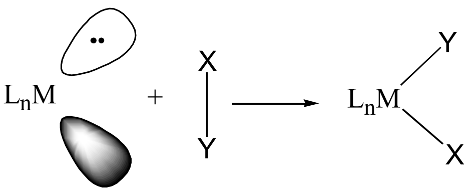
CHEM3012 - Core Chemistry 3

Reaction Mechanisms in Organometallic Chemistry

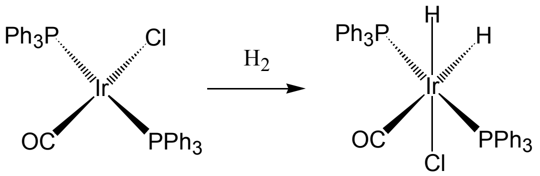
In an earlier section of this lecture course we considered the mechanisms of substitution reactions in organometallic species, and noted that the consequence of the 18 electron rule was to favour dissociative substitution reactions. In the lecture course *Organometallic Reaction Chemistry* in module CHEM3021 *Inorganic Concepts and Applications* we discussed electrophilic addition, nucleophilic addition, electrophilic abstraction and nucleophilic abstraction reactions of organometallic species, noting how these can be used to change the ligands attached to a metal, and the role of the metal centre in directing the chemistry, often changing the reactivity of an organic ligand from what would be observed for the free organic.

We now consider the two most fundamental reactions of organometallic chemistry, namely *insertion* (and its reverse *elimination*) and *oxidative addition* (and its reverse *reductive elimination*). Combining these two reactions in appropriate sequence with appropriate substrates gives rise to the enormous subject of transition metal catalysis.

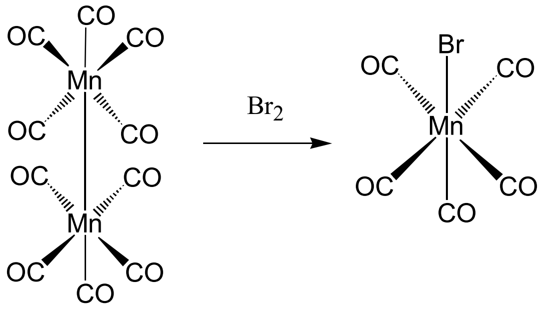
6. Oxidative addition and reductive elimination



We have seen how various 2e ligands can enter the coordination sphere of a metal by *substitution*. We now look at a general method for simultaneously introducing pairs of 1e ligands, A and B, by the *oxidative addition* of an A-B molecule, a reaction of great importance both in synthesis and in catalysis. The reverse reaction, *reductive elimination*, leads to the extrusion of A--B from an M(A)(B) complex and is often the product-forming step in a catalytic reaction. In the oxidative direction, we break the A-B bond and form an M-A and an M-B bond. Since A and B are 1e X^- type ligands, the oxidation state, electron count, and coordination number all increase by two units during the reaction. It is the change in formal oxidation state that gives the reaction the name oxidative addition.



Oxidative additions proceed by a great variety of mechanisms, but because the electron count increases by two units, a vacant 2e site is usually required on the metal. We can either start with a 16e complex, or a 2e site can be opened up in an 18e complex by the loss of a ligand. The change in oxidation state means that a metal complex of a given oxidation state must also have a stable oxidation state two units higher to undergo oxidative addition (and vice versa for reductive elimination).



There is also a binuclear variant of oxidative addition, in which each of two metals changes its oxidation state, electron count, and coordination number by one unit instead of two. This typically occurs in the case of a 17e complex which has a stable oxidation state more positive by one unit, or in the reaction of metal-metal bonded species.

In the overall process of Oxidative Addition, whatever the mechanism adopted, there is a net transfer of a pair of electrons from the metal into the σ^* orbital of the A-B bond, and of the A-B σ electrons to the metal. This cleaves the A-B bond and makes an M-A and an M-B bond. The reaction is promoted by starting with a metal in a reduced state; only rarely do metals in an oxidation state higher than (II) retain sufficient reducing character to undergo oxidative addition, except with powerful oxidants like Cl_2. Conversely, a highly oxidised metal is more likely to undergo reductive elimination.

