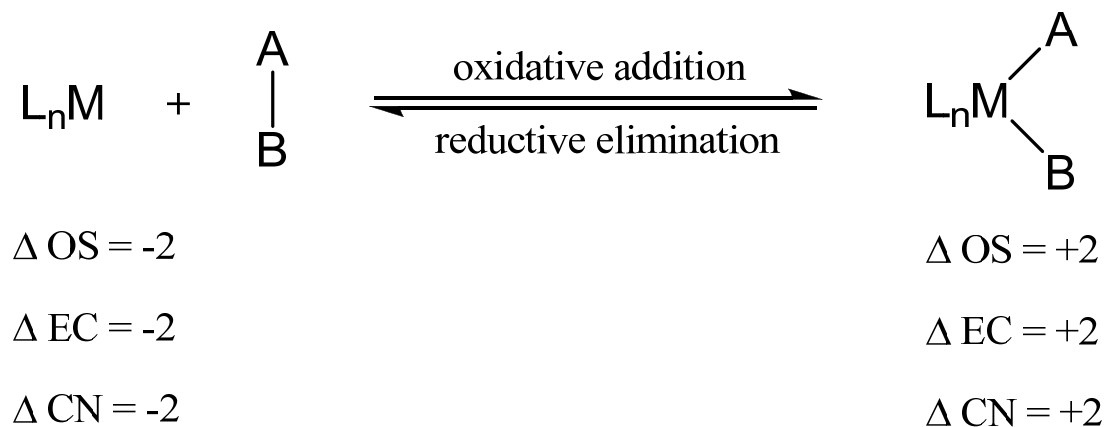# Oxidative Addition

- We have seen how neutral ligands such as C_2H_4 or CO can enter the coordination sphere of a metal by substitution. We now look at a general method for simultaneously introducing pairs of anionic ligands, A and B, by the **oxidative addition** of an A−B molecule such as H_2 or CH_3-I.

$$L_nM \ + \ \overset{A}{\underset{B}{|}} \ \underset{\text{reductive elimination}}{\overset{\text{oxidative addition}}{\rightleftharpoons}} \ L_nM\overset{A}{\underset{B}{<}}$$

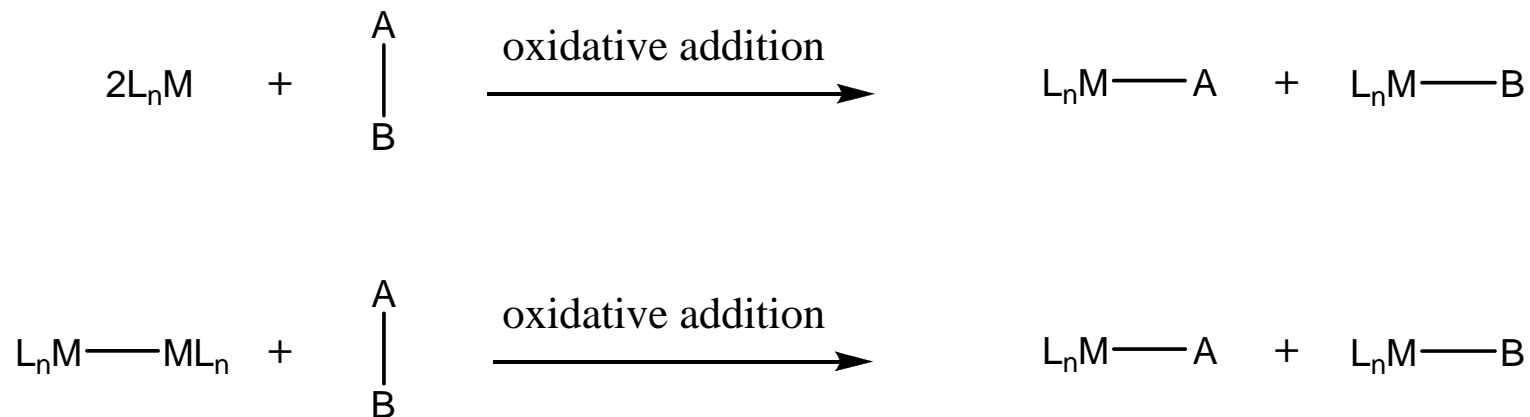| Δ OS = -2 | Δ OS = +2 |
| Δ EC = -2 | Δ EC = +2 |
| Δ CN = -2 | Δ CN = +2 |

- 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 addition direction, we break the A−B bond and form an M−A and an M−B bond.

- The oxidation state (OS), electron count (EC), and coordination number (CN) all increase by two units during the reaction.

- It is the change in formal oxidation state (OS) that gives rise to the oxidative and reductive part of the reaction names.

- Oxidative additions proceed by a great variety of mechanisms, however, *a vacant 2e site is always required on the metal*.

- We can either start with a 16e complex *or a 2e site must be opened up in an 18e complex by the loss of a ligand* producing a 16e intermediate species*.*

- The change in oxidation state means that the starting 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*).

Binuclear oxidative addition

- Each of two metals change their oxidation states, electron count, and coordination number by one unit each.

$$2L_nM \quad + \quad \underset{B}{\overset{A}{|}} \quad \xrightarrow{\text{oxidative addition}} \quad L_nM\text{——}A \quad + \quad L_nM\text{——}B$$

$$L_nM\text{——}ML_n \quad + \quad \underset{B}{\overset{A}{|}} \quad \xrightarrow{\text{oxidative addition}} \quad L_nM\text{——}A \quad + \quad L_nM\text{——}B$$

$$\Delta\, OS = +1$$

$$\Delta\, EC = +1$$

$$\Delta\, CN = +1$$

- This typically occurs in the case of a 17e complex or a binuclear 18e complex with an M−M bond where the metal has *a stable oxidation state more positive by one unit*.

- Whatever the mechanism, there is *a net transfer of two electrons* into the σ^* orbital of the A−B bond, and the two A−B σ electrons are divided between both metals.

