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REACTION MECHANISMS IN HOMOGENEOUS CATALYSIS

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INTRODUCTION

Many chemical products are made in the petrochemical industry by the addition of oxygen or oxygen containing molecules to unsaturated hydrocarbons. For instance ethylene oxide is synthesized from oxygen and ethylene, acetic acid from carbon-monoxide and methanol, aldehydes are made from carbonmonoxide, hydrogen and olefins, while alcohols are obtained by a subsequent hydrogenation. In some of these cases catalytic processes are involved that operate in a homogeneous phase, such as in the hydroformylation process, the Wacker process and in the carbonyla-tion of methanol. In the past decade much knowledge has been gathered on the chemistry involved in homogeneous catalysis and in some areas the level of understanding has even further advanced than in comparable areas in heterogeneous catalysis. Before discussing specific reactions, however, we will start with a review of the elementary reaction steps, such as substitution, insertion and oxidative addition, that take place in nearly all homogeneous reactions.

BASIC REACTIONS

Ligand substitution

Ligand substitution of a ligand by one that takes part in the chemical reaction is a step that occurs in many organo-transition metal reactions. Mainly two reaction mechanisms are observed for ligand substitution, an associative and a dissociative

mechanism [1]. Four coordinate square-planar complexes react by
the associative mechanism, a five coordinate complex being the
transition state. As far as they have been studied, reactions
of five coordinate trigonal-bipyramidal complexes are independent
of the concentration of the entering ligand and therefore the
reactions must be of the dissociative type. Six coordinate
octahedral complexes also react by the dissociative mechanism.
An example of ligand substitution on a hexa-coordinated manganese
complex will be encountered in the following section.

Insertion

Insertion reactions are reactions of the type

$$M-L + X \longrightarrow M-X-L$$
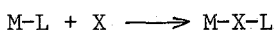
in which an organic group X is so-to-speak 'inserted' between the
metal atom and a ligand of a metalorganic compound. One could
also say that the metal containing compound is added to the
organic substrate and one speaks of 1,1 addition when both M and
L are linked to the same atom in the final product and of 1,2
addition if they are linked to neighbouring atoms:

$$M-L + X = Y \longrightarrow M-X-Y-L$$
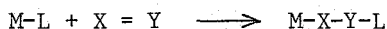
Addition reactions - and also the reverse reactions, the
elimination reactions - play an important role in the homogeneous
hydrogenation and polymerisation of olefins, in the formation of
metal-carbene complexes, in the rearrangement reactions of metal
carbonyls, and in many other reactions. In the literature of the
last two decades numerous examples of addition reactions can be
found with all kinds of groups X, Y and L and with many
transition-metal atoms. Some examples are given in Table I.
Of the reactions presented in Table I we will discuss in some
detail the 1,1 addition to CO and the 1,2 addition to olefins.

The 1,1 addition of an organometallic compound to CO, or
as this reaction is often called the insertion of CO into a
metal-carbon bond, has been extensively studied. From a mechanistic
point of view especially methyl pentacarbonyl manganese has been
well studied. Addition of strong donor ligands to this compound
induces a reaction that can be called a CO insertion between the
manganese atom and the methylgroup or the 1,1 addition of
methylmanganese to CO:

$$H_3C-Mn(CO)_5 + L \longrightarrow H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-Mn(CO)_4L$$
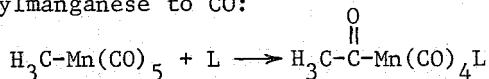
(L = CO, amine, phosphine)

metal-ligand bond	organic substrate	product
M–C	1,1 CO, CNR, CR_2, $SnCl_2$ 1,2 C_2H_4, C_2H_2, O_2, CO_2	M(COR), M–C(R)=NR' M–C_2H_4–R, M–C(O)–OR
M–H	1,2 C_2H_4	M–C_2H_5
M–NR_2	1,2 CO_2 1,3 CS_2	M–O–C(O)–NR_2 M(S_2C–NR_2)
M–Cl	1,1 CR_2, $SnCl_2$	
M–M	1,1 $SnCl_2$ 1,2 SO_2	M–$SnCl_2$–M M–O–S(O)–M

Table 1 Examples of 1,1 and 1,2 additions of organometallic
   compounds to organic substrates.

The reaction kinetics indicate that a two-step mechanism is
operative. In first instance the methyl group migrates to one of
the cis CO ligands and forms an acetyl group, followed by
addition of L to the vacated site

R   P
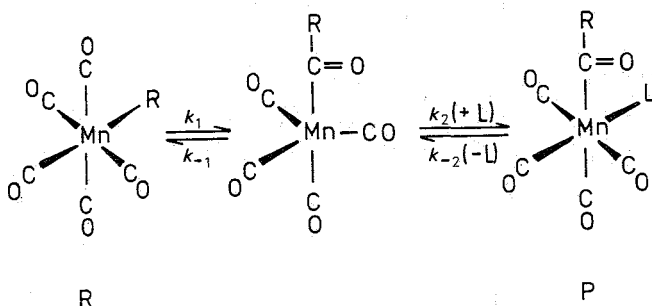
Assuming a steady state approximation for the acetyl intermediate
and neglecting the back reaction k_{-2} we obtain

$$\frac{d(P)}{dt} = \frac{k_1 k_2}{k_{-1} + k_2(L)} \cdot (R) \cdot (L)$$

For small concentrations of L one indeed finds a first order
dependence in both (R) and (L), while at high concentrations of
L the reaction is first order in (R) and zero order in (L).

   A very important question in the CO insertion reaction is the
question: how does the first step take place? Does the CO insert
into the Mn–CH_3 bond or does the methyl group migrate to the CO
ligand. The latter has been shown to be the case in very clever

labelling experiments by Noack and Calderazzo [2].

