

1

Fundamental Reactions to Cleave Carbon–Carbon σ -Bonds with Transition Metal Complexes

Masahiro Murakami and Naoki Ishida

1.1

Introduction

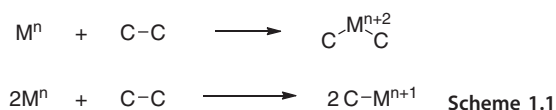
Transition metal-catalyzed reactions proceed through multiple elementary steps in general and, consequently, the mechanisms are often complicated, especially when backbone structures are reconstructed through a sequence of cleavage and formation of C–C bonds. A step-by-step understanding of elementary steps would be valuable to understand such catalytic transformations. This chapter focuses on elementary steps during which carbon–carbon σ -bonds are cleaved by means of organometallic complexes.

An elementary step to cleave C–C bonds is a reverse process of a C–C bond forming process. Oxidative addition of a C–C bond to a low-valent transition metal complex is a reverse process of reductive elimination, which occurs with a high-valent diorganometal, forming a C–C bond. β -Carbon elimination is a reverse process of insertion of an unsaturated bond into a carbon–metal bond, that is, carbometallation, or 1,2-addition of an organometal across a double bond. Such fundamental reactions are described along with typical examples. Besides this chapter, there are some excellent reviews on C–C bond cleavage available [1].

1.2

Oxidative Addition

Oxidative addition is insertion of a metal into a covalent bond. It involves formal two-electron oxidation of the metal center or one-electron oxidation of two metal centers (Scheme 1.1).



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Oxidative addition offers a direct method to cleave a covalent bond. Although a wide variety of bonds, such as C–I and C–Br, are known to readily undergo oxidative addition reactions to low-valent transition metal complexes, examples of oxidative addition of C–C single bonds are far more rare. The scarcity is in part associated with the thermodynamic stability of C–C bonds. Whereas oxidative addition of C–Br and C–I bonds to low-valent metals is thermodynamically favored in general, that of a C–C single bond is often thermodynamically disfavored.

The kinetic reason for the difficulty in breaking C–C single bonds is the constrained directionality of their σ -orbital. Figure 1.1 shows the interaction of a metal orbital with a C–C single bond. The interactions with C–C double bonds and C–H single bonds are also depicted for comparison. The π -orbital of a C–C double bond is oriented sideways, and thus it interacts with a metal orbital without significant strain and severe steric repulsion. The σ -orbital connecting hydrogen and carbon atoms lies along the bond axis and the directionality is less matched with the metal orbital. However, the constituent 1s orbital of the hydrogen atom is spherical, and can interact with a metal orbital from any direction without distortion. The hydrogen atom has no other substituents except the bonded carbon, thus sterically rendering the direct approach of the metal center less cumbersome. On the other hand, the σ -orbital of a C–C single bond possesses high directionality along the bond axis. Moreover, there are several substituents on both ends, which sterically prevent the approach of metal orbitals. Thus, interaction of such a C–C σ -orbital with a metal orbital is much more difficult than those of a C–C double bond and a C–H bond. Not only the thermodynamic stability, but also this kinetic barrier renders C–C σ -bonds considerably inert.

Despite the intrinsic difficulties mentioned above, a number of strategies have been devised to realize oxidative addition of C–C σ -bonds. For example, release of ring strain of a substrate molecule affords both kinetic and thermodynamic drive for oxidative addition. A chelating effect also assists both kinetically and

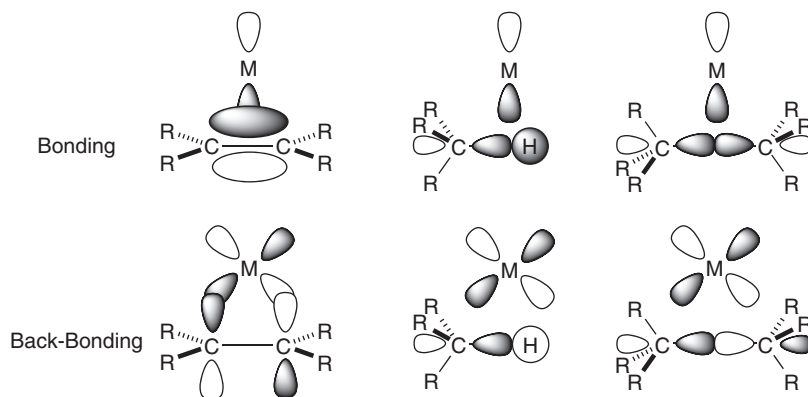


Figure 1.1 Orbital interactions of a metal with C=C, C–H, C–C bonds.

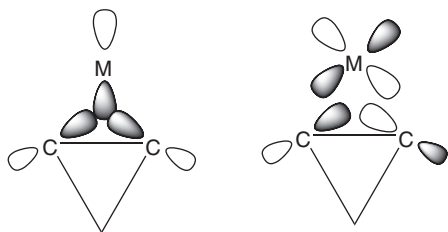


Figure 1.2 Orbital interactions of a metal with a C–C bond of cyclopropane.

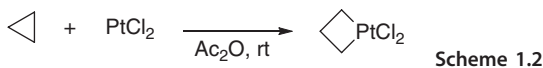
thermodynamically. Aromatization is also exploited as the driving force for oxidative addition of a C–C bond. Each case is exemplified in the following sections.

1.2.1

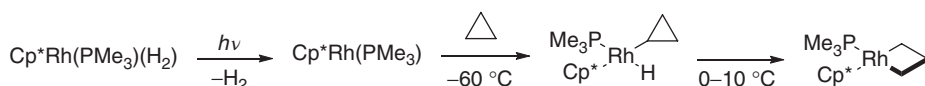
Oxidative Addition Utilizing Ring Strain

The orbitals of cyclopropane C–C bonds form “banana bonds”, which protrude away from the bond axis between the two carbon atoms (Figure 1.2). Consequently a metal center can interact with them similarly, to some extent, to the case of a metal–olefin interaction. This interaction lowers the kinetic barrier of the C–C oxidative addition. In addition, the enlargement of the three-membered cyclopropane ring to a four-membered metallacyclobutane relieves the structural strain owing to its constrained bond angles. Thus, the use of cyclopropanes as substrates for oxidative addition of C–C bonds is advantageous both kinetically and thermodynamically.

In fact, PtCl_2 reacted with cyclopropane to form platinacyclobutanes (Scheme 1.2) [2]. Cyclopropanes substituted with more electron-donating groups reacted faster and cyano and keto-substituted cyclopropanes remained intact [3].



It is often observed that C–H activation precedes C–C activation. For instance, photoirradiation of $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{H}_2)$ generated coordinatively unsaturated $\text{Cp}^*\text{Rh}(\text{PMe}_3)$ with liberation of dihydrogen (Scheme 1.3) [4]. The rhodium complex reacted with cyclopropane at -60°C to furnish a C–H oxidative addition product. No cleavage of a C–C bond was observed at this low temperature. Upon raising the temperature to 0 – 10°C , the cyclopropylrhodium rearranged to a rhodacyclobutane. This result indicates that oxidative addition of a C–H bond is kinetically favored and oxidative addition of a C–C bond is



Scheme 1.3

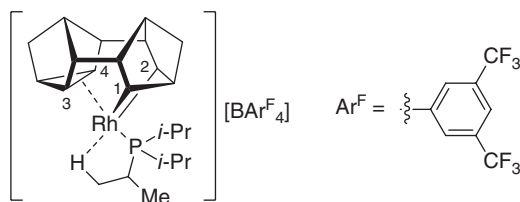
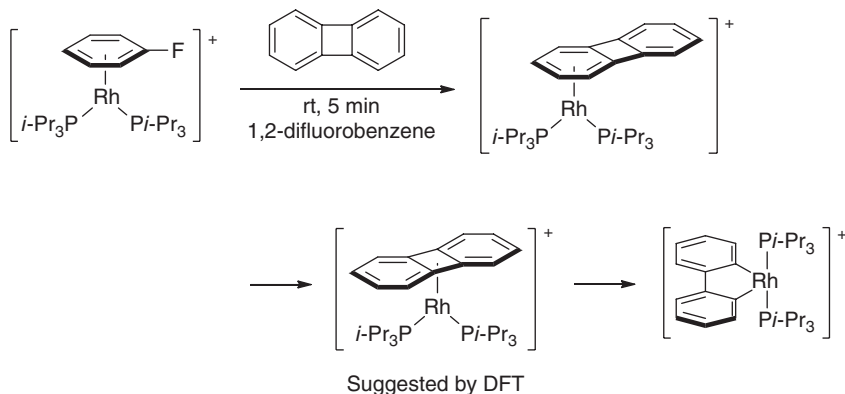


Figure 1.3 A rhodium complex with an agostic interaction with a C–C bond.

thermodynamically favored in this case. The kinetic preference for the oxidative addition of the C–H bond demonstrates the greater steric accessibility of the C–H bond compared with the C–C bond. The analogous rearrangement of a (cyclobutyl)(hydride)rhodium complex into rhodacyclopentane has also been reported [5].

Oxidative addition would proceed via coordination of the σ -bond to the metal (agostic interaction). A rhodium complex with an agostic interaction between a cyclopropane C–C σ -bond and a rhodium center has been reported (Figure 1.3) [6]. The bond lengths of Rh–C3 and Rh–C4 are 2.352 and 2.369 Å, longer than typical Rh–C single bonds, but within the sum of the van der Waals radii of Rh and C. The C3–C4 bond (1.6 Å) is longer than typical cyclopropane C–C bonds (about 1.5 Å), but again within the sum of the van der Waals radii of two carbons. The bonding between Rh and C3–C4 indicates that it might be the precursory structure for oxidative addition of cyclopropane C–C bonds.

