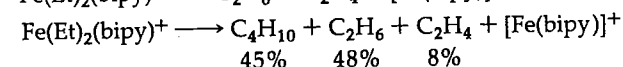
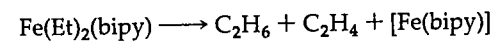
adding group	oxidation number
SCN^-	0.26
I^-	0.37
PPh_3	0.47
CH_3I	2.58
HCl	3.00
Cl_2	3.00

[W. J. Louw, D. J. A. de Waal, T. I. A. Gerber, C. M. Demanet, and R. G. Copperthwaite, *Inorg. Chem.* **21**, 1667 (1982).]

6. (a) The complex $\text{CH}_3\text{Rh}(\text{PPh}_3)_3$ is cleaved by H_2 to give methane and $\text{HRh}(\text{PPh}_3)_3$. If $\text{CH}_3\text{Rh}(\text{PPh}_3)_3$ is heated by itself, methane is again evolved, and the orange complex isolated analyzes approximately as $1\text{Rh}:3\text{PPh}_3$. Suggest the structure and the mechanism of CH_4 formation.
 (b) The orange complex from (a) reacts with CO to give a new complex that analyzes as $1\text{Rh}:3\text{PPh}_3:2\text{CO}$ and has IR peaks at 1965 and 1620 cm^{-1} . Suggest structures for this product.
7. (a) Treating $\text{Ir}(\text{CO})\text{CpPPh}_3$ with CH_3I yields a white solid that is soluble in fairly polar solvents, completely insoluble in benzene, has a ν_{CO} at 2050 cm^{-1} , and analyzes as $\text{IrC}_{25}\text{H}_{23}\text{IOP}$. Suggest a structure of the product.
 (b) Similar reactions of the cobalt and rhodium analogs $\text{M}(\text{CO})\text{Cp}(\text{PPh}_3)_3$ with CH_3I yield products that are colored, somewhat soluble in nonpolar solvents, and have ν_{CO} between 1650 and 1666 cm^{-1} . However, the analyses are the same as in (a). Suggest structures.
 (c) Compare $\text{Ir}(\text{CO})\text{CpPPh}_3$ with Vaska's compound, $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$. What is the key difference between them? How does this affect the nature of their reactions with CH_3I ? (Their activation parameters are very similar.)
8. Reaction of a macrocyclic rhodium complex with various alkyl halides showed the following dependence on the alkyl group: methyl > ethyl > secondary > cyclohexyl. In addition, reaction of *n*-butyl bromide in the presence of LiCl led to only the *trans*-chloro rhodium alkyl complex under conditions where the *trans*-bromo rhodium alkyl does not exchange with LiCl. Present a mechanism that accounts for these facts.
9. Reaction of *cis*- $\text{Me}_2\text{Pd}(\text{PPh}_3)_2$ with PhCH_2Br leads primarily to *trans*- $\text{MePd}(\text{PPh}_3)_2\text{Br}$ and PhCH_2CH_3 . Starting with α -deuteriobenzylbromide leads to α -deuterioethylbenzene with overall inversion of configuration at the benzylic carbon. Discuss the implications of this work. [D. Milstein and J. K. Stille, *J. Am. Chem. Soc.* **101**, 4981 (1979).]

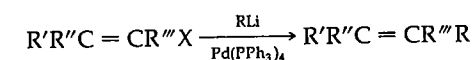
10. Reaction of $\text{Ni}(\text{Et})_2(\text{dppe})$ with CO leads to ethylene, ethane, acetone, and propionaldehyde. Account for these products. [T. Yamamoto, T. Kohara, and A. Yamamoto, *Chem. Lett.* 1217 (1976).]

11. Similar reactions have been observed on iron(II) complexes.



The rates of the reactions vary with half-lives of 15 days, 38 min, and 10^{-3} s for Fe(II), Fe(III), and Fe(IV), respectively. Account for the product distribution and rates of reaction.

12. A stereoselective synthetic route to alkenes has been presented as shown in the following reaction:



Suggest a mechanistic scheme.

Homogeneous Catalysis by Transition Metal Complexes

Homogeneous catalysis has been an important part of the explosion of interest in organometallic chemistry, providing a practical application for the complexes prepared. Homogeneous catalysis has not yet reached its full potential, but already a number of industrial processes employ homogeneous catalysts.^{1,2} Recent advances in synthesis-gas chemistry and asymmetric hydrogenations show considerable potential for industrial application.³⁻⁶ In this chapter we shall consider the mechanisms that have been suggested for several homogeneously catalyzed reactions such as homogeneous hydrogenations, hydroformylation, polymerization, olefin metathesis, and methanol homologation. As we discuss these mechanisms and the supporting data, it is important to remember that a catalytic cycle is composed of many reactions that may be equilibria and are usually impossible to investigate completely. Thus the mechanisms suggested will be the simplest that satisfactorily describe the data.

GENERAL CONSIDERATIONS

A catalyst accelerates the rate of a reaction without changing the thermodynamic stability of the reactants or products. The catalyst lowers the activation energy and thereby speeds the reaction (Figure 6.1). By lowering the activation energy, a catalyst increases the rate of reaction in both directions; that is, it increases the rate of attainment of equilibrium. Therefore only for reactions with favorable equilibria is a catalyst useful.

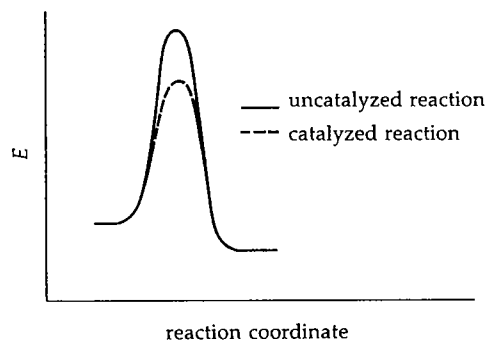


FIGURE 6.1. The effect of a catalyst on the reaction profile.

Reactions may be catalyzed heterogeneously or homogeneously. Heterogeneous catalysts operate in a different phase than the reactants. For the reactions that we shall discuss, heterogeneous catalysts are most often metals or metal oxides. Homogeneous catalysts function in the same phase as the reactants; for our considerations the homogeneous catalyst is usually a metal complex in solution. Heterogeneous catalysts, which are more commonly used in industry, have advantages in stability, generality for different reactions, and ease of separation from the products. Homogeneous catalysts often require lower temperature and pressure conditions and are more selective for a given product.⁷ Advantages of homogeneous catalysts have made them very attractive as raw materials have become scarce. An additional advantage of homogeneous catalysts is they can be studied and the reaction mechanism investigated by spectroscopic techniques.⁸

In order to function as a catalyst a complex must have open coordination sites or be capable of easily generating coordination sites. Most catalysts have involved square planar complexes or complexes with readily dissociable ligands.^{1,2,7,8} Saturated complexes with tightly bound ligands do not function in catalytic cycles. The transition metal also must hold the substrate molecules within the coordination sphere in a position appropriate for reaction. In some cases the catalyst holds the substrate molecules in position for stereospecific reactions. This is termed a template effect.⁹ A structure illustrating the potential of metal complexes for a template effect is shown in Figure 6.2.¹⁰ The tetranickel cluster is a catalyst for the cyclotrimerization of alkynes.¹⁰ In the structure the alkynes are held along the basal three nickel atoms in a position for trimerization; thus the catalyst brings the three acetylenes together as a template.¹⁰ It has been suggested that four acetylene molecules are simultaneously coordinated to nickel in the Ni(II) catalyzed cyclotetramerization of

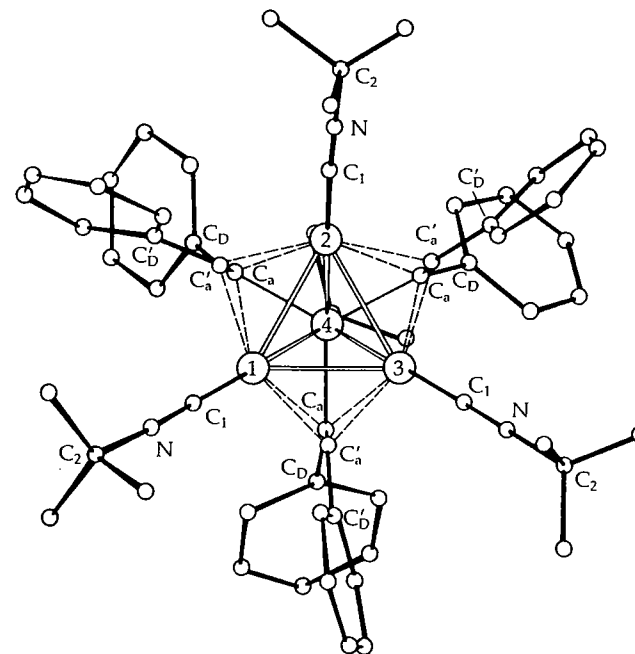
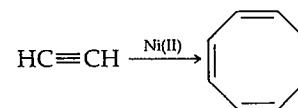


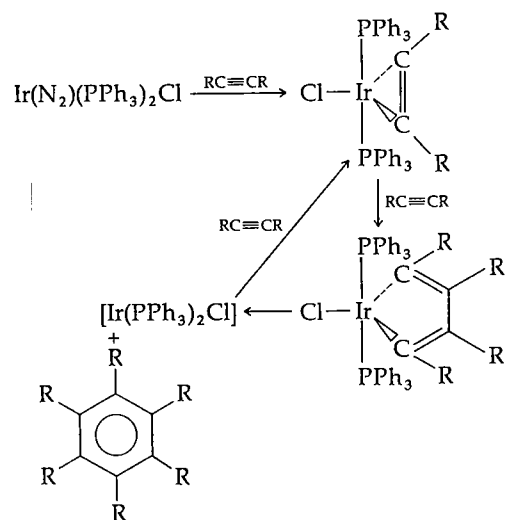
FIGURE 6.2. Structure illustrating the template effect for catalytic reactions. The $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4[\mu_3(\eta^2)\text{-C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]_3$ molecule is viewed normal to the triangular base along the idealized threefold axis. Nickel atoms are represented by large numbered open circles and carbon and nitrogen atoms by small open circles. [Reprinted with permission from M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.* 98, 4645 (1976). Copyright 1976 American Chemical Society.]

acetylene forming cyclooctatetraene,¹¹



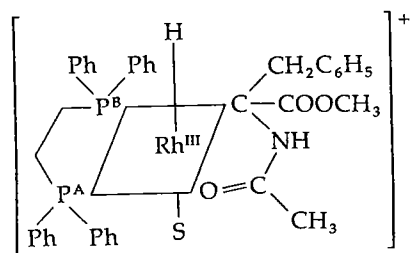
6.1

and successive coordination of alkynes was suggested in the cyclotrimerization on Ir(I).¹² The mechanistic distinction between simultaneous and successive coordination is not always straightforward. The important feature is that the metal complex must be able to coordinate the substrate(s) in the proper position for further reaction.



6.2

Studying catalytic reactions is different from studying the stoichiometric reactions we have discussed in earlier chapters. For catalytic reactions, interpretation of product distribution is very important; kinetic studies are less significant. Identification of intermediates is usually impossible. In fact the postulate has been advanced that if a complex is reactive enough to participate in a catalytic cycle, then it is not stable enough to be observed.⁸ This postulate suggests the difficulty of trying to define a catalytic cycle. Evidence cited in support of this postulate is the observation of the intermediate shown in Figure 6.3, which was intercepted from the catalytic cycle as shown in Figure 6.4 but which has the wrong configuration for the primary product.^{8,13}



S = CH₃OH or CH₃CN

FIGURE 6.3. An alkyl hydride intermediate that was intercepted from a cycle for catalytic hydrogenation. [Reprinted with permission from A. S. C. Chan and J. Halpern, *J. Am. Chem. Soc.* 102, 838 (1980). Copyright 1980 American Chemical Society.]

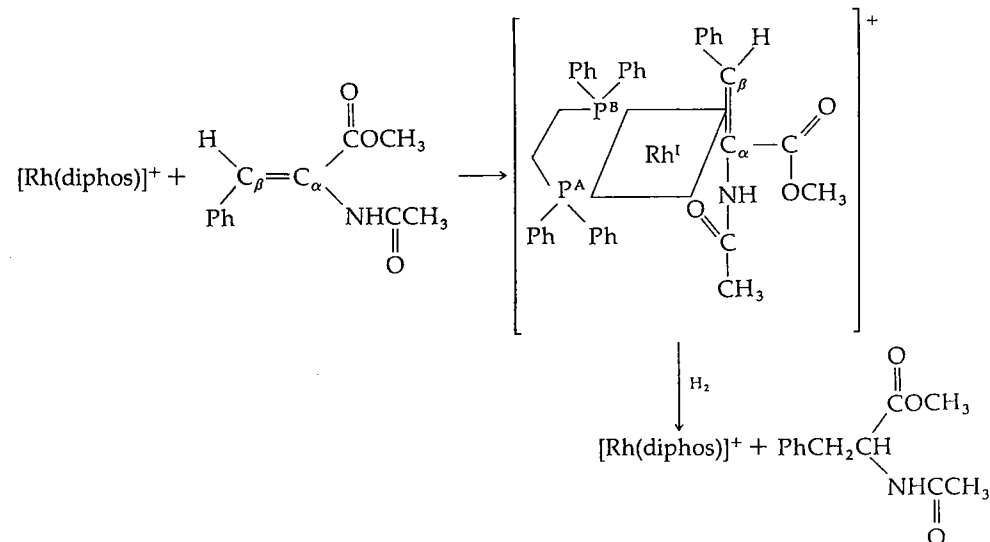
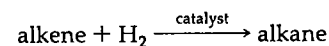


FIGURE 6.4. Cycle for the catalytic hydrogenation of methyl(Z)- α -acetamidocinnamate by Rh(diphos)⁺.¹¹

The mechanisms described in this chapter are those accepted for the different catalytic reactions. The simplest mechanism that fits all of the experimental data is the mechanism that we shall present.

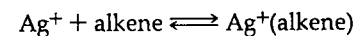
HOMOGENEOUS HYDROGENATION OF ALKENES

A catalyst must accomplish four things in homogeneous hydrogenations: (1) it must coordinate the alkene; (2) it must coordinate hydrogen; (3) it must allow the hydrogen to add to the alkene; and (4) it must eliminate the hydrogenated product.



6.3

Coordination of alkenes has been studied often beginning in the early nineteenth century with Zeise's salt, KPtCl₃(C₂H₄).¹⁴ Many alkene complexes have been prepared, and the stability of the alkene-metal bond evaluated.^{15,16} Stability constants determined for the reaction

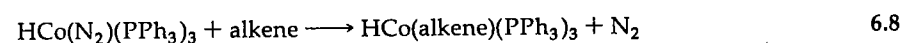


6.4

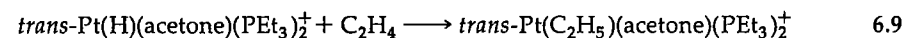
Stability Constants for Alkene Complexation.

<u>alkene</u>	<u>K^a</u>
C ₂ H ₄	17.5
CH ₃ CH=CH ₂	7.5
C ₂ H ₅ CH=CH ₂	8.8
C ₃ H ₇ CH=CH ₂	6.7
C ₄ H ₉ CH=CH ₂	4.3
C ₅ H ₁₁ CH=CH ₂	3.2
<i>cis</i> -CH ₃ CH=CHCH ₃	4.9
<i>trans</i> -CH ₃ CH=CHCH ₃	1.6
(CH ₃) ₂ C=CHCH ₃	1.01
(CH ₃) ₂ C=C(CH ₃) ₂	0.34

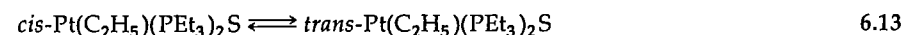
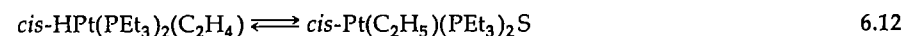
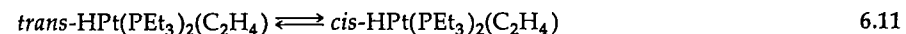
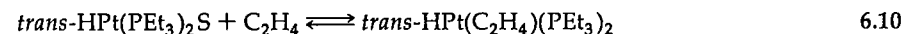
Hydrogen activation has also been commonly observed (see Chapter 5). Heterolytic activation has sometimes been observed¹⁷ although oxidative-addition is the most commonly observed means of activation (Chapter 5). Transfer of hydrogen to a coordinated alkene has not been as thoroughly investigated. The transfer must occur in two steps.


$$\begin{array}{ccc} \text{CpRh}(\text{C}_2\text{H}_4)\text{PMe}_3 + \text{HBF}_4 & \longrightarrow & [\text{CpRhH}(\text{C}_2\text{H}_4)\text{PMe}_3]\text{BF}_4 \\ & & \downarrow \uparrow \\ & & [\text{CpRh}(\text{C}_2\text{H}_5)\text{PMe}_3]\text{BF}_4 \end{array} \quad 6.7$$


6.8 the alkene and the hydride are in *trans* positions, and the alkyl is not formed.¹⁹ Insertion of ethylene into a Pt-H bond has been investigated in some detail.²⁰



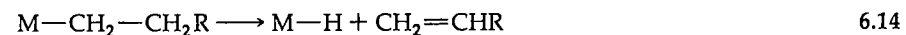
The rate expression precluded coordination of the ethylene and insertion into the Pt-H bond in the five-coordinate intermediate. The following mechanism was suggested:²⁰



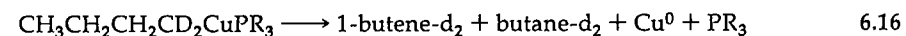
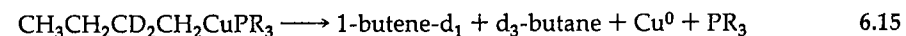
The intermediate, *trans*-HPt(C₇H₄)(PEt₃)₂, was observed by NMR.

➔ The stoichiometric hydrogenation of activated alkenes by Cp_2MoH_2 showed the stereochemistry of the alkene insertion to be *cis* by reaction of Cp_2MoD_2 with dimethyl fumarate, which leads to threo- $\text{Cp}_2\text{MoD}[\text{CH}(\text{CO}_2\text{Me})\text{CHD}(\text{CO}_2\text{Me})]$ or with dimethylmaleate, which leads to the erythro isomer. The isomers were identified by NMR.²¹ Since the stereochemistry of the Cp_2MoRH was known, the stereochemistry of the reductive-elimination could also be investigated and proceeded with retention of configuration at the sigma-bonded carbon.²¹ The stereochemistry is shown in Figure 6.5. This was in agreement with the results on reductive-elimination described in Chapter 5.

The reverse of reaction 6.5 is considered to occur by β -elimination, a general reaction of transition metal alkyl complexes. The reaction can be represented in the general case as



where the alkyl which possesses β -hydrogen is converted to a metal hydride and an alkene. That the β -hydrogen is transferred to the metal was shown by reaction of $(n\text{-Bu})\text{Cu}[\text{P}(n\text{-Bu})_3]$.²²⁻²⁴


$$R = Bu$$

Beta-elimination of deuterium from reaction 6.15 yields DCuPR_3 , which produces d_3 -butane in a binuclear reductive-elimination with the alkyl complex. Beta-elimination of hydrogen from reaction 6.16 yields the hydrido

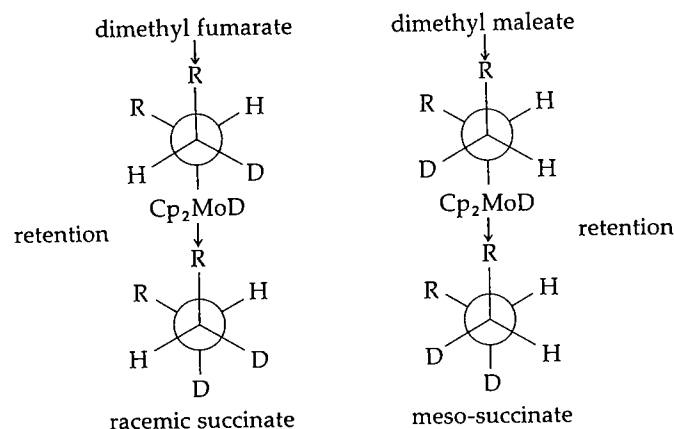
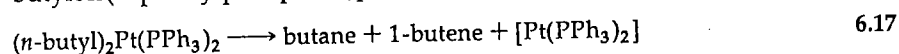
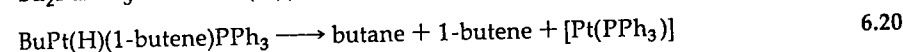
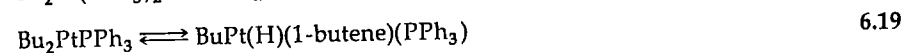


FIGURE 6.5. Stereochemistry of the stoichiometric hydrogenation of dimethyl fumarate or dimethyl maleate by Cp_2MoH_2 .¹⁹

species and the d_2 -butane and 1-butene.²² The mechanism of β -elimination has been most carefully investigated for the thermal decomposition of di-*n*-butylbis(triphenylphosphine)platinum(II).²³



The data indicate a first order intramolecular process that is slowed by the presence of excess PPh_3 . The following mechanism has been suggested:²³



Scrambling of the deuterium label indicated that the reactions could occur several times and probably also lead to the 2-butene isomer as a transient species. Since the rate-determining step for this reaction involved PPh_3 loss, no deuterium isotope effect was seen.²³ A kinetic isotope effect was evaluated for β -elimination from (*n*-octyl) $\text{Ir}(\text{CO})(\text{PPh}_3)_2$.²⁴ The value of 2.3 ± 0.2 is consistent with iridium inserting into a β -C-H bond. Beta-elimination is involved in (alkene) isomerization reactions, which accompany most homogeneous hydrogenation reactions.

$\text{Rh}(\text{PPh}_3)_3\text{Cl}$

Tris(triphenylphosphine)rhodiumchloride is one of the most active homogeneous hydrogenation catalysts known and has been often studied.²⁵⁻³² It is a square planar 16-electron complex that readily undergoes oxidative-

addition reactions and functions as a hydrogenation catalyst at ambient conditions.²⁵ The rates of hydrogenation of several alkenes are reported in Table 6.2.²⁷ The data show that less hindered olefins are hydrogenated more rapidly.²⁷ This order is very similar to that expected for olefin coordination stability.^{18,19}

TABLE 6.2

Hydrogenation of Alkenes with $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ at 25°C in Benzene Solution.

alkene	$k(10^2\text{M}^{-1}\text{s}^{-1})$
1-hexene	29.1
2-methylpent-1-ene	26.6
cis-4-methylpent-2-ene	9.9
trans-4-methylpent-2-ene	1.8
cyclohexene	31.6
1-methylcyclohexene	0.6
styrene	93.0

Oxidative-addition of H_2 to $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ has been studied by proton and phosphorus-31 NMR.³⁰ Addition at -25°C led quantitatively to $\text{H}_2\text{Rh}(\text{PPh}_3)_3\text{Cl}$ with the stereochemistry shown in Figure 6.6. Upon warming to 30°C , the coupling from Rh to P_1 and from P_1 to P_2 is lost while the Rh to P_2 coupling is retained. This is consistent with rapid dissociation of the

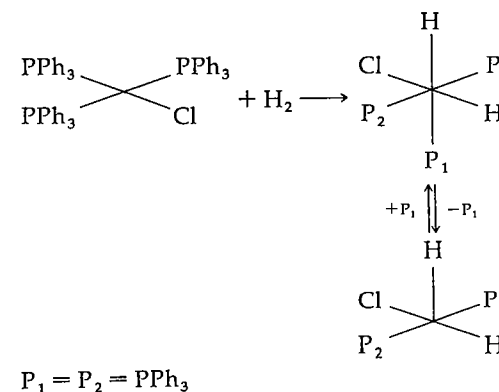
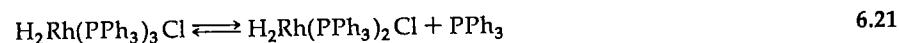
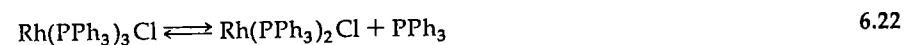


FIGURE 6.6. Stereochemistry of H_2 addition to $\text{Rh}(\text{PPh}_3)_3\text{Cl}$.²³

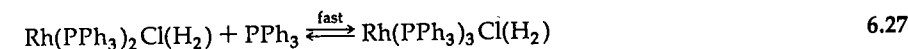
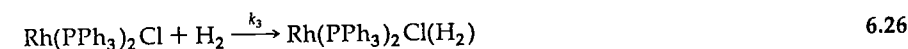
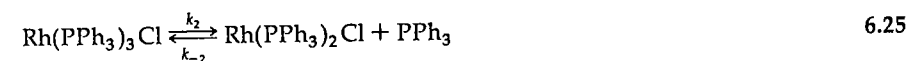
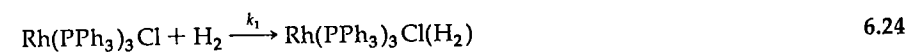
PPh_3 represented as P_1 . The rate constant for the reaction



was estimated as 200 s^{-1} at 30° by line shape analysis.³⁰ Although the equilibrium is rapidly established, it must greatly favor the six-coordinate species since there was no evidence for free PPh_3 or the five-coordinate complex. Studies of the kinetics of these reactions are complicated by the following reactions:



Both products react with H_2 and can participate in the catalytic cycle. An excess of PPh_3 inhibits reactions 6.22 and 6.23 allowing the kinetics of the hydrogen addition to $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ to be studied.³¹ The results are consistent with the following reactions:



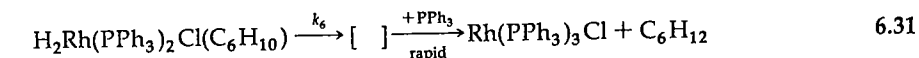
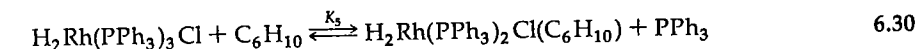
The rate law was derived

$$\frac{-d[\text{Rh}(\text{PPh}_3)_3\text{Cl}]}{dt} = \left(k_1 + \frac{k_2 k_3}{k_{-2}[\text{PPh}_3] + k_3[\text{H}_2]} \right) [\text{H}_2][\text{Rh}(\text{PPh}_3)_3\text{Cl}] \quad 6.28$$

with the rate constants, $k_1 = 4.8 \text{ M}^{-1}\text{s}^{-1}$, $k_2 = 0.71 \text{ s}^{-1}$ and $k_{-2}/k_3 = 1.1$.³¹ The remainder of the catalytic reaction, the transfer of H_2 from $\text{H}_2\text{Rh}(\text{PPh}_3)_3\text{Cl}$ to an alkene, was studied for cyclohexene.³² The rate law

$$\frac{-d[\text{H}_2\text{Rh}(\text{PPh}_3)_3\text{Cl}]}{dt} = \left(\frac{K_5 k_6 [\text{C}_6\text{H}_{10}]}{[\text{PPh}_3] + K_5 [\text{C}_6\text{H}_{10}]} \right) [\text{H}_2\text{Rh}(\text{PPh}_3)_3\text{Cl}] \quad 6.29$$

where the constants are defined by the following equations:



Equation 6.30 would be a rapid preequilibrium described by the equilibrium.

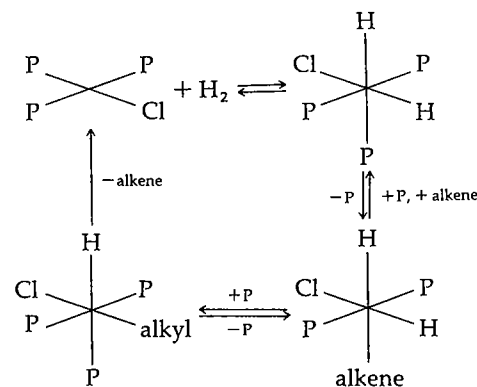
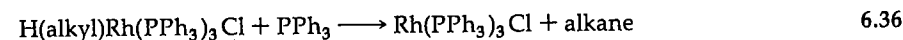
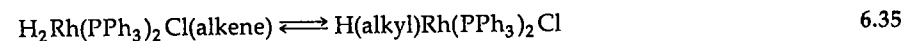
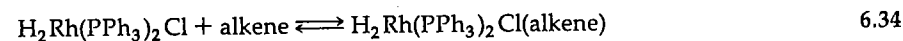
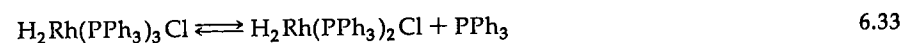
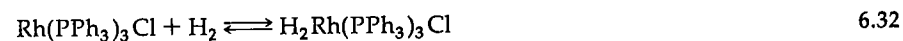
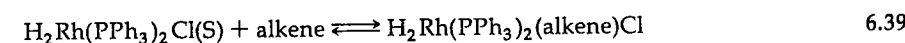
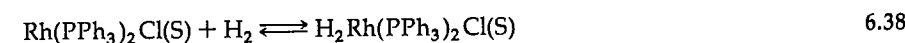
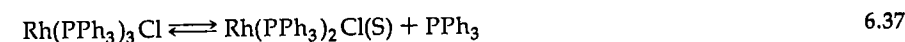


FIGURE 6.7. Stereochemistry at rhodium for catalytic hydrogenation by $\text{Rh}(\text{PPh}_3)_3\text{Cl}$.

constant K_5 . The reaction represented by k_6 is the rate-determining step. A complete catalytic cycle is represented by reactions 6.32–6.36; the stereochemistries are shown in Figure 6.7.



These reactions may be termed oxidative-addition (equation 6.32) ligand substitution (equations 6.33 and 6.34), alkene insertion into the rhodium-hydride bond (equation 6.35) and reductive-elimination of alkane. With the exception of the final step each reaction is reversible, and isomerization of alkenes does occur. At low concentrations of PPh_3 the following three reactions may replace reactions 6.32–6.34.³¹



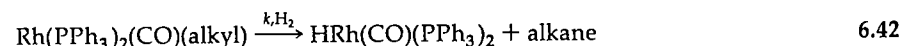
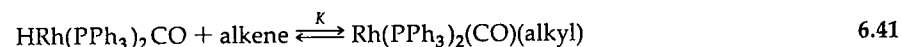
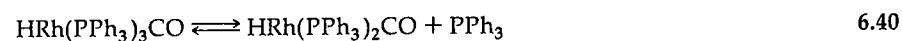
S = solvent

Although $\text{Rh}(\text{PPh}_3)_2\text{Cl}(\text{S})$ is of such low concentration that it cannot be detected in the catalytic system, the very rapid reaction with H_2 allows

$\text{Rh}(\text{PPh}_3)_2\text{Cl}(\text{S})$ to contribute to the catalytic reaction. There has been active discussion about whether PPh_3 dissociation occurs before or after oxidative-addition of hydrogen.²⁹ This is an extremely difficult question to resolve since the two products $\text{H}_2\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and $\text{H}_2\text{Rh}(\text{PPh}_3)_2\text{Cl}$ are both present in solution. The kinetics study indicated that both reactions contribute to formation of $\text{H}_2\text{Rh}(\text{PPh}_3)_3\text{Cl}$.

$\text{HRh}(\text{PPh}_3)_3\text{CO}$

Just as $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ serves as a model for catalytic hydrogenations by square planar 16-electron complexes, $\text{HRh}(\text{PPh}_3)_3\text{CO}$ serves as a model for hydrogenations by 18-electron hydride complexes.³³ The geometry is trigonal bipyramidal with equatorial PPh_3 ligands as shown in Figure 6.8.^{34,35} An 18-electron complex must open a coordination site for the alkene as an initial step; PPh_3 readily dissociates from $\text{HRh}(\text{PPh}_3)_3(\text{CO})$ under mild conditions.^{36,37} The proposed mechanism is as follows:



The rate shows a first order dependence on the concentration of hydrogen and rhodium complex and dependence between zero and first order in alkene.³⁸ The rate law for the mechanism of reactions 6.40–6.42 shows these characteristics.

$$\text{rate} = \frac{kK[\text{Rh}][\text{alkene}][\text{H}_2]}{1 + K[\text{alkene}]} \quad 6.43$$

The presence of PPh_3 inhibits the reaction by reversing reaction 6.40, leaving no coordination site for the alkene. None of the intermediates has been isolated or spectroscopically characterized. Evidence for the first two steps is shown by the exchange of hydrogen from the alkene to rhodium in the absence of H_2 .³⁹

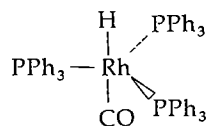
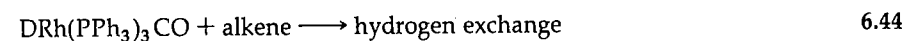


FIGURE 6.8. Structure of $\text{HRh}(\text{PPh}_3)_3(\text{CO})$.