First they studied the CO insertion and de-insertion by means
of infrared spectroscopy.
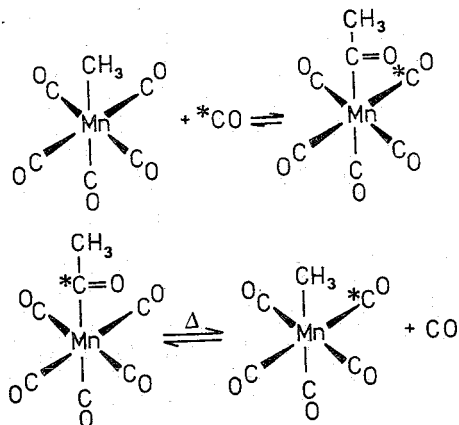
Since the products formed are exclusively the ones indicated in
the figure, CO insertion and de-insertion must be intramolecular
and regiospecific to the cis coordination site. These experiments
in itself do not decide on the two mechanisms, however. An analysis
of the decarbonylation products of acetylmanganese pentacarbonyl,
with one ^{13}CO group, now allows a distinction to be made between
carbonyl insertion and methyl migration. According to the schemes
given below the two pathways would give different product
distributions. Experimentally a cis-to-trans $CH_3Mn(CO)_4{}^{13}CO$ ratio
of 2:1 was found, proving that methyl migration is the correct
mechanism.

CO insertion
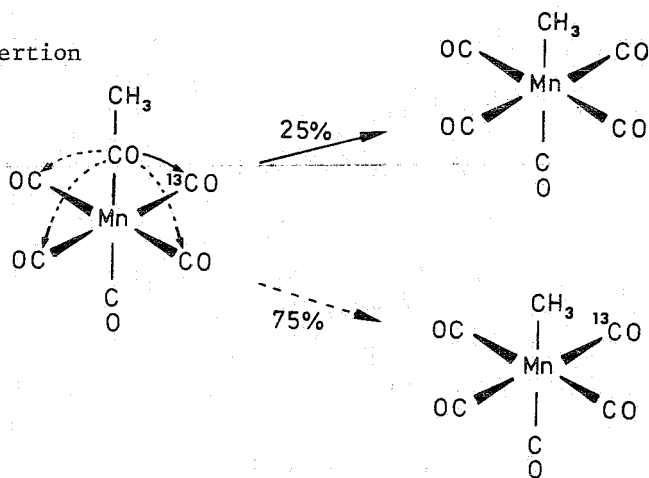
CH$_3$ migration
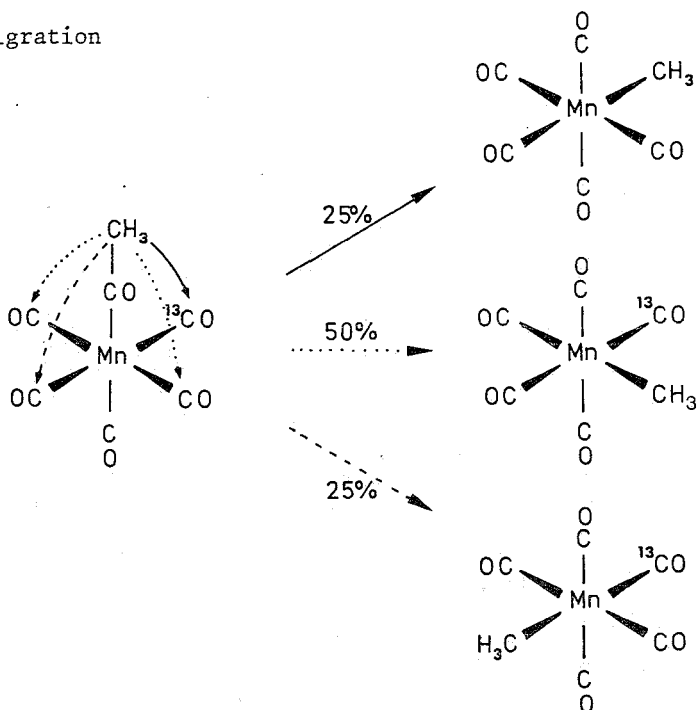
Furthermore carbonylation of cis-CH$_3$Mn(CO)$_4$^{13}CO with natural CO gave acetylmanganese pentacarbonyl with cis, trans and ^{13}COCH$_3$ products in the ratio 2:1:1, as expected for the methyl migration route. Carbonyl insertion would have given cis and ^{13}COCH$_3$ products in the ratio 3:1 and no trans isomer.

Another elegant proof of alkyl migration is found in the decarbonylation of the following iron compound
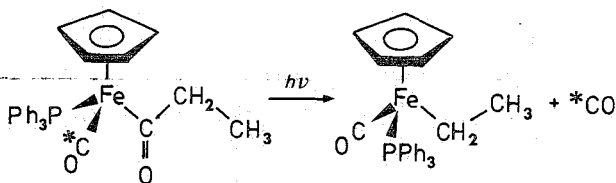
The iron acyl compound is chiral, with the iron atom as the center of chirality. Upon decarbonylation the chirality of the complex is inverted. This can only be explained by assuming that the labelled CO group has left the complex and that the alkyl group has migrated to the vacated site [3].