Biphenylenes undergo oxidative addition to various low-valent metals to form the corresponding dibenzometalloles [7]. The reaction with $\text{Cp}^*\text{Rh}(\text{PMe}_3)$ involved C–H activation prior to C–C activation, as with the case of C–C activation of cyclopropane [7c]. On the other hand, the reaction with $[\text{Rh}(\text{Pi-Pr}_3)_2]^+$ initially formed the η^6 -arene complex, which led to the dibenzorhodacycle [7g]. Density functional theory (DFT) calculation suggested the C–C activation proceeds via the rhodium η^4 -cyclobutadiene intermediate (Scheme 1.4).



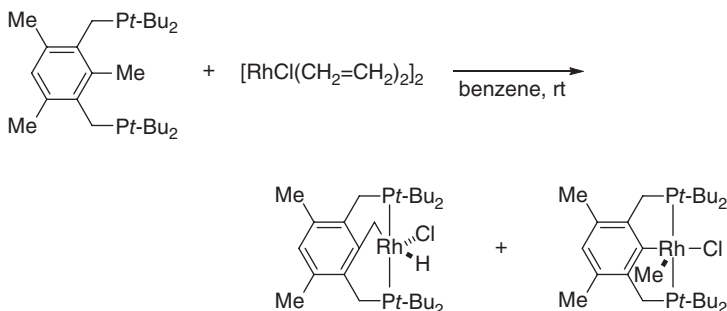
Scheme 1.4

A wide variety of strained C–C bonds, such as methylenecyclopropanes [8], vinylcyclopropanes [9], perfluorocyclopropenes [10], and cubane [11], also undergo oxidative addition. The oxidative addition of small ring molecules serves for initiation of their catalytic transformations (Chapters 2 and 3).

1.2.2

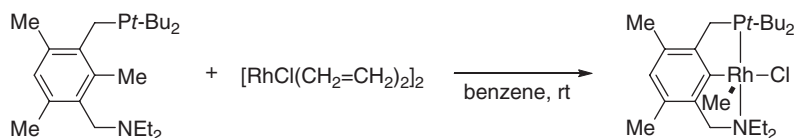
Chelation-Assisted Oxidative Addition

The Lewis basic functionalities, like phosphines, facilely coordinate to a metal, whereby the metal center is brought into proximity to a specific C–C bond. The coordination facilitates insertion of the metal into a C–C bond both kinetically and thermodynamically. For example, a system consisting of $[\text{RhCl}(\text{olefin})_2]_2$ and a bulky, pincer diphosphine ligand led to site-selective metal insertion into an aryl–methyl bond at room temperature (Scheme 1.5) [12]. Initially, the simultaneous formation of a C–H activated complex and a C–C activated complex was observed. The C–H activated complex was gradually converted to the C–C activated complex at room temperature, demonstrating that the C–C activated complex is thermodynamically more stable than the C–H activated product. Furthermore, a kinetic study revealed that, if the numbers of bonds available for activation are taken into account, metal insertion into the C–C bond is also kinetically preferred over the competing insertion into the C–H bond in this case. Electronic perturbation of the aromatic ring by introduction of a methoxy group had no significant influence on the reaction rate and the product ratio, suggesting that the C–C oxidative addition proceeds via a three-centered nonpolar transition state similar to that postulated for C–H bond activation.



Scheme 1.5

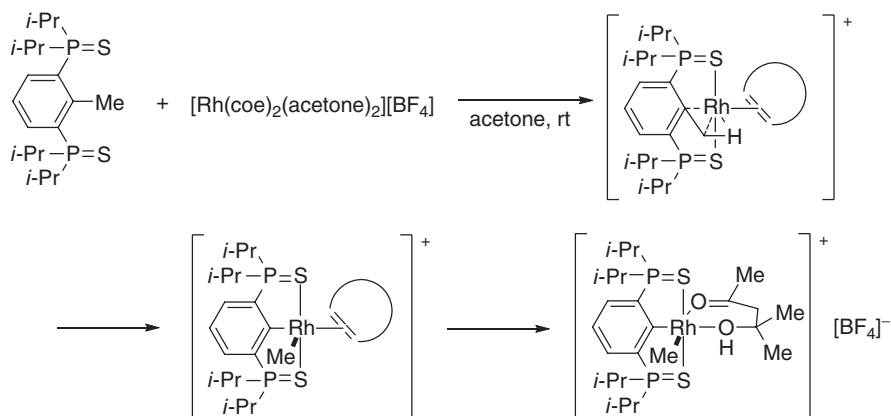
Other pincer systems also undergo oxidative addition of C–C bonds. A phosphine-amine pincer ligand reacted with a rhodium olefin complex more easily than diphosphine pincer ligands to give a C–C bond activated complex in minutes at room temperature (Scheme 1.6) [13]. In this case, the formation of a C–H activated complex was not observed upon monitoring the reaction, even at -50°C . It was proposed that the failure to observe the C–H activated product is attributed to the rapid, reversible dissociation of the amine ligand;



Scheme 1.6

the dissociation would lower the electron density on the rhodium center to significantly facilitate the C–H reductive elimination process.

The presence of a C–C–H η^3 -agostic interaction was proposed as the intermediate for oxidative addition of an SCS-pincer rhodium complex on the basis of the DFT calculation (Scheme 1.7) [14]. Both the C–C and C–H σ -bonds donate bonding electrons to the d orbital of rhodium (Figure 1.4). The olefin ligand located at the *trans*-position accepts electrons, which reinforces electron donation from C–C and C–H σ -bonds. The agostic complex is the intermediate leading to both C–C and C–H activations.



Scheme 1.7

1.2.3

Oxidative Addition Driven by Aromatization

Aromatization brings significant stabilization to molecules. Consequently, the formation of an aromatic molecule assists C–C bond cleavage thermodynamically. For example, an η^4 -(*endo*-ethylcyclopentadienyl)molybdenum

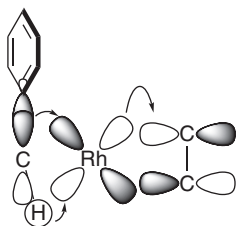


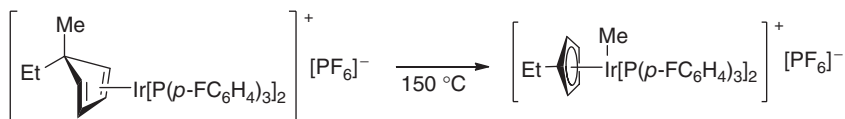
Figure 1.4 Schematic model of orbital interaction in a rhodium complex with a C–C–H η^3 -agostic interaction.

complex rearranged with oxidative addition of the Cp–Et bond to an η^5 -(cyclopentadienyl)(ethyl)molybdenum complex upon treatment with thallium tetrafluoroborate (Scheme 1.8) [15].



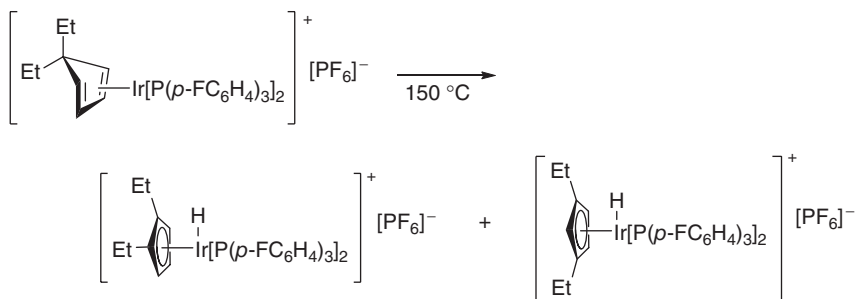
Scheme 1.8

Analogous oxidative addition reactions have been reported with nickel, iron, manganese, rhenium, and iridium complexes [16]. Crabtree *et al.* have reported the stereochemistry of the migration of the alkyl group on the Cp ring on iridium (Scheme 1.9) [16e]. When the *endo*-methyl complex was heated at 150°C , the methyl group selectively migrated onto the iridium. On the other hand, the corresponding *exo*-methyl derivative afforded a complex mixture.



Scheme 1.9

Heating of the 1,1-diethyl complex caused isomerization to form a mixture of 1,2- and 1,3-diethyl complex [16]. This isomerization reaction may indicate microscopic reversibility of the oxidative addition/reductive elimination of the C–C bond (Scheme 1.10).



Scheme 1.10

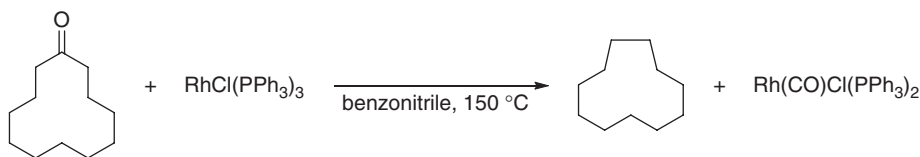
1.2.4

Oxidative Addition of Ketones

The carbonyl sp^2 carbon is trigonal planar so that it is sterically less hindered than tetrahedral sp^3 carbons. Additionally, the lone pair and π -electrons of the carbonyl

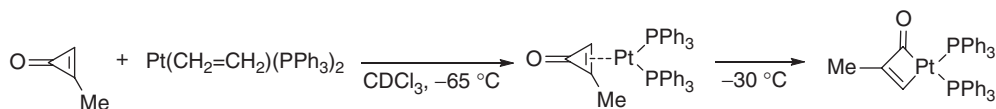
group can interact with the metal center to locate the metal in proximity to the C(carbonyl)–C bond. Therefore, oxidative addition of C(carbonyl)–C bonds is kinetically more favored than that of ordinary C–C bonds.

It is difficult to observe oxidative addition of C(carbonyl)–C bonds of ordinary ketones directly because of spontaneous carbonyl extrusion to form a metal carbonyl complex with elimination of a decarbonylated organic fragment. An early example of the oxidative addition is seen in a reaction of rhodium(III) chloride with triphenylphosphine in refluxing cyclohexanone, producing $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ [17]. Although other products derived from cyclohexanone are not identified, the carbonyl ligand of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ would originate from cyclohexanone via cleavage of the C(carbonyl)–C bond. A more explicit example is a decarbonylation reaction of cyclododecanone by Wilkinson complex, which afforded cycloundecane and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (Scheme 1.11) [18]. Decarbonylation of benzophenones and calcone took place upon treatment with a cyclopentadienylrhodium(I) complex [19].