The scheme shown in equations 6.40–6.42 includes reactions that probably occur in more than one step. The sequence can be described as: PPh_3 dissociation (equation 6.40); addition of alkene followed by insertion of the alkene into a Rh-H bond (equation 6.41); and oxidative-addition of H_2 followed by reductive-elimination of alkane (equation 6.42). The key differences mechanistically between $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and $\text{HRh}(\text{PPh}_3)_3\text{CO}$ lie in the electron count; the 16-electron $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ may undergo oxidative-addition, but the 18-electron $\text{HRh}(\text{PPh}_3)_3\text{CO}$ complex must initially undergo PPh_3 dissociation. The presence of the hydride ligand in $\text{HRh}(\text{PPh}_3)_3\text{CO}$ allows the alkene to add and insert into the Rh-H bond retaining the coordination site (no further dissociation is necessary); $\text{H}_2\text{Rh}(\text{PPh}_3)_3\text{Cl}$ must undergo PPh_3 dissociation to open a site for alkene.

The carbonyl complex $\text{HRh}(\text{PPh}_3)_3\text{CO}$ shows considerably more selectivity towards terminal alkenes, but is only about half as active as $\text{Rh}(\text{PPh}_3)_3\text{Cl}$. The results for several olefins are shown in Table 6.3³⁸ and may be compared to the data in Table 6.2.

TABLE 6.3

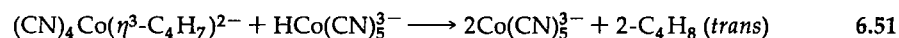
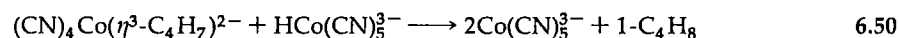
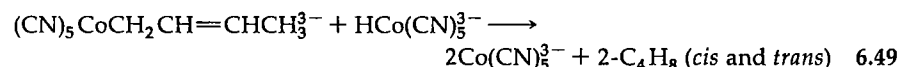
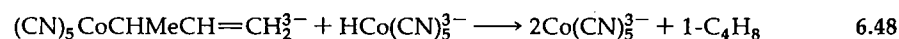
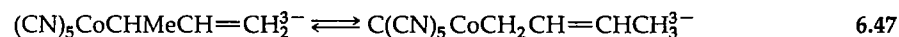
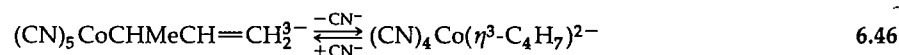
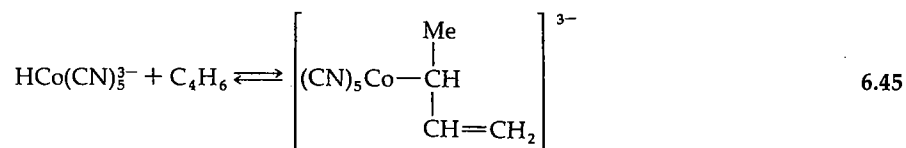
Rate of Hydrogenation of Several Olefins by $\text{HRh}(\text{PPh}_3)_3\text{CO}$ at 25°C.

alkene	rate (ml min^{-1})
1-hexene	16.7
ethylene	35
styrene	1.4
allyl benzene	11.1
cyclohexene	<0.1
cis-2-heptene	<0.1

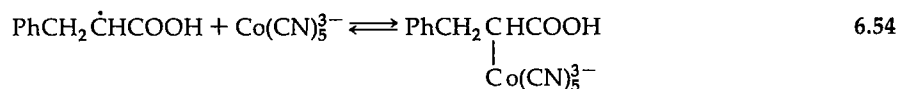
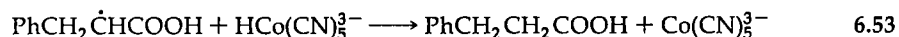
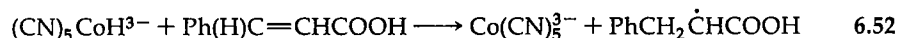
$\text{HCo}(\text{CN})_5^{3-}$

Much of the earliest research on mechanisms of homogeneous hydrogenation of alkenes by transition metal complexes derived from studies of $\text{HCo}(\text{CN})_5^{3-}$, which hydrogenates activated carbon-carbon double bonds.⁴⁰ Two mechanisms have been suggested depending on the substrate. For hydrogenation of conjugated dienes to monoenes, illustrated by 1,3-butadiene here, the mechanism involves an alkyl complex similar to the mechanisms considered above. The products of the hydrogenation of 1,3-butadiene are 1-butene and *cis*- and *trans*-2-butene with 1-butene dominant at high concentrations of CN^- and *trans*-2-butene dominant at low concentrations of

CN^- .⁴⁰ A detailed mechanism has been suggested for the hydrogenation of 1,3-butadiene by $\text{HCo}(\text{CN})_5^{3-}$.



The rate constants were calculated for each step of this catalytic cycle (the cycle is completed by $2\text{Co}(\text{CN})_5^{3-} + \text{H}_2 \rightarrow 2\text{HCo}(\text{CN})_5^{3-}$). The products of the hydrogenation of several conjugated dienes are shown in Table 6.4.⁴⁰ The hydrogenation of α,β -unsaturated acids by $\text{HCo}(\text{CN})_5^{3-}$ has been suggested to occur by a free radical mechanism.⁴⁰ The reduction of cinnamic acid to β -phenylpropionic acid can serve as an example:



Kinetic analysis rules out the mechanism involved in hydrogenation of conjugated dienes (reactions 6.45–6.51) for hydrogenation of α,β -unsaturated acids. The complex $\text{HCo}(\text{CN})_5^{3-}$ is an active hydrogenation catalyst for many activated carbon-carbon double bonds. It serves as a model for a free radical mechanism in homogeneous catalysis by transition metal complexes.

$\text{CH}_3\text{Co}(\text{CO})_2[\text{P}(\text{OMe})_3]_2$

Perhaps the most important requirement for an active catalyst is the ability to coordinate both alkene and hydrogen. An alkyl carbonyl complex may open two coordination sites if the carbonylation-decarbonylation reac-

TABLE 6.4

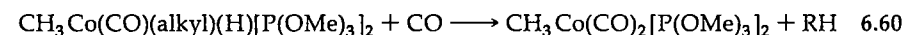
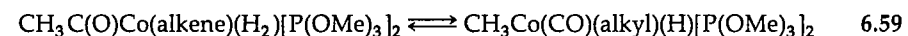
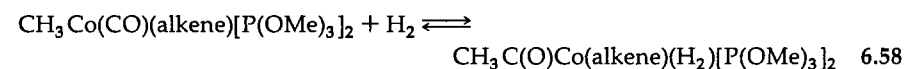
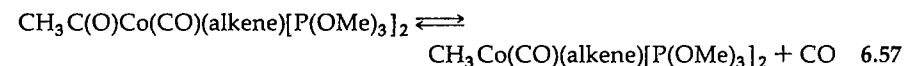
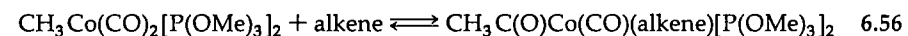
Products of the Hydrogenation of Conjugated Dienes by $\text{HCo}(\text{CN})_5^{3-}$.

alkene	products
butadiene	1-butene and 2-butene
1,3-pentadiene	1-pentene and <i>trans</i> -2-pentene
2,4-hexadiene	2-hexenes
norbornadiene	nortricyclene and norbornene
cyclopentadiene	cyclopentene
1,3-cyclohexadiene	cyclohexene

tion is a rapid equilibrium:



One coordination site is opened by the migration of the alkyl to a CO and the second by dissociative loss of a ligand from the acyl complex. A catalytic system for hydrogenation of alkenes has been developed using this concept of carbonylation-decarbonylation to open the coordination sites necessary.⁴¹ The catalyst, $\text{CH}_3\text{Co}(\text{CO})_2[\text{P}(\text{OMe})_3]_2$, is active for the hydrogenation of terminal alkenes at the rate of 450 turnovers per hour. In both rate and selectivity this alkyl complex is very similar to $\text{HRh}(\text{PPh}_3)_3(\text{CO})$. The rates of hydrogenation of several alkenes are shown in Table 6.5.⁴¹ The following cycle has been suggested for these catalytic reactions:⁴¹



Each of the intermediates in this scheme contains 18 electrons. An understanding of why alkane instead of CH_4 is reductively eliminated in the last step can only come from consideration of the possible geometries. The sug-

TABLE 6.5

The Rates of Hydrogenation of Alkenes by $\text{CH}_3\text{Co}(\text{CO})_2[\text{P}(\text{OMe})_3]_2$.

alkene	turnovers/hour
1-hexene	450
cyclohexene	11
2-hexene	4
1-octene	>100
styrene	>100
1,7-octadiene	>100
3-hexene	<1
cyclohexenone	<1

gested geometries for reaction 6.59 are shown in Figure 6.9. The CH_3 group is *trans* to H while the alkyl group is *cis*, thus the selectivity for reductive-elimination of alkane. If the phosphite donors are constrained to be *cis* as in the complex $\text{CH}_3\text{Co}(\text{CO})_2(\text{Pom-Pom})$, the catalyst has a much shorter lifetime, and the rate of CH_4 elimination is increased [$\text{Pom-Pom} = (\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$].⁴²

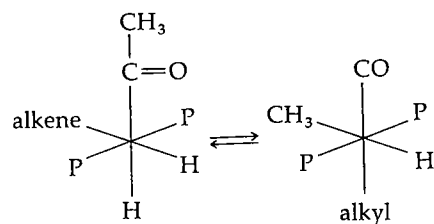
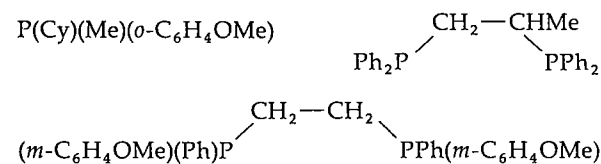


FIGURE 6.9. Stereochemistry of reaction 6.32.

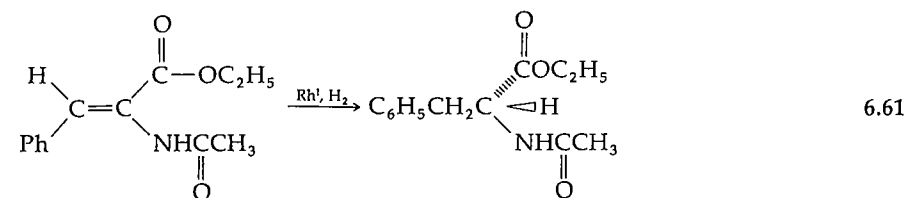
Asymmetric Hydrogenation

One of the most promising areas of application for homogeneous hydrogenation catalysis is in the use of chiral catalysts to effect the asymmetric hydrogenation of prochiral alkene functionality with high optical yields. The commercial synthesis of L-DOPA is accomplished by such an asymmetric hydrogenation. The chirality in the catalyst derives from a chiral ligand

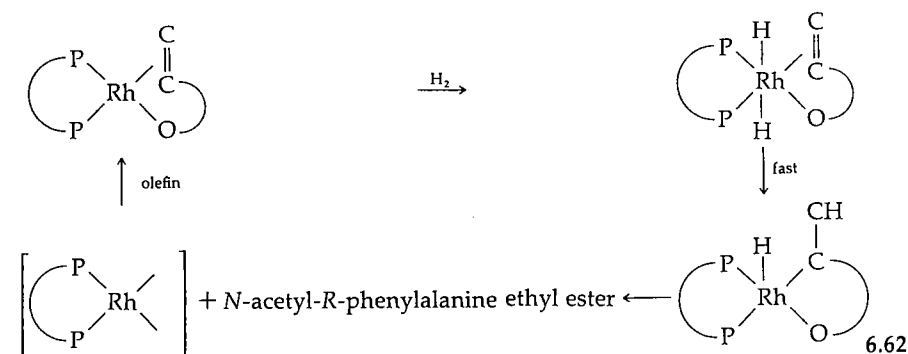
coordinated to the catalytic center. Several examples of such ligands are shown below.⁸



When these ligands are coordinated to Rh(I), they provide active catalysts that may give greater than 90% optical yields in the hydrogenation of olefinic substrates such as α -acylaminoacrylic acid and α -acetamidocinnamate derivatives.⁸ The mechanism of the hydrogenation reaction,



has been examined and the scheme below suggested:⁸



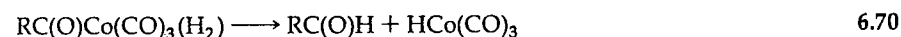
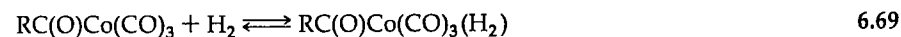
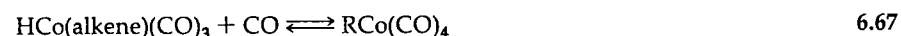
where $\widehat{\text{P}}\widehat{\text{P}}$ is a bidentate phosphine ligand and the ethyl-(Z)- α -acetamidocinnamate is functioning as a bidentate ligand through the alkene and an oxygen. At low temperature the monohydride alkyl complex could be characterized.¹³ From this reaction it was suggested that the enantiomeric selectivity in hydrogenation does not arise from a preferred mode of bonding of the prochiral olefin but rather arises from differences in the rates of the subsequent reactions.⁸ Asymmetric homogeneous hydrogenation should be a very productive research area in organic synthesis and mechanistic organometallic chemistry in the near future.

HYDROFORMYLATION REACTION

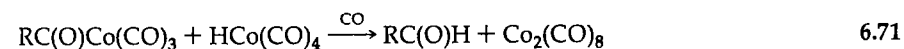
Hydroformylation involves the conversion of an alkene to an aldehyde with one additional carbon atom in the presence of synthesis gas, a mixture of CO and H₂.



This reaction is of considerable industrial importance as a means to functionalize alkenes.⁴³ The traditional catalyst is HCo(CO)₄, derived from Co₂(CO)₈ and H₂ under the reaction conditions. The extra selectivity to straight-chain aldehydes exhibited by HRh(PPh₃)₃CO has led industrial processes to shift to this catalyst.⁴⁴ Hydroformylation by the cobalt system is first order in [Co] and first order in alkene. The rate increases with increasing H₂ pressure and decreases with increasing CO pressure.⁴⁵ The conditions required are rather strenuous, over 100°C and over 200 atm pressure.^{44,45} Based on these observations and a number of other reactions, the following sequence was proposed for hydroformylation of alkenes by Co₂(CO)₈.⁴⁶



Primary side products are alkane, isomerized alkene, nonlinear aldehydes and alcohols, all logical products of the proposed scheme.⁴³ Each reaction involves two-electron transitions, either 16- or 18-electron complexes. Infrared studies of a hydroformylation reaction have suggested that reactions 6.69 and 6.70 should be replaced by a binuclear reaction (see Chapter 5).⁴⁷



Considering the relative ease of Co(CO)₄ formation from HCo(CO)₄, it is surprising that radical mechanisms have not received more attention. Photolysis was recently shown to inhibit the hydroformylation reaction, a difficult observation to justify in terms of a radical mechanism.⁴⁸

Terminal alkenes are hydroformylated more rapidly than more highly substituted alkenes.⁴⁵ Pertinent data (Table 6.6)⁴⁵ show that the degree of substitution at the olefinic carbons is the most important consideration in

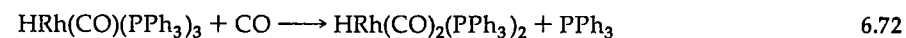
rates of hydroformylation. This would correspond to the ease of coordination of the alkene as discussed earlier.

TABLE 6.6

Rates of Hydroformylation of Alkenes by HCo(CO)₄ at 110°.

alkene	k(×10 ⁵ s ⁻¹)
1-hexene	110
1-octene	109
2-hexene	30
2-octene	31
2-methyl-1-pentene	13
4-methyl-1-pentene	107
2-methyl-2-pentene	8.1
cyclohexene	9.7

Both associative and dissociative mechanisms have been suggested for hydroformylation by HRh(CO)(PPh₃)₃.^{49,50} Schemes are shown in Figure 6.10. The active species in either scheme is HRh(CO)₂(PPh₃)₂ formed by reaction of HRh(CO)(PPh₃)₃ with CO.⁴⁹



The relative rates of hydroformylation of several alkenes are shown in Table 6.7.⁴⁹ Comparison of the data in Tables 6.6 and 6.7 indicates that the rhodium

TABLE 6.7

Rates of Hydroformylation of Alkenes by HRh(CO)(PPh₃)₃ in Benzene at 25°C.

alkene	rate (gas uptake in ml/min)
1-hexene	3.52
1-pentene	3.74
1-heptene	3.50
2-pentene	0.15
cis-2-heptene	0.12
2-methyl-1-pentene	0.06

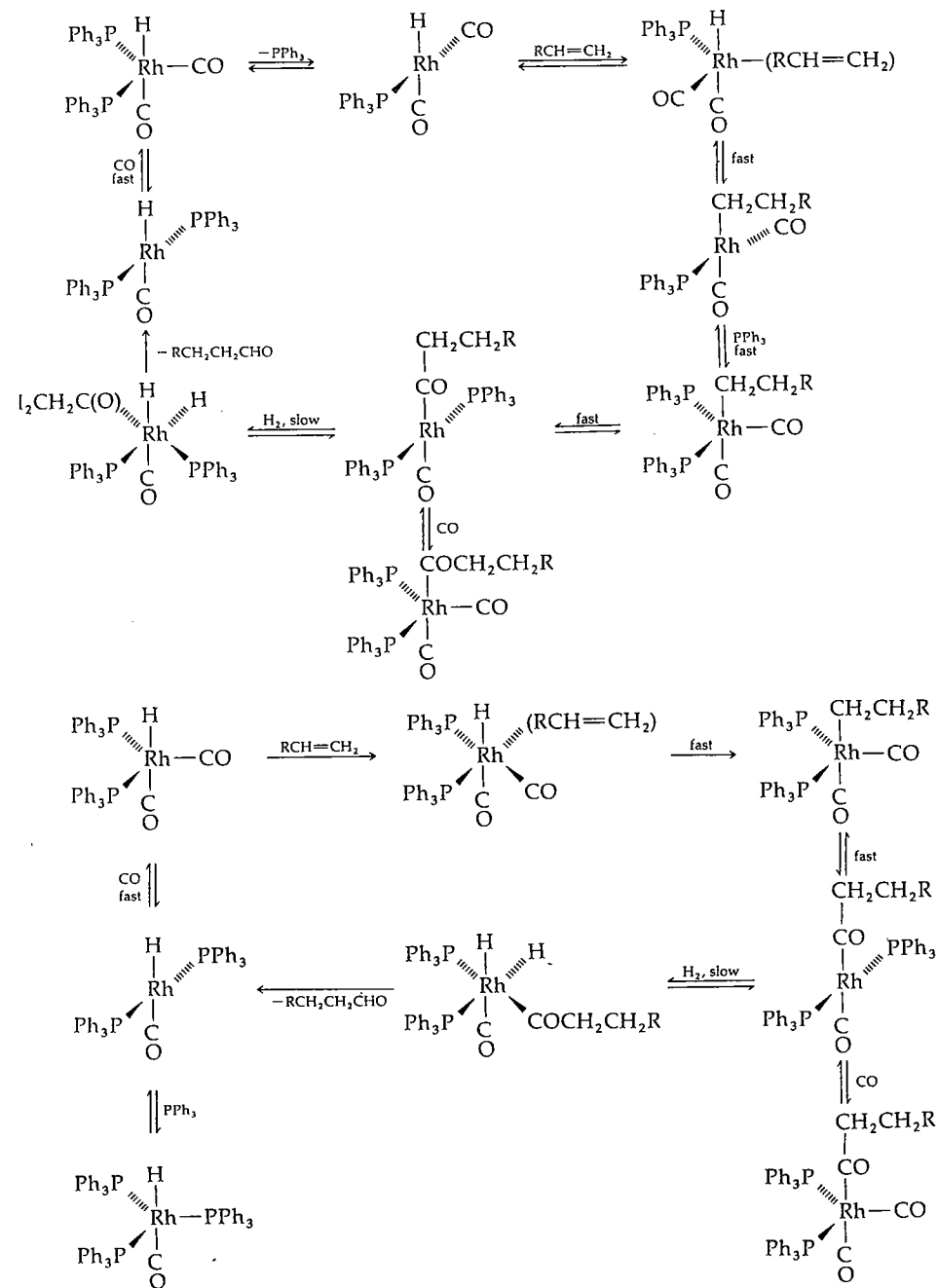


FIG. 6.10. Proposed mechanisms for the hydroformylation of alkenes by $(\text{CO})_2(\text{PPh}_3)_2$: (a) dissociative and (b) associative.

complex is considerably more selective for terminal alkenes and reacts at milder conditions.^{49,50} The rhodium system also produces fewer side products as shown in Table 6.8.⁵⁰ The advantages of rhodium catalysts in mild conditions and greater specificity (hydroformylation of 1-hexene produces heptanal in >90% yield on rhodium while cobalt produces a lower yield of the straight-chain aldehyde) are very attractive for industrial processes and offset the extra expense of rhodium over cobalt.

Other metal carbonyl species that have been investigated show reactivity quite dependent on the metal center.⁵⁰

metal:	Rh	Co	Ru	Mn	Fe	Cr, Mo, W, Ni
relative rate:	$10^3 - 10^4$	1	10^{-2}	10^{-4}	10^{-6}	0

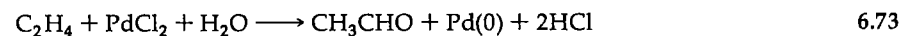
TABLE 6.8

Products from the Hydroformylation of Propylene for Cobalt and Rhodium-Based Catalysts.

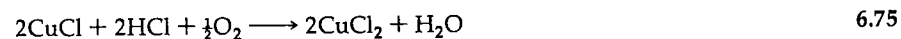
product	Co	Rh
aldehyde	80%	97%
alcohol	11%	trace
butylformate	2%	trace
propane	2%	2%
others	5%	<1%

WACKER ACETALDEHYDE SYNTHESIS

The Wacker process, which was one of the first industrial applications of homogeneous catalysis, led to the displacement of acetylene as the starting material for manufacture of organic chemicals. The efficient conversion of ethylene to acetaldehyde using PdCl_2 in a catalytic sequence was accomplished in the mid 1950s.^{1,51} The stoichiometric reaction



had been known since 1894. Combination with two reactions to regenerate the palladium chloride allowed a catalytic synthesis of acetaldehyde from ethylene.



Addition of the three reactions gives the net reaction

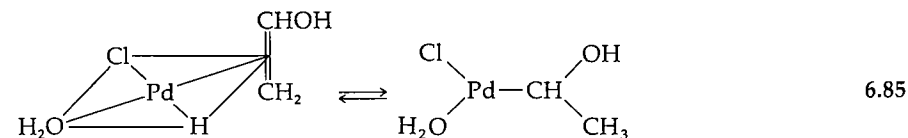
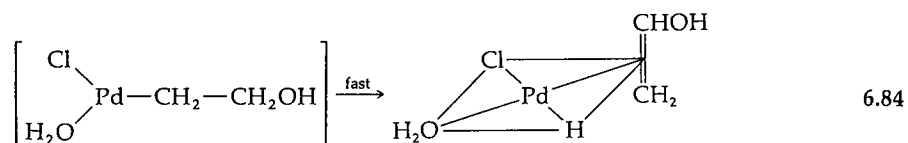
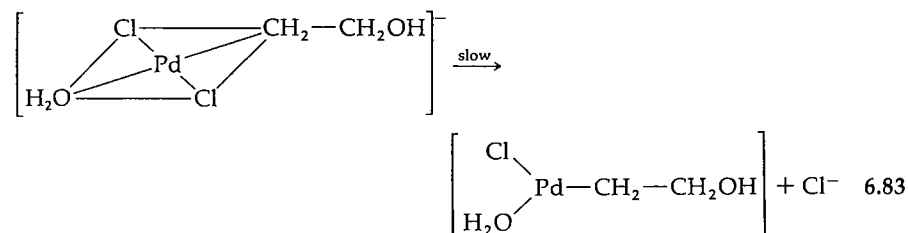
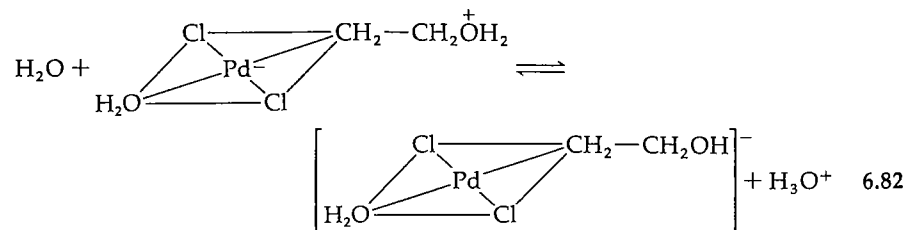
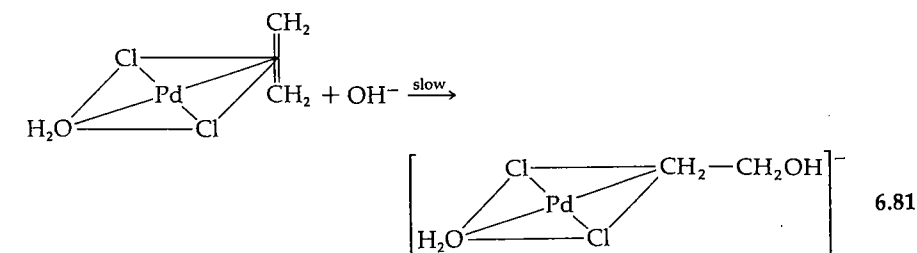
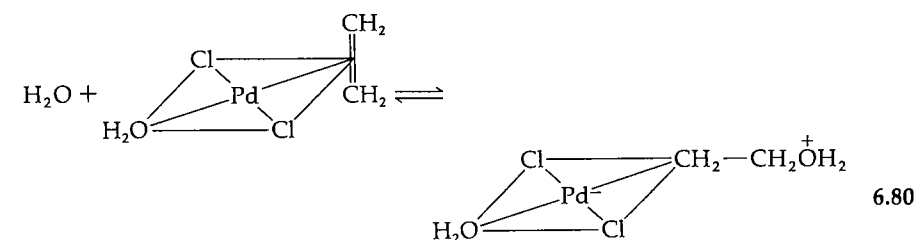
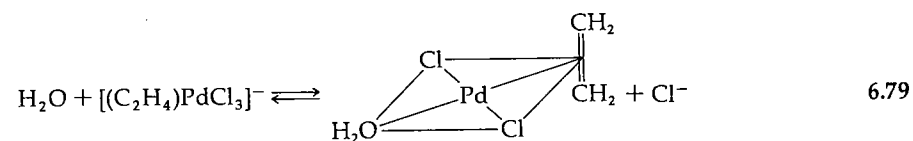
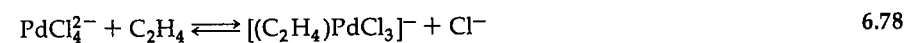


in which ethylene is converted by oxygen to acetaldehyde. While reactions 6.74 and 6.75 are essential to the catalytic sequence, they are electron transfer processes as discussed in Chapter 8. The conversion of ethylene into acetaldehyde occurs in reaction 6.73, which we shall examine in more detail.

The rate law for product formation in the Wacker process

$$\frac{-d[\text{C}_2\text{H}_4]}{dt} = \frac{k[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]}{[\text{H}^+][\text{Cl}^-]^2} \quad 6.77$$

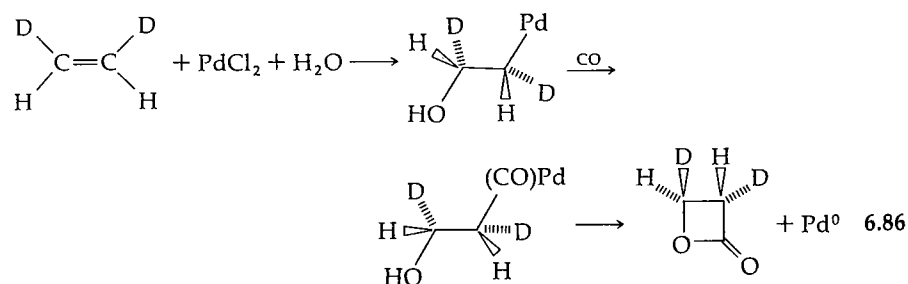
has led to the following mechanism for acetaldehyde formation.^{1,51,52}



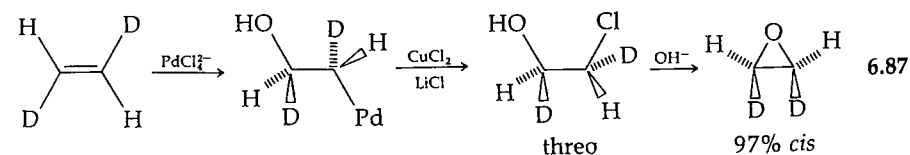
The first two reactions are ligand substitutions at a square planar center (Chapter 2). Note that the strong *trans* effect of the C_2H_4 leads to the *trans* product.^{52,53} Reaction 6.81 and reactions 6.80 and 6.82 involve attack of OH^- or H_2O on coordinated ethylene in what has been called a hydroxypalladation. The mechanism of this step has been demonstrated to be attack of hydroxide or water from outside the coordination sphere on coordinated ethylene by using specifically deuterium-labeled ethylenes.^{52,53} Beta-hydrogen elimination (reaction 6.84) leads to the olefin complex that may rearrange to a second sigma-bonded isomer (reaction 6.85). Acetaldehyde is formed by

β -elimination of the hydrogen on oxygen. The palladium hydride decomposes to palladium metal and HCl.

The primary discussion in recent years has centered on the hydroxypalladation reaction that converts the coordinated ethylene into the sigma alkyl (Pd-CH₂CH₂OH).^{52,53} The earlier suggestion of ethylene insertion into a Pd-OH bond was shown to be inconsistent with two separate stereochemical studies. The hydroxypalladation of *cis*-1,2-dideuterioethylene under CO allowed the trapping of the β -hydroxyethylpalladium complex and determination of the stereochemistry.⁵²



Since the insertion of carbon monoxide into a carbon-palladium sigma-bond occurs with retention of configuration at carbon, the hydroxypalladation proceeds with *anti* stereochemistry, indicating that attack on the coordinated ethylene takes place outside of the coordination sphere of the complex.⁵² A similar conclusion was obtained from studies of *trans*-1,2-dideuterioethylene with the stereochemistry determined for chloroethanol and the corresponding epoxide.⁵³



The formation of the epoxide is known to proceed with inversion of configuration at one carbon. Thus external attack on the coordinated olefin is confirmed.⁵³

The Wacker chemistry can also be used for other alkenes. Terminal alkenes produce methylketones, and acetone can be readily produced from

propene. The rates and yields decrease with increasing chain length of the alkene. Cyclic alkenes produce good yields of cyclic ketones, but other internal alkenes give mixtures of products.

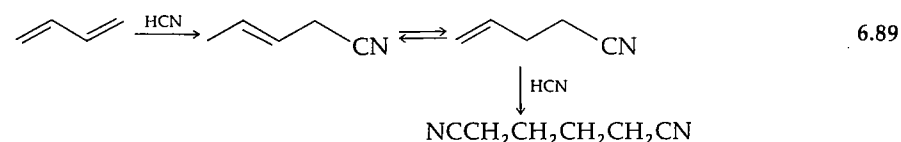
The Wacker process has been a very important reaction in transition metal homogeneous catalysis for the production of acetic acid as a building block of industrial organic chemistry. This process may soon be replaced by synthesis gas (CO and H₂) chemistry in industry, but it will remain a model for the adaptation of known chemistry into a useful catalytic cycle.¹

HYDROCYANATION OF 1,3-BUTADIENE

The synthesis of 6,6-nylon involves an elimination polymerization that requires 1,6-hexanediamine. 1,6-Hexanediamine can be readily produced by hydrogenation of adiponitrile using heterogeneous catalysts.



Thus the convenient production of adiponitrile has been an active area of research.^{1,54} A commercial route using homogeneous hydrocyanation of 1,3-butadiene has been developed and investigated mechanistically.⁵⁴



These reactions are catalyzed by Ni(0) complexes. The catalytic cycle is composed of three separate reactions: hydrocyanation of an activated olefin, isomerization, and hydrocyanation. We shall examine each of these reactions independently and then the cycle in its entirety.

The catalyst is a tetrahedral nickel complex, NiL₄, where L is a phosphite ligand.⁵⁴ Since NiL₄ is an 18-electron complex, ligand dissociation is important in initiating the catalytic reaction.



