

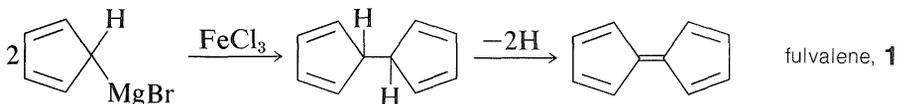
TRANSITION-METAL ORGANIC COMPOUNDS

In the 85 years following Kekulé's brilliant proposal for the structure of benzene, organic chemistry underwent a tremendous expansion, and in the process a wide variety of paradigms or working hypotheses were developed about what kinds of compounds could "exist" and what kinds of reactions could occur. In many cases, acceptance of these hypotheses appeared to stifle many possible lines of investigation and caused contrary evidence to be pigeonholed as "interesting but not conclusive." As one example, the paradigm of angle strain was believed to wholly preclude substances that we know now are either stable or important reaction intermediates, such as cubane (Section 12-10), cyclopropanone (Section 17-11), and benzyne (Sections 14-6C and 23-8).

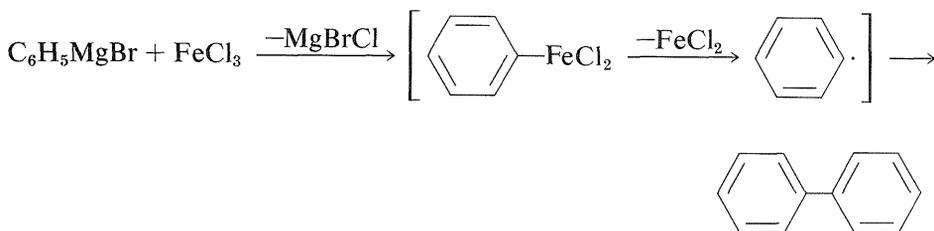
No paradigm did more to retard the development of organic chemistry than the notion that, with a "few" exceptions, compounds with bonds between carbon and transition metals (Fe, Co, Ni, Ti, and so on) are inherently unstable. This idea was swept away in 1951 with the discovery of *ferrocene*, $(C_5H_5)_2Fe$, by P. L. Pauson. Ferrocene has unheard of properties for an organoiron compound, stable to more than 500° and able to be dissolved in, and recovered from, concentrated sulfuric acid! Pauson's work started an avalanche of research on transition metals in the general area between organic and inorganic chemistry, which has flourished ever since and has led to an improved understanding of important biochemical processes.

31-1 METALLOCENES

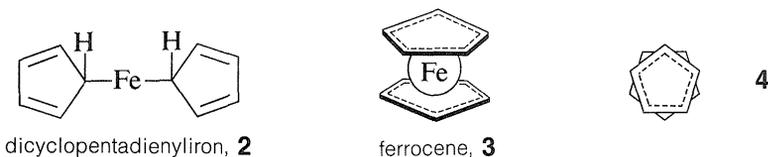
The discovery of ferrocene was one of those fortuitous accidents that was wholly unforeseeable—the kind of discovery which, over and over again, has changed the course of science. Pauson was trying to synthesize fulvalene, **1**, by first coupling two molecules of cyclopentadienylmagnesium bromide with FeCl_3 and then dehydrogenating the product:



The rationale for the coupling reaction was that phenylmagnesium bromide with FeCl_3 gives high yields of biphenyl, presumably by way of an unstable phenyliron compound:



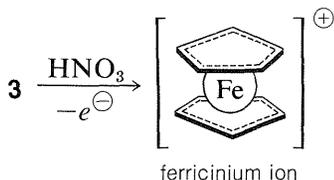
The reaction product was a beautifully crystalline, highly stable, orange substance, $\text{C}_{10}\text{H}_{10}\text{Fe}$, which Pauson formulated as a simple combination of two cyclopentadienide anions and *ferrous* ion with two C–Fe bonds, **2**. However, the product soon was shown by a variety of physical methods to have the “sandwich” structure, **3**:



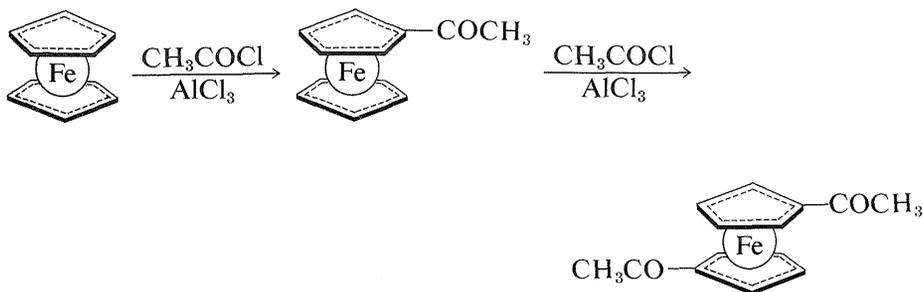
The bonding between the metal and the cyclopentadiene rings involves the π electrons of the two rings, all carbons being equally bonded to the central ferrous ion. The latter, in accepting a share of 12 π electrons from two cyclopentadienyl anions, achieves the 18 outer-shell electron configuration¹ of the inert gas, krypton. Analysis of the structure of crystalline ferrocene shows

¹Figure 6-4 (p. 154) shows that iron(0) has 8 electrons in the 4s and 3d orbitals. Ferrous ion ($\text{Fe}^{2\oplus}$) then will have 6 outer-shell electrons. This 6 plus the 12 π electrons of the two cyclopentadienide rings makes the 18-electron total and the krypton electronic configuration.

that when you look down on the molecule along the ring-iron-ring axis the cyclopentadiene rings are seen to be staggered with respect to one another, as shown in **4**. Ferrocene has mp 173° and, although stable to sulfuric acid, it is readily oxidized by nitric acid to the less stable ferricinium ion:



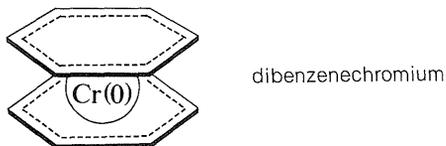
Like benzene, ferrocene does not react easily by addition but does undergo electrophilic substitution. For example, Friedel-Crafts acylation (Section 22-4F) with CH_3COCl gives both a monoethanoylferrocene and a diethanoylferrocene. The two acyl groups become attached to two different rings and, because only one diethanoylferrocene can be isolated, the cyclopentadienyl groups appear to be free to rotate about the axis of the carbon-iron bonds:



Ferrocene is only one of a large number of compounds of transition metals with the cyclopentadienyl anion. Other metals that form sandwich-type structures similar to ferrocene include nickel, titanium, cobalt, ruthenium, zirconium, and osmium. The stability of metallocenes varies greatly with the metal and its oxidation state; ferrocene, ruthenocene, and osmocene are particularly stable because in each the metal achieves the electronic configuration of an inert gas. Almost the ultimate in resistance to oxidative attack is reached in $(\text{C}_5\text{H}_5)_2\text{Co}^{\oplus}$, cobalticinium ion, which can be recovered from boiling *aqua regia* (a mixture of concentrated nitric and hydrochloric acids named for its ability to dissolve platinum and gold). In cobalticinium ion, the metal has the 18 outer-shell electrons characteristic of krypton.