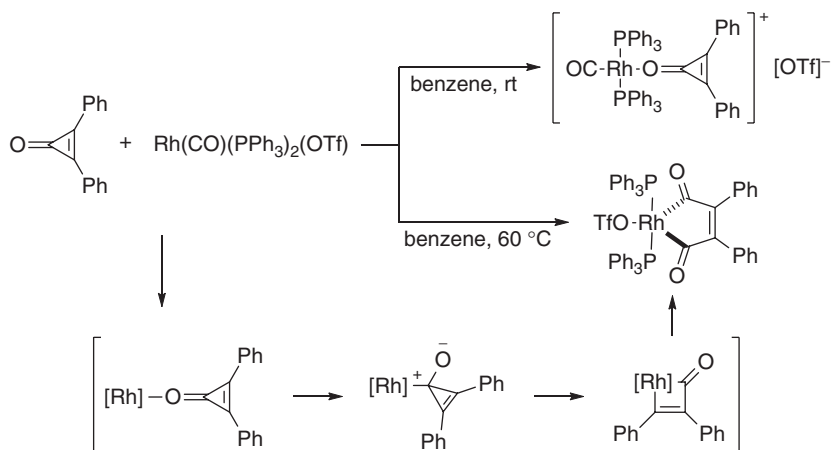
Scheme 1.11

Oxidative addition of a C(carbonyl)–C bond has been observed directly with highly strained unsaturated ketones. When a platinum(0) ethylene complex was treated with a cyclopropenone, the ethylene ligand was replaced with the olefin moiety of the cyclopropenone to produce a platinum η^2 -cyclopropenone complex. The platinum center then inserted site-selectively into the sterically less-crowded C(carbonyl)–C bond of the cyclopropenone to form a platinacyclobutenone (Scheme 1.12) [20].



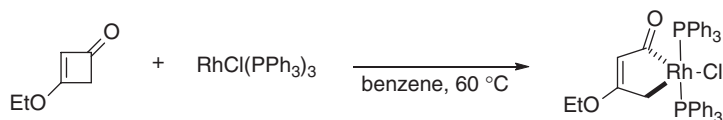
Scheme 1.12

Treatment of a cyclopropenone with a rhodium(I) complex initially generated the corresponding O-bound complex (Scheme 1.13) [21]. Heating of the O-bound complex at 60–65 °C led to the formation of the rhodacyclopentenenediones. It was proposed that the oxidative addition takes place via nucleophilic attack of the rhodium center on the carbonyl group and subsequent 1,2-migration of the C(sp²) atom from carbon to rhodium. Subsequent insertion of a carbon monoxide ligand into the C–Rh bond furnishes the rhodacyclopentenenedione.



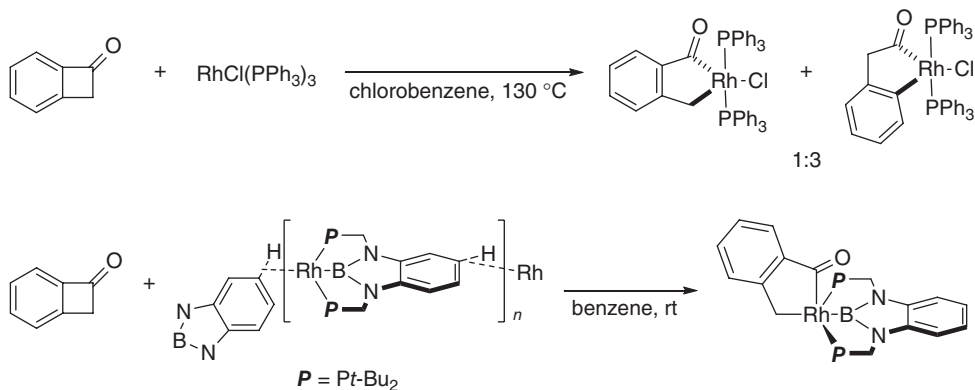
Scheme 1.13

Cyclobutenones undergo oxidative addition to rhodium(I) and cobalt(I) (Scheme 1.14) [22]. The metals inserted site-selectively into the C(carbonyl)–C(sp³) bond to form the corresponding metallacyclopentenones.



Scheme 1.14

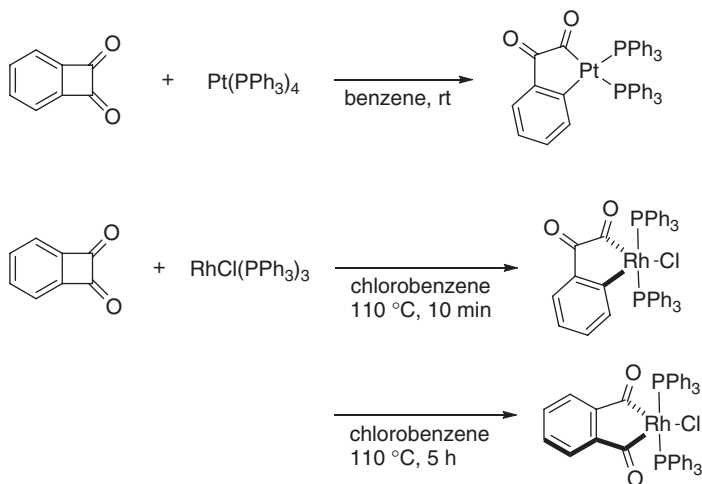
A reaction of benzocyclobutenone with Wilkinson complex took place at 130 °C to afford a regioisomeric mixture of oxidative addition products (Scheme 1.15) [22]. On the other hand, a reaction with an electron-rich rhodium(I) complex



Scheme 1.15

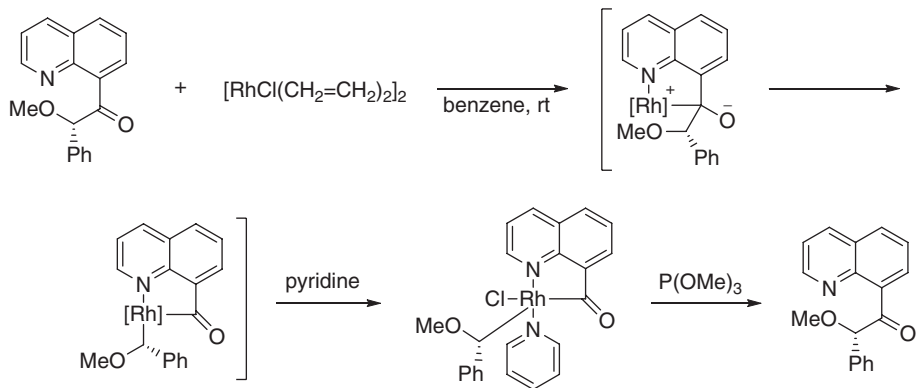
equipped with a PBP-pincer ligand proceeded, even at room temperature, to give a 2-rhodaindan-1-one exclusively [23].

Cyclobuten-1,2-diones underwent oxidative addition to various low-valent metals such as $\text{Pt}(\text{PPh}_3)_4$ and $\text{RhCl}(\text{PPh}_3)_3$ with site-selective cleavage of the C(arene)–C(carbonyl) bond (Scheme 1.16) [24]. The rhodium complex subsequently underwent rearrangement to furnish the phthaloylmethyl metal complexes.



Scheme 1.16

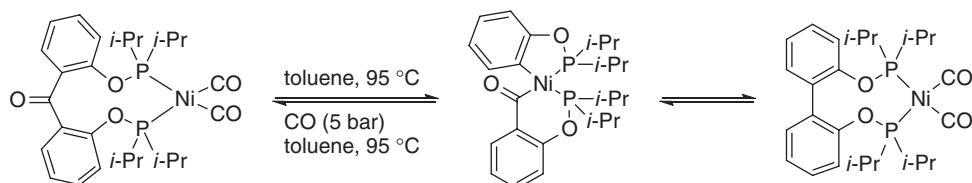
Chelation facilitates oxidative addition of unstrained C(carbonyl)–C bonds. For example, 8-quinolyl alkyl ketones underwent oxidative addition to rhodium(I) (Scheme 1.17) [25]. Addition of phosphorus ligands to the rhodacycle induced reductive elimination [26]. The stereochemistry of the α -carbon was retained during the oxidative addition/reductive elimination [27]. It was proposed that a tetrahedral intermediate arises by nucleophilic attack of rhodium on the carbonyl



Scheme 1.17

carbon en route to C–C bond cleavage without the intervention of a C–H activation process. This direct pathway contrasts with the sequential oxidative addition of C–H and C–C bonds observed with cyclopropanes [4] and biphenylenes [7].

Phosphorus also functions as a chelating group. The carbonyl group of a phosphine-tethered benzophenone/nickel complex was extruded upon heating to give a biaryl (Scheme 1.18) [28]. The extrusion/insertion of CO was reversible, indicating that the aryl–aryl bond also adds to nickel(0) facily. The related oxidative addition reaction to iridium(I) and rhodium(I) was also reported [29].



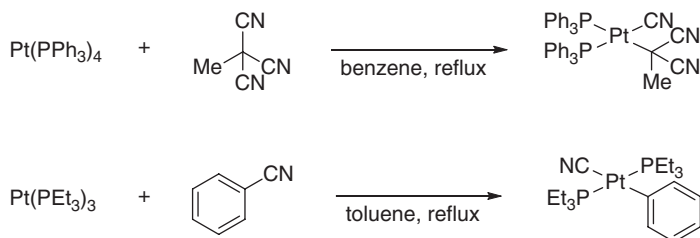
Scheme 1.18

Oxidative addition of C–C(carbonyl) bonds has been applied to various catalytic reactions, which are described in Chapter 6.