The equilibrium constants for the ligand dissociation of L from NiL₄ given in Table 6.9, indicate the importance of steric interactions. Hydrogen cyanide oxidatively adds to the NiL₃ complex.

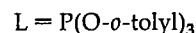
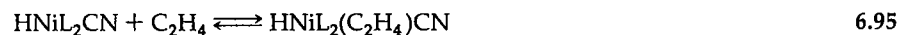


TABLE 6.9

Equilibrium Constants for Ligand Dissociation from NiL_4 in Benzene at 25°C.

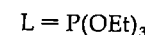
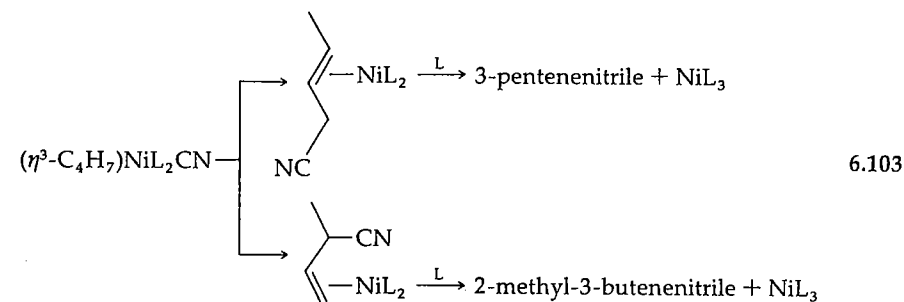
L	$K(M)$
P(OEt)_3	$< 10^{-10}$ (at 70°C)
$\text{P(O-}i\text{-Pr)}_3$	6×10^{-10}
$\text{P(O-}i\text{-Pr)}_3$	2.7×10^{-5}
$\text{P(O-}o\text{-tolyl)}_3$	4.0×10^{-2}

The hydridocyanonickel complexes could be spectroscopically characterized.⁵⁴ The hydrocyanation of ethylene can be used as a model for the mechanism of a nonactivated olefin.



The hydridocyano and ethylcyano complexes could be spectroscopically identified in the catalytic cycle.⁵⁴ This scheme involves a sequence of 16- and 18-electron conversions.

Hydrocyanation of a conjugated alkene is considered to be slightly different. Addition of the first molecule of HCN to 1,3-butadiene has been studied for $\text{Ni}[\text{P(OEt)}_3]_4$.



The η^3 -allyl group combines with the cyanide in two ways to form the desired linear 3-pentenitrile and the branched 2-methyl-3-butenitrile. The path leading to linear product was favored by a small rate factor.

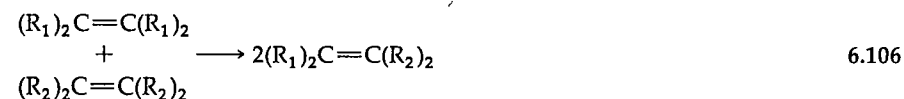
The catalytic conversion of 1,3-butadiene to adiponitrile with HCN in the presence of nickel(0) complexes is completed by the addition of BPh_3 , a Lewis acid promoter. The BPh_3 coordinates to the nitrogen of the coordinated cyanide and has three beneficial effects on the production of adiponitrile: (1) the rate of hydrogenation of unactivated olefins is enhanced; (2) the amount of linear product is increased; and (3) the catalyst lifetime is enhanced, presumably because a second oxidative-addition of HCN to form NiL_2CN_2 is prevented.⁵⁴



Each of the proposed steps in the hydrocyanation of 1,3-butadiene with NiL_4 (L = phosphite ligand) is suggested to occur by 16- and 18-electron intermediates.

OLEFIN METATHESIS

The olefin metathesis reaction involves the transfer of alkylidene units between two alkenes.⁵⁵⁻⁵⁸



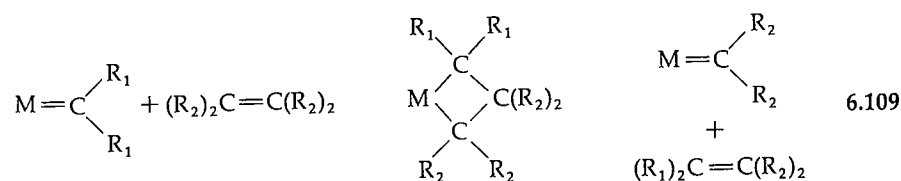
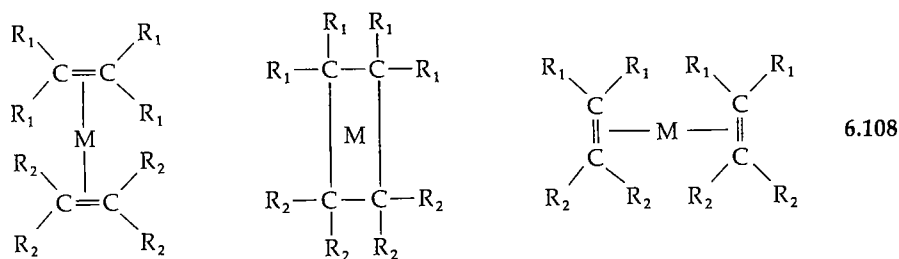
The olefin metathesis reaction is of considerable industrial importance.⁵⁷

Propylene is converted to ethylene and 2-butene in a commercial process, and cycloolefins polymerize to linear unsaturated polyalkenamers.⁵⁷

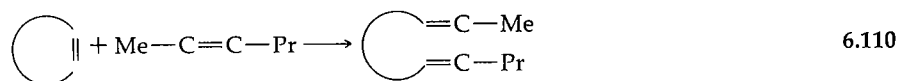


The importance of olefin metathesis led to extensive investigation that produced mechanistic understanding only 15 years after first reports on the reaction. A primary difference from the other catalytic systems that we have examined is that the catalyst for olefin metathesis is not well defined. The most active catalysts are combinations (WCl_6 , EtOH , EtAlCl_2 ; and $\text{Mo}(\text{PPh}_3)_2(\text{NO})_2\text{Cl}_2$, $\text{Me}_3\text{Al}_2\text{Cl}_3$). Despite this uncertainty in the coordination around the active metal center, the primary steps are now understood.

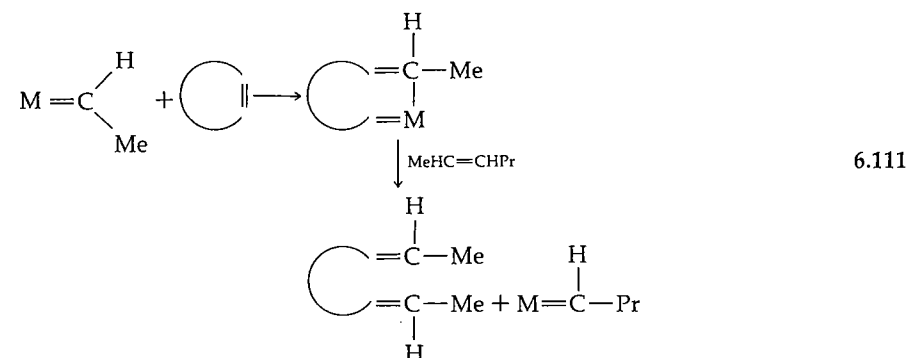
A number of experiments have been devised to differentiate between the two suggested mechanisms.^{55,59-60}



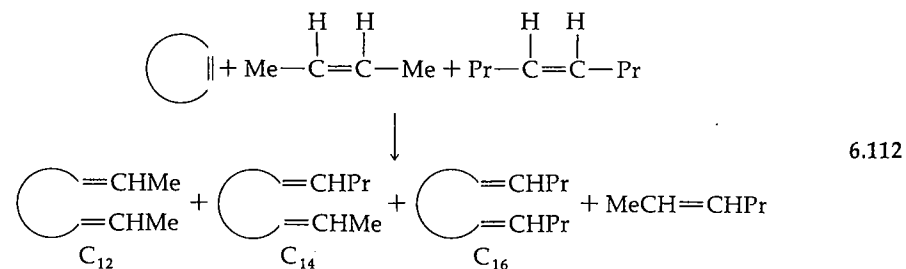
The first mechanism (equation 6.108) is the cyclobutane mechanism, and the second is the metallocyclobutane or carbene mechanism. Reactions in which a mixture of a cycloalkene and an alkene undergo metathesis allow these two mechanisms to be distinguished and have shown the cyclobutane mechanism to be unsatisfactory.⁵⁵ Metathesis of cyclooctene with 2-hexene was examined for the relative amounts of C_{12} , C_{14} and C_{16} dialkenes. For the cyclobutane mechanism only C_{14} would be expected since both alkenes would be coordinated to the metal.⁵⁵



For the metallocyclobutane mechanism more possibilities are available. One reaction is shown below:

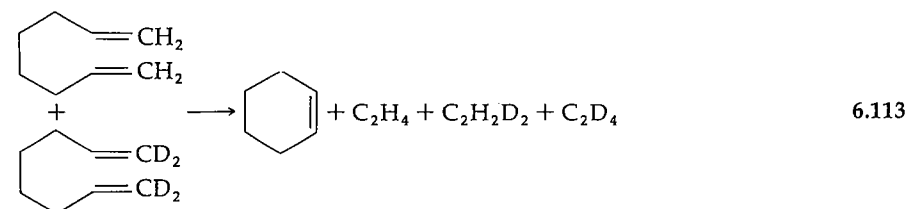


With this mechanism one expects a statistical distribution, 1 : 2 : 1 for C_{12} , C_{14} and C_{16} dialkenes.⁵⁵ Since the alkenes formed could undergo further metathesis, the significant observation to distinguish the mechanism must be made early in the reaction. The ratios, $[\text{C}_{12}]/[\text{C}_{14}]$ and $[\text{C}_{16}]/[\text{C}_{14}]$, extrapolated to $t = 0$ are nonzero in confirmation of the metallocyclobutane mechanism. Similar experiments with three alkenes, cyclooctene, 2-butene, and 4-octene, were performed.⁵⁵

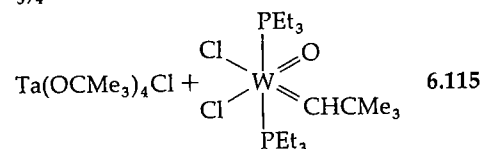
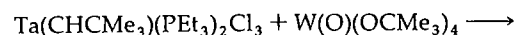


For the cyclobutane mechanism no C_{14} dialkene should form initially, but for the metallocyclobutane one would again expect a statistical ratio of $\text{C}_{12}:\text{C}_{14}:\text{C}_{16}$, 1 : 2 : 1. In plots extrapolated to $t = 0$ the amount of C_{14} was invariably larger than the amount of C_{12} or C_{16} . A sample plot is shown in Figure 6.11.⁵⁵

Another experiment to distinguish between the metallocyclobutane and the cyclobutane mechanism involved the metathesis of 1,7-octadiene.⁶⁰



tathesis has appeared.⁶³ Many metals have been used, but the most active catalysts are based on tungsten, molybdenum, and rhenium.⁵⁸ The alkylidene complex, $(\text{CO})_5\text{W}=\text{C}(\text{Ph})_2$, functions as a catalyst but much more slowly than other catalysts.⁵⁹ It has been suggested that the slowness of this alkylidene is attributable to the saturation of the coordination around the tungsten; CO dissociation is required to open a coordination site before the alkene can be coordinated.⁵⁹ The most active catalysts are based on transition metal halides and alkylaluminum species and probably proceed initially to a transition metal alkyl complex. In a few cases α -hydrogen abstraction has been observed from an alkyl to form an alkylidene.⁶⁴ A tungsten alkylidene that may serve as a model for alkylidenes formed when tungsten oxides or chlorides are treated with alkylaluminums has been isolated by the following reaction:⁶⁵



The oxoalkylidene complex is an active catalyst for the metathesis of alkenes. Reaction with 1-butene in the presence of AlCl_3 for one to two hours led to 3,3-dimethyl-1-butene (1 equiv.), 3-hexenes (1–2 equiv.), and an undetermined amount of C_2H_4 . The alkylidene product was predominantly the propylidene product although some methylidene product was observed. It was suggested that the metallocyclobutane A is more stable than B.



In several active catalyst systems—such as $\text{Mo}(\text{PPh}_3)_2\text{Cl}_2(\text{NO})_2$, $\text{Me}_3\text{Al}_2\text{Cl}_3$; WCl_6 , SnMe_4 ; and WCl_6 , ZnMe_2 —methane and ethylene are eliminated in the absence of alkene, evidence for methylidene formation.⁵⁸ Further evidence for methylidene intermediacy is shown by the initial formation of propylene in the metathesis of 2-alkenes.⁵⁸ Labeling showed that the methylidene of the propylene arose from the cocatalyst and the ethylidene arose from the 2-alkene.⁵⁸

Research on olefin metathesis supports the metallocyclobutane mechanism. The nature of the alkene products and the rates of alkene reactions are

fully consistent with the mechanism. The nature of the catalyst centers is not clearly defined, but in several cases there is evidence of alkylidene formation in the catalytic systems.

POLYMERIZATION OF ALKENES

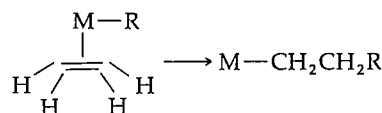
Polymerization remains one of the most important industrial applications of homogeneous catalysis.^{1,2} The polymerization of simple derivatives of ethylene leads to a number of important products as shown in Table 6.11. The discovery of alkene polymerization by Ziegler–Natta catalysts is one of the milestones of organometallic chemistry. Ziegler–Natta catalyst systems, composed of a transition metal halide and a main group alkyl (usually an aluminum alkyl), are poorly defined in terms of the coordination sphere of the transition metal. In this respect they are similar to olefin metathesis catalysts.

TABLE 6.11

Products from the Polymerization of Ethylene Derivatives.

alkene	polymer (application)
$\text{CH}_2=\text{CH}_2$	polyethylene (plastic bags)
$\text{CF}_2=\text{CF}_2$	teflon (pan coating)
$\text{CH}_2=\text{CHCl}$	polyvinylchloride (phonograph records)
$\text{CH}_2=\text{CHCN}$	orlon (rug fibers)
$\text{CH}_2=\text{CHPh}$	polystyrene (combs)

At the current time the two most plausible mechanisms for polymer growth on a transition metal cannot be differentiated on the basis of experimental data on the catalytic polymerization reaction. One proposed scheme involves insertion of an alkene into a metal alkyl bond, similar to insertion of an alkene into a metal-hydride bond as discussed for hydrogenation and hydroformylation.



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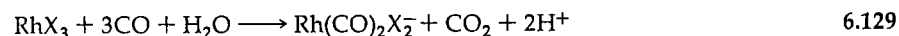
METHANOL CARBONYLATION

The conversion of methanol to acetic acid is a reaction of considerable importance.⁷⁰



Commercial processes based on cobalt and rhodium complexes exist. Mechanistic work has been accomplished on the rhodium system, and the cycle is understood.⁷⁰ Use of any of a number of rhodium complexes as starting compounds produces equivalent catalytic behavior, suggesting that the catalyst is formed under the reaction conditions, 180°C and 30–40 atm of CO. The iodide promoter that is also required may be in any of several different forms, CH₃I, HI, or I₂. Kinetic studies show a first order dependence on rhodium concentration and on the concentration of iodide promoter. The rate was independent of the partial pressure of CO, the concentration of CH₃OH, and the concentration of CH₃C(O)OH.

Carbonylation of RhX₃ leads to the carbonyl anions, Rh(CO)₂X₂[−], at lower temperatures.



The same anionic species forms under the reaction conditions for a number of rhodium precursors.⁷⁰ A sample withdrawn from a reactor initially charged with Rh(PPh₃)₂(CO)Cl showed Rh(CO)₂I₂[−] to be present. A catalytic cycle can be constructed for the carbonylation of CH₃OH based on Rh(CO)₂I₂[−] from the reactions we have previously discussed. The scheme is shown in Figure 6.13. The first step is one expected in reactions of square planar 16-electron complexes, oxidative-addition of CH₃I. The methyl iodide is present as the promoter or is formed from methanol.



The next step is an alkyl migration to coordinated CO with CO taking up the open coordination site. Reductive-elimination of acetyl iodide regenerates the catalyst, Rh(CO)₂I₂[−]. Reaction of acetyl iodide with H₂O leads to CH₃C(O)OH and HI completing the catalytic reaction.

Room temperature reaction of Rh(CO)₂I₂[−] with CH₃I leads directly to an acetyl complex that was isolated and characterized as a dimer.⁷⁰

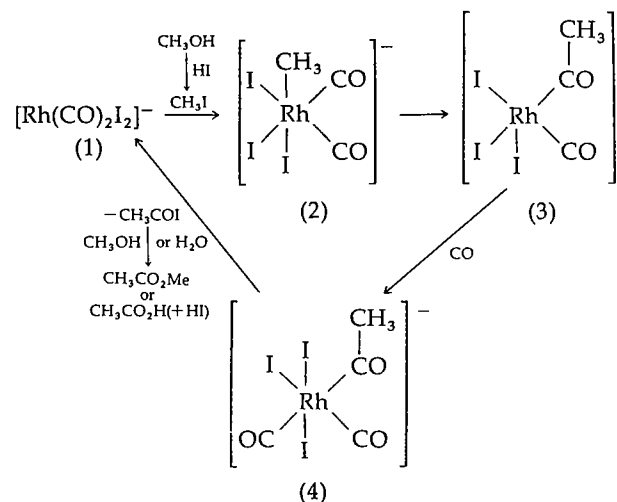
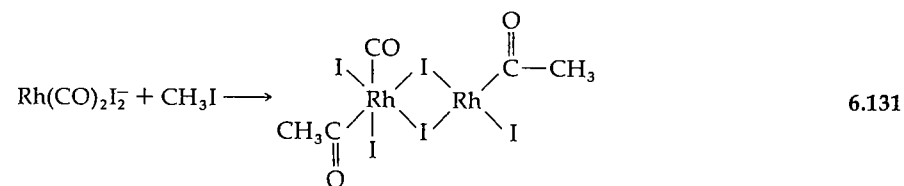


FIGURE 6.13. Proposed catalytic cycle for the carbonylation of methanol.⁴⁸

The dimer readily reacts with CO to form an acetyl carbonyl complex that is unstable towards reductive-elimination of CH₃C(O)I. The kinetic dependences indicate that oxidative-addition of methyl iodide to Rh(CO)₂I₂[−] is the rate-determining step. This is also indicated since Rh(CO)₂I₂[−] is the predominant rhodium species present under catalytic conditions.

Thus the proposed cycle accounts for the products and the observed kinetics. In addition each step of the catalytic cycle can be independently shown to occur at low temperature and pressure, so that the cycle is unusually well characterized, especially for a reaction that occurs at high temperature and pressure.⁷⁰

SUMMARY

We have examined the proposed mechanisms of several homogeneously catalyzed reactions. Although the reactions are different, the basic catalytic steps at the metal center are composed of steps that we have examined in earlier chapters: oxidative-addition, ligand dissociation, ligand addition to 16-electron complexes, insertion reactions, and reductive-elimination.

REFERENCES

1. G. W. Parshall, *Homogeneous Catalysis* (New York: John Wiley and Sons, 1980).
2. C. Masters, *Homogeneous Transition-Metal Catalysis: A Gentle Art* (London: Chapman and Hall, 1980).
3. E. L. Muetterties and J. Stein, *Chem. Rev.* **79**, 479 (1979).
4. C. Masters, *Adv. Organomet. Chem.* **17**, 61 (1979).
5. M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.* **100**, 5491 (1978).
6. K. E. Koenig and W. S. Knowles, *J. Am. Chem. Soc.* **100**, 7561 (1978).
7. E. L. Muetterties, *Inorg. Chim. Acta* **50**, 1 (1981).
8. J. Halpern, *Inorg. Chim. Acta* **50**, 11 (1981).
9. R. E. Harmon, S. K. Gupta, and D. J. Brown, *Chem. Rev.* **73**, 21 (1973).
10. M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.* **98**, 4645 (1976).
11. S. Eichler, *Chem. Ber.* **95**, 550 (1962).
12. J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.* **7**, 1298 (1968).
13. A. S. C. Chan and J. Halpern, *J. Am. Chem. Soc.* **102**, 838 (1980).
14. J. S. Thayer, *J. Chem. Ed.* **46**, 442 (1969) and references therein.
15. F. R. Hartley, *Chem. Rev.* **73**, 163 (1973).
16. F. R. Hartley, *Angew. Chem. Int. Ed. Engl.* **11**, 596 (1972).
17. J. Halpern, *Pure and Appl. Chem.* **51**, 2171 (1979).
18. H. Werner and R. Feser, *Angew. Chem. Int. Ed. Engl.* **18**, 157 (1979).
19. Y. Kubo, A. Yamamoto, and S. Ikeda, *J. Organomet. Chem.* **60**, 165 (1973).
20. H. C. Clark and C. R. Jablonski, *Inorg. Chem.* **13**, 2213 (1974).
21. A. Nakamura and S. Otsuka, *J. Am. Chem. Soc.* **95**, 7262 (1973).
22. G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. S. Filipp, Jr., *J. Am. Chem. Soc.* **92**, 1426 (1970).
23. G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Am. Chem. Soc.* **94**, 5258 (1972).
24. J. Evans, J. Schwartz, and P. W. Urquhart, *J. Organomet. Chem.* **81**, C37 (1974).
25. J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1711 (1966).
26. J. F. Mague and G. Wilkinson, *J. Chem. Soc. (A)*, 1736 (1966).
27. F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, 1574 (1967).
28. S. Montelatini, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, 1054 (1968).
29. F. H. Jardine, *Prog. Inorg. Chem.* **28**, 63 (1981).
30. P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Am. Chem. Soc.* **94**, 3240 (1972).
31. J. Halpern and C. S. Wong, *J. Chem. Soc. Chem. Comm.*, 629 (1973).
32. J. Halpern, T. Okamoto, and A. Zakhariev, *J. Mol. Catal.* **2**, 65 (1976).
33. B. R. James, *Homogeneous Hydrogenation* (New York: John Wiley and Sons, 1973).
34. L. Vaska, *J. Am. Chem. Soc.* **88**, 4100 (1966).
35. S. J. LaPlaca and J. A. Ibers, *Acta Cryst.* **18**, 511 (1965).
36. L. Vaska, *Inorg. Nucl. Chem. Lett.* **1**, 89 (1965).
37. D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. (A)*, 2660 (1968).
38. C. O'Connor and G. Wilkinson, *J. Chem. Soc. (A)*, 2665 (1968).
39. M. Yagupsky and G. Wilkinson, *J. Chem. Soc. (A)*, 941 (1970).
40. B. R. James, *Homogeneous Hydrogenation* (New York: John Wiley and Sons, 1973) p. 106.
41. T. S. Janik, M. F. Pyszczyk, and J. D. Atwood, *J. Mol. Catal.* **11**, 33 (1981).
42. P. Sullivan, M. F. Pyszczyk, T. S. Janik, and J. D. Atwood, *Annals of N. Y. Academy of Sciences* **415**, 259 (1983).
43. A. J. Chalk and J. F. Harrod, *Adv. Organomet. Chem.* **6**, 119 (1968).
44. R. L. Pruett, *Adv. Organomet. Chem.* **17**, 1 (1979).
45. I. Wender, S. Metlin, S. Ergun, H. W. Sternberg, and H. Greenfield, *J. Am. Chem. Soc.* **78**, 5401 (1956).
46. R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.* **83**, 4023 (1961).
47. N. H. Alemdarogly, J. L. M. Penniger, and E. Ostay, *Monatschrift für Chemie* **107**, 1153 (1976).
48. M. J. Mirbach, M. F. Mirbach, A. Saus, N. Topalsavoglou, and T. N. Phu, *J. Am. Chem. Soc.* **103**, 7590 (1981).
49. C. K. Brown and G. Wilkinson, *J. Chem. Soc. (A)*, 2753 (1970).
50. R. L. Pruett, *Adv. Organomet. Chem.* **17**, 1 (1979).
51. G. Henrici-Olivé and S. Olivé, *Coordination and Catalysis* (Weinheim: Verlag Chemie, 1977).
52. J. K. Stille and R. Divakaruni, *J. Organomet. Chem.* **169**, 239 (1979).
53. J. E. Backvall, B. Akermarck, and S. O. Ljunggren, *J. Am. Chem. Soc.* **101**, 2411 (1979).
54. W. C. Seidel and C. A. Tolman, *Annals of New York Academy of Sciences* **415**, 201 (1983).
55. T. J. Katz, *Adv. Organomet. Chem.* **16**, 283 (1978).
56. N. Calderon, *Acc. Chem. Res.* **5**, 127 (1972).
57. R. J. Haines and G. J. Leigh, *Chem. Soc. Rev.* **4**, 155 (1975).
58. N. Calderon, J. P. Lawrence, and E. A. Ofstead, *Adv. Organomet. Chem.* **17**, 449 (1979).
59. C. P. Casey, H. E. Tuinstra, and M. C. Sueman, *J. Am. Chem. Soc.* **98**, 608 (1976).
60. R. H. Grubbs, D. D. Carr, C. Hoppin and P. L. Burk, *J. Am. Chem. Soc.* **98**, 3478 (1976).
61. C. P. Casey, L. D. Albin, and T. J. Burkhardt, *J. Am. Chem. Soc.* **99**, 2533 (1977).
62. C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.* **96**, 7808 (1974).
63. A. K. Rappe and W. A. Goddard III, *J. Am. Chem. Soc.* **104**, 448 (1982).
64. R. R. Schrock, *Acc. Chem. Res.* **12**, 98 (1979).

65. J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, and W. J. Youngs, *J. Am. Chem. Soc.* **102**, 4515 (1980).
66. P. L. Watson, *J. Am. Chem. Soc.* **104**, 337 (1982).
67. E. R. Evitt and R. G. Bergman, *J. Am. Chem. Soc.* **101**, 3973 (1979).
68. M. L. H. Green, *Pure and Appl. Chem.* **50**, 27 (1978).
69. K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, *J. Chem. Soc. Chem. Comm.* 604 (1978).
70. D. Forster, *Adv. Organomet. Chem.* **17**, 255 (1978).

PROBLEMS

1. Write the balanced equation for each of the following homogeneously catalyzed reactions:

(a) hydrogenation	(e) olefin metathesis
(b) asymmetric hydrogenation	(f) methanol carbonylation
(c) hydroformylation	(g) polymerization of an alkene
(d) hydrocyanation of 1,3-butadiene	
2. Suggest a catalyst and appropriate reaction conditions for each reaction in Problem 1.
3. Replacing PPh_3 by PBu_3 in $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ causes a loss of catalytic activity. Combining the information from Chapter 5, suggest a reason for this loss of activity.
4. Reaction of diphenylacetylene with Cp_2MoH_2 led to *cis*-1,2-diphenylethylene and $\text{Cp}_2\text{Mo}(\text{PhCCPh})$. Suggest a mechanism. [A. Nakamura and S. Otsuka, *J. Am. Chem. Soc.* **94**, 1886 (1972).]
5. Reaction of Cp_2NbCl_2 with $(n\text{-C}_3\text{H}_7)\text{MgCl}$ gives an 18-electron mononuclear complex that adds one equivalent of CO to form $\text{Cp}_2\text{Nb}(\text{CO})\text{C}_3\text{H}_7$. Present a scheme to account for these observations. [A. H. Klazinga and J. H. Teuben, *J. Organomet. Chem.* **194**, 309 (1980).]
6. Most homogeneous catalysts show a selectivity in hydrogenation of alkenes (Tables 6.2, 6.3, and 6.4). Suggest a reason for this.
7. The complex $\text{H}_3\text{Co}(\text{PPh}_3)_3$ is an active hydrogenation catalyst. Suggest the mechanism for the reaction. (Refer to reaction 6.4 and the relevant discussion.)
8. Asymmetric hydrogenations are accomplished by an optically active center on the metal complex. Suggest at least two different ways to generate an optically active center on a square planar rhodium complex. [See J. M. Brown and D. Parker, *Organometallics* **1**, 950 (1982) and references therein.]
9. Look at the hydroformylation mechanism catalyzed by $\text{HCo}(\text{CO})_4$ (equations 6.35–6.41). Discuss the assumptions made for this mechanism, and account for the formation of the major impurities (alkane, alcohol, etc.).
10. The addition of PBu_3 to a $\text{Co}_2(\text{CO})_8$ hydroformylation mixture leads to a catalyst that is more selective for 1-alkenes to *n*-aldehydes, that produces alcohols, and that is active at more moderate conditions. Account for these observations. [L. H. Slauch and R. D. Mullineaux, *J. Organomet. Chem.* **13**, 469 (1968).]
11. There are several similarities between the mechanisms of alkene hydrogenation

by $\text{CH}_3\text{Co}(\text{CO})_2(\text{P}(\text{OMe})_3)_2$, hydroformylation by $\text{HCo}(\text{CO})_4$, and hydroformylation by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$. Compare and contrast these mechanisms.

12. Explain the evidence that implicates metal alkylidenes (carbenes) in olefin metathesis.
13. Explain in some detail the steric interactions in the metallocyclobutane intermediate that lead to specificity in the metathesis reactions.
14. How does the mechanism suggested for methanol carbonylation account for the observed dependences on the added reagents?

Stereochemical Nonrigidity

Molecules that interchange rapidly between different structures are said to be stereochemically nonrigid. If the conversion(s) leads to a chemically distinguishable species, the process is **isomerization**; if the conversion(s) leads to a chemically indistinguishable configuration, the process is **fluxionality**. The primary technique for studying stereochemically nonrigid molecules is NMR spectroscopy, which is convenient for rates from 10^2 to 10^5 s^{-1} . (See Chapter 1 for a discussion of kinetic studies by NMR.) In this chapter we shall consider three types of stereochemical nonrigidity: coordination number isomerization, "ring-whizzing," or migration of a metal around an unsaturated ring, and rearrangements in metal clusters.

COORDINATION NUMBER ISOMERIZATION

Transition metal complexes of coordination number four to nine have at least two possible geometries.^{1,2} These geometries may interconvert (leading to either isomerization or fluxional behavior) at quite different rates depending on the coordination number.^{1,3} The rearrangement mechanisms have been defined by consideration of solid state structures that lie on the reaction coordinate between two or more distinct geometries.³⁻⁵ Often the rearrangements involve movement along the normal vibrational modes. We shall consider the interconversions for each coordination number separately.

Four-Coordinate Complexes

Four-coordinate complexes, in which the metal contains eight *d*-electrons, may be either square planar or tetrahedral. Platinum and palladium complexes are invariably square planar, but the smaller nickel may be tetrahedral, square planar, or an intermediate along the reaction coordinate between these two primary geometries.^{1,2} Electronic factors (CFSE) favor square planar complexes, but steric interactions favor tetrahedral ones. Our discussion will center on complexes of nickel, for which the energy differences between square planar and tetrahedral are relatively small and interconversions are possible.

The interconversion between tetrahedral and square planar geometries lies along a vibrational mode and involves relatively little molecular motion (Figure 7.1). The small molecular motion required suggests rapid interconversion. However a spin change is also involved since tetrahedral complexes are paramagnetic with two unpaired electrons and square planar complexes are diamagnetic. Thus the interconversion between tetrahedral and square planar complexes is relatively slow and can be conveniently studied.

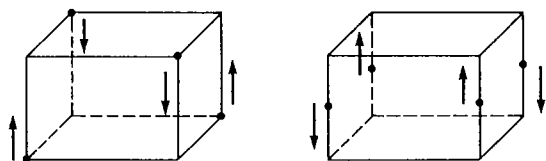


FIGURE 7.1. Molecular motion involved in conversion of tetrahedral to square planar geometry.

Complexes of the formula NiL_2X_2 , where L is a phosphorus donor and X is a halide, have been observed as tetrahedral, as square planar, and as mixtures of the two isomers.^{1,2,6,7} Table 7.1 lists the percentage of tetrahedral isomer for several different complexes.^{6,7} The data indicate that the nature of the ligands on nickel affects the geometry in a similar set of complexes.^{6,7} Many of the data suggest the preference of larger ligands for tetrahedral geometry in which the ligand-ligand interactions are reduced. For $\text{Ni}(\text{PPh}_2\text{R})_2\text{Cl}_2$, as R changes from Me to Et, Pr, and Ph, the structures become 31, 40, 47 and 100% tetrahedral, respectively. The halide dependence also indicates the preference of larger ligands for tetrahedral geometry with 31, 59 and 73% tetrahedral for the chloro, bromo and iodo complexes, respectively. That electronic properties are also important is indicated by the results on *para* substituted phenylphosphines.