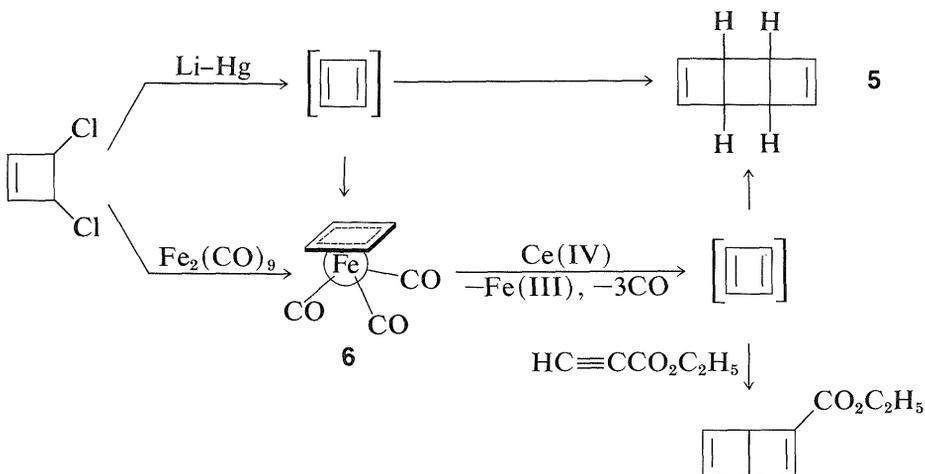
Many other unsaturated organic compounds can form π complexes with transition metals. A substance that is in some ways analogous to ferrocene is the complex of two benzene molecules with chromium metal, called dibenzenechromium. The bonding involves zerovalent chromium and the π electrons of

the two benzene rings. In dibenzenechromium, the electronic configuration of the chromium atom is similar to that of krypton:



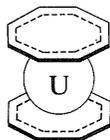
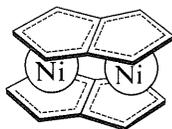
Although dibenzenechromium is thermally quite stable, it is less so than ferrocene and melts with decomposition at 285° to give benzene and metallic chromium. Furthermore, it appears to lack the aromatic character of either benzene or ferrocene as judged by the fact that it is destroyed by reagents used for electrophilic substitution reactions.

Several transition-metal complexes of cyclobutadiene have been prepared, and this is all the more remarkable because of the instability of the parent hydrocarbon. Reactions that logically should lead to cyclobutadiene give dimeric products instead. Thus, 3,4-dichlorocyclobutene has been dechlorinated with lithium amalgam in ether, and the hydrocarbon product is a dimer of cyclobutadiene, **5**. However, 3,4-dichlorocyclobutene reacts with diiron nonacarbonyl, $\text{Fe}_2(\text{CO})_9$, to give a stable iron tricarbonyl complex of cyclobutadiene, **6**, whose structure has been established by x-ray analysis. The π -electron system of cyclobutadiene is considerably stabilized by complex formation with iron, which again attains the electronic configuration of krypton.

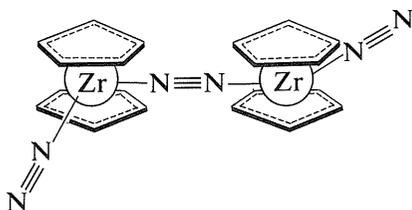


Oxidation of **6** with ceric iron, Ce(IV) , releases cyclobutadiene which quickly dimerizes, but can be trapped by good dienophiles such as ethyl propynoate to give a cycloadduct.

Many metallocene derivatives are known of other conjugated cyclic polyenes. Examples are bis(cyclooctatetraene)uranium (uranocene, **7**) and bis(pentalenylnickel), **8** (see Section 22-12B):

uranocene, **7**bis(pentalenylnickel), **8**

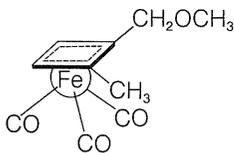
Many of the metallocene compounds display unusual reactivities and reactions, of which none is more startling than the discovery by the Russian chemist, M. E. Vol'pin, of absorption of dinitrogen, N_2 , by titanocene, $(C_5H_5)_2Ti$, to form a complex or complexes that can be reduced easily to form ammonia. The nature of these complexes is in doubt, but very clear evidence has been obtained by J. E. Bercaw for the structure of the complex **9** formed from decamethylzirconocene and dinitrogen:

**9** (for clarity, the 20 methyl groups on the rings have been omitted)

This complex treated with acids gives NH_2-NH_2 and some NH_3 .

Exercise 31-1 If the ferrocene rings in **3** were *not* free to rotate, how many different dichloroferrocene isomers would be expected (including chiral forms)? How could the substitution method (Section 1-1F) be used to determine which of the isomers was which?

Exercise 31-2 The cyclobutadiene iron complex, **10**, has been prepared *optically active*, and when oxidized with Ce(IV) in the presence of tetracyanoethene gives a mixture of *cyclobutadiene* cycloadducts, all of which are *optically inactive*.

**10** (one chiral form)

a. Draw the other chiral form of **10**.

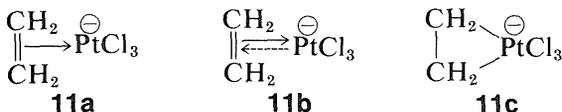
- b.** Write structures for the cycloadducts that would be expected to be formed if **10** were oxidized with Ce(IV) in the presence of tetracyanoethene.
- c.** How does formation of optically inactive products indicate that the cycloadducts are formed from the cyclobutadiene corresponding to **10**?
- d.** Is cycloaddition of an alkene to cyclobutadiene best regarded as a $[2 + 2]$ or a $[4 + 2]$ reaction?

Exercise 31-3* Assuming the molecular formula of **9** is established as $C_{40}H_{60}N_6Zr_2$, explain how the proposed structure is consistent with ^{15}N nmr spectra as follows. Made with $^{15}N \equiv ^{14}N$, **9** shows three widely separated resonance lines of equal intensity. However, when **9** is made with $^{15}N \equiv ^{15}N$, two of the peaks become doublets with a spacing of 6 Hz.

31-2 OTHER ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS

31-2A π -Type Alkene and Cycloalkene Complexes

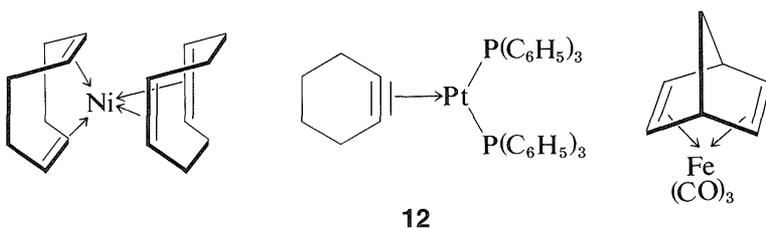
Not all organometallic compounds of transition metals date from the discovery of ferrocene. Many have been known for a long time but their structures were not understood. A conspicuous example is the anion of a substance known as Zeise's salt, which is formed from the reaction of ethanol with chloroplatinic acid, H_2PtCl_6 . The anion has the formula $Pt(C_2H_4)Cl_3^-$. Although known since 1830, it finally was shown to have a structure with *both* ethene carbons bonded to platinum. The carbon-to-metal bonding usually is formulated as a π complex, **11a**, or charge-transfer complex (Section 22-4D). Alternatively, we can think of the bonding in **11a** as between platinum as a Lewis acid (electron-pair acceptor) and ethene as a Lewis base (electron-pair donor):



The arrow in **11a** symbolizes donation of π electrons. However, because the stability of the ion is much greater than would be expected for either a simple acid-base or charge-transfer complex, it is postulated that unshared d electrons from the metal participate in the bonding. This is symbolized by the dashed arrow in **11b**, which stands for donation of d electrons into the π^* orbital of the double bond or, as it is often called, "back bonding." Perhaps most simple is **11c**, where the C-Pt bonding is formulated as a three-

membered ring with essentially C–Pt σ bonds. In this formulation, full participation of a platinum electron pair is assumed.