Oxidative addition is the inverse of reductive elimination and vice versa. In principle each reaction is reversible, but in practice they tend to go in the oxidative or reductive direction only. The position of equilibrium in any particular case is governed by the overall thermodynamics; this in turn depends on the relative stabilities of the two oxidation states and the balance of the A-B versus the M-A and M-B bond strengths. Alkyl hydride complexes commonly eliminate alkane, but only rarely do alkanes oxidatively add to a metal. Conversely, alkyl halides commonly add to metal complexes, but the adducts rarely reductively eliminate the alkyl halide. Third- row elements, which tend to have stronger metal- ligand bonds tend to give more stable adducts. Occasionally, an equilibrium is established so that both the forward and back reactions are observed. The addition of H_2 to give the metal dihydride is an example.

$$[Ir(COD)_2]^+ + H_2 \rightleftharpoons [IrH_2(COD)_2]^+ \text{ (COD = 1,4-cyclooctadiene)}$$

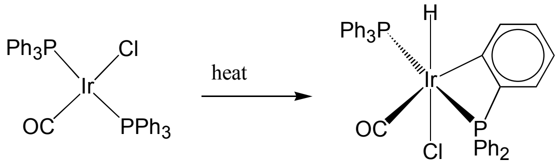
These reactions are not limited to transition metals, perhaps the most familiar oxidative addition is the formation of Grignard reagents, but it can occur whenever an element has two accessible oxidation states two units apart. The equations illustrate oxidative addition to Mg(0), P(III), and C(-II).

$$\text{Me-Br} + \text{Mg} \rightarrow \text{Me-Mg-Br}$$

$$\text{Cl-Cl} + PCl_3 \rightarrow PCl_5$$

$$\text{RCOO-H} + :CH_2 \rightarrow \text{RCOO-}CH_2\text{-H}$$

The unusual feature of oxidative addition reactions of transition metals is the wide range of addenda A-B that can be involved, including such normally unreactive molecules as silanes, H_2, and even alkanes and C-H bonds, as in the ortho-metallation example shown here. Oxidative additions are a very diverse group of reactions from the point of view of mechanism, and we shall therefore look at them type by type.



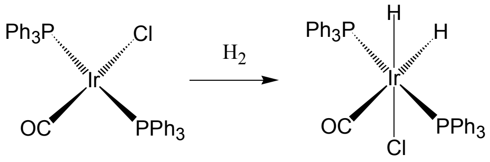
6.1. Kinetics and rate law of oxidative addition

Two typical reactions are used to illustrate.

6.1.1. Oxidative addition of H_2 to Vaska's complex.

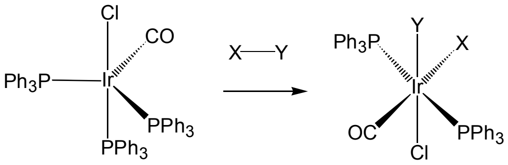
This is a 16 electron d^8 square planar complex, so it is already coordinatively and electronically unsaturated.

Rate = $k_2[Ir(I)][H_2]$ hence simple second order kinetics



6.1.2. Oxidative addition to an 18 electron complex

In this case the 18 electron complex needs to dissociate a ligand before the oxidative addition can occur. A more complex rate law is observed:



$$\text{Rate} = \frac{k_1k_2[Ir(1)][X - Y]}{k_{-1}[PPh_3] + k_2[X - Y]}$$

As you should be aware from earlier lecture courses, such a rate law is typical for a reaction which involves an equilibrium step (k_1 and k_{-1}) followed by an irreversible step (k_2).

$$Ir(CO)Cl(PPh_3)_3 \rightleftharpoons Ir(CO)Cl(PPh_3)_2 + PPh_3$$

$$Ir(CO)Cl(PPh_3)_2 + X\text{-}Y \rightarrow Ir(CO)Cl(X)(Y)(PPh_3)_2$$

6.2. Mechanisms of oxidative addition

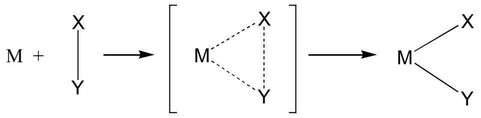
The following mechanisms are known:

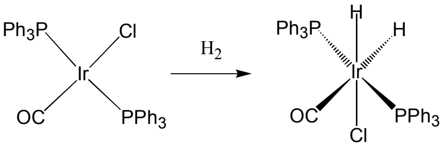
- Concerted
- Nucleophilic S_N2
- Nucleophilic ionic (has some of the character of S_N1)
- Radical chain mechanism
- Stepwise Radical mechanism

The mechanism which applies in an particular case will depend on the substrate which is adding to the metal, the nature of the metal centre including other ligands, and the solvent. We will discuss each mechanism in turn.

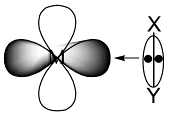
6.2.1. Concerted Oxidative addition

Nonpolar addenda, such as H_2 and R_3SiH, tend to react by a three-centred transition state or intermediate of the type shown below. The best studied case is the addition of H_2 to 16e square p1anar d^8 species, such as *Vaska's complex.* The products are 18e d^6 octahedral dihydrides.

