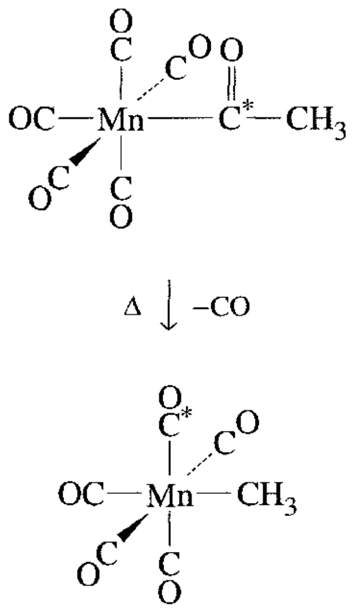
CHAPTER

14

Organometallic Reactions and Catalysis



Organometallic compounds undergo a rich variety of reactions, comparable in diversity to the reactions of organic molecules. These may involve loss or gain of ligands (or both), molecular rearrangement, formation or breaking of metal-metal bonds, or reactions at the ligands themselves. Often, reaction mechanisms involve multiple steps and, frequently, reactions yield not one but a variety of products. Sequences of reactions may be combined into catalytic cycles that may be useful, in some cases commercially. In this chapter, we will not attempt to cover all possible types of organometallic reactions but will concentrate on those that have proved most common and useful, particularly for synthetic and catalytic processes. We will discuss organometallic reactions according to the following outline:

I. Reactions involving gain or loss of ligands
   A. Ligand dissociation and substitution
   B. Oxidative addition
   C. Reductive elimination
   D. Nucleophilic displacement

II. Reactions involving modification of ligands
   A. Insertion
   B. Carbonyl insertion (alkyl migration)
   C. Hydride elimination
   D. Abstraction

14-1 REACTIONS INVOLVING GAIN OR LOSS OF LIGANDS

Some of the most important reactions of organometallic compounds involve a change in coordination number of the metal by a gain or loss of ligands. If the formal oxidation state of the metal is retained, these reactions are considered addition or dissociation reactions; if the formal oxidation state is changed, they are termed oxidative additions or reductive eliminations.

Type of Reaction	*Change in Coordination Number*	*Change in Formal Oxidation State of Metal*
Addition	Increase	None
Dissociation	Decrease	None
Oxidative addition	Increase	Increase
Reductive elimination	Decrease	Decrease

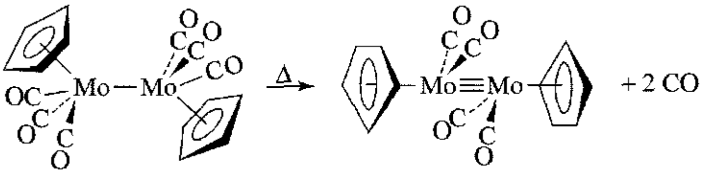
In classifying these reactions, it will frequently be necessary to determine formal oxidation states of the metals in organometallic compounds. In general, method A (the donor pair method) described in Chapter 13 can be used in assigning oxidation states. Examples will be given later in this chapter in the discussion of oxidative addition reactions.

We will first consider ligand dissociation reactions. When coupled with addition reactions, dissociation reactions can be useful synthetically, providing an avenue to replace ligands such as carbon monoxide and phosphines by other ligands.

14-1-1 LIGAND DISSOCIATION AND SUBSTITUTION

CO dissociation

Chapter 13 gave a brief introduction to carbonyl dissociation reactions, in which CO may be lost thermally or photochemically. Such a reaction may result in rearrangement of the remaining molecule or replacement of CO by another ligand:



$$Fe(CO)_5 + P(CH_3)_3 \xrightarrow{\Delta} Fe(CO)_4(P(CH_3)_3) + CO$$

The second type of reaction, involving ligand replacement, is an important way to introduce new ligands into complexes and deserves further discussion.

Most thermal reactions involving replacement of CO by another ligand, L, have rates that are independent of the concentration of L; they are first order with respect to the metal complex. This behavior is consistent with a **dissociative** mechanism involving slow loss of CO, followed by rapid reaction with L:

$$\underset{18\,e^-}{Ni(CO)_4} \longrightarrow \underset{16\,e^-}{Ni(CO)_3} + CO \quad \text{(slow)} \quad \text{loss of CO from 18-electron complex}$$

$$\underset{16\,e^-}{Ni(CO)_3} + L \longrightarrow \underset{18\,e^-}{Ni(CO)_3L} \quad \text{(fast)} \quad \text{addition of L to 16-electron intermediate}$$

Loss of CO from the stable, 18-electron $Ni(CO)_4$ is slow relative to the addition of L to the more reactive, 16-electron $Ni(CO)_3$. Consequently, the first step is rate limiting, and this mechanism has the following rate law:

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

Some reactions show more complicated kinetics. For example, study of the reaction

$$Mo(CO)_6 + L \xrightarrow{\Delta} Mo(CO)_5L + CO \qquad (L = \text{phosphine})$$

has shown that, for some phosphine ligands, the rate law has the following form:

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

The two terms in the rate law imply parallel pathways for the formation of $\text{Mo(CO)}_5\text{L}$. The first term is again consistent with a dissociative mechanism:

$$\text{Mo(CO)}_6 \xrightarrow{k_1} \text{Mo(CO)}_5 + \text{CO} \qquad \text{(slow)}$$

$$\text{Mo(CO)}_5 + \text{L} \longrightarrow \text{Mo(CO)}_5\text{L} \qquad \text{(fast)}$$

$$\text{Rate}_1 = k_1[\text{Mo(CO)}_6]$$

The second term in the rate law is consistent with an **associative** process involving a bimolecular reaction of Mo(CO)_6 and L to form a transition state that then loses CO:

$$\text{Mo(CO)}_6 + \text{L} \xrightarrow{k_2} [\text{Mo(CO)}_6\text{---L}] \qquad \text{association of Mo(CO)}_6\text{ and L}$$

$$[\text{Mo(CO)}_6\text{---L}] \longrightarrow \text{Mo(CO)}_5\text{L} + \text{CO} \qquad \text{loss of CO from transition state}$$

Formation of the transition state is the rate-limiting step in this mechanism; the rate law for this pathway is therefore

$$\text{Rate}_2 = k_2[\text{Mo(CO)}_6][\text{L}]$$

There is also strong evidence that solvent is involved in the first-order mechanism for the replacement of CO; however, because the solvent is in great excess, it does not appear in the rate law, and the observed rate law obtained in this case is the same as that shown above.[1]

Because of the two pathways, the overall rate of formation of $\text{Mo(CO)}_5\text{L}$ is the sum of the rates of the unimolecular and bimolecular mechanisms, $\text{Rate}_1 + \text{Rate}_2$.

Although most CO substitution reactions proceed primarily by a dissociative mechanism, an associative path is more likely for complexes of large metals (providing favorable sites for incoming ligands to attack) and for reactions involving highly nucleophilic ligands.

As pointed out in the introduction to this section, even though ligand dissociation and association involve changes in coordination number, they do not involve changes in the oxidation state of the metal.[2]

Dissociation of phosphine

Carbon monoxide is by no means the only ligand that can undergo dissociation from metal complexes. Many other ligands can dissociate, with the ease of dissociation a function of the strength of metal-ligand bonding and, in some cases, the degree of crowding of ligands around the metal. These steric effects have been investigated for a variety of ligands, especially phosphines and similar ligands.

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[1] W. D. Covey and T. L. Brown, *Inorg. Chem.*, **1973**, *12*, 2820.

[2] Assuming that no oxidation-reduction reaction occurs between the ligand and the metal.

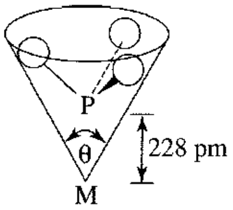


FIGURE 14-1 Ligand Cone Angle.

TABLE 14-1
Ligand Cone Angles

Ligand	*Cone Angle θ*	*Ligand*	*Cone Angle θ*
PH_3	87°	$P(CH_3)(C_6H_5)_2$	136°
PF_3	104°	$P(CF_3)_3$	137°
$P(OCH_3)_3$	107°	$P(C_6H_5)_3$	145°
$P(OC_2H_5)_3$	109°	$P(cyclo\text{-}C_6H_{11})_3$	170°
$P(CH_3)_3$	118°	$P(t\text{-}C_4H_9)_3$	182°
PCl_3	124°	$P(C_6F_5)_3$	184°
PBr_3	131°	$P(o\text{-}C_6H_4CH_3)_3$	194°
$P(C_2H_5)_3$	132°		

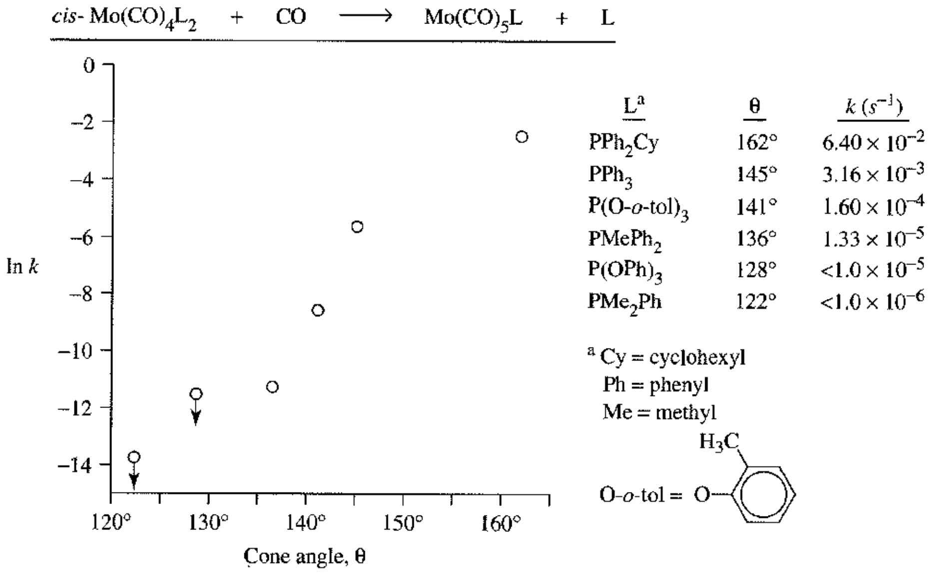
To describe steric effects, Tolman has defined the cone angle as the apex angle, θ, of a cone that encompasses the van der Waals radii of the outermost atoms of a ligand, as shown in Figure 14-1.[3] Values of cone angles of selected ligands are given in Table 14-1.

As might be expected, the presence of bulky ligands, having large cone angles, can lead to more rapid ligand dissociation as a consequence of crowding around the metal. For example, the rate of the reaction

$$cis\text{-Mo(CO)}_4\text{L}_2 + \text{CO} \longrightarrow \text{Mo(CO)}_5\text{L} + \text{L} \qquad (\text{L} = \text{phosphine or phosphite})$$

which is first order in *cis*-$Mo(CO)_4L_2$, increases with increasing ligand bulk, as shown in Figure 14-2; the larger the cone angle, the more rapidly the phosphine or phosphite is lost.[4] The overall effect is substantial; for example, the rate for the most bulky ligand shown is more than four orders of magnitude greater than that for the least bulky ligand.

Many other examples of the effect of ligand bulk on the dissociation of ligands have been reported in the chemical literature.[5] For many dissociation reactions, the effect of ligand crowding may be more important than electronic effects in determining reaction rates.



$$cis\text{-}Mo(CO)_4L_2 + CO \longrightarrow Mo(CO)_5L + L$$

L[a]	θ	k (s⁻¹)
PPh_2Cy	162°	6.40×10^{-2}
PPh_3	145°	3.16×10^{-3}
$P(O\text{-}o\text{-}tol)_3$	141°	1.60×10^{-4}
$PMePh_2$	136°	1.33×10^{-5}
$P(OPh)_3$	128°	$<1.0 \times 10^{-5}$
PMe_2Ph	122°	$<1.0 \times 10^{-6}$

[a] Cy = cyclohexyl
Ph = phenyl
Me = methyl

FIGURE 14-2 Reaction Rate Constant Versus Cone Angle for Phosphine Dissociation.

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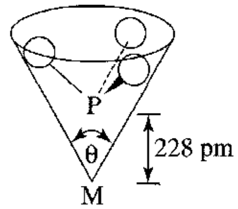
[3] C. A. Tolman, *J. Am. Chem. Soc.*, **1970**, *92*, 2953; *Chem. Rev.*, **1977**, *77*, 313.

[4] D. J. Darensbourg and A. H. Graves, *Inorg. Chem.*, **1979**, *18*, 1257.

[5] For example, M. J. Wovkulich and J. D. Atwood, *Organometallics*, **1982**, *1*, 1316; J. D. Atwood, M. J. Wovkulich, and D. C. Sonnenberger, *Acc. Chem. Res.*, **1983**, *16*, 350.



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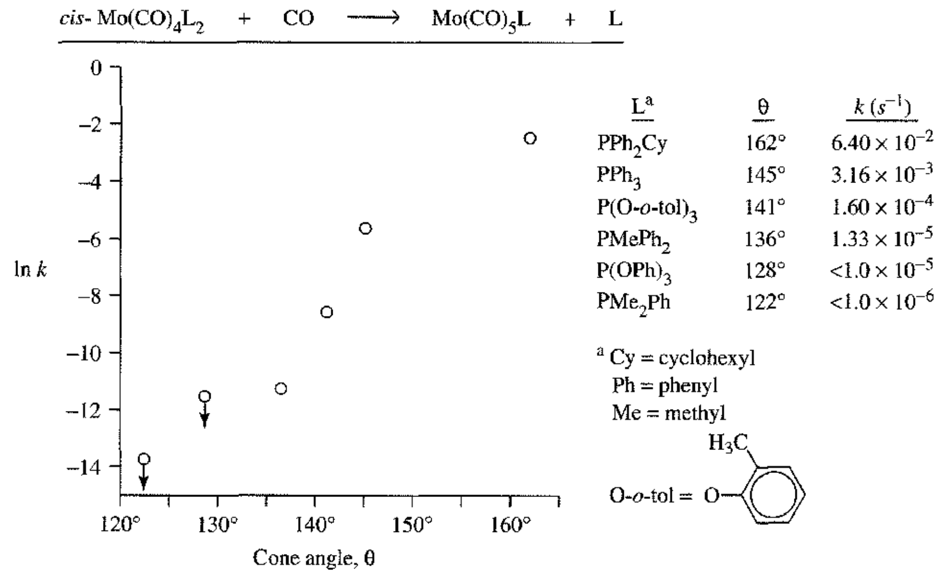

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[3] C. A. Tolman, *J. Am. Chem. Soc.*, **1970**, *92*, 2953; *Chem. Rev.*, **1977**, *77*, 313.