- This cleaves the A−B bond and makes an M−A and an M−B bond.

| Change in d^n Configuration	Change in Coordination Geometry	Examples	Group	Remarks
$d^{10} \rightarrow d^8$	Lin. $\xrightarrow{X_2}$ Sq. Pl.	Au(I) $\rightarrow$ (III)	11	
	Tet. $\xrightarrow{-2L,\,X_2}$ Sq. Pl.	Pt, Pd(0) $\rightarrow$ (II)	10	
$d^8 \rightarrow d^6$	Sq. Pl. $\xrightarrow{X_2}$ Oct.	M(II) $\rightarrow$ (IV)	10	M = Pd, Pt
		Rh, Ir(I) $\rightarrow$ (III)	9	Very common
		M(0) $\rightarrow$ (II)	8	Rare
	TBP. $\xrightarrow{-L,\,X_2}$ Oct.	M(I) $\rightarrow$ (III)	9	
		M(0) $\rightarrow$ (II)	8	
$d^7 \rightarrow d^6$	2Sq. Pyr. $\xrightarrow{X_2}$ 2Oct.	2Co(II) $\rightarrow$ (III)	8	Binuclear
	2Oct. $\xrightarrow{-L,\,X_2}$ 2Oct.	2Co(II) $\rightarrow$ (III)	8	Binuclear
$d^6 \rightarrow d^4$	Oct. $\xrightarrow{-L,\,X_2}$ 7-c	Re(I) $\rightarrow$ (III)	7	
		M(0) $\rightarrow$ (II)	6	
		V($-$I) $\rightarrow$ (I)	5	
$d^4 \rightarrow d^3$	2Sq. Pyr. $\xrightarrow{X_2}$ 2Oct.	2Cr(II) $\rightarrow$ (III)	6	Binuclear
	2Oct. $\xrightarrow{-L,X_2}$ 2Oct.	2Cr(II) $\rightarrow$ (III)	6	Binuclear
$d^4 \rightarrow d^2$	Oct. $\xrightarrow{X_2}$ 8-c	Mo, W(II) $\rightarrow$ (IV)	6	
$d^2 \rightarrow d^0$	Various	M(III) $\rightarrow$ (V)	5	
		M(II) $\rightarrow$ (IV)	4	

- As we have seen, oxidative addition is the inverse of reductive elimination and vice versa.

- In principle, these reactions are 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

Relative stabilities of the two oxidation states

Balance of the A−B vs. the M−A and M−B bond strengths

- Alkyl hydride complexes commonly undergo reductive elimination of an alkane, but rarely does oxidative addition of alkanes occur.

- Conversely, alkyl halides commonly undergo oxidative addition, but the adducts rarely reductively eliminate the alkyl halide.

- Rare examples of equilibrium do exist, but are thermodynamically controlled:
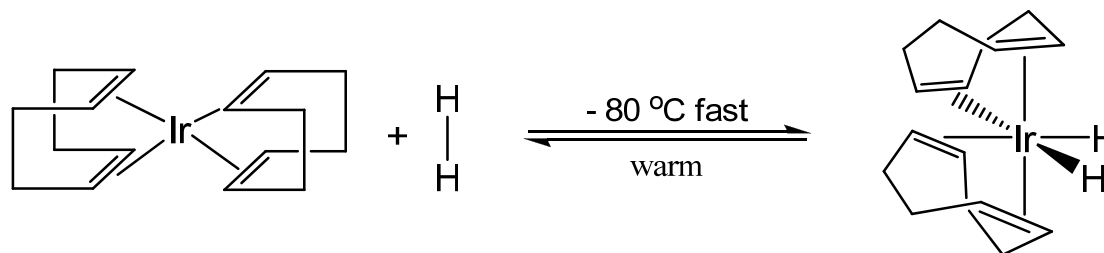
- Oxidative addition is usually favored by strongly donating ligands because these stabilize the increased oxidation state of the central metal.

- While the change in formal oxidation state is always +2 (apart from binuclear oxidative addition) , the real charge on the metal changes much less because ligands A and B do not end up with pure −1 charges in $L_nM(A)(B)$ – *electroneutrality principle !*

- *The real change in charge at the metal and ligands depends mostly on the electronegativity of A and B* so that the following reagents are more oxidizing in the order: $H_2 < HCl < Cl_2$.

- We can estimate the oxidizing power of different reagents experimentally by measuring $v(CO)$ on going from $IrCl(CO)L_2$ to $Ir(A)(B)Cl(CO)L_2$ because a more oxidizing reagent will reduce M−CO back bonding.

Reagent	$v(CO)$ (cm^{-1})	$\Delta v(CO)$ (cm^{-1})
None	1967	0
O_2	2015	48
$D_2{}^a$	2034	67
HCl	2046	79
MeI	2047	80
C_2F_4	2052	85
I_2	2067	100
Cl_2	2075	108

[a] The D isotope is used because the Ir−H stretching vibrations have a similar frequency to $v(CO)$
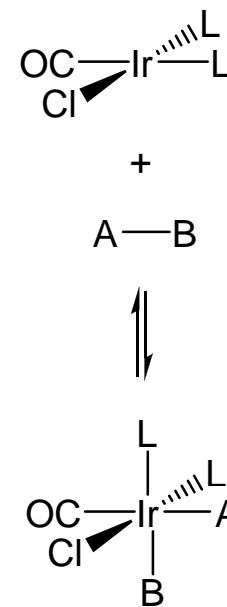
- Oxidative additions are very diverse mechanistically, and we therefore consider each type separately.

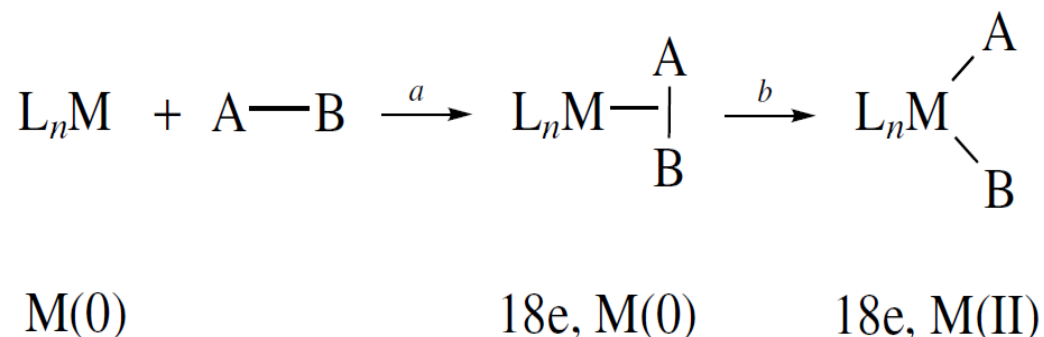1. **Concerted, or three-center, oxidative addition mechanism**

2. **S_N2 mechanism**

3. **Radical mechanisms**

4. **Ionic Mechanisms**

1. Concerted Mechanism

- Concerted, or three-center, oxidative addition is really an **associative reaction** in which the incoming ligand first binds as a **σ complex** *and* then undergoes bond breaking as a result of strong back donation from the metal into the σ^* orbital.

- Non-polar reagents, such as H_2, or compounds containing C−H and Si−H bonds all tend to react via a **σ complex transition state** (or even an intermediate) of this type.

- The associative **step a** involves formation of a *σ complex; sometimes* this is stable and the reaction stops here.

