CH$_3$Mn(CO)$_4$THF has been identified, so the conjecture that THF and DMF behave in a manner that is different from the other solvents is not without some justification. Additional work on the influence of the solvent could yield additional insight regarding the mechanisms of this and other reactions of coordinated ligands.

22.2 **HOMOGENEOUS CATALYSIS**

Few areas of chemistry have changed as rapidly as the field of homogeneous catalysis by coordination compounds. Not only is the chemistry fascinating and diverse, but also it is immensely practical. The ability to carry out hydrogenations, isomerizations, and other processes at or near ambient conditions is sufficient motivation to ensure that knowledge will develop rapidly. That has certainly been the case. From a few rather sparse reactions has come a well-developed and rapidly growing field. Commensurate with that growth has been the expansion of the literature of the field. Numerous books have been written on the subject, some of which are listed as references at the end of this chapter. It is impossible in a textbook to do more than describe a few of the most important types of processes and show the general nature of the field. The interested reader should consult additional sources to become familiar with the details of the catalytic processes. In the sections that follow, several types of reactions will be described, and the role of the complexes that function as catalysts will be shown. Keep in mind that each of the schemes is made up of a series of steps, most of which are identical to some of the types of reactions described earlier.

22.2.1 **Hydrogenation**

In order for a complex to function as a hydrogenation catalyst, it is necessary for it to be able to bond to hydrogen and to the alkene. This requires the complex to be able to add hydrogen in an oxidative
addition reaction, and that process is characteristic of a metal in a low oxidation state. After the hydrogen and alkene are part of the coordination sphere of the metal, a facile means must be available for them to react. The overall reaction can be written as

\[
\text{H}_2 + \text{alkene} \rightarrow \text{alkane}
\]  

(22.26)

A complex that meets the requirements for a hydrogenation catalyst is \( \text{RhCl}(\text{P} \phi \text{3}) \), where \( \phi \) is a phenyl group, \( \text{C}_6\text{H}_5 \). This complex is a coordinatively unsaturated 16-electron species that has become known as Wilkinson’s catalyst because it was developed and utilized by the late Sir Geoffrey Wilkinson (who also received a Nobel Prize in 1973 for work on the structure of ferrocene). This versatile catalyst is effective in the hydrogenation of several types of compounds, which include alkenes and alkynes. Figure 22.8 shows the process that leads to hydrogenation of ethylene. Although the catalytic scheme is illustrated as if the hydrogenation of ethylene were occurring, more useful reactions involve hydrogenating longer-chain alkenes. In fact, ethylene does not undergo hydrogenation very readily under these conditions, but replacing a hydrogen atom on the \( \text{C}_2\text{H}_4 \) group with an alkyl group, \( \text{R} \), makes the scheme fit the general case.

The overall catalytic process can be considered as a series of steps. The first step involves the oxidative addition of hydrogen to give a complex having octahedral coordination. Addition of the alkene could occur by either an associative or dissociative pathway in which a molecule of \( \text{P} \phi \text{3} \) leaves. However, on the basis of NMR studies, it is believed that a small amount of this complex undergoes loss of one of the \( \text{P} \phi \text{3} \) ligands to give a five-bonded complex. It is also believed that it is possible for this intermediate to be interconverted between trigonal bipyramid and square-base pyramid structures, as shown in Eq. (22.27), because it is of a fluxional nature. It may be that the loss of the \( \text{P} \phi \text{3} \) ligand \textit{trans} to \( \text{H} \) is facilitated as a result of a \textit{trans} effect. It is to this intermediate that the alkene attaches. In order to form the
reactive intermediate, a ligand must be lost, and the large size of the P\(_{03}\) ligand seems to be one factor that enhances its dissociation.

\[ \text{Rh}_3L_3Cl \overset{\text{H}}{\longrightarrow} \text{RhL}_2^+ \text{L}^- \]