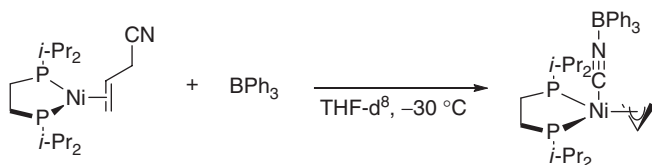
1.2.5

Oxidative Addition of Nitriles

A C–N triple bond coordinates to metals in either an endo-on or a side-on mode, which kinetically facilitates the access of the metal center to the C–CN bond. Furthermore, the metal cyanide bond is generally thermodynamically stable. Consequently, various C–CN bonds underwent oxidative addition, particularly to zerovalent Group 10 metals (Scheme 1.19) [30]. The oxidative addition reaction was facilitated by addition of Lewis acids (Scheme 1.20).

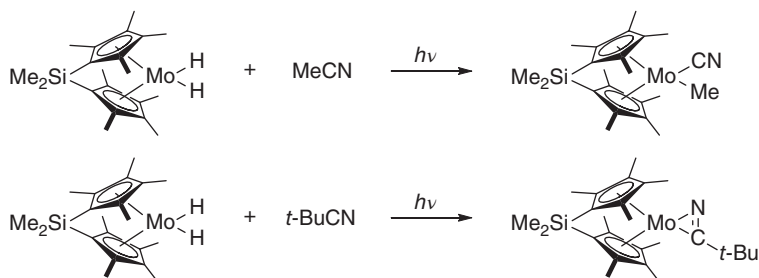


Scheme 1.19



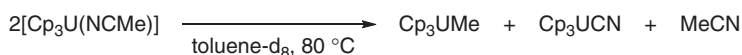
Scheme 1.20

In addition to zerovalent Group 10 metals, ansa-molybdenocene dihydride reacted with nitriles upon liberation of dihydrogen by photoirradiation (Scheme 1.21) [31]. Acetonitrile underwent oxidative addition of the C–CN bond to the molybdenum center. On the other hand, when the complex was treated with bulkier pivalonitrile, the side-on coordination complex was formed.



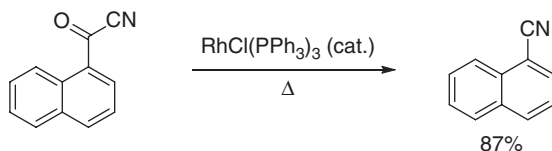
Scheme 1.21

Oxidative addition with formal one-electron oxidation of the metal center has been observed with a uranium complex (Scheme 1.22) [32]. Heating of an end-on acetonitrile complex of Cp^3U afforded a mixture of the methyl and the cyanide complexes with liberation of one molecule of acetonitrile.

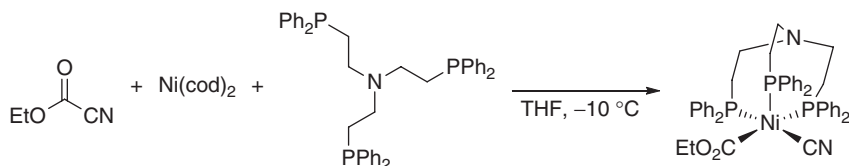


Scheme 1.22

The C(carbonyl)–CN bonds also undergo oxidative addition to late-transition metals like nickel(0), rhodium(I), and palladium(0) [33]. For example, aroyl cyanides underwent decarbonylation in the presence of a rhodium(I) catalyst, probably through oxidative addition, deinsertion of CO and reductive elimination (Scheme 1.23) [33a]. The oxidative addition of a C(carbonyl)–CN bond was directly observed in the reaction of a cyanofornate with a nickel(0) complex (Scheme 1.24) [33c].



Scheme 1.23

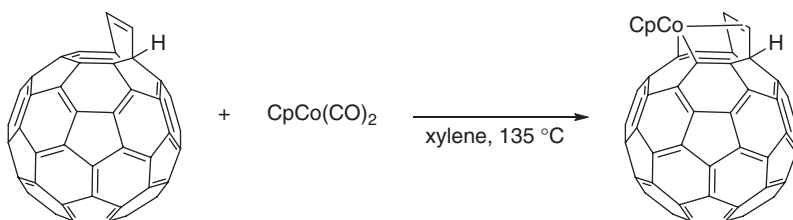


Scheme 1.24

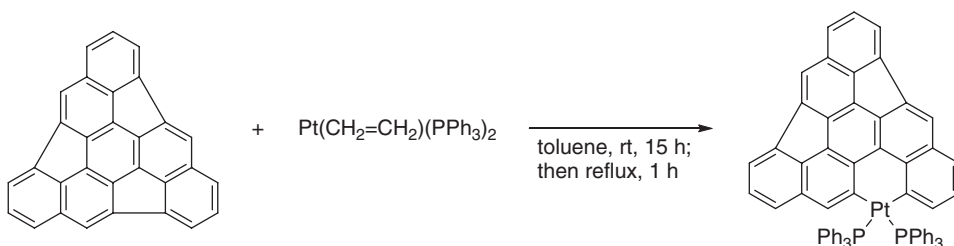
1.2.6

Others

Curved polyaromatic hydrocarbons undergo oxidative addition. A strained five-membered ring of a C₆₀-derived molecule reacted with a CpCo fragment (Scheme 1.25) [34]. Analogously, a bowl-shaped fullerene subunit reacted with a platinum(0) complex (Scheme 1.26) [35].

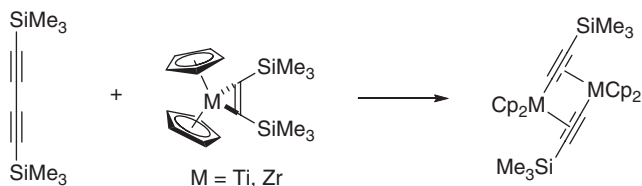


Scheme 1.25



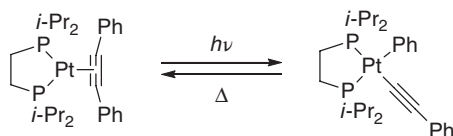
Scheme 1.26

Cleavage of a C(sp)–C(sp) single bond by low-valent titanocene and zirconocene has been reported [36]. Treatment of a diyne with those metallocenes in tetrahydrofuran (THF) produced the dimer of the alkynylmetallocene complex, in which the alkyne moiety was bonded to the metal center in both σ - and π -fashions (Scheme 1.27).



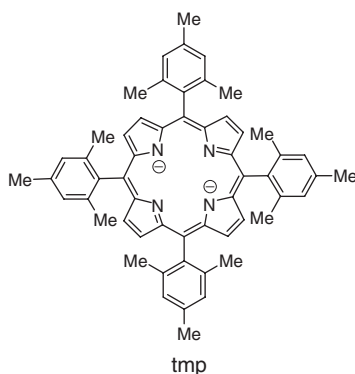
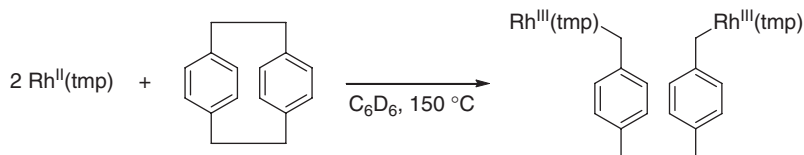
Scheme 1.27

A C(sp)–C(sp²) single bond of arylalkynes was cleaved by photoirradiation of a platinum–alkyne complex (Scheme 1.28) [37]. The oxidative addition product was reverted to the starting η^2 -alkyne complex upon heating. This result indicates the photochemical oxidative addition is an endergonic process.



Scheme 1.28

Oxidative addition of a C(sp³)–C(sp³) bond to two metals with one-electron oxidation was also reported (Scheme 1.29) [38]. A Rh(II)-porphyrin complex reacts with [2.2]-paracyclophane to give a bisalkylrhodium(III) species.

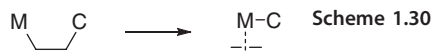


Scheme 1.29

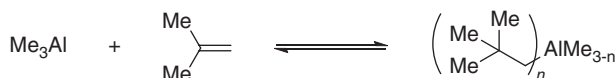
1.3

β -Carbon Elimination

β -Carbon elimination is a process eliminating a carbon atom connected to the β -position of a metal. The bond between β - and γ -carbons is cleaved to result in an organometallic species along with unsaturated bonds (Scheme 1.30). It is a reverse process of insertion of unsaturated bonds into a carbon–metal bond, that is, carbometallation.



The reversibility of carbometallation/ β -carbon elimination was first demonstrated by a reaction of methylaluminum with isobutylene, which is in equilibrium with neopentylaluminum (Scheme 1.31) [39].



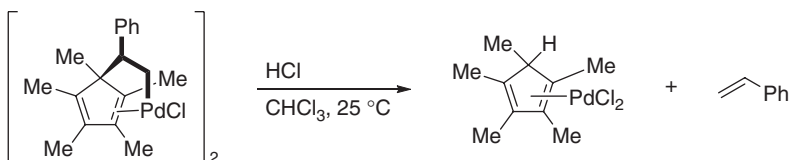
Scheme 1.31

Since then, various β -carbon elimination reactions have been reported. This section describes important examples of β -carbon elimination reactions.

1.3.1

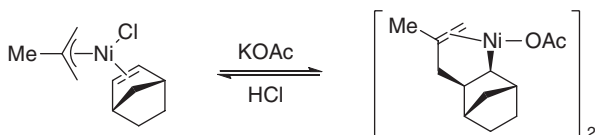
β -Carbon Elimination of Late Transition Metal Alkyls

Acid treatment of an alkylpalladium complex having a cyclopentadiene moiety gives an early example of β -carbon elimination of late transition metal alkyls (Scheme 1.32) [40]. A palladium–cyclopentadiene complex was generated together with elimination of styrene.