- **Step b** *is the oxidative part of the* reaction in which metal electrons are formally transferred to the σ^* orbital of A−B.
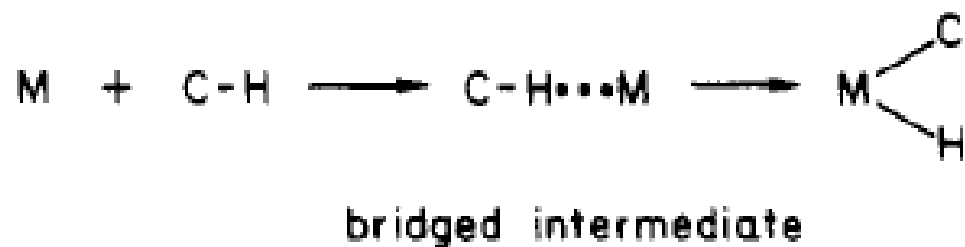
$$L_nM \; + \; A\!-\!B \xrightarrow{\;a\;} L_nM\!-\!\begin{matrix} A \\ | \\ B \end{matrix} \xrightarrow{\;b\;} L_nM\!\!\begin{matrix} \diagup A \\ \diagdown B \end{matrix}$$

$$M(0) \qquad\qquad 18e,\, M(0) \qquad 18e,\, M(II)$$

- There are many examples, however, one of the most-studied cases is the addition of H_2 to the 16e square planar d^8 species $IrCl(CO)(PPh_3)_2$ [*aka* Vaska's complex] to give the 18e d^6 octahedral dihydride $IrCl(H_2)(CO)(PPh_3)_2$.
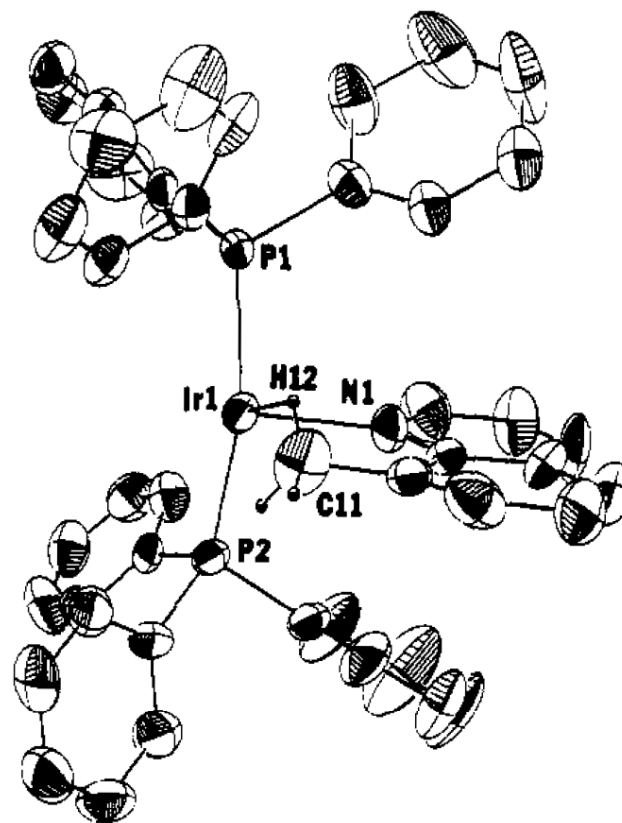

square planar
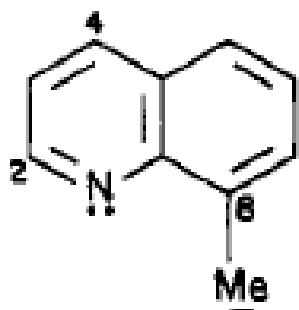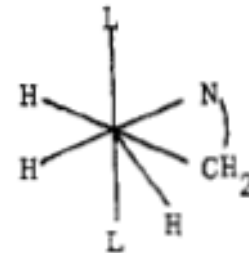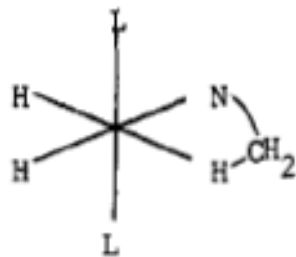16e, Ir(I)

trig. bipyramid
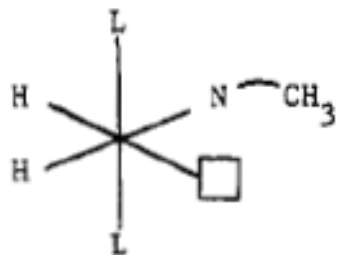18e, Ir(I)

octahedral
18e, Ir(III)
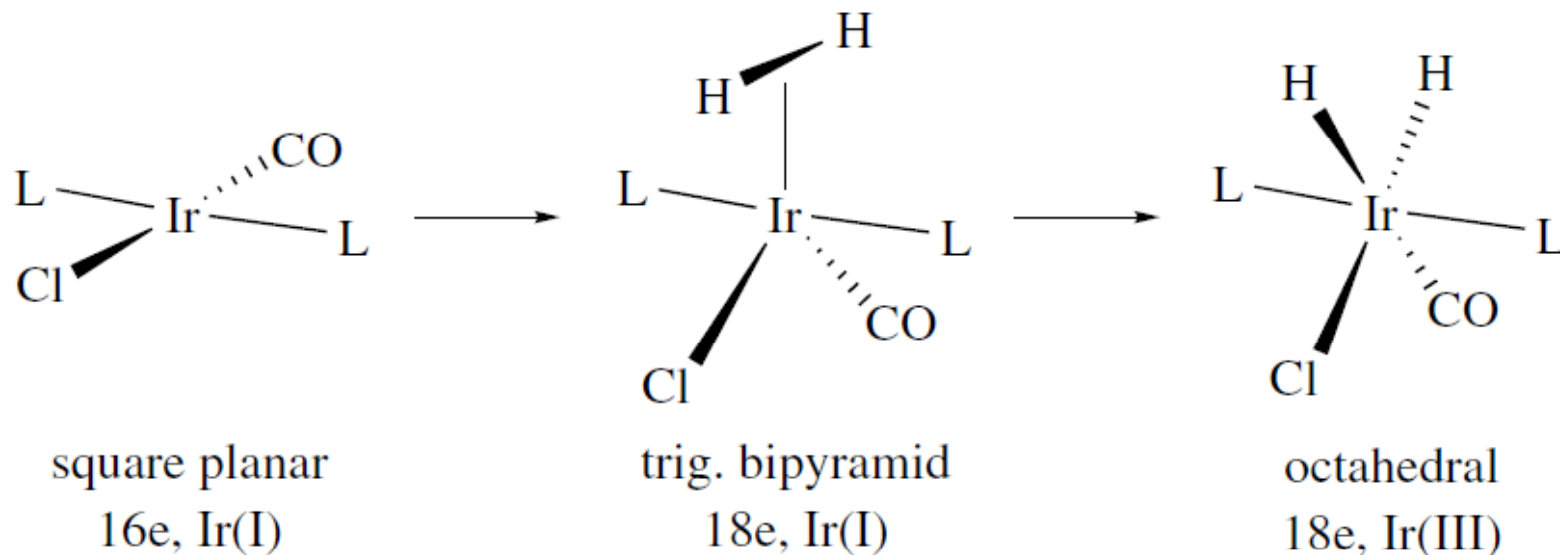
- Normally two ligands that are *trans* in the Ir(I) complex fold back to give the *cis* dihydride isomer, but subsequent rearrangement can occur.

