Unit-V: Reactions and Catalysis by Organometallics

Organic compounds incorporating carbon-metal bonds are called organometallic compounds. Unique properties have been widely used to effect synthetic transformations. Depending on the reduction potential of the metal, the reactivity of organometallic compounds varies markedly, the most reactive requiring low to moderate temperatures and inert conditions (atmosphere and solvents) for preparation and use. In general, the reactivity parallels the ionic character of the carbon-metal bond.

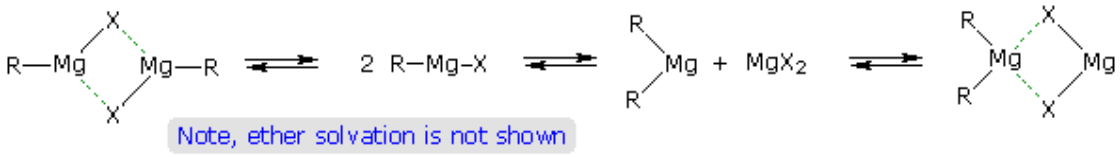
% Ionic Character of H_3C **– M**etal.,
$(CH_3)_2Hg < (CH_3)_2Cd < (CH_3)_2Zn < (CH_3)_2Mg < CH_3Li$

The first reported organometallic compounds were prepared by the reductive substitution of alkyl halides. Halide reactivity increases in the order: Cl < Br < I.

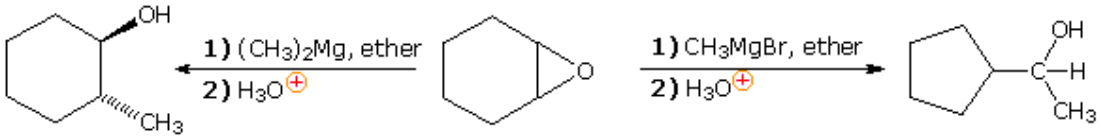
R-X + Zn ⟶ R-Zn-X An Alkyl Zinc Reagent

R-X + Mg ⟶ R-Mg-X A Grignard Reagent

R-X + 2Li ⟶ R-Li + LiX An Alkyl Lithium Reagent

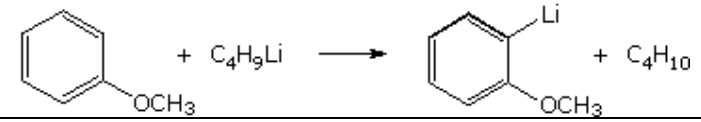
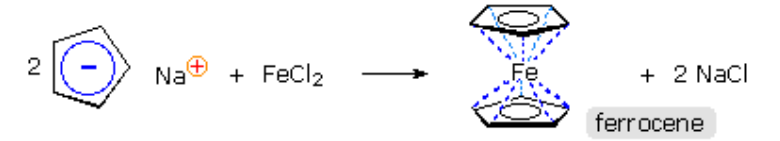


Pure dialkylmagnesium reagents may be prepared by alternative routes or by removing the magnesium halide by precipitation.



Metal Exchange Reactions

Alternative methods of preparing a wide variety of organometallic compounds generally involve an exchange reaction in which a given metal is either moved to a new location or replaced by a new metal, which may include B, Al, Ti, V, Fe, Ni, Cu, Mo, Ru, Pd, Sn, Pt, Hg & Pb. Five such exchange methods are outlined in the following table.

General Reaction & Comments	Examples
R–M + R'–H ⇌ R–H + R'–M **This equilibrium favors the weaker C-H acid.** Equation 1 illustrates the most common method of converting terminal alkynes to Grignard reagents. The corresponding alkynylsodium reagents are similarly prepared by reaction with $NaNH_2$. The other equations are examples of common lithiation reactions.	**1)** $R{-}C{\equiv}C{-}H + C_2H_5MgBr \longrightarrow R{-}C{\equiv}C{-}MgBr + C_2H_6$ **2)** **3)** 
R–M + M' ⇌ R–M' + M **This equilibrium favors the elemental metal having the less negative reduction potential.** Although highly toxic, dialkylmercury compounds are relatively stable and may be purified by distillation. This exchange is the best way of preparing halogen free organometallic compounds.	R–M is often a dialkylmercury compound. **1)** $3\,(C_6H_5)_2Hg + 2\,Al \longrightarrow 2\,(C_6H_5)_3Al + 3\,Hg$ **2)** $(C_2H_5)_2Hg + Mg \longrightarrow 2\,(C_2H_5)_2Mg + Hg$
R–M + M'X ⇌ R–M' + MX **This equilibrium favors the metal halide in which the metal has the greater negative reduction potential.** Sodium and potassium alkyls are often prepared by the exchange shown in equation 1. Many metallocenes similar to ferrocene have been made by procedure 2. The cadmium and copper reagents shown in equations 3 & 4 have reduced and modified reactivity compared with the magnesium and lithium reagents from which they are made.	**1)** $CH_3(CH_2)_3{-}Li + KOC(CH_3)_3 \longrightarrow CH_3(CH_2)_3{-}K + LiOC(CH_3)_3$ **2)**  **3)** $2\,CH_3CH_2MgBr + CdCl_2 \longrightarrow (CH_3CH_2)_2Cd + 2\,MgBrCl$ **4)** $2\,C_2H_5Li + CuI \longrightarrow (C_2H_5)_2CuLi + LiI$ a Gilman reagent

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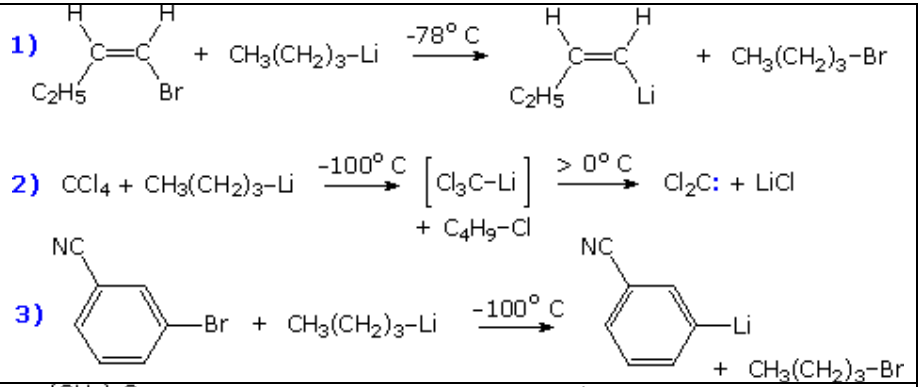
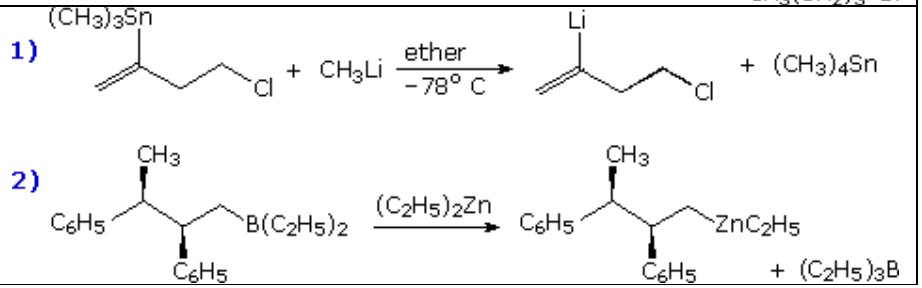
$R^{-}M + R'^{-}X \rightleftharpoons R^{-}X + R'^{-}M$ **M is usually Li and X is generally Br or I.** This is one of the best methods of preparing a wide range of organolithium reagents having well defined structures. The exchange usually occurs with retention of configuration. The low temperature serves to prevent competitive reactions, such as addition of butyl lithium to the nitrile group in reaction 3, or the decomposition of reactive compounds, such as Cl_3CLi in reaction 2. Free radical intermediates have been detected.	
$R^{-}M + R'^{-}M' \rightleftharpoons R^{-}M' + R'^{-}M$ **This equilibrium varies with the participating compounds.** Metal-metal exchanges of this kind are less commonly employed than the previous techniques. They are particularly useful when boron and tin compounds must be converted to more reactive organometallic intermediates. In example 1 metal-metal exchange proved faster than metal-chlorine exchange.	

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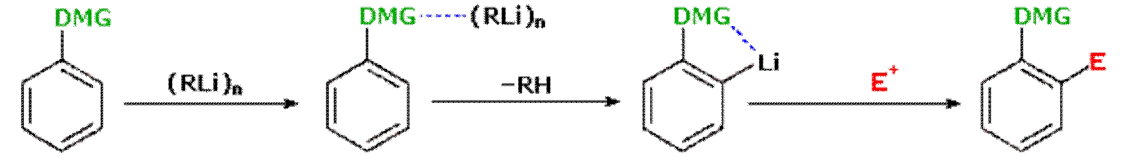
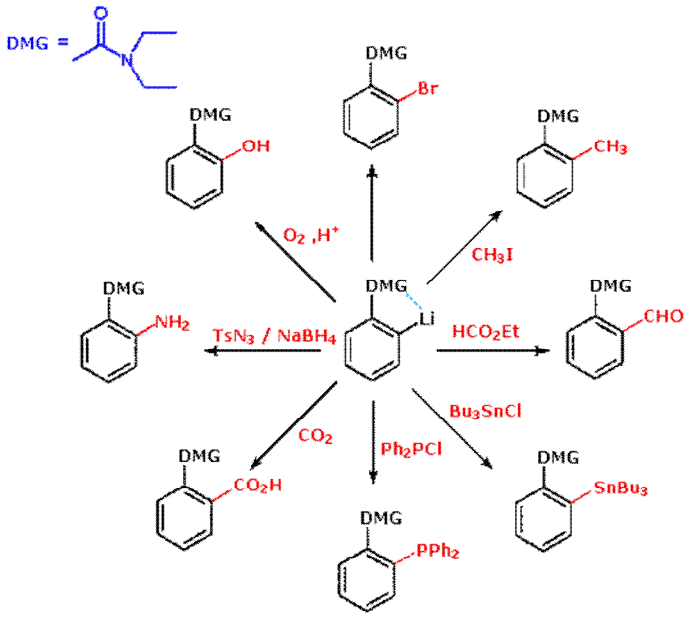
Directed ortho-Metalation

Organometallic reagents function as powerful nucleophiles, selective metal hydrogen exchange, Metalation, would represent a powerful first step to that end. The organometal species produced in this way could then react with a variety of common electrophilic reagents (e.g. alkyl halides, carbonyl compounds and halogens). However, with the exception of terminal alkynes such metalations are rare and usually non-specific. The ortho-lithiation of functionally substituted aromatic rings has proven to be a powerful technique for regioselective synthesis. The following equation illustrates this Directed ortho Metalation (DoM) reaction, where DMG refers to a directing metalation group and E^+ is an electrophile.