Scheme 1.32

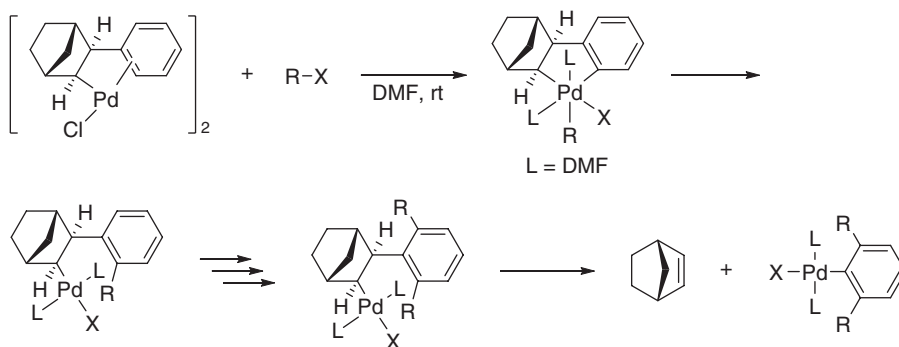
Insertion of norbornene into a C–M bond is often reversible. For example, a π -allylnickel norbornene complex was in equilibrium with inserted alkyl-nickel species (Scheme 1.33) [41]. Whereas the chloride complex favored the π -allylnickel form, the acetate complex favored the inserted alkyl-nickel species.



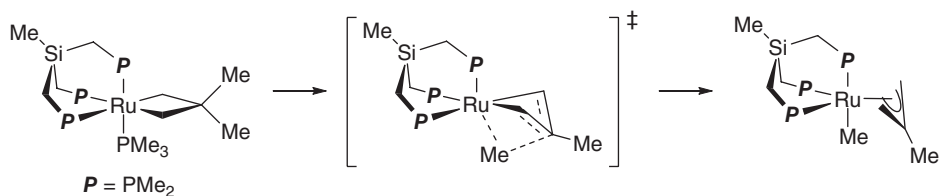
Scheme 1.33

A palladacycle reacted with alkyl halides to afford a sterically bulky arylpalladium complex with liberation of norbornene (Scheme 1.34) [42]. β -Aryl elimination from the norbornylpalladium intermediate would be responsible for the formation of these products.

A ruthenacyclobutane complex underwent β -carbon elimination to form a π -allyl(methyl)ruthenium complex (Scheme 1.35) [43]. Kinetic studies revealed that



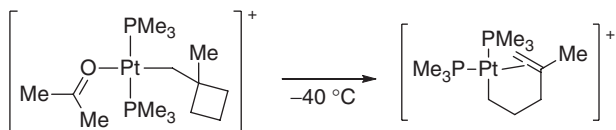
Scheme 1.34



Scheme 1.35

the entropy of activation was negative, indicating the more ordered unimolecular transition state.

Relief of ring strain facilitates β -carbon elimination both thermodynamically and kinetically, as is the case with oxidative addition. Thus, a cyclobutylmethylplatinum complex underwent β -carbon elimination, even at -40°C , to furnish a ring-opened product (Scheme 1.36) [44].



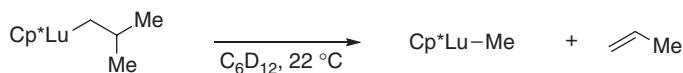
Scheme 1.36

β -Carbon elimination of late transition metal alkyls is involved in various multi-step catalytic reactions. See the following chapters for more examples.

1.3.2

β -Carbon Elimination from Early Transition Metal Alkyls

β -Carbon elimination from early transition metal alkyls has been extensively studied since it is related to chain termination of olefin polymerization. An early example is thermal decomposition of an isobutyltitanium complex, which formed a methyltitanium complex along with various byproducts (Scheme 1.37)



Scheme 1.37

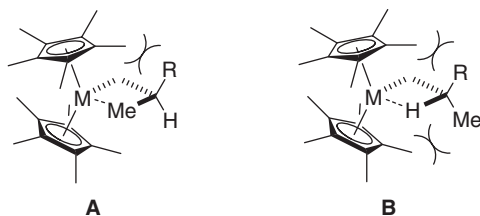


Figure 1.5 Conformations of alkylmetallocenes.

[45]. A concerted four-center transition state was proposed based on the fact that the reverse reaction (addition reaction of $\text{Lu}-\text{C}$ to olefins) was a concerted process.

Similar reactivity has been observed with a bridged scandocene [46], cationic zirconocene and hafnocene [47], and a samarocene [48]. Interestingly, β -methyl elimination occurs even in the presence of a β -hydrogen. The reason was considered from the viewpoint of sterics [49]. The orientation **A**, in which the β -Me substituent is located in proximity to the Cp^*M wedge, is more favorable than the orientation **B** due to steric interactions (Figure 1.5). In addition, the presence of hyperconjugation between the highly electrophilic d^0 metal center and the methyl group electronically facilitates the β -methyl elimination [50].

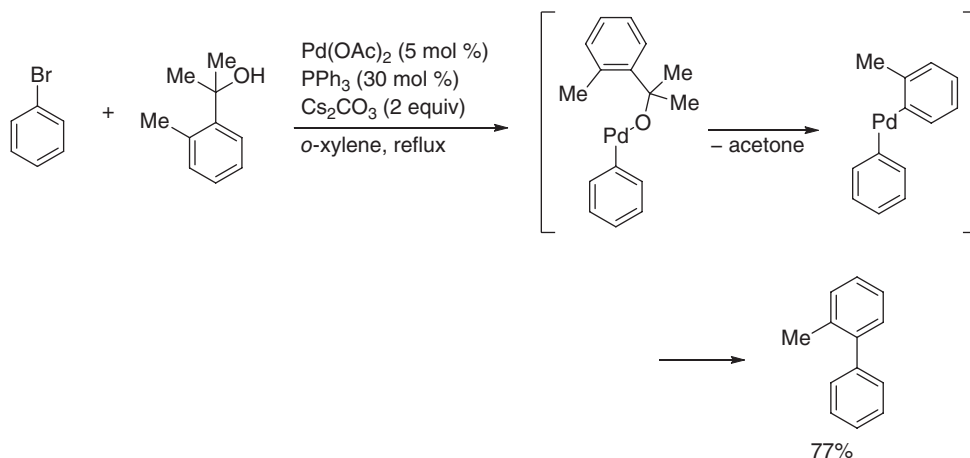
β -Carbon elimination of early transition metals has been applied to ring opening polymerization of methylenecyclopropanes [51] and methylenecyclobutenes [52]. Cyclopolymerization of 2-methyl-1,5-hexadienes [53] and isomerization of 1,4-dienes [54] also involve β -carbon elimination.

1.3.3

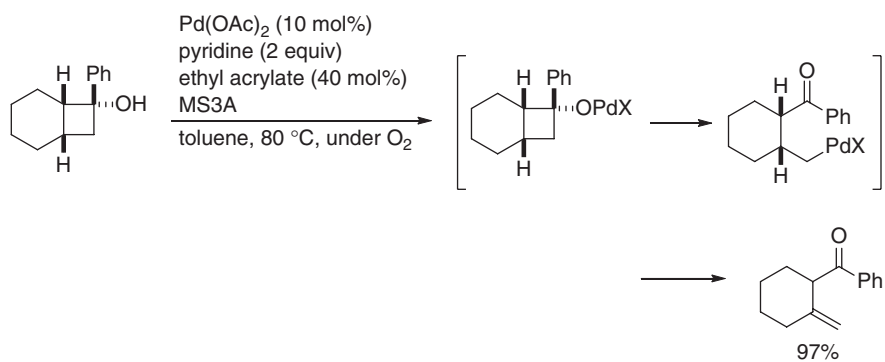
β -Carbon Elimination of Late Transition Metal Alcoholates

β -Carbon elimination of late transition metal alcoholates has been studied mainly in the context of catalytic transformations [55]. For example, tertiary benzyl alcohols reacted with aryl bromides in the presence of a palladium catalyst to give biaryls and ketones (Scheme 1.38) [56]. The formation of biaryl was explained by the mechanism involving β -carbon elimination of the putative palladium alkoxide intermediate. Tertiary cyclobutanols underwent ring opening more facily owing to relief of the ring strain of the four-membered ring (Schemes 1.39 and 1.40) [57, 58]. This ring opening process was further extended to multi-step transformations (Chapters 2–4).

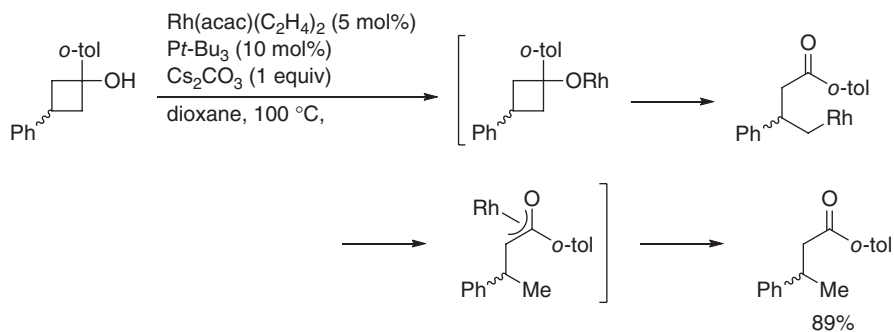
An explicit example of β -carbon elimination was observed with a rhodium alcoholate complex [59]. When a rhodium triphenylmethanolate was heated at $50\text{ }^\circ\text{C}$