- Conversely, in a reductive elimination such as the loss of H_2 from the dihydride, the two ligands to be eliminated normally have to be *cis* to one another.

  (consider the reverse of the reaction above)

- 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 oxidative addition because of the high thermodynamic stability of the aryl hydride adduct.

- Agostic complexes, *σ complexes of C−H bonds, can be thought of as lying* along the pathway for oxidative addition but arrested at different points.

- A study of the structures of a series of these complexes allowed the kinetic pathway and reaction trajectories to be mapped out.

  ➢ The C−H bond seems to approach with the H atom pointing toward the metal.

  ➢ The C−H bond then pivots around the hydrogen to bring the carbon closer to the metal in a side-on arrangement, followed by C−H bond cleavage.

$$M \; + \; C\text{-}H \longrightarrow C\text{-}H \cdots M \longrightarrow M \Big\langle {}^{C}_{H}$$

bridged intermediate

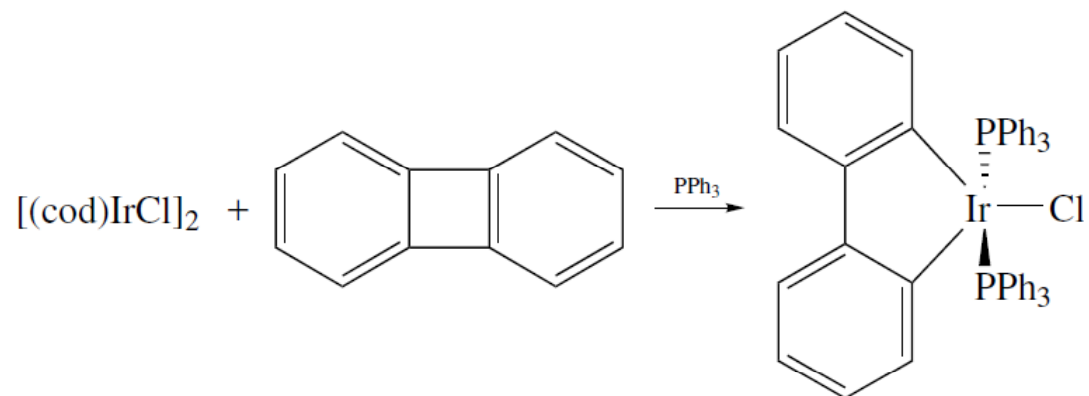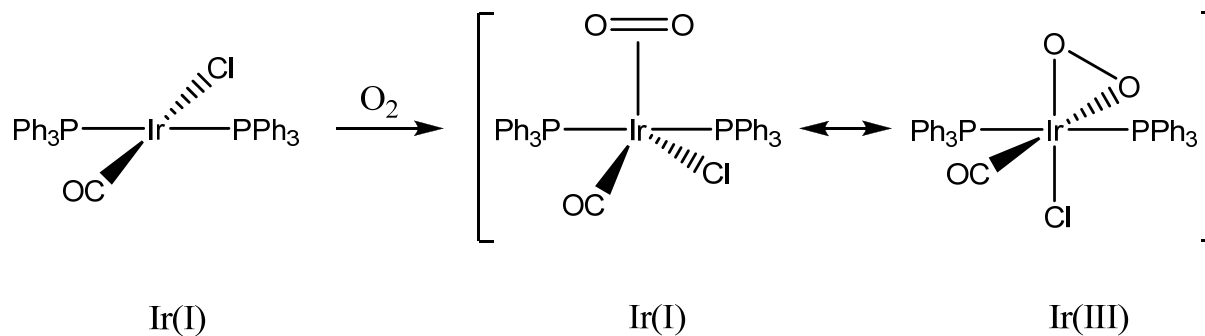Crabtree et al. *Inorg. Chem. 1985, 24, 1986-1992*

- Carbon–carbon bonds do not normally oxidatively add, but a classic early case, the reaction of cyclopropane with Pt(II) to give a Pt(IV) metalacyclobutane shown below, illustrates how *the reaction can be driven by ring strain*.
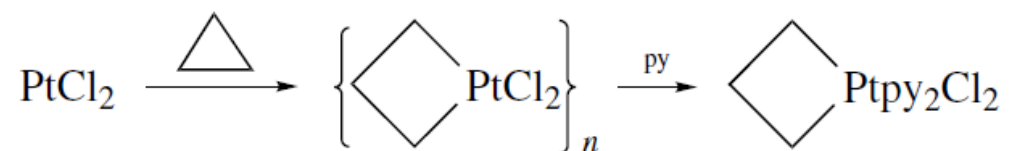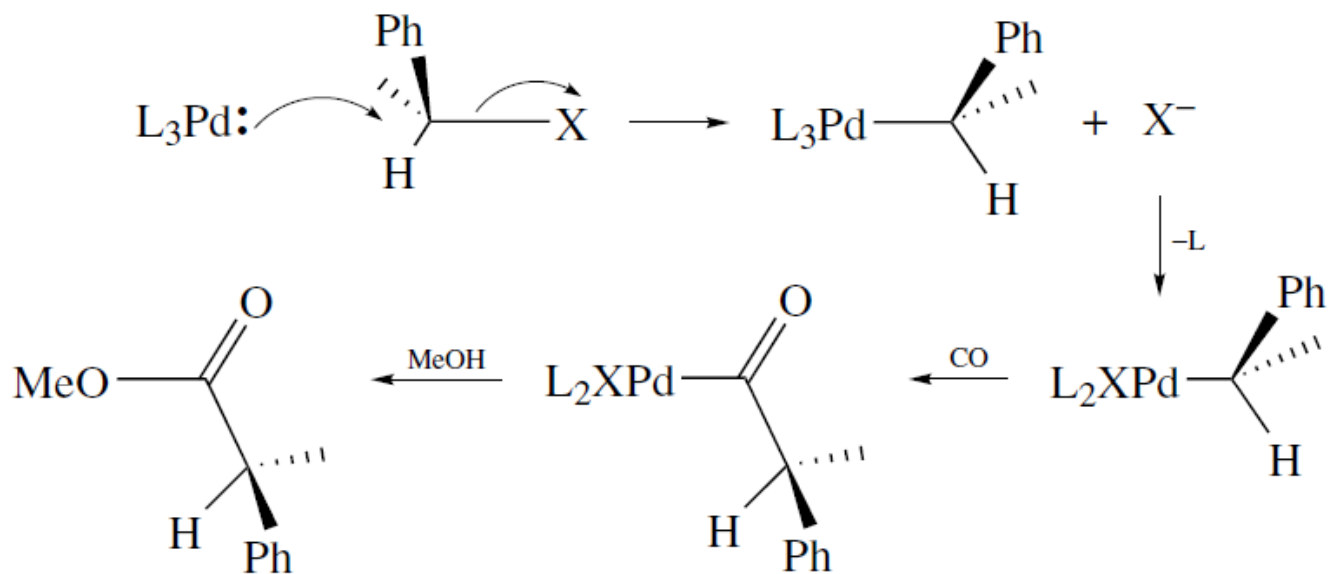