Many complexes of alkenes, cycloalkenes, alkynes, and cycloalkynes with transition metals are now known. Some examples are:

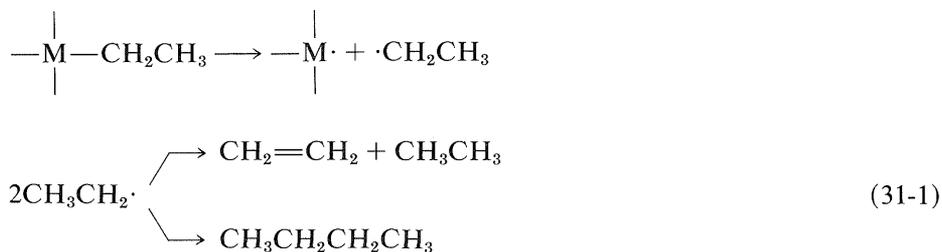


Many substances of this type have potential synthetic usefulness as catalysts or as reagents.

Exercise 31-4 The diphenylethyne complex with Pt(0), analogous to **12**, has been shown by x-ray diffraction analysis to have C—C≡C bond angles of about 140° and a central C—C bond distance of 1.32Å. Explain which of the formulations, **11a**, **11b**, or **11c**, seems most reasonable to account for the x-ray data for this complex.

31-2B Alkyl–Transition-Metal Bonds

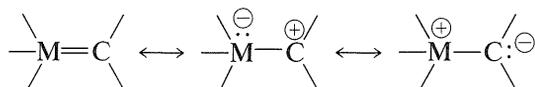
Organometallic compounds of transition metals with alkyl-to-metal bonds for many years were regarded as highly unstable substances and prone to dissociate into radicals that would couple or disproportionate, as illustrated by the following sequence:



The fact is that the stability depends on the character of the attached alkyl groups. Transition-metal compounds with CH₃—, (CH₃)₃CCH₂—, and C₆H₅CH₂— groups are in many cases very much more stable than those with CH₃CH₂—, (CH₃)₂CH—, and (CH₃)₃C— groups, even though the ease of formation of radicals by dissociation would be expected to be especially favorable with the C₆H₅CH₂— group. Furthermore, decompositions that give alkene and metal hydride or disproportionation products (alkene and alkane) may fail to give coupling products altogether. These facts and many others

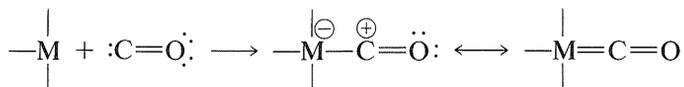
31-2C Carbene–Metal Complexes

Bonding between a transition-metal atom and one sp^2 -hybridized carbon can be represented by the following valence-bond structures:

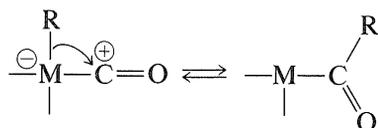


Stable transition-metal complexes of this type are known and others have been recognized as likely intermediates in a number of reactions. Rightly or wrongly, they are called **carbene-metal complexes**, although they also can be regarded either as metal-stabilized carbocations or as metal-stabilized ylides (Section 16-4A).

Perhaps the most common examples of this type of carbon–metal bonding are the metal carbonyls, in which the carbon monoxide ligand functions as the “carbene”:



When represented in this way the chemistry of carbonyl complexes of transition metals becomes easier to understand. Hydroformylation reactions and other carbonylations that are catalyzed by transition-metal complexes frequently involve hydride or alkyl transfers from the metal atom to the “positive” carbonyl carbon (Sections 16-9G, 31-3, and 31-4):



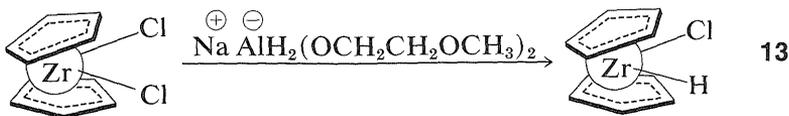
We now proceed to describe some selected reactions that can be understood within this framework of σ -, π -, and carbene-type bonding between the metal and carbon.

31-3 TRANSITION-METAL COMPOUNDS AS REAGENTS FOR ORGANIC SYNTHESSES

31-3A Reactions of Zirconocene Chlorohydride

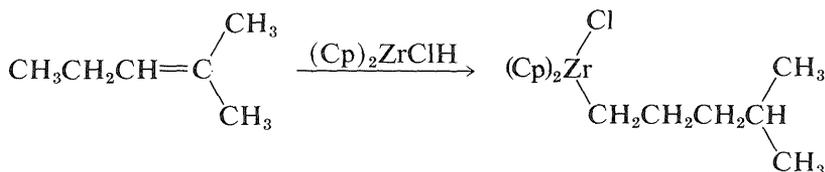
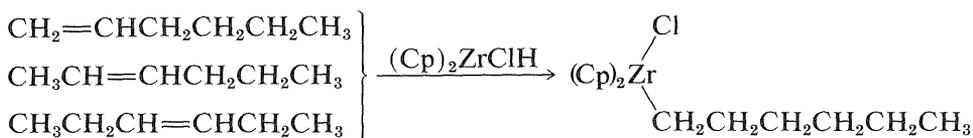
Some transition-metal hydrides show promise as synthetic reagents of the same general applicability as the boron hydrides (Section 11-6). An excellent illustration is provided by the work of J. Schwartz with zirconocene chloro-

hydride, **13**, which is available by reduction of zirconocene dichloride:

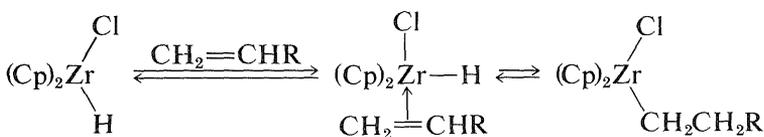


(The cyclopentadienide rings in **13** are shown as being nonparallel and this is in accord with x-ray diffraction studies of metallocenes that have extra substituents on the metal.) Henceforth we will abbreviate the structure **13** by (Cp)₂ZrClH.

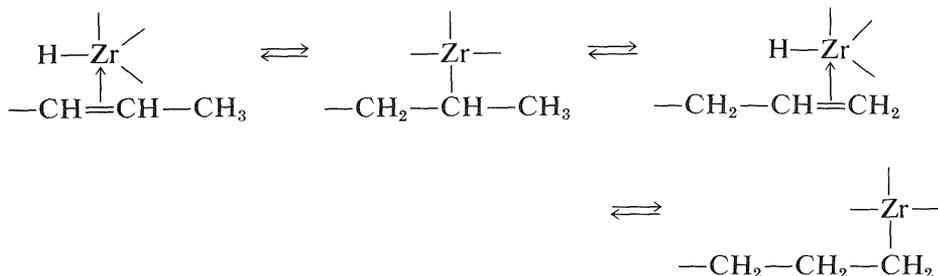
Alkenes react with (Cp)₂ZrClH to form alkyl-Zr bonds with zirconium becoming attached to the *least-hindered primary carbon*:



The initial step in this kind of reaction is formation of the π -alkene complex followed by hydride transfer:



These reactions must be reversible for an alkene with an *internal* double bond to form an adduct with the metal atom at the *end* of the chain. The process is seen as a series of interconversions between π and σ complexes, which permits the metal atom to move to the least-hindered (primary) carbon:



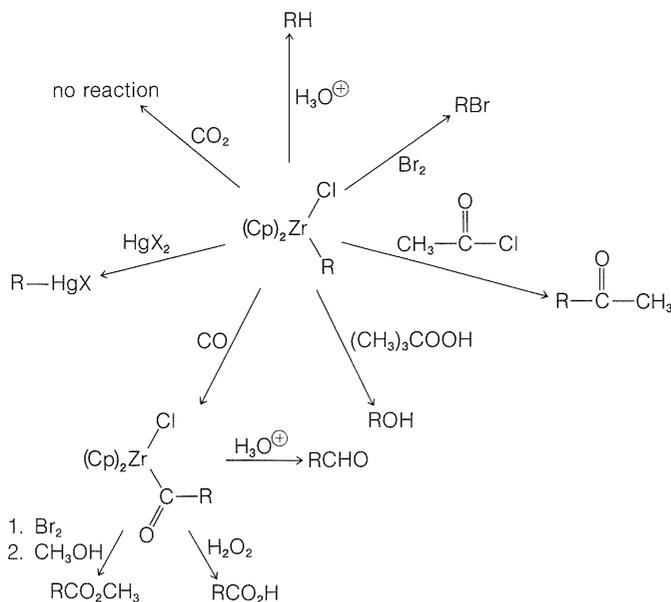
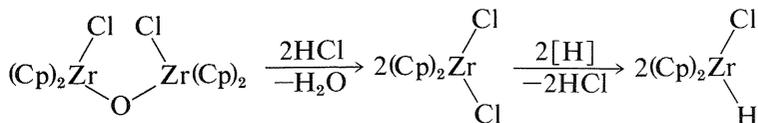


Figure 31-1 Synthetic reactions of alkylzirconocenes. In general, the reactions parallel those of the boranes (Sections 11-6 and 16-9G).

The alkyl chlorozirconium compounds undergo a variety of useful reactions, as can be seen from Figure 31-1. Similar reactions also can be carried out with alkynes by way of complexes such as $(Cp)_2Zr(Cl)CH=CH_2$.

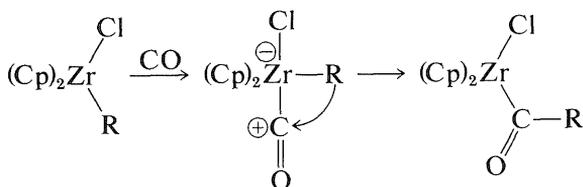
One of the elegant features of these reactions is the formation of crystalline $[(Cp)_2Zr(Cl)]_2O$ on treatment of the reaction products with water. This substance can be converted back to zirconocene dichloride with HCl and thence back to $(Cp)_2ZrClH$:



A very important reaction of alkyl transition-metal complexes with carbon monoxide results in formation of an acyl derivative, as can be seen for

$(Cp)_2Zr \begin{matrix} \text{H} \\ | \\ \text{R} \end{matrix}$ in Figure 31-1. This reaction proceeds by way of a carbon-

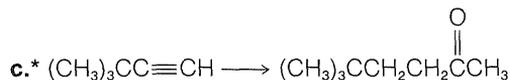
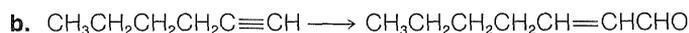
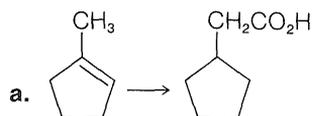
monoxide complex of the metal, which then rearranges by an alkyl shift:



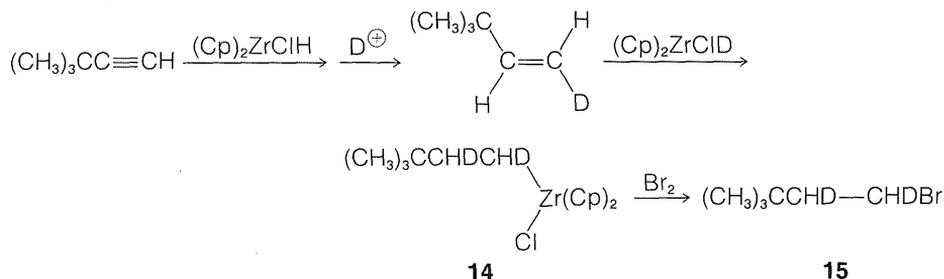
This sequence of steps is an important part of the mechanism of the hydroformylation of alkenes (oxo reaction), to be discussed in Section 31-4B, and also is related to the carbonylation reactions of boranes discussed in Section 16-9G.

Exercise 31-5 Write the sequence of steps whereby $(\text{Cp})_2\text{ZrClH}$ reacts with 2-methyl-2-pentene to form $(\text{Cp})_2\text{Zr}(\text{Cl})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$. Why is there no appreciable amount of $(\text{Cp})_2\text{Zr}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ in the product?

Exercise 31-6 Show how $(\text{Cp})_2\text{ZrClH}$ could be used to achieve the following conversions:



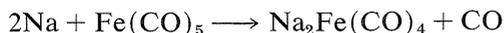
Exercise 31-7* The stereochemistry of reactions in which Zr–C bonds are formed and cleaved can be deduced from the results of the following reactions, where D is hydrogen of mass 2.



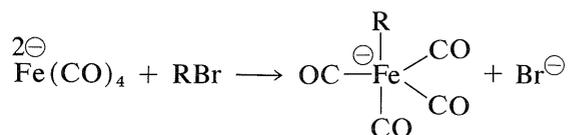
The CH—CH coupling constants in the proton nmr spectra of **14** and **15** are about 13 Hz. Work out the favorable conformations and the likely configurations of **14** and **15** and the stereochemistry of the addition and cleavage reactions. (Review Section 9-10H.)

31-3B A Nucleophilic Transition-Metal Reagent. Sodium Tetracarbonylferrate(−II)

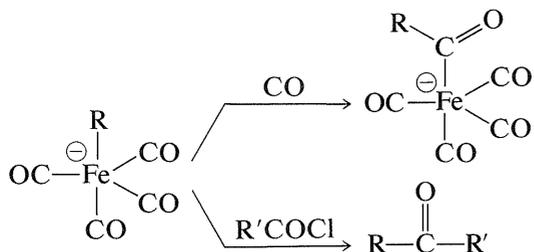
Sodium reacts with iron pentacarbonyl to produce a salt known as sodium tetracarbonylferrate(−II)², $\text{Na}_2\text{Fe}(\text{CO})_4$, which has been shown by J. P. Collman and co-workers to have considerable potential as a reagent for organic synthesis.



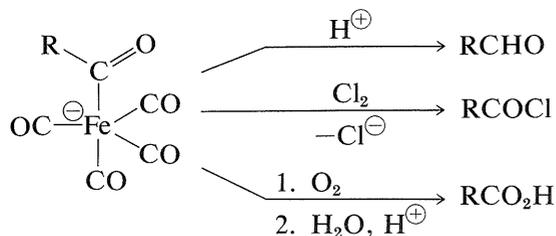
The tetracarbonylferrate dianion is a good nucleophile and reacts with alkyl halides or alkyl sulfonate esters by the $\text{S}_{\text{N}}2$ mechanism (with inversion) to form C–Fe bonds:



The resulting anion undergoes insertion with carbon monoxide or ketone formation with acyl halides in a manner similar to alkylchlorozirconocenes (Section 31-3A):



The product of CO insertion has the potential of transferring $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}:^{\ominus}$, and is converted to RCHO with acids, to RCOCl with halogens, or to RCO_2H by oxidation:



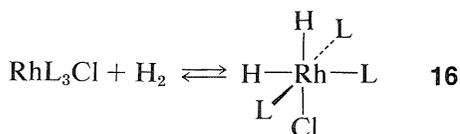
²The designation (−II) indicates that the iron in this substance can be regarded as being in the −2 oxidation state.