The kinetics of these reactions are studied by NMR techniques (as described in Chapter 1). A typical set of data is shown in Figure 7.2 for

TABLE 7.1

Structures of Several NiL_2Cl_2 Complexes Given as the Percentage of Tetrahedral Isomer.

complex	percentage tetrahedral at 0°C
$\text{Ni}(\text{PEt}_3)_2\text{Cl}_2$	0
$\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$	100
$\text{Ni}(\text{PPh}_2\text{Me})_2\text{Cl}_2$	31
$\text{Ni}(\text{PPh}_2\text{Et})_2\text{Cl}_2$	40
$\text{Ni}(\text{PPh}_2\text{Pr})_2\text{Cl}_2$	47
$\text{Ni}[(p\text{-ClC}_6\text{H}_4)_2\text{PMe}]_2\text{Cl}_2$	10
$\text{Ni}[(p\text{-MeC}_6\text{H}_4)_2\text{PMe}]_2\text{Cl}_2$	35
$\text{Ni}(\text{PPh}_2\text{Me})_2\text{Br}_2$	59
$\text{Ni}(\text{PPh}_2\text{Me})_2\text{I}_2$	73

$\text{Ni}(\text{PPh}_2\text{Me})_2\text{Br}_2$.⁷ The resonances for the paramagnetic tetrahedral complex are contact shifted; those for the diamagnetic square planar complex occur in the normal aromatic region. The kinetic parameters for the interconversion of $\text{Ni}(\text{PPh}_2\text{R})_2\text{X}_2$ are shown in Table 7.2.⁷ The rate of isomerization depends on

TABLE 7.2

Rate Constants and Activation Parameters for the Conversion from Tetrahedral to Square Planar Geometry for $\text{Ni}(\text{PPh}_2\text{R})_2\text{X}_2$.

R	X	$k(10^{-5}\text{s}^{-1})$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
Me	Cl	2.6	9	-4
	Br	0.45	9.3	-6.1
	I	29	8.5	-0.6
Et	Cl	9.2	9.0	-1
	Br	1.6	9.0	-4.7
	I	> 10	7.	-5
Pr	Cl	6.6	9.4	-0.6
	Br	1.3	9.8	-2.4
	I	> 10	8	-3

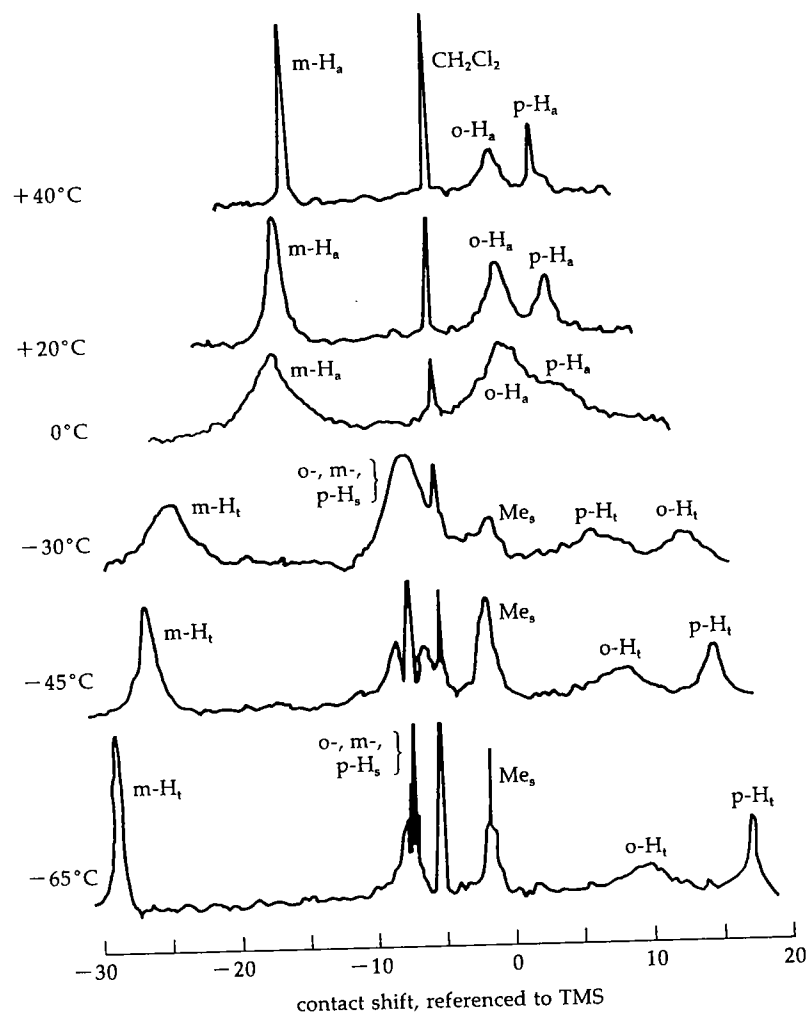


FIGURE 7.2. Proton NMR traces of $[\text{MeP}(\text{Ph})_2]_2\text{NiBr}_2$ in CD_2Cl_2 as a function of temperature. The H_a refer to averaged resonances, the H_t to tetrahedral, and the H_s to square planar. [Reprinted with permission from G. N. LaMar and E. O. Sherman, *J. Am. Chem. Soc.* 92, 2691 (1970). Copyright 1970 American Chemical Society.]

both R and X although not in a readily explainable manner. For fixed R the rate depends on the halide ($\text{Br} < \text{Cl} < \text{I}$); for constant X, the R group dependence is $\text{Me} < \text{Pr} < \text{Et}$. Apparently the factors determining the kinetics are complex and involve a combination of steric and electronic effects. This is in

contrast to the thermodynamics where the preference for tetrahedral ($\text{X} = \text{Cl} < \text{Br} < \text{I}$ and $\text{L} = \text{R}_3\text{P} < \text{ArR}_2\text{P} < \text{Ar}_2\text{RP} < \text{Ar}_3\text{P}$) is clearly understandable in terms of steric effects.

Five-Coordinate Complexes

Five-coordinate rearrangements are important for five-coordinate complexes and for intermediates in dissociative reactions of six-coordinate complexes.⁸⁻¹⁰ Two geometries are observed in five-coordination, trigonal bipyramidal and square pyramidal. Both geometries and the interconversion between them are shown in Figure 7.3. Five-coordinate complexes are usually trigonal bipyramidal; but five-coordinate intermediates generated by dissociation from six-coordinate complexes are often square pyramidal.

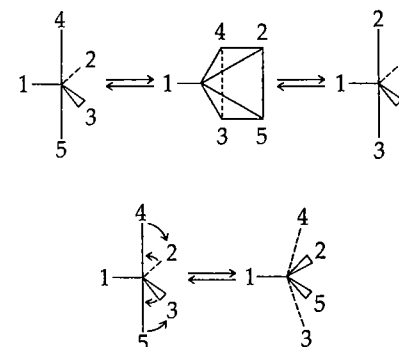


FIGURE 7.3. The interconversion between trigonal bipyramidal and square pyramidal geometries.

For five-coordinate complexes of trigonal bipyramidal geometry there are two symmetry-distinct coordination positions; the three equatorial positions are equivalent (1, 2 and 3 of Figure 7.3) but distinct from the two axial positions (4 and 5 in Figure 7.3). The two different environments should be detectable by experimental measurements. X-ray diffraction experiments do confirm the geometry and show bond differences between the axial and equatorial ligands. NMR studies of molecules such as PF_5 and $\text{Fe}(\text{CO})_5$ (^{19}F and ^{13}C respectively) show only one resonance.⁸⁻¹⁰ This indicates that there is a chemical process that averages the environments of the axial and equatorial positions on the NMR time scale but not on the X-ray time scale.

There are two primary sources of five-coordinate complexes, Group V species and d^8 transition metal complexes. Species of both types undergo rapid intramolecular rearrangements. Since in many cases the exchange can-

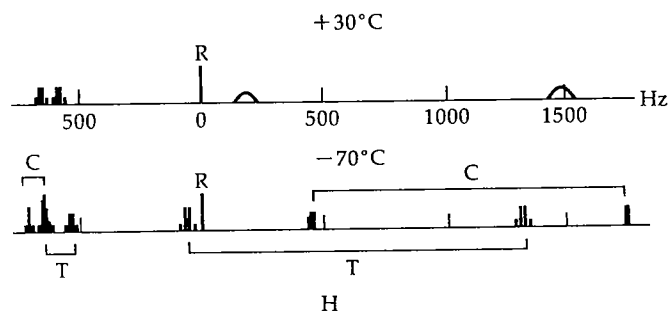


FIGURE 7.4. Fluorine NMR spectra of $\text{CF}_3\text{Co}(\text{CO})_3(\text{PF}_3)$ at 30° and -70° (reference, CFCl_3). [Reprinted with permission from C. A. Udovich and R. J. Clark, *J. Am. Chem. Soc.* 91, 526 (1969). Copyright 1969 American Chemical Society.]

not be stopped (on the NMR time scale) at temperatures as low as -150°C , the activation barrier must be quite low (see Chapter 1). A mechanism involving pseudorotation along the normal coordinates as illustrated in the bottom of Figure 7.3 has been suggested.¹¹ The procedure may be viewed as holding one equatorial position of the trigonal bipyramid fixed and bending the other two equatorial positions apart. The two axial positions bend away from the one stationary equatorial site, leading to the square pyramid. The reaction may proceed to a new trigonal bipyramidal configuration or return to the starting configuration.

For many five-coordinate complexes the exchange cannot be stopped on the NMR time scale.⁸⁻¹¹ One of the first that was investigated was $\text{CF}_3\text{Co}(\text{CO})_3\text{PF}_3$.¹² The room temperature ^{19}F NMR spectrum shows an averaged environment for the complex, as shown schematically in Figure 7.4 where the methyl fluorines are downfield from the reference and the PF_3 resonances are broad and upfield. Lowering the temperature to -70°C stops the exchange and leads to the two isomers shown in Figure 7.5.¹²

A number of HML_4 complexes have also been investigated; the temperature-dependent NMR spectra are shown in Figure 7.6 for $\text{HRh}(\text{P}(\text{OEt})_3)_4$.¹³

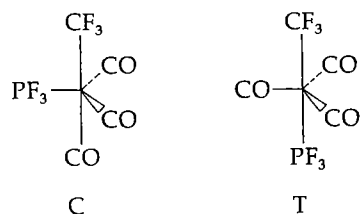


FIGURE 7.5. Suggested structures of the two low-temperature isomers of $\text{CF}_3\text{Co}(\text{CO})_3\text{PF}_3$.

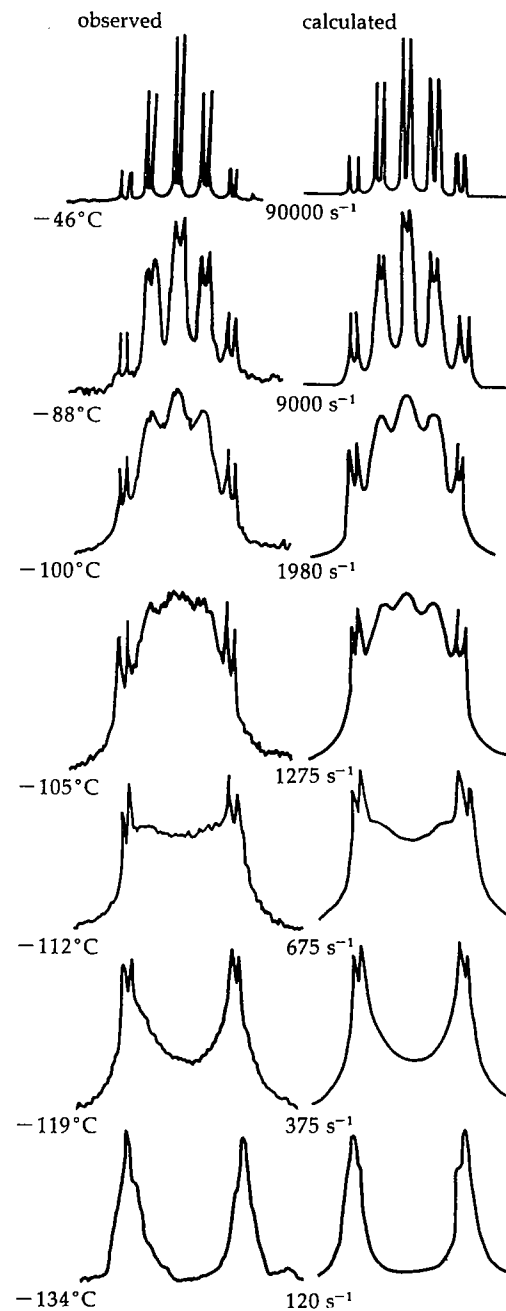


FIGURE 7.6. Observed and calculated hydride region proton (90 MHz) NMR spectra for $\text{HRh}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$ in CHClF_2 . [Reprinted with permission from P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Am. Chem. Soc.* 94, 5271 (1972). Copyright 1972 American Chemical Society.]

The -134°C spectrum does not represent a low-temperature limit spectrum but does indicate a C_{3v} ground state. The calculated lineshapes shown in Figure 7.6 were obtained assuming a first order low-temperature limit corresponding to a C_{3v} geometry with the NMR parameters $J_{\text{HRh}} = 9$ Hz, $J_{\text{HP}_{\text{ax}}} = 152$ Hz, and $J_{\text{HP}_{\text{eq}}} = 5$ Hz.¹³ The kinetic parameters ($\Delta H^{\ddagger} = 5.2$ kcal/mole and $\Delta S^{\ddagger} = -11.9$ eu) were also obtained. By similar techniques the activation barriers of the five coordinate HML_4 species shown in Table 7.3 were obtained.¹³ These data illustrate one feature that is commonly observed: The rate of intramolecular interchange is first row $>$ second row $>$ third row. These hydrido complexes, HML_4 , are best described as a tetrahedral arrangement of phosphorus ligands with the hydride capping a tetrahedral face, and a hydride tunneling mechanism is favored.¹³

TABLE 7.3

Activation Barriers for a Series of HML_4 Complexes Obtained from Dynamic NMR Investigations.

compound	$\Delta G^{\ddagger}$ (kcal/mole)
$\text{HRh}[\text{P}(\text{OEt})_3]_4$	7.25
$\text{HIr}(\text{CO})_2(\text{PPh}_3)_2$	8.4
$\text{Fe}(\text{PF}_3)_5$	<5
$\text{Ru}(\text{PF}_3)_5$	<5
$\text{Os}(\text{PF}_3)_5$	<5
$\text{HFe}(\text{PF}_3)_4^-$	<5
$\text{HRu}(\text{PF}_3)_4^-$	7.0
$\text{HOs}(\text{PF}_3)_4^-$	8.0
$\text{HCo}(\text{PF}_3)_4$	5.5
$\text{HRh}(\text{PF}_3)_4$	9.0
$\text{HIr}(\text{PF}_3)_4$	10.0

In cases where steric interactions may be involved, $\text{M}[\text{P}(\text{OMe})_3]_5$, the order of dependence on the metal is altered as shown by the data in Table 7.4.¹⁴ The ruthenium complex has the lowest activation barrier in contrast to the trends shown in Table 7.3 where steric interactions are not as important. The steric interaction is shown nicely by the increase in activation barrier for $\text{Fe}[\text{P}(\text{OEt})_3]_5$ over that of $\text{Fe}[\text{P}(\text{OMe})_3]_5$.

The rate of exchange in $\text{Fe}(\text{CO})_5$ is too rapid to be investigated directly by NMR. However the exchange frequency was calculated from time-averaged chemical shifts and weighting factors obtained from infrared data.¹⁵ The

TABLE 7.4

Activation Parameters for Intramolecular Rearrangement in ML_5 Systems.

complex	$\Delta G^{\ddagger}$
$\text{Fe}[\text{P}(\text{OMe})_3]_5$	8.8
$\text{Ru}[\text{P}(\text{OMe})_3]_5$	7.2
$\text{Os}[\text{P}(\text{OMe})_3]_5$	7.6
$\text{Fe}[\text{P}(\text{OEt})_3]_5$	11.3

value determined, $1.1 \times 10^{10} \text{ s}^{-1}$, is very rapid and suggests an exchange mechanism based on normal vibrational modes.

Most of the studies of five-coordinate complexes have centered on 18-electron species because these are readily accessible. A few studies have been accomplished on intermediates generated by ligand dissociation from six-coordinate complexes. For these intermediates the important question is whether the intermediate exists long enough to undergo rearrangement. The best estimate of the lifetime for an intermediate from ligand dissociation is 10^{-5} s. This is about the rate observed for intramolecular rearrangement in 18-electron five-coordinate complexes. As discussed in Chapter 4, CO dissociation from $\text{Mn}(\text{CO})_5\text{Br}$ leads to $\text{Mn}(\text{CO})_4\text{Br}$, which does undergo intramolecular rearrangement.¹⁶ This is in contrast to $\text{Mo}(\text{CO})_4\text{PPh}_3$, which apparently is rigid.¹⁷ The only conclusion possible for 16-electron five-coordinate complexes is that one should be aware of the possibility for intramolecular rearrangement in intermediates generated by dissociation from six-coordinate complexes. Too little information exists to make further generalizations at this point.

Six-Coordinate Complexes

Six-coordinate complexes differ from four-coordinate and five-coordinate complexes in that they have one predominant isomer.^{1,2} Complexes that are octahedral do not rearrange to trigonal prismatic species with any finite lifetime. The reactions that we shall consider are isomerization and racemization of octahedral complexes. Often these processes occur by dissociation of the ligands from an octahedron. Because this process is not distinct from ligand substitution as discussed in Chapter 3, we shall not be concerned with it here. The reactions to be considered in this section involve rearrangement without complete dissociation of a ligand from the coordination sphere. Two types of mechanism will be considered, one involving dissociation of one end

of a chelating ligand and the second involving twists of the intact octahedral complex. In both cases the most informative examples involve tris-chelate complexes that are substitutionally inert.¹⁸⁻²⁰

The bond-rupture mechanism involves dissociation of one end of a chelate ligand leading to a five-coordinate intermediate followed by reattachment of the chelate. The five-coordinate intermediate may be either a trigonal bipyramid or a square pyramid, and it may be either rigid or fluxional. These possibilities can lead to racemization for a symmetrical chelate or to racemization and isomerization for an unsymmetrical one. The case for an unsymmetrical chelate is shown in Figure 7.7. The analysis is further complicated by the possibility of mixtures of intermediates.

The twist mechanism can be considered as a rotation of one trigonal face of an octahedron while the opposite face remains in its original position.¹⁸ Two possibilities are shown in Figure 7.8. The rotation about the real C_3 axis, which leads to inversion of configuration without isomerization, is called a trigonal twist. The twist mechanisms can be thought of as

octahedral $\rightleftharpoons$ [trigonal prismatic] $\rightleftharpoons$ octahedral

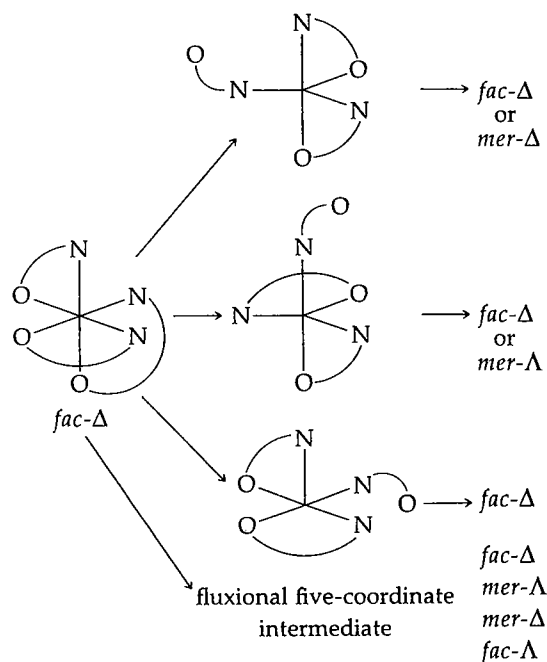


FIGURE 7.7. Possible isomerizations and racemization of a facial unsymmetrical tris-chelate complex undergoing bond rupture.

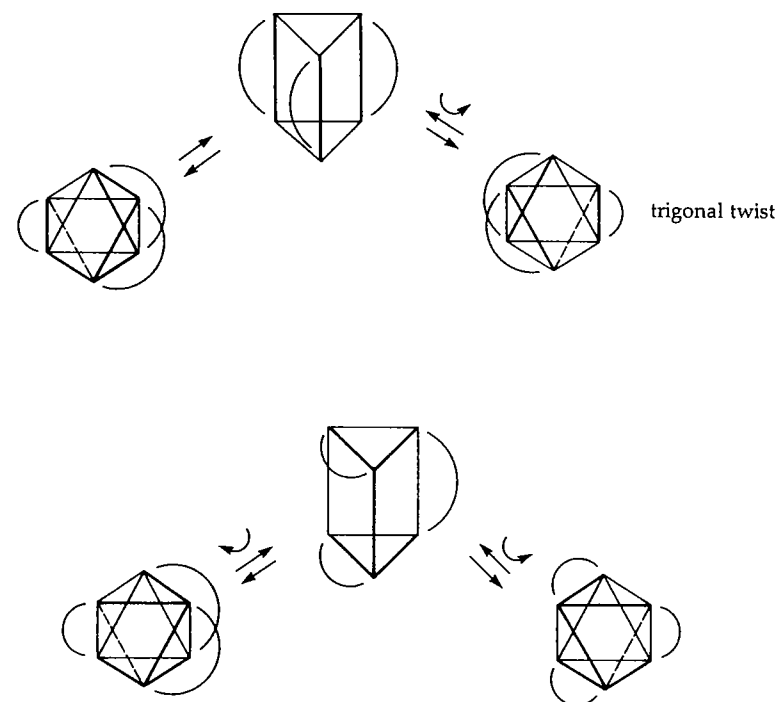
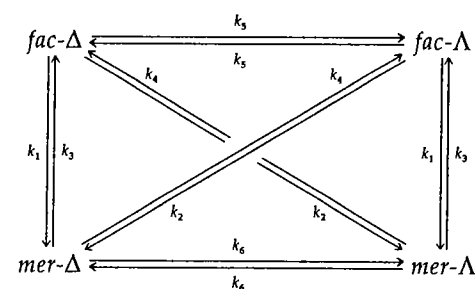


FIGURE 7.8. Possible twist mechanisms in isomerization and racemization of tris-chelate complexes. [Based on J. C. Bailor, Jr., *J. Inorg. Nucl. Chem.* 8, 165 (1958).]

reactions in which the trigonal prismatic structure represents the transition state.¹⁸

Sorting out the different intramolecular rearrangements for complexes is not simple.¹⁸⁻²⁰ The isomerization and racemization of unsymmetrical tris-chelate complexes can be described in general for the four possible isomers shown in Figure 7.9.²⁰



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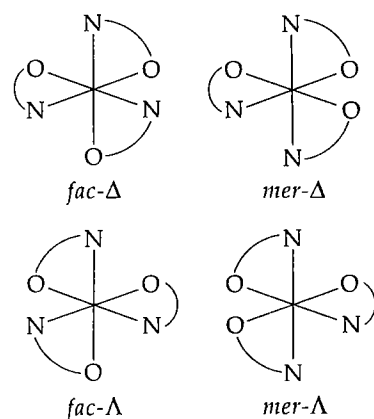


FIGURE 7.9. Four possible isomers of unsymmetrical tris-chelate complexes.

The rate constants have been evaluated for two Co(III) complexes, tris(*S*-methylhexane-2,4-dionato)cobalt(III), Co(mhd)_3 , and tris(benzoylacetate)cobalt(III), Co(bzac)_3 (Table 7.5).²¹⁻²² The data show differences for the *cis* and *trans* isomers, the *cis* isomers undergoing primarily isomerization and inversion ($k_2 \gg k_1, k_5$) and the *trans* isomer undergoing inversion and inversion with isomerization at comparable rates ($k_6 > k_4 \gg k_3$). These rate data cannot readily be accommodated into one mechanistic path. It has been concluded on the basis of these rate constants that Co(mhd)_3 follows a bond-rupture mechanism primarily through a trigonal bipyramidal transition state with the unidentate chelate occupying an axial site. However, some of the

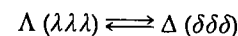
TABLE 7.5

Rate Constants for Isomerization and Racemization of Two Unsymmetrical Tris-chelate Complexes. The Rate Constants Are as Defined in Scheme 7.1.

$k(10^4\text{s}^{-1})$	Co(mhd)_3	Co(bzac)_3
k_1	0.11	0.02
k_2	0.96	1.81
k_3	0.05	0.01
k_4	0.46	0.67
k_5	~0	0.44
k_6	0.86	1.29

transition states are trigonal bipyramidal with the unidentate chelate in an equatorial site (10%) and some are square pyramidal with the unidentate chelate in the axial site (20%).²⁰ The other complex Co(bzac)_3 could be accommodated equally well by bond rupture with 80% axially substituted trigonal bipyramidal and 20% axially substituted square pyramidal intermediate and by a twist mechanism with 20% trigonal twist.²⁰ The best way to differentiate between the two mechanisms is by comparing rates and activation parameters for the isomerization (racemization) to those for dissociation of the chelate. The oxalate complex of Rh^{3+} , Rh(ox)_3^{3-} , illustrates this comparison. The similarity in activation parameters for aquation, for ^{18}O exchange of the bound oxygen of oxalate, and for racemization strongly suggests that bond rupture is the mechanism. The comparison is shown in Table 7.6.²⁰ The activation parameters indicate a similar rate-determining step for the three reactions, probably a bond rupture. Bond rupture must be the mechanism for the exchange of the coordinated oxygen of oxalate for free ^{18}O , and it can be involved in the replacement of oxalate (aquation). The comparison suggests that racemization also occurs by bond rupture.

Racemization of Ni(en)_3^{2+} was investigated



and found to occur at a rate of $5.5 \times 10^3\text{s}^{-1}$ ($\Delta G^\ddagger = 15.7$ kcal/mole) at 100°C .²⁰ Comparison to *N,N'*-dimethylethylenediamine, where bond rupture would lead to an interconversion of the *dl* and meso isomers that is not observed, suggests that the racemization occurs by a twist mechanism.

Intramolecular racemization and isomerization of octahedral complexes occur relatively slowly either by dissociation to five-coordinate intermediates or by a twist mechanism (rotation of one octahedral face with respect to the other).

The complex $\text{H}_2\text{Fe(P(OEt)}_3)_4$ has been investigated by variable-tempera-

TABLE 7.6

Comparison of Rate Data for Three Reactions of Rh(ox)_3^{3-} .

reaction	$k_{\text{obs}}(10^6\text{s}^{-1})$	$\Delta H^\ddagger(\text{kcal/mole})$	$\Delta S^\ddagger(\text{eu})$
^{18}O exchange ^a	14.7	23.4	-6.3
aquation	0.9	25.5	-7.8
racemization	19.7	23.3	-8.2

^a This is exchange of the coordinated oxygen on oxalate for free ^{18}O .

ture NMR.²³ The changes in the spectrum with temperature are shown in Figure 7.10. The high-temperature spectrum (68°C) clearly shows the equivalence of the phosphorus nuclei; the low-temperature spectrum indicates the *cis* stereochemistry of the rigid molecule. A number of mechanisms including twists were investigated, but the only mechanism giving satisfactory agree-

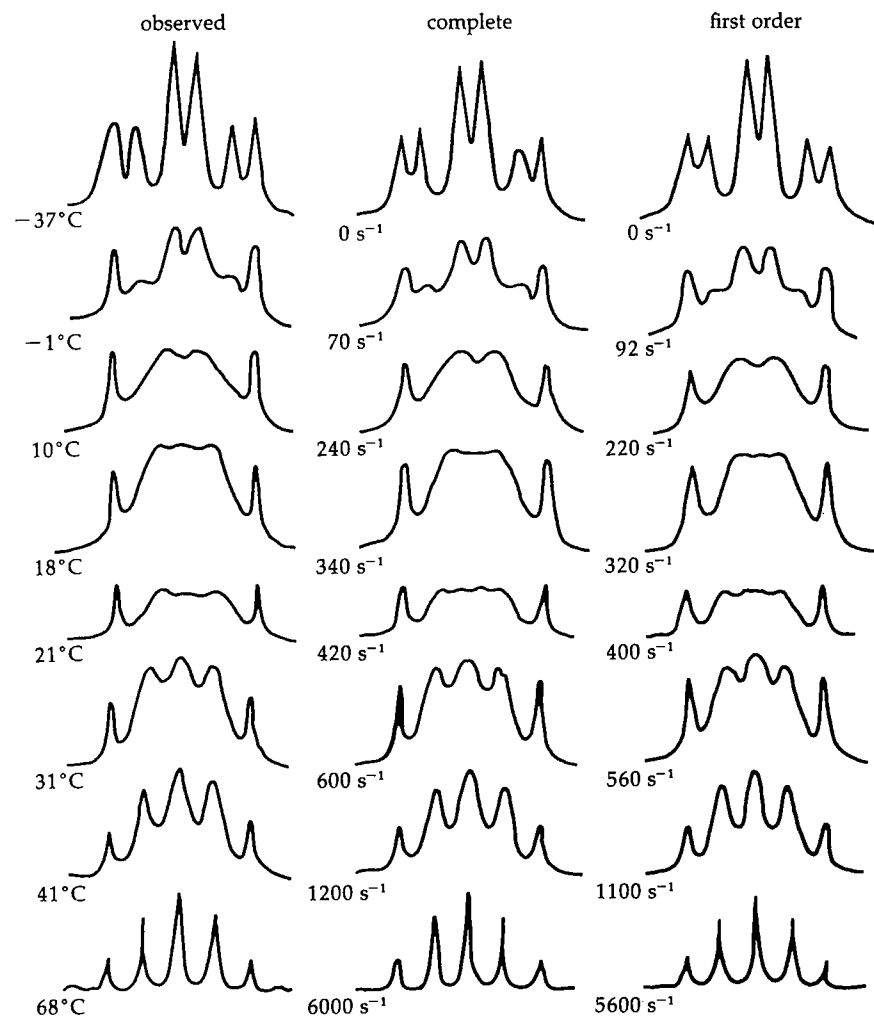


FIGURE 7.10. Calculated and observed NMR spectra of $\text{H}_2\text{Fe}[\text{P}(\text{OEt})_3]_4$ at various temperatures. [Reprinted with permission from P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Am. Chem. Soc.* **93**, 4701 (1971). Copyright 1971 American Chemical Society.]

ment involves a hydrogen migrating from one face of the pseudotetrahedral arrangement to another.²³ It is significant that the octahedral complex undergoes rearrangement with a substantially higher barrier (13.7 kcal/mole) than HMP_4 complexes (Table 7.3). This can also be seen in the higher temperature required for the fast-exchange limit.

Seven-Coordinate Complexes

Seven-coordinate complexes are not often observed, but they are of considerable interest as intermediates in associative reactions of six-coordinate complexes and in dissociative reactions of eight-coordinate complexes.^{1,2} Three geometries are commonly found, a pentagonal bipyramid derived from the octahedral arrangement by addition to an edge, a capped octahedron with the seventh ligand occupying a face position of an octahedron, and a capped trigonal prism with a square face capped.²⁴ These possibilities are shown in Figure 7.11. The energy differences between these geometries are small as only minor movement is required to interconvert (Figure 7.12). Calculations show barriers to interconversion between these three isomers of 0–4 kcal/mole.²⁴ Values for several complexes are shown in Table 7.7. Thus, under most experimental conditions seven-coordinate complexes are stereochemically nonrigid.