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[5] For example, M. J. Wovkulich and J. D. Atwood, *Organometallics*, **1982**, *1*, 1316; J. D. Atwood, M. J. Wovkulich, and D. C. Sonnenberger, *Acc. Chem. Res.*, **1983**, *16*, 350.

14-1-2 OXIDATIVE ADDITION

These reactions, as the name suggests, involve an increase in both the formal oxidation state and the coordination number of the metal. Oxidative addition (OA) reactions are among the most important of organometallic reactions and are essential steps in many catalytic processes. The reverse type of reaction, designated reductive elimination (RE), is also very important. These reactions can be described schematically by the equation:

$$L_nM + X{-}Y \underset{\text{RE}}{\overset{\text{OA}}{\rightleftharpoons}} L_nM\begin{matrix}\diagup X\\ \diagdown Y\end{matrix}$$

For example, heating $Fe(CO)_5$ in the presence of I_2 leads to formation of *cis*-$I_2Fe(CO)_4$. The reaction has two steps:

$$Fe(CO)_5 \xrightarrow{\Delta} Fe(CO)_4 + CO$$

$$\underset{16\,e^-}{Fe(CO)_4} + I_2 \longrightarrow \underset{18\,e^-}{cis\text{-}I_2Fe(CO)_4} \qquad \text{(oxidative addition)}$$

The first step involves dissociation of CO to give a 4-coordinate iron(0) intermediate. In the second step, iron is formally oxidized to iron(II) and the coordination number expanded by the addition of two iodo ligands. This second step is an example of oxidative addition. Like most oxidative additions, this step involves an increase by 2 in both the oxidation state and coordination number of the metal.

It may be useful at this point to review briefly the assignment of oxidation states. Coordinated ligands are generally assigned the charges of the free ligand (e.g., zero for neutral ligands such as CO, 1− for Cl^-, CN^-). Hydrogen atom ligands and organic radicals are treated as anions:

H^-	CH_3^-	$C_6H_5^-$	$C_5H_5^-$
hydride	methyl	phenyl	η^5-C_5H_5

(The assigned charges on these ligands may have little chemical significance. For example, in methyl complexes, the carbon-metal bond is largely covalent, and such complexes should not be viewed as containing the free ion CH_3^-. The assignment of these charges is a formalism, another electron-counting scheme.)

OA reactions of square-planar d^8 complexes have special chemical significance, and we will therefore use one such complex, *trans*-$Ir(CO)Cl(PEt_3)_2$, to illustrate these reactions (Figure 14-3).

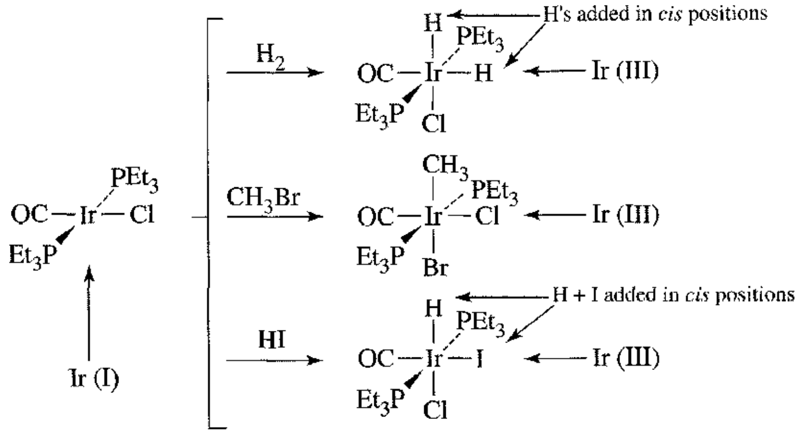


FIGURE 14-3 Examples of Oxidative Addition Reactions.

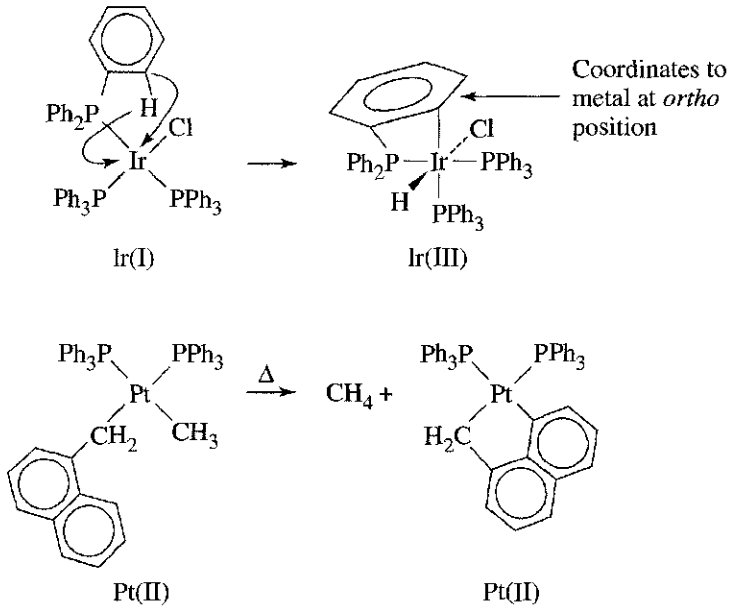


FIGURE 14-4 Cyclometallation Reactions.

In each of the examples shown, the formal oxidation state of iridium increases from (I) to (III), and its coordination number increases from 4 to 6. The new ligands may add in a *cis* or *trans* fashion, with their orientation a function of the mechanistic pathway involved. An important feature of such reactions is that, in the expansion of the coordination number of the metal, the newly added ligands are brought into close proximity to the original ligands; this may enable chemical reactions to occur between ligands. Such reactions, encountered frequently in the mechanisms of catalytic cycles involving organometallic compounds, will be discussed later in this chapter.

Cyclometallations

These are reactions that incorporate metals into organic rings. The most common of these are orthometallations, oxidative additions in which the *ortho* position of an aromatic ring becomes attached to the metal. The first example in Figure 14-4 is an OA in which an *ortho* carbon and the hydrogen originally in the *ortho* position add to iridium.

Not all cyclometallation reactions are OAs; the second example in Figure 14-4 shows a cyclometallation that is not an OA overall (although one step in the mechanism may be OA).

14-1-3 REDUCTIVE ELIMINATION

Reductive elimination is the reverse of oxidative addition. To illustrate this distinction, consider the following equilibrium:

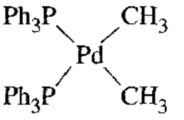
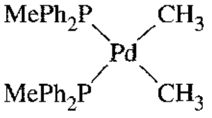
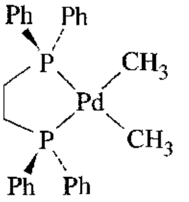
$$\underset{\text{Ta(III)}}{(\eta^5\text{-}C_5H_5)_2TaH} + H_2 \underset{\text{RE}}{\overset{\text{OA}}{\rightleftharpoons}} \underset{\text{Ta(V)}}{(\eta^5\text{-}C_5H_5)_2TaH_3}$$

The forward reaction involves formal oxidation of the metal, accompanied by an increase in coordination number; it is an OA. The reverse reaction is an example of RE, which involves a decrease in both oxidation number and coordination number.

RE reactions often involve elimination of molecules such as

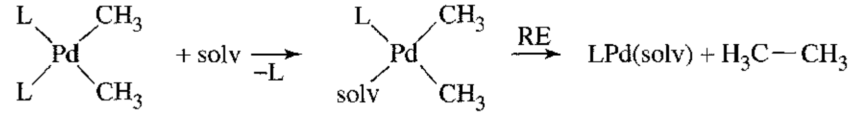
R—H R—R′ R—X H—H (R, R′ = alkyl, aryl; X = halogen)

TABLE 14-2
Relative Rates of Reductive Elimination

Complex	*Rate Constant* (s^{-1})	T(°C)
	1.04×10^{-3}	60
	9.62×10^{-5}	60
	4.78×10^{-7}	80

The products eliminated by these reactions may be important and useful organic compounds (R—H, R—R′, R—X). In some cases, the organic fragments (R, R′) undergo rearrangement or other reactions while coordinated to the metal. Examples of this phenomenon will be discussed later in this chapter.

As might be expected, the rates of RE reactions are also affected by ligand bulk. An example of this effect is shown in Table 14-2. The three *cis*-dimethyl complexes shown undergo RE following replacement of a phosphine ligand by a solvent molecule (solv):



RE yields ethane in each case. The most crowded complex, $Pd(CH_3)_2(PPh_3)_2$, undergoes reductive elimination the most rapidly.[6]

14-1-4 NUCLEOPHILIC DISPLACEMENT

Ligand displacement reactions may be described as nucleophilic substitutions, involving incoming ligands as nucleophiles. Organometallic complexes, especially those carrying negative charges, may themselves behave as nucleophiles in displacement reactions. For example, the anion $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ can displace iodide from methyl iodide:

$$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^- + CH_3I \longrightarrow [(\eta^5\text{-}C_5H_5)(CH_3)Mo(CO)_3] + I^-$$

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[6] A. Gillie and J. K. Stille, *J. Am. Chem. Soc.*, **1980**, *102*, 4933. Rates of other reductive elimination reactions are also reported in this reference.

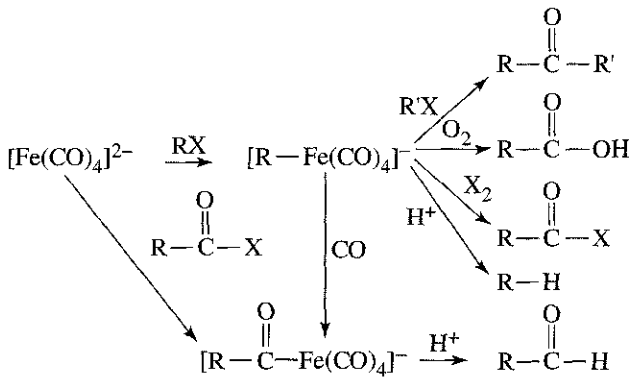


FIGURE 14-5 Synthetic Pathways Using $[Fe(CO)_4]^{2-}$.

$[Fe(CO)_4]^{2-}$ is an extremely useful organometallic nucleophile. Cooke and Collman developed the synthesis for the parent compound of this nucleophile, $Na_2Fe(CO)_4$, commonly known as Collman's reagent, by reacting sodium with $Fe(CO)_5$ in dioxane:[7]

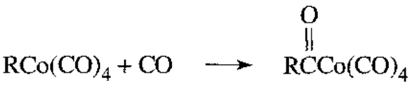
$$2\,Na + Fe(CO)_5 \xrightarrow{\text{dioxane}} Na_2Fe(CO)_4 \cdot 1.5\ \text{dioxane} + CO$$

The product of this reaction can be used to synthesize a variety of organic compounds. For example, the nucleophilic attack of $[Fe(CO)_4]^{2-}$ on an organic halide RX yields $[RFe(CO)_4]^-$, which can subsequently be converted to alkanes, ketones, carboxylic acids, aldehydes, acid halides, or other organic products. These reactions are outlined in Figure 14-5; note that $[RFe(CO)_4]^-$ undergoes other types of reactions in addition to nucleophilic displacements, as shown for some examples in the figure. Additional details of these reactions can be found in the literature.[8]

Another useful anionic nucleophile is $[Co(CO)_4]^-$, whose chemistry has been developed by Heck.[9] A rather mild nucleophile, $[Co(CO)_4]^-$ can be synthesized by the reduction of $Co_2(CO)_8$ by sodium; it reacts with organic halides to generate alkyl complexes:

$$[Co(CO)_4]^- + RX \longrightarrow RCo(CO)_4 + X^-$$

The alkyl complex reacts with carbon monoxide to apparently insert CO into the cobalt-alkyl bond (insertion reactions will be discussed later in this chapter) to give an acyl complex (containing a —C(=O)R ligand):



$$RCo(CO)_4 + CO \longrightarrow R\overset{\overset{\large O}{\|}}{C}Co(CO)_4$$

The acyl complex can then react with alcohols to generate esters:

$$R\overset{\overset{\large O}{\|}}{C}Co(CO)_4 + R'OH \longrightarrow R\overset{\overset{\large O}{\|}}{C}OR' + HCo(CO)_4$$

Reaction of $HCo(CO)_4$, a strong acid, with base can regenerate the $[Co(CO)_4]^-$ to make the overall process catalytic.

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[7] M. P. Cooke, *J. Am. Chem. Soc.*, **1970**, *92*, 6080; J. P. Collman, *Acc. Chem. Res.*, **1975**, *8*, 342; R. G. Finke and T. N. Sorrell, *Org. Synth.*, **1979**, *59*, 102.

[8] J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **1977**, *99*, 2515; *J. Am. Chem. Soc.*, **1978**, *100*, 4766.

[9] R. F. Heck, in I. Wender and P. Pino, eds., *Organic Synthesis via Metal Carbonyls*, Vol. 1, Wiley, New York, 1968, pp. 373–404.

Many other nucleophilic anionic organometallic complexes have been studied, and the relative nucleophilicities of various carbonyl anions have been reported.[10] Parallels between these anions and anions of main group elements will be discussed in Chapter 15.

14-2 REACTIONS INVOLVING MODIFICATION OF LIGANDS

Many cases are known in which a ligand or molecular fragment appears to insert itself into a metal-ligand bond. Although some of these reactions are believed to occur by direct, single-step insertion, many "insertion" reactions are much more complicated and do not involve a direct insertion step at all. The most studied of these reactions are the carbonyl insertions; these will be discussed following a brief introduction to some common insertion reactions.

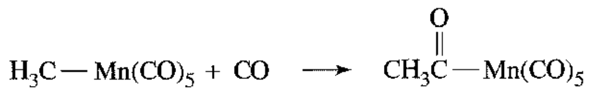
14-2-1 INSERTION

The reactions in Figure 14-6 may be designated as 1,1 insertions, indicating that both bonds to the inserted molecule are made to the same atom in that molecule. For example, in the second reaction, both the Mn and CH_3 are bonded to the sulfur of the inserted SO_2.

1,2 insertions give products in which bonds to the inserted molecule are made to adjacent atoms in that molecule. For example, in the reaction of $HCo(CO)_4$ with tetrafluorethylene, as shown in Figure 14-7, the product has the $Co(CO)_4$ group attached to one carbon and H attached to the neighboring carbon.

