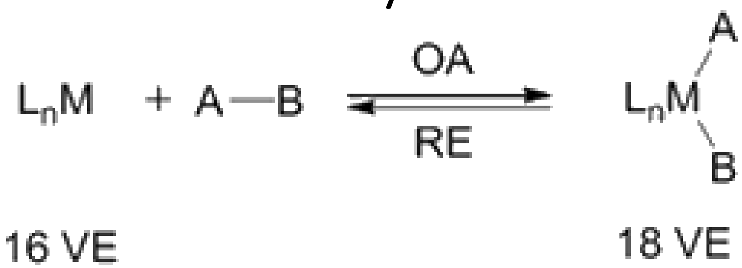
Oxidative Addition

- Oxidative addition (OA) is a process that **adds two anionic ligands** *e. g*. A and B, that originally are a part of a A-B molecule, like in H_2 or Me−I, on to a metal center and is of significant importance from the perspective of both synthesis and catalysis.

- The exact reverse of the same process, in which the two ligands, A and B, are eliminated from the metal center forming back the A−B molecule, is called the **reductive elimination (RA)**.

- As A and B are anionic X type ligands, the oxidative addition is accompanied by an increase in the **coordination number**, valence electron count as well as in the formal oxidation state of the metal center by two units.

- The oxidative addition step may proceed by a variety of pathways. It requires the metal center to be both **coordinatively unsaturated** and **electron deficient**.



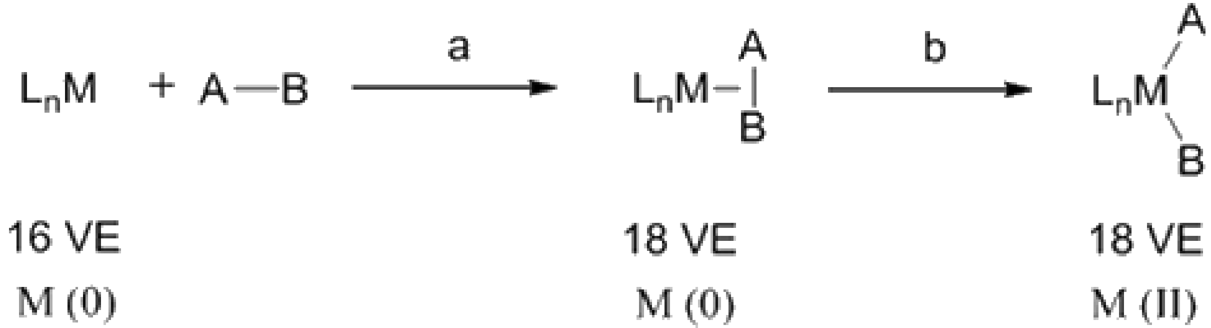
Change in d^n Configuration	Change in Coordination Geometry	Examples	Group
$d^{10} \rightarrow d^8$	Lin. $\xrightarrow{X_2}$ Sq. Pl.	Au(I) $\rightarrow$ (III)	11
	Tet. $\xrightarrow{-2L,\ X_2}$ Sq. Pl.	Pt, Pd(0) $\rightarrow$ (II)	10
$d^8 \rightarrow d^6$	Sq. Pl. $\xrightarrow{X_2}$ Oct.	Pt, Pd(II) $\rightarrow$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

Concerted oxidative addition pathway

- Oxidative addition may proceed by a concerted **3–centered associative** mechanism involving the incoming ligand with the metal center.

- Specifically, the addition proceeds by the **formation** of a **σ–complex** upon binding of an incoming ligand say, H_2, followed by the **cleavage** of the H–H bond as a result of the back donation of electrons from the metal to the σ*–orbital of the H–H bond.

- Such type of addition is common for the H–H, C–H and Si–H bonds. As expected these proceed by two steps
  a) the formation of a σ–complex and
  b) the oxidation step. For example, the oxidative addition of H_2 to Vaska's complex $(PMe_3)_2Ir(CO)Cl$ proceeds by this pathways.