TABLE 7.7

Calculated Relative Values of the Energy of the Pentagonal Bipyramid, Capped Octahedron, and Capped Trigonal Prism for d^4 -Configurations.

geometry	MCl_7	$\text{M}(\text{CO})_7$
pentagonal bipyramid	0	0
capped octahedron	1	5
capped trigonal prism	2	4

The chromium complex $\text{Cr}[\text{P}(\text{OMe})_3]_5\text{H}_2$ has a pentagonal bipyramidal structure with the two hydrogens in the pentagonal plane as shown by ^{31}P NMR at -130°C . The high-temperature limit spectra show a triplet for the ^{31}P and a sextet for the ^1H . Detailed analysis of the mechanism for the intramolecular exchange was not offered, but a scheme involving simultaneous exchange of two axial phosphorus ligands with two equatorial ligands would be consistent with the variable-temperature NMR.²⁵

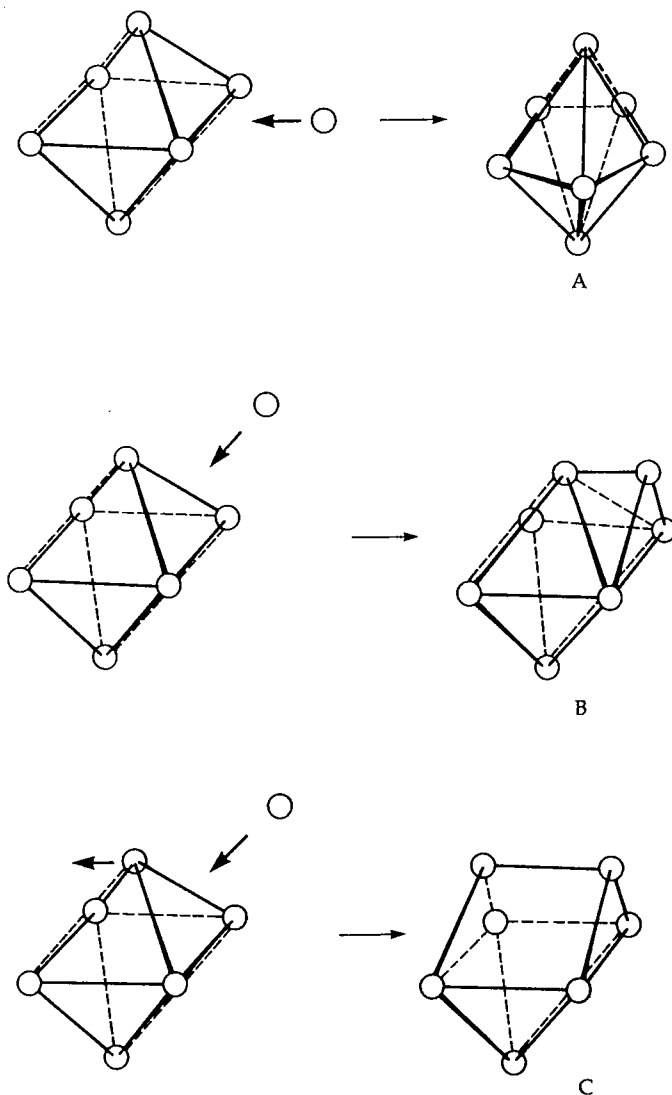


FIGURE 7.11. Seven-coordinate geometries as derived from an octahedron.

The reaction dynamics of bis[1,2-bis(dimethylphosphino)ethane]tricarbonyltitanium, $\text{Ti}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2(\text{CO})_3$, have been investigated by variable-temperature NMR.²⁶ The structure of this analogue of $\text{Ti}(\text{CO})_7$ was shown to be a capped octahedron (structure B in Figure 7.11) in which a CO is

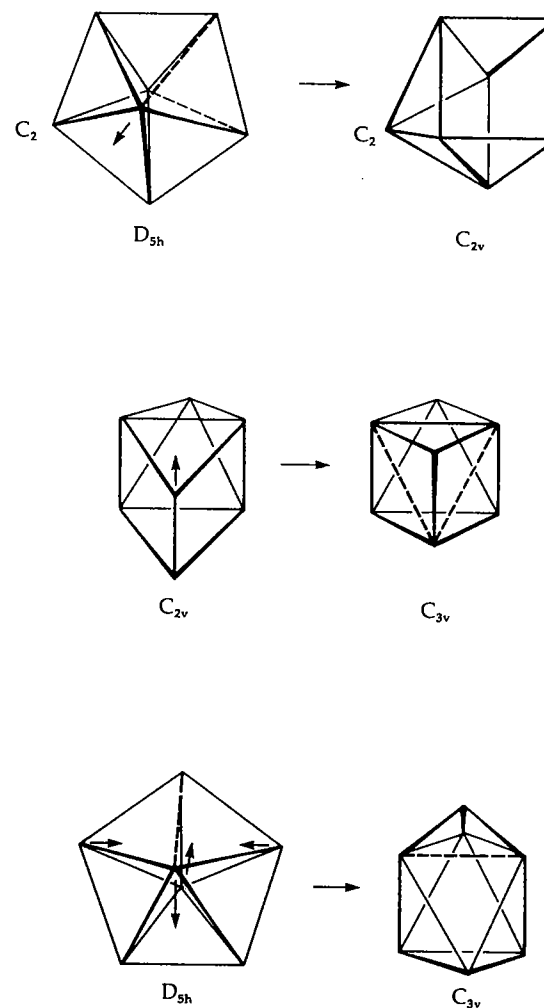


FIGURE 7.12. Rearrangements of the idealized seven-coordinate geometries. [Based on R. Hoffman, B. F. Beier, E. L. Muetterties and A. R. Rossi, *Inorg. Chem.* 16, 311 (1977).]

the capping group. Both ^{13}C and ^{31}P spectra were investigated at variable temperatures, and the exchange was stopped at -115°C where the ^{31}P spectrum showed four distinct, equally intense resonances. This is one of the few seven-coordinate complexes in which the exchange can be stopped and investigated. The change in the resonances as the temperature was raised to

-60° allowed determination of the activation parameters for the dynamic behavior ($\Delta G^\ddagger = 7.8$ kcal/mole; $\Delta H^\ddagger = 8.6$ kcal/mole; $\Delta S^\ddagger = 4$ eu).²⁶ A trigonal twist of the face of the octahedron occupied by three phosphorus ligands was suggested as the simplest mechanism consistent with the NMR data.

Eight-Coordinate Complexes

Eight-coordinate complexes are commonly observed for the high oxidation state (+4, +5) of the early transition metals.^{1,2} Two geometrical forms are observed, the square antiprism and the dodecahedron (Figure 7.13). Each of these structures can be readily derived from a cube, the square antiprism by rotating one face by 45° relative to the opposite face and the dodecahedron by closing the cube along opposite faces. Conversion between the two occurs relatively rapidly along vibrational modes.²⁷ A possible scheme is shown in Figure 7.14. The $\text{Mo}(\text{CN})_8^{4-}$ complex shows a dodecahedral arrangement of cyanides around molybdenum that would give two different environments for the two CN^- groups. In solution only one ^{13}C NMR signal is seen. This is most readily explained by a rapid equilibration as shown in Figure 7.14.²⁷

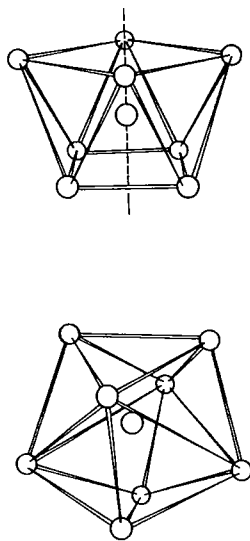


FIGURE 7.13. The square antiprism and the dodecahedron for eight-coordinate complexes. [Reprinted with permission from S. J. Lippard, *Progress Inorganic Chemistry* 8, 115 (1976). Copyright 1976 S. J. Lippard.]

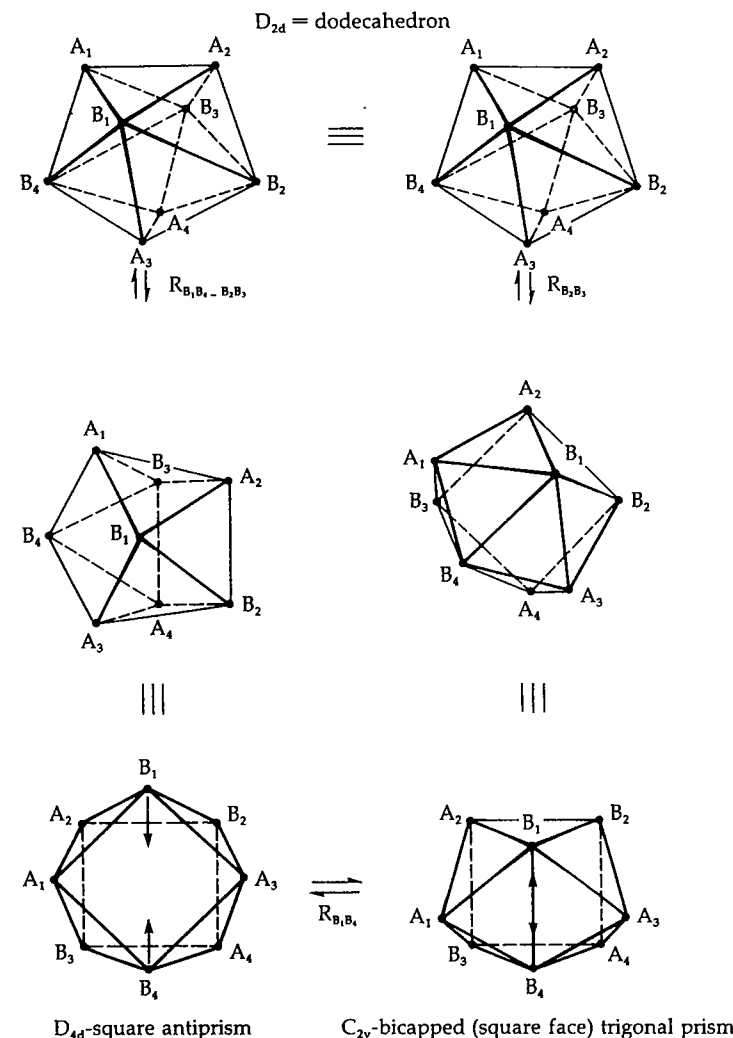


FIGURE 7.14. Rearrangement in eight-coordination. [Based on E. L. Muetterties, *Inorg. Chem.* 4, 769 (1965).]

Nine-Coordinate Complexes

Nine-coordinate complexes have not been very extensively investigated.^{1,2} The geometry observed for almost all nine-coordinate complexes is the symmetrically tricapped trigonal prism.²⁸ This geometry is related by a stretching motion to the monocapped square antiprism. The rearrangement is

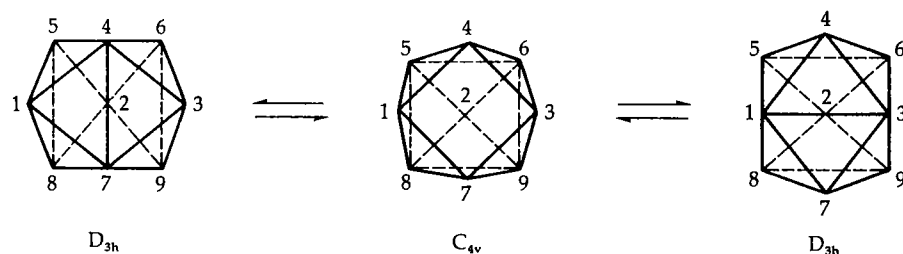


FIGURE 7.15. The suggested intramolecular path for stereochemical nonrigidity in nine-coordinate complexes. [Reprinted with permission from L. J. Guggenberger and E. L. Muetterties, *J. Am. Chem. Soc.* **98**, 7221 (1976). Copyright 1976 American Chemical Society.]

shown in Figure 7.15. The barrier to this intramolecular rearrangement is calculated to be very small, but experimental data demonstrating the rearrangement have not been presented.²⁸

METAL MIGRATION IN AN UNSATURATED RING—RING WHIZZERS

When a metal coordinates to a ring with more than one equivalent position, characterization by NMR often indicates an equilibration. The cyclopentadienyl ring, $\eta^1\text{-C}_5\text{H}_5$, serves as an example (Figure 7.16). Only one resonance is seen in the proton NMR despite the existence of three nonequivalent sites in the static structure.²⁸ The process that equilibrates the three sites is metal migration around the ring, and complexes that show such behavior are commonly termed "ring whizzers." We shall examine several examples that illustrate different ring whizzers.

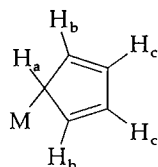
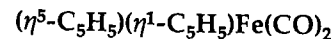
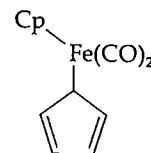


FIGURE 7.16. Nonequivalent hydrogens in a static structure on an $\eta^1\text{-C}_5\text{H}_5$ complex.



One of the first complexes that demonstrated fluxional behavior for a ring complex was $(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$,



which shows two singlet resonances of equal intensity at room temperature.²⁹ The NMR spectra at several temperatures are shown in Figure 7.17. At -80°C the spectrum shows a sharp single resonance from $\eta^5\text{-C}_5\text{H}_5$ and a singlet from the unique hydrogen on $\eta^1\text{-C}_5\text{H}_5$. The assignment of the two multiplets is crucial to the mechanistic interpretation; the downfield signal is assigned to the H_b hydrogens as defined in Figure 7.16.²⁹ As the spectra in Figure 7.17 show, the collapse of the low-temperature spectrum is unsymmetrical (the H_b hydrogens are exchanging more rapidly than H_c 's). This rules out a random process or any process in which all sites become equivalent and limits the reasonable mechanistic possibilities to a 1,2 metal migration or a 1,3

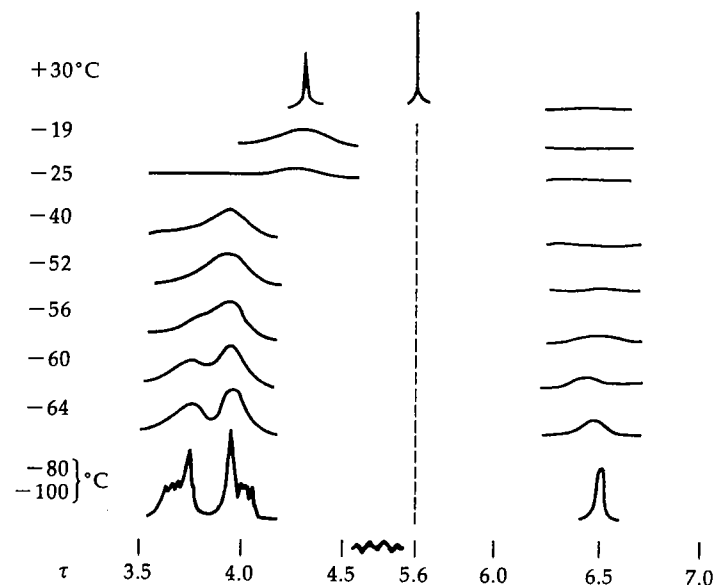


FIGURE 7.17. Variable-temperature proton NMR spectra of $(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ in CS_2 . [Reprinted with permission from F. A. Cotton, *Acc. Chem. Res.* **1**, 257 (1968). Copyright 1968 American Chemical Society.]

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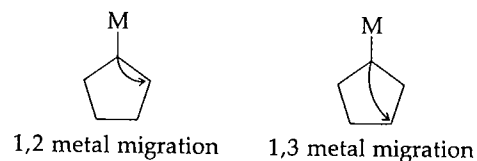
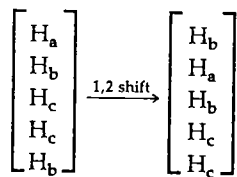
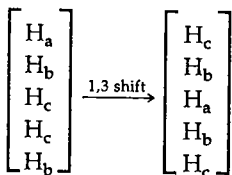


FIGURE 7.18. The definition of 1,2 and 1,3 metal migration for fluxional isomerism in $\eta^1\text{-C}_5\text{H}_5$ complexes.

metal migration as shown in Figure 7.18. The effect of a 1,2 shift on the hydrogen positions can be illustrated as shown below.



With the 1,2 shift both H_b 's are equilibrated in a single migration while only one H_c is equilibrated. Thus the H_b would exchange more rapidly than H_c as observed in the NMR spectrum. The 1,3 shift would lead to more rapid equilibration of H_c than H_b .



The 1,2 shift is thus demonstrated for the metal migration in the η^1 -cyclopentadienyl ring of $(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$.²⁹



Cyclooctatetraene complexes also allow for metal migration around the unsaturated ring. The complex $(\eta^4\text{-C}_8\text{H}_8)\text{Ru}(\text{CO})_3$ (Figure 7.19) serves as an example.^{29,30} The NMR spectrum at low temperature (-147°C) shows four distinct resonances of equal intensity, but at room temperature there is only one sharp resonance, indicating complete equilibration.³⁰ The spectra at different temperatures are shown in Figure 7.20. An unsymmetrical collapse like that of $(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ is observed. After assignment of the spectra and interpretation of the possibilities, a 1,2 shift was again suggested.

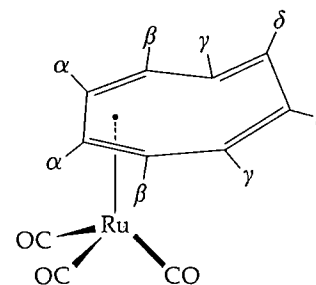


FIGURE 7.19. Static structure of $(\eta^4\text{-C}_8\text{H}_8)\text{Ru}(\text{CO})_3$ showing the four different hydrogen positions. [Reprinted with permission from F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *J. Am. Chem. Soc.* 91, 6598 (1969). Copyright 1969 American Chemical Society.]

The activation energy of 9.4 kcal/mol indicates the ease of metal migration along the unsaturated C_8H_8 ring.

Cycloheptatriene Complexes

The predominant mechanism for metal migration in unsaturated ring systems is the 1,2 shift. This mechanism is observed for $\eta^1\text{-C}_5\text{H}_5$ complexes, $(\eta^1\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5$, $\eta^3\text{-C}_7\text{H}_7$ complexes, $\eta^4\text{-C}_6\text{R}_6$ rhodium complexes, $\eta^4\text{-C}_8\text{H}_8$ complexes, $\eta^5\text{-C}_7\text{H}_7$ complexes, and some $\eta^6\text{-C}_8\text{H}_4\text{Me}_4$ complexes. In this section we shall examine two cycloheptatrienyl complexes in which 1,3 and 1,4 shifts are suggested.^{31,32} For a cycloheptatriene complex such as $(\eta^4\text{-C}_7\text{H}_8)\text{Fe}(\text{CO})_3$, a simple 1,2 shift is not possible and the proton NMR spectrum shows no line broadening up to 100°C . However a high energy process does exchange the environments.³¹ Two possible mechanisms are shown in Figure 7.21. The 1,2 shift must be accompanied by ring closure to the norcaradiene intermediate. The alternative is a 1,3 shift through an unsaturated intermediate. The mechanism of rearrangement was investigated by spin saturation transfer of the proton NMR.³¹ A number of mechanisms can be ruled out based on the lack of scrambling of the exo and endo substituents in the d_7 complex. The free energy of activation is 22.3 kcal/mol.³¹ The selective nature of the averaging process was only consistent with a 1,3 shift. The results of an extended Hückel molecular orbital calculation suggested an η^2 transition state/intermediate with the iron shifted toward the interior of the cycloheptatriene.³¹

The rearrangement of the cycloheptatrienyl complex $\text{CpRu}(\text{CO})_2\text{-(}\eta^1\text{-C}_7\text{H}_7\text{)}$ has been interpreted in terms of two concurrent modes, a 1,2 shift

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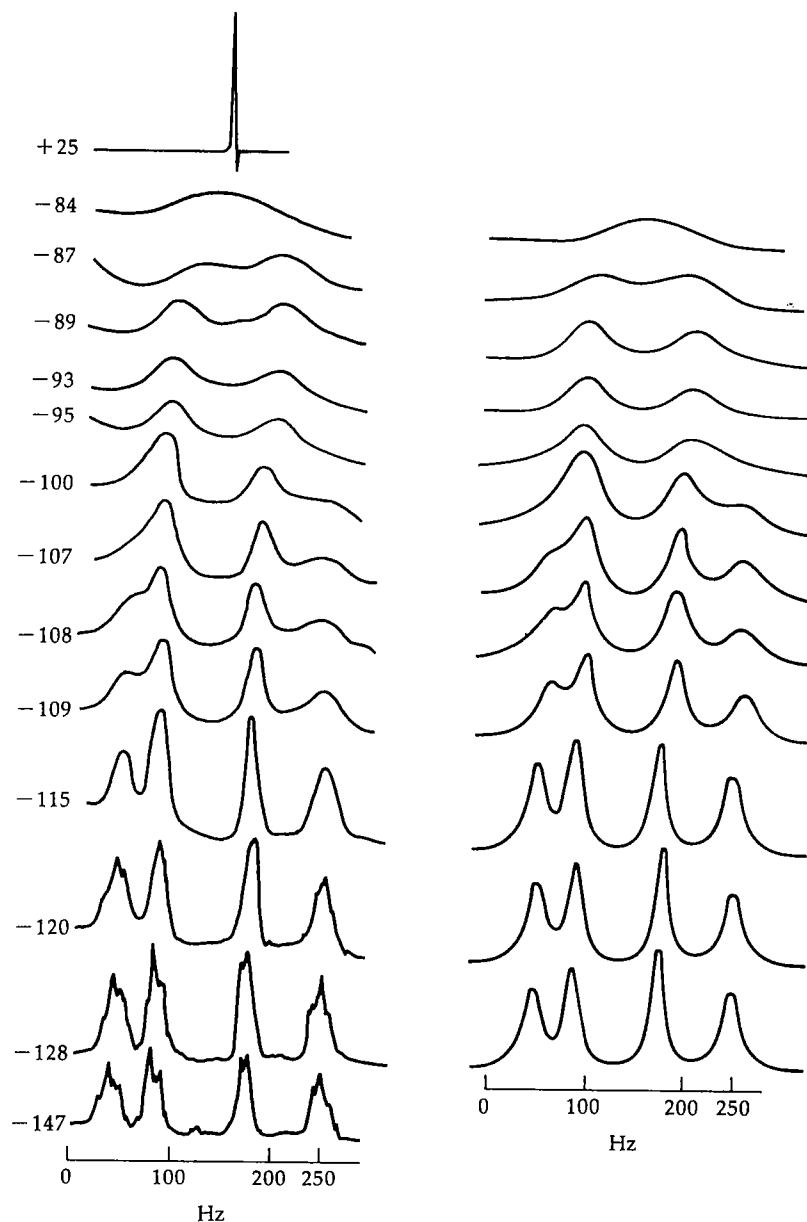


FIGURE 7.20. The variable-temperature NMR spectra of $(\eta^4\text{-C}_8\text{H}_8)\text{Ru}(\text{CO})_3$ with computer simulation for a 1,2 shift at the right. [Reprinted with permission from F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *J. Am. Chem. Soc.* 91, 6598 (1969). Copyright 1969 American Chemical Society.]

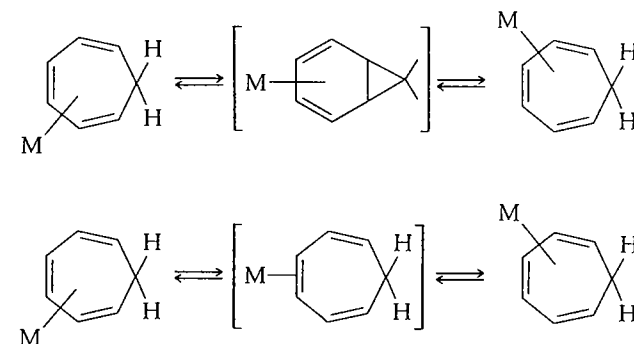


FIGURE 7.21. Possible mechanisms for rearrangement of cycloheptatriene complexes.

and a 1,4 shift.³² The structure of $\text{CpRu}(\text{CO})_2(\eta^1\text{-C}_7\text{H}_7)$ is shown in Figure 7.22. The spin saturation transfer technique was used to explore the possible migration pathways.³² Rate constants for the different possibilities were calculated from the ^{13}C NMR data; for the 1,2 shift $k = 1.7 \times 10^{-2} \text{ s}^{-1}$, for the 1,3 shift $k \approx 0$, and for the 1,4 shift $k = 0.3 \text{ s}^{-1}$.³² This suggests that the 1,2 and 1,4 shifts are of comparable energy ($\Delta G^\ddagger \approx 19 \text{ kcal/mol}$).

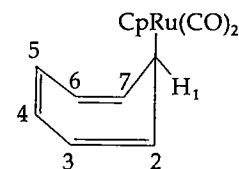


FIGURE 7.22. The structure of $\text{CpRu}(\text{CO})_2(\eta^1\text{-C}_7\text{H}_7)$ with the numbering scheme.

An allene complex (this is not formally an unsaturated ring system) also undergoes fluxional behavior.³³ The structure of $(\eta^2\text{-Me}_2\text{C}=\text{C}=\text{CMe}_2)\text{Fe}(\text{CO})_4$ is shown in Figure 7.23. The proton NMR spectrum at room temperature shows only one resonance although at low temperature the spectrum is resolved.³³ The rearrangement must involve migration of the iron from coordination to one double bond to coordination to the orthogonal double bond. This is illustrated in Figure 7.23. The activation energy for the process was determined as 9.0 kcal.³³

The examples illustrate the ease of metal migration in unsaturated systems where there are equivalent structural forms. The most common mechanism is a 1,2 shift, but others may be possible, especially if the 1,2 shift is energetically unfavorable. The metal remains coordinated during the process

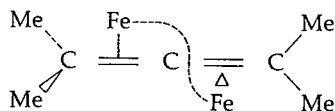


FIGURE 7.23. The structure of $(\eta^2\text{-Me}_2\text{C}=\text{C}=\text{CMe}_2)\text{Fe}(\text{CO})_4$ and migration in its fluxional behavior.³³

and must migrate along the electron density from one energy minimum to another.

METAL-METAL BONDED SYSTEMS

In systems that involve more than one metal center, the exchange of ligands between metal centers is commonly observed. This type of stereochemical nonrigidity has been investigated extensively as a possible model to surface mobility of chemisorbed species.³⁴ The fluxional behavior of metal carbonyl clusters is the most frequently studied of the metal-metal bonded complexes. The bonding of carbon monoxide in metal clusters may take different forms as shown in Figure 7.24. These structures are models for carbon monoxide mobility on clusters and for the rearrangements of other ligands such as nitric oxide, isocyanides, and hydrides. We shall examine the fluxional processes in a few cluster compounds.

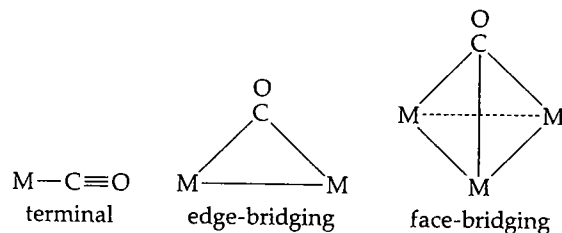


FIGURE 7.24. Bonding modes of terminal, edge-bridging and face-bridging carbon monoxide in metal clusters.

Metal Carbonyl Dimers

Dimers are not clusters but the intramolecular rearrangements of dimers provide data on exchange of ligands between two metal centers. For $\text{Co}_2(\text{CO})_8$ in solution, infrared spectroscopy reveals two forms, one bridged and one nonbridged (Figure 7.25). This molecule is fluxional on the NMR

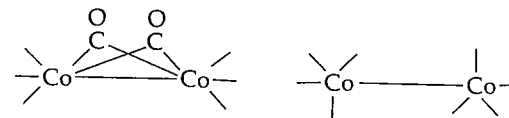


FIGURE 7.25. The solution structures of $\text{Co}_2(\text{CO})_8$.

time scale below -90°C , but the mechanism has not been established.³⁴ Conversion of the bridged isomer to the unbridged and back would be logical steps.

The iron dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ has been investigated extensively by a number of techniques; of these NMR is the most informative.^{34,35} The complex exhibits only one resonance in the ^1H spectrum down to -48°C , but the peak splits to two singlets at lower temperatures.^{35,36} These two singlets are assigned to *cis* and *trans* isomers as shown in Figure 7.26. The NMR spectra at different temperatures are shown in Figure 7.27. Note the slight preference for the *cis* isomer. The interconversion between the two isomers occurs with a rather low activation barrier ($\Delta G^\ddagger = 10.4$ kcal/mole). Carbon-13 NMR has shown that bridge-terminal CO exchange in the *cis* complex occurs with an activation barrier very similar to that for isomerization, but the bridge-terminal CO exchange of the *trans* complex was considerably more facile. These data suggest a simultaneous breaking of the two bridge bonds with a CO moving to a terminal position on each iron. Bridge-terminal exchange in the *trans* isomer would occur by just this process, leading to an intermediate as shown in the top part of Figure 7.28 where all four COs are equivalent. *Cis-trans* isomerization and bridge-terminal exchange in the *cis* isomer require simultaneous breaking of two bridge bonds and rotation of one iron by 120° with respect to the other. This rotation requires an additional activation barrier and slows these processes relative to the bridge-terminal exchange in the *trans* isomer. In the larger ruthenium analogue, the *cis-trans* isomerization could not be stopped at the lowest temperature investigated.³⁶ In a complex where the cyclopentadienyls are linked and cannot rotate, $(\eta^{10}\text{-C}_{10}\text{H}_8\text{-C}_{10}\text{H}_8)\text{Fe}_2(\text{CO})_4$ (Figure 7.29), exchange of bridge and terminal COs occurs only above 80°C .³⁴

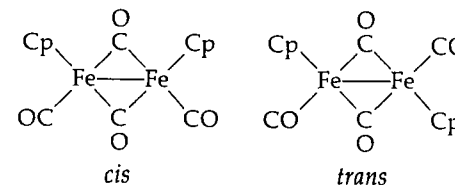


FIGURE 7.26. The *cis* and *trans* isomers of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$.

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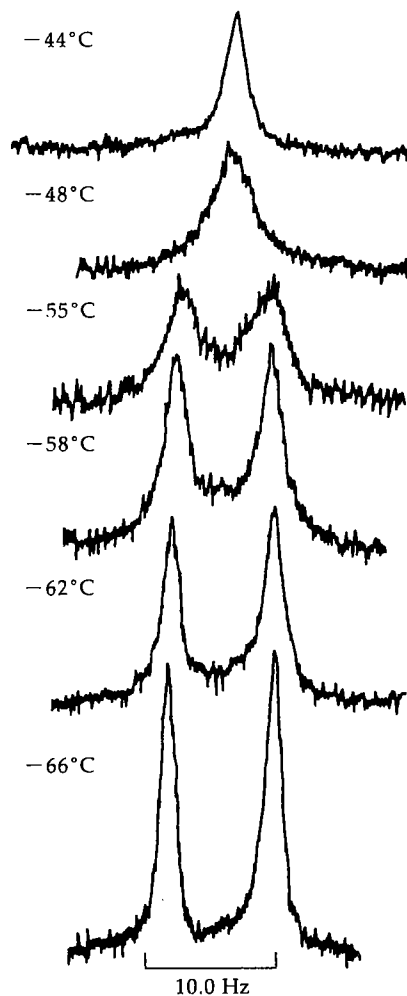


FIGURE 7.27. The proton NMR spectrum of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ shows the interconversion between *cis* and *trans* isomers that equilibrates the environment of the hydrogens. [Reprinted with permission from J. G. Bullitt, F. A. Cotton and T. J. Marks, *Inorg. Chem.* 11, 671 (1972). Copyright 1972 American Chemical Society.]

Trinuclear Clusters

The trimetaldodecacarbonyls are diverse in structure and fluxional behavior.³⁴ The iron complex adopts the bridged structure; the ruthenium and osmium complexes have the nonbridged structure as shown in Figure 7.30.

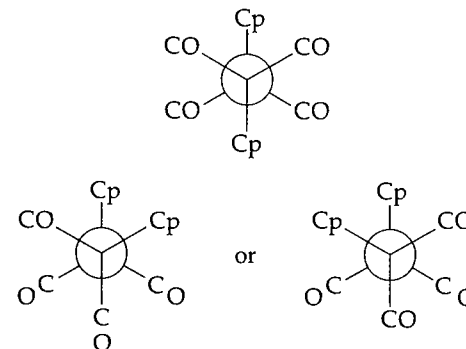


FIGURE 7.28. The nonbridged intermediates in the fluxional behavior of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$. The *trans* isomer leads only to the top possibility in which the four COs are equivalent. The *cis* isomer may lead to either of the lower possibilities. Since the COs are nonequivalent in the *cis* isomer, rotation must occur for bridge-terminal exchange.³⁶

The iron and ruthenium complexes in solution are fluxional to -100°C showing only a single resonance in the ^{13}C NMR; the osmium complex is rigid at room temperature.³⁴ No mechanistic detail has been obtained for the $\text{M}_3(\text{CO})_{12}$ species in solution.

The exchange process has been investigated for the trimer $\text{Cp}_3\text{Rh}_3(\text{CO})_3$, which exists in two isomeric forms (Figure 7.31).³⁷ Both isomers undergo fluxional processes without converting into each other. This is surprising since a primary suggestion for fluxional behavior of (b) is termed the merry-go-round for which (a) would be an intermediate.³⁴ The ^{13}C NMR spectra of (b) at different temperatures were investigated; spectra at two temperatures are shown in Figure 7.32.³⁷ The quartet at room temperature indicates complete randomization of the three CO groups with the quartet arising from

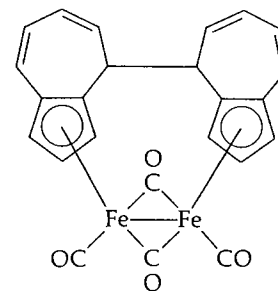


FIGURE 7.29. The structure of the iron dimer with linked cyclopentadienyls.