14-2-2 CARBONYL INSERTION (ALKYL MIGRATION)

Perhaps the most well-studied insertion reaction is carbonyl insertion, which involves the reaction of CO with an alkyl complex to give an acyl [$—C(=O)R$] product. For example, the reaction of $CH_3Mn(CO)_5$ with CO has the following stoichiometry:



$$H_3C—Mn(CO)_5 + CO \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}—Mn(CO)_5$$

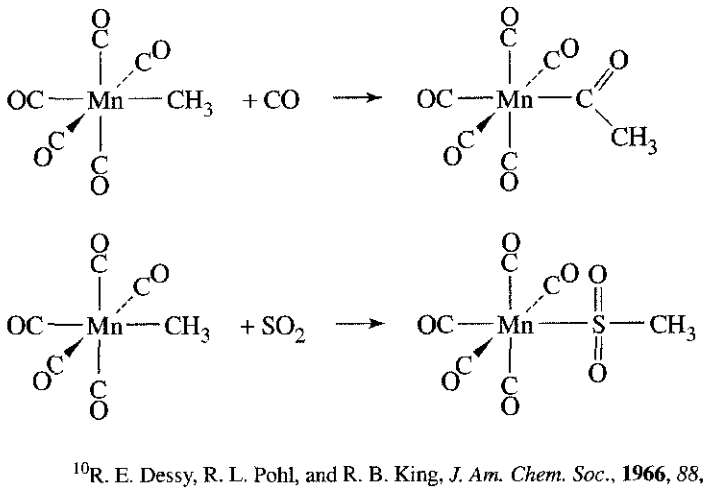


FIGURE 14-6 Examples of 1,1 Insertion Reactions.

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[10] R. E. Dessy, R. L. Pohl, and R. B. King, *J. Am. Chem. Soc.*, **1966**, *88*, 5121.

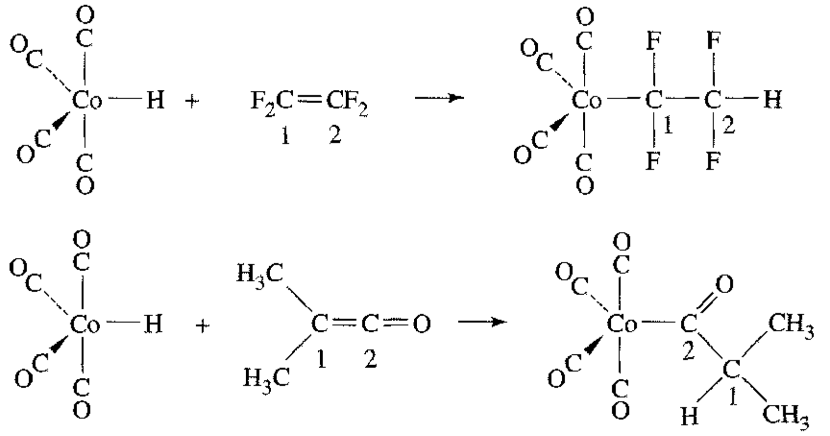


FIGURE 14-7 Examples of 1,2 Insertion Reactions.

The insertion of CO into a metal-carbon bond in alkyl complexes is of particular interest in its potential applications to organic synthesis and catalysis (examples will be discussed in Section 14-3), and its mechanism deserves careful consideration.

From the net equation, we might expect that the CO inserts directly into the Mn—CH_3 bond. However, other mechanisms are possible that would give the overall reaction stoichiometry while involving steps other than the insertion of an incoming CO. Three plausible mechanisms have been suggested for this reaction:

Mechanism 1: CO Insertion
Direct insertion of CO into metal-carbon bond.

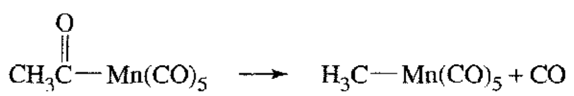
Mechanism 2: CO Migration
Migration of CO to give intramolecular CO insertion. This would yield a 5-coordinate intermediate, with a vacant site available for attachment of an incoming CO.

Mechanism 3: Alkyl Migration
In this case, the alkyl group would migrate, rather than the CO, and attach itself to a CO *cis* to the alkyl. This would also give a 5-coordinate intermediate with a vacant site available for an incoming CO.

These mechanisms are described schematically in Figure 14-8. In both Mechanisms 2 and 3, the intramolecular migration is considered to occur to one of the migrating group's nearest neighbors, located in *cis* positions.

Experimental evidence that may be used to evaluate these mechanisms includes the following:[11]

1. Reaction of $CH_3Mn(CO)_5$ with ^{13}CO gives a product with the labeled CO in carbonyl ligands only; *none* is found in the acyl position.
2. The reverse reaction



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}—Mn(CO)_5 \longrightarrow H_3C—Mn(CO)_5 + CO$$

which occurs readily on heating $CH_3C(=O)Mn(CO)_5$, when carried out with ^{13}C in the acyl position, yields product $CH_3Mn(CO)_5$ with the labeled CO entirely *cis* to CH_3. No labeled CO is lost in this reaction.

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[11] T. C. Flood, J. E. Jensen, and J. A. Statler, *J. Am. Chem. Soc.*, **1981**, *103*, 4410, and references therein.

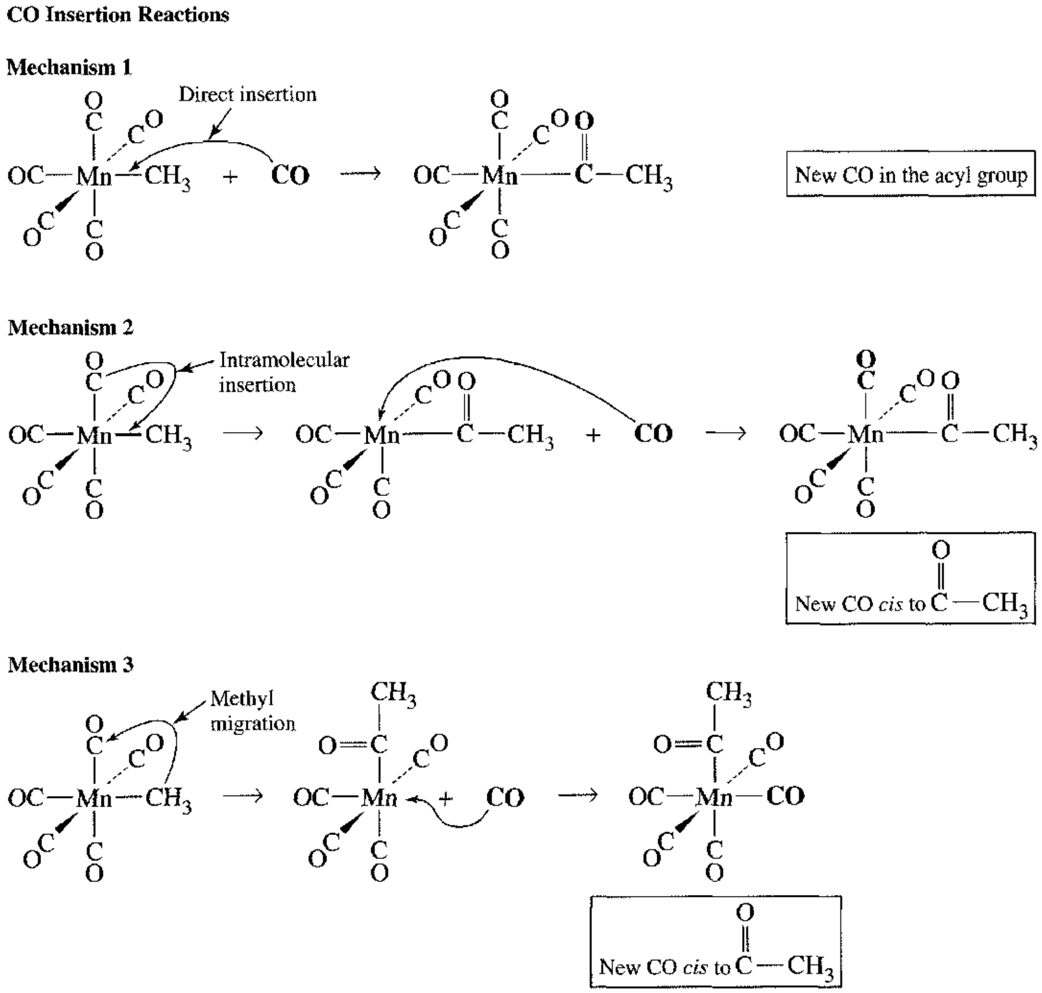


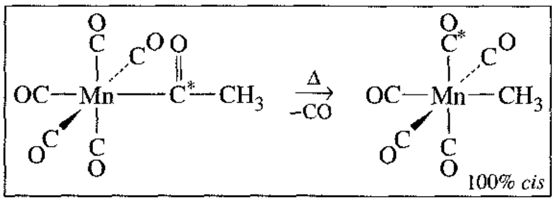
FIGURE 14-8 Possible Mechanisms for CO Insertion Reactions. Acyl groups are shown as $-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ for clarity; the actual geometry around acyl carbons is trigonal.

3. The reverse reaction, when carried out with ^{13}C in a carbonyl ligand *cis* to the acyl group, gives a product that has a 2 : 1 ratio of *cis* to *trans* product (*cis* and *trans* referring to the position of labeled CO relative to CH_3 in the product). Some labeled CO is also lost in this reaction.

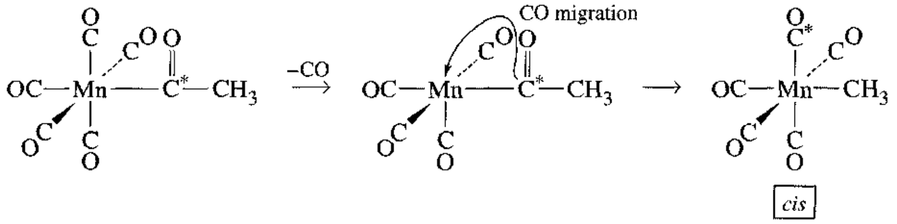
The mechanisms can now be evaluated on the basis of these data. First, Mechanism 1 is definitely ruled out by the first experiment. Direct insertion of ^{13}CO must result in ^{13}C in the acyl ligand; because none is found, the mechanism cannot be a direct insertion. Mechanisms 2 and 3, on the other hand, are both compatible with the results of this experiment.

The principle of microscopic reversibility requires that any reversible reaction must have identical pathways for the forward and reverse reactions, simply proceeding in opposite directions. (This principle is similar to the idea that the lowest pathway over a mountain chain must be the same regardless of the direction of travel.) If the forward reaction is carbonyl migration (Mechanism 2), the reverse reaction must proceed by loss of a CO ligand, followed by migration of CO from the acyl ligand to the empty site. Because this migration is unlikely to occur to a *trans* position, all the product should be

Mechanism 2 versus Mechanism 3



Mechanism 2



Mechanism 3

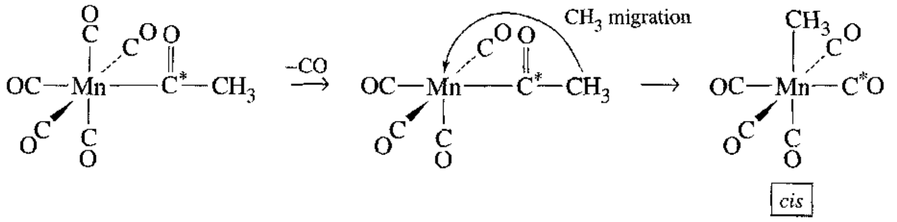
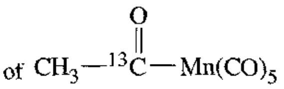


FIGURE 14-9 Mechanisms of Reverse Reactions for CO Migration and Alkyl Insertion (1). C* indicates the location of ^{13}C.

cis. If the mechanism is alkyl migration (Mechanism 3), the reverse reaction must proceed by loss of a CO ligand, followed by migration of the alkyl portion of the acyl ligand to the vacant site. Again, all the product should be *cis*. Both Mechanisms 2 and 3 would transfer labeled CO in the acyl group to a *cis* position and are therefore consistent with the experimental data for the second experiment (Figure 14-9).

EXERCISE 14-1

Show that heating of  $CH_3{-}^{13}\overset{\overset{\displaystyle O}{\|}}{C}{-}Mn(CO)_5$ would not be expected to give the *cis* product by Mechanism 1.

The third experiment differentiates conclusively between Mechanisms 2 and 3. The CO migration of Mechanism 2, with ^{13}CO *cis* to the acyl ligand, requires migration of CO from the acyl ligand to the vacant site. As a result, 25% of the product should have no ^{13}CO label and 75% should have the labeled CO *cis* to the alkyl, as shown in Figure 14-10. On the other hand, alkyl migration (Mechanism 3) should yield 25% with no label, 50% with the label *cis* to the alkyl, and 25% with the label *trans* to the alkyl. Because this is the ratio of *cis* to *trans* found in the experiment, the evidence supports Mechanism 3, which is the accepted pathway for this reaction.