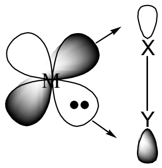




The *cis* isomer is formed first, but subsequent rearrangement **can** give the *trans* dihydride. The lumo in a d^8 square planar complex has $d_{x^2-y^2}$ character, and so tends to lie in the plane of the ligands. However, the metal may re-hybridise by folding back two of the mutually trans ligands to direct an empty orbital in the direction of the incoming H_2 ligand. The oxidative addition then proceeds by donation of the X-Y bond pair into this vacant orbital, and back-donation from a filled metal d orbital to the X-Y σ* orbital. A vacant site capable of accepting two electrons must be present on the metal for the reaction to occur, so that in 18e complexes ligand dissociation must take place first.



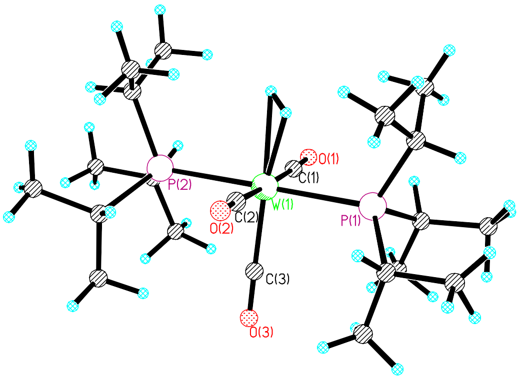
Donation from X–Y sigma
to empty metal d orbital



Donation from metal
to X–Y σ*

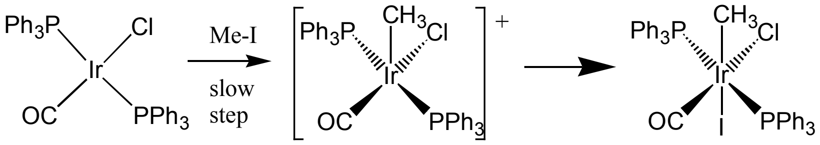
The reactions are usually second order. They are little affected by the polarity of the solvent, but may be accelerated to some extent by electron- releasing phosphines. The C-H and Si-H bonds of various hydrocarbons and silanes can also oxidatively add to metals. Among different types of C-H bonds, those of arenes are particularly prone to do this because of the high thermodynamic stability of the aryl hydride adduct.

Sometimes the metal centre is a good σ acceptor but a poor π-donor and in these cases the oxidative addition is then frozen in a partially completed sense, and then molecular dihydrogen complexes can be isolated and studied. Some of these even appear to be in equilibrium with the oxidative addition product: a classical dihydride. The first characterised η^2-H_2 complex was $W(P^iPr_3)_2(CO)_3(H_2)$, whose molecular structure (determined by neutron diffraction) is shown here.



6.2.2. S_N2 Reactions

The S_N2 mechanism is often found in the addition of methyl, allyl, acyl, and benzyl halides (polar X-Y bonds) to species such as Vaska's complex. Like the concerted type, they are second-order reactions, but they are accelerated by using polar solvents, and show a more negative $\Delta S^{\ddagger}$. All this is consistent with an ordered, polar transition state, and is very similar to what is seen for S_N2 reactions in organic chemistry. The reaction as discussed here leads to specifically trans addition.



Of the two steps in this reaction, the first involves oxidation by two units, but no change in the electron count (Me^+ is a 0e reagent), and the second, an increase by 2e in the electron count (Cl^- is a 2e reagent), but no change in the oxidation state. Only the two steps together constitute the full oxidative addition.

If the R group is chiral at the carbon bearing the halogen, this mechanism leads to inversion at the chiral centre.

When an 18e complex is involved, the first step can proceed without the necessity of losing a ligand first. Only the second step requires a vacant 2e site. In some cases the product of the first step is stable and does not lose a ligand to admit the halide anion. This is sometimes loosely called an oxidative addition, but it is better considered as an electrophilic attack at the metal.

$$(C_5H_5)Ir(CO)L + MeI \rightarrow [(C_5H_5)Ir(CO)LM]^+ I^-$$

The more nucleophilic the metal, the greater its reactivity in S_N2 additions, as illustrated by the reactivity order for some Ni(0) complexes:

$$Ni(PR_3)_4 > Ni(PAr_3)_4 > Ni(PR_3)_2(alkene) > Ni(PAr_3)_2(alkene) > Ni(cod)_2 \text{ (R = alkyl; Ar = aryl).}$$

Steric hindrance at carbon slows the reaction, so we find the reactivity order:

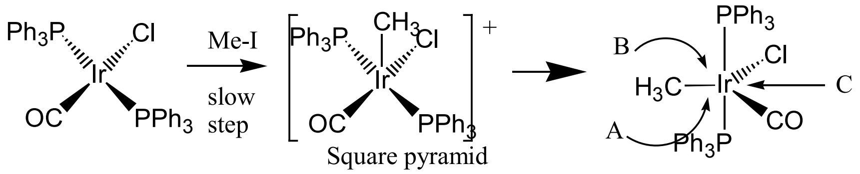
$$MeI > EtI > i\text{- }PrI.$$

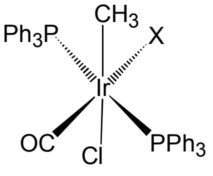
A better leaving group, X at carbon, accelerates the reaction, which gives rise to the reactivity order:

$$ROSO_2(C_6H_4Me) > RI > RBr > RCl.$$

6.2.3. Ionic oxidative addition mechanism

This reaction mechanism is very similar to the previous one, but occurs in more polar solvents, such as methanol. Under these conditions the 5 coordinate square-based pyramid intermediate, formed by nucleophilic attack of the metal on the substrate, has sufficient lifetime to rearrange to a trigonal bipyramid before the halide ion attacks.





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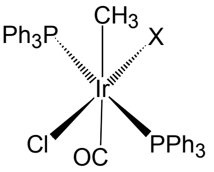

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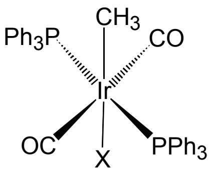

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6.2.4. Radical Mechanisms

Radical mechanisms in oxidative additions were recognised later than the S_N2 and the concerted processes. A troublesome feature of these pathways is that minor changes in the structure of the substrate or of the complex, or in impurities present in the reagents or solvents, can sometimes be enough to change the rate, and even the predominant mechanism, of a given reaction. Sharp disagreements have turned on questions of repeatability and on what types of experimental evidence should be considered as valid mechanistic criteria. For example, the use of radical traps, such as RNO, has been criticised on the grounds that these may initiate a radical pathway for a reaction that otherwise would have followed a non-radical mechanism. Much needs to be more firmly established in this difficult area.

Two subtypes of radical processes are now distinguished: the non-chain and the chain.

6.2.4.(a). Non-chain radical mechanism

This variant is believed to operate in the additions of certain alkyl halides, RX, to $Pt(PPh_3)_3$ (R = Me, Et; X = I. R = $PhCH_2$; X = Br).

$PtL_3 \rightarrow PtL_2$ this reaction is fast

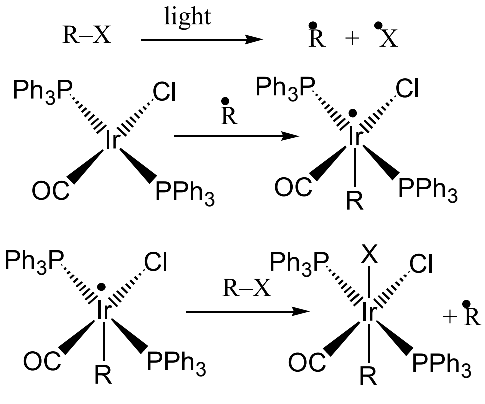
$PtL_2 + RX \rightarrow PtXL_2 + R\bullet$ slow

$PtXL_2 + R\bullet \rightarrow RPtXL_2$ this reaction is fast

The key feature is the 1e oxidation of the metal by the alkyl halide as a result of an X atom transfer from RX to the metal. This produces the pair of radicals, which combine to give the product. As in the S_N2 process, a reaction following the radical mechanism goes faster the more reducing (basic) the metal and the more oxidisable the substrate which gives the reactivity order RI > RBr > RCl. Unlike the S_N2 process, the reaction is very slow for tosylates [e.g., $ROSO_2(C_6H_4Me)$] and goes faster the more stable the $R^{\cdot}$ radical, giving rise to the order of R group reactivity: $3^{o} > 2^{o} > 1^{o} > \text{Me}$.

6.2.4.(b). Radical chain mechanism

This has been identified in the case of the reaction of EtBr and $PhCH_2Br$ with the PMe_3 analogue of Vaska's complex. A radical initiator $Q^{\cdot}$ (e.g., a trace of air or peroxide in the solvent) is required to set the process going by addition to the metal. The resulting metal-centred radical abstracts X from the halide and leaves $R^{\cdot}$, which is believed to be the chain carrier. The alkyl group therefore loses any stereochemistry at the α-carbon (because $RR'R''C^{\cdot}$ is planar at the α-carbon). The reactions slow down or stop in the presence of radical inhibitors such as hindered phenols, ArOH; these quench the chain-carrier radical $R^{\cdot}$ to give R--H and the stable, and therefore unreactive, aryloxy radical, $ArO^{\cdot}$.