- Similarly, biphenylene readily reacts in the same way.

Ir(I)   Ir(I)   Ir(III)

- Upon addition of O_2, Ir(I) reduces the O_2 to O_2^{2-}, the peroxide ion, which coordinates to the Ir(III).

- Why not envisage the reaction as a ligand addition by regarding O_2 as a 2e donor such as ethylene?

- This is a result of the different formal oxidation states assigned to the L and X_2 extreme pictures of binding.

- In fact, ethylene is much closer to the L extreme while O_2 is very close to the X_2 extreme.

- This means that the conventional descriptions of ethylene binding as a ligand addition and of O_2 binding as an oxidative addition are the most appropriate.

- For ligands, such as $CF_2=CH_2$, which bind in a fashion that is approximately equidistant between the two extremes, there is a gray area in which the choice between the two descriptions is arbitrary.

- ***This emphasizes that categories such as "oxidative addition" are mental constructs and have their limitations.***

2. S$_N$2 Mechanism (*non-concerted*)

- In all oxidative additions, a pair of electrons from the metal is used to break the A−B bond in the reagent.

- In the S$_N$2 pathway, adopted for polarized A-B substrates such as alkyl halides, the *metal electron pair of L$_n$M directly attacks the A−B σ∗ orbital by an in-line attack at the least electronegative atom (where σ∗ is largest) formally to give L$_n$M^{2+} , A$^−$, and B$^−$ fragments (ionic model).*

- The S$_N$2 mechanism is often found in the addition of methyl, allyl, acyl, and benzyl halides.

- Like the concerted type, they are *second-order reactions*, but they are accelerated in polar solvents and show negative entropies of activation (ΔS).

- This is consistent with an *ordered, polar transition state, as in organic S$_N$2 reactions*.

- **Inversion at carbon** has been found in suitably substituted halides.

$$L_3Pd: \quad \overset{Ph}{\underset{H}{\diagup}} \cdots X \quad \longrightarrow \quad L_3Pd\overset{Ph}{\underset{H}{\diagdown}} \quad + \quad X^-$$

$$\downarrow_{-L}$$

$$MeO\overset{O}{\diagdown}\underset{\underset{Ph}{H}}{\cdots} \quad \overset{MeOH}{\longleftarrow} \quad L_2XPd\overset{O}{\diagdown}\underset{\underset{Ph}{H}}{\cdots} \quad \overset{CO}{\longleftarrow} \quad L_2XPd\overset{Ph}{\underset{H}{\diagdown}}$$

- The stereochemistry at the carbon of the oxidative addition product was determined by carbonylation to give the metal acyl followed by methanolysis to give the ester.

- Both of these reactions are known to leave the configuration at carbon unchanged, and the configuration of the ester can be determined unambiguously from the measured optical rotation of the final organic product.
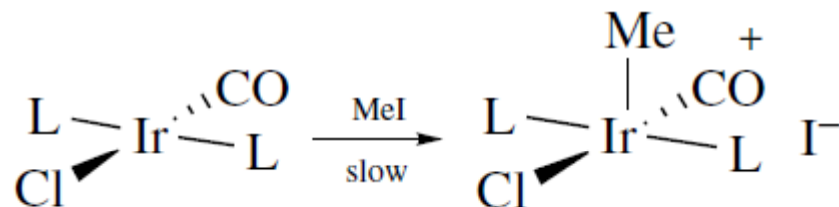
- R and X may end up ***cis or trans*** to one another in the final product, as expected for the recombination of the ion pair formed in the first step.
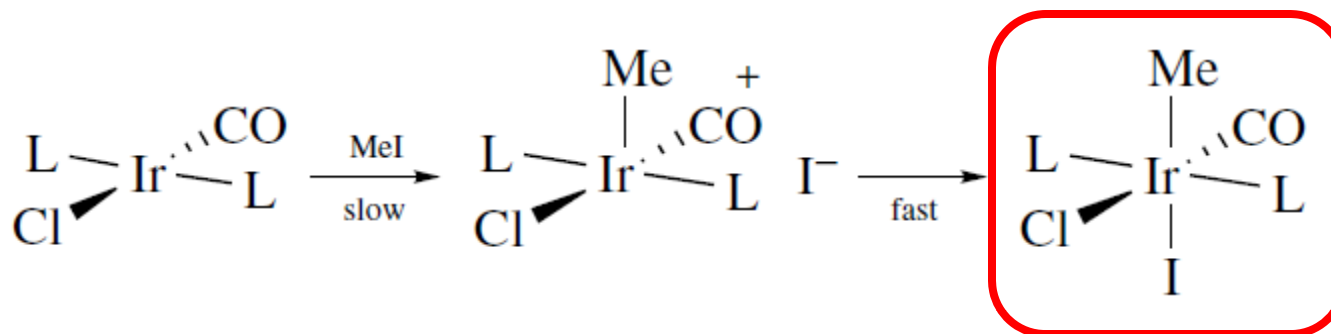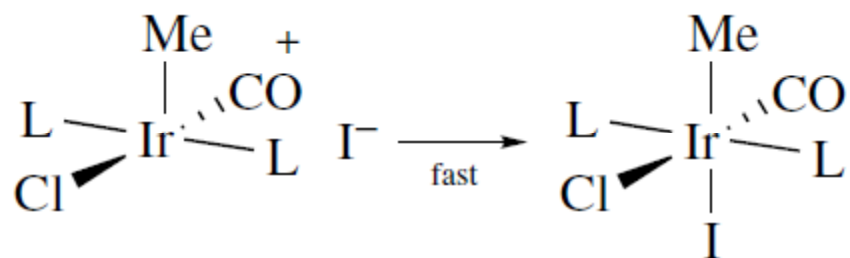