The reaction scheme shown in Figure 22.8 consists of a series of steps that represents the types of elementary reactions described earlier. The first step is the oxidative addition of hydrogen with the hydrogen atoms occupying cis positions. Subsequently, the entry of a molecule of triphenylphosphine into the coordination sphere occurs as a hydrogen transfer to the alkene occurs. This is followed by another hydrogen transfer that occurs in conjunction with reductive elimination of the alkane to regenerate the catalyst. Part of the interest and utility of this hydrogenation scheme is that it can be carried out at essentially ambient conditions. This represents a radical departure from the high temperature and pressure required when metal catalysts are used in hydrogenation. The mechanism shown in Figure 22.8 is only one of at least three that have been proposed, and it may deviate in some details from the actual mechanism (see the following structures). Keep in mind that positions indicated as being vacant may be occupied by a coordinated solvent molecule.

In the scheme shown in Figure 22.8, the rate-determining step is alkene insertion (viewed by some as hydrogen transfer). Because the hydride ion is a nucleophile, the reaction can be considered as a nucleophilic attack, which is influenced by the electron density in the alkene. A most interesting and important study dealing with this issue was reported by Nelson, Li, and Brammer (2005), in which the ionization potentials of a series of alkenes (a measure of electron density and availability) were correlated with the relative rate of reaction. The alkene that served as an index for comparing the rates was CH\(_2\)C=CHCH\(_3\), for which the \(k\) was set equal to 100. Rates for reactions of other alkenes (expressed by the \(k_{rel}\) values) were compared to that value, and they ranged from 1.4 for (CH\(_3\))\(_2\)C=CH\(_3\) to 410 for CH\(_3\)C=CH\(_3\). Plots of ionization potential versus log \(k_{rel}\) were generally linear, and especially so for a series of terminal alkenes. The negative slope of the plots is consistent with nucleophilic attack of hydride on the alkene that causes the alkene to change from \(\eta^2\) to \(\eta^1\) bonding. Other good correlations were established for the relative rate of hydrogenation of alkenes and the energy of the lowest unoccupied molecular orbital (LUMO). Although the correlations do not distinguish between mechanisms with regard to the possible transition states, they demonstrate that nucleophilic attack of hydride on the alkene is the rate-determining step in the process.
Some disagreement exists regarding the structure of the transition state (whether H or $P\phi_3$ is trans to the alkene) and whether or not solvent molecules occupy sites that are apparently vacant. In spite of some uncertainty regarding these details, the major issues regarding the catalyzed hydrogenation of alkenes using Wilkinson’s catalyst are fairly well understood.

Following the success of Wilkinson’s catalyst, other complexes having similar characteristics were studied. These include RhH($P\phi_3$)$_3$, RhHCl($P\phi_3$)$_3$, and RhH(CO)($P\phi_3$)$_3$. The last two of these are 18-electron complexes, so it is necessary for a ligand to leave in order to form a bond to a molecule of the reacting alkene. Hydride complexes contain one hydrogen atom that can transfer to the alkene (or to which the alkyl group can transfer) to form an alkyl group. After the transfer, the reaction with gaseous hydrogen reforms the hydride complex, and a second hydrogen transfer during which reductive elimination of the alkane occurs completes the process. Some catalysts have been designed that contain a different ratio of $P\phi_3$ to rhodium, and others have been studied that contain different phosphine ligands having a different basicity than $P\phi_3$. These catalysts and those that contain more basic phosphines have not been found to be more effective than the intermediates shown in Eq. (22.27). The nature of the alkene is also a factor in the catalytic process.

Another important use for Wilkinson’s catalyst is in the production of materials that are optically active (by what is known as enantioselective hydrogenation). When the phosphine ligand is a chiral molecule and the alkene is one that can complex to the metal to form a structure that has R or S chirality, the two possible complexes will represent two different energy states. One will be more reactive than the other, so hydrogenation will lead to a product that contains predominantly only one of the diastereomers.