31-4 SOME HOMOGENEOUS CATALYTIC REACTIONS INVOLVING TRANSITION-METAL COMPLEXES

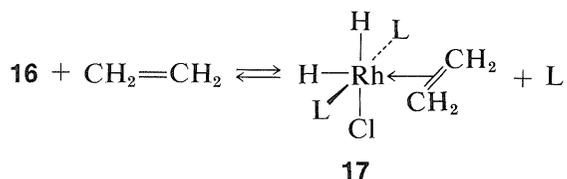
31-4A Hydrogenation

The mechanisms of hydrogenation of alkenes over finely divided metals such as nickel, platinum, and so on (Section 11-2) now are understood in a general way. However, these reactions are extremely difficult to study because they occur on a metallic surface whose structure is hard to define. In contrast, the mechanisms of hydrogenation with homogeneous catalysts are known in considerable detail and provide insight into their heterogeneous counterparts.

Homogeneous hydrogenation catalyzed by the four-coordinated rhodium complex, $\text{Rh}[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Cl}$, has been particularly well investigated. With this catalyst, the first step is formation of the six-coordinated rhodium hydride of known configuration, **16**, in which we abbreviate the ligand, triphenylphosphine, $(\text{C}_6\text{H}_5)_3\text{P}$, as L:

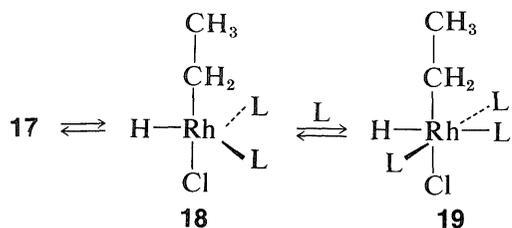


The next step is coordination of the alkene (here ethene) with **16** with loss of L to give the π complex **17**, also of known configuration:



Stable ethene complexes of Rh similar to **17** have been isolated and shown to have the π -complex structure. Formation of **17** must be an equilibrium process because addition of extra L reduces the rate of hydrogenation by shifting the equilibrium to the left.

Hydrogenation proceeds by hydride rearrangement of **17** to a five-coordinated ethyl-rhodium complex, **18**. This complex regains a ligand molecule to replace the one lost previously, thereby giving the six-coordinated complex, **19**:



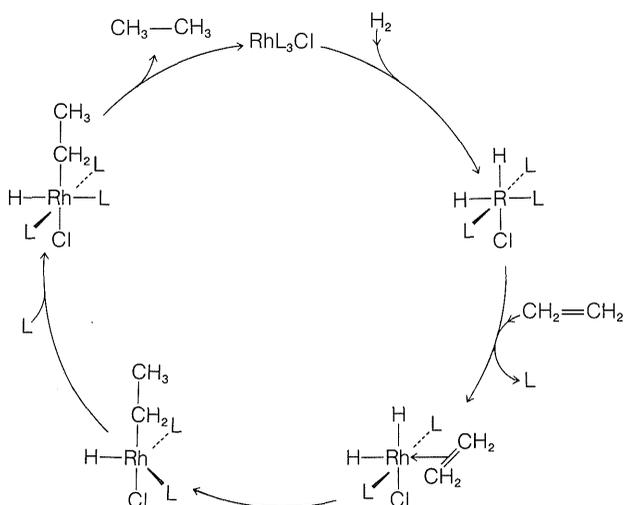


Figure 31-2 Merry-go-round diagram that summarizes the steps in the hydrogenation of ethene by $\text{Rh}[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Cl}$. The key features are the flow of reactants into and the products out of the cycle, the loss and re-gaining of the ligand, and the regeneration of the catalyst. The ligand triphenylphosphine is represented by L.

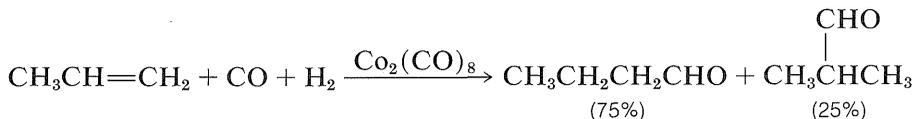
Stable complexes with $\text{Rh}-\text{CH}_2\text{CH}_3$ bonds similar to **19** have been well characterized. The final step is formation of ethane from **19** with regeneration of RhL_3Cl :



Although we abbreviate $(\text{C}_6\text{H}_5)_3\text{P}$ as L and show little role for it or for the Cl attached to rhodium in the reaction, these ligands play a very important role in providing the electronic and steric environment around the rhodium, which makes efficient catalysis possible. A useful diagram of how the catalyst functions in the overall reaction is shown in Figure 31-2.

31-4B Hydroformylation of Alkenes (Oxo Reaction)

The conversion of alkenes to aldehydes with carbon monoxide and hydrogen in the presence of a cobalt catalyst is an important reaction (Section 16-9F):



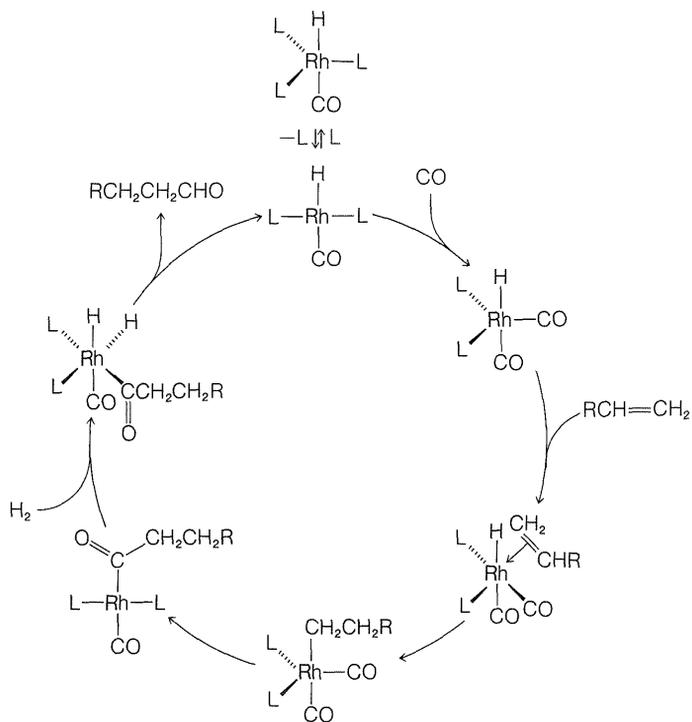
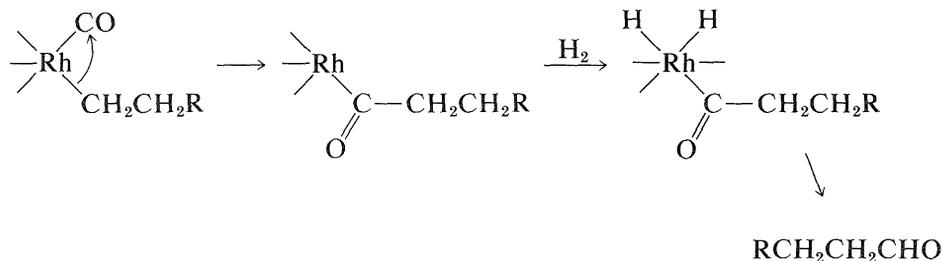


Figure 31-3 Catalytic cycle for the hydroformylation of alkenes as developed by G. Wilkinson. The stereochemical configurations of the participants in the cycle are uncertain.