Of the 1,2 addition reactions the addition of a metalhydride to an olefin, or in other words the insertion of an olefin into a metal-hydrogen bond, is studied most. This reaction plays an important role in the hydrogenation of olefins, in the formation of aldehydes from olefins via the hydroformylation reaction, and in the polymerisation of olefins via the Ziegler-Natta reaction. An example of olefin insertion into a metal-hydrogen bond is the reaction of olefins with trans-$PtHCl(PEt_3)_2$. At 95^0C and 80 atm of ethylene there is a 25% conversion to the σ-bonded ethyl group, while heating in vacuo induces the reverse reaction [4].

$$\begin{array}{ccccc}
PEt_3 & & & & PEt_3 \\
| & & & & | \\
Cl-Pt-H & + & C_2H_4 \rightleftharpoons & & Cl-Pt-C_2H_5 \\
| & & & & | \\
PEt_3 & & & & PEt_3
\end{array}$$
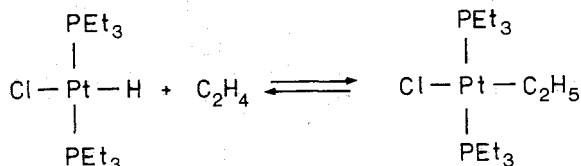
Heating the deuterated complex trans-$Pt(CD_2CH_3)Cl(PEt_3)_2$ gave a platinum product with both Pt-H and Pt-D bonds. This demonstrates that the addition or elimination of the olefin proceeds through a symmetrical transition state, the hydrido ethylene platinum complex: The equilibrium between metalhydride and olefin on one hand and the metal-alkyl complex on the other hand lies more to the olefin side for the larger olefins than for ethylene. For instance, with octene-1 no platinumoctyl complex is formed. That olefin addition and elimination does occur, however, was proved by the conversion of trans-$PtDCl(PEt_3)_2$ into trans-$PtHCl(PEt_3)_2$ when heated with octene-1 at 130^0C for 48 hours.
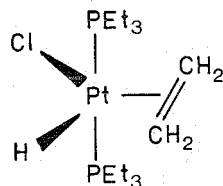
Although it is usually assumed that the 1,2 addition of M-H to C_2H_4 goes via complex formation between the reactants:

$$L_nMH + H_2C=CH_2 \rightleftharpoons \left[L_nM\text{-----}\begin{array}{c} H \quad CH_2 \\ || \\ CH_2 \end{array} \right] \rightleftharpoons L_nM\text{----}\begin{array}{c} H\text{----}CH_2 \\ || \\ CH_2 \end{array} \rightarrow L_nM\text{-}CH_2CH_3$$
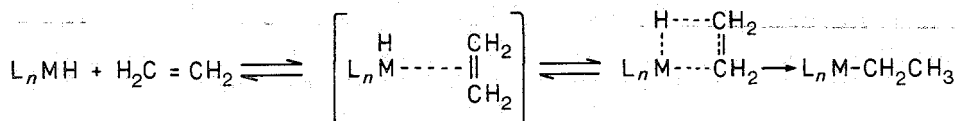
only very few hydrido-ethylene-metal complexes have been isolated. Recently an hydrido-ethylene-rhodium complex has been prepared which in nitromethane solution proved to be in equilibrium with the σ-ethyl complex [5].

$$[(C_5H_5)RhH(C_2H_4)PMe_3]^+ \xrightleftharpoons \quad [(C_5H_5)Rh(C_2H_5)PMe_3]^+$$
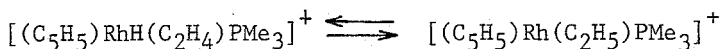
At -20°C the proton-NMR spectrum shows sharp signals for the C_2H_4 and H protons, the former being splitted into two multiplets and the latter into a doublet of doublets by the interaction with the rhodium and phosphorus nuclear spins $\frac{1}{2}$. At room temperature and above the hydrido and ethylene protons appear as broad bands indicating that exchange between these groups occurs. This is confirmed by an experiment in which D_2O is added to the solution at -20 C. The ^{1}H-NMR signals of the hydrido and ethylene protons disappear and analysis of the solution demonstrates that $[(C_5H_5)RhD(C_2D_4)PMe_3]^+$ has been formed. The equilibrium between the hydrido-ethylene-rhodium and ethyl-rhodium complexes is shifted to the right by the addition of ethylene

$$[(C_5H_5)RhH(C_2H_4)PMe_3]^+ + C_2H_4 \rightleftharpoons [(C_5H_5)Rh(C_2H_5)(C_2H_4)PMe_3]^+$$
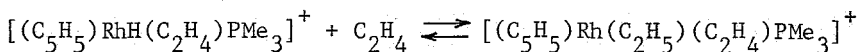
Apparently the ethylene is bonded to the vacant site that is created by the transformation of $H-Rh-C_2H_4$ into $Rh-C_2H_5$.

Hydrido-olefin-metal complexes are rarely observed but also alkyl-metal complexes are hard to isolate. For a long time this has been ascribed to a weak transition-metal-carbon σ-bond, but now it is generally agreed that the reason is kinetic rather than thermodynamic. Alkyl transition-metal complexes are very susceptible to the so-called β-H-elimination reaction, the reverse of the olefin insertion reaction given above. Stable transition-metal alkyls can be prepared but they must either have no β hydrogen atoms, or the coordination around the metal atom must be complete so that the β hydrogen atom cannot be added to the metal atom. For alkyl-metal complexes with vacant coordination sites the β-H-elimination usually is rapid, but bulky ligands may slow it down.

Dimerisation, oligomerisation and Ziegler-Natta polymerisation of olefins have long been assumed to involve insertion of the olefin into the metal-carbon bond of an intermediate metal-alkyl [6]. Green, Rooney and coworkers have pointed out, however, that there are no unambiguous examples where a well characterised alkyl-olefin-metal complex has been observed to react to the expected insertion product [7]. This has led them to suggest an alternative mechanism for apparent insertion reactions which involves α-elimination of hydrogen atoms to form a transient carbene complex and carbon-carbon formation via reaction between the carbene and the π-bonded olefin, analogous to the reaction in metathesis. The polymerisation of propene is then described by the following scheme:
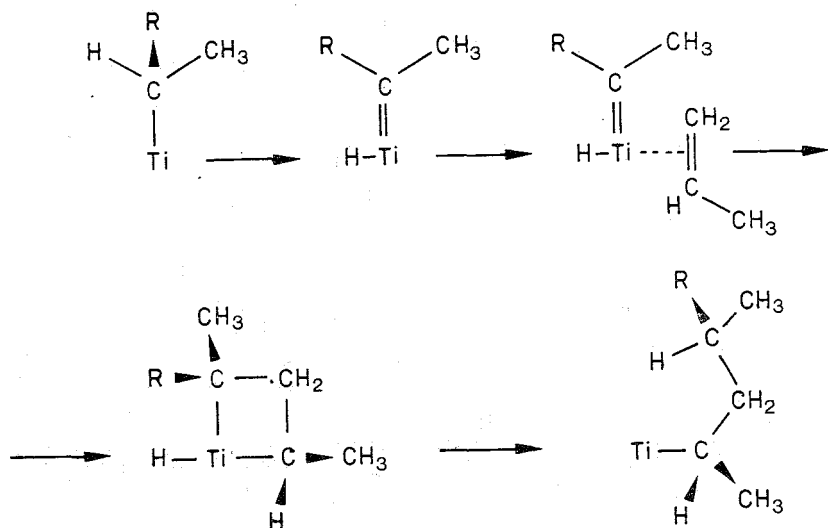
On the other hand, Evitt and Bergman have recently clearly
demonstrated that the formation of propene and methane in the
reaction of ethylene with η^5-cyclopentadienyl(triphenylphosphine)-
dimethylcobalt is due to insertion rather than α-elimination [8]:

$$CpCo(PPh_3)(CH_3)_2 + 2\ C_2H_4 \longrightarrow CpCo(PPh_3)(C_2H_4) + CH_4 + C_3H_6$$
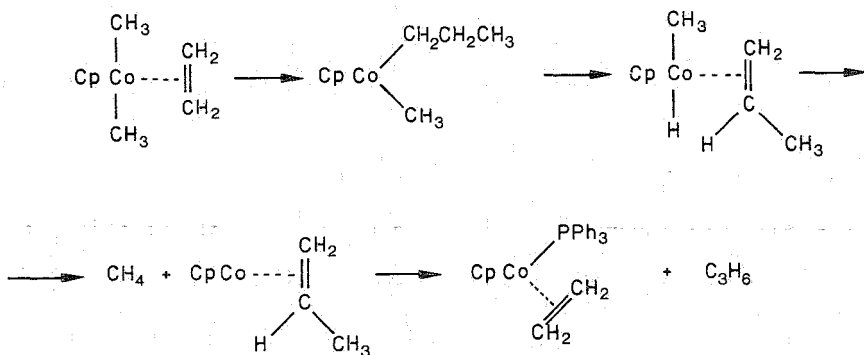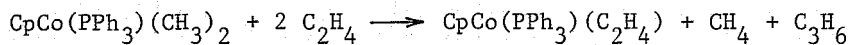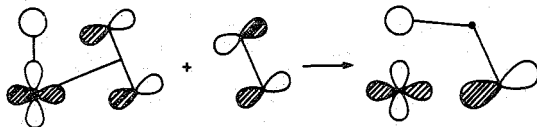
When the perdeutero cobalt complex was treated with C_2H_4 mass spectral analysis showed CD_3H and propene-d_3 to be formed, while in the reaction of C_2D_4 with the perdeutero cobalt complex CD_4 was formed. Apparently, the hydrogen atom that is added to the methyl group to form methane is derived from the ethylene and not from other hydrogen sources in the system, and a complete methyl group is transferred to the ethylene in the formation of propene. Since in the insertion pathway three of the methane hydrogens derive from the initial methyl group and the fourth from ethylene, whereas in the α-elimination pathway the fourth hydrogen comes from the second methyl group and a methylene is transferred to ethylene, the experimental results demonstrate that insertion rather than α-elimination is responsible for the methylation of ethylene by the cobalt complex.
Although this single example of course does not prove that the α-elimination pathway has to be excluded for all apparent insertion reactions, it certainly has brought back confidence in the 'old' insertion pathway.

The olefin insertion reaction has attracted also the attention of theoreticians and in a recent article Thorn and Hoffmann give a lucid explanation of the factors that make the transition from a π-bonded olefin into a σ-bonded alkyl group possible [9]. They argue that the approach of a hydrido ion to an ethylene molecule, in the absence of a transition metal atom, leads to a repulsive interaction between the H ion and the approaching C atom because of the fact that the highest occupied molecular orbital is an antibonding combination between the ethylene π and the hydrido 1s orbitals
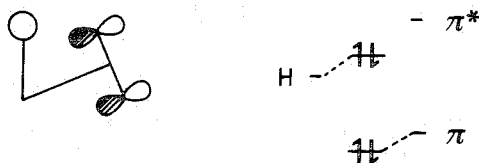
Adding a transition metal atom to the scene leads to a diminished repulsive interaction between the hydrido ion and the approaching C atom. The hydrido-π olefine molecular orbital now forms bonding and antibonding combinations with the $d_{x^2-y^2}$ orbital. At the same time this d orbital will combine with the ethylene π* orbital. This results in some mixing of the π and π* orbitals and in a weakening of the repulsion between the approaching H and C atoms. Concurrently the orbital develops into a bonding Pt-C orbital

The interaction of the $d_{x^2-y^2}$ orbital with both π and π^* orbitals, which is allowed by the low symmetry in the transition state, in effect leads to a rehybridisation of the π and π^* orbitals back into two 2p orbitals localised on the two carbon atoms. The energy increase that would go with the rehybridisation is largely surpressed by the interaction with the d orbitals of the metal atom

$$d_{x^2-y^2} \quad \text{---} \quad \text{---} \quad -\pi^*$$
$$\text{---} \quad -H$$
$$\text{---} \quad -\pi$$

The antibonding combination of $d_{x^2-y^2}$, π and π^* is highly unfavourable. As a consequence this orbital must be empty for the total energy of the system to remain low. This explains why the olefin insertion proceeds especially smoothly in square planar d^8 complexes. It also means that the reverse reaction, the β-H-elimination, can only proceed when the resulting H atom and π-bonded olefin are able to form part of a square planar arrangement around the metal atom. Dissociation of a phosphine ligand from $Pt(C_4H_9)_2(PR_3)_2$ thus is a prerequisite for β-elimination and added phosphine can surpress it entirely [10]. The related macrocyclic compound is much more stable since the coplanar $Pt-CH_2-CHR-H$ orientation cannot be achieved [11].