Although there is a large amount of interesting chemistry associated with the $Co(CN)_5^{3-}$ ion, it is the ability to function as a catalyst in homogeneous systems that is the issue in this chapter. Because $Co(CN)_5^{3-}$ has the ability to split hydrogen (as shown in Eq. (22.10)), it is not surprising that it can function as a catalyst in hydrogenation reactions. The hydrogenation of 1,3-butadiene is illustrated in Figure 22.9.

![FIGURE 22.9](image-url) A plausible mechanism for hydrogenation of 1,3-butadiene catalyzed by $Co(CN)_5^{3-}$. 
As shown earlier, Co(CN)$_5^{3-}$ has the ability to split hydrogen molecules as a result of an oxidative addition reaction.

\[ \text{H}_2 + 2 \text{Co(CN)}_5^{3-} \rightarrow 2 \text{HCo(CN)}_5^{3-} \]  

(22.28)

Consequently, it is HCo(CN)$_5^{3-}$ that functions as a catalyst in hydrogenation processes. In the first step of the process shown in Figure 22.9, the alkene coordinates to HCo(CN)$_5^{3-}$ as one hydrogen atom is added to the molecule so that only one double bond remains. The monoene is bonded to the cobalt in \( \eta^1 \) fashion. In the second step, another HCo(CN)$_5^{3-}$ transfers hydrogen to the alkene, which undergoes reductive elimination and leaves, having been converted to 1-butene.

One of the interesting aspects of this process is that the nature of the product depends on the concentration of CN\(^{-}\) in the solution. When the concentration of CN\(^{-}\) is high, the product is 1-butene, but at low concentrations of CN\(^{-}\), the product is 2-butene. The explanation for this difference seems to be that when the cyanide ion concentration is low, the alkene changes bonding mode from \( \eta^2 \) to \( \eta^3 \) to complete the coordination sphere of the metal ion. The result is that the hydrogen atom from the second HCo(CN)$_5^{3-}$ is added to the terminal carbon atom in the \( \eta^3 \) arrangement and the product is 2-butene. In the presence of an excess of CN\(^{-}\), the alkene maintains the \( \eta^1 \) bonding, and the hydrogen atom from the second HCo(CN)$_5^{3-}$ is added to carbon atom adjacent to the methyl group, which produces 1-butene.

### 22.2.2 Isomerization of Alkenes

The isomerization of alkenes is an industrially important process that can be used to prepare specific isomers used as monomers in polymerization. One step in the isomerization process involves a change in bonding mode of an alkene. For example, isomerization of 1-alkenes to produce 2-alkenes may take place as the alkene changes from \( \eta^2 \) to \( \eta^1 \) in the transition state. This mechanism can be shown as

\[
\begin{align*}
\text{RCH}_2\text{CH}=\text{CH}_2 & \rightleftharpoons \text{H}_2\text{C}-\text{CH}_2\text{M} \rightleftharpoons \text{RCH}=\text{CH}_2\text{M} \rightleftharpoons \text{RCH}=\text{CH}_2\text{M} \\
\end{align*}
\]

(22.29)

One of the effective catalysts for isomerization of alkenes is a square planar complex of Rh\(^{3+}\). That complex undergoes replacement of a ligand in the coordination sphere as shown in the reaction scheme presented in Figure 22.10.

The isomerization process can be considered as taking place in a series of steps that involves a substitution reaction in which the alkene replaces a ligand L followed by the addition of H\(^+\) and L to form a six-bonded complex. A hydrogen transfer changes the alkene from \( \eta^2 \) to \( \eta^1 \), which is reversed as the alkyl group is converted into a 2-ene as a ligand L enters the coordination sphere of the metal. Reductive elimination by loss of L and H\(^+\) leads to a square planar complex in which the alkene is present as the 2-ene. Elimination of RCH=CH$_2$CH$_3$ as L enters the coordination sphere liberates the product and reforms the catalyst.
22.2.3 Polymerization of Alkenes (the Ziegler-Natta Process)

Ethylene and propylene are two monomers that are used in enormous quantities to produce polyethylene and polypropylene. These polymers are used for making a large variety of containers and other items. As a result, there has been a great deal of interest for many years in the reactions that yield these polymers.