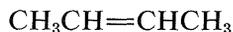
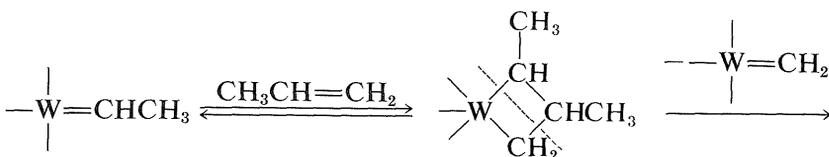
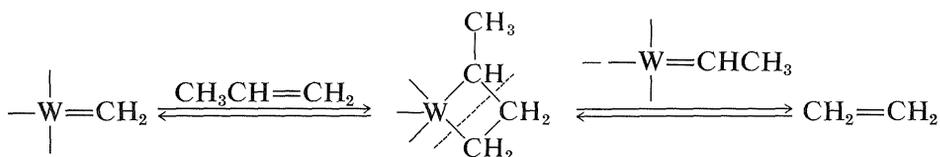
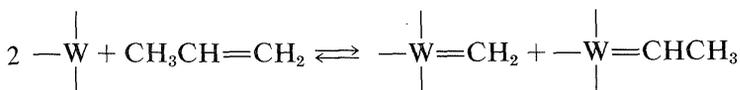
A mechanism for this kind of transformation has been established by G. Wilkinson for a rhodium catalyst, $\text{RhL}_3\text{H}(\text{CO})$, in which L is $(\text{C}_6\text{H}_5)_3\text{P}$, in accord with the cycle of Figure 31-3. This cycle shows that the reaction is closely related to the hydrogenation cycle of Figure 31-2. The new steps are



Exercise 31-8 Explain how 2-methylpropanal could be formed in substantial amount in the cycle of Figure 31-3 with propene as the starting alkene.

The reaction products are those expected if cyclobutanes were intermediates, but formation and cleavage of cyclobutanes is not the correct mechanism because cyclobutanes generally are not converted to alkenes over alkene-metathesis catalysts.

After a great deal of research on the mechanism of this reaction, it now appears likely that the crucial step is the formation of carbene metal complexes and that the products are formed by recombination of the carbenes with alkene in the various possible ways:

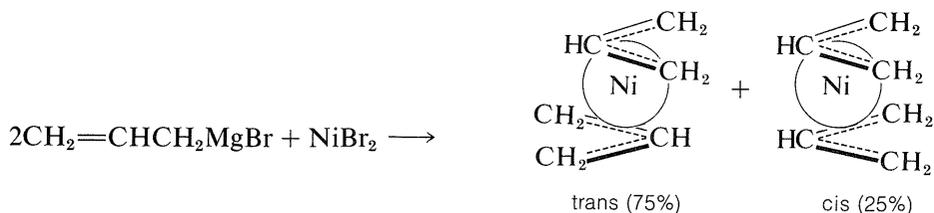


Exercise 31-9 Explain how an alkene-metathesis catalyst might convert a cycloalkene into (a) a long-chain unsaturated polymer, (b) a mixture of large-ring polymers, and (c) a catenane (interlocking carbon rings like two links in a chain).

31-5 π -PROPENYL COMPLEXES OF NICKEL

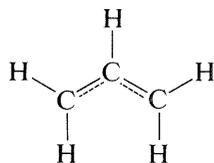
A considerable body of highly useful chemistry based on nickel has been developed, largely by the German chemist, G. Wilke. Many of these reactions involve what are called π -propenyl (π -allyl) complexes and their formation

has a close analogy in the formation of ferrocene from cyclopentadienyl-magnesium compounds and ferric chloride (Section 31-1). Treatment of NiBr_2 with two moles of 2-propenylmagnesium bromide gives a stable (albeit oxygen sensitive) substance of composition $(\text{C}_3\text{H}_5)_2\text{Ni}$:

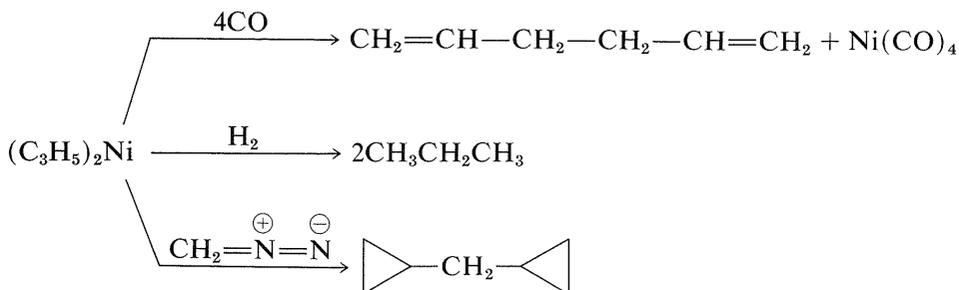


20

Unlike $\text{C}_3\text{H}_5\text{MgBr}$, the metal compound has a very complex proton nmr spectrum (see Exercise 31-10). Analysis of the spectrum indicates it arises from a mixture (75:25) of two $(\text{C}_3\text{H}_5)_2\text{Ni}$ isomers with each isomer having its C_3H_5 groups in a rigid planar arrangement as follows:

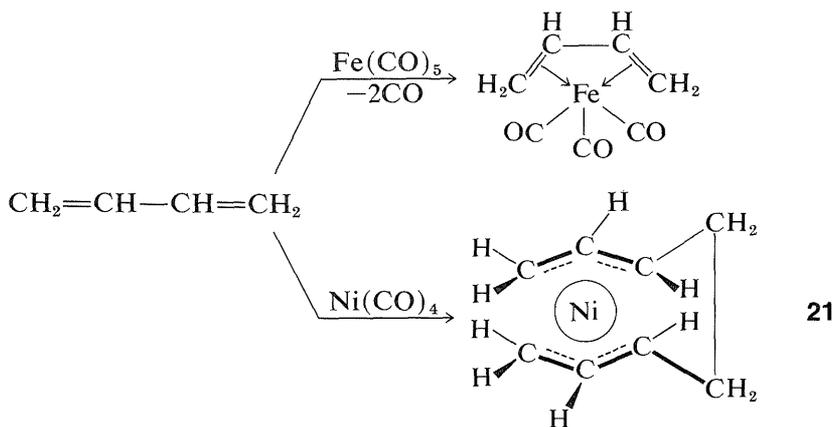


These facts can be accommodated by the *trans*- and *cis*-di- π -propenylnickel structures, **20**. Di- π -propenylnickel has many interesting reactions, among which are the following examples:

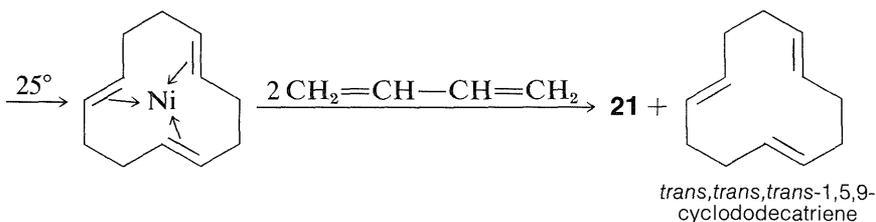
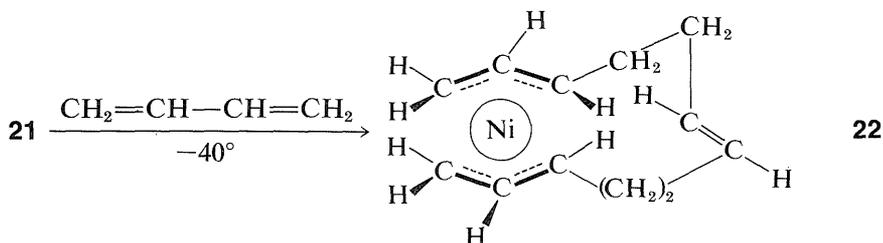


The π -propenyl-type structures are more stable for nickel than for other metals such as iron. With 1,3-butadiene, $\text{Fe}(\text{CO})_5$ forms a double