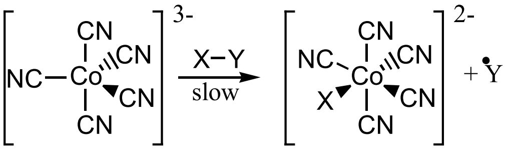


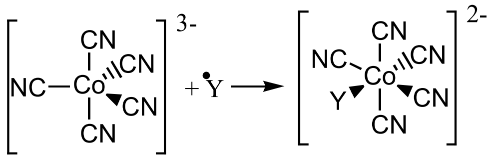
6.2.4.(c). Stepwise radical oxidative addition

Binuclear oxidative additions, because they involve 1e rather than 2e changes at the metals, often go via radicals. One of the best known examples is shown here. The rate-determining step is the first reaction.

Typical examples of X-Y are:

H_2, Br_2, H-OH, HO-OH, RI, I-CN, H_2N-OH





6.3. Oxidative addition of hydrogen halides

Hydrogen halides tend to react by an ionic mechanism in solution, where they are often largely dissociated. Two variants have been recognised. Polar solvents encourage both types, examples of which are shown below.

In the more common type, the complex is basic enough to be protonated, after which the anion binds to give the final product. The first route is favoured by basic ligands and a low oxidation state.

$$\mathrm{Pt(PPh_3)_4 + H^+ + Cl^- \rightarrow [HPt(PPh_3)_3]^+ + Cl^- + PPh_3 \rightarrow [HPt(PPh_3)_2Cl] + PPh_3}$$

18e d^{10} tetrahedral 16e d^8 square planar 16e d^8 square planar

This reaction follows rate = k[complex][H^+] suggesting that protonation is the slow step. This can be carried out independently by using an acid with a non-coordinating anion: HBF_4 and HPF_6 are the most often used. The anions in these acids {BF_4^- and PF_6^-} have insufficient nucleophilicity to carry out the second step and so the intermediate (e.g., $[HPtL_3]BF_4$) can be isolated.

The opposite case, in which the halide ion attacks first followed by protonation of the intermediate, is rarer, and is promoted by electron acceptor ligands and by a net positive charge on the metal.

$$\mathrm{[Ir(COD)L_2]^+ + Cl^- + H^+ \rightarrow IrCl(COD)L_2 + H^+ \rightarrow [IrHCl(COD)L_2]^+}$$

16e d^8 square planar 18e d^8 trigonal bipyramid 18e d^6 octahedral

The rate of this type usually follows rate = k[complex][Cl^-], suggesting that Cl^- addition is the slow step. This step can be carried out independently with LiCl alone, but no reaction is observed with HBF_4 alone, because the cationic iridium complex is not basic enough to be protonated and BF_4^- is a non-coordinating anion.

6.4. Reductive Elimination

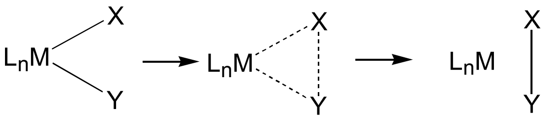
In spite of its great importance, reductive elimination has received less detailed study than oxidative addition. The reaction is most often seen in higher oxidation states, because the formal oxidation state of the metal is reduced by two units in the reaction. However, in very high oxidation states the rate may begin to go down as the d orbitals become too stabilised to participate. The reaction is especially efficient for intermediate oxidation states, such as the d^8 metals Ni(II), Pd(II), and Au(III) and the d^6 metals Pt(IV), Pd(IV), Ir(III), and Rh(III). Certain groups are more easily eliminated than others; for example, the following reactions are commonly seen, probably for thermodynamic reasons.

$L_nMRH \rightarrow L_nM + R\text{-}H$	alkyl hydride gives alkyl
$L_nMR_2 \rightarrow L_nM + R\text{-}R$	dialkyl gives alkane
$L_nMH(COR) \rightarrow L_nM + RCHO$	acyl hydride give aldehyde
$L_nMR(COR) \rightarrow L_nM + R_2CO$	acyl alkyl gives ketone
$L_nMRX \rightarrow L_nM + R\text{-}X$	alkyl halide elimination

The elimination reaction is thus promoted by:

- high metal oxidation state
- high coordination number
- formation of a strong X-Y bond (H_2, RH, R-R, R-X, RCO-X)

The fate of the L_nM fragment does not concern us here, but in the catalysis of organic reactions a reductive elimination is often the last step in a catalytic cycle and the resulting L_nM fragment must be able to survive long enough to react with the substrates for the organic reaction and so re-enter the cycle. The eliminations