The result is that a reaction that initially appears to involve CO insertion, and is often so designated, does not involve CO insertion at all! It is not uncommon, on close study, for reactions to differ substantially from how they might at first appear; the "carbonyl insertion" reaction may in fact be more complicated than described here. In this reaction, as well as in all chemical reactions, it is extremely important for chemists to be willing to undertake mechanistic studies and to keep an open mind about possible

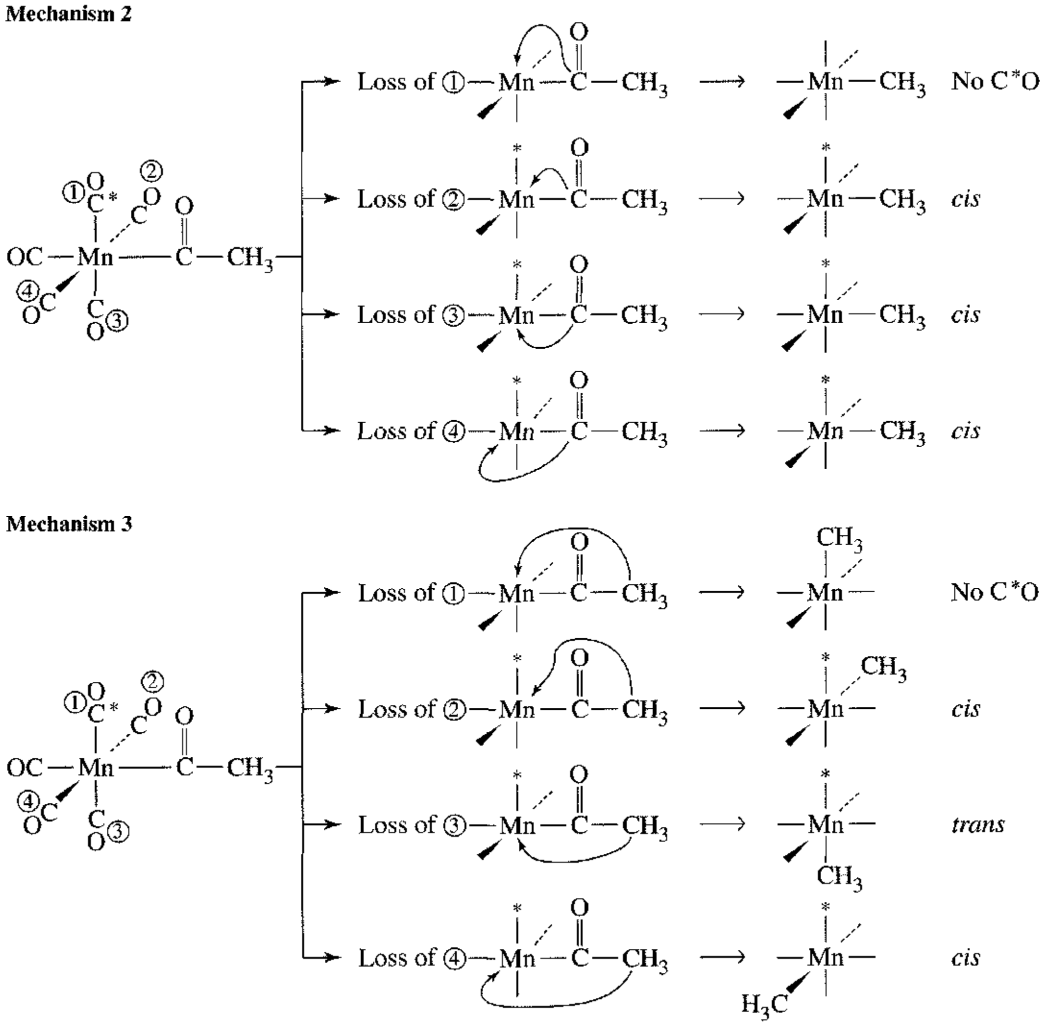


FIGURE 14-10 Mechanisms of Reverse Reactions for CO Migration and Alkyl Insertion (2). C* indicates the location of ^{13}C.

alternative mechanisms. No mechanism can be proved; it is always possible to suggest alternatives consistent with the known data.

One final point about the mechanism of these reactions should be made. In the previous discussion of Mechanisms 2 and 3, it was assumed that the intermediate was a square pyramid and that no rearrangement to other geometries (such as trigonal-bipyramidal) occurred. Other labeling studies, involving reactions of labeled $CH_3Mn(CO)_5$ with phosphines, have supported a square-pyramidal intermediate.[12]

EXERCISE 14-2

Predict the product distribution for the reaction of *cis*-$CH_3Mn(CO)_4(^{13}CO)$ with $PR_3(R = C_2H_5)$.

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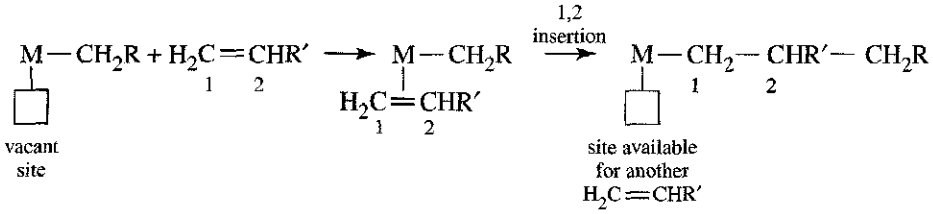
[12] T. C. Flood, J. E. Jensen, and J. A. Statler, *J. Am. Chem. Soc.*, **1981**, *103*, 4410 and references therein.

14-2-3 1,2 INSERTIONS

Two examples of 1,2 insertions have been shown in Figure 14-7. An important application of 1,2 insertions of alkenes into metal-alkyl bonds is in the formation of polymers. One such process is the Cossee-Arlman mechanism,[13] proposed for the Ziegler-Natta polymerization of alkenes (also discussed in Section 14-4-1). According to this mechanism, a polymer chain can grow as a consequence of repeated 1,2 insertions into a vacant coordination site, as follows:



$$\underset{\square}{\mathrm{M{-}CH_2R}} + \underset{1}{\mathrm{H_2C}}{=}\underset{2}{\mathrm{CHR'}} \longrightarrow \underset{\underset{1\qquad 2}{\mathrm{H_2C{=}CHR'}}}{\mathrm{M{-}CH_2R}} \xrightarrow{\text{1,2 insertion}} \underset{\square}{\mathrm{M}}{-}\underset{1}{\mathrm{CH_2}}{-}\underset{2}{\mathrm{CHR'}}{-}\mathrm{CH_2R}$$

14-2-4 HYDRIDE ELIMINATION

Hydride elimination reactions are characterized by the transfer of a hydrogen atom from a ligand to a metal. Effectively, this may be considered an oxidative addition, with both the coordination number and the formal oxidation state of the metal being increased (the hydrogen transferred is formally considered as hydride, H^-). The most common type is **β elimination**, with a proton in a β position[14] on an alkyl ligand being transferred to the metal by way of an intermediate in which the metal, the α and β carbons, and the hydride are coplanar. An example is shown in Figure 14-11. β Elimination is the reverse of 1,2-insertion.

EXERCISE 14-3

Show that the reverse of the reaction shown in Figure 14-11 would be 1,2 insertion.

β Eliminations, as will be seen later in this chapter, are important in many catalytic processes involving organometallic complexes.

Several general comments can be made about β-elimination reactions. First, because only complexes that have β hydrogens can undergo these reactions, alkyl complexes that lack β hydrogens tend to be more stable thermally than those that have such hydrogens (although the former may undergo other types of reactions). Furthermore, coordinatively saturated complexes (complexes in which all coordination sites are filled) containing β hydrogens are in general more thermally stable than complexes

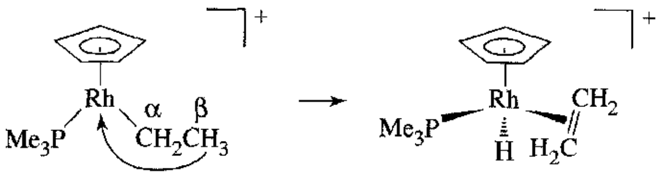


FIGURE 14-11 β Elimination.

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[13] P. Cossee, *J. Catal.*, **1964**, *3*, 80; E. J. Arlman and P. Cossee, *J. Catal.*, **1964**, *3*, 99.

[14] The Greek letter α is used to designate the carbon atom directly attached to the metal, β is used for the next carbon atom, and so forth.

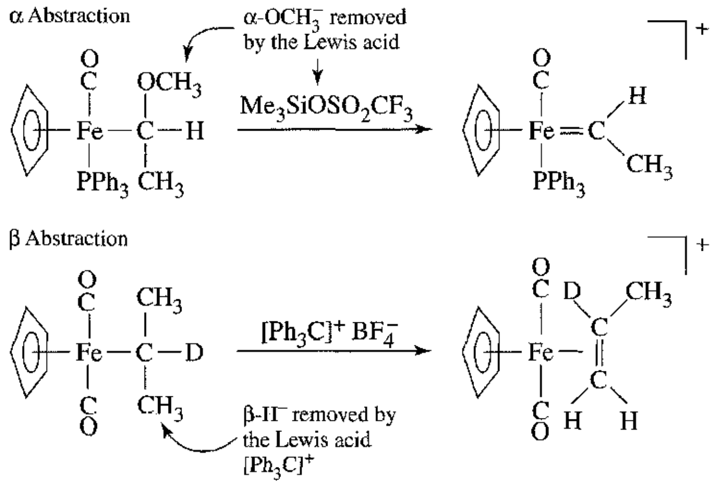

FIGURE 14-12 Abstraction Reactions.

having empty coordination sites; the β-elimination mechanism requires transfer of a hydrogen to an empty coordination site. Finally, other types of elimination reactions are also known (such as the elimination of hydrogen from α and γ positions); the interested reader is referred to other sources for examples of such reactions.[15]

14-2-5 ABSTRACTION

Abstraction reactions are elimination reactions in which the coordination number of the metal does not change. In general, they involve removal of a substituent from a ligand, often by the action of an external reagent, such as a Lewis acid. Two types of abstractions, α and β abstractions, are illustrated in Figure 14-12; they involve, respectively, removal of substituents from the α and β positions (with respect to the metal) of coordinating ligands. α-Abstraction has been encountered previously, in the synthesis of carbyne complexes discussed in Section 13-6-3.

14-3 ORGANOMETALLIC CATALYSTS

In addition to having an intrinsic interest for chemists, organometallic reactions are also of great interest industrially, especially in the development of catalysts for reactions of commercial importance. The commercial interest in catalysis has been spurred by the fundamental problem of how to convert relatively inexpensive feedstocks (e.g., coal, petroleum, and water) into molecules of greater commercial value. This frequently involves, as part of the industrial process, conversion of simple molecules into more complex molecules (e.g., ethylene into acetaldehyde, methanol into acetic acid, or organic monomers into polymers), conversion of one molecule into another of the same type (one alkene into another), or a selective reaction at a particular molecular site (e.g., replacement of hydrogen by deuterium, selective hydrogenation of a specific double bond). Historically, many catalysts have been heterogeneous in nature—that is, solid materials having catalytically active sites on their surface, with only the surface in contact with the reactants. Homogeneous catalysts, soluble in the reaction medium, are molecular species that are easier to study

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[15] J. D. Fellmann, R. R. Schrock, and D. D. Traficante, *Organometallics*, **1982**, *1*, 481; J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, and references therein.

and modify for specific applications than heterogeneous catalysts. Appropriate design of catalyst molecules may provide high selectivity in the processes catalyzed; it is not surprising that development of highly selective homogeneous catalysts has been of considerable industrial interest. Not every catalytic cycle, however, is efficient or profitable enough to be commercially feasible.

In the examples of catalysis that follow, the reader will find it useful to identify the catalysts, the species regenerated in each complete reaction cycle. In addition, the individual steps in these cycles will provide examples of the various types of organometallic reactions introduced earlier in this chapter. In each case, the proposed mechanisms presented in this section should be viewed as subject to modification as additional research is conducted.

14-3-1 EXAMPLE OF CATALYSIS: CATALYTIC DEUTERATION

If deuterium gas (D_2) is bubbled through a benzene solution of $(\eta^5\text{-}C_5H_5)_2TaH_3$ at an elevated temperature, the hydrogen atoms of benzene are slowly replaced by deuterium; eventually, perdeuterobenzene, C_6D_6, can be obtained (for use, for example, as an NMR solvent).[16] Replacement of H by D occurs in a series of alternating reductive elimination and oxidative addition steps, as outlined in Figure 14-13.

The initial step in this process is loss of H_2 (formally, reductive elimination) from the 18-electron $(\eta^5\text{-}C_5H_5)_2TaH_3$ to give the 16-electron $(\eta^5\text{-}C_5H_5)_2TaH$. $(\eta^5\text{-}C_5H_5)_2TaH$ can then react with benzene in the second step (oxidative addition) to give an 18-electron species containing a phenyl group σ-bonded to the metal. This species can undergo a second loss of H_2 to give another 16-electron species, $(\eta^5\text{-}C_5H_5)_2TaH{-}C_6H_5$. $(\eta^5\text{-}C_5H_5)_2TaH{-}C_6H_5$ subsequently adds D_2 (another oxidative addition) to form an 18-electron species (Step 4), which in the last step eliminates C_6H_5D. Repetition of this sequence in the presence of excess D_2 eventually leads to C_6D_6. In each subsequent cycle, the catalytic species $(\eta^5\text{-}C_5H_5)_2TaD$ is regenerated.

14-3-2 HYDROFORMYLATION

The hydroformylation, or oxo, process is commercially useful for converting terminal alkenes into a variety of other organic products, especially those having their carbon chain increased by one. One of these processes, the conversion of an alkene of formula $R_2C{=}CH_2$ into an aldehyde, $R_2CH{-}CH_2{-}CHO$, is outlined in Figure 14-14.[17]

Each step of the hydroformylation cycle may be categorized according to its characteristic type of organometallic reaction, as indicated in the figure. The cobalt-containing intermediates in this cycle alternate between 18- and 16-electron species. The 18-electron species react to formally reduce their electron count by 2 (by ligand dissociation, 1,2 insertion of coordinated alkene, alkyl migration, reductive elimination), whereas the 16-electron species can increase their formal electron count (by coordination of alkene or CO or by oxidative addition). Such a pattern is commonly encountered in catalytic cycles involving organometallic complexes, with the catalytic activity in large part a consequence of the capability of the metal to react by way of a variety of 18- and 16-electron intermediates.

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[16] J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **1976**, *98*, 1729, and references therein.

[17] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **1961**, *83*, 4023; see also F. Heck, *Adv. Organomet. Chem.*, **1966**, *4*, 243.