vs. concerted mechanism
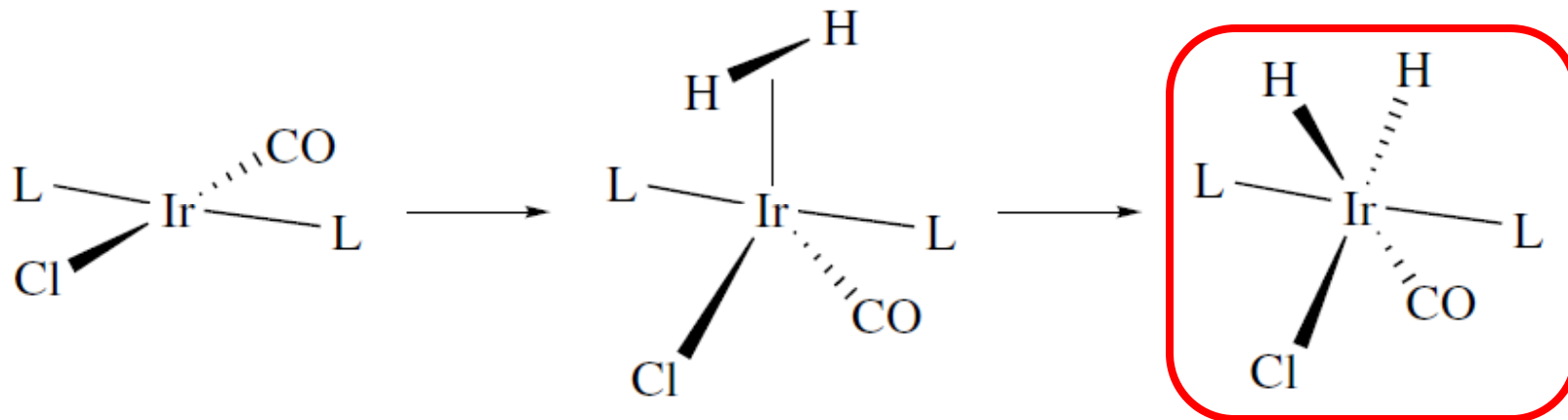
- Of the two steps, the first involves ***oxidation by two units but no change in the electron count*** (Me$^+$ is a 0e reagent)

- The second step involves an ***increase by 2e in the electron count*** (I$^-$ is a 2e reagent) but no change in the oxidation state.

- **Only the two steps together constitute the full oxidative addition.**

- When an 18e complex is involved, the first step can therefore proceed without the necessity of losing a ligand first.

- Only the second step requires a vacant 2e site.

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

$$Ni(PR_3)_4 > Ni(PAr_3)_4 > Ni(PR_3)_2(alkene) > Ni(PAr_3)_2(alkene) > Ni(cod)_2 \quad (R = alkyl)$$

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

$$Me\text{-}I > Et\text{-}I > {}^iPr\text{-}I$$

- *A better leaving group accelerates the reaction*, which gives rise to the reactivity order:

$$R\text{-}OSO_2(C_6H_4Me) > R\text{-}I > R\text{-}Br > R\text{-}Cl$$
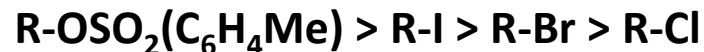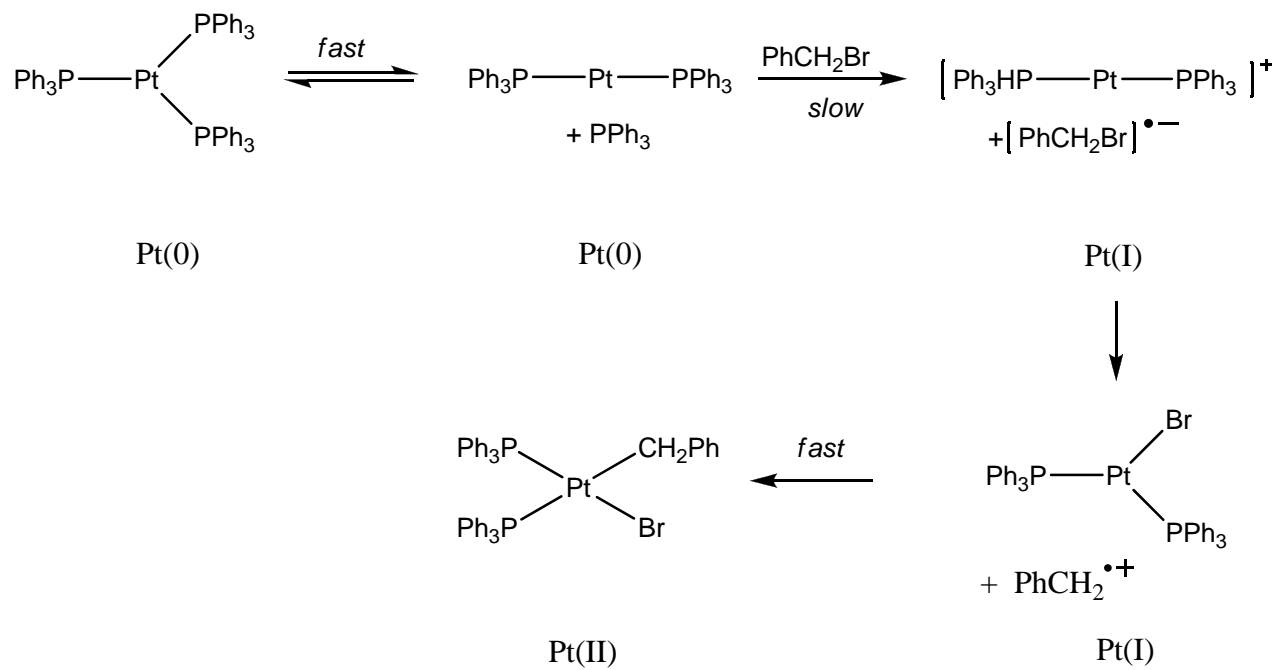
3. Radical mechanism

- Radical mechanisms in oxidative additions were recognized later than the S_N2 and the concerted processes.

- They can also be ***photoinitiated.***

- A troublesome feature of these reactions is that minor changes in the structure of the substrate, the complex, or in impurities present in the reagents of 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$^\bullet$, has been criticized on the grounds that these may initiate a radical pathway for a reaction that otherwise would have followed a non-radical mechanism in the absence of trap.