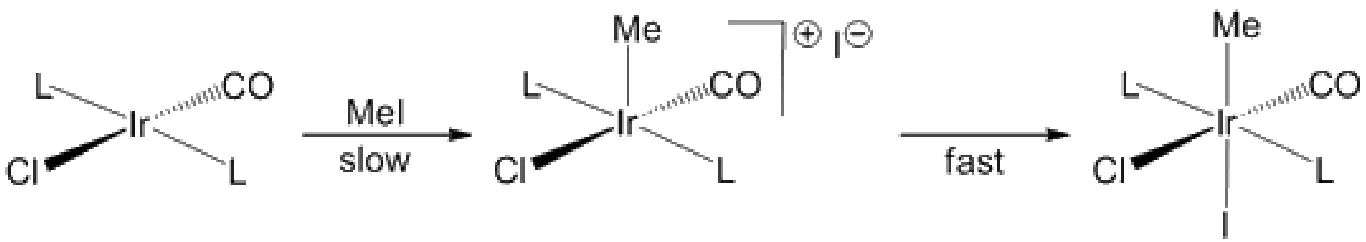


S_N2 pathway

- This pathway of oxidative addition is operational for the polarized AB type of ligand substrates like the alkyl, acyl, allyl and benzyl halides.

- In this mechanism, the L_nM fragment directly **donates electrons to the σ*−orbital** of the A−B bond by attacking the least electronegative atom, say A, of the AB molecule and concurrently initiating the elimination of the most electronegative atom of the AB molecule in its anionic form, B^-.

- These reactions proceed *via* a polar transition state that is accompanied by an inversion of the stereochemistry at the atom of attack by the metal center and are usually accelerated in polar solvents.



one bond is broken and one bond is formed synchronously, i.e., in one step. S_{N2} is a kind of nucleophilic substitution reaction mechanism

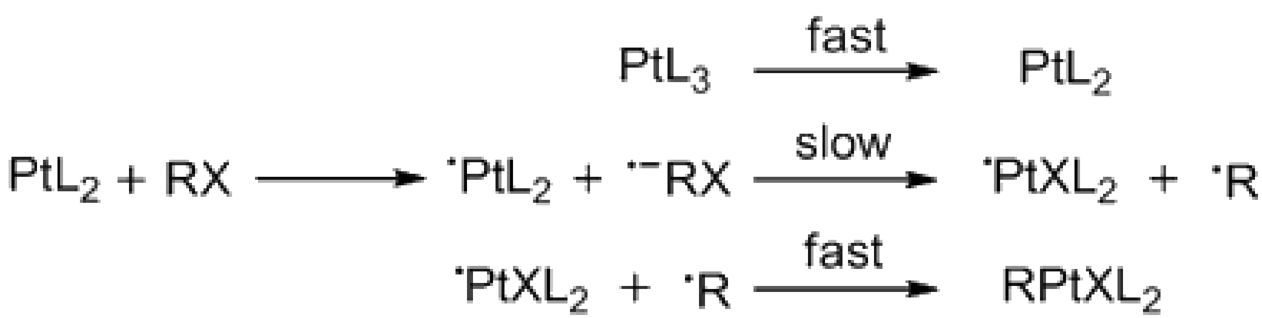
Radical pathway

- This type of oxidative addition proceeds *via* a by radical pathway that generally are vulnerable to the presence of impurities.

- The radical processes can be of non−chain and chain types. In a non−chain type of mechanism, the metal (M) transfer **one electron to the σ*−orbital of the RX bond** resulting in the formation of a radical cation $M^{+\bullet}$ and a radical anion $RX^{-\bullet}$.

- The generation of the two radical fragments occurs by the way of the elimination of the anion X^- from the radical anion $RX^{-\bullet}$ leaving behind the radical $R^\bullet$ while the subsequent reaction of X^- anion with the radical cation $M^{+\bullet}$ generates the other radical $MX^\bullet$ in the course of the reaction.

- Such type of non−chain type of oxidative addition is observed for the addition of the alkyl halide to $Pt(PPh_3)_3$ complexes.



Ionic pathway

This is kind of pathway for the oxidative addition reaction is common to the addition of **hydrogen halides** (HX) in its dissociated H^+ and X^- forms. The ionic pathways are usually of the following two types:

(i) the ones in which the starting metal complex adds to H^+ prior to the addition of the halide $X^-$and

(ii) the other type, in which the halide anion X^- adds to the starting metal complex first, and then the addition of proton H^+ occurs on the metal complex.

$$Pt(PPh_3)_4 + H^+ + Cl^- \xrightarrow{-PPh_3} [HPt(PPh_3)_3]^+ + Cl^- \xrightarrow{-PPh_3} [HPtCl(PPh_3)_2]$$

$Pt(PPh_3)_4$	$[HPt(PPh_3)_3]^+$	$[HPtCl(PPh_3)_2]$
18 VE, d^{10}	16 VE, d^8	16 VE, d^8
tetrahedral	square planar	square planar

$$[Ir(cod)L_2]^+ + Cl^- + H^+ \longrightarrow [IrCl(cod)L_2] + H^+ \longrightarrow [IrHCl(cod)L_2]^+$$