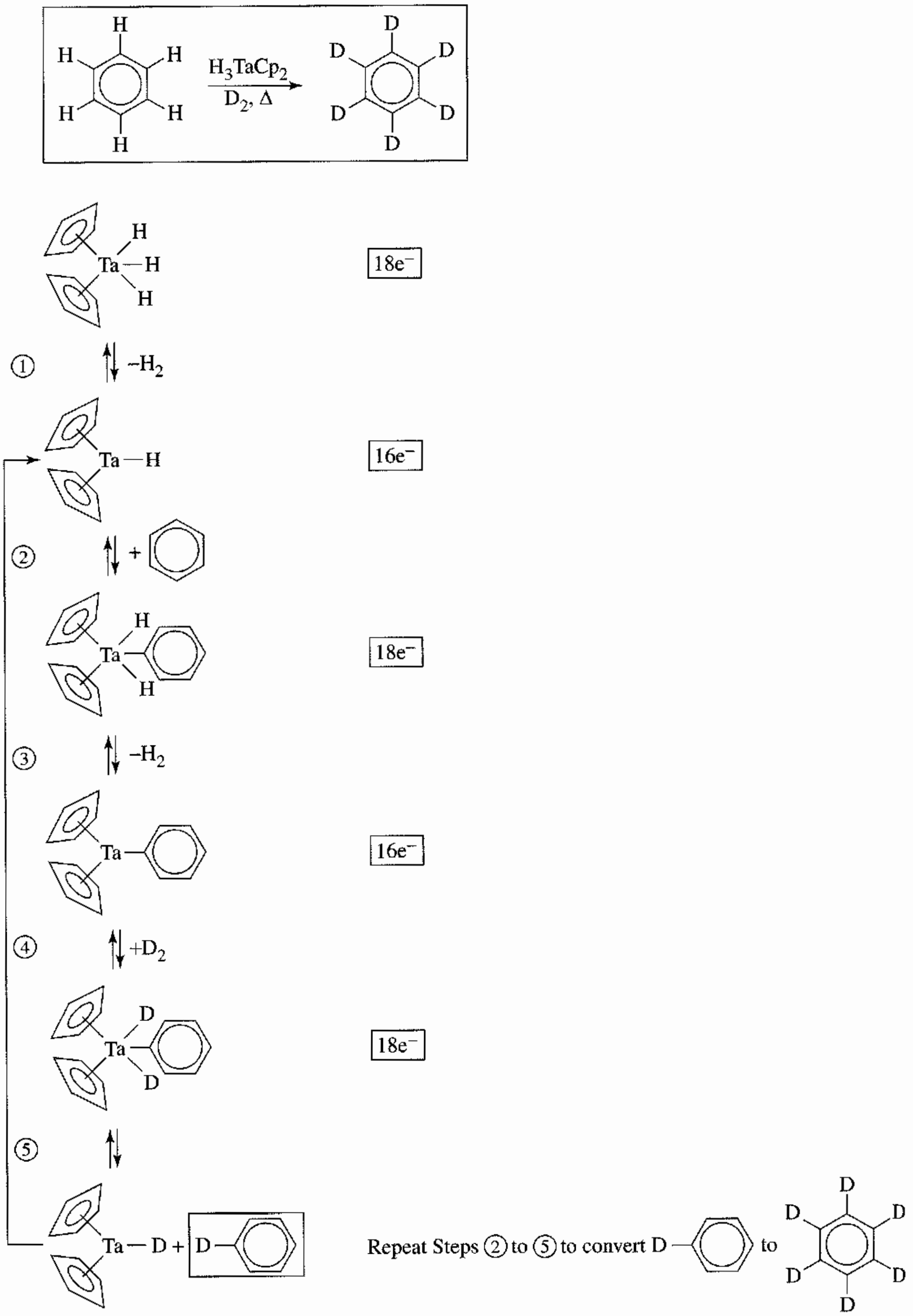
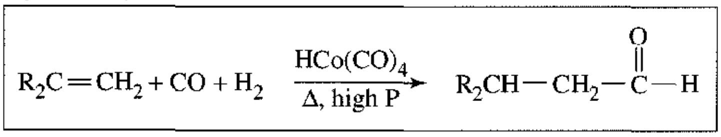


FIGURE 14-13 Catalytic Deuteration.

Hydroformylation (Oxo) Process



$$R_2C{=}CH_2 + CO + H_2 \xrightarrow[\Delta,\ \text{high P}]{HCo(CO)_4} R_2CH{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

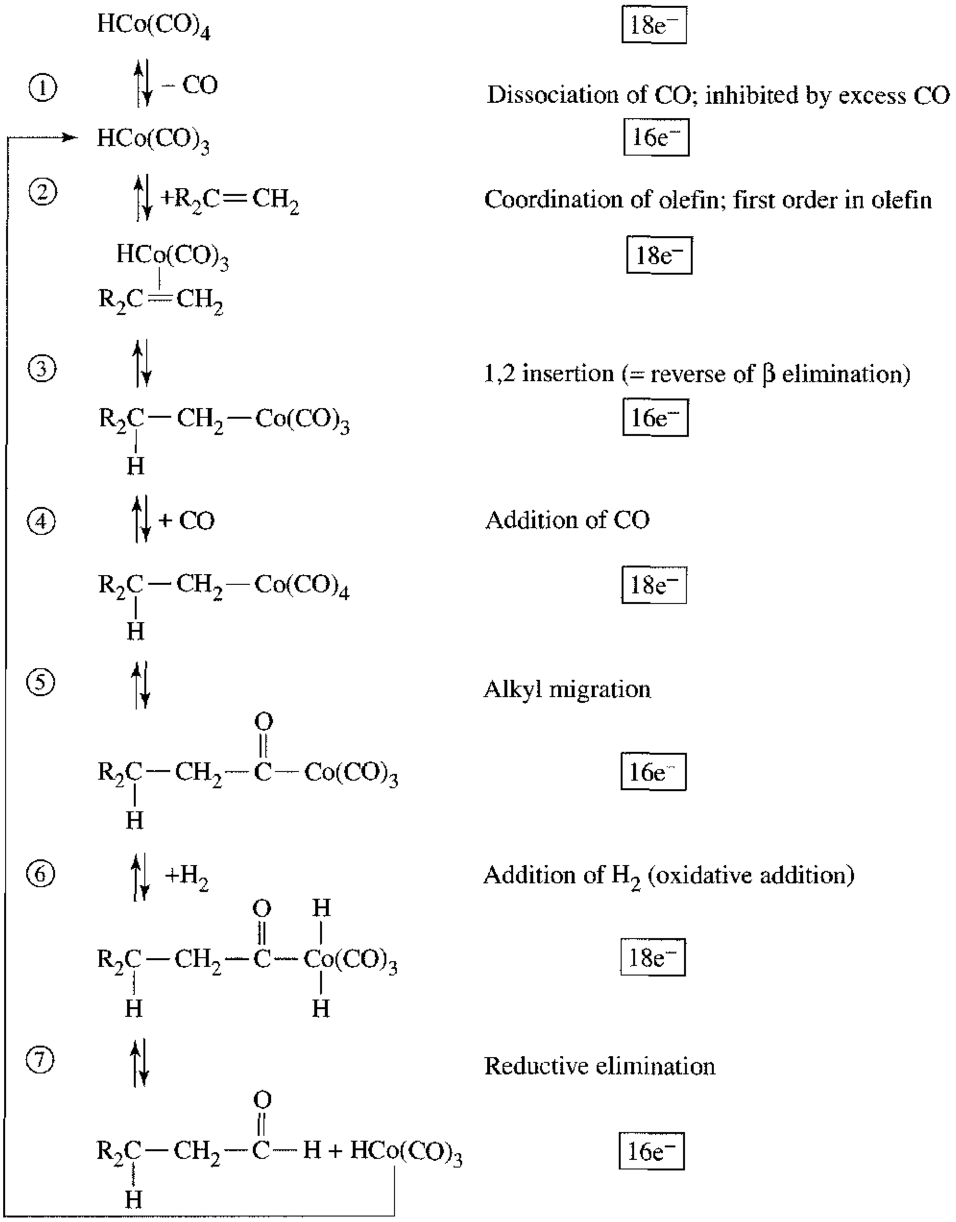


FIGURE 14-14 Hydroformylation Process.

A few steps of the hydroformylation process are worth comment. The first step, involving dissociation of CO from $HCo(CO)_4$, is inhibited by high CO pressure, yet the fourth step requires CO; thus, careful control of this pressure is necessary for optimum yields and rates.[18] The second step is first order in alkene; it is the slow (rate-determining) step. In Step 3, the product is formed preferentially with a CH_2 group rather than a CR_2 group bonded to the metal; this preference for CH_2 bonding to metal is enhanced by bulky R groups. Step 6 involves addition of H_2 (OA); however, high H_2 pressure can lead to

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[18] For more information on reaction conditions, see G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, 2nd ed., John Wiley & Sons, New York, 1992, pp. 106–111.

addition of H_2 to the 16-electron intermediate from Step 3, which would then eliminate an alkane:

$$\underset{16\,e^-}{R_2CH{-}CH_2{-}Co(CO)_3} + H_2 \longrightarrow \underset{18\,e^-}{R_2CH{-}CH_2{-}Co(H)_2(CO)_3} \qquad \text{oxidative addition}$$

$$\underset{18\,e^-}{R_2CH{-}CH_2{-}Co(H)_2(CO)_3} \longrightarrow R_2CH{-}CH_3 + \underset{16\,e^-}{HCo(CO)_4} \qquad \text{reductive elimination}$$

Again, careful control of the experimental conditions is necessary to maximize yield of the desired products.[19] The actual catalytic species in this mechanism is the 16-electron $HCo(CO)_3$.

The main industrial application of hydroformylation is in the production of butanal from propene ($CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_2CHO$). Subsequent hydrogenation gives butanol, an important industrial solvent. Other aldehydes are also produced industrially by hydroformylation, using either cobalt catalysts such as the one in Figure 14-14 or rhodium-based catalysts.

EXERCISE 14-4

Show how $(CH_3)_2CHCH_2CHO$ can be prepared from $(CH_3)_2C{=}CH_2$ by the hydroformylation process.

A shortcoming of the cobalt carbonyl-based hydroformylation process outlined in Figure 14-14 is that it produces only about 80% of the much more valuable linear aldehydes, with the remainder having branched chains. Modifying the catalyst by replacing one of the CO ligands of the starting complex by PBu_3 (Bu = *n*-butyl) to give $HCO(CO)_3(PBu_3)$[20] increases the selectivity of the process to give a ratio of linear to branched aldehydes of approximately 9 : 1. Finally, replacing the cobalt with rhodium yields far more active catalysts (much less catalyst needs to be present) that can function with higher linear and branched selectivity at significantly lower temperatures and pressures than cobalt-based catalysts.[21] A proposed mechanism for an example of such a catalytic process using $HRh(CO)_2(PPh_3)_2$ is shown in Figure 14-15.[22]

EXERCISE 14-5

Classify each step of the mechanism in Figure 14-15 according to its reaction type.

14-3-3 MONSANTO ACETIC ACID PROCESS

The synthesis of acetic acid from methanol and CO is a process that has been used with great commercial success by Monsanto since 1971. The mechanism of this process is complex; a proposed outline is shown in Figure 14-16. As in the hydroformylation process, the individual steps of this mechanism are the characteristic types of

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[19] For a discussion of additional details, including possible alternative steps in this mechanism, see T. Ziegler and L. Versluis, "The Tricarbonylhydridocobalt-Based Hydroformylation Reaction," in W. R. Moser and D. W. Slocum, eds., *Homogeneous Transition Metal-Catalyzed Reactions*, American Chemical Society, Washington, DC, 1992, pp. 75–93.

[20] L. H. Slaugh and R. D. Mullineaux, *J. Organomet. Chem.*, **1968**, *13*, 469.

[21] J. A. Osborne, J. F. Young, and G. Wilkinson, *Chem. Commun. (Cambridge)*, **1965**, 17; C. K. Brown and G. Wilkinson, *J. Chem. Soc., A*, **1970**, 2753.

[22] For a more detailed outline of the various cobalt- and rhodium-based hydroformylation catalysts and for additional related references, see G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, pp. 257–265.

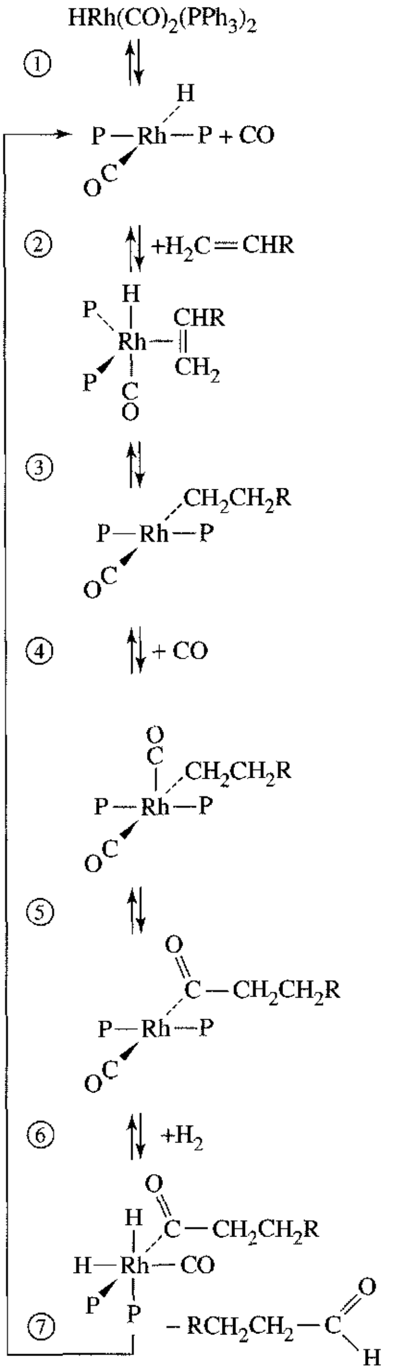

FIGURE 14-15 Hydroformylation using HRh(CO)$_2$(PPh$_3$)$_3$. P = PPh$_3$. From C. K. Brown and G. Wilkinson, *J. Chem. Soc., A*, **1970**, 2753.

organometallic reactions described previously in this chapter; the intermediates are 18- or 16-electron species having the capability to lose or gain, respectively, 2 electrons. (Solvent molecules may occupy empty coordination sites in the 4- and 5-coordinate 16-electron intermediates.) The first step, oxidative addition of CH_3I to $[RhI_2(CO)_2]^-$, is rate determining.[23]

The final step involving rhodium is reductive elimination of $IC(=O)CH_3$. Acetic acid is formed by hydrolysis of this compound. The catalytic species,

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[23] A discussion of the mechanism of this reaction can be found in D. Forster and T. W. Deklava, *J. Chem. Ed.*, **1986**, *63*, 204, and references therein.