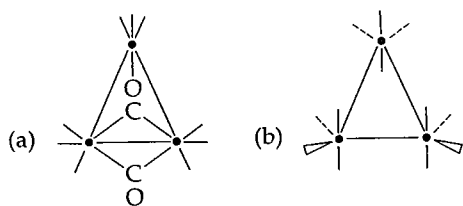


FIGURE 7.30. Structures of the trimetaldodecacarbonyls. The bridged structure (a) is for $\text{Fe}_3(\text{CO})_{12}$, and the unbridged (b) for $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$.

coupling to three equivalent rhodium centers. The spectrum recorded at -125°C is consistent with a pairwise bridge-opening mechanism for the exchange process. The activation energy, $\Delta G^\ddagger = 8.9$ kcal/mol, was derived from the intermediate-exchange spectra.³⁷ The limiting slow-exchange spectrum could not be obtained, but the broadening at -156°C led to an estimate of 4.8 kcal/mol for $\Delta G^\ddagger$ for the low-temperature process. An additional process occurred at high temperature converting (b) into (a). The scheme in Figure 7.33 was suggested to account for these observations. The essential feature is the conversion of an edge-bridging carbonyl to a face-bridging one. The upper part of the scheme accounts for the low-temperature process in which carbonyl A is always bridging but B and C are terminal part of the time, explaining the -125°C spectrum. The conversion from X into Y, a face-to-face interconversion through an edge-bridged intermediate, may be an important step in carbonyl scrambling on clusters in general.

Tetranuclear Clusters

Tetranuclear carbonyl clusters, $\text{M}_4(\text{CO})_{12}$, $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$, also exhibit nonrigid behavior.³⁴ These complexes adopt one of the two structures shown in Figure 7.34. Cobalt and rhodium have bridged structures; iridium has the unbridged structure. The energy difference between the two structures is

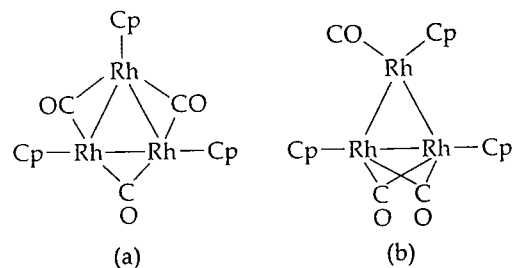


FIGURE 7.31. Two isomers of $\text{Cp}_3\text{Rh}_3(\text{CO})_3$.³⁷



FIGURE 7.32. Carbon-13 NMR spectra of the B isomer of $\text{Cp}_3\text{Rh}_3(\text{CO})_3$ at room temperature and at -125°C . [Reprinted with permission from R. J. Lawson and J. R. Shapley, *Inorg. Chem.* 17, 772 (1978). Copyright 1978 American Chemical Society.]

probably not large, and the two may be considered intermediates for the fluxional behavior of the other structure. The rhodium complex $\text{Rh}_4(\text{CO})_{12}$ shows only a broad resonance in the ^{13}C NMR at room temperature.³⁸ Heating to 63°C leads to a quintet as expected for complete equilibration of the

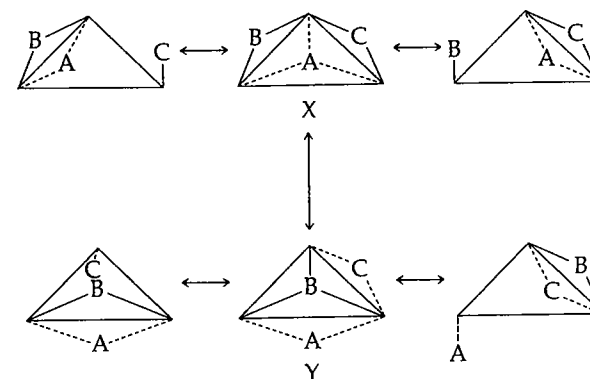


FIGURE 7.33. Scheme for the scrambling processes in $\text{Cp}_3\text{Rh}_3(\text{CO})_3$. [Reprinted with permission from R. J. Lawson and J. R. Shapley, *Inorg. Chem.* 17, 772 (1978). Copyright 1978 American Chemical Society.]

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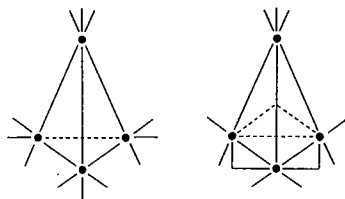


FIGURE 7.34. Structures of the tetrametaldodecacarbonyls.

carbonyls. The collapse of this spectrum as the temperature is lowered is symmetrical, indicating no site selectivity and consistent with an interconversion between the bridged and unbridged structures in Figure 7.34.³⁸ The low-temperature (-65°C) spectrum shows four doublets of equal intensity consistent with the bridged structure for $\text{Rh}_4(\text{CO})_{12}$.³⁹

The tetra-iridium complexes are interesting in that substitution of one carbonyl by a phosphorus donor changes the structure from the unbridged

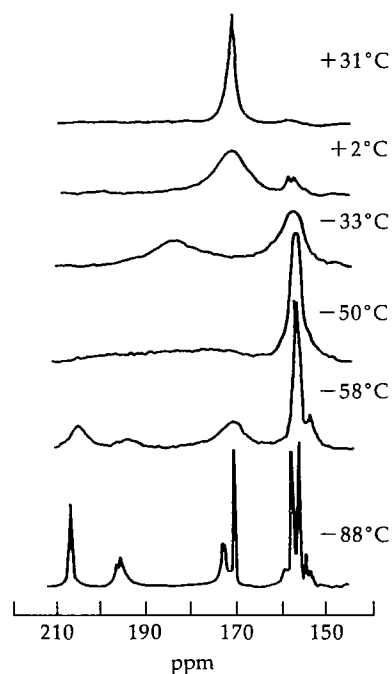


FIGURE 7.35. The variable-temperature carbon-13 NMR spectra of $\text{Ir}_4(\text{CO})_{11}\text{PPh}_2\text{Me}$ showing three averaging processes. [Reprinted with permission from G. F. Stuntz and J. R. Shapley, *J. Am. Chem. Soc.* **99**, 607 (1977). Copyright 1977 American Chemical Society.]

isomer to the bridged with the phosphorus donor in the basal plane. The fluxional behavior of $\text{Ir}_4(\text{CO})_{11}\text{PPh}_2\text{Me}$ has been investigated.⁴⁰ The NMR spectrum indicates three distinct averaging processes as the temperature is raised from -88°C (Figure 7.35). The low-temperature process equilibrates the bridging carbonyls with the basal radial carbonyls (defined in Figure 4.11). The next process (about -50°C) equilibrates the two axial carbonyls on the basal iridiums with two carbonyls on the apical iridium. The remaining carbonyl is equilibrated in a process above 0°C . Each of these processes apparently occurs by bridging-terminal exchange with energy differences governed by location of the phosphine.⁴⁰

Hydrido Cluster Compounds

The introduction of a hydride ligand offers further possibilities for the nonrigidity of metal clusters.⁴¹ Hydrides are commonly either bridging or terminal, and the exchange between the two is usually facile. The complexes $\text{H}_2\text{Os}_3(\text{CO})_{11}$ and $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{PMe}_2\text{Ph}$ serve as examples of the exchange. The bridging and terminal hydrides have been investigated by proton NMR.^{42,43} The reaction is shown in Figure 7.36. The free energies of activation show very small dependence on the ligand L in $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$ for a wide variety of different L groups.⁴³ A smaller value of $\Delta G^\ddagger$ for exchange of bridge and terminal hydrides was observed for smaller or more basic ligands. It has been suggested that the transition state for bridge-terminal exchange involved a double bridging configuration of one osmium-osmium bond.⁴³ The series of $\text{P}(\text{OMe})_3$ substituted derivatives of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ are all fluxional down to -100°C indicating the facility of hydrogen exchange.⁴⁴ This facility has led to very little clear mechanistic evidence on hydrogen movement on clusters. Variable-temperature NMR spectra of $[\text{AsPh}_4][\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ showed the exchange process, but the line shapes could not be fit by a simple mechanism.⁴⁵

Three dynamic processes were observed for hydride equilibration on $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\mu\text{-diphos})$.⁴⁶ The lowest energy process (observed between -92 and -131°C) was considered to be the movement of a hydride from one

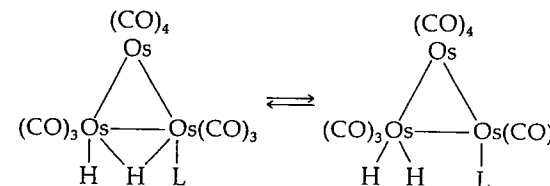


FIGURE 7.36. The bridging-terminal hydride exchange in $\text{H}_2\text{Os}_3(\text{CO})_{11}$ and $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{PMe}_2\text{Ph}$.⁴² L = CO, PMe_2Ph

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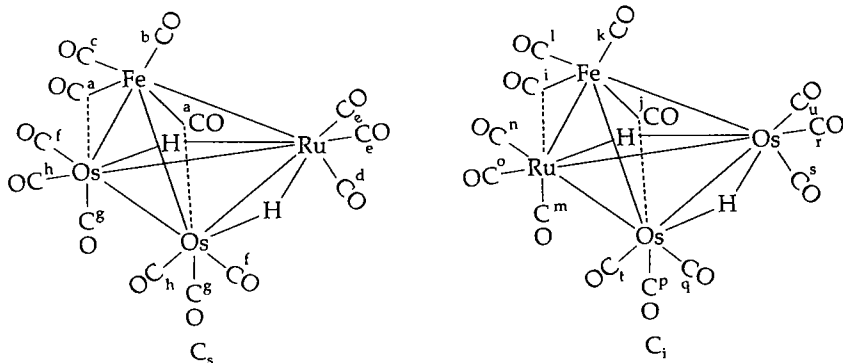


FIGURE 7.37. Carbonyl labeling scheme for the C_s and C_i isomers of $H_2FeRuOs_2(CO)_{13}$. [Reprinted with permission from W. L. Gladfelter and G. L. Geoffroy, *Inorg. Chem.* 19, 2579 (1980). Copyright 1980 American Chemical Society.]

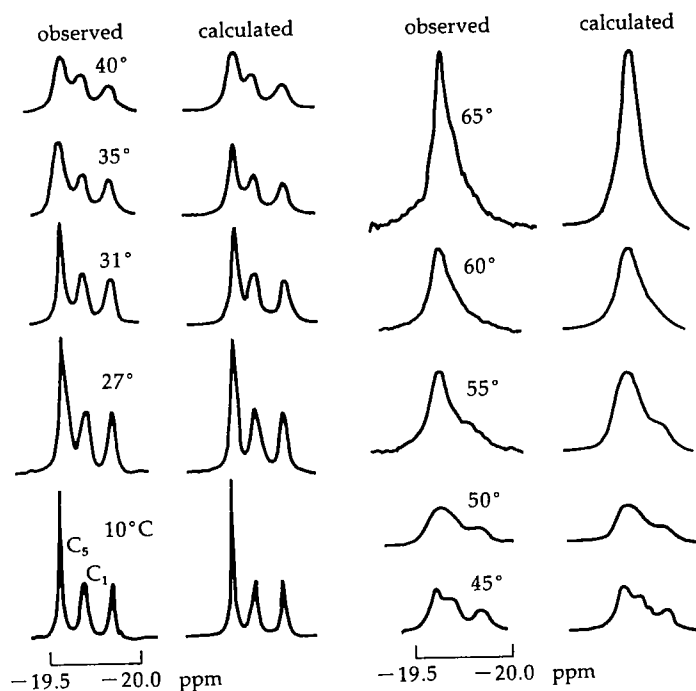


FIGURE 7.38. Variable-temperature proton NMR spectra for $H_2FeRuOs_2(CO)_{13}$. [Reprinted with permission from W. L. Gladfelter and G. L. Geoffroy, *Inorg. Chem.* 19, 2579 (1980). Copyright 1980 American Chemical Society.]

edge-bridging position to another. This process was observable because the backbone of the diphos ligand is asymmetric.⁴⁶ The second process (-74 to -92°C) was considered to involve conformational changes of the diphos ligand with a free energy of 9.1 kcal/mole. The final process (-40 to -70°C) equilibrated all four hydrides, but the precise mechanism could not be determined.⁴⁶

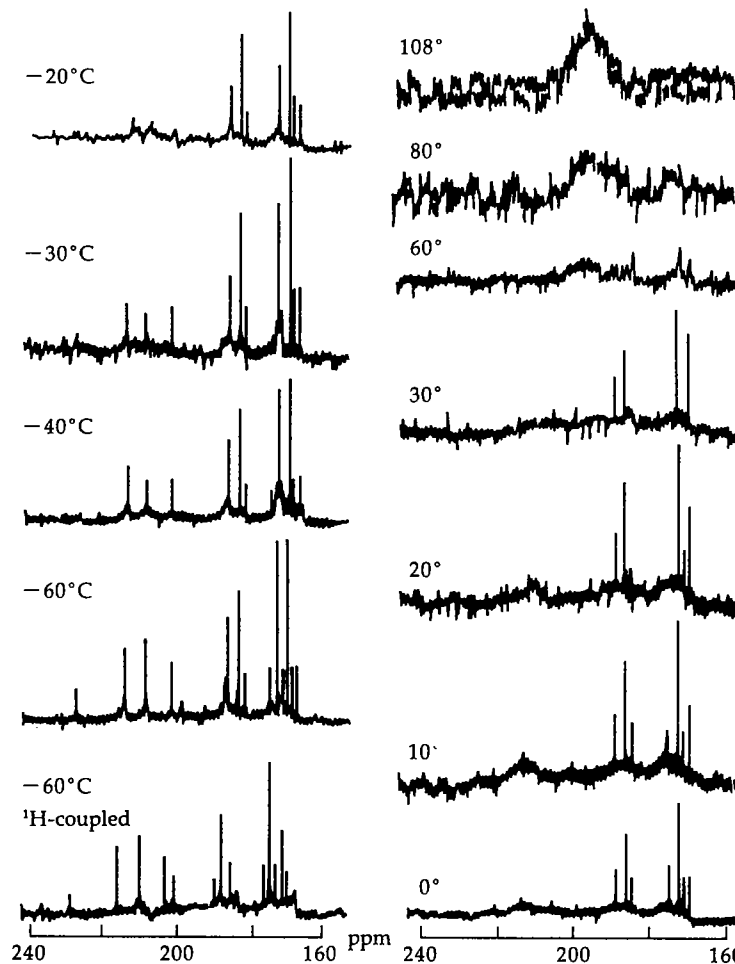


FIGURE 7.39. Variable-temperature carbon-13 NMR spectra of $H_2FeRuOs_2(CO)_{13}$. [Reprinted with permission from W. L. Gladfelter and G. L. Geoffroy, *Inorg. Chem.* 19, 2579 (1980). Copyright 1980 American Chemical Society.]

The hydrido mixed metal clusters $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$, $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and $\text{H}_3\text{FeRuOs}_2(\text{CO})_{13}$ provide the most thoroughly investigated examples of fluxional behavior in metal-cluster complexes.⁴⁷ The structures and labeling scheme for the latter are shown in Figure 7.37. The asymmetry provided by the different metal centers allows considerable mechanistic interpretation from variable temperature proton and ^{13}C NMR spectra. The spectra for $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ shown in Figures 7.38 and 7.39 indicate several different exchange processes.⁴⁷ The carbonyl environments are equilibrated in three distinct exchange processes. The first is exchange of bridge and terminal carbonyls on the iron, probably by the opening of one carbonyl bridge, a trigonal twist of the $\text{Fe}(\text{CO})_3$ unit, and re-formation of the CO bridge. The second carbonyl exchange process equilibrates the COs around the Fe-M-M triangle that contains the bridging COs. A cyclical movement of the COs around the triangular face (a type of merry-go-round) has been suggested for this fluxional reaction.⁴⁵ As indicated by the proton NMR, the hydrogen atoms are not involved in the two low-temperature exchange processes. The third process is involved in isomerization, H exchange, and total CO scrambling. This was considered a cluster framework rearrangement (Figure 7.40) with the iron moving away from Os_1 toward Os_2 and H_b moving simultaneously. The combination of framework rearrangement and cyclic CO exchange allows total exchange of carbonyls and hydrogens in $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$. Examination of the three clusters $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$,

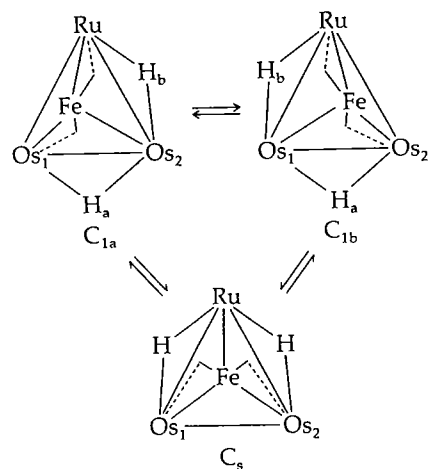


FIGURE 7.40. Skeletal rearrangement for the fluxional behavior of $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$. [Reprinted with permission from W. L. Gladfelter and G. L. Geoffroy, *Inorg. Chem.* 19, 2579 (1980). Copyright 1980 American Chemical Society.]

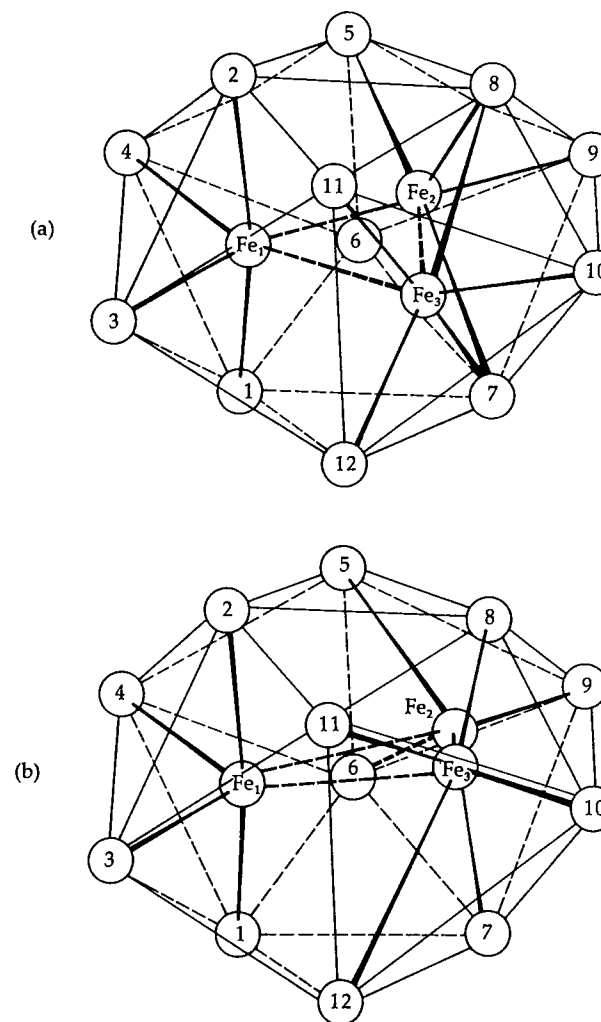


FIGURE 7.41. Possible orientations of the iron triangle within an icosahedral arrangement of COs: (a) the observed structure of $\text{Fe}_3(\text{CO})_{12}$; (b) the observed structure of $\text{Os}_3(\text{CO})_{12}$. [Reprinted with permission from B. F. G. Johnson, *J. Chem. Soc. Chem. Comm.* 703 (1976). Copyright 1976 Royal Society of Chemistry.]

$\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ showed identical exchange processes except that the activation barrier for each process increased with the osmium content of the cluster.⁴⁷

The ligand scrambling on larger cluster compounds is more complicated

to study. The migration of the hydride ligands on $\text{Rh}_{13}(\text{CO})_{24}\text{H}_3^{3-}$ and $\text{Rh}_{13}(\text{CO})_{24}\text{H}_2^{2-}$ indicates that the hydrides move rapidly on the inside of the hexagonal close-packed structure while carbonyl fluxionality occurred by the "normal" bridge-terminal exchange.⁴⁸ The movement of hydrogen atoms on the inside of the metal framework is directly applicable to hydrogen diffusion in metals and warrants further investigation.

Metal Rotations within the Ligand Polyhedron

An alternative postulated mechanism for metal-cluster fluxionality involves reorganization of the metal framework within the polyhedron of ligand atoms. This process has been described in some detail for $\text{Fe}_3(\text{CO})_{12}$.⁴⁹ In the ground state structure the 12 carbonyls describe an icosahedron, and the iron atoms lie within this icosahedron as shown in Figure 7.41a. Rotation by 30° would lead to the isomer with all COs equivalent and terminal (Figure 7.41b).⁵⁰ Similar rotations can lead to other structures. This scheme has the advantage of equilibrating the COs in a single step involving relatively minor atom motion—as required for reactions with very low activation barriers.⁴⁹ At this time there is no evidence to differentiate between ligand motion and metal motion for the stereochemical nonrigidity of extremely facile systems in solution. However, the solid state carbon-13 NMR spectrum of $\text{Fe}_3(\text{CO})_{12}$ showed six resonances of equal intensity, inconsistent with a static structure and suggesting time averaging of the two disordered molecules observed crystallographically.* It has been suggested that the two molecules interconvert by a 60° rotation of the iron triangle, a transition that is very rapid on the NMR time scale.⁵⁰

SUMMARY

Certain classes of metal complexes can be expected to exhibit stereochemical nonrigidity at moderate conditions without undergoing ligand loss. These include five- and seven-coordinate complexes, unsaturated ring complexes, and metal clusters. In each case a combination of NMR spectra and computer simulation has allowed reasonable mechanistic interpretation of the fluxional behavior.

* Note that on the X-ray crystallography time scale (10^{-18}s) $\text{Fe}_3(\text{CO})_{12}$ in the solid state is in the slow-exchange limit, while on the NMR time scale (10^{-1} – 10^{-9}s) a fast-exchange spectrum is observed.

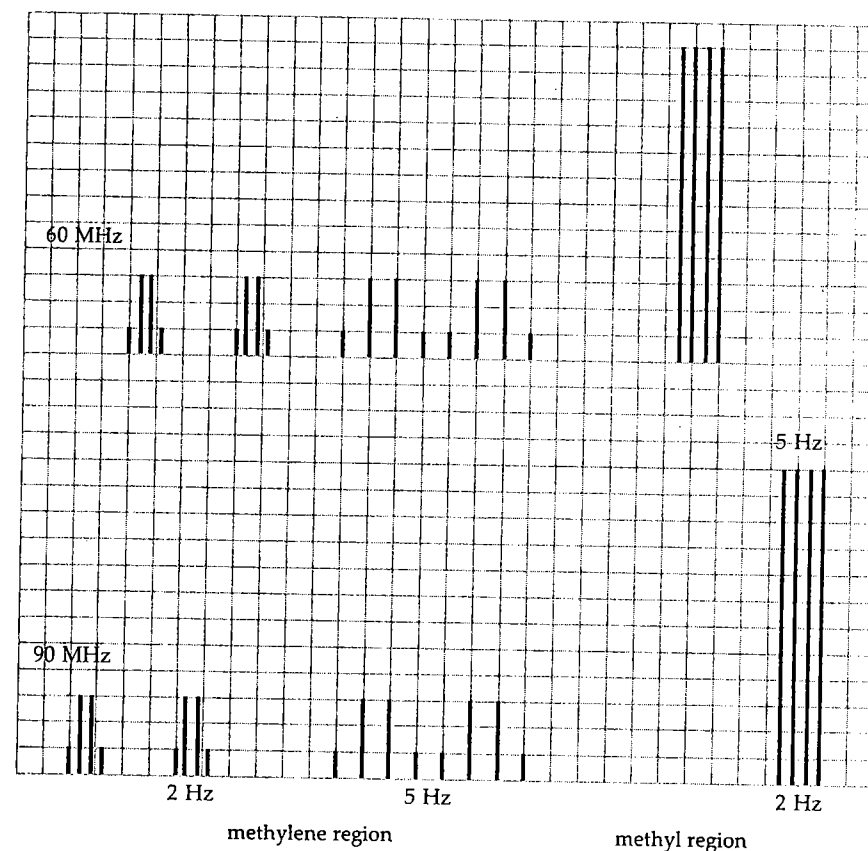
REFERENCES

1. K. F. Purcell and J. C. Kotz, *Inorganic Chemistry* (Philadelphia; W. B. Saunders, 1977).
2. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (New York: Interscience, 1972).
3. E. L. Muetterties, *Tetrahedron* 30, 1595 (1974).
4. E. L. Muetterties, *J. Am. Chem. Soc.* 91, 1636 (1969).
5. E. L. Muetterties, *Acc. Chem. Res.* 3, 266 (1970).
6. L. H. Pignolet, W. DeW. Horrocks, Jr., and R. H. Holm, *J. Am. Chem. Soc.* 92, 1855 (1970).
7. G. N. LaMar and E. O. Sherman, *J. Am. Chem. Soc.* 92, 2691 (1970).
8. R. R. Holmes, Sr., R. M. Deiters, and J. A. Golen, *Inorg. Chem.* 8, 2612 (1969).
9. J. R. Shapley and J. A. Osborn, *Acc. Chem. Res.* 6, 305 (1973).
10. R. R. Holmes, *Acc. Chem. Res.* 5, 296 (1972).
11. R. S. Berry, *J. Chem. Phys.* 32, 933 (1960).
12. C. A. Udovich and R. J. Clark, *J. Am. Chem. Soc.* 91, 526 (1969).
13. P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Am. Chem. Soc.* 94, 5271 (1972).
14. J. P. Jesson and P. Meakin, *J. Am. Chem. Soc.* 96, 5760 (1974).
15. H. Mahnke, R. J. Clark, R. Rosanske, and R. K. Sheline, *J. Chem. Phys.* 60, 2997 (1974).
16. J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.* 97, 3380 (1975).
17. D. J. Darensbourg and A. H. Graves, *Inorg. Chem.* 18, 1257 (1979).
18. J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.* 8, 165 (1958).
19. R. H. Holm, *Acc. Chem. Res.* 2, 307 (1969).
20. N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.* 17, 391 (1972) and references therein.
21. J. G. Gordon II and R. H. Holm, *J. Am. Chem. Soc.* 92, 5319 (1970).
22. A. Y. Girgis and R. C. Fay, *J. Am. Chem. Soc.* 92, 7061 (1970).
23. P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Am. Chem. Soc.* 93, 4701 (1971).
24. R. Hoffman, B. F. Beier, E. L. Muetterties, and A. R. Rossi, *Inorg. Chem.* 16, 511 (1977).
25. F. A. Van-Catledge, S. D. Ittel, C. A. Tolman, and J. P. Jesson, *J. Chem. Soc. Chem. Comm.*, 254 (1980).
26. P. J. Domaille, R. L. Harlow, and S. S. Wreford, *Organometallics* 1, 935 (1982).
27. E. L. Muetterties, *Inorg. Chem.* 4, 769 (1965).
28. L. G. Guggenberger and E. L. Muetterties, *J. Am. Chem. Soc.* 98, 7221 (1976).
29. F. A. Cotton, *Acc. Chem. Res.* 1, 257 (1968) and references therein.
30. F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *J. Am. Chem. Soc.* 91, 6598 (1969).

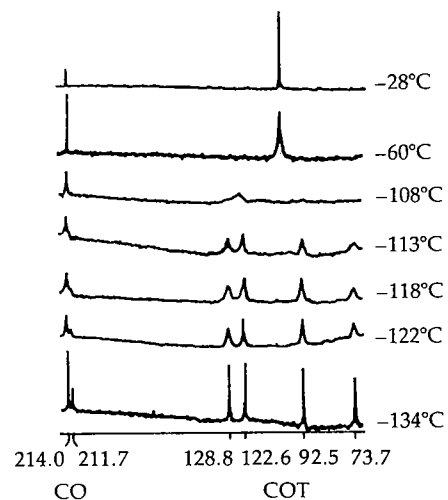
31. K. J. Karel, T. A. Albright, and M. Brookhart, *Organometallics* **1**, 419 (1982).
32. D. M. Heinekey and W. A. G. Graham, *J. Am. Chem. Soc.* **104**, 915 (1982).
33. R. Ben-Shoshan and R. Pettit, *J. Am. Chem. Soc.* **89**, 2231 (1967).
34. E. Band and E. L. Muetterties, *Chem. Rev.* **78**, 639 (1978) and references therein.
35. R. D. Adams and F. A. Cotton, *J. Am. Chem. Soc.* **95**, 6589 (1973).
36. J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.* **11**, 671 (1972).
37. R. J. Lawson and J. R. Shapley, *Inorg. Chem.* **17**, 772 (1978).
38. F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Am. Chem. Soc.* **94**, 6191 (1972).
39. J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J. Chem. Soc. Chem. Comm.* 807 (1973).
40. G. F. Stuntz and J. R. Shapley, *J. Am. Chem. Soc.* **99**, 607 (1977).
41. J. Evans, *Adv. Organomet. Chem.* **16**, 319 (1977) and references therein.
42. J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. DeBoer, *J. Am. Chem. Soc.* **97**, 4145 (1975).
43. J. B. Keister and J. R. Shapley, *Inorg. Chem.* **21**, 3304 (1982).
44. S. A. R. Knox and H. D. Kaesz, *J. Am. Chem. Soc.* **93**, 4594 (1971).
45. J. W. Koepke, J. R. Johnson, S. A. R. Knox, and H. D. Kaesz, *J. Am. Chem. Soc.* **97**, 3947 (1975).
46. M. R. Churchill, R. A. Lashewycz, J. R. Shapley, and S. I. Richter, *Inorg. Chem.* **17**, 1277 (1980).
47. W. L. Gladfelter and G. L. Geoffroy, *Inorg. Chem.* **19**, 2579 (1980).
48. S. Martinengo, B. T. Heaton, R. J. Goodfellow, and P. Chini, *J. Chem. Soc. Chem. Comm.* 39 (1977).
49. B. F. G. Johnson, *J. Chem. Soc. Chem. Comm.* 703 (1976).
50. H. Dorn, B. E. Hanson, and E. Modell, *Inorg. Chem. Acta.* **54**, L71 (1981).

PROBLEMS

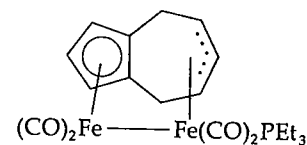
1. Reaction of NiCl_2 with excess PEt_3 leads to $\text{Ni}(\text{PEt}_3)_2\text{Cl}_2$, which can be isolated and further reacted with a phosphorus ligand, $\text{P}(\text{CF}_3)\text{F}(\text{Cl})$, to yield $\text{Ni}[\text{P}(\text{CF}_3)\text{F}(\text{Cl})](\text{PEt}_3)\text{Cl}_2$ as yellow crystals. Describe this complex in detail given the following data:
 - (a) Magnetic susceptibility at 25°C is 0.3 B.M.; at 65° , 1.2 B.M.; and at -100° , 0.0 B.M.
 - (b) Molecular weight studies show that no association or dissociation occurs from -100°C to $+100^\circ\text{C}$.
 - (c) The proton NMR spectrum for the complex in C_6D_6 at 20° is a broad resonance displaced substantially from the typical C-H proton region.
 - (d) The proton NMR at -100°C (at both 60 MHz and 90 MHz) is as shown below. Assume rotation about all bonds is infinitely fast at -100°C and that the only magnetic nuclei are ^1H .



- The optically active complex $R\text{-cis-Co(en)}_2\text{Cl}_2^+$ undergoes both racemization and isomerization in CH_3OH . Based on the observation that racemization is somewhat more rapid than isomerization, describe the most likely mechanism.
- The analysis of the mechanism of coordination sphere isomerization is more complicated in general than we have presented. The separation of different possibilities is very difficult. For five-coordinate complexes an alternative possibility is termed the "turnstile" mechanism. Consider the theoretical differences between the Berry pseudorotation and the turnstile mechanism; evaluate the possibility of differentiating between the two mechanisms experimentally. [J. I. Musher, *J. Am. Chem. Soc.* **94**, 5662 (1972)].
- Why do five- and seven-coordinate complexes undergo such rapid equilibration?
- The Bailar twist of a tris-chelate complex formally involves rotation around the C_3 axis. There exist two other unique faces about which rotation can occur. Show for the three different faces what isomerization occurs for a *fac-R-tris*-unsymmetrical bidentate metal complex.
- What is the order of reactivity toward coordination sphere isomerization for different coordination numbers? Explain.
- The ^{13}C NMR of $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$ are shown below at different temperatures. Based on these spectra and on the similarity of activation parameters to those for the $(\eta^4\text{-C}_8\text{H}_8)\text{Ru}(\text{CO})_3$ complex, assign the spectra and offer a mechanism for the ring-whizzing phenomenon. [F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc.* **98**, 1413 (1976).]