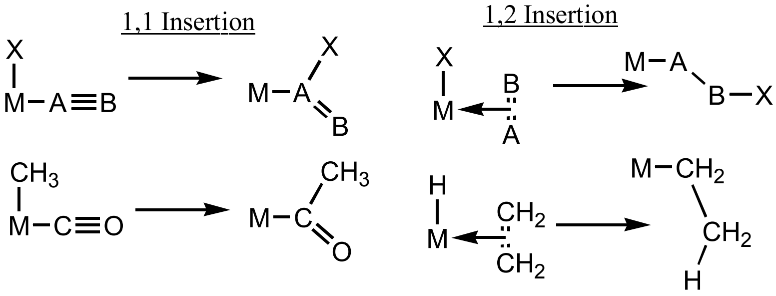


above are analogous to the 3-centre oxidative additions in that they are believed to proceed by a non-polar, non-radical 3-centre transition state. Retention of stereochemistry at carbon is a characteristic feature of this group of reactions. This mechanism requires that X and Y are cis to each other in the complex.

Dialkyls containing β-hydrogens often β-eliminate to give an alkyl hydride and alkene before they reductively eliminate R-H. This is an extremely important reaction. An interesting case is $PdEt_2(PR_3)_2$: the cis isomer reductively eliminates butane, but in the trans isomer, in which the two R groups are not properly oriented for reductive elimination, the β-elimination/reductive elimination path is followed to give ethylene and ethane. See the next section for β-elimination.

7. Insertion and elimination

Oxidative addition and **substitution** allow us to assemble 1e and 2e ligands on the metal. With **insertion**, and its reverse reaction **elimination**, we can now combine and transform these ligands within the coordination sphere, and then expel these transformed ligands to form free organic compounds. In insertion, a coordinated 2e ligand AB can insert itself into an M-X bond to give M-(AB)-X, in which new bonds have been formed between AB and both M and X. There are two main types of insertion 1,1- and 1,2- as shown below, in which the metal and the X ligand end up bound to the same (1,1) or adjacent (1,2) atoms of the L type ligand, shown as A=B.

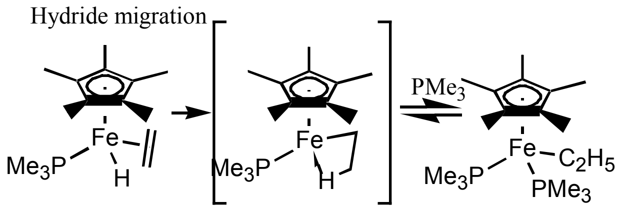


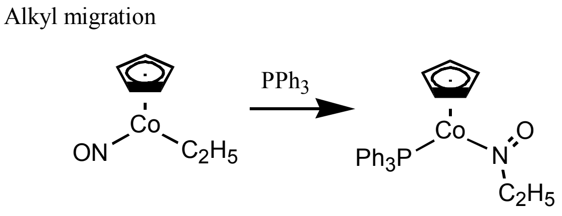
The type of insertion observed in any given case depends on the nature of the 2e inserting ligand. For example, CO gives only 1,1-insertion; that is, both the M and the X group end up attached to the CO carbon. On the other hand, ethylene gives only 1,2- insertion, in which the M and the X end up on adjacent atoms of the 2e ligand. In general, η^1 ligands tend to give 1,1- insertion and η^2 ligands, 1,2-insertion. Sulphur dioxide is the only common ligand that can give both types; as a ligand, SO_2 can bind in both η^1 (S) and η^2 (S, O) forms.

In principle, insertion reactions are reversible, but as we saw for oxidative addition and reductive elimination, for many ligands only one of the two possible directions is observed in practice. For example, SO_2 commonly inserts into M-R bonds to give alkyl sulphinate complexes, but these rarely eliminate SO_2. Conversely, diazoarene complexes readily eliminate N_2, but N_2 has not yet been observed to insert into a metal-aryl bond (this would be a extremely useful reaction!).