- Two subtypes of radical process are now distinguished:

  ➢ *non-chain*

  ➢ *chain*

- The *non-chain variant* is believed to operate in the additions of certain alkyl halides, R-X, to Pt(PPh$_3$)$_3$ (R = Me, Et; X = I; R = PhCH$_2$; X = Br).

Pt(0)   Pt(0)   Pt(I)

Pt(II)   Pt(I)

- The key feature is one electron transfer from M to the R-X σ* orbital to form M^+ and $(R-X)^{\bullet -}$.

- After X^- transfer to M^+, the $R^{\bullet +}$ radical is liberated.

- Like the S_N2 process, the radical mechanism is faster the more basic the metal, and the more readily electron transfer takes place, which gives the reactivity order

R-I > R-Br > R-Cl

- Unlike the S_N2 process, the reaction is very slow for alkyl tosylates [e.g., $ROSO_2(C_6H_4Me)$], and it goes faster as the alkyl radical, R, becomes more stable and so easier to form, giving rise to the order of R group reactivity:
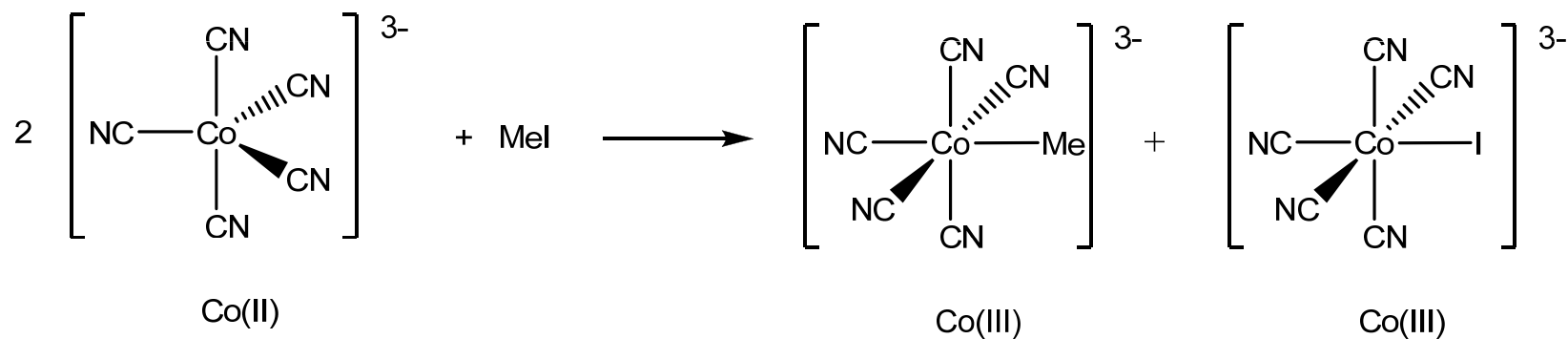
3° > 2° > 1° > Me
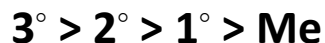
- ***The second general kind of reaction is the radical chain.***

- This has been identified in the case of the reaction of Et-Br and $PhCH_2Br$ with the PMe_3 analog of Vaska's complex, $IrCl(CO)(PMe_3)_2$.

- A chain process occurs if ***the radicals formed escape from the solvent cage without recombination***.

- Otherwise, a radical initiator, $Q^\bullet$, (e.g., a trace of air) may be required to set the process going. This can lead to an induction period (a period of dead time before the reaction starts).

- In either case, a metal-centered radical abstracts $X^\bullet$ from the halide, to leave the chain carrier $R^\bullet$.

Ir(I)   Ir(II)   Ir(III)
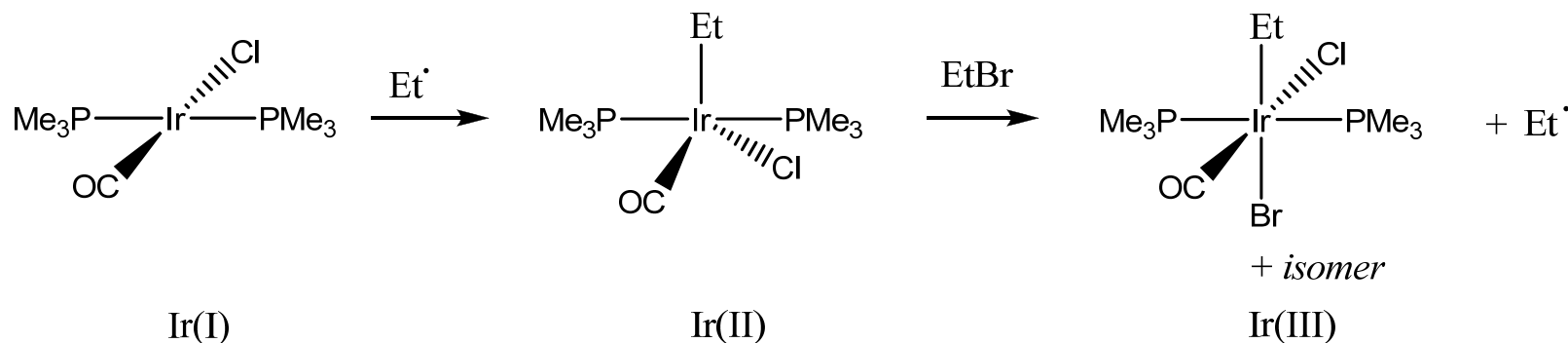
- Chain termination steps limit the number of cycles possible per R$^\bullet$.

$$2R\bullet \longrightarrow R_2$$
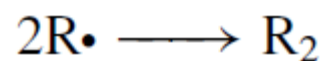
- The alkyl group always loses any stereochemistry at the α carbon because RR′R′′C$^\bullet$ is planar at the central carbon.

- Unlike the non-chain case, the reactions slow down or stop in the presence of radical inhibitors, such as the hindered phenol, 2,6-di-t-butylphenol.

- These quench the radical R$^\bullet$ to give R–H and the stable, and therefore unreactive, aryloxy radical, ArO$^\bullet$.

- *Binuclear oxidative additions*, because they involve 1e rather than 2e changes at the metals, *often go via radical mechanisms*.

$$2\ \begin{bmatrix} NC-Co \cdots CN \\ CN \end{bmatrix}^{3-} + \ MeI \longrightarrow \begin{bmatrix} NC-Co-Me \end{bmatrix}^{3-} + \begin{bmatrix} NC-Co-I \end{bmatrix}^{3-}$$

Co(II)   Co(III)   Co(III)

4. Ionic mechanism

- Hydrogen halides are often largely dissociated in solution, and the ***anion and proton tend to add to metal complexes in separate steps***.

- ***Two variants have been recognized***.

1. In the more common one, the complex is basic enough to protonate, after which the anion binds to give the final product.