Scheme 1.38

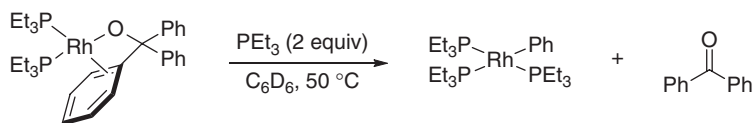


Scheme 1.39



Scheme 1.40

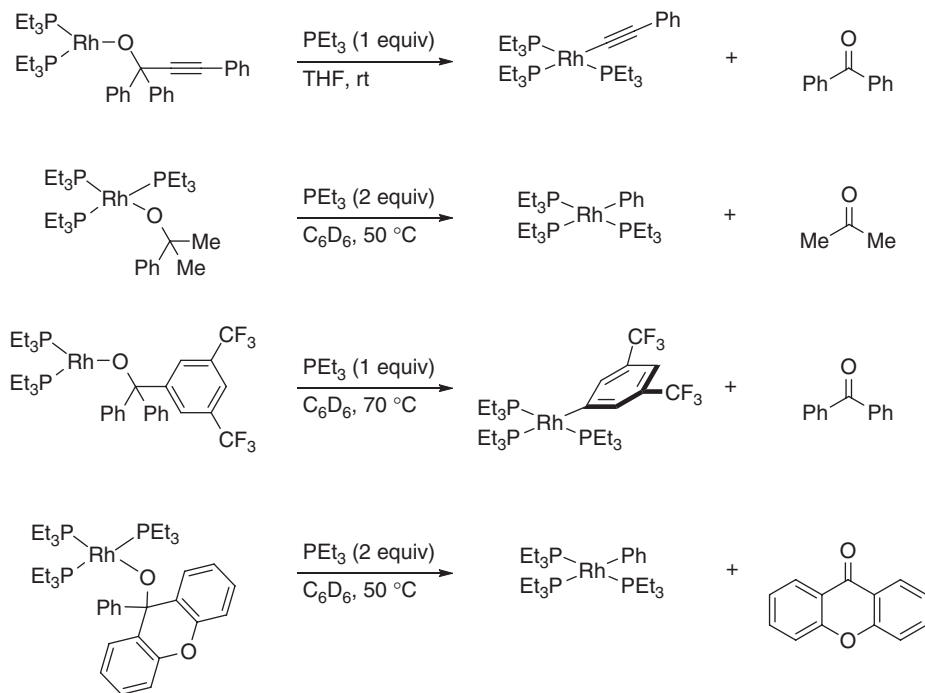
in the presence of PEt_3 , a phenylrhodium species was generated together with benzophenone (Scheme 1.41).



Scheme 1.41

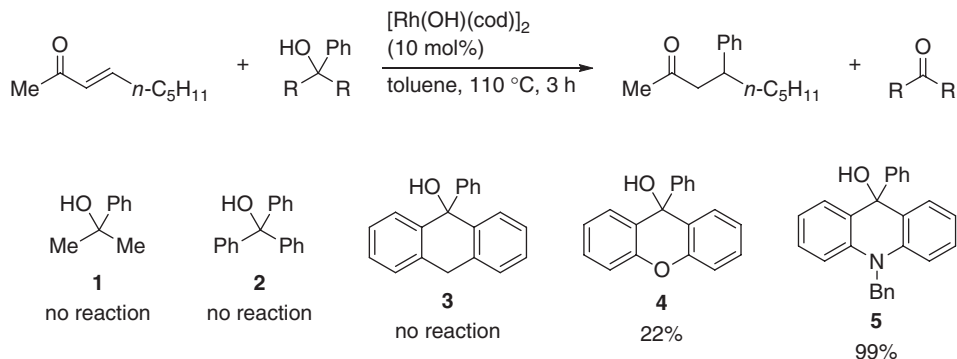
The crystal structure of the rhodium triphenylmethanolate delineated the pathway of β -carbon elimination. The rhodium complex possessed a pseudo-square planar geometry with two cis-oriented phosphine ligands. One phenyl group bound to rhodium in an η^2 -fashion. Among the three $\text{C}(\text{phenyl})\text{--C}(\text{sp}^3)$ bonds, the one of the phenyl group bound to rhodium was longer (1.552 \AA) than the others ($1.528\text{--}1.530\text{ \AA}$). This structural feature suggests the potential intermediacy of the π -complex in the β -carbon elimination pathway.

The migratory aptitude in β -carbon elimination was examined by competitive experiments (Scheme 1.42) [59b]. The tendency was in the order of alkynyl $>$ aryl \gg alkyl. Among the aryl groups, one having an electron-deficient substituent migrated preferentially. In the case of cyclic alcohols, the isolated phenyl group exclusively migrated.



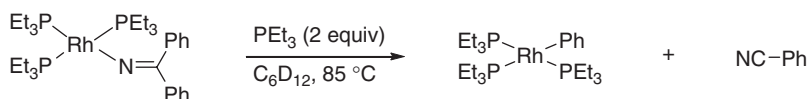
Scheme 1.42

The α -substituents on the tertiary alcohol also affect the reaction rate (Scheme 1.43). Whereas alcohols **1–3** were unreactive in the rhodium-catalyzed phenyl transfer reaction to enones, acridone-derived **5** reacted almost quantitatively under the otherwise same reaction conditions [60].



Scheme 1.43

Related to the β -carbon elimination of late transition metal alcoholates, β -carbon elimination from rhodium iminyl complexes has also been reported (Scheme 1.44) [61]. Aryl nitriles were eliminated to form arylrhodium species.

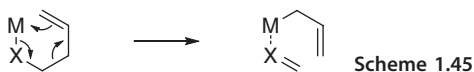


Scheme 1.44

1.4

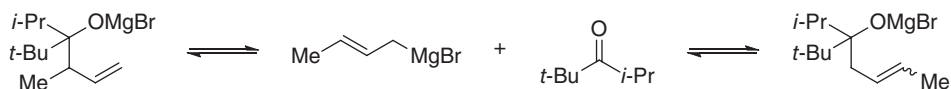
Retroallylation

Reactions of some allylmetals with carbonyl compounds are reversible. The reverse process is called “*retroallylation*.” The bond between β - and γ -carbons is cleaved in conjunction with the formation of a carbon–metal bond at the vinyl terminus through a six-membered transition state (Scheme 1.45). The retroallylation reaction can be considered as a variant of β -carbon elimination, but it proceeds more facilely, in general, owing to the six-membered transition state, which is typically less-strained than the four-membered transition state.



Scheme 1.45

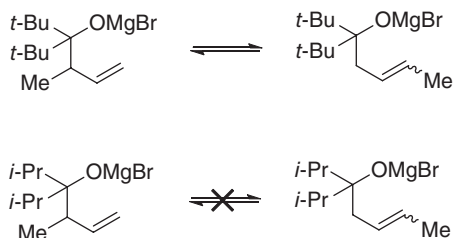
The reversibility of carbonyl allylation reactions was initially discovered in the reaction of crotylmagnesium bromide with *tert*-butyl isopropyl ketone



Scheme 1.46

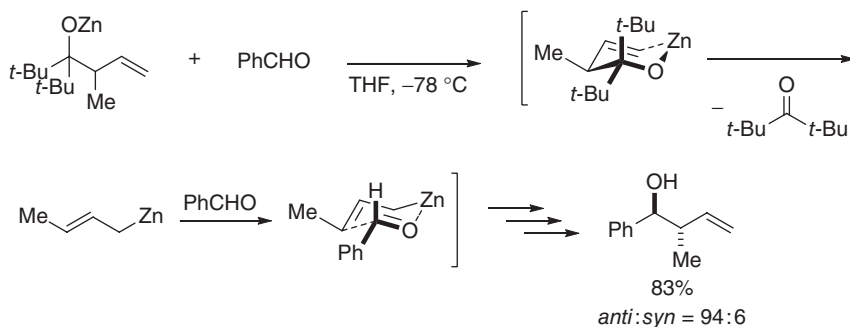
(Scheme 1.46) [62]. The resulting alcoholate gradually isomerized to the sterically less congested one via a retroallylation/allylation process.

The steric congestion around the cleaved C–C bond facilitates the retroallylation process. For example, whereas α -methylallyldi-*tert*-butylcarboxymagnesium bromide underwent facile isomerization, α -methylallyldiisopropylcarboxymagnesium bromide remained unchanged under the identical reaction conditions (Scheme 1.47).



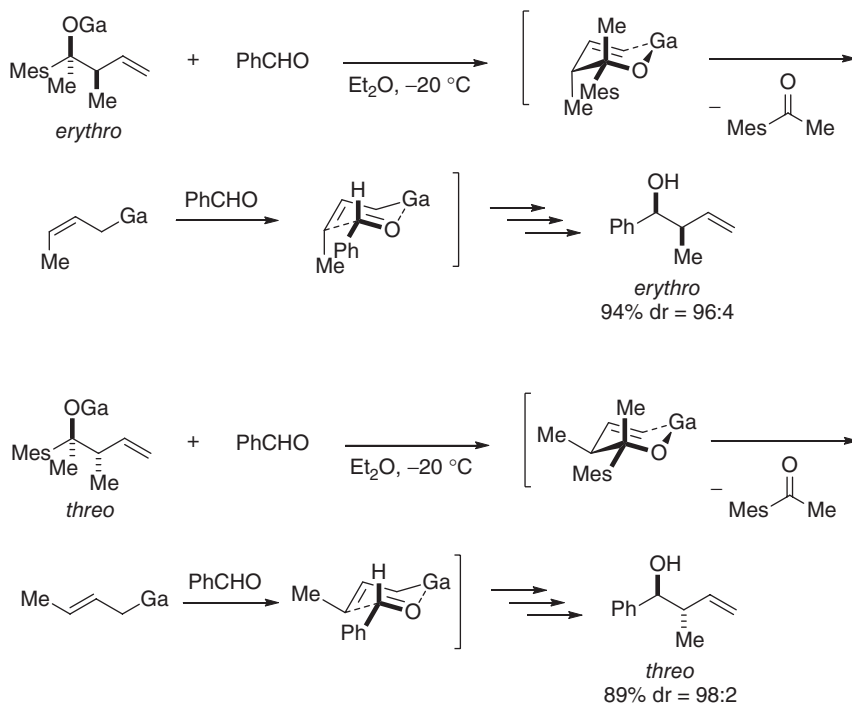
Scheme 1.47

Various metal homoallyl alcoholates undergo retroallylation [63]. For instance, a zinc homoallyl alcoholate stereoselectively reacted with benzaldehyde through retroallylation to afford an *anti*-homoallyl alcohol as the major product (Scheme 1.48) [63c]. It is assumed that the retroallylation reaction proceeds through a six-membered chair-like transition state, in which the methyl substituent takes the equatorial position to avoid 1,3-diaxial repulsion. The resulting (*E*)-crotylzinc species adds to benzaldehyde again through a six-membered chair-like transition state, in which both the phenyl group and the methyl group take the equatorial position.