$$P$$
$$|$$
$$P \text{---} Pt \text{---} CH_2$$
$$|\qquad|$$
$$H_2C \quad CH_2$$
$$\quad CH_2$$

Oxidative addition

Oxidative addition reactions are a class of reactions of transition-metal complexes in which ligands are added to the metal atom and in which the formal charge of the central metal increases. These reactions can also be described as 1,1 addition to the metal atom

$$XY + M\text{-}L \rightleftharpoons \overset{\displaystyle L}{\underset{\displaystyle}{X\text{-}M\text{-}Y}}$$

The following reactions constitute examples of oxidative additions:

In the second reaction the oxidative addition of methyliodide is followed by methyl migration (CO insertion). With regard to the stereochemistry of oxidative addition, in all cases studied up to now hydrogen has been found to add in a cis fashion, while the addition of alkylhalides has been reported to be both cis and trans, but most often trans.

The oxidative addition reactions can be understood by looking at the effective number of valence electrons (NVE) around the metal atom. Usually the d^8 complexes of Ru(0), Rh(I), Ir(I), Pd(II) and Pt(II) are square planar complexes with 16 valence electrons or they are trigonal bipyramidal 18 electron complexes. Species such as H_2, X_2, HX, RX, RCOX, RSnX can add to these compounds. Addition to the square planar, 16 electron, d^8 complexes leads directly to octahedral, 18 electron, d^6 complexes whereas addition to the five coordinate, 18 electron, d^8 complexes leads to octahedral complexes only after dissociation of one of the original ligands.

The influence of the metal atom in oxidative addition reactions can be rationalised by taking into account its nucleophilicity. A high electron density on the metal atom favours oxidative addition and the largest metals of the third row, in the lowest oxidation state, therefore show the greatest tendency to undergo oxidative addition [12]. By a similar reasoning it is understandable that strongly donating ligands like carbonyls and phosphines promote the oxidative addition.

The influence of metal basicity is evident when comparing two metals like iridium and rhodium. With $IrCl(CO)(PPh_3)_2$ the addition of CH_3I is complete and irreversible, while for the rhodium analog it is quite reversible. The reverse reaction is called reductive elimination and together with oxidative addition

it plays an important role in the homogeneous catalysis of hydro-
formylation and of the carbonylation of methanol to acetic acid.

REACTION MECHANISMS

    Having discussed the basic reactions, we will in this section
clarify part of the chemistry involved in homogeneous catalysis
and in particular we will discuss the hydrogenation of olefins,
the carbonylation reaction (as used in the hydroformylation
and methanol carbonylation processes), and the oxidation of
ethylene to acetaldehyde.

Olefin hydrogenation

    Many metal complexes are able to activate hydrogen, some of
the best known are $RuCl_6^{3-}$, $Co(CN)_5^{3-}$, and $RhCl(PPh_3)_3$. Especially
the latter complex, the so-called Wilkinson's complex, is very
effective in homogeneous hydrogenation. Although some details
are still to be clarified, it is generally believed that the
activity of this catalyst in the hydrogenation of olefins is
explained by the following scheme [13].
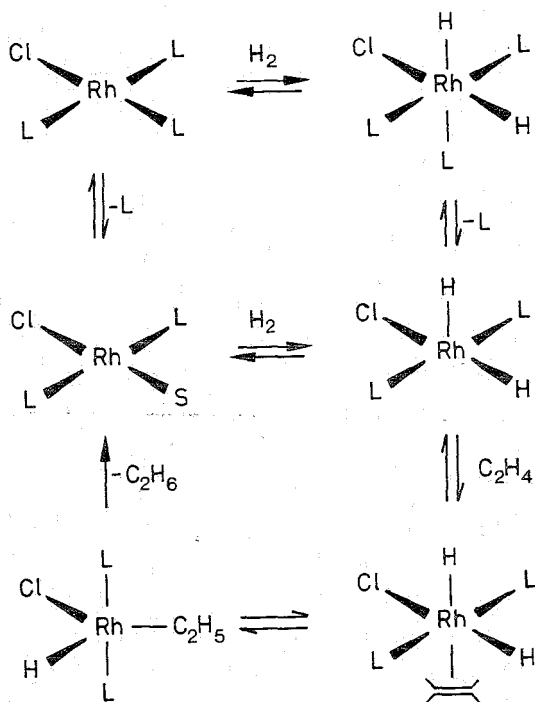
The first step is oxidative addition of H_2 to the rhodium complex
followed by ligand dissociation, or vice versa. Then complex
formation with the olefin takes place and insertion of the
olefin into the Rh-H bond. Reductive elimination of the alkane
regenerates the catalytically active species. Note that whenever
an oxidative addition occurs in a catalytic cycle a reductive
elimination has to follow in order to close the catalytic cycle.

Carbonylation

     A reaction that is of great industrial importance is the
hydroformylation reaction of α olefins to aldehydes. The aldehydes
are further hydrogenated to alcohols which can be used as such as
solvents or can be further processed to plasticisers and detergents.
Whereas cobalt carbonyl is still the most widely used catalyst
new processes use a rhodium catalyst such as $RhCl(CO)(PPh_3)_2$.
Rhodium catalysts are very active and, even more important, can
be used at much lower pressures. They also give a higher ratio
of linear-to-branched aldehydes.