➢ **protonation – anionation**

2. Rarer is the opposite case in which the halide ion attacks first, followed by protonation of the intermediate.

➢ **anionation - protonation**

- In the ***more common mechanism of protonation followed by anionation***, the complex is basic enough to protonate, after which the anion binds to give the final product.
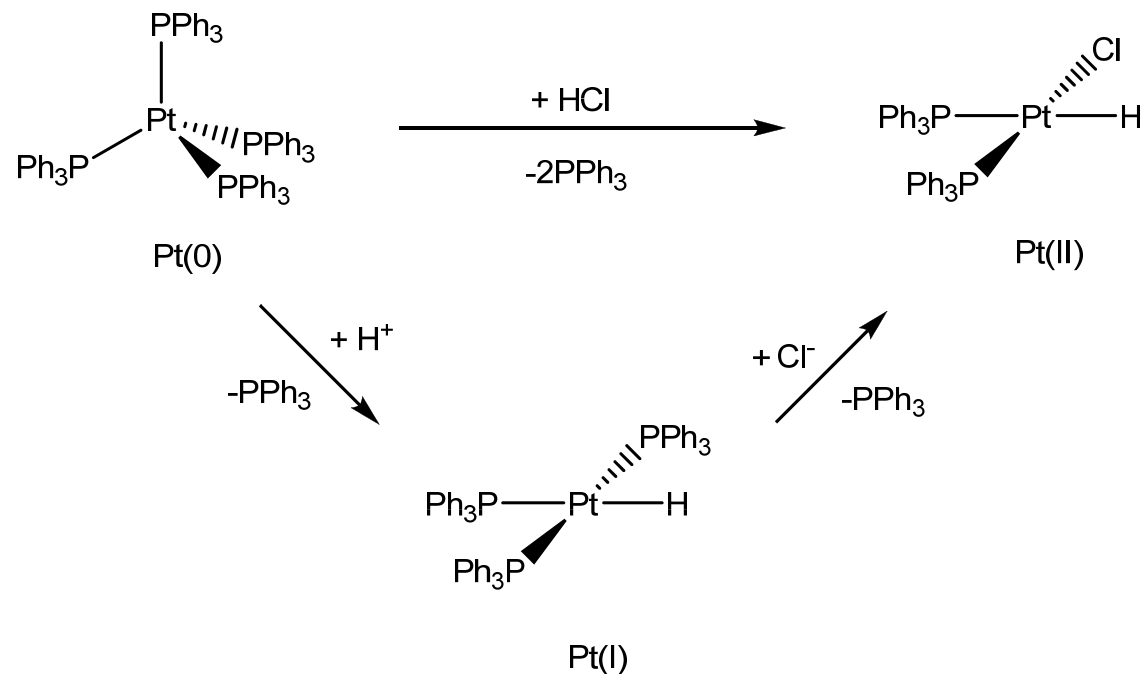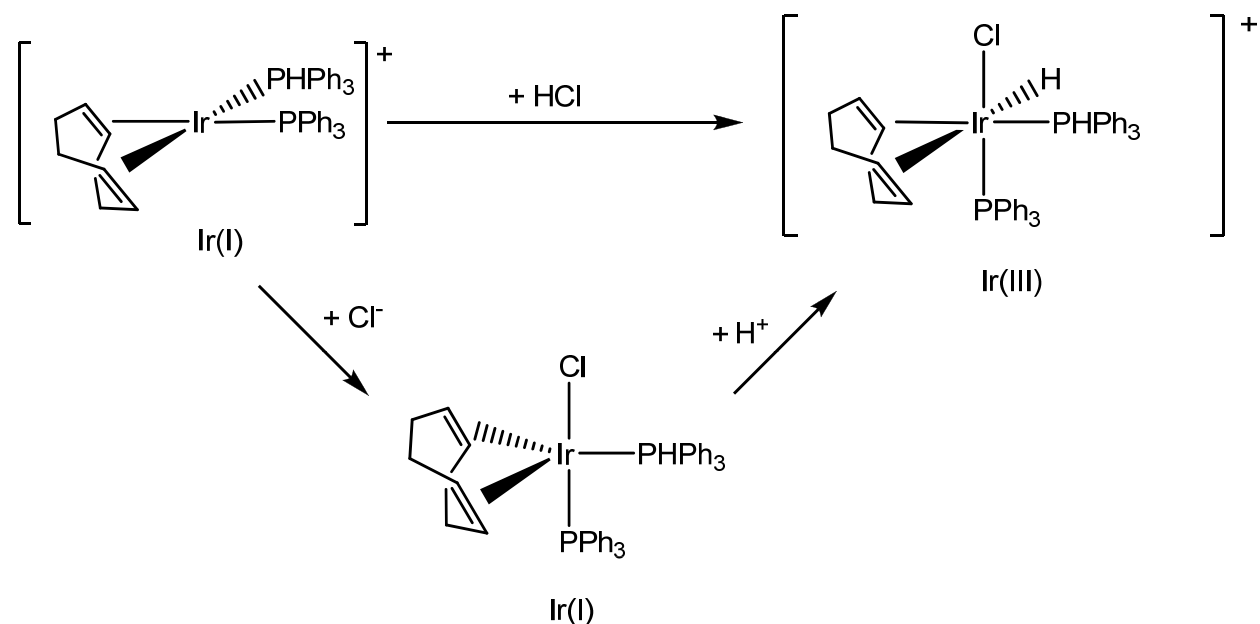

- This route is favored by

  ➢ polar solvents

  ➢ basic ligands

  ➢ a low-oxidation-state metal

- Like the concerted and S_N2 mechanisms the ionic mechanism is **second order** in rate. **Protonation is the rate determining step:**

$$\text{Rate} = k[\text{complex}][\text{H}^+]$$

- 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 anion has insufficient nucleophilicity to carry out the second step, and so the **intermediate can be isolated!!**

- This is an example of a general strategy in which a "non-coordinating" anion is used to isolate reactive cations as stable salts.

- Rarer is the case of *anionation followed by protonation* where the halide ion attacks first, followed by protonation of the intermediate.

- This route is favored by

  ➢ polar solvents

  ➢ electron-acceptor ligands

  ➢ a net positive charge on the complex

- *Polar solvents encourage both ionic mechanisms – why?*

- Again this is a ***second order*** reaction but now follows a rate dependent upon the counterion concentration as X^- addition is the rate limiting step.

$$\text{Rate} = k[\text{complex}][\text{Cl}^-]$$

- Similar to the first type mechanism, this step can be carried out independently with LiCl alone.

- No reaction is observed with HBF_4 alone!

  ➢ because the cationic iridium complex is not basic enough to protonate and BF_4^- is a non-coordinating anion.