- The fluxional behavior of the complex $(\eta^1\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5$ was investigated by the spin saturation transfer technique. Irradiation of the one position (Figure 7.22) caused the two and seven position resonances to decrease in intensity with a $\Delta H^\ddagger$ of 18.1 kcal/mole and $\Delta S^\ddagger = -5.7$ eu. Interpret this observation mechanistically. [D. M. Heinekey and W. A. G. Graham, *J. Am. Chem. Soc.* **101**, 6115 (1979).]
- Cyclopropenium complexes are another example of ring whizzing. This behavior has been considered in detail for triphenylcyclopropenium complexes of nickel and palladium. Suggest a reasonable mechanism, and illustrate the transition state. [C. Mealli, S. Midollini, S. Moneti, L. Sacconi, J. Silvestre, and T. A. Albright, *J. Am. Chem. Soc.* **104**, 95 (1982).]
- The complex $\text{Ir}_4(\text{CO})_{11}(\text{CNCMe}_3)$, which has the unbridged structure, undergoes two processes, a low-temperature one that equilibrates ten carbonyls and a higher-temperature process that equilibrates the remaining carbonyl with the ten. Describe the processes that are probably occurring. [G. F. Stuntz and J. R. Shapley, *J. Organomet. Chem.* **213**, 389 (1981).]
- The ligands that occupy the equatorial site of a trimetal cluster have an important effect on the merry-go-round process. Why? What ligand characteristics provide for facile equilibration?
- The tetranickel cluster $\text{Ni}_4(\text{CNCMe}_3)_7$ undergoes a fluxional process that scrambles the isocyanides. The complex contains four terminal and three edge-bridging isocyanides. Suggest a mechanism for the fluxional behavior.
- In the dinuclear indenyl complex $(\text{C}_{10}\text{H}_8)\text{Fe}_2(\text{CO})_4\text{PEt}_3$ that contains no bridging carbonyls,

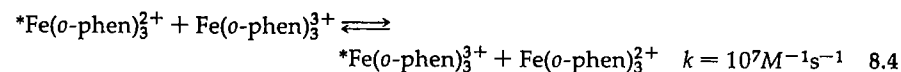
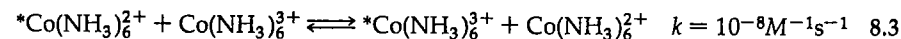
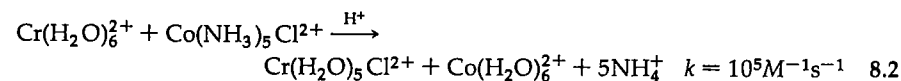
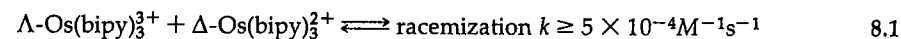


internuclear CO exchange is observed. Suggest a scheme that incorporates electron redistribution of the rings.

Oxidation-Reduction Reactions — Electron Transfer

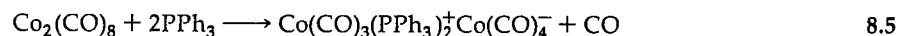
Many inorganic reactions involve a change in the oxidation states of metals. The ability of metals to assume a variety of oxidation states (the chromium subgroup has been observed in oxidation states from -4 to $+6$) makes this a common reaction often utilized in synthetic sequences.¹⁻⁴ Oxidation-reduction (redox) reactions involve two species that change in oxidation state, one increasing (losing an electron) and the other decreasing (gaining an electron). The thermodynamics of electron transfer depends on the reduction potentials of the reactants. This topic is treated in general chemistry courses and will not be covered in this chapter. The complexes that we shall consider are thermodynamically accessible, but they may have a kinetic barrier to reaction. The kinetic barrier and the mechanism will be our primary focus.

Several examples of electron transfer in inorganic reactions are shown in the following equations:



These equations indicate the types of reaction and the diversity of rates observed among electron transfer reactions in inorganic systems. Reactions such as 8.3 and 8.4, which were investigated in the 1950s as radioisotopes became available, form an important part of the electron transfer

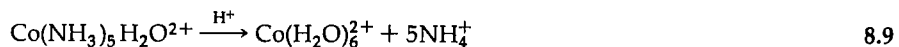
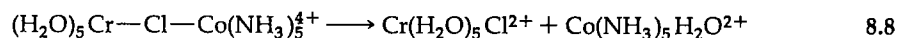
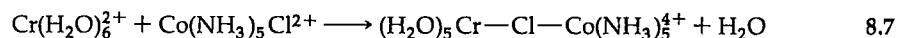
chemistry.¹⁻⁴ Electron transfer has not been as fully studied in organometallic reactions although some reactions certainly involve electron transfer.



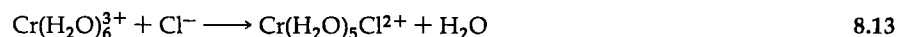
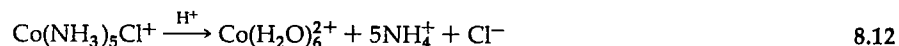
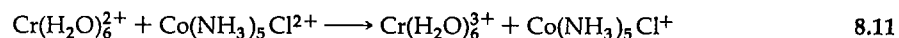
Recently the reactivity of organometallic complexes has been enhanced by electron transfer reagents.^{5,6}

The mechanisms for redox reactions fall into two classifications. An **inner sphere electron transfer** is accompanied by marked changes in the coordination sphere of the transition state, usually with a ligand bridging the two metal centers. In an **outer sphere electron transfer** mechanism the coordination spheres of the reactants remain intact. Differentiating between the two mechanistic types is in general not easy. Reaction rates for exchange that are more rapid than for substitution at the metal (as in equation 8.4) are good evidence for an outer sphere reaction. In describing the product distribution it is necessary to understand the ligand substitutional lability of the metal centers (Chapter 3). Reaction 8.2 provides an example of the importance of the metal center on the products. The reactant metal complexes involve a Cr^{2+} , which is extremely labile, and Co^{3+} , which is inert; the products are Cr^{3+} , which is inert, and Co^{2+} , which is labile. Thus the loss of ligands from the cobalt product is a natural consequence of the lability of the Co^{2+} . Either an inner sphere or an outer sphere mechanism would give the same products.

Inner sphere:



Outer sphere:



Thus simple product distribution is not a good means of distinguishing mechanistic type in electron transfer reactions.*

All electron transfer reactions are first order in oxidant and reductant,

$$\text{rate} = k[\text{oxidant}][\text{reductant}] \quad 8.14$$

allowing no distinction between inner sphere and outer sphere processes based on the rate law.^{3,4,7-12} Activation enthalpies are usually low, with outer sphere mechanisms a bit lower than inner sphere ones; both have negative entropies of activation. The standard kinetic parameters are not very useful in differentiating electron transfer mechanisms. Special considerations are required to distinguish between inner and outer sphere mechanisms. In later sections we shall consider each mechanism for electron transfer.

THEORETICAL CONSIDERATIONS

Electron transfer by either type of mechanism is subject to the restrictions of the Franck-Condon principle. The electron weighs much less than the nuclei and therefore moves rapidly compared to nuclei. Thus during the time of electron transfer the nuclei remain stationary and bond distances cannot change. Before electron transfer from one center to another can take place, the coordination spheres must adjust so that the energy of the system is unaltered on electron transfer. This is most easily considered for self-exchange reactions like those of equations 8.3 and 8.4. The M-L bond distance is shorter for the higher oxidation state metal.† Several examples are shown in Table 8.1. Before the self-exchange electron transfer can take place the metal of higher oxidation state must lengthen its bonds and the one with lower oxidation state must shorten its bonds. The amount of distortion required to reach a common state is inversely related to the rate of electron transfer. If large changes are required, then the rate of electron transfer may be very slow. Coupled with the principles of electronic structures of transition

* Use of $^{36}\text{Cl}^-$ free in solution initially showed no incorporation into the chromium product, indicating an inner sphere mechanism. In this case, because $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ is inert, isotope labeling allows mechanistic differentiation.

† A shorter M-L bond distance for the higher oxidation state metal presumes that pi back-bonding is not important in the metal-ligand bond. When pi-bonding is important, the lower oxidation state M-L bond may be shorter. An example is $\text{V}(\text{CO})_6$ and $\text{V}(\text{CO})_6^-$ in which the V-C distances are 2.001 and 1.931 Å, respectively.^{13,14} In general the metal-ligand bond distance does change with oxidation state of the metal. In our discussion we shall consider the metal of higher oxidation state to have the shorter M-L bond.

TABLE 8.1

Changes in Metal-Ligand Bond Distances as the Oxidation State Changes.

M	L	M ^{II} -L	M ^{III} -L	ref
Ru	NH ₃	2.144(4)	2.104(4)	15
Ru	H ₂ O	2.122(16)	2.029(7)	16
Co	NH ₃	2.114(9)	1.936(15)	15
Fe	bipy	1.97(1)	1.963	17
Co	bipy	2.128(8)	1.93(2)	17

metal complexes this concept allows an understanding of some of the reactivity changes in electron transfer reactions. The self-exchange between $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_6^{2+}$ is quite slow as shown in reaction 8.3. Since the Co^{3+} is a low spin d^6 and the Co^{2+} is a high spin d^7 , the electron transfer involves a spin change and the reaction would be expected to be very slow. The e_g orbitals are anti-bonding with respect to the metal-ligand sigma bonding framework while the t_{2g} orbitals are nonbonding. Changing the number of e_g electrons has a relatively larger effect on the bonding than does changing the number of t_{2g} electrons. Typically electron transfer into or out of the e_g orbital is slower than transitions involving t_{2g} electrons. Reactions that involve very small M-L changes with oxidation state may undergo very rapid electron transfer. Note that the smallest M-L changes with oxidation state involve differences in t_{2g} electrons (t_{2g}^6 and t_{2g}^5).

Since electron transfer involves rearrangement of the coordination sphere along a normal coordinate, isotope changes should affect the rate. This has been addressed in recent experiments.^{17,18} Kinetic isotope effects were measured for redox reactions of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, $\text{Fe}(\text{D}_2\text{O})_6^{2+}$ and $\text{Fe}(\text{OH}_2)_6^{2+}$ with $\text{M}(\text{bipy})_3^{3+}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Cr}$). The oxygen kinetic isotope effect of $k_{16}/k_{18} = 1.08$ for chromium was readily predicted as the product of an electronic interaction and Franck-Condon factors for vibrational modes as given by the effect of mass change on the frequency of the symmetric metal-ligand stretching mode. The substitution of deuterium for hydrogen in the ligand caused a larger kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.3$) than could be explained by the change in metal-ligand frequency. It has been suggested that the O-H modes were also involved in the electron transfer.¹⁷

OUTER SPHERE ELECTRON TRANSFER

An outer sphere electron transfer may be considered as the following steps:



where the brackets indicate the reactants are in close proximity (an encounter complex). Reaction 8.16 involves the structural rearrangement necessary for electron transfer; reaction 8.17 indicates the electron transfer; and the final reaction is the movement of the products apart. Since outer sphere reactions involve no bond-breaking or bond-making they are amenable to theoretical treatment.^{3,8,19,20} In Marcus's interpretation, for a reaction with $\Delta G^0 = 0$, the free energy of activation is the sum of several contributions.²¹

$$\Delta G^\ddagger = RT \ln \frac{kT}{hZ} + \Delta G_a^\ddagger + \Delta G_i^\ddagger + \Delta G_o^\ddagger \quad 8.19$$

The first term allows for the loss of translational and rotational free energy on forming the collision complex from the reactants. This term involves constants (Z is the effective collision number) and can be calculated. The $\Delta G_a^\ddagger$ represents the free energy change due to electrostatic interaction between the reactants at the separation distance in the activated complex compared to the interaction at infinite separation. The term $\Delta G_i^\ddagger$ represents the free energy change that is required for rearrangement of the coordination sphere—elongation or contraction of the metal-ligand bonds in the activated complex and perhaps also rearrangement of the ligand. This normally occurs along the vibrational normal modes for the molecule. The $\Delta G_o^\ddagger$ represents solvent sphere rearrangement. The solvent would certainly be more attracted to the higher oxidation state and must rearrange prior to electron transfer. This term is relatively constant for different $\text{M}(\text{H}_2\text{O})_6$ complexes in the same oxidation state. The $\Delta G_o^\ddagger$ may be quite different for different ligand systems. A few examples for hexaquo complexes are shown in Table 8.2.⁸ In complexes that do not differ greatly in oxidation state or ligands, differences in outer sphere reactivity cannot arise from $\Delta G_a^\ddagger$ or $\Delta G_o^\ddagger$ and so must arise from changes in $\Delta G_i^\ddagger$. A measure of $\Delta G_i^\ddagger$ is the metal-ligand bond distance changes as shown in Table 8.1 for the different oxidation states. For complexes whose structures are known, the energy barrier for electron transfer can be calculated from the

TABLE 8.2

Enthalpies of Solvation for Hexaaquo Ions.

$M(H_2O)_6^{2+}$	ΔH (kcal/mole)	$M(H_2O)_6^{3+}$	ΔH (kcal/mole)
V ²⁺	-267	V ³⁺	-610
Cr ²⁺	-274	Cr ³⁺	-662
Mn ²⁺	-259	Mn ³⁺	-655
Fe ²⁺	-282	Fe ³⁺	-629

following classical equations:

$$E = 3k_m(r^\ddagger - r_m)^2 + 3k_n(r_n - r^\ddagger)^2 \quad 8.20$$

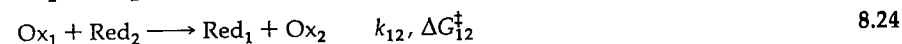
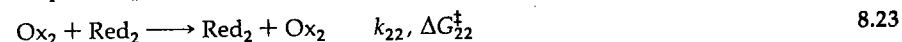
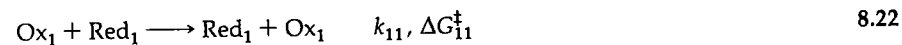
$$r^\ddagger = \frac{k_m r_m + k_n r_n}{k_m + k_n} \quad 8.21$$

where k_m and k_n are force constants, r_m and r_n are the metal-ligand bond distances and $r^\ddagger$ is the bond distance necessary for electron transfer.^{3,8,20} Using these equations for $Co(NH_3)_6^{2+}/Co(NH_3)_6^{3+}$ gives an energy barrier of 6.8 kcal/mole; the value for $Ru(NH_3)_6^{2+}/Ru(NH_3)_6^{3+}$ is negligible since the radius difference is only 0.04 Å.¹⁶ This small radius change illustrates the small effect when a "nonbonding" t_{2g} electron is removed. The difference in self-exchange rates for these two systems is a factor of 10^{15} , and 7 kcal/mole is insufficient to account for such a large difference. The cobalt complex also must undergo a spin change with a calculated energy difference of 24.6 kcal/mole. Thus the reorganization energy for the cobalt-ligand bond is small compared to the spin-change energy. Similar considerations for the species $Fe(H_2O)_6^{2+}/Fe(H_2O)_6^{3+}$ and $Ru(H_2O)_6^{2+}/Ru(H_2O)_6^{3+}$ show that the reactivity order

$$k \text{ for } Fe(H_2O)_6^{2+}/Fe(H_2O)_6^{3+} < k \text{ for } Ru(H_2O)_6^{2+}/Ru(H_2O)_6^{3+} \\ < k \text{ for } Ru(NH_3)_6^{2+}/Ru(NH_3)_6^{3+}$$

is readily accounted for by the reorganization energies during self-exchange.¹⁶

A useful variation of Marcus's theory called the relative Marcus theory utilizes self-exchange reactions to calculate the barrier for cross reactions.^{3,8}

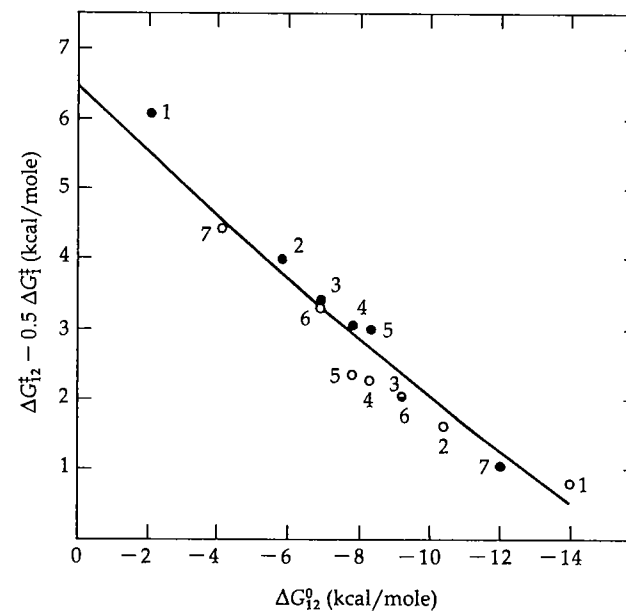


The barrier to the self-exchange reaction is considered to contribute to the cross reaction as shown below.

$$\Delta G_{12}^\ddagger = 0.5 \Delta G_{11}^\ddagger + 0.5 \Delta G_{22}^\ddagger + 0.5 \Delta G_{12}^0 \quad 8.25$$

The $\Delta G_{12}^\ddagger$ is lower than the average of the self-exchange free energies because of the favorable free energy change, ΔG_{12}^0 .⁸ For a series of closely related reactions (a common oxidant or reductant) a plot of $\Delta G_{12}^\ddagger$ versus ΔG_{12}^0 should be linear with a slope of 0.5. This has been demonstrated in the oxidation of a series of iron phenanthroline complexes by Ce(IV) as shown in Figure 8.1.²² The expression for the rate constant is

$$k_{12} = (k_{11} k_{22} K_{12} f)^{1/2} \quad 8.26$$



1. tris(3,4,7,8-tetramethyl-1,10-phenanthroline)
2. tris(5,6-dimethyl-1,10-phenanthroline)
3. tris(5-methyl-1, 10-phenanthroline)
4. tris(1,10-phenanthroline)
5. tris(5-phenyl-1, 10-phenanthroline)
6. tris(5-chloro-1, 10-phenanthroline)
7. tris(5-nitro-1,10-phenanthroline)

FIGURE 8.1. Relation between $\Delta G_{12}^\ddagger - 0.5\Delta G_{11}^\ddagger$ and the standard free energy change of the oxidation-reduction reactions at 25.0°C: open circles, $Fe(phen)_3^{2+}$ -Ce(IV) reactions in 0.50 F H_2SO_4 ; closed circles, Fe^{2+} - $Fe(phen)_3^{3+}$ reactions in 0.50 F $HClO_4$.

where f is defined as

$$\log f = \frac{(\log K_{12})^2}{[4 \log (k_{11}k_{22}/Z^2)]} \quad 8.27$$

which becomes significant only if K_{12} , the cross reaction equilibrium constant, is large. Equation 8.26 is more usefully represented as

$$\log k_{12} = 0.5 \left(\log k_{11} + \log k_{22} + \frac{\Delta E^0}{0.059} + \log f \right) \quad 8.28$$

at 25°C. Table 8.3 shows the utility of this approach to modeling outer sphere electron transfer reactions.⁸ It should be emphasized that the calculation of rate constants is a difficult task. The success for outer sphere electron transfer reactions further emphasizes the special nature of these reactions.

TABLE 8.3

Comparison of Calculated and Observed Rate Constants for Outer Sphere Cross Reactions.

reaction	observed	calculated
$\text{IrCl}_6^{2-} + \text{W}(\text{CN})_8^{4-}$	6.1×10^7	6.1×10^7
$\text{IrCl}_6^{2-} + \text{Fe}(\text{CN})_6^{4-}$	3.8×10^5	7×10^5
$\text{Mo}(\text{CN})_8^{3-} + \text{W}(\text{CN})_8^{4-}$	5.0×10^6	4.8×10^6
$\text{Fe}(\text{CN})_6^{4-} + \text{MnO}_4^-$	1.3×10^4	5×10^3
$\text{V}(\text{H}_2\text{O})_6^{2+} + \text{Ru}(\text{NH}_3)_6^{3+}$	1.5×10^3	4.2×10^3
$\text{Ru}(\text{en})_3^{2+} + \text{Fe}(\text{H}_2\text{O})_6^{3+}$	8.4×10^4	4.2×10^5
$\text{Fe}(\text{H}_2\text{O})_6^{2+} + \text{Mn}(\text{H}_2\text{O})_6^{3+}$	1.5×10^4	3×10^4

The validity of the Marcus treatment has been demonstrated in so many cases that deviations from the expectation are usually indicative of a mechanistic change.²³ Reaction of $\text{Co}(\text{H}_2\text{O})_6^{3+}$ with a number of reductants occurs by an outer sphere mechanism. The parameters from these reactions can be utilized to calculate the $\text{Co}(\text{H}_2\text{O})_6^{3+}$ self-exchange rates, which are 12 orders of magnitude smaller than the experimental value. This has been used to suggest an inner sphere mechanism through a water-bridged pathway for the self-exchange.²³

It has been shown that the selectivities of the rates of outer sphere redox processes (as shown in Table 8.4) do not depend on the free energy gain for reactions where the reorganization energy is small compared to the exother-

TABLE 8.4

Kinetic Data for the Reaction of Binuclear Cobalt (Substituted Carboxylato) with Some Reductants (Structure in Figure 8.2).²²

reductant	R				E^0
	CH_3	CH_2F	CHF_2	CF_3	
$\text{Ru}(\text{NH}_3)_6^{2+}$	0.035	0.12	0.21	0.36	0.10
$\text{Cr}(\text{H}_2\text{O})_6^{2+}$	1.46×10^{-3}	2.79×10^{-3}	3.97×10^{-3}	6.3×10^{-3}	-0.45
$\text{Zn}^+(\text{aq})$	5.5×10^8	7.6×10^8	1.0×10^9	1.2×10^7	-2.0

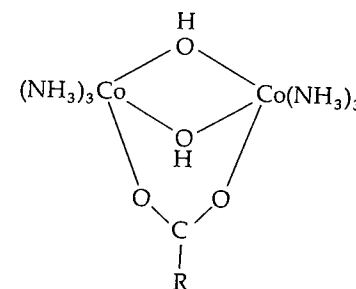
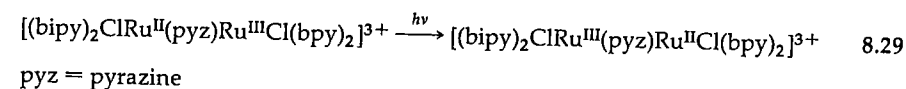


FIGURE 8.2. Structure of the dinuclear carbonato complexes that are oxidants in the reaction described in Table 8.4.

mic contribution.²⁴ The Marcus theory accommodated the free energy gain completely when quadratic terms were included.²⁴

Both charge transfer and intervalence transitions can be used to provide information on thermal electron transfer.²⁵⁻²⁷ The relationship between electron transfer and intervalence transitions is shown graphically in Figure 8.3.²⁵ The intervalence transfer leads to an excited vibrational state through a photochemical reaction. As a long-range, directed electron transfer process between separated redox sites, intervalence transfer may provide an experimental basis for relating optical and thermal electron transfer. Most studies have centered on Ru^{2+} , Ru^{3+} complexes bridged by aromatic nitrogen donor ligands.²⁵



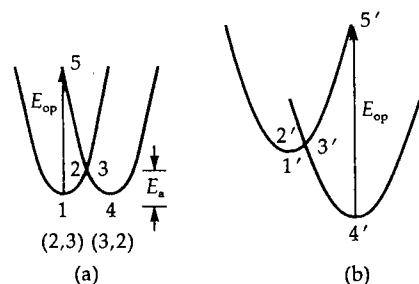
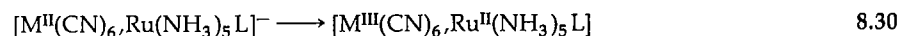


FIGURE 8.3. Reaction coordinate diagrams for electron transfer showing the optical transitions for (a) $\Delta G^\circ = 0$ and (b) ΔG° negative.

The theories of Marcus and Hush relate the energy of the intervalence transfer to the energy of the electron transfer. Outer sphere charge transfer transitions have been investigated for a series of mixed-metal ion pairs and used to compare to the enthalpy change associated with the electron transfer. Some data are shown in Table 8.5.²⁶ Plots of the energy of the optical transition versus the enthalpy change for the charge transfer



show linear relationships (Figure 8.4), indicating the value of charge-transfer transitions to the understanding of outer sphere electron transfer mechanisms. It has been suggested that outer sphere contact between $\text{M}(\text{CN})_6^{4-}$ and an ammine face of the $\text{Ru}(\text{NH}_3)_5 \text{L}^{3+}$ occurs.²⁶

TABLE 8.5

Spectral and Enthalpy Data for Outer Sphere Charge Transfer in $[M^{II}(\text{CN})_6, \text{Ru}^{III}(\text{NH}_3)_5 \text{L}]^-$.²⁷

M	L	λ	ΔH
Fe	py	910	11.0
Fe	4-Mepy	898	11.1
Fe	4-Brpy	932	10.7
Ru	py	643	10.7
Ru	4-Mepy	627	15.9
Ru	4-Brpy	653	15.3
Os	py	658	15.3
Os	4-Mepy	626	16.0
Os	4-Brpy	670	14.9

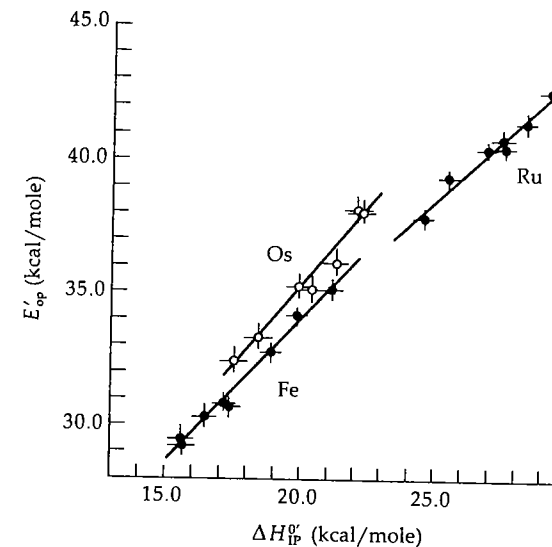


FIGURE 8.4. A plot of the optical transition versus the enthalpy change for the charge transfer transition (reaction 8.30).

One feature allows the definite assignment of an electron transfer as outer sphere: If the rate of electron transfer is more rapid than substitution at the metal centers, the mechanism can be assigned as outer sphere. This is because inner sphere electron transfer requires loss of a ligand to open a coordination site while outer sphere needs no such change in coordination. Thus a reactant such as $\text{Co}(\text{NH}_3)_6^{3+}$ or $\text{Ru}(\text{bipy})_3^{3+}$ that is inert to substitution and does not contain a possible bridging ligand will undergo outer sphere electron transfer. The examples shown in Table 8.3 further illustrate this feature. Although Cl^- or CN^- can function as a bridging ligand, neither IrCl_6^{2-} with an Ir^{4+} center nor $\text{W}(\text{CN})_8^{4-}$ undergoes substitution on the same time scale as the electron transfer. Similar considerations apply to the other examples.

Much of the recent interest in outer sphere electron transfer has been in the area of bioinorganic reactions. Cross reactions between nickel(II) peptides and nickel(III) peptides have been used to evaluate the self-exchange rate constants for a number of different complexes.²⁸ The self-exchange reaction rates varied with peptide structure, but they could be broadly classified according to the protonation, triply deprotonated peptides reacting at $1.2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ and doubly deprotonated peptides reacting at $1.3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$. It was suggested that the approach of the complexes was close, probably from an axial direction.²⁸ Reactions between blue copper proteins — stellacyanin, plastocyanin, and azurin — and inorganic redox reagents —

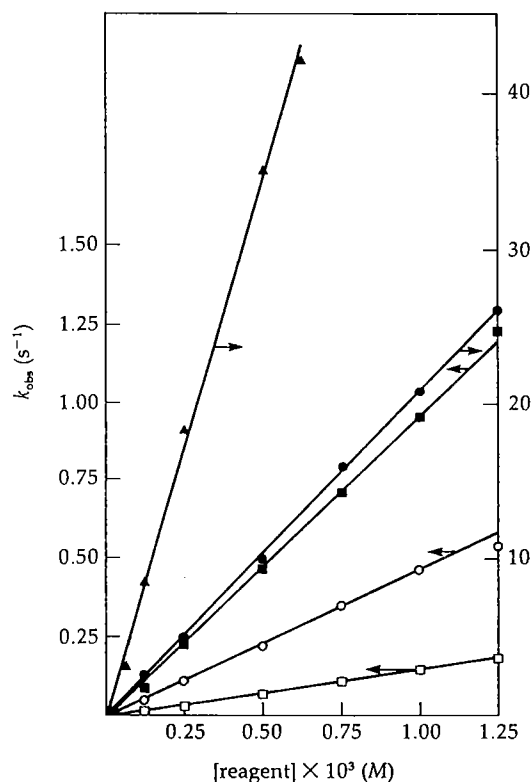


FIGURE 8.5. Dependences of the observed rate constants on reagent concentration at 25°C. [pH 7.0 (phosphate); $\mu = 0.2$ M]. (■) $\text{Fe}(\text{dipic})_2^{2-}$ -azurin(II); (□) $\text{Co}(\text{dipic})_2^{2-}$ -azurin(I); (●) $\text{Fe}(\text{dipic})_2^{2-}$ -plastocyanin(II); (○) $\text{Co}(\text{dipic})_2^{2-}$ -plastocyanin(I); (▲) $\text{Fe}(\text{dipic})_2^{2-}$ -stellacyanin(II).

bis(dipicolinate) complexes of cobalt(III) and iron(II)—have been examined.²⁹ The rate data indicate well-behaved reactions (Figure 8.5). The electron transfer distance of 2–3 Å suggests that the hydrophobic ligand penetrates the hydrophobic region of the copper-histidine redox unit.

INNER SPHERE MECHANISMS

Inner sphere mechanisms are characterized by the formation of a binuclear transition state/intermediate during the electron transfer reaction.^{1–4,30} A very important facet of the inner sphere process is the bridging ligand that forms part of the coordination spheres of both the oxidizing and the reducing

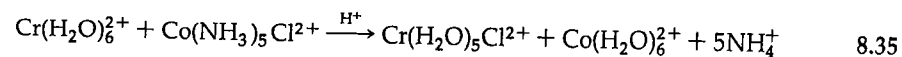
metal ions.¹² The bridging ligand must function as a Lewis base toward both metal centers—it must have two pairs of electrons that can be donated to different metal centers. The electron transfer can be considered as several individual reactions.



The first reaction is the diffusion-controlled formation of a collision complex. The second reaction is the formation of a complex, termed the precursor complex, in which the ligand bridges the two metal centers but the electron has not been transferred. Reaction 8.33 is the electron transfer leading to the successor complex. The last reaction is the dissociation of the successor complex to the products. Any of these reactions may be rate determining as shown by the reaction profiles in Figure 8.6. If reaction 8.32 or 8.34 is rate determining, the reaction is substitutionally controlled; if the electron transfer is rate determining, as is most commonly observed, the middle profile is observed, and reaction 8.33 is rate determining. The scheme shown in reactions 8.31–8.34 represents an atom transfer in which the bridging ligand is transferred to a different metal center. Atom transfer is not a requirement for an inner sphere mechanism, but it is a consequence of the kinetic labilities of the two metal centers in the successor complex. The bridging ligand remains with the more inert metal center.

The same theoretical considerations apply for inner sphere reactions as for outer sphere—bond lengths must adjust—but the same theoretical treatment cannot be accomplished because the reaction also involves bond dissociation. The most important consideration for inner sphere reactions is the bridging ligand.

It is instructive to consider an example that illustrates an inner sphere reaction, the reaction of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ with $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, for which the substitutional reactivities are known. The $\text{Co}(\text{III})$ complex is substitutionally inert in acidic solution, and the $\text{Cr}(\text{II})$ complex exchanges extremely rapidly. In the products of the electron transfer the substitutional labilities at the two centers are reversed, the $\text{Co}(\text{II})$ center being very labile and substitution on $\text{Cr}(\text{III})$ quite slow.