π complex, whereas $\text{Ni}(\text{CO})_4$ produces a bis- π -propenyl-type structure, **21**:



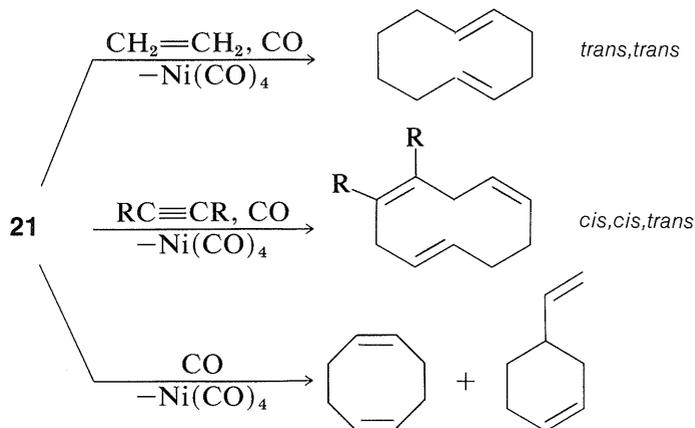
With more 1,3-butadiene, **21** is converted first to **22**, which after rearrangement reacts with 1,3-butadiene to give back **21** with liberation of *trans,trans,trans*-1,5,9-cyclododecatriene:



The overall sequence thus provides a catalytic route for the *cyclic trimerization* of 1,3-butadiene.

Ethene and alkynes react with **21** in the presence of excess carbon monoxide to give ten-membered ring compounds, whereas the reaction of **21**

with excess carbon monoxide results in formation of a mixture of six- and eight-membered rings:



Exercise 31-10 The nmr spectrum of 2-propenylmagnesium bromide in ether is shown in Figure 31-4. With the aid of the discussion in Sections 9-10C and 9-10E and the knowledge that the CH_2 resonance of ethylmagnesium bromide comes at 38 Hz *upfield* from tetramethylsilane, sketch the nmr spectrum you would expect for $\text{CH}_2=\text{CHCH}_2\text{MgBr}$. Consider possible ways of reconciling your expected spectrum with the actual spectrum shown in Figure 31-4. (Review Section 27-2.)

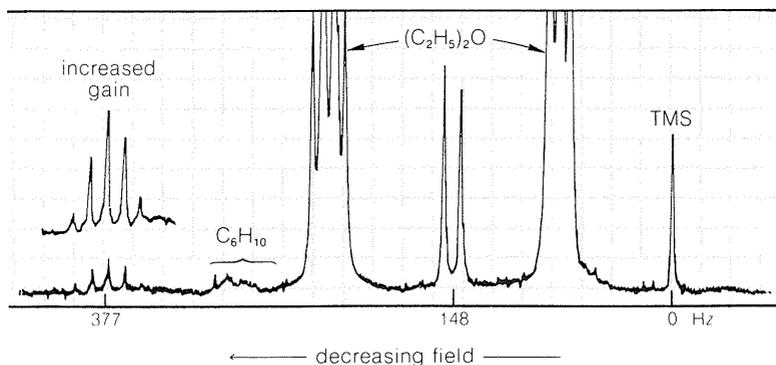


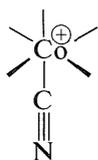
Figure 31-4 Nmr spectrum of 2-propenylmagnesium bromide in diethyl ether solution at 60 MHz with reference to tetramethylsilane at 0 Hz. The off-scale bands are due to the diethyl ether, and the signals designated C_6H_{10} are due to 1,5-hexadiene (coupling product resulting during formation of the Grignard reagent).

Exercise 31-11 When one mole of azabenzene (pyridine), which is a good ligand, is added to a solution of one mole of **20** in diethyl ether, a complex of composition $(C_3H_5)_2NiNC_5H_5$ is formed in which the very complex proton spectrum of the C_3H_5 groups of **20** becomes greatly simplified and essentially like that of Figure 31-4. Explain how complexation of one mole of azabenzene with nickel in **20** could so greatly simplify the proton nmr spectrum.

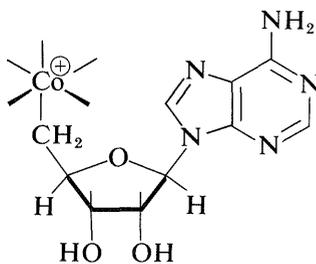
Exercise 31-12* π -Propenyl(ethyl)nickel decomposes at -70° to give propene and ethene. If the ethyl group is labeled with deuterium as $-CH_2-CD_3$, the products are C_3H_5D and $CD_2=CH_2$. If it is labeled as $-CD_2-CH_3$, the products are $C_3H_6 + CD_2=CH_2$. Are these the products expected of a radical decomposition, or of a *reversible* hydride-shift followed by decomposition as in the mechanism of Section 31-2B? Suppose the hydride-shift step were not reversible, what products would you expect then?

31-6 VITAMIN B₁₂ AS AN ORGANOMETALLIC COMPOUND

The structure of vitamin B₁₂ shown in Section 30-6B with a cyanide ion coordinated with cobalt is not the active form of the vitamin but is a particularly stable form, convenient to isolate and handle. The active form is a coenzyme that is remarkable in having a carbon-cobalt bond to an essentially alkyl-type carbon. The carbon-cobalt bond is to a 5'-deoxyadenosyl group, and if we abbreviate vitamin B₁₂ coordinated to cyanide as **23**, the coenzyme can be written, in the same style, as **24**. (You will notice that **23** is an abbreviation of the formula of Section 30-6B turned 180°.)



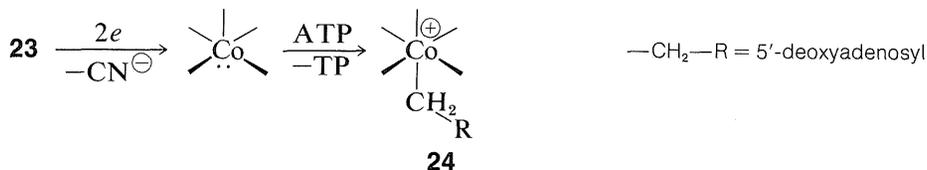
cyanocobalamin, **23**



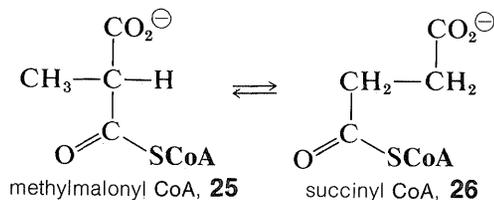
deoxyadenosylcobalamin, **24**

Both **23** and the B₁₂ coenzyme, **24**, are compounds of Co(III) and both substances have all electrons paired. B₁₂ can be reduced to a form with Co(II) which has an unpaired electron and gives an esr signal (Section 27-9). The cobalt-carbon bond of **24** appears to be formed from **23** by removal of the cyano group and a *two-electron* reduction to Co(I). The reduced cobalt is