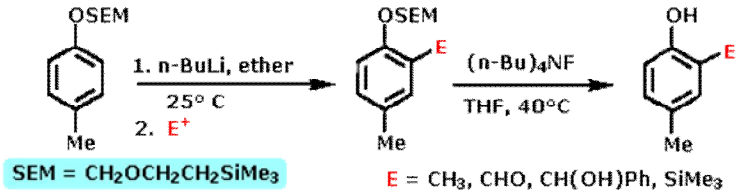
Electrophilic substitution of aromatic rings generally gives a mixture of ortho and para substitution products when an existing substituent activates the ring or meta products when the substituent is deactivating. In the case of anisole the methoxy substituent is a strongly activating group. Electrophilic iodination by the action of molecular iodine in the presence of sodium nitrate and acetic acid (a source of iodinium cation) gives a high yield of para-iodoanisole. By clicking once on the equation, iodination via directed ortho metalation of anisole will be shown. The ortho isomer is the sole product provided excess iodine is avoided.

The strongly deactivating sulfonic acid substituent is easily converted to a DMG by amide formation. Clicking the above equation a second time shows the DoM of such an amide. Direct electrophilic substitution would normally occur at the meta position, so the action of the amide DMG is particularly noteworthy. A similar amide derivative of a carboxylic acid substituent may be used for DoM, as shown in the following diagram.



Many derivatives of common functional groups may serve as DMGs. Some examples will be displayed above by clicking on the diagram. Common oxygen protective groups, such

as SEM (2-trimethylsilylethoxymethyl), have proven to be excellent DMGs. Two examples of this function are drawn below. The second will be shown by clicking on the diagram.

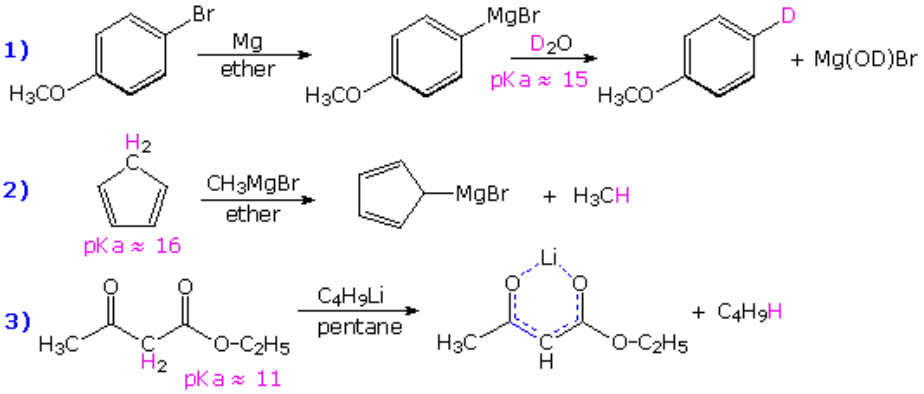


Reactions of Simple Organometallic Compounds

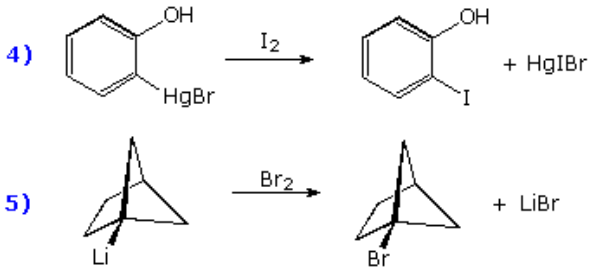
Reactions of organometallic compounds reflect the nucleophilic character of the carbon atom bonded to the metal. Alkyllithium compounds are the most reactive of the commonly used compounds in this class, having metal-carbon bonds that are roughly 30% ionic. The carbon-magnesium bond of Grignard reagents is about 20% ionic, and they have proven to be somewhat less reactive. Dialkylzinc reagents have significantly reduced reactivity, and fail to react with carbon dioxide, esters and many aldehydes and ketones. Alkylmercury and lead compounds are the least reactive commonly studied organometallics. The ionic character of the carbon-mercury bond is estimated to be less than 10%. Such compounds react with mineral acids, but not with water or alcohols. Some examples of the reactions of organometallic compounds with a variety of electrophilic functions are provided in the following three-part chart.

Organometallic compounds having significant carbanion-like behavior are subject to oxidation by suitable cations. The most important and widely used reaction of of organometallic reagents is undoubtedly their addition to carbonyl and nitrile functional groups.

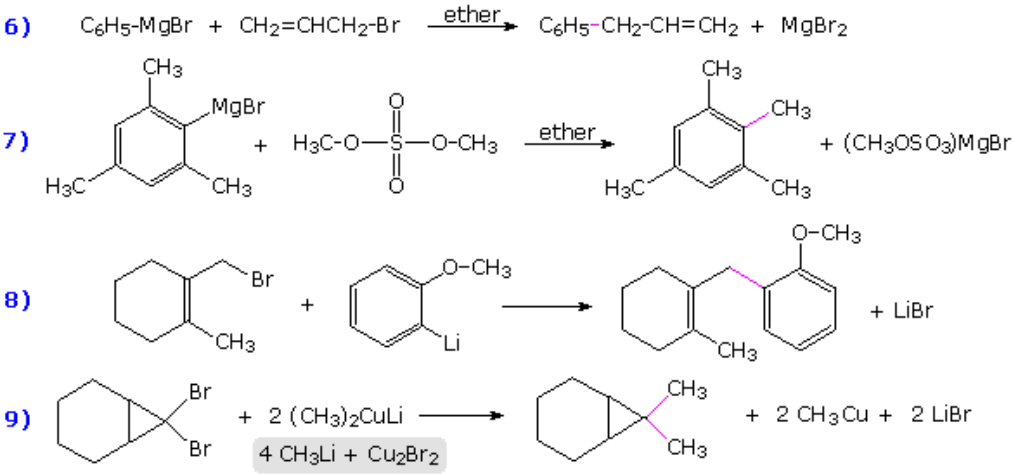
I. Reaction with Electrophilic (Acidic) Hydrogen



II. Reaction with Electrophilic Halogen



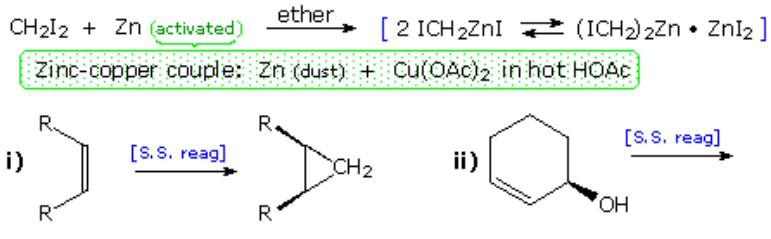
III. Other Electrophilic Substitutions



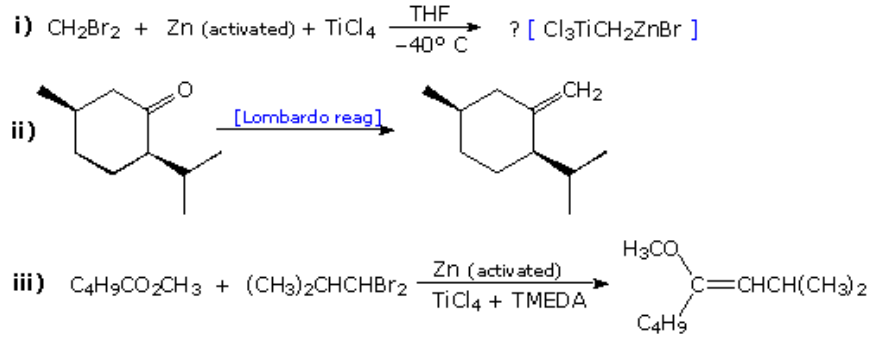
Organometallic Reagents from Geminal Dihalides

The successful preparation of organometallic reagents from dihalides is dependent on the number of carbon atoms separating the halogen groups. For example, 1,4-dibromobutane and para-dibromobenzene react with excess magnesium in ether to generate di-Grignard reagents that may be used in the same manner as any simple Grignard reagent. In the case of para-chlorobromobenzene, the greater reactivity of bromine permits the preparation of para-chlorophenylmagnesium bromide in good yield.

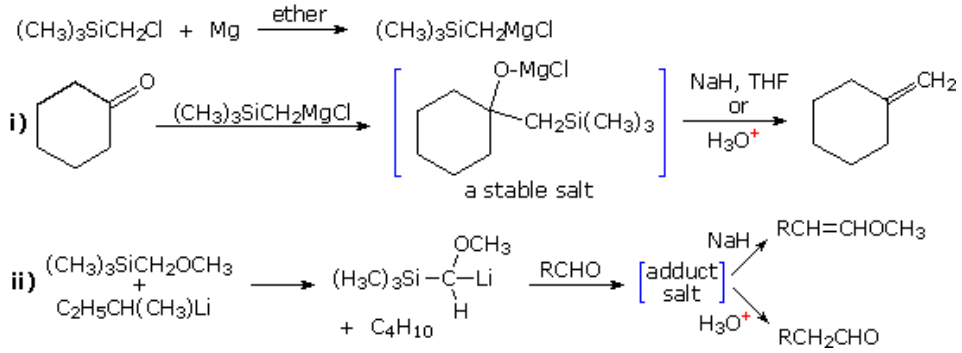
Simmons-Smith Reagent



Lombardo's Reagent



Peterson Reaction

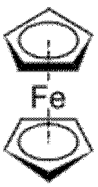


Types of Organometallic Reactions

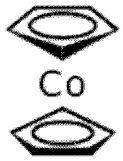
Organometallic reactions can usually be classified as one of the following classes:

- ligand dissociation/ligand association
- reductive elimination/oxidative addition
- σ bond metathesis/4-centered reaction
- insertion/de-insertion
- Lewis acid activation of electrophile

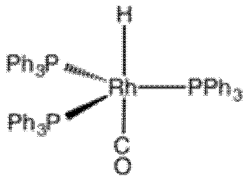
Organometallic Compounds



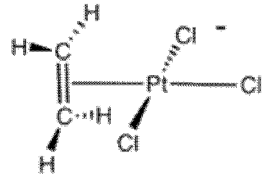
Ferrocene is an archetypal organoiron complex.