Since the chromium(II) complex is quite labile, the precursor complex can easily be formed. The electron transfer also occurs readily. In the successor complex the $\text{Cr}(\text{III})$ center is the more inert and the chloride-chromium bond

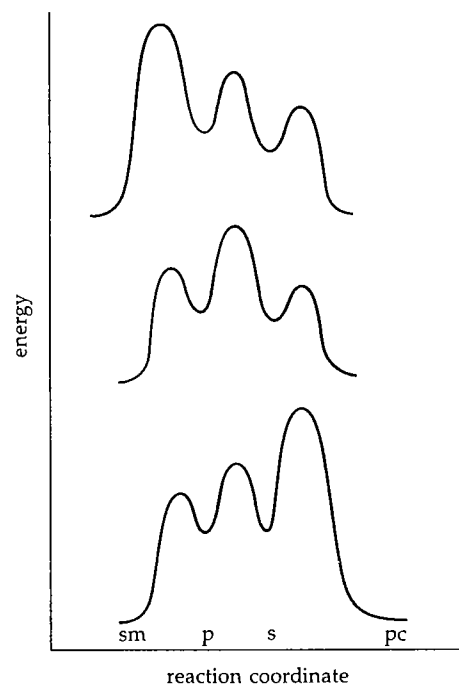


FIGURE 8.6. Possible energy profiles for inner sphere electron transfer. The relative minima correspond to the starting complexes (sm), the precursor (p), the successor complex (s), and the product complexes (pc). In the top profile the precursor formation is rate determining, in the middle one the electron transfer is rate determining, and in the bottom profile the successor decomposition is rate determining.

remains while the labile Co(II) loses chloride. That the chloride is transferred directly is shown by the absence of $^{36}\text{Cl}^-$ incorporation when the reaction is run in the presence of free $^{36}\text{Cl}^-$.*

Nature of the Bridging Ligand

The bridging ligand can be very important in inner sphere reactions. Some data for reduction of $\text{Co(NH}_3)_5\text{L}^{3+}$ by Cr^{2+} are shown in Table 8.6.³ The order observed for the halides represents the ability of the ligand to

* Use of $^{36}\text{Cl}^-$ free in solution initially showed no incorporation into the chromium product, indicating an inner sphere mechanism. In this case, because $\text{Cr(H}_2\text{O)}_5\text{Cl}^{2+}$ is inert, isotope labeling allows mechanistic differentiation.

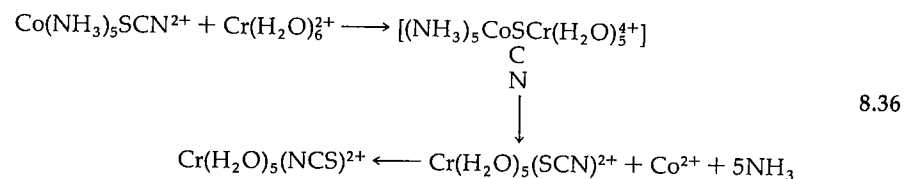
TABLE 8.6

Rate Constants for Reduction of $\text{Co(NH}_3)_5\text{L}^{3+}$ by $\text{Cr(H}_2\text{O)}_6^{2+}$.

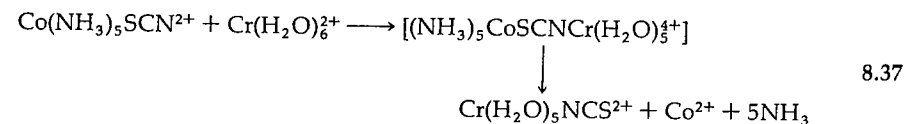
L	k
NH_3	8.0×10^{-5}
F^-	2.5×10^5
Cl^-	6.0×10^5
Br^-	1.4×10^6
I^-	3.0×10^6
N_3^-	3.0×10^5
OH^-	1.5×10^6
NCS^-	19
SCN^-	1.9×10^5
H_2O	~ 0.1

donate to two metal centers. Water has two electron pairs that could be used to bridge metal centers, but an inverse dependence on the $[\text{H}^+]$ indicates that OH^- is the actual bridging ligand. The 10^5 increase in rate for OH^- over H_2O adds to the plausibility of this interpretation.^{11,12}

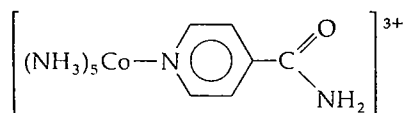
When a halide atom functions as the bridging ligand, it is obvious that a single atom is involved. When a ligand such as SCN^- functions as a bridging ligand, there are two possibilities.¹¹ If the second metal bonds to sulfur, the reaction is referred to as adjacent attack; if the second metal bonds to nitrogen, it is referred to as remote attack. Attack at both possible sites has been observed for Cr^{2+} as the reductant. Adjacent attack leads to the unstable sulfur-bonded isomer, which rearranges to the more stable nitrogen bonded form.³¹



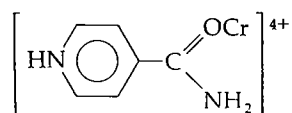
For remote attack the stable nitrogen-bonded isomer forms directly



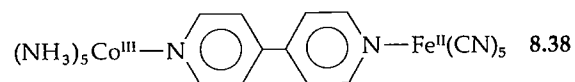
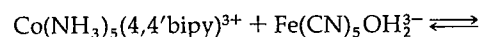
In 1 M H⁺, 30% of the electron transfer occurred by adjacent attack.^{30,31} It is difficult to prove that remote attack has occurred in some systems. The reaction of



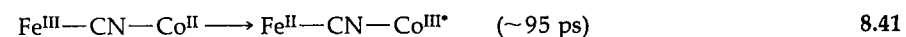
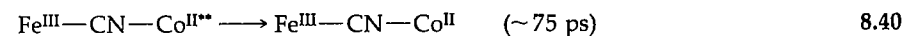
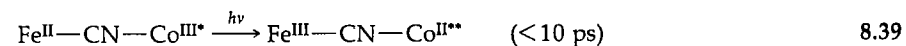
with Cr²⁺ in acid solution leads to the product



This product can't arise by interaction of Cr(H₂O)₆³⁺ with the free ligand since the product is unstable with respect to the free amide and Cr(H₂O)₆³⁺, although the reaction is slow enough that it is possible to characterize the intermediate.¹¹ In a few cases it has been possible to characterize the binuclear species formed in electron transfer reactions.^{30,32-34} For the reaction of 4,4'-bipyridinepentaaminecobalt(III) with aquopentacyanoferrate(II), the rate of formation and dissociation of the precursor were measured.³²



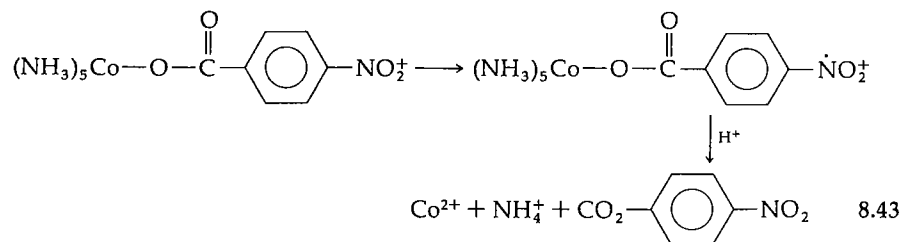
The rate of dissociation and electron transfer in the precursor were comparable. The electron transfer in binuclear (NC)₅Fe^{II}-CN-Co^{III} (chelate) complexes has been observed by picosecond absorption spectroscopy. The following scheme has been suggested based on these data.³³



The first reaction is excitation into the charge transfer band, which leads to Co^{II} in a $t_{2g}^6 e_g^1$ excited state. The next reaction is the rearrangement to $t_{2g}^5 e_g^2$. The third reaction is the spin-allowed back electron transfer leading to Co^{III} in an excited state ($t_{2g}^5 e_g^1$) that slowly relaxes to the singlet groundstate.³³

After the precursor complex forms, there are two possible roles for the bridging ligand in the actual electron transfer.⁷ The electron could be transferred to the ligand forming a radical that, in a subsequent step, would

transfer the electron to the second metal. Alternatively the electron might spend no time on the bridging ligand, which would function merely as a mediator for the electron transfer. Pulse radiolysis of *p*-nitrobenzoato-pentaamine cobalt(III) led to the formation of a metastable intermediate ascribed to the cobalt(III) complex of the radical ion, which decayed to the cobalt(II) complex in a first order process.¹²



Because detection of radical ligand species is not usually possible, a rate test has been developed to distinguish the role of the bridging ligand by comparing reductions of cobalt(III) and chromium(III) with the same reductant and bridging ligand.¹² For the radical mechanism electron transfer takes place from the reductant to the ligand; the nature of the oxidant will therefore have a small effect on the rate. When the ligand is merely mediating the electron transfer, the nature of the oxidant should be much more important. Data in Table 8.7 demonstrate this procedure for distinguishing the role of the bridging ligand in inner sphere electron transfer.¹² For the ligands that would not

TABLE 8.7

Rates of Reaction of Cr(II) with Co(III) and Cr(III) Complexes, Co(NH₃)₅L²⁺ or Cr(H₂O)₅L²⁺. L = Bridging Ligand.

L	$k(\text{Co})/k(\text{Cr})$
NCS^-	1.4×10^5
F^-	3.4×10^7
OH^-	2.3×10^6
$\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CHCO}_2\text{H}(\text{trans})$	0.4
$\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CHCO}_2\text{H}(\text{cis})$	50

be expected to form a radical, the ratio $k(\text{Co})/k(\text{Cr})$ is $\sim 10^6$, indicating an important effect on the nature of the oxidant. Fumarate and maleate have a much smaller dependence on the nature of the oxidant, and it has been concluded that these reductions occur through a ligand-centered radical.¹²

The ability of a ligand to mediate an electron transfer has been ascribed to a matching of the symmetry of metal and ligand orbitals.¹² When the symmetry of the orbitals of the metal ions that donate and accept the electron are the same, ligands with orbitals of matching symmetry may provide a lower energy pathway for electron transfer. Thus if the reductant donates an e_g electron to an e_g orbital, a ligand such as chloride (a sigma carrier) would be a better bridging ligand than azide or acetate. Electron transfer involving a t_{2g} orbital would be better accommodated by an azide or an acetate, presumably because of better overlap of the t_{2g} orbital with the pi system of azide or acetate. Existing data are in agreement with these suggestions, but they are insufficient to test the concepts adequately.

It has proved difficult to prepare complexes in which the effect of the nature of the bridging ligand on the rate of electron transfer can be investigated, usually because one of these metal centers is labile and the rate of formation of the precursor is difficult to separate from the rate of electron transfer. An ingenious approach to circumvent this problem involved the preparation of binuclear Ru(III)-Co(III) complexes, which were then reacted with a rapid one-electron reducing agent.³⁵ This produced the binuclear precursor complex,

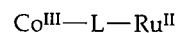
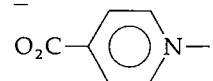
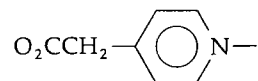
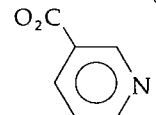


TABLE 8.8

Rate Constants for Intramolecular Electron Transfer in $(\text{NH}_3)_5\text{Co}^{\text{III}}-\text{L}-\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{H}_2\text{O})^{4+}$ Where L = Pyridinecarboxylate.

L	k
	1×10^2
	1.6×10^{-2}
	1.6×10^{-3}

which could be used to measure the rate of electron transfer between the Ru^{II} and the Co^{III} centers. The results for bridging pyridine carboxylate ligands are shown in Table 8.8.¹² These results show an inhibiting effect of the CH_2 group and the importance of conjugation in the bridging ligand.

Other Considerations for Inner Sphere Reactions

The role of the bridging ligand is the most important feature of inner sphere reactions and has dominated research on reactivity towards electron transfer by an inner sphere mechanism. The *cis* ligand has a very small effect if the data in Table 8.9 are indicative of inner sphere processes in general.⁸ The electronic requirements of inner sphere electron transfer for macrocyclic ligands have been discussed in terms of a three-center transition state bonding scheme.³⁶

TABLE 8.9

Rates of Electron Transfer between Cr^{2+} and *cis*- $\text{Co}(\text{en})_2\text{LCI}^{2+}$.

L	$k(M^{-1}s^{-1})$
NH_3	2.3×10^5
H_2O	4.2×10^5
Py	9.4×10^5
Cl^-	7.7×10^5
F^-	9×10^5

Discussions of inner sphere reactions are complicated by the fact that any of the three components may be rate determining. The possibilities in the free energy profiles are shown in Figure 8.6. In the first case the rate-determining step is formation of the precursor complex (equation 8.32). In the second case the rate-determining step is the electron transfer, and in the third case decomposition of the successor complex is rate determining. Each type has been observed, but the second is the most common, involving the rearrangement of the coordination sphere as discussed earlier.

LONG-RANGE ELECTRON TRANSFER

One of the most active research areas in electron transfer involves long-range electron transfer, transfers in which the distance between the oxidant and the reductant may be up to 25 Å.³⁷ The primary impetus for the research lies in a

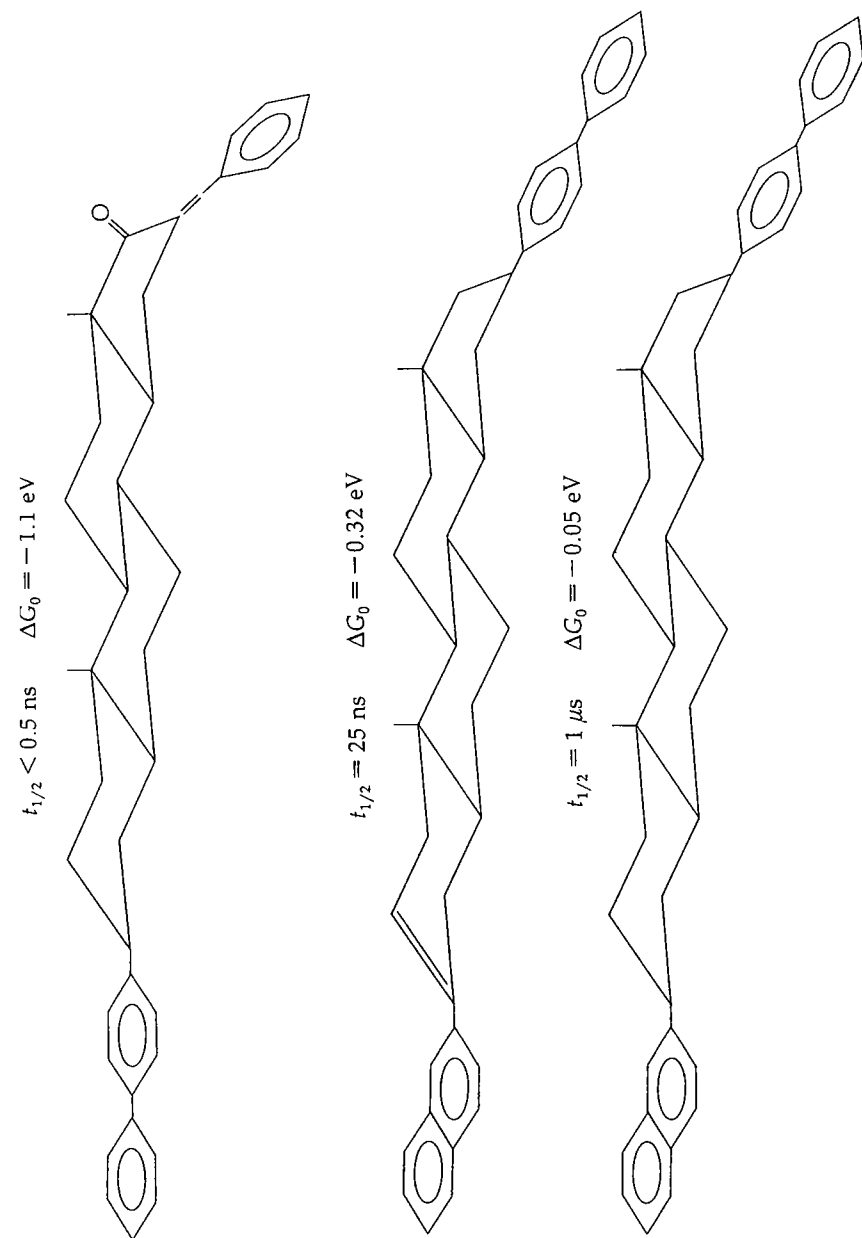


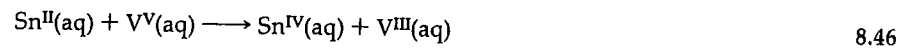
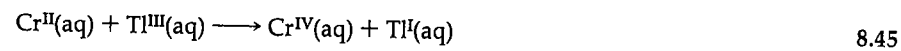
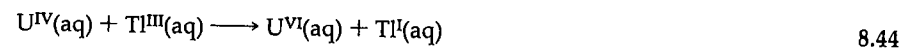
FIGURE 8.7. Systems in which long-range electron transfer has been studied. The half-lives and free energies for intramolecular electron transfer are shown above each diended steroid.

wish to understand electron transfer in biological systems where electron transfer often takes place over considerable distances.³⁷ The capability for rapid electron transfer between organic donor and acceptor sites separated by rigid saturated hydrocarbon groups has been investigated.³⁸ The types of complexes are shown in Figure 8.7. These complexes were treated with solvated electrons, and the approach to equilibrium between the two ends was investigated. As shown on Figure 8.7 the rates for electron transfer from one end to the other range from half-lives of $< 0.5 \text{ ns}$ to $1 \mu\text{s}$.³⁸ This fast electron transfer is surprising considering the long distances ($\sim 15 \text{ \AA}$) and the insulating nature of the organic backbone, but it certainly makes the electron transfer between metal centers in biological molecules more understandable. The distance from the redox site to the surface in several metalloproteins was estimated from the reaction with $\text{Fe}(\text{EDTA})^{2-}$.³⁹ The calculations indicated electron transfer distances ranging from 3 to $10 \text{ \AA}$ depending on the protein and inorganic redox reagent.³⁹ Electron transfer has been observed in a Zn^{II} , Fe^{III} hybrid hemoglobin at $25 \text{ \AA}$.⁴⁰ The electron transfer was initiated by flash photoexcitation forming Zn^{III} which is a good reductant for Fe^{III} in the long-range process. The distance is known from crystallography to be $25 \text{ \AA}$ in a rigid structure, and the rate constant was $60 \pm 25 \text{ s}^{-1}$.⁴⁰ Similar experiments on pentaammineruthenium(III)(histidine-33)-ferricytochrome C have shown electron transfer between the metal centers $15 \text{ \AA}$ apart at a rate of 20 s^{-1} .⁴¹

There is considerable theoretical and experimental interest in these long-range electron transfers, but at this point a full explanation is not available.³⁷ The application to biological systems will certainly keep this an active research area.

MULTIELECTRON TRANSFER

A number of electron transfer reactions yield products that have changed by more than one electron.⁴²



It is usually difficult to determine whether a two-electron transfer occurs simultaneously or in steps. The absence of large amounts of $\text{Cr}^{\text{III}}(\text{aq})$ in reaction 8.45 is evidence that two electrons may be transferred. A more recent report has suggested that a four-electron "simultaneous" transfer occurs

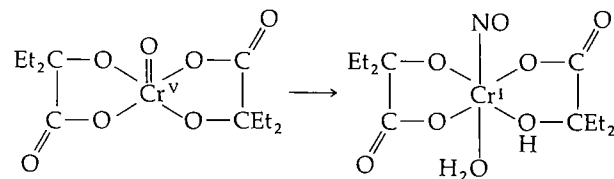


FIGURE 8.8. A reaction that has been suggested to proceed by a four-electron transfer.

from a chelated chromium(V) complex.⁴⁴ The reaction is shown in Figure 8.8. The suggested scheme involved formation of a hydroxylamine precursor followed by a four-electron transfer.

SUMMARY

Electron transfer is one of the primary reactions of transition metal complexes. Its rate depends on the concentration of the oxidant and the reductant. Electron transfer mechanisms are of two basic types: an outer sphere mechanism between metal centers with intact coordination spheres and an inner sphere mechanism in which a ligand bridges the two metal centers. In either case a primary consideration in the rate is the changes in the bond lengths and angles necessary before electron transfer can occur. Outer sphere reactions can be adequately described by theoretical methods. The nature of the bridging ligand is important for inner sphere reactions. Conjugation in a bridging ligand aids electron transfer, although electron transfer can occur over very long distances even in the absence of conjugation.

REFERENCES

1. K. F. Purcell and J. C. Kotz, *Inorganic Chemistry* (Philadelphia: W. B. Saunders, 1977).
2. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (New York: Interscience, 1972).
3. R. G. Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes* (Boston: Allyn and Bacon, 1974).
4. F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* (New York: John Wiley and Co., 1968).
5. J. W. Hersberger, R. J. Klinger, and J. K. Kochi, *J. Am. Chem. Soc.* **105**, 61 (1983).
6. M. O. Alpers, N. J. Coville, T. V. Ashworth, E. Singleton, and H. E. Swanepoel, *J. Organomet. Chem.* **199**, 55 (1980).
7. H. Taube, *J. Chem. Ed.* **45**, 452 (1968).
8. L. E. Bennett, *Prog. Inorg. Chem.* **18**, 2 (1973).
9. J. E. Earley, *Prog. Inorg. Chem.* **13**, 243 (1970).
10. N. Sutin, *Acc. Chem. Res.* **1**, 225 (1968).
11. H. Taube and E. S. Gould, *Acc. Chem. Res.* **2**, 321 (1969).
12. A. Haim, *Acc. Chem. Res.* **8**, 264 (1975).
13. S. Bellard, K. A. Robinson, and G. M. Sheldrick, *Acta Cryst.* **B35**, 271 (1979).
14. R. D. Wilson and R. Bau, *J. Am. Chem. Soc.* **96**, 7601 (1974).
15. H. C. Stynes and J. A. Ibers, *Inorg. Chem.* **10**, 2304 (1971).
16. P. Bernhard, H.-B. Burgi, J. Hauser, H. Lehmann, and A. Ludi, *Inorg. Chem.* **21**, 3936 (1982).
17. J. Guarr, E. Buhks, and G. McLendon, *J. Am. Chem. Soc.* **105**, 3764 (1983).
18. E. Buhks, M. Bixon, and J. Jortner, *J. Phys. Chem.* **85**, 3763 (1981).
19. F. Moattar, J. R. Walton, and L. E. Bennett, *Inorg. Chem.* **22**, 550 (1983).
20. N. Sutin, *Prog. Inorg. Chem.* **36**, 441 (1983).
21. R. A. Marcus, *Ann. Rev. Phys. Chem.* **15**, 155 (1964).
22. G. Dulz and N. Sutin, *Inorg. Chem.* **2**, 917 (1963).
23. J. F. Endicott, B. Durham, and K. Kumar, *Inorg. Chem.* **21**, 2437 (1982).
24. H. Cohen, S. Efrima, D. Meyerstein, M. Nutkovich, and K. Wieghardt, *Inorg. Chem.* **22**, 688 (1983).
25. T. J. Meyer, *Acc. Chem. Res.* **11**, 94 (1978).
26. J. C. Curtis and T. J. Meyer, *Inorg. Chem.* **21**, 1562 (1982).
27. T. J. Meyer, *Prog. Inorg. Chem.* **30**, 389 (1983).
28. C. K. Murray and D. W. Margerum, *Inorg. Chem.* **22**, 463 (1983).
29. A. G. Mauk, E. Bordignon, and H. B. Gray, *J. Am. Chem. Soc.* **104**, 7654 (1982).
30. A. Haim, *Prog. Inorg. Chem.* **30**, 273 (1983).
31. C. Shea and A. Haim, *J. Am. Chem. Soc.* **93**, 3055 (1971).
32. D. Gaswick and A. Haim, *J. Am. Chem. Soc.* **96**, 7845 (1974).

33. B. T. Reágor, D. F. Kelley, D. H. Huchital, and P. M. Rentzepis, *J. Am. Chem. Soc.* **104**, 7400 (1982).
34. R. W. Craft and R. G. Gaunter, *Inorg. Chem.* **14**, 1283 (1975).
35. S. S. Isied and H. Taube, *J. Am. Chem. Soc.* **95**, 8198 (1973).
36. F. P. Rotzinger, K. Kumar, and J. F. Endicott, *Inorg. Chem.* **21**, 4111 (1982).
37. D. Devault, *Quart. Rev. Biophy.* **13**, 390 (1980).
38. L. T. Calcaterra, G. L. Closs, and J. R. Miller, *J. Am. Chem. Soc.* **105**, 670 (1983).
39. A. G. Mauk, R. A. Scott, and H. B. Gray, *J. Am. Chem. Soc.* **102**, 4360 (1980).
40. J. L. McGourty, N. V. Blough, and B. M. Hoffman, *J. Am. Chem. Soc.* **105**, 4470 (1983).
41. J. R. Winkler, D. G. Nocera, K. M. Yocom, E. Bordinon, and H. B. Gray, *J. Am. Chem. Soc.* **104**, 5798 (1982).
42. A. G. Sykes, *Kinetics of Inorganic Reactions* (Oxford: Pergamon, 1966) Chapter 8.
43. N. Rajasekar, R. Subramaniam, and E. S. Gould, *Inorg. Chem.* **21**, 4110 (1982).

PROBLEMS

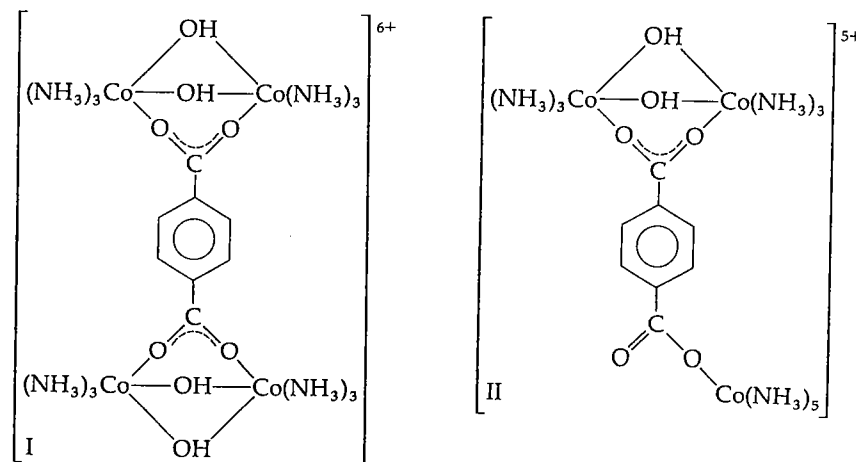
1. Write inner and outer sphere mechanisms for the reaction of $\text{V}(\text{H}_2\text{O})_6^{2+}$ with $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$. Suggest data that could be used to differentiate between the two.
2. Use the following data for the isotopic exchange reactions to calculate the rate constants for the cross reactions:

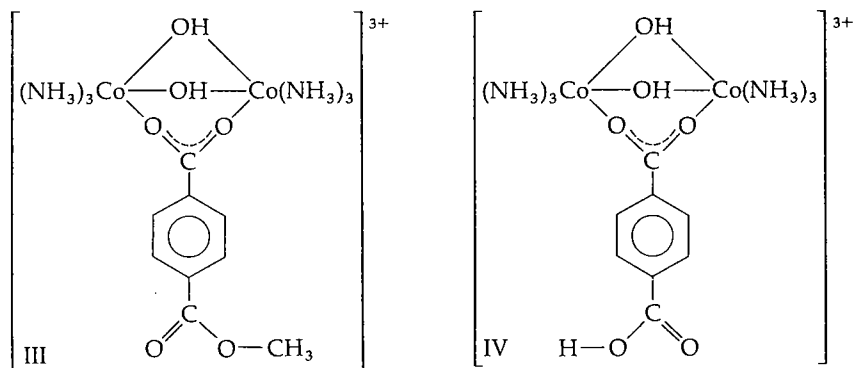
	E_0	k
$^*\text{Ce}^{\text{IV}}(\text{aq}) + \text{Ce}^{\text{III}}(\text{aq}) \rightleftharpoons \text{Ce}^{\text{IV}}(\text{aq}) + ^*\text{Ce}^{\text{III}}(\text{aq})$	1.44	4.6
$^*\text{Fe}(\text{CN})_6^{3-} + \text{Fe}(\text{CN})_6^{4-} \rightleftharpoons \text{Fe}(\text{CN})_6^{3-} + ^*\text{Fe}(\text{CN})_6^{4-}$	0.68	300
$^*\text{MnO}_4^- + \text{MnO}_4^{2-} \rightleftharpoons \text{MnO}_4^- + ^*\text{MnO}_4^{2-}$	0.56	3.6×10^3

3. Use the data in Table 7.1 to estimate the rate of self-exchange for $\text{Ru}(\text{H}_2\text{O})_6^{2+,3+}$. [P. Bernhard, H.-B. Burgi, J. Hauser, H. Lehmann, and A. Ludi, *Inorg. Chem.* **21**, 3936 (1982).]
4. Consider the following data:

Second Order Rate Constants for the Reductions of Complexes I–IV by Chromium(II) and Vanadium(II) at 25°C, $\mu = 1.0 \text{ M}$ (LiClO_4).

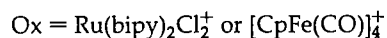
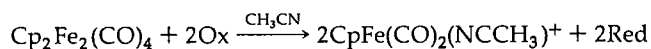
complex	$k_{\text{Cr}} \times 10^3 (\text{M}^{-1}\text{s}^{-1})$	$k_{\text{V}} (\text{M}^{-1}\text{s}^{-1})$	$k_{\text{Cr}}/k_{\text{V}}$
I	1.16 ± 0.09	0.056 ± 0.005	0.021
II	1.15 ± 0.03	0.065 ± 0.005	0.018
III	1.66 ± 0.02	0.085 ± 0.003	0.020
IV	1.89 ± 0.09	0.096 ± 0.005	0.020





Suggest mechanisms based on these data. [M. Hery and K. Wieghardt, *Inorg. Chem.* 15, 2315 (1976).]

- The transfer of electrons between centers in biological molecules has been modeled by attaching an oxidizing agent to a protein containing Fe(III). Briefly describe the nature of the experiment. [S. S. Isied, G. Worosila, and S. J. Atherton, *J. Am. Chem. Soc.* 104, 7659 (1982).]
- For reactions of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ with oxidants



the rate law is

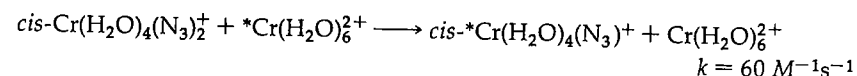
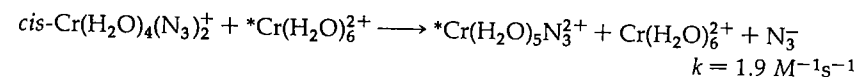
$$-\frac{d[\text{Cp}_2\text{Fe}_2(\text{CO})_4]}{dt} = k[\text{Ox}][\text{Cp}_2\text{Fe}_2(\text{CO})_4]$$

and activation parameters,

Ox	$\Delta H^\ddagger$	$\Delta S^\ddagger$
$\text{Ru}(\text{bipy})_2\text{Cl}_2^+$	6.2	-17.
$[\text{CpFe}(\text{CO})]_4^+$	1.8	-31.

Suggest a mechanism. [J. N. Braddock and T. J. Meyer, *Inorg. Chem.* 12, 723 (1973).]

- The activation enthalpy for reduction of $\text{cis-Co}(\text{en})_2\text{Cl}_2^+$ by Cr^{2+} is -6 ± 4 kcal/mole. Explain the negative value. [R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.* 9, 23 (1970).]
- Explain the following two reactions:



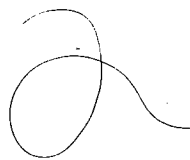
[T. J. Swift and T. A. Stephenson, *Inorg. Chem.* 5, 1100 (1966).]

- Why is $\text{Co}(\text{CN})_5^{3-}$ a common choice for preparation of a bridged redox species?
- The reaction of $\text{Co}(\text{NH}_3)_6^{3+}$ with $\text{Co}(\text{CN})_5^{3-}$ occurs at approximately the same rate as that of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ with $\text{Co}(\text{CN})_5^{3-}$. What does this indicate about the mechanism?
- In the reaction of $\text{Co}(\text{NH}_3)_5\text{SCN}^{2+}$ with $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ the intermediate $\text{Fe}(\text{H}_2\text{O})_5(\text{NCS})^{2+}$ can be detected. Suggest a mechanism.
- The reduction of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ by $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ occurs at a rate of ~ 0.1 ; $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ is reduced by $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ at a rate of 1.5×10^6 (all rates expressed in $\text{M}^{-1}\text{s}^{-1}$). Reduction of these two oxidants by $\text{Ru}(\text{NH}_3)_6^{2+}$ led to rate constants of 3.0 and 0.04 for the aquo and hydroxo complexes, respectively. What do these data suggest for the mechanisms of these redox reactions?

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