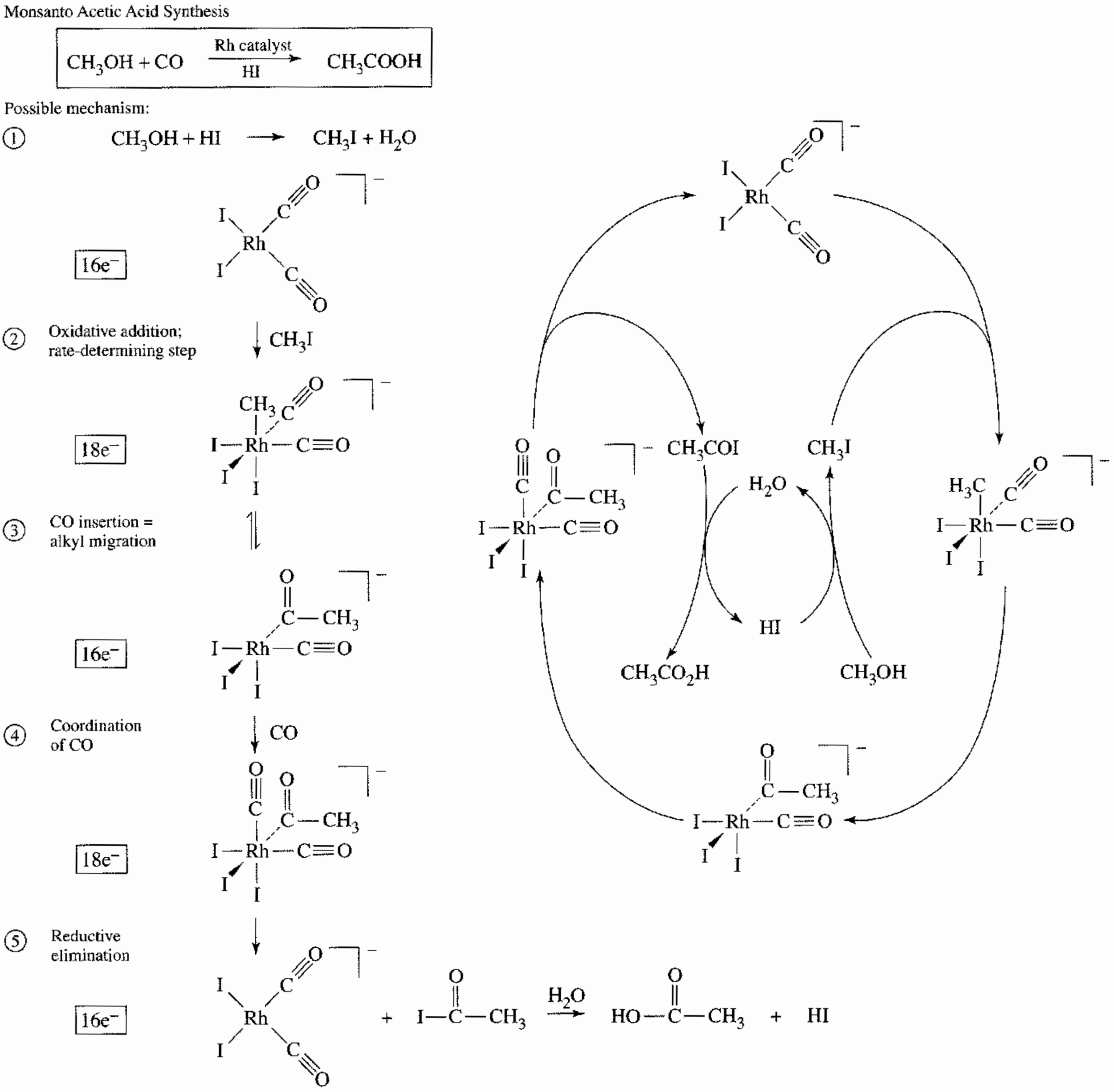

FIGURE 14-16 Monsanto Acetic Acid Process. (References: A. Haynes, B. E. Mann, D. J. Gulliver, G. E. Morris, and P. M. Maitlis, *J. Am. Chem. Soc.*, **1991**, *113*, 8567, and M. Cheong, R. Schmid, and T. Ziegler, *Organometallics*, **2000**, *19*, 1973.)

$[Rh(CO)I_2]^-$ (which may contain solvent in the empty coordination sites) is regenerated, as shown in the figure.

In addition to rhodium-based catalysts, iridium-based catalysts have also been developed in a process known as the Cativa process. The iridium system follows a cycle similar to the rhodium system in Figure 14-16, beginning with oxidative addition of CH_3I to $[Ir(CO)_2I_2]^-$. The first step in the iridium system is much more rapid than in the Monsanto process and the second step is much slower; the second step, involving alkyl migration, is rate determining for the Cativa process.[24]

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[24] M. Cheong, R. Schmid, and T. Ziegler, *Organometallics*, **2000**, *19*, 1973, and references therein.

14-3-4 WACKER (SMIDT) PROCESS

The Wacker or Smidt process, used to synthesize acetaldehyde from ethylene, involves a catalytic cycle that uses $PdCl_4{}^{2-}$. A brief outline of a cycle proposed for this process is shown in Figure 14-17. The fourth step in this cycle is substantially more complex than that shown in the figure and has been the subject of much study.[25]

An important feature of this process is that it uses the ability of palladium to form complexes with the reactant ethylene, with the important chemistry of ethylene occurring while it is attached to the metal. In other words, the palladium modifies the chemical behavior of ethylene to enable reactions to occur that would not be possible for free ethylene. Incidentally, the first ethylene complex with palladium in Figure 14-17 is isoelectronic with Zeise's complex, $[PtCl_3(\eta^2\text{-}H_2C{=}CH_2)]^-$.

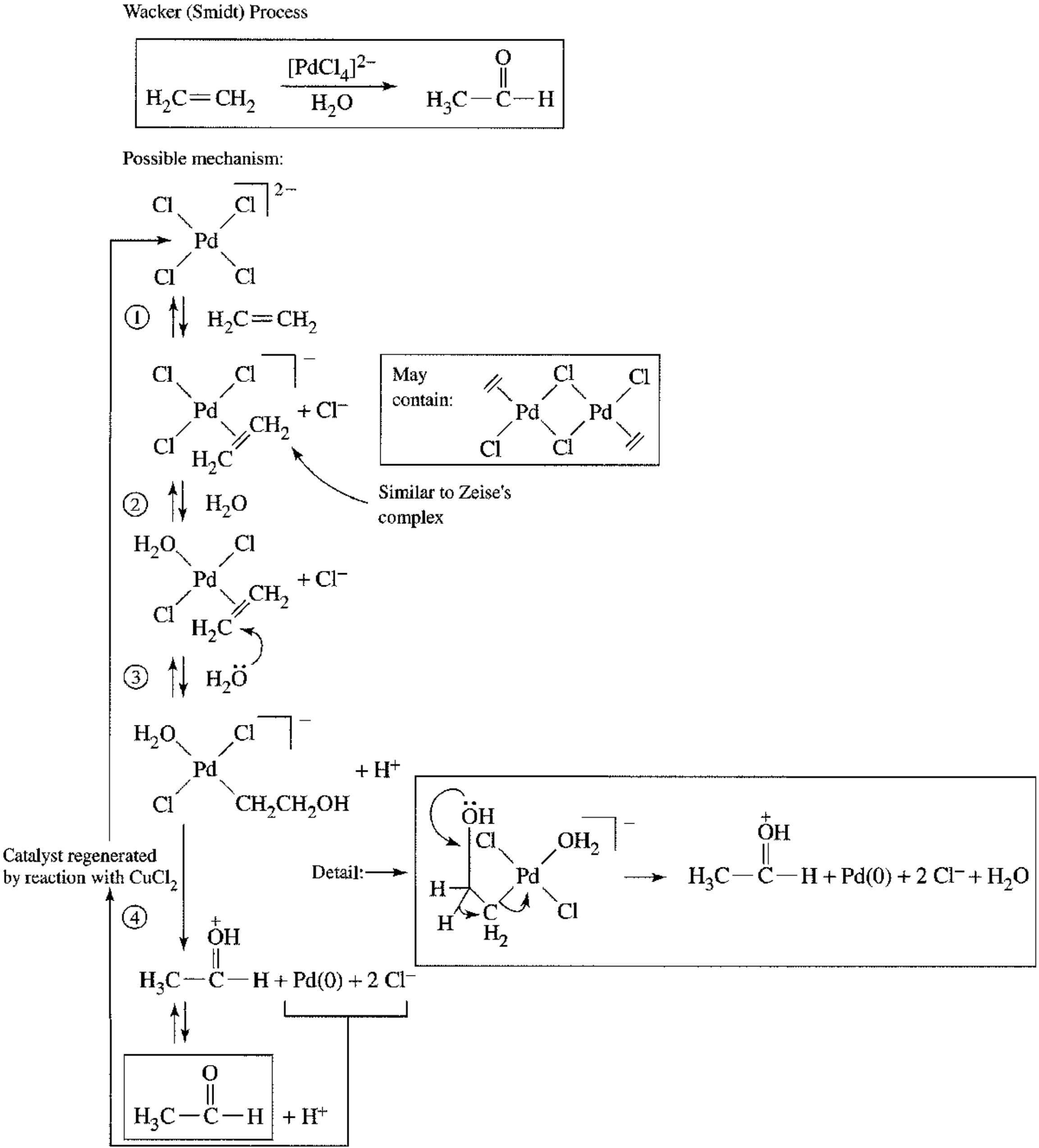

FIGURE 14-17 Wacker (Smidt) Process.

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[25] For example, see J. M. Francis and P. M. Henry, *Organometallics*, **1991**, *10*, 3498; **1992**, *11*, 2832.

14-3-5 HYDROGENATION BY WILKINSON'S CATALYST

Wilkinson's catalyst, $RhCl(PPh_3)_3$, is not itself an organometallic compound but participates in the same types of reactions as expected for 4-coordinate organometallic compounds; for example, many reactions bear similarities to Vaska's catalyst, *trans*-$IrCl(CO)(PPh_3)_2$. $RhCl(PPh_3)_3$ participates in a wide variety of catalytic and noncatalytic processes. The bulky phosphine ligands play an important role in making the complex selective—for example, they limit coordination of Rh to unhindered positions on alkenes. One example, involving catalytic hydrogenation of an alkene, is shown in Figure 14-18.[26]

Hydrogenation Using Wilkinson's Catalyst

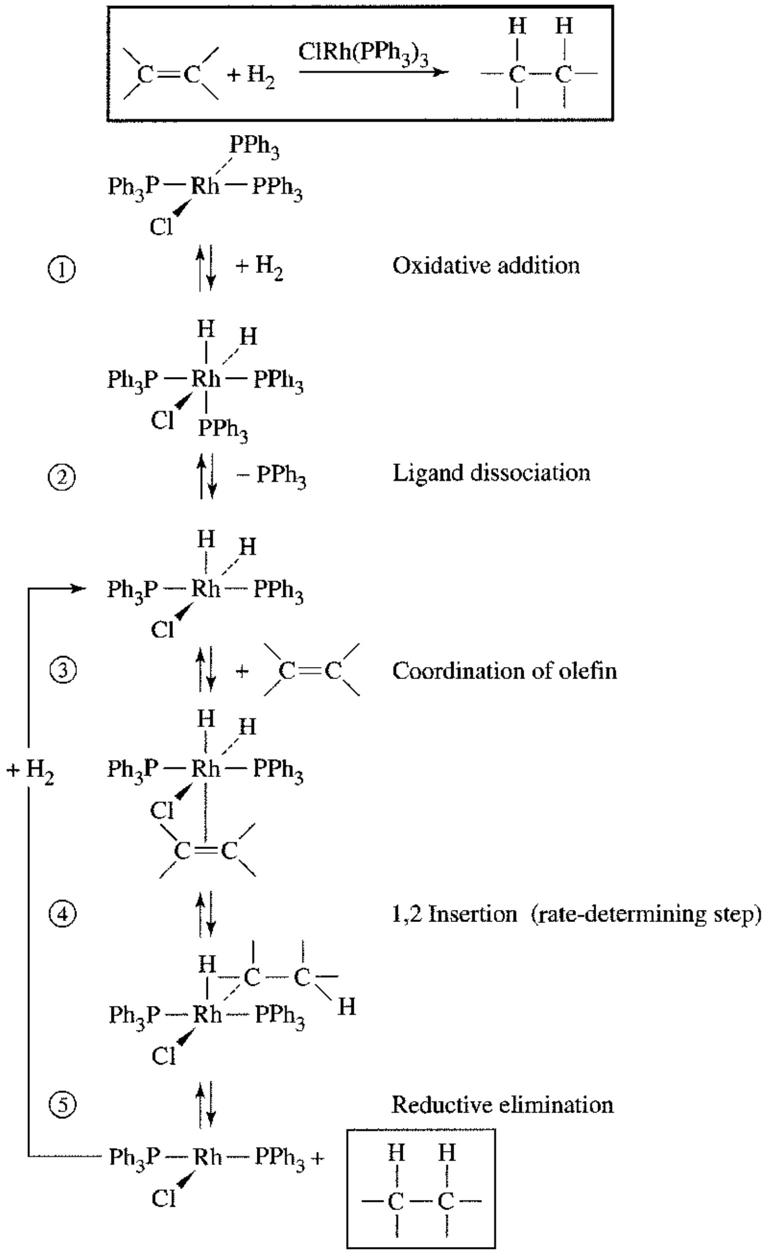
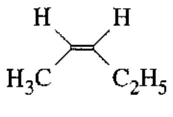
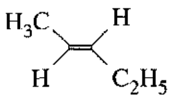
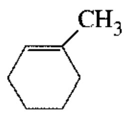
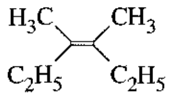


FIGURE 14-18 Catalytic Hydrogenation Involving Wilkinson's Catalyst.

[26] B. R. James, *Adv. Organomet. Chem.*, **1979**, *17*, 319; see also J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, pp. 531–535, and references therein.

TABLE 14-3
Relative Rates of Hydrogenation Using Wilkinson's Catalyst at 25°C

Compound Hydrogenated	*Rate Constant × 100 (L mol^{-1} s^{-1})*
	31.6
 	9.9
 	1.8
 	0.6
 	<0.1

SOURCE: A. J. Birch and D. H. Williamson, *Org. React.*, **1976**, *24*, 1.

The first two steps in this process give the catalytic species $RhCl(H)_2(PPh_3)_2$, which has a vacant coordination site. A $C{=}C$ double bond can coordinate to this site, gain the two hydrogens coordinated to Rh, and subsequently leave, if the double bond is not sterically hindered. This effect is illustrated in Table 14-3, which shows relative rates of hydrogenation using Wilkinson's catalyst.

In molecules containing several double bonds, the least hindered double bonds are reduced. The most hindered positions cannot coordinate effectively to Rh (largely because of the presence of the bulky phosphines) and hence do not react as rapidly. Consequently, Wilkinson's catalyst is useful for selective hydrogenations of $C{=}C$ bonds that are not sterically hindered. Examples are shown in Figure 14-19.

Because the selectivity of Wilkinson's catalyst is largely a consequence of the bulky triphenylphosphine ligands, the selectivity can be fine-tuned somewhat by using phosphines having different cone angles than PPh_3. Wilkinson's catalyst and similar compounds having different phosphine ligands are useful in a variety of other catalytic cycles.

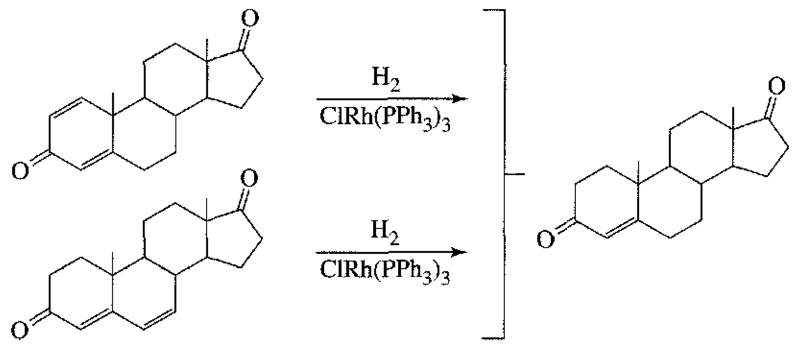
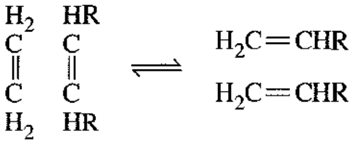


FIGURE 14-19 Selective Hydrogenation by Wilkinson's Catalyst.