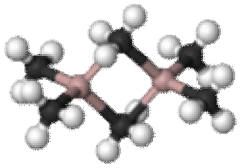
Cobaltocene is a structural analogue of ferrocene, but is highly reactive toward air.



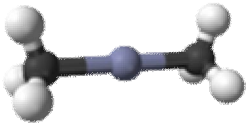
Tris(triphenylphosphine)rhodium carbonyl hydride is used in the commercial production of many aldehyde-based fragrances.



Zeise's salt is an example of a transition metal alkene complex.



Trimethylaluminium is an organometallic compound with a bridging methyl group. It is used in the industrial production of some alcohols

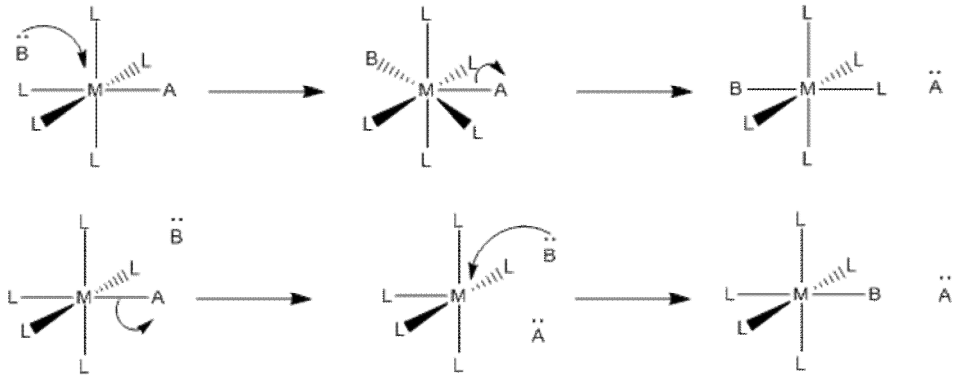


Dimethylzinc has a linear coordination. It is a volatile pyrophoric liquid that is used in the preparation of semiconducting films.

Ligand Substitution in Coordination Complexes

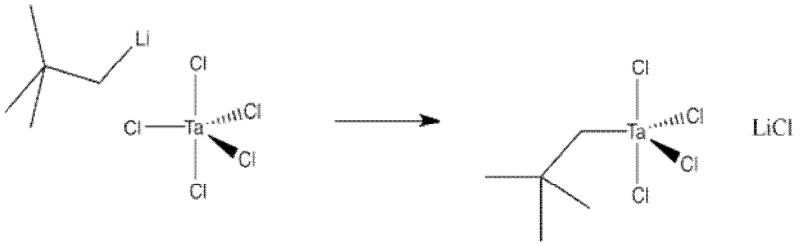
There are two basic steps in ligand substitution: association and dissociation. Association, in this case, refers to the binding of a ligand to the metal. The ligand donates an electron pair to the metal and the two molecules come together to form a new bond. Dissociation, in this case, refers to the release of a ligand from a metal. The metal-ligand bond breaks and the ligand leaves with its electron pair.

Two mechanistic possibilities seem pretty obvious. Either the new ligand binds first and then the old one leaves, or the old ligand leaves first and then the new one binds.

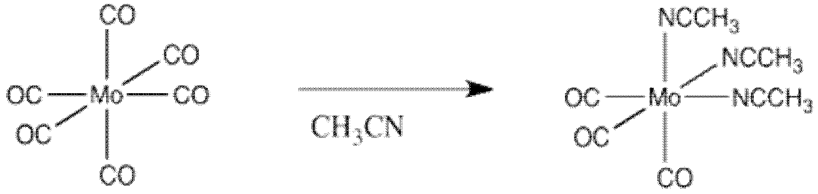


- Associative mechanism is association first. The new ligand binds and then the old one leaves.
- Dissociative mechanism is dissociation first. The old ligand leaves and then the new one binds.

Assume an associative mechanism.

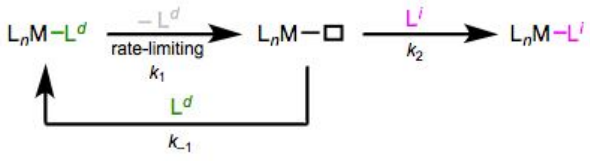


Assume a dissociative mechanism.



Dissociative Ligand Substitution

Associative substitution is unlikely for saturated, 18-electron complexes—coordination of another ligand would produce a 20-electron intermediate. For 18-electron complexes, dissociative substitution mechanisms involving 16-electron intermediates are more likely. The incoming ligand then enters the coordination sphere of the metal to generate the product. For the remainder of this post, we'll focus on the kinetics of the reaction and the nature of the unsaturated intermediate. The reverse of the first step, re-coordination of the departing ligand (rate constant k_{-1}), is often competitive with dissociation.

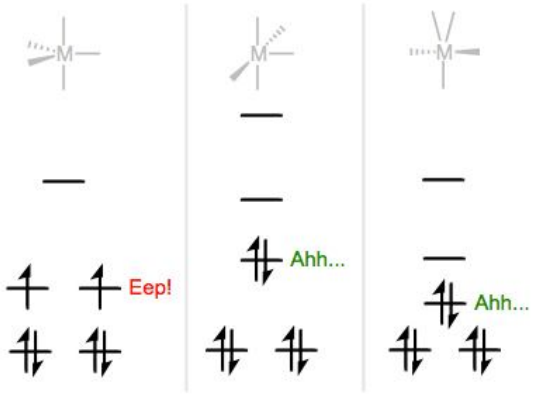


A general scheme for dissociative ligand substitution.

Typical of dissociative reactions like S_N1.

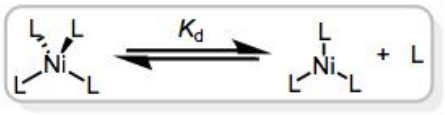
$$\text{rate} = k_1[L_nM\text{–}L^d]$$

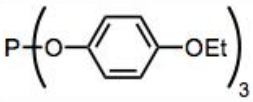
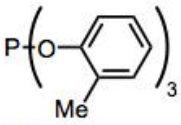
The trigonal bipyramidal geometry presents electronic problems (unpaired electrons) for 6 *d* electrons, as the figure below shows. The orbital energy levels come from crystal field theory. Distortion to a square pyramid or a distorted TBP geometry removes the electronic issue, and so five-coordinate d^6 complexes typically have square pyramidal or distorted TBP geometries. This is just the geometry prediction process in action!



dissociative substitution, are: d^8 TBP > d^{10} tetrahedral > d^6 octahedral

Destabilization of the starting complex is commonly accomplished by adding steric bulk to its ligands. Naoturally, dissociation relieves steric congestion in the starting complex. Chelation has the opposite effect, and tends to steel the starting complex against dissociation.



L	Cone Angle	K_d
$P(OEt)_3$	109	$< 10^{-10}$
	128	$6 * 10^{-10}$
$P(Oi\text{-}Pr)_3$	130	$2.7 * 10^{-5}$
	141	$4 * 10^{-2}$
PPh_3	145	huge

Dissociative substitution describes a pathway by which compounds interchange ligands. This pathway can be well described by the cis effect, or the labilization of CO ligands in the cis position. The opposite pathway is associative substitution. Intermediate pathways exist between the pure dissociative and pure associative pathways, these are called interchange mechanisms.

Dissociative interchange pathway

Intermediates are not observed, which is more common than pure dissociative pathways. If the reaction rate is insensitive to the nature of the attacking nucleophile, the process is called dissociative interchange.

$$[Co(NH_3)_5(H_2O)]^{3+} + SCN^- \rightleftharpoons \{[Co(NH_3)_5(H_2O)], NCS\}^{2+}$$
$$\{[Co(NH_3)_5(H_2O)], NCS\}^{2+} \rightleftharpoons [Co(NH_3)_5NCS]^{2+} + H_2O$$

The rate for the hydrolysis of cobalt(III) ammine (NH_3-containing) halide complexes are deceptive, appearing to be associative but proceeding by a pathway that is dissociative in character. The hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ follows second order kinetics: the rate increases linearly with concentration of hydroxide as well as the starting complex.

Oxidative Addition

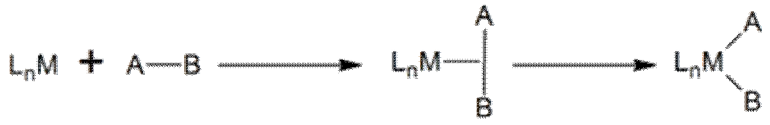
Oxidative addition and reductive elimination are two important and related classes of reactions in organometallic chemistry. Oxidative addition is a process that increases both the oxidation state and coordination number of a metal centre. Oxidative addition is often a step in catalytic cycles, in conjunction with its reverse reaction, reductive elimination. Oxidative addition is favored for metals that are (i) basic and/or (ii) easily oxidized. Metals with a relatively low oxidation state often satisfy one of these requirements, but even high oxidation state metals undergo oxidative addition, as illustrated by the oxidation of Pt(II) with chlorine:

$$[PtCl_4]^{2-} + Cl_2 \rightarrow [PtCl_6]^{2-}$$

Oxidative additions proceed via many pathways that depend on the metal center and the substrates.

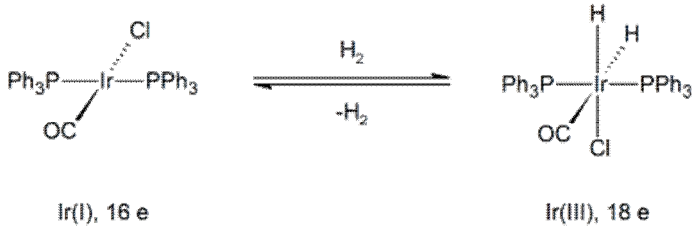
Concerted pathway

Oxidative additions of nonpolar substrates such as hydrogen and hydrocarbons appear to proceed via concerted pathways. Such substrates lack π-bonds, consequently a three-centered σ complex is invoked, followed by intramolecular ligand bond cleavage of the ligand (probably by donation of electron pair into the sigma* orbital of the inter ligand bond) to form the oxidized complex. The resulting ligands will be mutually *cis*,[2] although subsequent isomerization may occur.



This mechanism applies to the addition of homonuclear diatomic molecules such as H_2. Many C–H activation reactions also follow a concerted mechanism through the formation of an M–(C–H) agostic complex.[2]

A representative example is the reaction of hydrogen with Vaska's complex, *trans*-$IrCl(CO)[P(C_6H_5)_3]_2$. In this transformation, iridium changes its formal oxidation state from +1 to +3. The product is formally bound to three anions: one chloride and two hydride ligands. As shown below, the initial metal complex has 16 valence electrons and a coordination number of four whereas the product is a six-coordinate 18 electron complex.