Scheme 1.48

A gallium-mediated allyl transfer reaction proceeds in a stereospecific manner (Scheme 1.49) [63g]. An *erythro-tert*-homoallyl alcoholate reacted with benzaldehyde to afford an *erythro-sec*-homoallyl alcohol. On the other hand, the reaction of a *threo-tert*-homoallyl alcoholate provided a *threo-sec*-homoallyl alcohol. A six-membered transition state with the bulky mesityl substituent at the equatorial position was assumed for the stereospecificity.



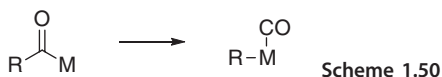
Scheme 1.49

In addition to stoichiometric reactions, transition metals catalyze retroallylation reactions of homoallyl alcohols [64]. Homopropargyl [65], allenylmethyl [64f], and allenylethyl ones [66] also undergo analogous C–C cleavage. See Chapter 5 for catalytic reactions.

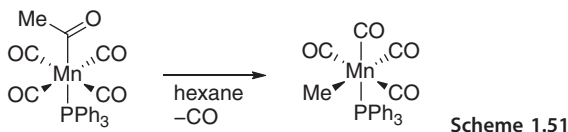
1.5

Migratory Deinsertion of a Carbonyl Group

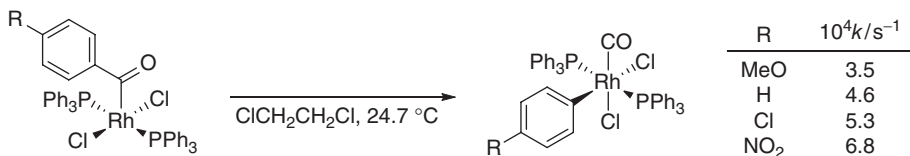
Migratory insertion of a carbonyl group into a carbon–metal bond is a well-established carbon–carbon bond forming reaction, which is found in various catalytic reactions such as hydroformylation. Migratory deinsertion of a carbonyl group is a reverse process of the carbonyl migratory insertion; an acylmetal species generates an alkylmetal carbonyl complex with cleavage of the R–CO bond (Scheme 1.50).



An explicit example was observed with a manganese carbonyl complex [67]. The octahedral *trans*-acetylmanganese complex underwent migratory deinsertion of the carbonyl group to afford the *cis*-methylmanganese complex (Scheme 1.51). The alkyl group migrates onto the metal center and the carbonyl group stays at the original position on the metal.

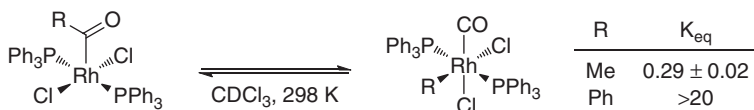


The influence of the electronics on the rate of the migratory deinsertion was measured with para-substituted benzoylrhodium(III) complexes (Scheme 1.52) [68]. An electron-deficient aryl group migrated faster than an electron-rich one. The rate of the migratory deinsertion was also affected by the spectator ligand; migratory deinsertion of the chloride complex was faster than that of the bromide complex.



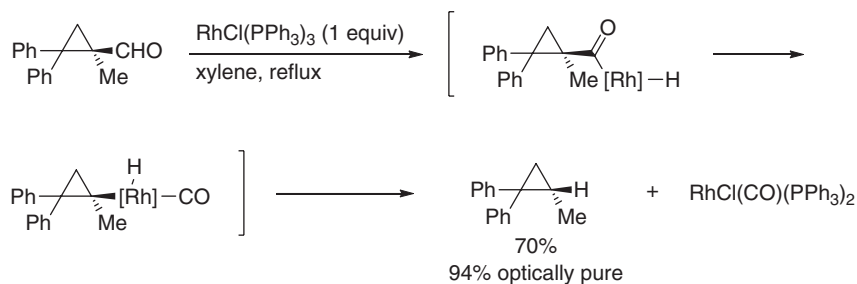
Scheme 1.52

The equilibrium constants vary with the structures of the organorhodium(III) complexes (Scheme 1.53) [69]. Whereas the acetyl complex favors the acyl form, the benzoyl complex favors the carbonyl form. This result can be ascribed to the strength of the resulting carbon–rhodium bond; the phenyl–rhodium bond is stronger than the methyl–rhodium bond.



Scheme 1.53

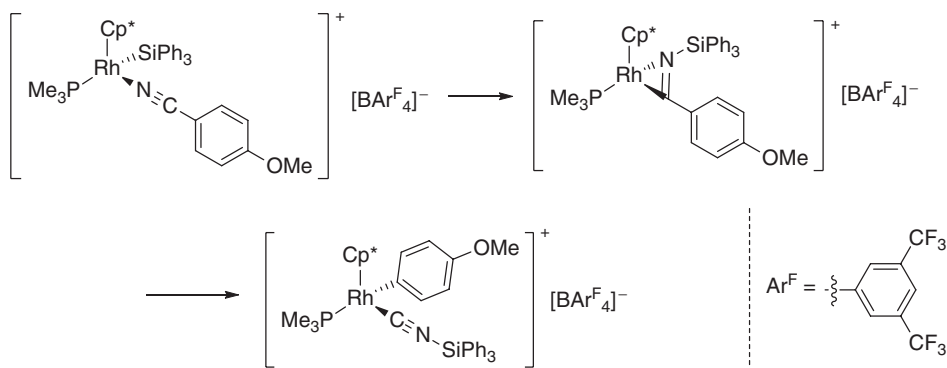
The migratory deinsertion process is important in the context of the transition metal-catalyzed or -mediated extrusion of the carbonyl group from aldehydes, ketones, and acid derivatives [70]. For example, treatment of aldehydes with a rhodium complex induced decarbonylation through oxidative addition of the



Scheme 1.54

aldehydic C–H bond, followed by migratory deinsertion of CO and reductive elimination (Scheme 1.54) [71]. It proceeded with retention of the stereochemistry of the migrating alkyl group. See Section 7.2 for related reactions and Section 8.12 for the application to total synthesis of natural products.

An analogous mode of reaction is observed in the C–CN cleavage of benzonitriles with silylmethyl complexes [72]. For example, a silylrhodium complex initially forms an η^2 -iminoacylrhodium complex (Scheme 1.55). The aryl group of the iminoacyl moiety migrates onto rhodium to form a rhodium isocyanide complex.



Scheme 1.55

This activation process is also extended to various catalytic substitution reactions of nitriles (Chapter 6).

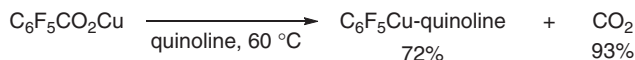
1.6

Decarboxylation

Decarboxylation is a process that releases CO_2 . Metal carboxylates undergo decarboxylation through cleavage of the C–CO bond to generate new organometallic species (Scheme 1.56).



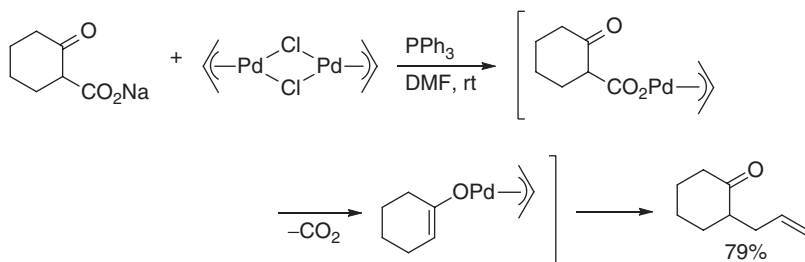
It has long been known that aromatic acids undergo decarboxylation to produce arenes when rigorously heated in the presence of copper and quinoline [73]. This reaction would involve decarboxylation of a copper carboxylate intermediate. A more explicit example has been reported with copper(I) pentafluorobenzoate (Scheme 1.57) [74]. When copper(I) pentafluorobenzoate was heated at 60 °C in quinoline, pentafluorophenylcopper was produced with liberation of CO₂.



Scheme 1.57

Alkynyl acids also underwent analogous decarboxylation facily [75]. These decarboxylation processes have been extended to catalytic decarboxylative transformations (Chapter 4).

A sodium β-ketocarboxylate does not undergo spontaneous decarboxylation at room temperature. On the other hand, it reacted with π-allylpalladium chloride to form a π-allylpalladium carboxylate, which underwent facile decarboxylation to produce an α-allylated ketone (Scheme 1.58) [76].



Scheme 1.58

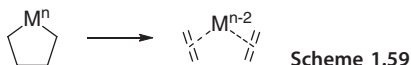
The decarboxylation reaction of β-ketocarboxylates has been applied to catalytic reactions. See Ref. [77] for examples.

1.7

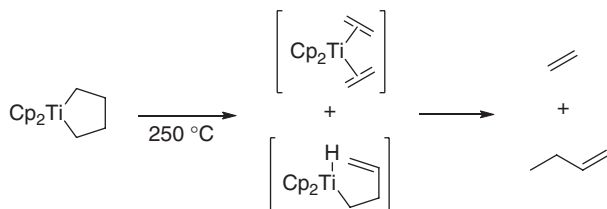
Retro-oxidative Cyclization

Oxidative cyclization is a reaction between a low-valent transition metal complex and two unsaturated bonds to form a five-membered metallacycle. One carbon–carbon and two carbon–metal bonds are formed simultaneously and the metal center is formally oxidized. A retro-oxidative cyclization reaction is the

reverse process, by which the metallacycle is fragmented into two unsaturated molecules and a low-valent metal complex through cleavage of a C–C bond (Scheme 1.59).