     The reaction mechanism is complex and, depending on the
concentration of phosphine, involves an associative mechanism in
which the olefin adds to a five coordinate rhodium complex or a
dissociative mechanism in which the olefin adds to a four
coordinate complex [14]. The reaction sequence mainly consists of
1) addition of the olefin followed by olefin insertion into the
   Rh-H bond
2) migration of the resulting alkyl group to a CO ligand (CO
   insertion)
3) oxidative addition of H_2 followed by reductive elimination of
   the aldehyde.
At high triphenylphosphine concentrations the lower catalytic cycle,
the associative route, is prefered. The olefin is added to a
five coordinated rhodium complex and the rather large steric
hindrance induces a high linear-to-branched ratio of the aldehyde
product. At too high phosphine concentrations the catalyst
activity decreases due to the formation of the inactive
$RhH(CO)(PPh_3)_3$ species. At low phosphine concentrations the
dissociative mechanism is dominant. Because of the fact that the
olefin is now added to a four coordinated species the aldehyde
product will have a lower linear-to-branched ratio. Too high
pressures of CO lead to the formation of $Rh(COR')(CO)_2(PPh_3)_2$
which is inable to undergo the oxidative addition of H_2. Since
the oxidative addition is assumed to be the rate determining
step high CO pressures will inhibit the reaction. In agreement
with this infrared experiments under high pressure have
demonstrated the presence of metal acyl complexes, indicating
that CO insertion is relatively fast and oxidative addition of
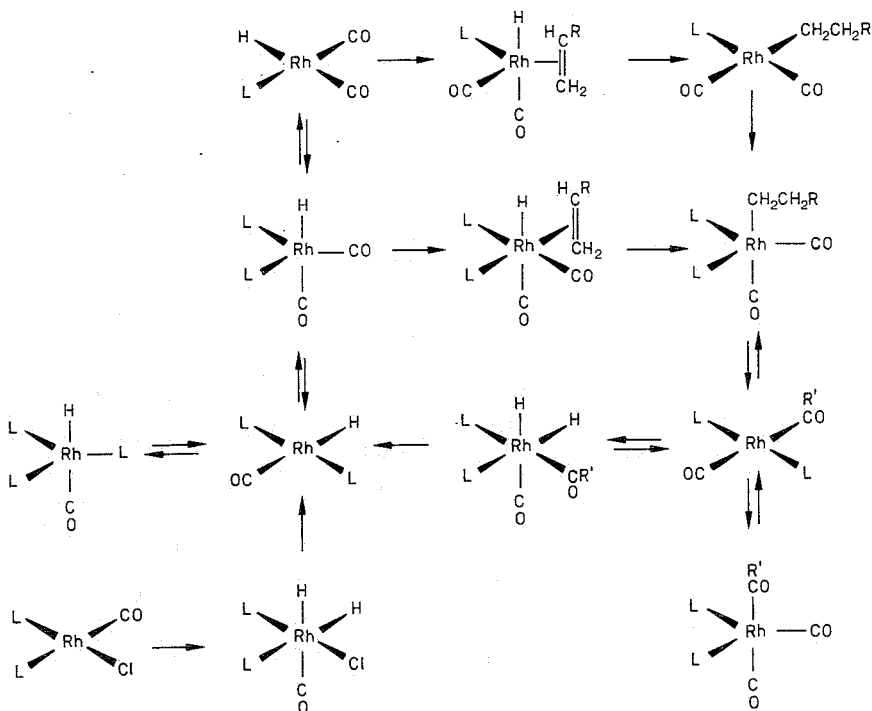
H_2 is slow. For internal olefins no metal acyl complex is observed but only the metal hydrido complex. Apparently the coordination or the insertion of internal olefins is slow.

The better activity of the rhodium catalyst compared to the cobalt catalyst undoubtedly arises from the larger tendency of rhodium for oxidative addition. Also iridium compounds are active catalysts and $HIr(CO)_3PR_3$ with R = isopropyl has been used by Whyman in a very instructive breakdown of the hydroformylation catalytic cycle in its individual steps [15]. By means of infrared spectroscopy he observed that when treating the iridium compound with 14 atm ethylene at $50°C$ after 30 minutes conversion into $(C_2H_5)Ir(CO)_3PR_3$ had occurred

$$HIr(CO)_3PR_3 + C_2H_4 \longrightarrow (C_2H_5)Ir(CO)_3PR_3$$

On venting the excess of ethylene from the solution and replacing it with 14 atm CO at $50°C$ new infrared bands appeared which demonstrated that CO insertion had occurred

$$(C_2H_5)Ir(CO)_3PR_3 + CO \longrightarrow (C_2H_5CO)Ir(CO)_3PR_3$$

Replacing the excess CO by 14 atm H_2 led to the disappearance of the acyl infrared bands, the appearance of a propionaldehyde band and the reappearance of the bands of the original iridium complex·

$$(C_2H_5CO)Ir(CO)_3PR_3 + H_2 \longrightarrow HIr(CO)_3PR_3 + C_2H_5CHO$$
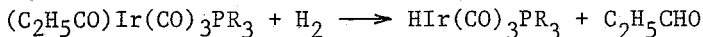
The sequence of reactions could be repeated many times by pressurising with the respective gases, the intensity of the aldehyde absorption band increasing at the end of each cycle. This clearly proofs that the above reaction steps form part of the hydroformylation sequence and that the catalyst in this case is a mononuclear iridium carbonylphosphine complex.