14-3-6 OLEFIN METATHESIS

Olefin metathesis, first discovered in the 1950s, involves the formal exchange of $:CR_2$ fragments ($R = H$ or alkyl) between alkenes. For example, metathesis between molecules of formula $H_2C{=}CH_2$ and $HRC{=}CHR$ would yield two molecules of $H_2C{=}CHR$:



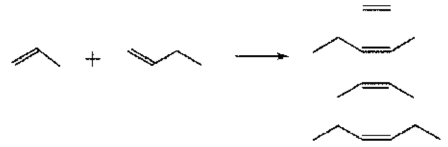
$$\begin{matrix} H_2 & HR \\ C & C \\ \| & \| \\ C & C \\ H_2 & HR \end{matrix} \rightleftharpoons \begin{matrix} H_2C{=}CHR \\ H_2C{=}CHR \end{matrix}$$

New double bonds are formed between the top and bottom two carbons in the diagram, and the original double bonds are severed.[27]

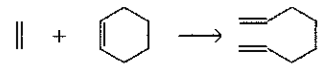
EXAMPLE

Predict the possible products of metathesis of the following olefins. Be sure to consider that two molecules of the same structure can also metathesize (undergo self-metathesis).

a. Between propene and 1-butene.



b. Between ethylene and cyclohexene.



Example b is an example of **ring-opening metathesis (ROM)**, in which metathesis opens a ring of a cyclic alkene. The reverse of this process is called, appropriately, **ring-closing metathesis (RCM)**. An example of ring-closing metathesis is shown in Figure 14-22.

EXERCISE 14-6

Predict the products of metathesis:

a. Between two molecules of propene.
b. Between propene and cyclopentene.

Metathesis, which is reversible and can be catalyzed by a variety of organometallic complexes, has been the subject of considerable investigation, and many reviews on this topic have been published.[28] In 1970, Hérisson and Chauvin proposed that these reactions are catalyzed by carbene (alkylidene) complexes that react with alkenes via the formation of metallacyclobutane intermediates, as shown in Figure 14-20.[29] This mechanism, now known as the "Chauvin mechanism," has received considerable support and is believed to be the pathway of the majority of transition metal–catalyzed olefin metathesis reactions.

---

[27] Discussions of the history of the metathesis reaction written by two of its discoverers can be found in R. L. Banks, *Chemtech*, **1986**, *16*, 112 and H. Eleuterio, *Chemtech*, **1991**, *21*, 92.

[28] For example, see T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, **2001**, *34*, 18, and A. Fürstner, *Angew. Chem., Int. Ed.*, **2000**, *39*, 3012.

[29] J.-L. Hérisson and Y. Chauvin, *Makromol. Chem.*, **1970**, *141*, 161.

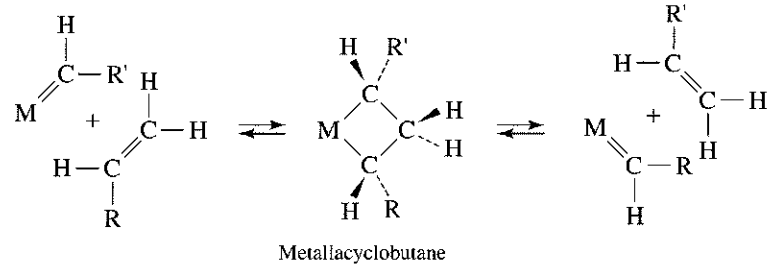


FIGURE 14-20 Olefin Metathesis.

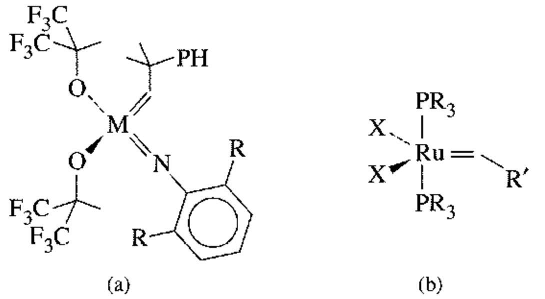


FIGURE 14-21 Metathesis Catalysts. (a) Schrock catalyst (M = Mo, W) (b) Grubbs catalyst (X = Cl, Br)

(a) (b)

In this mechanism, a metal carbene complex first reacts with an alkene to form a metallacyclobutane intermediate. This intermediate can either revert to reactants or form new products; because all steps in the process are equilibria, an equilibrium mixture of alkenes results.

The most thoroughly studied catalysts that effect alkene metathesis are of two types, shown in Figure 14-21. Schrock metathesis catalysts are the most effective of all metathesis catalysts but in general are highly sensitive to oxygen and water. These catalysts are now available commercially; the catalyst having M = Mo and R = isopropyl is sometimes called "Schrock's catalyst." An example of a reaction utilizing this catalyst is the final step of the synthesis of the natural product dactylol, shown in Figure 14-22.[30]

The reaction shown in Figure 14-22 is an example of ring-closing metathesis (RCM), in which the metathesis of two double bonds leads to ring formation. Like ordinary metathesis, ring-closing metathesis is believed to occur by way of a metallacyclobutane intermediate; this intermediate is responsible for joining the originally separate carbons into a ring.

Grubbs metathesis catalysts in general have less catalytic activity than Schrock catalysts, but are less sensitive to oxygen and water. They are also substantially less expensive than the molybdenum and tungsten catalysts. The catalyst having R = cyclohexyl, X = Cl, and R′ = phenyl has received particular attention and is marketed as Grubbs's catalyst. One requirement of these catalysts is the presence of

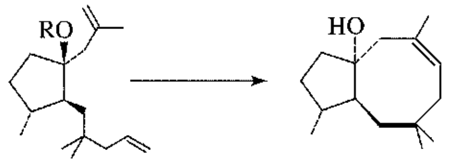


FIGURE 14-22 Ring-Closing Metathesis (RCM).

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[30] A. Fürstner and K. Langemann, *J. Org. Chem.*, **1996**, *61*, 8746.

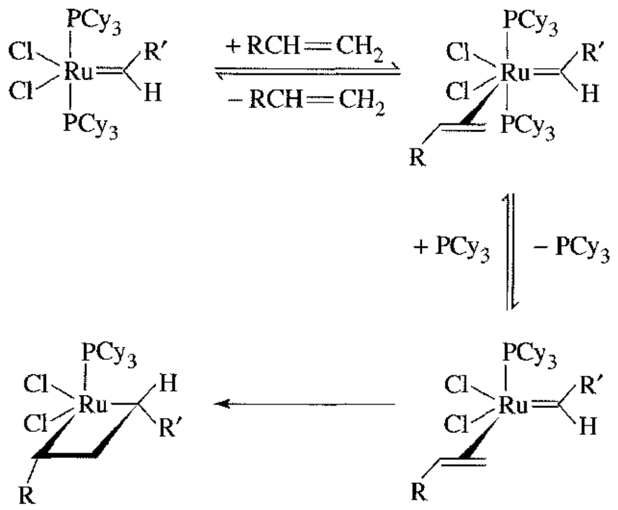

FIGURE 14-23 Proposed Mechanism for Formation of Metallacyclobutane from Ruthenium Catalyst.

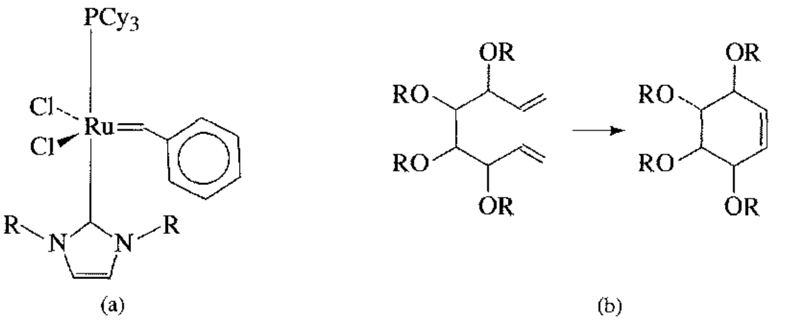

FIGURE 14-24 Ring-Closing Metathesis Catalyzed by the *N*-Heterocyclic Carbene Complex. (a) Catalyst (R = mesityl) (b) Ring-closing reaction (R = benzyl)

bulky phosphine ligands. This bulkiness facilitates phosphine dissociation, a key step in the proposed mechanism involving the Grubbs catalyst, shown in Figure 14-23.[31]

Although much research in the field of homogeneous metathesis catalysis has focused on complexes resembling those of Schrock and Grubbs, various other avenues have also been pursued. A promising recent development has been the introduction of catalysts that contain ruthenium and *N*-heterocyclic carbene ligands.[32] These ligands exceed trialkylphosphines in steric requirements and are more strongly electron donating;[33] both features support improved catalytic activity. An example of such a catalyst, and a ring-closing metathesis process that it catalyzes, are shown in Figure 14-24.[34]

Such catalysts compare favorably in activity with Schrock's catalyst and typically are thermally stable with low sensitivity toward oxygen and water. The process shown in Figure 14-24 has also been performed, using Schrock's catalyst and Grubbs's catalyst. As shown in Table 14-4, the *N*-heterocyclic catalyst compares favorably with Schrock's catalyst and is far superior to Grubbs's catalyst—at least for this reaction.

TABLE 14-4
Relative Activity of Metathesis Catalysts

Catalyst	*Reaction Time (h)*	*Yield (%)*
Schrock's catalyst	1	92
Grubbs's catalyst	60	32
Catalyst in Figure 14-24	2	89

[31] E. L. Dias, S. T. Nguyen, and R. H. Grubbs, *J. Am. Chem. Soc.*, **1997**, *119*, 3887.
[32] M. S. Sanford, J. A. Love, and R. H. Grubbs, *J. Am. Chem. Soc.*, **2001**, *123*, 6543.
[33] J. Huang, H.-J. Schanz, E. D. Stevens, and S. P. Nolan, *Organometallics*, **1999**, *18*, 2370.
[34] L. Ackermann, D. El Tom, and A. Fürstner, *Tetrahedron*, **2000**, *56*, 2195.

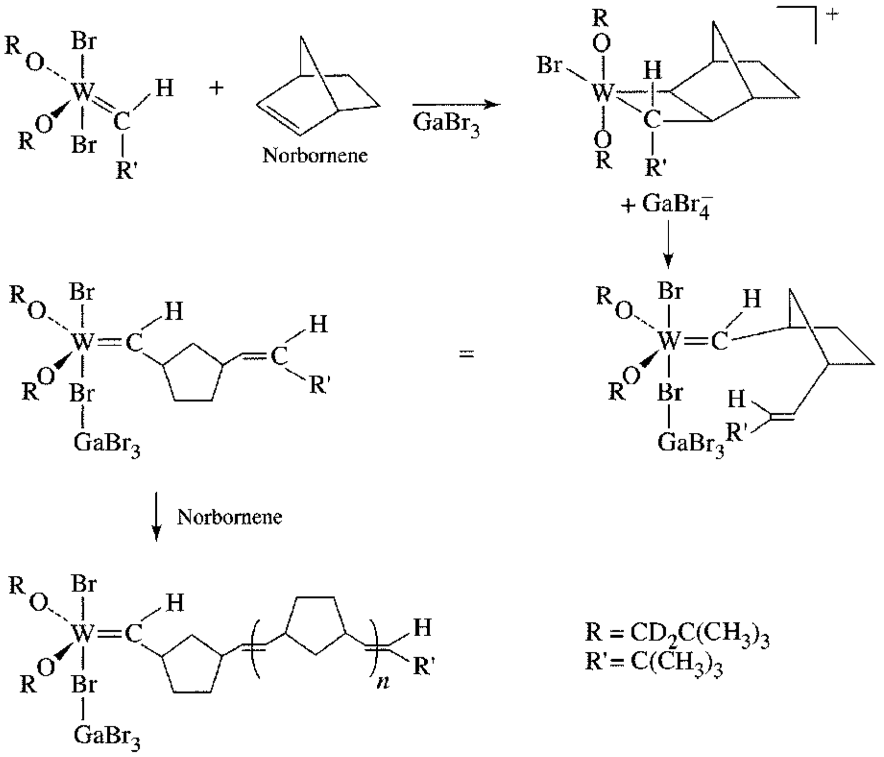

FIGURE 14-25 Polymerization of Norbornene Using Carbene Catalyst.

An interesting variation on olefin metathesis is the use of carbene complexes to catalyze alkene polymerization, also via a metallacyclobutane intermediate. An example is the use of W(CH—*t*-Bu)(OCD$_2$—*t*-Bu)$_2$Br$_2$ as a catalyst in the ring-opening polymerization of norbornene in the presence of GaBr$_3$, as shown in Figure 14-25.[35] Proton and ^{13}C NMR data are consistent with the proposed structure of the metallacyclobutane, as well as the polymer growing off the carbene carbon.

Alkynes can also undergo metathesis reactions catalyzed by transition metal carbyne complexes. The intermediates in these reactions are believed to be metallacyclobutadiene species, formed from the addition of an alkyne across a metal-carbon triple bond of the carbyne (Figure 14-26). The structures of a variety of metallacyclobutadiene complexes have been determined, and some have been shown to catalyze alkyne metathesis.[36]

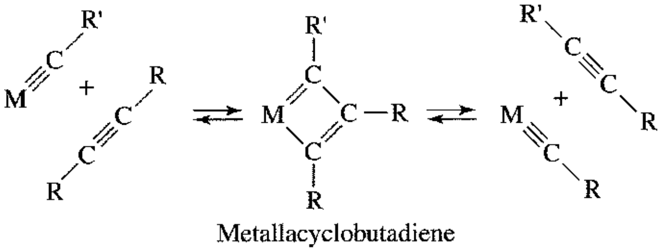

FIGURE 14-26 Alkyne Metathesis.

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[35] J. Kress, J. A. Osborn, R. M. E. Greene, K. J. Ivin, and J. J. Rooney, *J. Am. Chem. Soc.*, **1987**, *109*, 899.

[36] W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988, p. 311, and references therein; U. H. W. Bunz and L. Kloppenburg, *Angew. Chem., Int. Ed.*, **1999**, *38*, 478.