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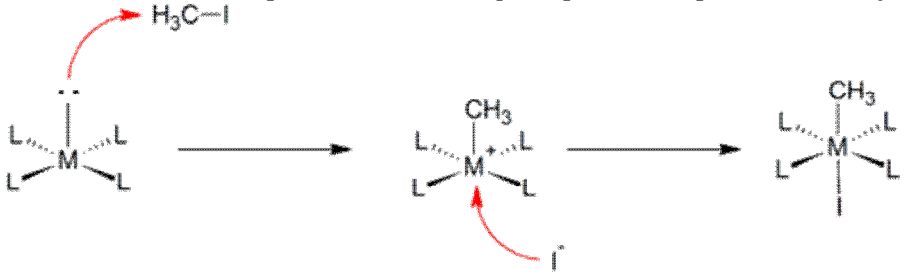
Formation of a trigonal bipyramidal dihydrogen intermediate is followed by cleavage of the H–H bond, due to electron back donation into the H–H σ*-orbital. This system is also in chemical equilibrium, with the reverse reaction proceeding by the elimination of hydrogen gas with simultaneous reduction of the metal center.

The electron back donation into the H–H σ*-orbital to cleave the H–H bond causes electron-rich metals to favor this reaction. The concerted mechanism produces a *cis* dihydride, while the stereochemistry of the other oxidative addition pathways do not usually produce *cis* adducts.

S_N2-type

Some oxidative additions proceed analogously to the well known bimolecular nucleophilic substitution reactions in organic chemistry. Nucleophillic attack by the metal center at the less electronegative atom in the substrate leads to cleavage of the R–X bond, to form an $[M–R]^+$ species. This step is followed by rapid coordination of the anion to the cationic metal center. For example, reaction of a square planar complex with methyl iodide:



This mechanism is often assumed in the addition of polar and electrophilic substrates, such as alkyl halides and halogens.

Applications

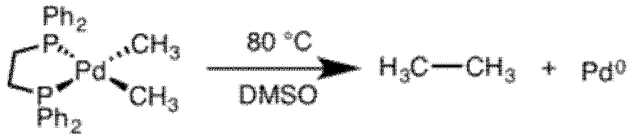
Oxidative addition and reductive elimination are invoked in many catalytic processes both in homogeneous catalysis such as the Monsanto process and alkene hydrogenation using Wilkinson's catalyst. Metals are however characterized by band structures, so oxidation states are not meaningful. Oxidative addition is also needed in order for nucleophilic addition of an alkyl group to occur. Oxidative insertion is also a crucial step in many cross-coupling reactions like the Suzuki coupling, Negishi coupling, and the Sonogashira coupling.

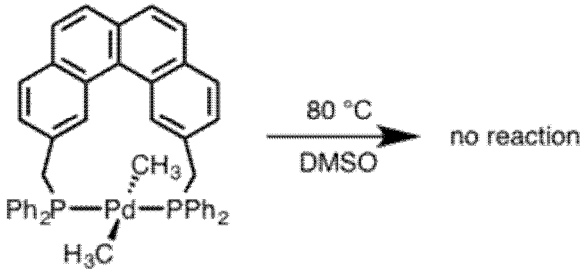
Reductive elimination

Reductive elimination is an elementary step in organometallic chemistry in which the oxidation state of the metal center decreases while forming a new covalent bond between two ligands. It is the microscopic reverse of oxidative addition, and is often the product-forming step in many catalytic processes. Since oxidative addition and reductive elimination are reverse reactions, the same mechanisms apply for both processes, and the product equilibrium depends on the thermodynamics of both directions.

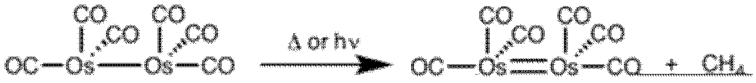
Reductive elimination is often seen in higher oxidation states, and can involve a two-electron change at a single metal center (mononuclear) or a one-electron change at each of two metal centers.

This pathway is common for d^8metals Ni(II), Pd(II), and Au(III) and d^6 metals Pt(IV), Pd(IV), Ir(III), and Rh(III). Additionally, mononuclear reductive elimination requires that the groups being eliminated must be cis to one another on the metal center.





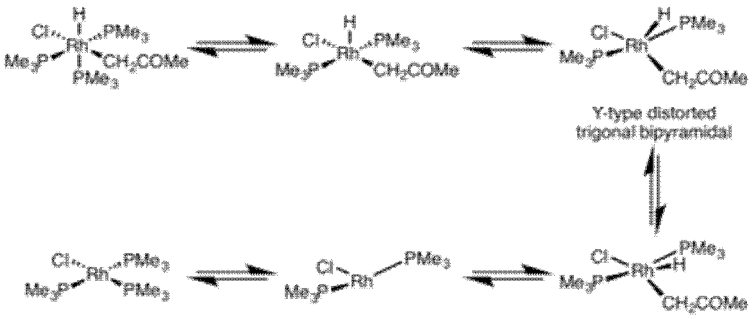
The oxidation state of each metal decreases by one, while the d-electron count of each metal increases by one. This type of reactivity is generally seen with first row metals, which prefer a one-unit change in oxidation state, but has been observed in both second and third row metals.



Oxidative addition, several mechanisms are possible with reductive elimination. The prominent mechanism is a concerted pathway, meaning that it is a nonpolar, three-centered transition state with retention of stereochemistry.

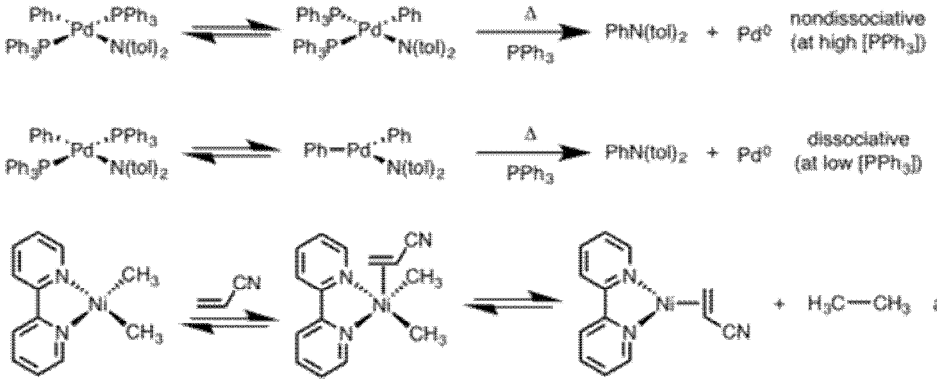
Octahedral complexes

The rate of reductive elimination is greatly influenced by the geometry of the metal complex. In octahedral complexes, reductive elimination can be very slow from the coordinatively saturated center, and often, reductive elimination only proceeds via a dissociative mechanism, where a ligand must initially dissociate to make a five-coordinate complex.



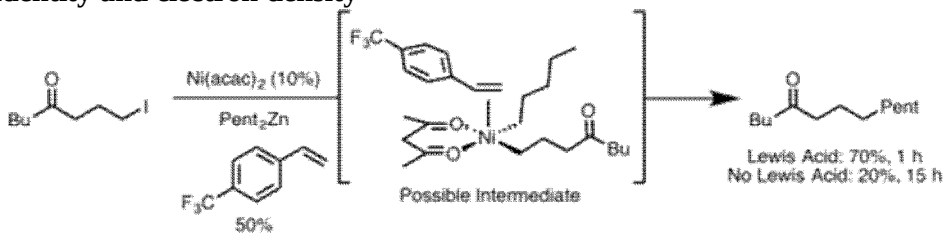
Square planar complexes

Reductive elimination of square planar complexes can progress through a variety of mechanisms: dissociative, nondissociative, and associative. If the eliminating ligands are trans to each other, the complex must first undergo a trans to cis isomerization before eliminating.

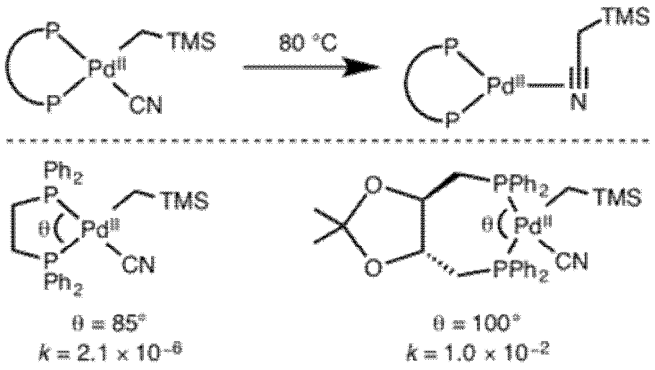


Factors affecting the reductive elimination

Metal identity and electron density

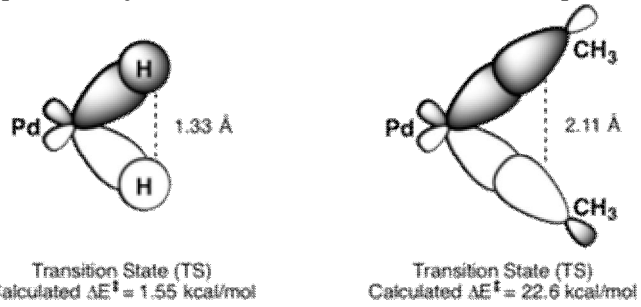


Sterics



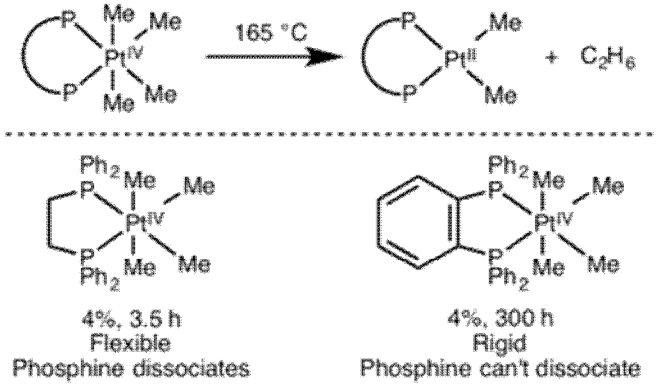
Participating ligands

Kinetics for reductive elimination are hard to predict, but reactions that involve hydrides are particularly fast due to effects of orbital overlap in the transition state.[10]



Coordination number

Reductive elimination occurs more rapidly for complexes of three- or five-coordinate metal centers than for four- or six-coordinate metal centers. For even coordination number complexes, reductive elimination leads to an intermediate with a strongly metal-ligand antibonding orbital. When reductive elimination occurs from odd coordination number complexes, the resulting intermediate occupies a nonbonding molecular orbital.