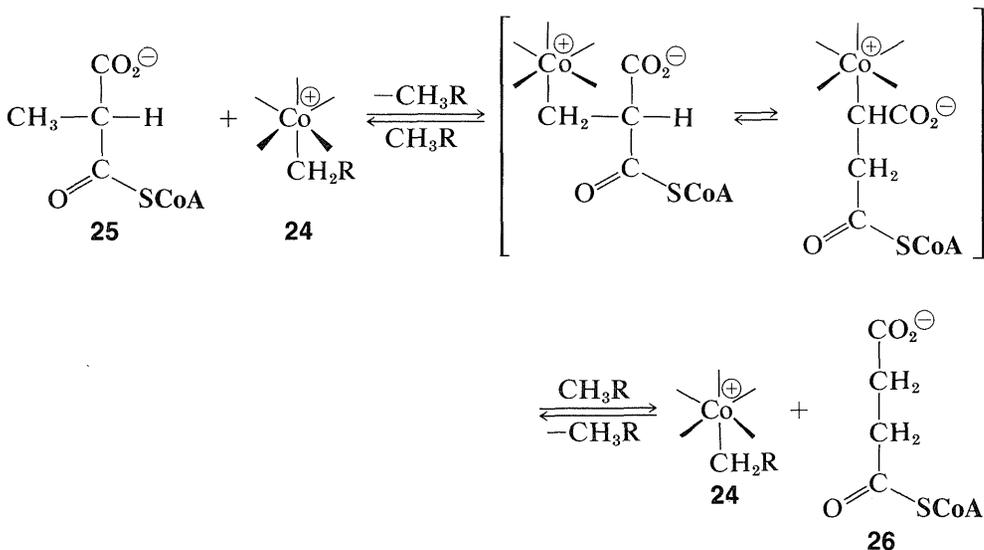
powerfully *nucleophilic* and probably is alkylated with adenosine triphosphate (ATP, Section 15-5F) to form **24**:



Vitamin B₁₂ coenzyme participates in several biological reactions but none is more unusual, or as hard to rationalize, as its role in the interconversion of methylpropanedioyl CoA (methylmalonyl CoA, **25**) to butanedioyl CoA (succinyl CoA, **26**):³



This rearrangement, which is important in the biochemical utilization of propanoic acid, has been shown to involve transfer of a hydrogen from the CH₃— group of **25** to the —CH₂R group of **24**. Then rearrangement and formation of **26** occurs along with reformation of **24**:



³For the structure of CoA, see Section 18-8F.

We formulate the intermediate oxidized forms of **25** and **26** with cobalt-to-carbon bonds, but there is no definitive evidence that this is correct. The overall reaction involves attack on the CH_3- of **25**, not an easy reaction to carry out in the laboratory, except with reagents such as Cl^- , because this CH_3 is not adjacent to a double bond or other activating group. Furthermore, there is no very good analogy for the rearrangement step. At present, although it is known that **24** is reduced to give CH_3-R , the details of this important biochemical mechanism remain to be elucidated by further research.

Additional Reading

F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed., Wiley-Interscience, New York, 1972, Chapter 23.

C. A. Tolman, "The 16 and 18 Electron Rule in Organometallic Chemistry and Homogeneous Catalysis," *Chem. Soc. Rev.* **1**, 337 (1972).

T. J. Katz and N. Acton, "Bis(pentalenylnickel)," *J. Amer. Chem. Soc.* **94**, 3281 (1972); J. Tsuji, "Carbon-Carbon Bond Formation via Palladium Complexes," *Accts. Chem. Res.* **2**, 144 (1969).

R. Cramer, "Transition-Metal Catalysis Exemplified by Some Rhodium-Promoted Reactions of Olefins," *Accts. Chem. Res.* **1**, 186 (1968).

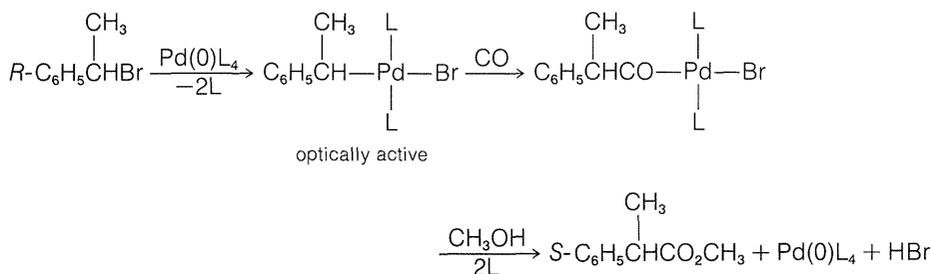
M. F. Semmelhack, "Formation of Carbon-Carbon Bonds via π -Allylnickel Compounds," *Organic Reactions* **19**, 115 (1972).

D. E. Bublitz and K. L. Rinehart, Jr., "The Synthesis of Substituted Ferrocenes and Other π -Cyclopentadienyl-Transition Metal Compounds," *Organic Reactions* **17**, 1 (1969).

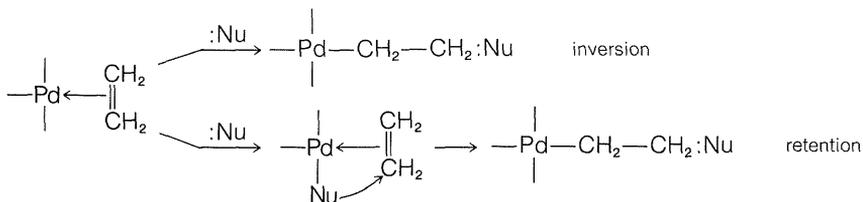
J. M. Swan and D. St. C. Black, *Organometallics in Organic Synthesis*, Chapman and Hall, London, 1974. This is an informative but concise account for the nonspecialist.

Supplementary Exercises

Exercise 31-13 Palladium has many interesting uses in organic syntheses. The following sequence of reactions also could be achieved by forming and carbonating a Grignard reagent, but would *not* be stereospecific as it is with palladium. Devise mechanistic steps for the reaction that account for the stereochemical result [L is $(\text{C}_6\text{H}_5)_3\text{P}$]. Review Sections 31-2, 31-3, and 31-4.



Exercise 31-14* a. When a metal is complexed with an alkene, there are two possible ways for nucleophiles to become attached to carbon, as illustrated here with palladium:

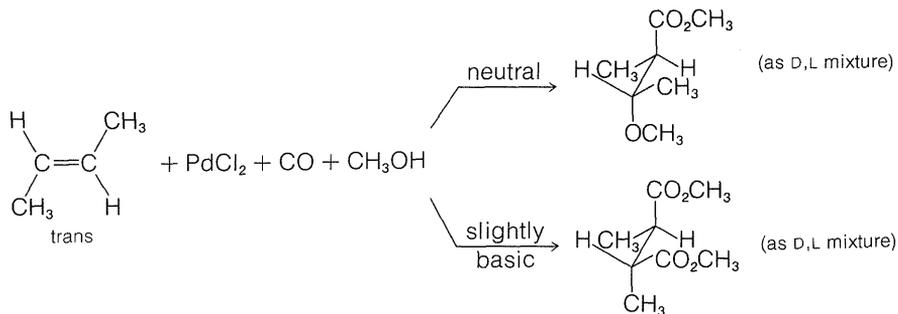


Show how these mechanisms in combination with others described in this chapter can explain how PdCl_2 can convert $\text{CH}_2=\text{CH}_2$ to CH_3CHO (Wacker process). Your mechanism must be in accord with the fact that, when the reaction is carried out in D_2O , there is *no* deuterium in the ethanal formed.



[This reaction is used for large-scale production by oxidizing the $\text{Pd}(0)$ back to $\text{Pd}(\text{II})$ with $\text{Cu}(\text{II})$. Thus $\text{Pd}(0) + 2\text{Cu}(\text{II}) \longrightarrow \text{Pd}(\text{II}) + 2\text{Cu}(\text{I})$, and then the $\text{Cu}(\text{I})$ is converted back to $\text{Cu}(\text{II})$ with O_2 . The overall result is $\text{CH}_2=\text{CH}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{CH}_3\text{CHO}$.]

b. The balance between the competitive nucleophilic reactions described in Part a is a delicate one as judged from the following results:



Write mechanistic steps that will account for the difference in stereochemical results of these reactions, noting that in one case there is a single carbonylation reaction and in the other a dicarbonylation reaction.