$[Ir(cod)L_2]^+$	$[IrCl(cod)L_2]$	$[IrHCl(cod)L_2]^+$
16 VE, d^8	18 VE, d^8	18 VE, d^6
square planar	TBP	octahedral

Heterogeneous catalysis

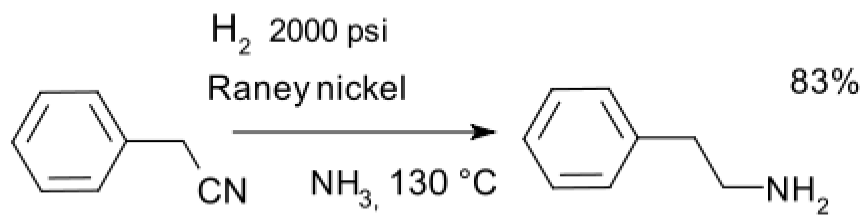
- **Heterogeneous** catalysis is the type of catalysis where the phase of the catalyst differs from the phase of the reactants.
- This contrasts with **homogeneous** catalysis where the reactants and catalyst exist in the same phase.
- Phase distinguishes between not only solid, liquid, and gas components, but also immiscible mixtures (e.g. oil and water), or anywhere an interface is present.
- Catalysts are useful because they increase the rate of a reaction without themselves being consumed and are therefore reusable.
- Heterogeneous catalysis typically involves solid phase catalysts and gas phase reactants.
- In this case, there is a cycle of molecular adsorption, reaction, and desorption occurring at the catalyst surface. Thermodynamics, mass transfer, and heat transfer influence the rate (kinetics) of reaction.

Some Industrial examples

Process	Reactants, Product(s)	Catalyst	Comment
Sulfuric acid synthesis (Contact process)	$SO_2 + O_2$, SO_3	vanadium oxides	Hydration of SO_3 gives H_2SO_4
Ammonia synthesis (Haber–Bosch process)	$N_2 + H_2$, NH_3	iron oxides on alumina(Al_2O_3)	Consumes 1% of world's industrial energy budget[3]
Nitric acid synthesis (Ostwald process)	$NH_3 + O_2$, HNO_3	unsupported Pt-Rh gauze	Direct routes from N_2 are uneconomical
Hydrogen production by Steam reforming	$CH_4 + H_2O$, $H_2 + CO_2$	Nickel or K_2O	Greener routes to H_2 by water splitting actively sought
Ethylene oxide synthesis	$C_2H_4 + O_2$, C_2H_4O	silver on alumina, with many promotors	Poorly applicable to other alkenes
Hydrogen cyanide synthesis (Andrussov oxidation)	$NH_3 + O_2 + CH_4$, HCN	Pt-Rh	Related ammoxidation process converts hydrocarbons to nitriles
Olefin polymerization Ziegler–Natta polymerization	propylene, polypropylene	$TiCl_3$ on $MgCl_2$	Many variations exist, including some homogeneous examples
Desulfurization of petroleum (hydrodesulfurization)	$H_2 + R_2S$ (idealized organosulfur impurity), $RH + H_2S$	Mo-Co on alumina	Produces low-sulfur hydrocarbons, sulfur recovered via the Claus process

Other examples

Reduction of nitriles in the synthesis of phenethylamine with Raney nickel catalyst and hydrogen in ammonia:



Nitrile hydrogenation
The cracking, isomerisation, and reformation of hydrocarbons to form appropriate and useful blends of petrol.

In automobiles, catalytic converters are used to catalyze three main reactions:

The oxidation of carbon monoxide to carbon dioxide:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

- The reduction of nitrogen monoxide back to nitrogen:

$$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$$

- The oxidation of hydrocarbons to water and carbon dioxide:

$$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6\ H_2O$$

- This process can occur with any of hydrocarbon, but most commonly is performed with petrol or diesel.

- Asymmetric heterogeneous catalysis facilitates the production of pure enantiomer compounds using chiral heterogeneous catalysts.

- The vast majority of heterogeneous catalysts are basedon metals or metal oxides; however, some chemical reactions can be catalyzed by carbon-based materials, e.g., oxidative dehydrogenations or selective oxidations.

$$\text{Ethylbenzene} + 1/2\ O_2 \rightarrow \text{Styrene} + H_2O$$

$$\text{Acrolein} + 1/2\ O_2 \rightarrow \text{Acrylic acid}$$