The polymerization of alkenes is one of the important processes in which coordination chemistry is involved in what is known as the Ziegler-Natta process. Although polymerization of ethylene can be carried out at high temperature and pressure, a process by which this could be accomplished at room temperature and atmospheric pressure was discovered by Karl Ziegler in 1952. The process utilized TiCl$_4$ and Al(C$_2$H$_5$)$_3$ in a hydrocarbon solvent. It was later found by Giulio Natta that by using other catalyst combinations, polymers having stereoregularity could be produced. Ziegler and Natta shared the 1963 Nobel Prize for their enormously important work.

The polymerization reaction can be carried out using other combinations of a metal halide and a metal alkyl. Generally, a halide of titanium, vanadium, or chromium is used in combination with an alkyl of beryllium, aluminum, or lithium. Although the details of the process are not completely understood, the mechanism involves the replacement of a chloride ion by an ethyl group or an ethyl group attaching at a vacant site as the initial step. After a molecule of ethylene is coordinated to the titanium, it undergoes migration and insertion in the bond between Ti and C$_2$H$_5$. Another ethylene molecule becomes coordinated at the vacant site in the coordination sphere of the Ti, and another insertion reaction occurs, which lengthens the chain, and so on. The reaction scheme shown in Figure 22.11 illustrates this process. The crucial step in the process is the insertion reaction by which the hydrocarbon chain is lengthened.

Another reaction involving combining alkenes is the dimerization of ethene. That reaction is catalyzed by a rhodium complex, RhClL$_3$ as is illustrated in Figure 22.12.
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The first step in this process is an oxidative addition that is followed by a hydrogen transfer to a coordinated ethene molecule to convert it to an ethyl group. The third step involves the addition of a ligand as the C\textsubscript{2}H\textsubscript{4} molecule undergoes an insertion reaction to give a coordinated butyl group.

22.2.4 Hydroformylation

Also referred to as the *oxo* process or *hydrocarbonylation*, *hydroformylation* is a route to producing an aldehyde from an alkene, hydrogen, and carbon monoxide. This process has been known for approximately 70 years, and it is still economically important because useful compounds are produced in enormous quantities by this means. The reaction is summarized by the following equation:

\[
4 \text{RCH=CH}_2 + 5 \text{H}_2 + 4 \text{CO} \rightarrow 2 \text{RCH}_2\text{CH}_2\text{CHO} + 2 \text{RCH}_2\text{CH(O)CH}_3
\]  

(22.30)

Figure 22.13 shows the scheme used to describe the hydroformylation process. The active catalyst is HCo(CO)\textsubscript{3}, which is a 16-electron species that is coordinatively unsaturated. After that species is generated, the first step of the catalyzed process involves the addition of the alkene to the catalyst. In the next step, an insertion reaction occurs in which the alkene is inserted in the Co–H bond (nucleophilic attack by H\textsuperscript{−} on the alkene would accomplish the same result as described
earlier), which changes the bonding from \( \eta^2 \) to \( \eta^1 \). This is followed by the migration of CO to the Co–alkyl bond, which generates the \( \text{RC(O)}-\text{Co} \) linkage. With the oxidative addition of \( \text{H}_2 \) and reductive elimination of the aldehyde, the process is complete. Although the cobalt carbonyl catalyst allows the reaction to be useful, it requires temperatures of approximately 150°C and a pressure of 200 atmospheres. It is also generally the case that branched aldehydes are produced in greater quantity than straight-chain products. This is a significant handicap because the linear aldehydes are converted to linear alcohols that are used in the manufacture of detergents. The oxo process is also important for the production of precursors for making polymers such as poly(vinyl chloride).