The chemistry of the carbonylation of methanol to acetic acid

$$CH_3OH + CO \longrightarrow CH_3C \overset{\displaystyle \nearrow O}{\underset{\displaystyle \searrow OH}{}}$$
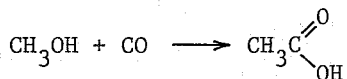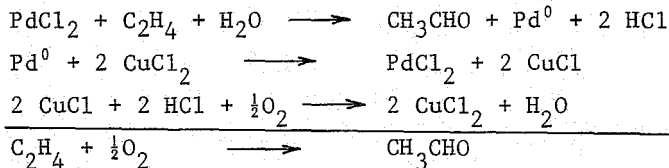
is related to hydroformylation chemistry. Also in this case rhodium is a better catalyst than cobalt, giving a higher selectivity at much lower pressure. The mechanism goes via oxidative addition of methyl iodide, insertion of CO into the Rh-methyl bond and reductive elimination of acetyliodide [16]. The acetyl iodide reacts further with methanol to acetic acid and methyl iodide, that reenters the catalytic cycle. Also here infrared spectroscopy proved helpful in demonstrating the occurrence of the separate reaction steps. When adding excess methyl iodide to a solution of $[Rh(CO)_2I_2]^-$ at room temperature, Forster [17] observed the infrared spectrum of $[(CH_3CO)Rh(CO)I_3]^-$. This anion could even be isolated in crystalline form, in the form of a dimer with a Rh-I bridge, when large organic cations were added as counterions. The reversibility of the CO insertion was demonstrated by heating of this crystalline material under vacuum. On bubbling CO through a solution of the rhodium acetyl complex very rapid formation of a new species is observed, followed by slow decomposition to the original $[Rh(CO)_2I_2]^-$ complex.

Kinetic data have shown that the methanol carbonylation reaction is first order in both rhodium and methyl iodide and zero order in CO, suggesting that the addition of methyl iodide is rate determining. Forster has confirmed this by observing that under in situ conditions only the infrared bands of $[Rh(CO)_2I_2]^-$ were present [17].

$$CH_3COI + CH_3OH \longrightarrow CH_3COOH + CH_3I$$
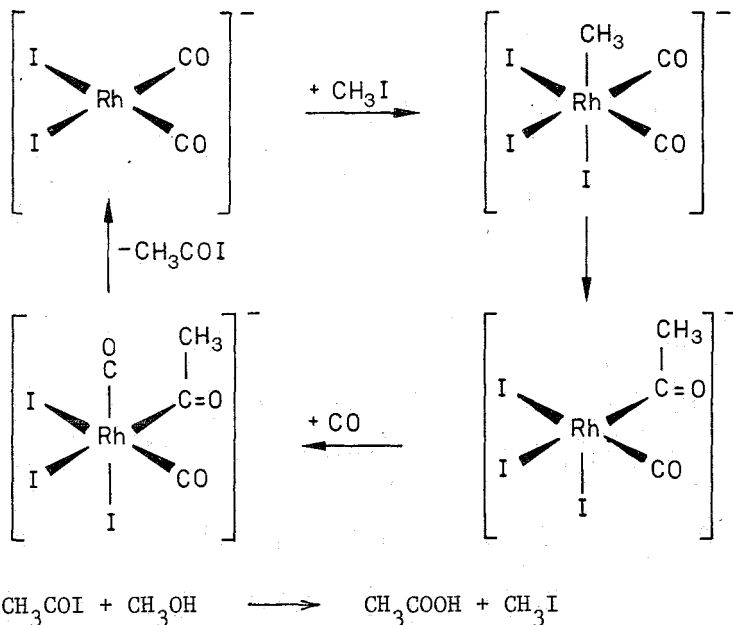
The Wacker process

The oxidation of ethylene to acetaldehyde with platinum group metals has been known since 1894. Bubbling ethylene through a solution of K_2PtCl_4 first the familiar Zeise's salt is formed $K[PtCl_3(C_2H_4)]$, but heating the solution results in the formation of acetaldehyde and metallic platinum. It lasted until the end of the fifties before Smidt c.s. discovered that the metal formed during the oxidation reaction can be reoxidised in situ by cupric chloride [18]. When combining this with the fast reoxidation of cuprous chloride by oxygen, the reaction sequence is turned into a catalytic cycle. This catalytic reaction is now known as the Wacker process, a very successful industrial process for producing acetaldehyde

$$PdCl_2 + C_2H_4 + H_2O \longrightarrow CH_3CHO + Pd^0 + 2\ HCl$$
$$Pd^0 + 2\ CuCl_2 \longrightarrow PdCl_2 + 2\ CuCl$$
$$\underline{2\ CuCl + 2\ HCl + \tfrac{1}{2}O_2 \longrightarrow 2\ CuCl_2 + H_2O}$$
$$C_2H_4 + \tfrac{1}{2}O_2 \longrightarrow CH_3CHO$$

Nickel and platinum show some activity in this reaction too, but they are inferior to palladium. Most probably nickel binds

ethylene too weakly and platinum binds ethylene too strongly.
This is another illustration of the rule that some bonding
between catalyst and substrate is required for catalysis, but
weak bonding is not good enough and too strong bonding is not
good either.

The mechanism of the Wacker reaction has attracted a great
deal of attention. Kinetic studies indicate that the rate is
described approximately by

$$\frac{d[H_3CCHO]}{dt} = \frac{k[C_2H_4][PdCl_4^{2-}]}{[H^+][Cl^-]^2}$$

This rate equation can be explained by assuming that there are
three pre-equilibria before the rate determining step:
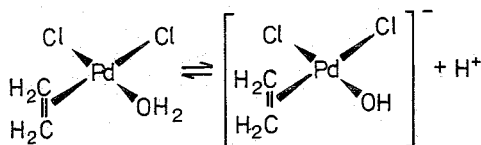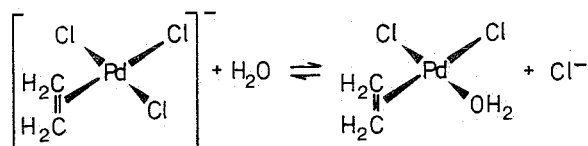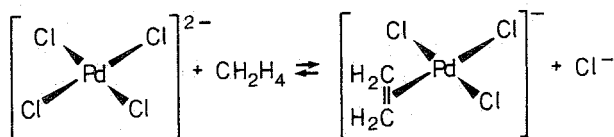
The rate determining step is the transformation of the hydroxy
ethylene palladium complex into the β-hydroxy-ethyl palladium
complex

$$[(C_2H_4)PdCl_2(OH)]^- + H_2O \longrightarrow [(HO-CH_2-CH_2)PdCl_2(H_2O)]^-.$$

The steric course of this rearrangement has long been assumed to
go via cis migration of the hydroxyl group to the coordinated
olefin (or to put it wrongly, insertion of the olefin into the
Pd-OH bond). Recent studies have cast doubt on this, however,
and have suggested that the rearrangement involves nucleophilic
trans attack of water from outside the coordination sphere of
the palladium [19, 20].