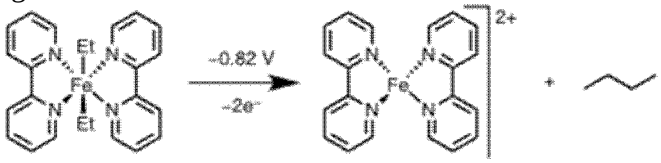


Geometry

Reductive elimination generally occurs faster for complexes whose structures resemble the product.

Photolysis/oxidation

Reductive elimination can be induced by oxidizing the metal center to a higher oxidation state via light or an oxidant.



Applications

Hydrogenation, Monsanto acetic acid process, hydroformylation and cross coupling reactions, Heck reaction and Wacker process, reductive elimination is involved only in catalyst regeneration..

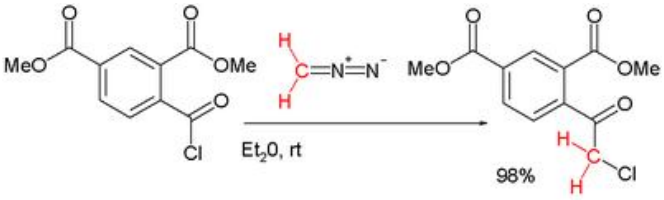
Insertion reaction

An insertion reaction is a chemical reaction where one chemical entity (a molecule or molecular fragment) interposes itself into an existing bond of typically a second chemical entity *e.g.*:

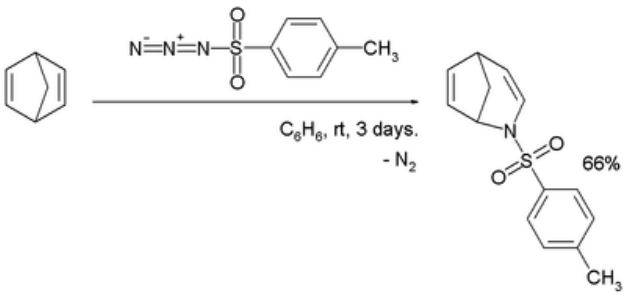
$$A + B–C \rightarrow B–A–C$$

The term only refers to the result of the reaction and does not suggest a mechanism. Insertion reactions are observed in organic, inorganic, and organometallic chemistry. The inserting molecule can act either as a nucleophile or as an electrophile to the metal complex.

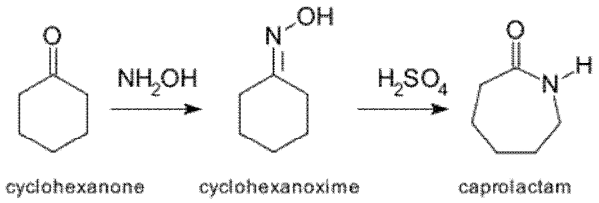
The Nierenstein reaction in which a diazomethane methylene group is inserted into the carbon-chlorine bond of an acid chloride to generate an α-chloromethyl ketone.



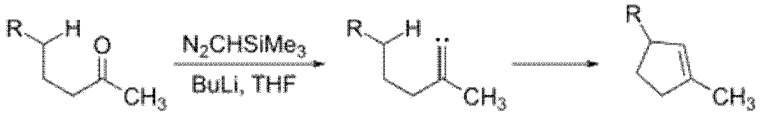
Organic azides also provide an example of an insertion reaction in organic synthesis and, like the above examples, the transformations proceed with loss of nitrogen gas. When tosyl azidereacts with norbornadiene, a ring expansion reaction takes place in which a nitrogen atom is inserted into a carbon-carbon bond α- to the bridge head.



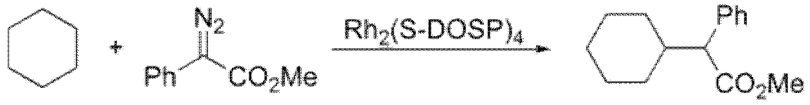
The Beckmann rearrangement is another example of a ring expanding reaction in which a heteroatom is inserted into a carbon-carbon bond.



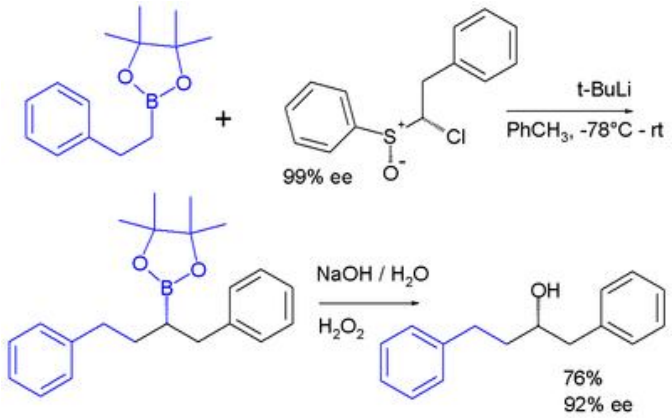
Carbenes undergo both intermolecular and intramolecular insertion reactions.



Carbene insertions into carbon-hydrogen bonds can also occur intermolecularly

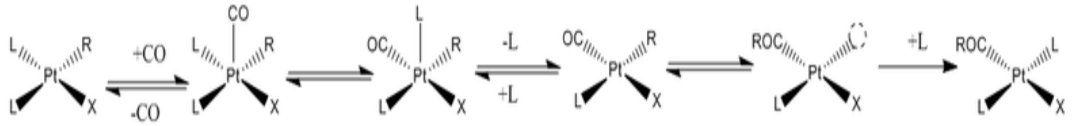


One example is the chloroalkyllithium carbenoid reagent prepared *in situ* from a sulfoxide and *t*-BuLiwhich inserts into the carbon-boron bond of a pinacol boronic ester.

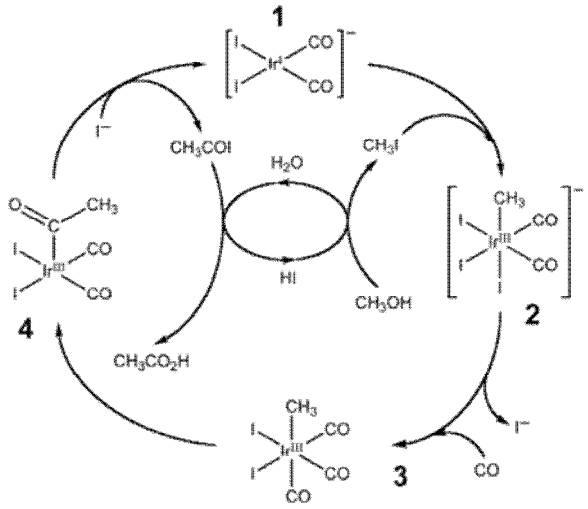


Carbonylations

The insertion of carbon monoxide and alkenes into metal-carbon bonds is a widely exploited reaction with major industrial applications.



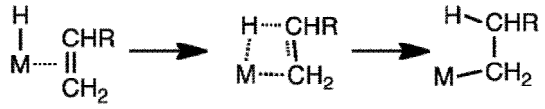
Nucleophilic insertion and rearrangement of a square planar complex such reactions are subject to the usual parameters that affect other reactions in coordination chemistry, but steric effects are especially important in determining the stereochemistry and regiochemistry of the reactions. The reverse reaction, the de-insertion of CO and alkenes, are of fundamental significance in many catalytic cycles as well. More traditional is the rhodium-based Monsanto acetic acid process, but this process has been superseded by the iridium-based Cativa process. By 2002, worldwide annual production of acetic acid stood at 6 million tons, of which approximately 60% is produced by the Cativa process.



The Cativa process catalytic cycle, shown above, includes both insertion and de-insertion steps. The oxidative addition reaction of methyl iodide with (**1**) involves the formal insertion of the iridium(I) centre into the carbon-iodine bond, whereas step (**3**) to (**4**) is an example of migratory insertion of carbon monoxide into the iridium-carbon bond. The active catalyst species is regenerated by the reductive elimination of acetyl iodide from (**4**), a de-insertion reaction.

Olefin insertion

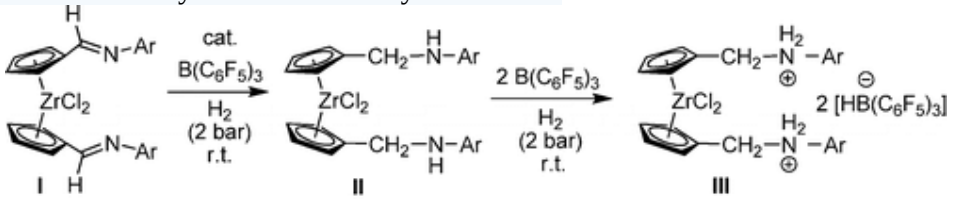
The insertion of ethylene and propylene into titanium alkyls is the cornerstone of Ziegler-Natta catalysis, the commercial route of polyethylene and polypropylene. The olefin can be coordinated to the metal before insertion. Depending on the ligand density of the metal, ligand dissociation may be necessary to provide a coordination site for the olefin.



Migratory insertion of an alkene into a metal hydride. The middle image depicts the transition state. Notice that the less substituted carbon becomes bonded to the metal, at least usually. The reverse reaction is called beta-hydride elimination.

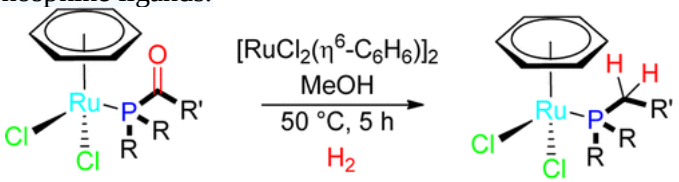
Hydrogenation

The bis(arylimino-Cp)$ZrCl_2$ complex (**I**) forms an "antagonistic" Lewis pair with $B(C_6F_5)_3$. Treatment with dihydrogen yields the aminomethyl-Cp hydrogenation product (**II**) by means of a quasi-autocatalytic process. The salt **III** is an efficient catalyst for the hydrogenation of bulky imines and of silyl enolethers.