In a more modern process, a rhodium complex having the structure

\[
\text{Rh} \quad \phi_3 \text{P} \quad \text{H} \quad \text{P} \quad \phi_3 \quad \text{Rh} \quad \text{C} \quad \text{O} \quad \phi_3 \text{P} \quad \phi_3
\]

is the starting complex for a catalytic cycle. The complete cycle is shown in Figure 22.14.

The first step in hydroformylation with the rhodium catalyst involves the loss of a \( \text{P} \phi_3 \) ligand followed by coordination of the alkene. This is followed by a hydrogen transfer that is accompanied by a change in bonding mode of the alkene to the metal from \( \eta^2 \) to \( \eta^1 \). After adding CO to a vacant site to give a five-bonded complex, migration of CO and insertion in the metal-carbon bond leads to formation of \( \text{M} \equiv \text{C(O)}\text{CH}_2\text{CH}_2\text{R} \). An oxad reaction of \( \text{H}_2 \) followed by reductive elimination of \( \text{RCH}_2\text{CH}_2\text{CHO} \) completes the process. Hydroformylation is one of the most important processes in which a complex functions as a catalyst.

### 22.2.5 Wacker Process

One of the important industrial processes is that by which ethylene is converted to acetaldehyde. This process involves the addition of oxygen to an alkene, and the equation for the overall process can be shown as

\[
\text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{PdCl}_2 \rightarrow \text{CH}_3\text{CHO} + \text{Pd} + 2 \text{HCl} \quad (22.31)
\]
It is believed that this reaction proceeds by the formation of a complex in which \( \text{C}_2\text{H}_4 \) is attached to the palladium.

\[
PdCl_2^{2-} + \text{C}_2\text{H}_4 \rightarrow [PdCl_2\text{C}_2\text{H}_4]^{2-} + \text{Cl}^{-} \tag{22.32}
\]

In that complex, it may be that water reacts with the coordinated \( \text{C}_2\text{H}_4 \) to produce a \( \sigma \)-bonded \( \text{CH}_2\text{CH}_2\text{OH} \) group rather than an insertion reaction involving an \( \text{OH} \) group. The aldehyde is formed as \( \text{H}^+ \) is lost, and the palladium is produced as shown in Eq. (22.31). The palladium chloride catalyst can be recovered (the price of palladium is almost $500/oz as this is written) by the reaction with \( \text{CuCl}_2 \).

\[
2 \text{CuCl}_2 + \text{Pd} \rightarrow \text{PdCl}_2 + 2 \text{CuCl} \tag{22.33}
\]

In order to complete the cyclic process, cuprous chloride is oxidized,

\[
4 \text{CuCl} + 4 \text{HCl} + \text{O}_2 \rightarrow 4 \text{CuCl}_2 + 2 \text{H}_2\text{O} \tag{22.34}
\]

The Wacker process was developed in the late 1950s and is not widely used because other processes are more effective.

### 22.2.6 Monsanto Process

Acetic acid is a major organic chemical that is manufactured in enormous quantities. It is used in numerous processes that include production of monomers as precursors for polymerization, as a solvent,
and many other industrial uses. One of the most important processes for the production of acetic acid is the Monsanto process. This method makes use of a rhodium catalyst that is obtained by a reaction involving \( \text{RhI}_3 \).

\[
\text{RhI}_3 + 3 \text{CO} + \text{H}_2\text{O} \rightarrow [\text{RhI}_2(\text{CO})_2]^+ + \text{CO}_2 + 2 \text{H}^+ + \text{I}^-
\]  

(22.35)

The rate-determining step in the process is believed to be oxidative addition of \( \text{CH}_3\text{I} \) to the rhodium complex, producing an octahedral rhodium +3 complex. The second step entails an insertion reaction in which CO is placed between the metal and the \( \text{CH}_3 \) group. This step could also involve migration of the \( \text{CH}_3 \) to a neighboring CO to give a \( \text{Rh}-\text{C(O)}\text{CH}_3 \) linkage or movement of the CO. After the addition of a molecule of CO, reductive elimination of \( \text{CH}_3\text{COI} \) generates the initial rhodium complex ion. The series of steps can be represented by the scheme shown in Figure 22.15.