Cis and trans additions to ethylene follow different steric
courses and by using dideutero-ethylene of a specific con-
figuration it should be possible to distinguish between these
two possibilities. Thus it has been found that when cis-1,2-
dideutero ethylene is used as a reactant in the Wacker reaction
a hydroxylethyl palladium complex is formed that can be trapped
with CO into the trans-2,3-dideutero propiolactone [20]. This
result implies that the hydroxylation of ethylene has taken place
from outside the coordination sphere of palladium.
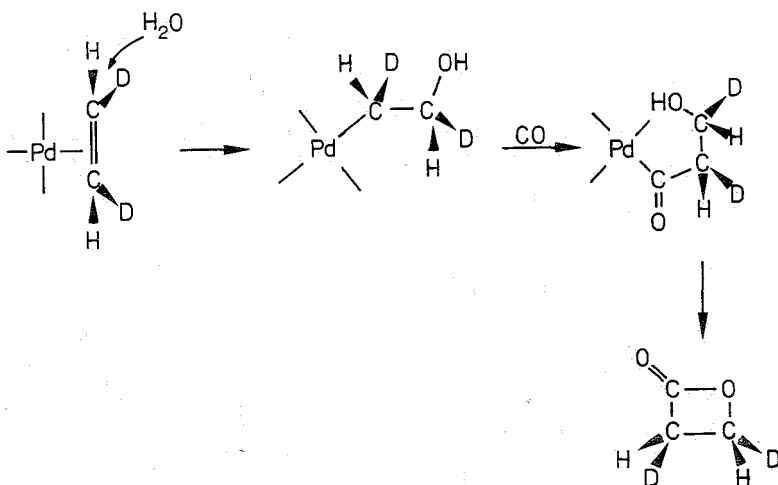
It may well be that both intra and inter molecular addition are
possible and that depending on the reaction conditions one or
the other route dominates. In that respect it has to be noted
that the insertion step in the Wacker reaction is different from
the examples given in hydroformylation and carbonylation chemistry
in that it is the only case in which a strongly nucleophilic
solvent is used. This may be the reason that in the Wacker
reaction trans attack by a solvent molecule can compete with cis
attack by a nucleophilic ligand inside the coordination sphere
of the metal.

Another point that is as yet unsolved is the rearrangement
of the β-hydroxy ethyl group into acetaldehyde. It may well be
that it proceeds via a reaction sequence of β-H-elimination,
migration of the H atom to the other carbon atom, followed
by β-H-elimination from the hydroxy group. In agreement with
this sequence the oxidation of C_2D_4 gives exclusively CD_3CDO.
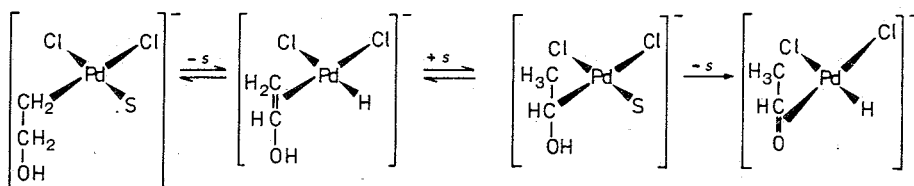
REFERENCES

1. R.F. Heck, 'Organotransition metal chemistry', Acad. Press, New York, 1974.
2. K. Noack and F. Calderazzo, J. Organometal. Chem. 10, 101 (1967).
3. A. Davison and N. Martinez, J. Organometal. Chem. 74, C17 (1974).
4. J. Chatt, R.S. Coffey, A. Gough and D.T. Thompson, J. Chem. Soc. A, 190 (1968).
5. H. Werner and R. Feser, Angew. Chem. 91, 171 (1979).
6. P. Cossee, J. Catal. 3, 80 (1964).
7. K.J. Ivin, J.J. Rooney, C.D. Stewart, M.L.H. Green and R. Mahtab, J.C.S. Chem. Comm. 604 (1978).
8. E.R. Evitt and R.G. Bergman, J. Am. Chem. Soc. 101, 3973 (1979).
9. D.L. Thorn and R. Hoffmann, J. Am. Chem. Soc. 100, 2079 (1978).
10. G.M. Whitesides, J.F. Gaasch and E.R. Stedronsky, J. Am. Chem. Soc. 94, 5258 (1972).
11. J.X. McDermott, J.F. White and G.M. Whitesides, J. Am. Chem. Soc. 98, 6521 (1976).
12. R.S. Nyholm and K. Vrieze, J. Chem. Soc. 5337 (1965).
13. J. Halpern, in 'Organotransition Metal Chemistry' (ed. Y. Ishii and M. Tsutsui), Plenum Press, New York, 1975, p. 109.
14. R.L. Pruett, Adv. Organometal. Chem. 17, 1 (1979).
15. R. Whyman, J. Organometal. Chem. 94, 303 (1975).
16. J.F. Roth, J.H. Craddock, A. Hershman and F.E. Paulik, Chem. Techn. 600 (1971).
17. D. Forster, J. Am. Chem. Soc. 98, 846 (1976); Adv. Organometal. Chem. 17, 225 (1979).
18. J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Rüttinger and H. Kojer, Angew. Chem. 71, 176 (1959); Angew. Chem. Int. Ed. 1, 80(1962).
19. J.E. Bäckvall, B. Åkermark and S.O. Ljunggren, J.C.S. Chem. Comm. 264 (1977).
20. J.K. Stille and R. Divakarumi, J. Organometal. Chem. 169, 239 (1979).