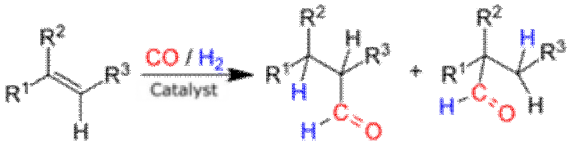
Ar = 2,6-di-*i*-propylphenyl

Hydrogenation of a benzene ruthenium chloride dimer in the presence of novel acylphosphine (phosphomide) ligands resulted in the formation of corresponding ruthenium(II)–benzyl phosphine complexes. Here, selective reduction of the carbonyl group to a methylene unit takes place with molecular hydrogen under mild conditions in good yield. This approach provides an alternative synthesis of ruthenium phosphine complexes of benzyl and heterobenzyl phosphine ligands.



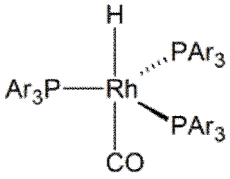
R = Cy
R' = Aryl, Heteroaryl

Hydroformylation

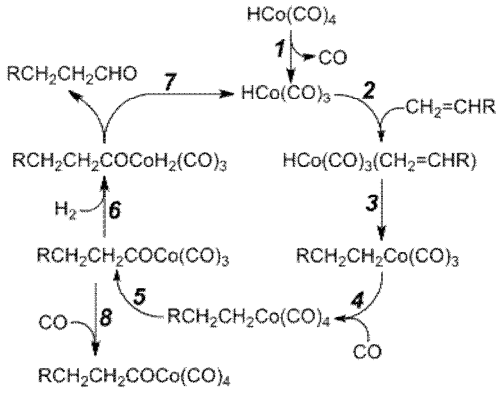


Hydroformylation of an Alkene (R1 to R3 organyl groups (i. e. Alkyl- or Aryl group) or hydrogen).

Hydroformylation, also known as oxo synthesis or oxo process, is an industrial process for the production of aldehydes from alkenes. This chemical reaction entails the net addition of a formyl group (CHO) and a hydrogen atom to a carbon-carbon double bond. Hydroformylation is also used in speciality chemicals, relevant to the organic synthesis of fragrancesand drugs.



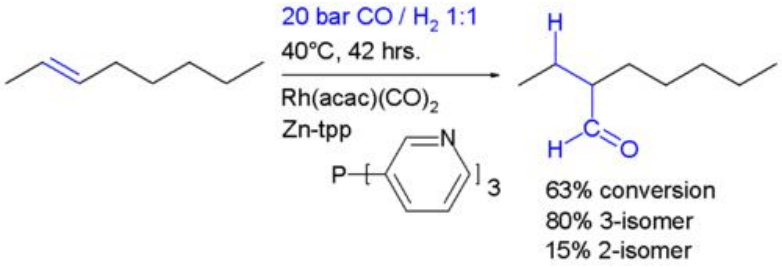
A generic rhodium catalyst, where PAr_3 = triphenylphosphine or its sulfonated analogue Tppts. See tris(triphenylphosphine)rhodium carbonyl hydride.



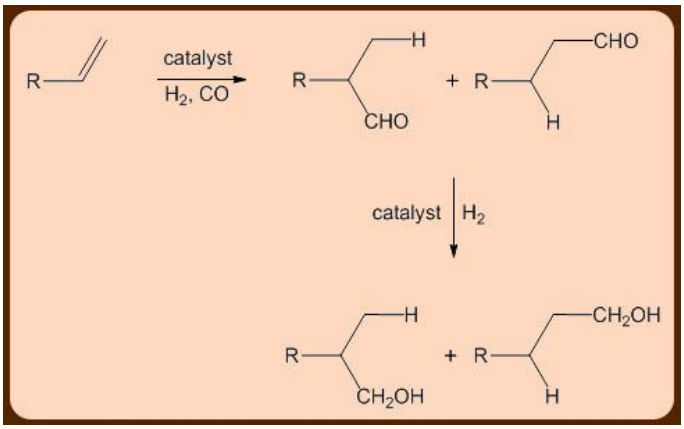
drmurugesanchemistry@gmail.com

Mechanism of cobalt-catalyzed hydroformylation. The process begins with dissociation of CO from cobalt tetracarbonyl hydride to give the 16-electron species (step **1**). Subsequent binding of alkene gives an 18e species (step **2**). In step **3**, the olefin inserts to give the 16e alkyl tricarbonyl. Coordination of another equivalent of CO gives alkyl tetracarbonyl (step **4**). Migratory insertion of CO gives the 16e acyl in step **5**. In step **6**, oxidative addition of hydrogen gives a dihydrido complex, which in step **7** releases aldehyde by reductive elimination. Step **8** is unproductive and reversible.

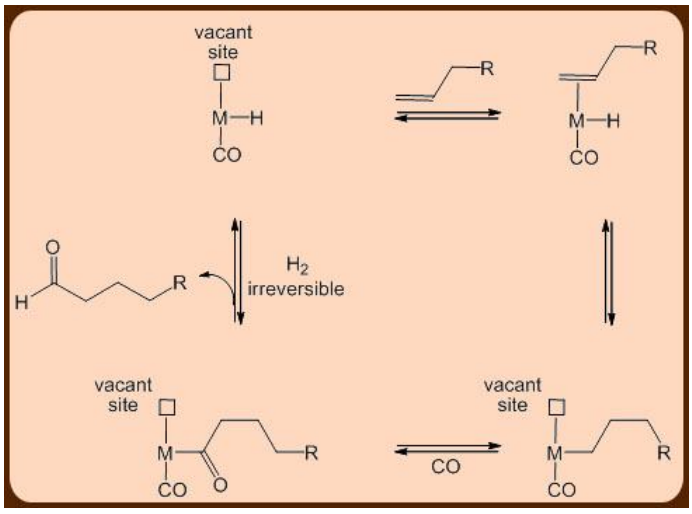
To suppress competing isomerization of the alkene, the rate of migatory insertion of the carbonyl into the carbon-metal bond of the alkyl be fast. The rate of insertion of the carbonyl carbon into the C-M bond is likely to be greater than the rate of beta-hydride elimination.[10]



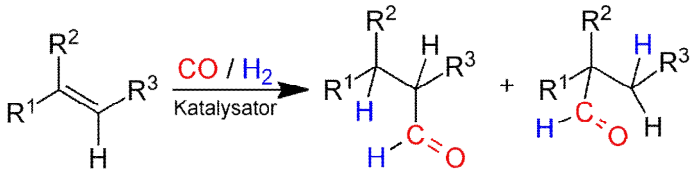
Hydroformylation, popularly known as the "oxo" process, is a Co or Rh catalyzed reaction of olefins with CO and H_2 to produce the value-added aldehydes.



The reaction, discovered by Otto Roelen in 1938, soon assumed an enormous proportion both in terms of the scope and scale of its application in the global production of aldehydes. The metal hydride complexes namely, the rhodium based $HRh(CO)(PPh_3)_3$ and the cobalt based $HCo(CO)_4$ complexes, catalyzed the hydroformylation reaction as shown below.

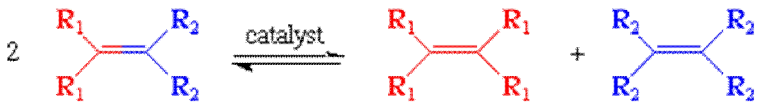


Hydroformylation, also known as oxo synthesis or oxo process, is an important homogeneously catalyzed industrial process for the production of aldehydes from alkenes.[1] This chemical reaction entails the addition of a formyl group (CHO) and a hydrogen atom to a carbon-carbon double bond. This process has undergone continuous growth since its invention in 1938: Production capacity reached 6.6×106 tons in 1995. It is important because the resulting aldehydes are easily converted into many secondary products. For example, the resulting aldehydes are hydrogenated to alcohols that are converted to plasticizers or detergents. Hydroformylation is also used in specialty chemicals, relevant to the organic synthesis of fragrances and natural products. The development of hydroformylation, which originated within the German coal-based industry, is considered one of the premier achievements of 20th-century industrial chemistry.



Olefin Metathesis

The olefin metathesis reaction can be thought of as a reaction in which all the carbon-carbon double bonds in an olefin (alkene) are cut and then rearranged in a statistical fashion:

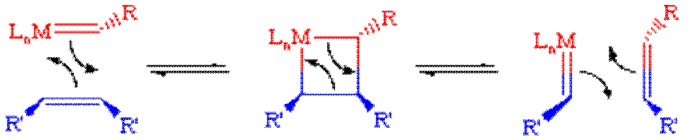


If one of the product alkenes is volatile (such as ethylene) or easily removed, then the reaction shown above can be driven completely to the right. Likewise, using a high pressure of ethylene, internal olefins can be converted to terminal olefins. There are a wide variety of variants on this reaction as is discussed below.

Mechanism

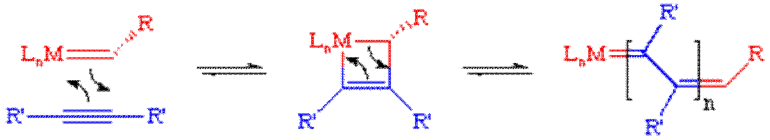
The commonly accepted mechanism for the olefin metathesis reaction was proposed by Chauvin and involves a [2+2] cycloaddition reaction between a transition metal alkylidene complex and the olefin to form an intermediate metallacyclobutane. This metallacycle then

breaks up in the opposite fashion to afford a new alkylidene and new olefin. If this process is repeated enough, eventually an equilibrium mixture of olefins will be obtained.

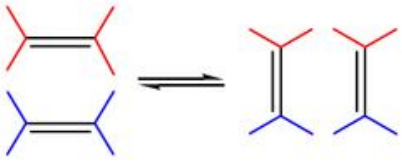


Such cycloaddition reactions between two alkenes to give cyclobutanes is symmetry forbidden and occurs only photochemically. However, the presence of d-orbitals on the metal alkylidene fragment breaks this symmetry and the reaction is quite facile.

When an acetylene is reacted with an alkylidene, a [2 + 2] cycloaddition occurs as with olefins, a metallacyclobut**e**ne is formed instead of a metallacyclobut**a**ne. If this metallacycle opens in a productive fashion, the result is a growing polymer chain:



This reaction typically only works well with 2-butyne or terminal acetylenes. Polymerization of terminal acetylenes is complicated by the potential for the R group to insert alpha or beta with respect to the metal. It is extremely challenging to always get a beta insertion and generate a polymer with reproducible properties.



Olefin metathesis is an organic reaction that entails the redistribution of fragments of alkenes (olefins) by the scission and regeneration of carbon-carbon double bonds. Because of the relative simplicity of olefin metathesis, it often creates fewer undesired by-products and hazardous wastes than alternative organic reactions.