14-4
HETEROGENEOUS CATALYSTS

In addition to the homogeneous catalytic processes described earlier, heterogeneous processes, involving solid catalytic species, are very important, although the exact nature of the reactions occurring on the surface of the catalyst may be extremely difficult to ascertain. Of the 20 organic chemicals produced in 1995 in greatest quantities in the United States, at least 14 were produced commercially by processes that involve metal catalysts; most of these processes involve heterogeneous catalysis. Selected examples from 2001 are given in (Table 14-5).[37]

TABLE 14-5
Leading Organic Compounds and Metal Catalysts

Compound	*U.S. Production 2001 (×10^9 kg)*	*Example of Metal-Containing Catalyst Used*
Ethylene	22.56	
Propylene	13.20	$TiCl_3$ or $TiCl_4$ + AlR_3 (R = alkyl)
Urea	12.65	
1,2-Dichloroethane	9.36	$FeCl_3$, $AlCl_3$
Benzene	6.42	Pt on Al_2O_3 support
Ethylbenzene	4.65	$AlCl_3$
Styrene	4.22	ZnO, Cr_2O_3
Ethylene oxide	3.35	Ag
Cumene	3.16	
1,3 Butadiene	1.72	Fe_2O_3 or other metal oxide
Acrylonitrile	1.35	$BiPMe_{12}O_{40}$
Vinyl acetate	1.26	Pd salts

In many cases, the methods of preparing the catalysts and information on their function are proprietary, the product of substantial corporate investment. Nevertheless, it is important to mention several of these processes as important practical applications of organometallic reactions.

14-4-1 ZIEGLER-NATTA POLYMERIZATIONS

In 1955, Ziegler and coworkers reported that solutions of $TiCl_4$ in hydrocarbon solvents in the presence of $Al(C_2H_5)_3$ gave heterogeneous solutions capable of polymerizing ethylene.[38] Subsequently, many other heterogeneous processes were developed for polymerizing alkenes, using aluminum alkyls in combination with transition metal complexes. An outline of a possible mechanism for the Ziegler-Natta process proposed by Cossee and Arlman is given in Figure 14-27.[39]

First, reaction of $TiCl_4$ with aluminum alkyl gives $TiCl_3$, which on further reaction with the aluminum alkyl gives a titanium alkyl complex, as shown in the figure. Ethylene (or propylene) can then insert into the titanium-carbon bond, forming a longer alkyl. This alkyl is further susceptible to insertion of ethylene to lengthen the chain. Although the mechanism of the Ziegler-Natta process has proved difficult to understand,

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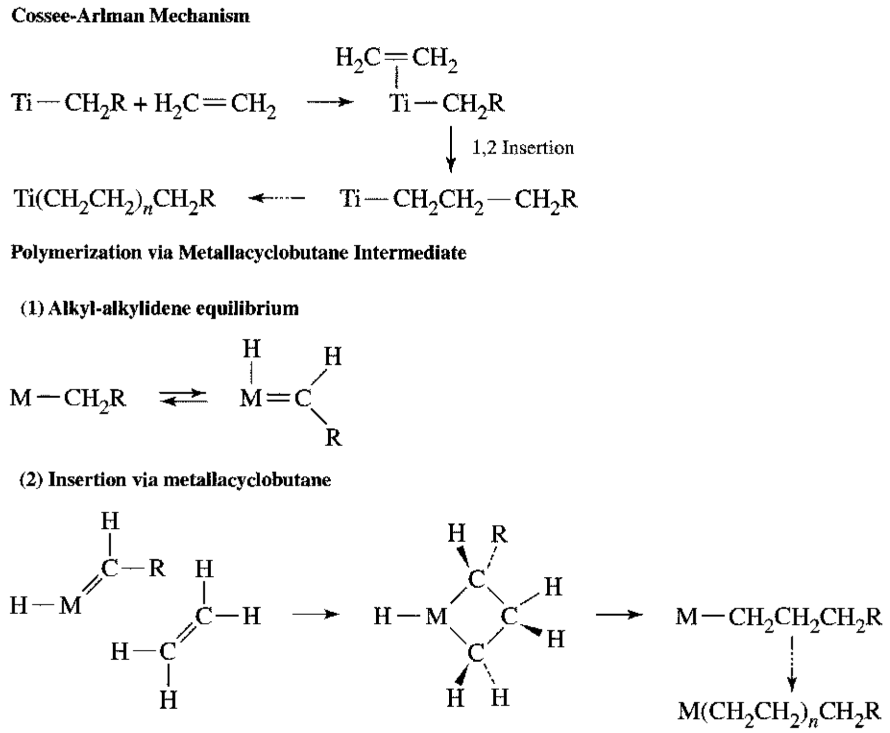
[37] R. Chang and W. Tikkanen, *The Top Fifty Industrial Chemicals*, Random House, New York, 1988; *Chem. Eng. News*, June 24, 2002, p. 61. The 1995 and 2001 data are not directly comparable because of differences in data collection.

[38] K. Ziegler, E. Holzkamp, H. Breiland, and H. Martin, *Angew. Chem.*, **1955**, *67*, 541.

[39] J. Cossee, *J. Catal.*, **1964**, *3*, 80; E. J. Arlman, *J. Catal.*, **1964**, *3*, 89; E. J. Arlman and J. Cossee, *J. Catal.*, **1964**, *3*, 99.



Cossee-Arlman Mechanism

Polymerization via Metallacyclobutane Intermediate

(1) Alkyl-alkylidene equilibrium

(2) Insertion via metallacyclobutane

FIGURE 14-27 Ziegler-Natta Polymerization.

direct insertions of multiply bonded organics into titanium-carbon bonds have been demonstrated, supporting the Cossee-Arlman mechanism.[40]

However, an alternative mechanism, involving a metallacyclobutane intermediate, has also been proposed.[41] This mechanism, also shown in Figure 14-27, involves the initial formation of alkylidene from a metal alkyl complex, followed by addition of ethylene to give the metallacyclobutane, which then yields a product having ethylene inserted into the original metal-carbon bond. Distinguishing between these mechanisms has been a long and difficult process, but experiments by Grubbs and coworkers have strongly supported the Cossee-Arlman mechanism as the likely pathway for polymerization in most cases.[42] In at least one example, however, there is strong evidence for ethene polymerization involving a metallacycle intermediate.[43]

14-4-2 WATER GAS REACTION

This reaction occurs at elevated temperatures and pressures between water (steam) and natural sources of carbon, such as coal or coke:

$$H_2O + C \longrightarrow H_2 + CO$$

---

[40] J. J. Eisch, A. M. Piotrowski, S. K. Brownstein, E. J. Gabe, and F. L. Lee, *J. Am. Chem. Soc.*, **1985**, *107*, 7219.

[41] K. J. Ivin, J. J. Rooney, C. D. Stewart, and M. L. H. Green, *Chem. Commun. (Cambridge)*, **1978**, 604.

[42] L. Clauson, J. Sato, S. L. Buchwald, M. L. Steigerwald, and R. H. Grubbs, *J. Am. Chem. Soc.*, **1985**, *107*, 3377. For a brief review of experiments used to distinguish between the two mechanisms, see G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, pp. 357–369.

[43] W. H. Turner and R. R. Schrock, *J. Am. Chem. Soc.*, **1982**, *104*, 2331.

The products of this reaction, an equimolar mixture of H_2 and CO (called "synthesis gas" or "syn gas"; some CO_2 may be produced as a by-product), can be used with metallic heterogeneous catalysts in the synthesis of a variety of useful organic products. For example, the **Fischer-Tropsch process**, developed by German chemists in the early 1900s, uses transition metal catalysts to prepare hydrocarbons, alcohols, alkenes, and other products from synthesis gas.[44] For example,

$$H_2 + CO \longrightarrow \text{Alkanes} \qquad \text{Co catalyst}$$

$$3\,H_2 + CO \longrightarrow CH_4 + H_2O \qquad \text{Ni catalyst}$$

$$2\,H_2 + CO \longrightarrow CH_3OH \qquad \text{Co or Zn/Cu catalyst}$$

Various heterogeneous catalysts are used industrially—for example, transition metals on Al_2O_3 and mixed transition metal oxides.

Most of these processes have been conducted under heterogenous conditions. However, there has been considerable interest in developing homogenous systems to catalyze the Fischer-Tropsch conversion.

These processes for obtaining synthetic fuels were used by a number of countries during World War II. They are, however, uneconomical in most cases, because hydrogen and carbon monoxide in sufficient quantities must be obtained from coal or petroleum sources. Currently, South Africa, which has large coal reserves, makes the greatest use of Fischer-Tropsch reactions in the synthesis of fuels in its Sasol plants.

In **steam reforming**, natural gas (consisting chiefly of methane) is mixed with steam at high temperatures and pressures over a heterogeneous catalyst to generate carbon monoxide and hydrogen:

$$CH_4 + H_2O \longrightarrow CO + 3\,H_2 \qquad \text{Ni catalyst, 700° to 1000°C}$$

(Other alkanes also react with steam to give mixtures of CO and H_2.) Steam reforming is the principal industrial source of hydrogen gas. Additional hydrogen can be produced by recycling the CO to react further with steam in the **water gas shift reaction**:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \text{Fe-Cr or Zn-Cu catalyst, 400°C}$$

This reaction is favored thermodynamically: at 400°C, $\Delta G° = -14.0\,\text{kJ/mol}$. Removal of CO_2 by chemical means from the product can yield hydrogen of greater than 99% purity. This reaction has been studied extensively with the objective of being able to catalyze formation of H_2 *homo*geneously.[45] An example is shown in Figure 14-28.[46] However, these processes have not yet proved efficient enough for commercial use.

In general, these processes, when performed using heterogeneous catalysts, require significantly elevated temperatures and pressures. Consequently, as in the case of the water gas shift reaction, there has been great interest in developing homogeneous catalysts that can perform the same functions under much milder conditions.

[44] E. Fischer and H. Tropsch, *Brennst. Chem.*, **1923**, *4*, 276.

[45] For example, see M. M. Taqui Khan, S. B. Halligudi, and S. Shukla, *Angew. Chem., Int. Ed.*, **1988**, *27*, 1735 and R. Ziessel, *Angew. Chem., Int. Ed.*, **1992**, *30*, 844.

[46] J. P. Collins, R. Ruppert, and J .P. Sauvage, *Nouv. J. Chim.*, **1985**, *9*, 395.

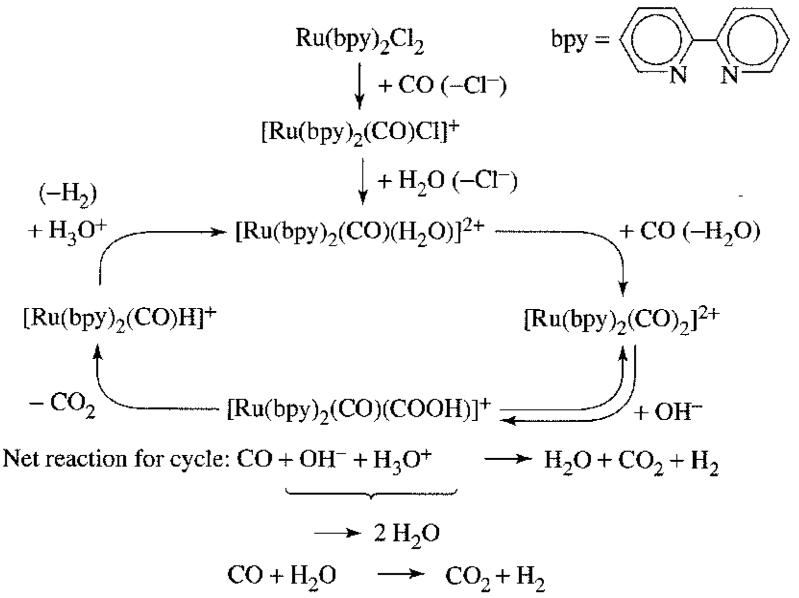


FIGURE 14-28 Homogeneous Catalysis of Water Gas Shift Reaction. (Adapted with permission from H. Ishida, K. Tanaka, M. Morimoto, and T. Tanaka, *Organometallics*, **1986**, *5*, 724. © 1986 American Chemical Society.)

GENERAL REFERENCES

J.P. Collman, L.S. Hegedus, J.R. Norton, and R.G Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, provides a detailed discussion, with numerous references, of many of the reactions and catalytic processes described in this chapter, as well as a variety of other types of organometallic reactions. In addition to providing extensive information on the structural and bonding properties of organometallic compounds, G. Wilkinson F. G. A. Stone, and E. W. Abel, eds, *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, and E. W. Abel, F. G. A. Stone, and G. Wilkinson, eds, *Comprehensive Organometallic Chemistry II*, Pergamon Press, Oxford, 1995, give the most comprehensive information on organometallic reactions, with numerous references to the original literature. S. T. Oyama and G. A. Somorjai, "Homogeneous, Heterogeneous, and Enzymatic Catalysis" in *J. Chem. Educ.*, **1988**, *65*, 765, gives examples of the types and amounts of catalysts used in a variety of industrial processes. The other references listed at the end of Chapter 13 are also useful in connection with this chapter.

PROBLEMS

14-1 Predict the transition metal-containing products of the following reactions:

a. $[Mn(CO)_5]^- + H_2C{=}CH{-}CH_2Cl \longrightarrow$ initial product $\xrightarrow{-CO}$ final product

b. *trans*-$Ir(CO)Cl(PPh_3)_2 + CH_3I \longrightarrow$

c. $Ir(PPh_3)_3Cl \xrightarrow{\Delta}$

d. $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_3) + PPh_3 \longrightarrow$

e. $(\eta^5\text{-}C_5H_5)Mo(CO)_3[C({=}O)CH_3] \xrightarrow{\Delta}$

f. $H_3C{-}Mn(CO)_5 + SO_2 \longrightarrow$ (no gases are evolved)

14-2 Predict the transition metal–containing products of the following reactions:

a. $H_3C{-}Mn(CO)_5 + P(CH_3)(C_6H_5)_2 \longrightarrow$ (no gases are evolved)

b. $[Mn(CO)_5]^- + (\eta^5\text{-}C_5H_5)Fe(CO)_2Br \xrightarrow{\Delta}$

c. *trans*-$Ir(CO)Cl(PPh_3)_2 + CH_3I \longrightarrow$

d. $W(CO)_6 + C_6H_5Li \longrightarrow$

e. *cis*-$Re(CH_3)(PEt_3)(CO)_4 + {}^{13}CO \longrightarrow$ (show all expected products, percentage of each)

f. *fac*-$Mn(CO)_3(CH_3)(PMe_3)_2 + {}^{13}CO \longrightarrow$ (show all expected products, percentage of each)