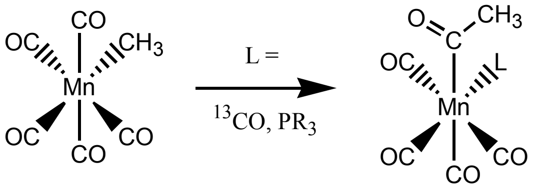
$M\text{-}R + SO_2 \rightarrow M\text{-}SO_2R$	insertion is favoured
$M\text{-}N{=}N\text{-}Ar \rightarrow M\text{-}Ar + N_2$	elimination is favoured

The immediate precursor species to the insertion product usually has both the 1e and 2e ligands coordinated. This means that a net 3e set of ligands is converted to a 1e insertion product, so that a 2e vacant site is generated by the insertion. This site can be occupied by an external 2e ligand and the insertion product trapped. Conversely, the elimination requires a vacant site, so that an 18e complex will not undergo the reaction unless a ligand first dissociates. The insertion also requires a cis arrangement of the 1e and 2e ligands, while the elimination generates a cis arrangement of these ligands. The formal oxidation state does not change during the reaction. Typical examples of hydride and alkyl migration are shown:





7.1. Insertion Reactions Involving CO



CO shows a strong tendency to insert into metal alkyl bonds to give metal acyls. The reaction has been carefully studied for a number of systems. Although the details may differ, most follow the pattern set by the best-known case, shown here.

The detailed mechanism of this reaction has been extensively studied by a number of workers using vibrational spectroscopy to study ^{13}C labelled species, and the products of phosphine promoted insertion.

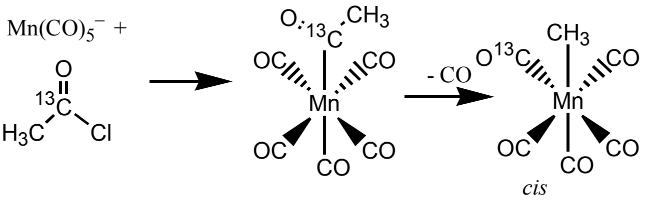
The reaction of $Mn(CO)_5Me$ with ^{13}CO or phosphine ligands shows that:

- the CO in the acetyl comes from the carbonyl ligands already attached to the metal;
- the incoming ligand ends up cis to the acetyl group.

Further support for this comes from the reaction of $Mn(CO)_5^-$ (from $Mn_2(CO)_{10}$ plus Na) with ^{13}C labelled acetyl chloride:

Two possible reaction mechanisms can be postulated:

1. CH_3 **migrates** to a *cis* carbonyl ligand
2. a *cis* CO **inserts** into the M-CH_3 bond

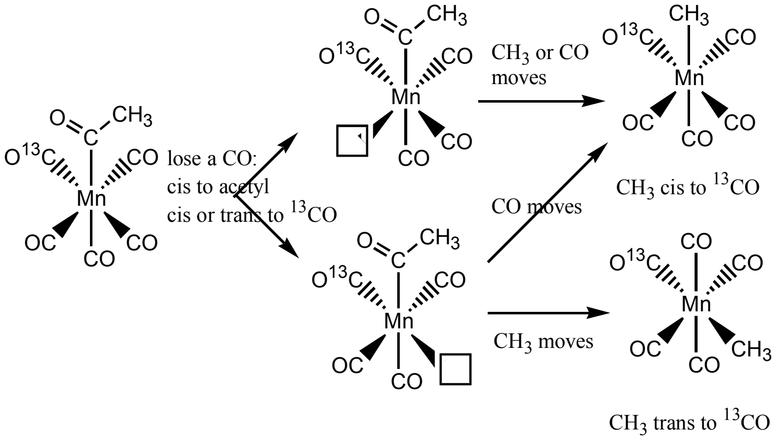


The experiment to test these possibilities is outlined here, using the reverse reaction (elimination) for a complex which is ^{13}CO labelled cis to the acyl ligand:

- If the methyl moves then it ends up both cis and trans to the ^{13}CO label
- If CO moves, then methyl ends up only cis to the ^{13}CO label.

Experimentally, the methyl moves.

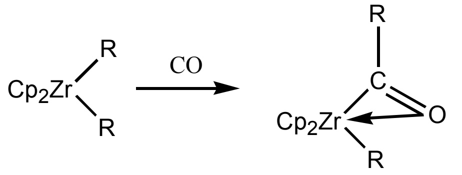
This observation implies that the methyl also moves when the reaction is carried out in the direction of insertion. This is the only feature of migratory insertion in $MeMn(CO)_5$ that does not reliably carry over to other systems, where the product acyl is occasionally found at the site originally occupied by the CO undergoing the insertion.



For the forward (insertion) reaction, the first step is the migration of the methyl group to a cis CO (hence the alternative name *migratory insertion* for this reaction). This generates a 2e site at the metal, which can be filled by the incoming ligand, typically CO or a phosphine. It is found that the more nucleophilic the ligand, the faster the reaction, and so it is believed that the first step is rapid and reversible and that trapping with phosphine (k_2) is the rate-determining step. When the incoming ligand is ^{13}CO, the product only contains one labelled CO, which is cis to the newly- formed acetyl group. This shows that the methyl group migrates to a coordinated CO, rather than a free CO attacking the Mn-Me bond.