Applications

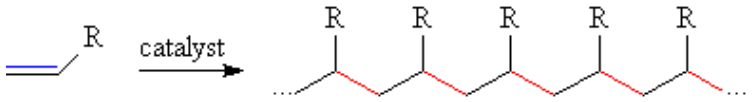
Olefin metathesis has several industrial applications. Almost all applications employ heterogeneous catalysts.[6] Representative processes include:[1]

- The Phillips Triolefin and the Olefin conversion technology. This process interconverts propylene with ethylene and 2-butenes. Rhenium and molybdenum catalysts are used. Nowadays, only the reverse reaction, i.e., the conversion of ethylene and 2-butene to propylene is industrially practiced, however [6].
- Shell higher olefin process (SHOP) produces (alpha-olefins) for conversion to detergents. The process recycles certain olefin fractions using metathesis.[7]
- Neohexene production, which involves ethenolysis of isobutene dimers. The catalyst is derived from tungsten trioxide supported on SiO_2 and MgO.

- 1,5-Hexadiene and 1,9-decadiene, useful crosslinking agents and synthetic intermediates, are produced commercially by ethenolysis of 1,5-cyclooctadiene and cyclooctene. The catalyst is derived from Re_2O_7 on alumina.
- Synthesis of pharmaceutical drugs,[8]
- Potential applications of homogeneous catalysts

Olefin Polymerization

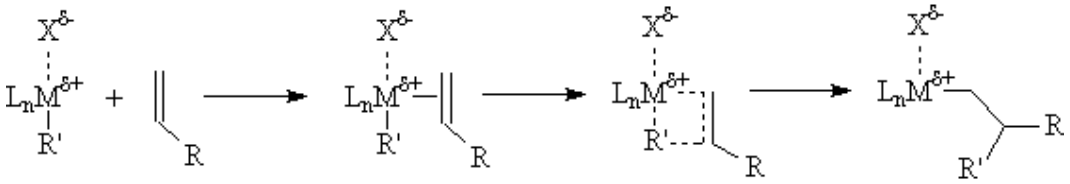
The transition metal catalyzed polymerizaion of olefins can be thought of as a reaction in which the carbon-carbon π-bond in α-olefins (1-alkenes) are cut and then remade as a carbon-carbon σ-bonds, linking the olefins together in long hydrocarbon chains. This reaction is exothermic by ~ 20 Kcal/mol, the energy difference between the carbon-carbon π- and σ-bonds. For typical early transition metal, d^0 catalysts, the activation energy is ~ 10 Kcal/mole, making this a very facile reaction.



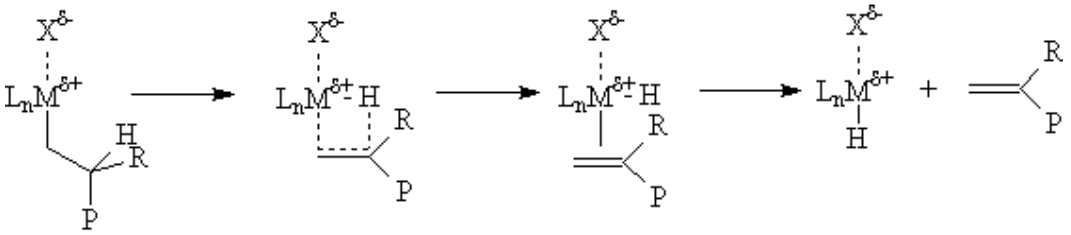
These long chain macromolecules are known as polymers (from the Greek, *poly* = many and *mer* = units) and are the principal constituents of many common plastics. Some familar plastics made via early transition metal catalyzed polymerization include: high density polyethylene (HDPE, R=H), linear low density polyethylene (LLDPE, R = mostly H with some Et, Bu or Hx), polypropylene (R = Me) and ethylene-propylene-diene-modified rubber (EPDM, R = H, Me and Alkenyl).

Mechanism

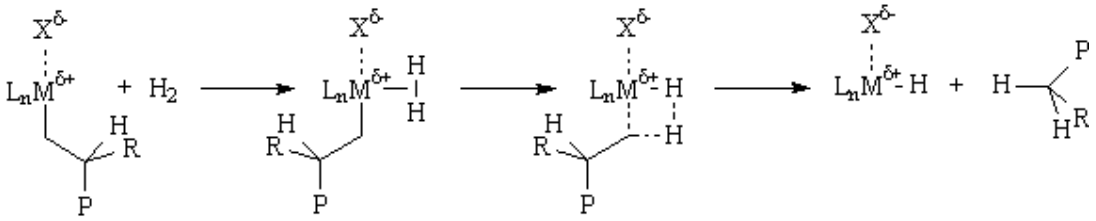
The commonly accepted mechanism for the olefin polymerization reaction is shown below. A severely electron deficient metal center coordinates the π-bond of an olefin to form a weakly bound olefin complex; the bond is weak because there are no d-electrons to form a π-bond. The bound olefin then inserts into a metal-carbon bond within the complex via a four center transition state, forming new metal-carbon and carbon-carbon bonds. This process then repeats, extending the chain indefinitely.



Chain growth can be terminated by a number of processes. One of the most impotant is β-hydride elimination. Since this is simply the reverse of insertion, the activation energy is ~ 30 Kcal/mole plus the energy difference between the metal-carbon and metal-hydrogen bonds. Catalysts with relatively strong M-C bonds give higher molecular weight polymers, while those with relatively strong M-H bonds give lower molecular weight polymers (waxes). Beta-hydride elimination leads to polymers with vinyl (R=H) or vinylidene (R=Me, Et, Pr...) end groups. The vinyl terminated polymers are, of course, α-olefins and may also be incorporated into the growing polymer chains giving "long chain branched" products under appropriate conditions.



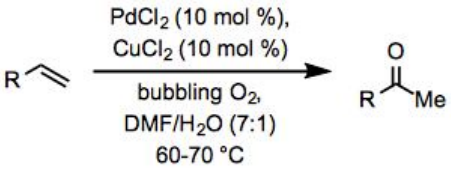
Another termination process of great practical use is hydrogenolysis. This sigma-bond metathesis reaction leads to polymers with saturated end groups:

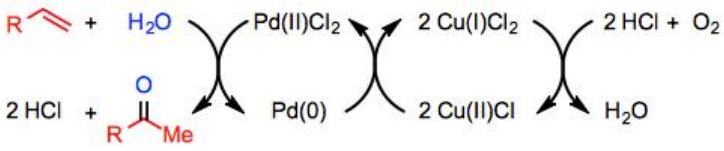


Wacker oxidation

The Wacker oxidation refers generally to the transformation of a terminal or 1,2-disubstituted alkene to a ketone through the action of catalytic palladium(II), water, and a co-oxidant. Variants of the reaction yield aldehydes, allylic/vinylic ethers, and allylic/vinylic amines. Because of the ease with which terminal alkenes may be prepared and the versatility of the methyl ketone group installed by the reaction, the Wacker oxidation has been employed extensively in organic synthesis.

The stoichiometric conversion of ethylene to acetaldehyde by an acidic, aqueous solution of $PdCl_2$ was discovered over a century ago, but fifty years passed between the discovery of this reaction and the development of a catalytic method. In 1959, researchers at Wacker Chemie reported that a similar transformation takes place in an aqueous, acidic solution of catalytic $PdCl_2$ and a stoichiometric amount of $CuCl_2$ through which oxygen is bubbled.



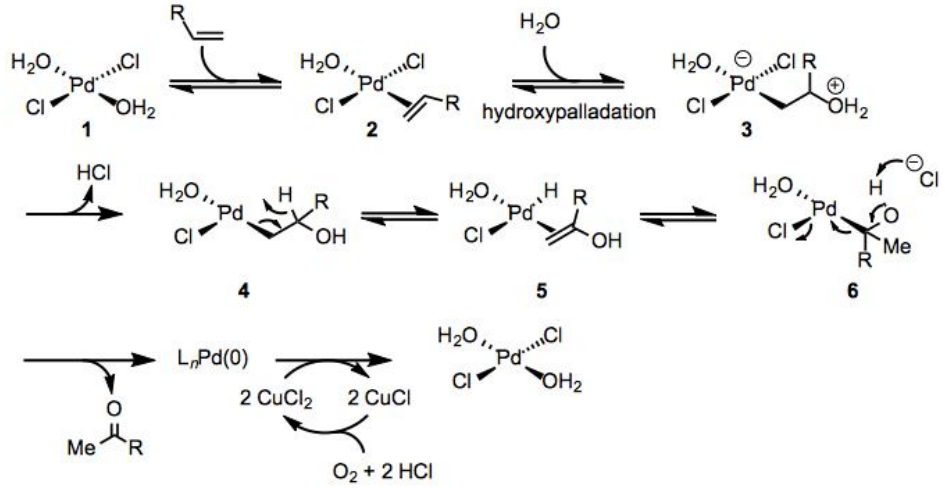


Since this initial report, the Wacker process has been widely applied in organic synthesis and has been extended to other classes of substrates and products. To encourage mixing of the organic reactants with the aqueous phase, a co-solvent is generally employed along with water. Dimethylformamide (DMF) is a common choice; when DMF is used as a co-solvent with a stoichiometric amount of CuCl under balloon pressure of oxygen, the reaction is called the "Tsuji-Wacker oxidation."[4] Applications of the Wacker oxidation to

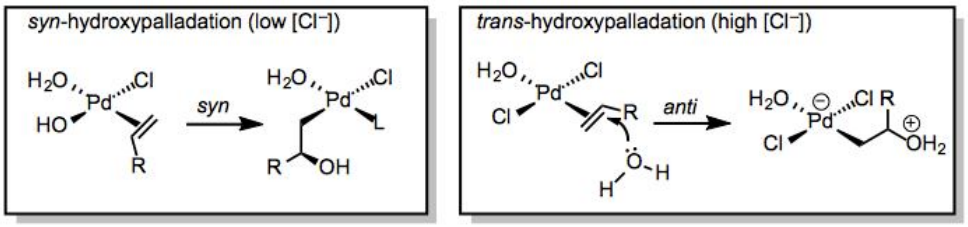
organic synthesis typically involve the installation of a methyl ketone moiety, which may subsequently undergo nucleophilic addition or deprotonation to form an enolate.