The acetyl iodide that is released in the last step of the process reacts with water to produce acetic acid,

\[
\text{CH}_3\text{COI} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HI}
\]  

(22.36)

In an alternate procedure, the acetyl iodide is converted to methyl acetate if methanol is the solvent for the process.

\[
\text{CH}_3\text{COI} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{COOCH}_3 + \text{HI}
\]  

(22.37)

Methyl iodide is regenerated by the reaction

\[
\text{CH}_3\text{OH} + \text{HI} \rightarrow \text{CH}_3\text{I} + \text{H}_2\text{O}
\]  

(22.38)

This reaction is efficient because of the soft-soft interaction of \( \text{CH}_3 \) and I and the hard-hard interaction that leads to the formation of water. As in the case of some other catalytic processes, the idealized
scheme shown in Figure 22.15 does not necessarily represent the complete details of the process. Other products are known to include dimethyl ether and methyl acetate.

The applications of coordination compounds in catalysis that have been shown are by no means the only important cases. In fact, there are numerous reactions in which homogeneous catalysis forms the basis for a great deal of chemistry. From the examples shown, it should be apparent that this is a vast and rapidly developing field. It is also one that is important from an economic standpoint. Although the basic principles have been described in this chapter, the literature related to catalysis is extensive. For further details and more comprehensive reviews of the literature, consult the references listed.

22.3 BIOINORGANIC CHEMISTRY

As analytical methods and techniques for determining molecular structure have become more sophisticated, so has the awareness that a small detail in a structure may have a major role in its function. It has become increasingly apparent that such a small detail may be a metal ion. Thus, the relationship between inorganic chemistry and biochemistry has grown into the recognized discipline of bioinorganic chemistry. Any separation between the fields of chemistry seems to have disappeared, although the distinction is a fine one. For example, adding an (inorganic) chlorine atom to a benzene molecule to produce chlorobenzene does not make it part of “inorganic” chemistry. But if a zinc atom is contained in an enzyme having a molecular weight of 36,000, it suddenly becomes a “bioinorganic” structure. To be sure the molecule contains a metal, but the vast majority of the molecule is still “biochemical” in nature and its reactions are biochemical reactions. Nevertheless, it is appropriate even in an “inorganic” book to show at least a few ways in which metal ions influence biochemical function.

From the outset it is apparent that any attempt to cover a significant part of a discipline as vast as bioinorganic chemistry in a chapter of a book on inorganic chemistry is doomed to failure. Entire volumes (even multiple volumes) have been written on the subject. Articles describing work in the field are published in numerous journals that deal with inorganic chemistry, biochemistry, and hybrid areas such as organometallics. Even organizing such a huge amount of information would be a daunting task. Although one may not be able to eat a whole pie, eating one piece can show the flavor and character of the pie. So it is when dealing with an enormous amount of material on a subject. In this section, the approach taken will be to concentrate on a few selected systems to show the flavor and character of the field, but with no attempt at presenting a survey of the whole field. That task is addressed in some of the monographs listed in the suggested references.

22.3.1 Metals and Toxicity

The vast majority of biochemical processes in which a metal plays a role involve a only a relatively small number of metals. Those metals include Na, K, Mg, Ca, Mo, or the first-row transition metals from V to Zn. Only molybdenum could be considered as a heavy metal. It should also be observed that the metal ions constitute those that can be considered as hard or borderline in hardness. It is a general property that ions of heavy metals having low charge (that is to say “soft”) are toxic. These include Hg, Pb, Cd, Tl, and numerous others. Some heavy metals bind to groups such as the sulfhydryl (–SH) group in enzymes, thereby destroying the ability of the enzyme to promote the reaction in a