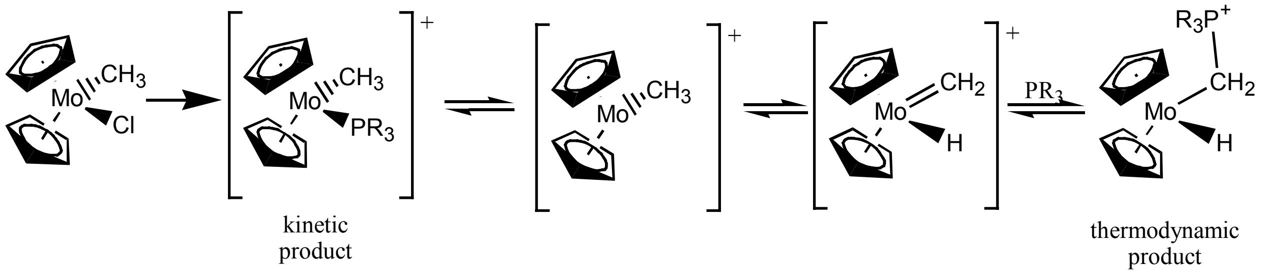
Given that the methyl group migrates to the CO, why stop there? Why does the resulting acyl group not migrate to another CO to give an MeCOCO ligand? The double insertion of CO has never been observed. If it happened repeatedly, we might even get the unknown $(CO)_n$, polymer as ligand, a material believed to be thermodynamically unstable with respect to CO itself. The complex that would have been formed in a double insertion can be made by an independent route from MeCOCOCl and $[Mn(CO)_5]^-$. It easily eliminates CO to give $MeCOMn(CO)_5$, which suggests that the double insertion product is thermodynamically unstable with respect to $MeCOMn(CO)_5$.

Lewis acids such as $AlCl_3$ or H^+ can increase the rate of migratory insertion by as much as 10^8 fold. Since the early transition metals are themselves strongly Lewis acidic, and oxophilic they can act as their own Lewis acid catalysts for insertion. The product in this case is an η^2-acyl, and this is a reaction of some synthetic importance.

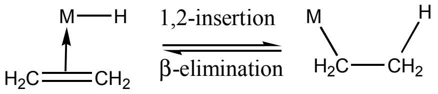


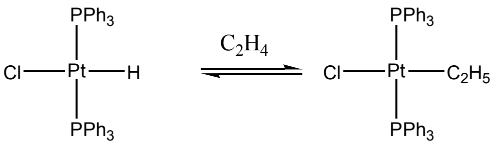
7.2. Metal alkyl eliminations

The α-elimination reaction is formally the opposite of a 1,1-insertion reaction. the α-elimination reaction is relatively common, but the products, alkylidene hydrides are very reactive and are rarely encountered as free species.



7.3. Insertions Involving Alkenes

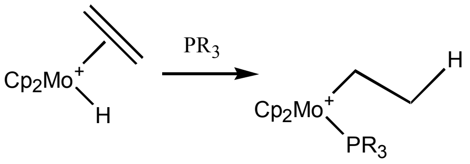




The insertion of coordinated alkenes into M--H bonds is a very important reaction because it gives alkyls and constitutes a key step in a variety of catalytic reactions, as you will see in later courses covering catalysis. As η^2 ligands, alkenes give 1,2-insertion. The reverse reaction is β-elimination, and the two are potentially in equilibrium. The position of equilibrium is decided by the thermodynamics of the particular system, and depends strongly on the alkene.

For simple alkenes such as ethylene, the equilibrium tends to lie to the left (i.e., the alkyl β-eliminates), but for alkenes with electron-withdrawing ligands (e.g., C_2F_4), the alkyl is particularly stable and the equilibrium lies entirely to the right.

The usual stereochemistry of the insertion is syn and so the stereochemistry at both carbons is retained. As we saw for CO insertions and eliminations, a 2e vacant site is generated by the insertion (and required for the elimination). The vacant site may be filled by a suitable ligand such as a phosphine.



The detailed mechanism for the insertion reactions of alkenes will be discussed in a later lecture course [Catalysis at Metal Centres], together with the relevance and importance of this reaction in the organometallic chemistry of alkenes.

8. Further reading

If you wish to read some text books which cover aspects of this course in more detail or which provide a different emphasis, then the following are recommended (in addition to chapters in many standard texts):

R. Henderson *The mechanisms of reactions at transition metal sites*, OUP Primer series

F. A. Cotton and G. Wilkinson *Advanced Inorganic Chemistry* Wiley Interscience. There is a chapter on reaction mechanisms and molecular rearrangements in complexes in the 4th and 5th editions (but not in the 6th edition).