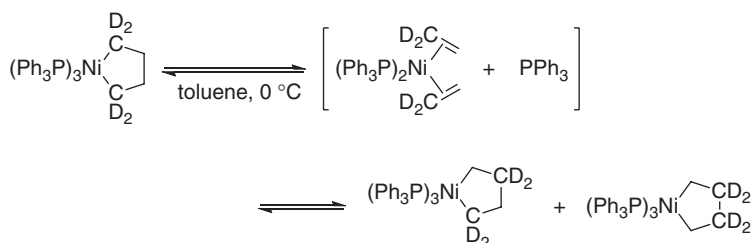


Retro-oxidative cyclization was initially reported in the thermolysis of titanacyclopentane, which generated ethylene together with 1-butene via β -hydride elimination (Scheme 1.60) [78]. Nickellacyclopentane also underwent retro-oxidative cyclization to afford ethylene, together with cyclobutane and 1-butene [79].

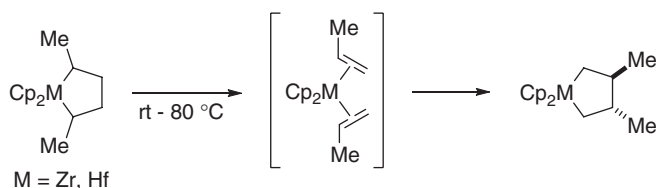


Scheme 1.60

Oxidative cyclization is reversible even under mild reaction conditions. For example, a deuterated nickellacyclopentane underwent deuterium scrambling even at 0 °C (Scheme 1.61) [80]. A 2,5-dimethylzirconacyclopentane undergoes rearrangement to afford a sterically less congested 3,4-dimethylzirconacyclopentane (Scheme 1.62) [81].

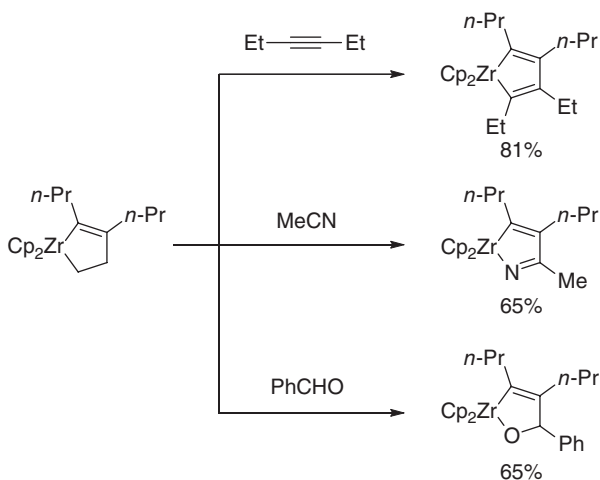
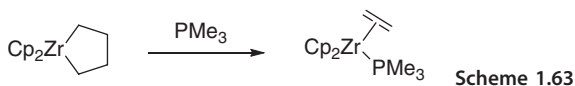


Scheme 1.61



Scheme 1.62

The ethylene moiety of zircona- and hafnacyclopentane can be replaced with more strongly coordinating ligands. Trimethylphosphine induces retro-oxidative cyclization of a zirconacyclopentane and replaces one ethylene ligand to afford a monoethylene trimethylphosphine complex (Scheme 1.63) [82]. Alkynes, nitriles, and aldehydes also substitute the olefin moiety through retro-oxidative cyclization and re-oxidative cyclization to afford thermodynamically more stable zirconacycles (Scheme 1.64) [83]. The replacement reaction has been applied to the selective synthesis of polysubstituted benzenes and pyridines [84].



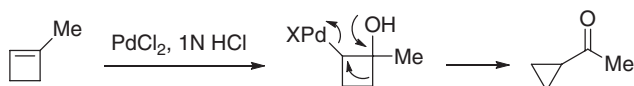
Scheme 1.64

Some catalytic reactions involving retro-oxidative addition have been reported so far. See Section 7.2 for examples.

1.8

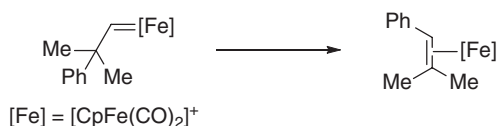
1,2-Migration

A Wagner–Meerwein rearrangement is a reaction in which an alkyl or aryl group migrates from a carbon to the neighboring carbocation. Reactions of alkenes and alkynes with a highly electrophilic metal center can produce an equivalent to a carbocationic intermediate, which prompts analogous 1,2-alkyl and aryl migration. For example, Wacker-type oxidation of cyclobutene afforded cyclopropyl ketone via 1,2-alkyl migration (Scheme 1.65) [85].



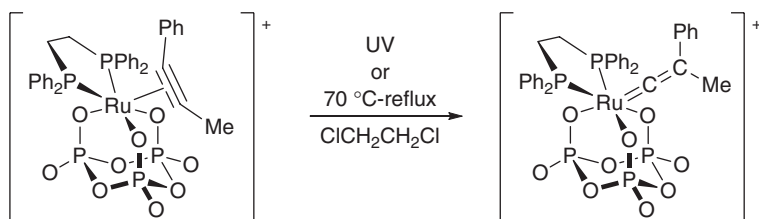
Scheme 1.65

Like free carbenes, a metal carbene complex prompts 1,2-alkyl migration. For example, an iron alkylidene complex bearing no β -hydrogen rearranged to an iron-alkene complex through 1,2-phenyl migration (Scheme 1.66) [86]. The migratory aptitude was in the order of $H > Ph > Me$. 1,2-Alkyl migration of tungsten alkylidene has also been reported [87].



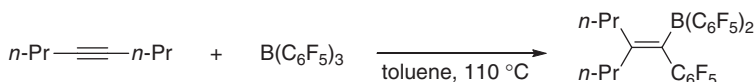
Scheme 1.66

It has been reported that internal alkynes react with organometallic compounds via 1,2-alkyl/aryl migration. When a ruthenium complex bearing an alkyne ligand was heated or irradiated, one substituent on the alkyne migrated onto the other alkyne carbon to form a vinylidene complex (Scheme 1.67) [88]. The migratory aptitude of the alkyne substituents was in the order of CO_2Et , p -EtOCOC₆H₄ > Me > Ph > p -MeC₆H₄ > p -MeOC₆H₄.



Scheme 1.67

Fluorinated organoboranes reacted with internal alkynes through 1,2-alkyl/aryl migration to afford tetrasubstituted alkenes bearing a boron atom (Scheme 1.68) [89]. In a formal sense, one substituent on the alkyne migrated to another alkyne carbon to result in a vinylidene, which was inserted into the C–B bond.



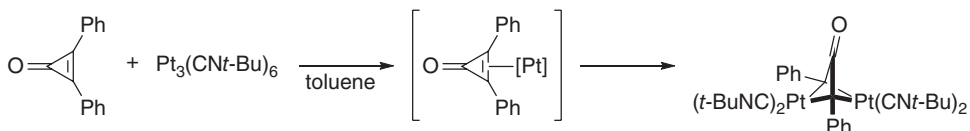
Scheme 1.68

The 1,2-alkyl/aryl migration reaction is found in various skeletal rearrangement reactions catalyzed by transition metals. See Section 7.2 and Ref. [90] for examples.

1.9

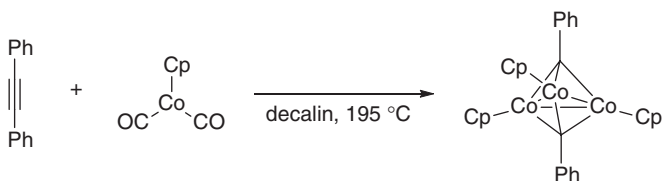
Cleavage of C–C Multiple Bonds

Coordination of C–C unsaturated bonds to a metal center generally induces elongation of the C–C bond. The coordination can be viewed as oxidative addition of the π -bond to the metal center. In some extreme cases, such interaction eventually leads to cleavage of the C–C σ -bond. For example, the C–C double bond of a cyclopropenone was cleaved upon treatment with $\text{Pt}_3(\text{CN}t\text{-Bu})_6$ (Scheme 1.69) [91]. Presumably, the η^2 -alkene complex is formed initially, and then it is attacked by $\text{Pt}(\text{CN}t\text{-Bu})_2$ from the opposite side to cause the C–C bond cleavage.



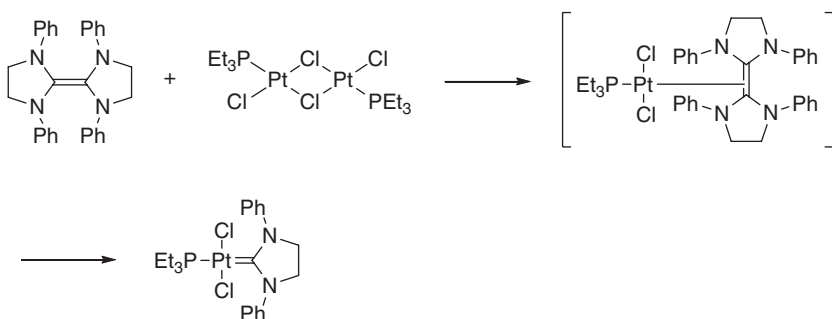
Scheme 1.69

A carbon–carbon triple bond of alkynes is cleaved with multiple metals to afford metal carbyne clusters. When diphenylacetylene is treated with $\text{CpCo}(\text{CO})_2$, a tricobalt cluster bearing two triply-bridging carbyne ligands is formed (Scheme 1.70) [92]. An analogous reaction proceeds with CpRh [93], $\text{Fe}_m(\text{CO})_n$ [94], and $\text{CpWOS}_3(\text{CO})_{10}$ [95].



Scheme 1.70

A C–C double bond of electron-rich olefins was cleaved by various palladium(II) and platinum(II) complexes to produce the carbene complexes (Scheme 1.71) [96]. It was assumed that the olefin–platinum complex was formed as the intermediate.



Scheme 1.71

1.10

Summary

This chapter describes fundamental reactions cleaving C–C bonds by means of organometallic complexes. Although C–C bonds are considered to be one of the least reactive functional groups, their cleavage is directly observed by elaborating the reaction system. Knowledge of these fundamental processes would be useful for understanding and designing catalytic multi-step transformations.

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