Mechanism and Stereochemistry

The mechanism of the Wacker oxidation has been studied both experimentally and theoretically. The first step of the Wacker oxidation involves coordination of the alkene to the palladium center to form π-complex **2**. Evidence for this step is provided by the relative sluggishness of electron-poor alkenes, which generally require higher catalyst loadings than unactivated alkenes. Hydroxypalladation then occurs to yield either zwitterionic complex **3** or neutral complex **4** depending on the mode of hydroxypalladation (see below). Studies employing deuterated substrates suggest that β-hydride elimination then occurs to afford enol complex **5**, which re-inserts into the Pd-H bond to afford complex **6**. Computational studies support the involvement of chloride-assisted deprotonation in the subsequent step, which affords the product and palladium(0). Oxidation of palladium(0) by copper(II) then occurs, regenerating palladium(II) species **1**. The role of copper(II) in the mechanism is poorly understood at present.



The mode of hydroxypalladation is an important issue for the Wacker oxidation. Hydroxypalladation may occur either in a *syn* fashion through an inner-sphere mechanism or in an *anti* fashion via nucleophilic attack on the coordinated alkene (Eq. 3). Although the stereocenter in **4** is ultimately destroyed upon elimination, the mode of hydroxypalladation can influence the site selectivity of the reaction. Markovnikov-type addition of water to the more substituted carbon of the alkene forms a methyl ketone, while attack of water at the less substituted position ultimately yields an aldehyde. The mode of hydroxypalladation has been shown to affect the distribution of ketone and aldehyde products, and is also important in stereoselective Wacker cyclization reactions.



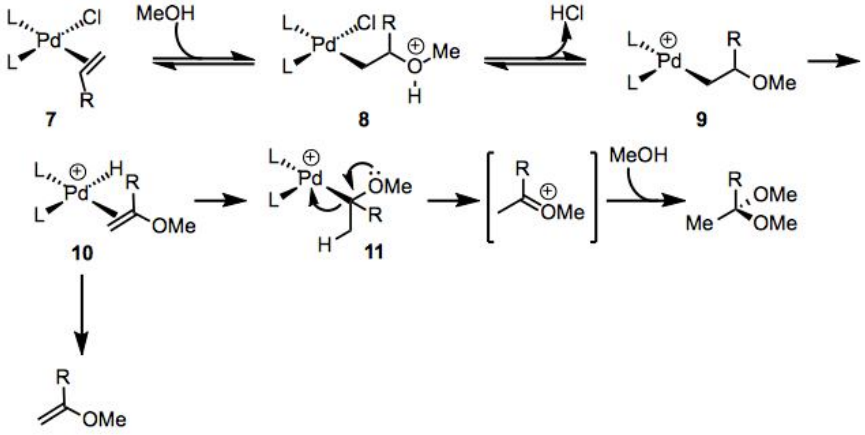
At low concentrations of chloride ion, *syn*-hydroxypalladation appears to be the norm. Water coordinates to the metal and migratory insertion into the Pd-OH bond occurs to

generate **4** directly. At high concentrations of chloride ion, chloride competes with hydroxide for binding at palladium, and thus *anti*-hydroxypalladation may occur.

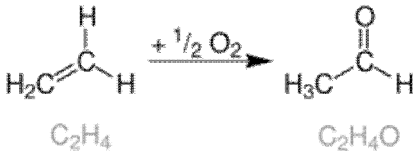
Mechanism:

Alcohols may also be employed as nucleophiles in the Wacker process. The initial steps of the mechanism are similar to those for the Wacker oxidation with water, but the mechanisms diverge at alkoxy complex **11** (Eq. 4). Elimination of palladium occurs to generate an oxocarbenium ion, which may be captured by solvent to generate an acetal. Small amounts of vinyl ether products support the intermediacy of complex **10**.

(4)



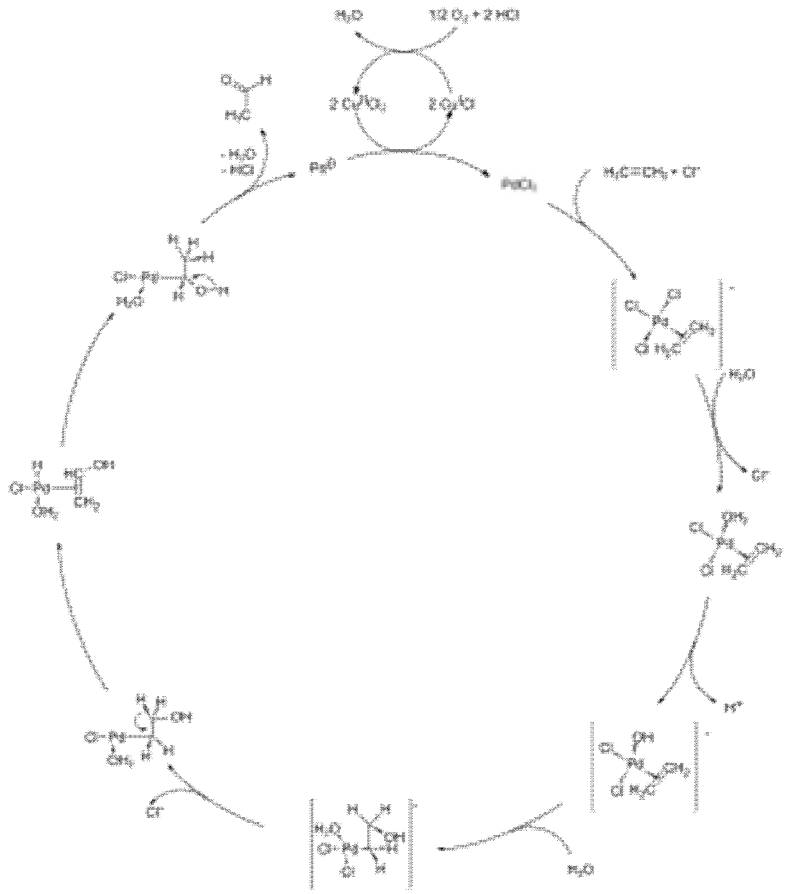
Wacker process



The Wacker process or the Hoechst-Wacker process refers to the oxidation of ethylene to acetaldehyde in the presence of palladium(II) chloride as the catalyst.[1] This chemical reaction was one of the first homogeneous catalysis with organopalladium chemistry applied on an industrial scale.

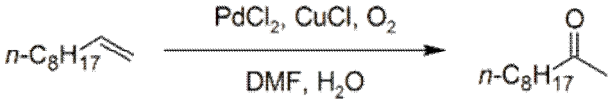
Reaction mechanism

The reaction mechanism for the industrial Wacker process (olefin oxidation via palladium(II) chloride) has received significant attention for several decades. Aspects of the mechanism are still debated. A modern formulation is described below:



Wacker–Tsuji oxidation

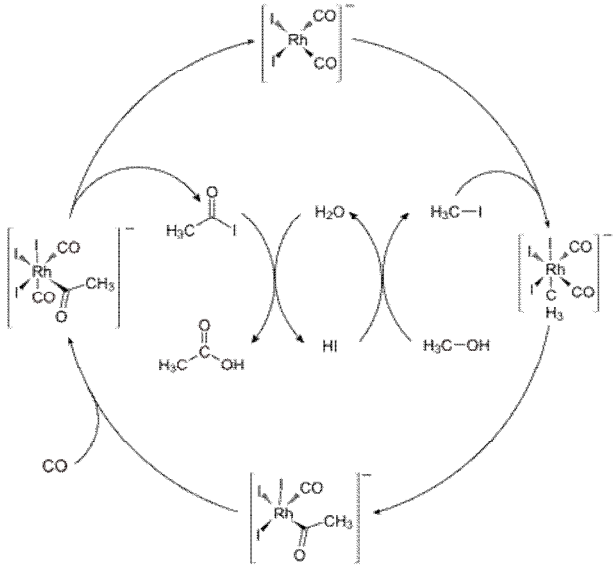
The so-called Wacker–Tsuji oxidation is the laboratory scale version of the above reaction, for example the conversion of 1-decene to 2-decanone with palladium(II) chloride and copper(I) chloride in a water / dimethylformamide solvent mixture in the presence of air:[28]



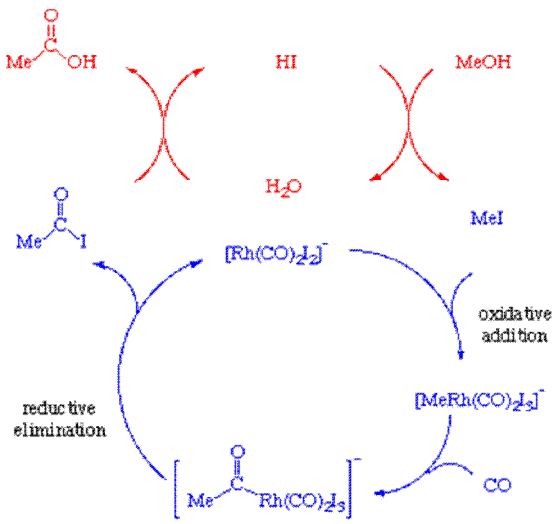
The Monsanto process is an industrial method for the manufacture of acetic acid by catalytic carbonylation of methanol. The Monsanto process has largely been supplanted by the Cativa process, a similar iridium-based process developed by BP Chemicals Ltd which is more economical and environmentally friendly.

This process operates at a pressure of 30–60 atm and a temperature of 150–200 °C and gives a selectivity greater than 99%. It was developed in 1960 by the German chemical company, BASF, and improved by the Monsanto Company in 1966, which introduced a new catalyst system.

Catalytic cycle



The catalytically active species is the anion *cis*-$[Rh(CO)_2I_2]^-$ (top of scheme).[3] The first organometallic step is the oxidative addition of methyl iodide to *cis*-$[Rh(CO)_2I_2]^-$ to form the hexacoordinate species $[(CH_3)Rh(CO)_2I_3]^-$. This anion rapidly transforms, via the migration of a methyl group to an adjacent carbonyl ligand, affording the pentacoordinate acetyl complex $[(CH_3CO)Rh(CO)I_3]^-$. This five-coordinate complex then reacts with carbon monoxide to form the six-coordinate dicarbonyl complex, which undergoes reductive elimination to release acetyl iodide ($CH_3C(O)I$). The catalytic cycle involves two non-organometallic steps: conversion of methanol to methyl iodide and the hydrolysis of the acetyl iodide to acetic acid and hydrogen iodide.[4]

The reaction has been shown to be first-order with respect to methyl iodide and $[Rh(CO)_2I_2]^-$. Hence the oxidative addition of methyl iodide is proposed as the rate-determining step.

Once methyl iodide has been generated, the catalytic cycle begins with the oxidative addition of methyl iodide to $[Rh(CO)_2I_2]^-$. Coordination and insertion of carbon monoxide leads an intermediate 18-electron acyl complex which can then undergo reductive elimination to yield acetyl iodide and regenerate our catalyst: