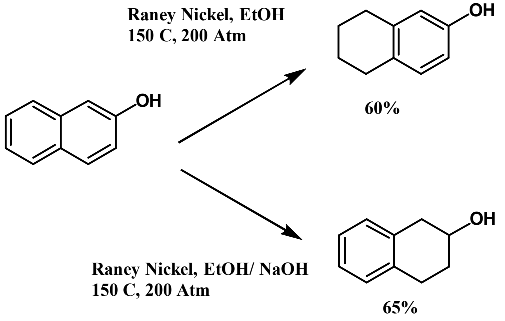
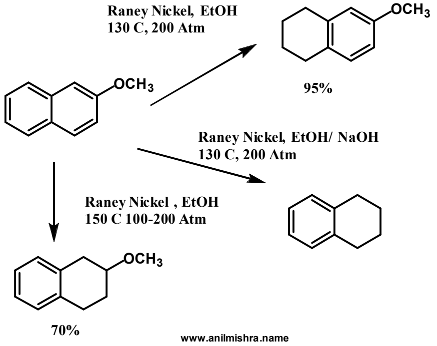
Selective Reduction

Ring Differentiation in Aromatic Reduction



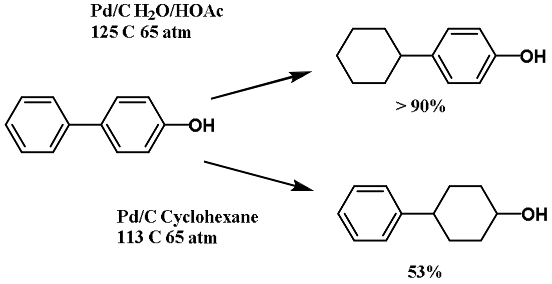
Selective Reduction

Ring Differentiation in Aromatic Reduction

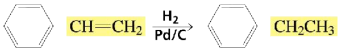


Selective Reduction

Ring Differentiation in Aromatic Reduction



Catalytic Hydrogenation



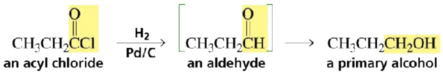
$CH_3CH_2CH{=}NCH_3 + H_2 \xrightarrow{Pd/C} CH_3CH_2CH_2NHCH_3$

methylpropylamine

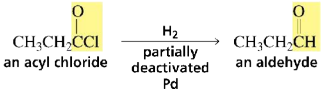
$CH_3CH_2CH_2C{\equiv}N + 2\,H_2 \xrightarrow{Pd/C} CH_3CH_2CH_2CH_2NH_2$

butylamine

Catalytic Hydrogenation



$\underset{\text{an acyl chloride}}{CH_3CH_2\overset{O}{\overset{\|}{C}}Cl} \xrightarrow[Pd/C]{H_2} \left[\underset{\text{an aldehyde}}{CH_3CH_2\overset{O}{\overset{\|}{C}}H}\right] \longrightarrow \underset{\text{a primary alcohol}}{CH_3CH_2CH_2OH}$



$\underset{\text{an acyl chloride}}{CH_3CH_2\overset{O}{\overset{\|}{C}}Cl} \xrightarrow[\text{partially deactivated Pd}]{H_2} \underset{\text{an aldehyde}}{CH_3CH_2\overset{O}{\overset{\|}{C}}H}$

Catalyst poisoning

- Catalyst poisoning refers to the partial or total deactivation of a catalyst caused by exposure to a range of chemical compounds.
  - ☐ Poisoning may be desirable when it results in improved selectivity
    - Lindlar's catalyst
  - ☐ It may be undesirable when the catalyst is rendered ineffective
    - Lead in catalytic converters
- Poisoning refers specifically to chemical deactivation, rather than other mechanism of catalyst degradation such as thermal decomposition or physical damage.

Catalyst Inhibitors and Poisons

- Inhibitors diminish the rate , but the effect can be reversed by washing it away.
- Poisons exert an appreciable inhibitory effect when present in small amounts.
- Both can be used to fine-tune the selectivity of a catalyst.

Catalyst Inhibitors and Poisons

- Metals and metals Salts
  - Mg, Ni Co have no effect on $PdCl_2$ reductions.
  - Al, Fe, Cu, Zn, Ag, Sn, Pb, Hg, Cr their oxides and carbonates inhibit Palladium.
  - Pt reductions inhibited by Al, Co, Bi.
  - Pt Reductions increased by Fe, Cu Zn, Ag, Pb
  - Raney nickel completely inhibited by mercuric chloride, but 50% inhibited by Ag_2SO_4

Catalyst Inhibitors and Poisons

- Halogen-Containing Compounds
  - Halide ions inhibit Ni, sometimes Pt, Pd In a concentration-dependent manner.
    - $I^- >> Br^- > Cl^- > F^-$
  - Corresponding acids just as potent, if anhydrous.

Catalyst Inhibitors and Poisons

- Halogen-Containing Compounds
  - Non-ionizable organic halides often do not inhibit Pt and Pd, except when directly bonded to the region of reduction
    - e.g. aromatic halides reduced to cyclohexane halides
  - Potent inhibitors (Ni): carbon tet, chloroform, chloral hydrate, trichloroethanol, di- and trichloroacetic acid, alkyl chloride, benzyl chloride, and acetyl chloride.

Advantages of Catalytic Poisons

- Normally, it is not possible to stop the hydrogenation of an alkyne at the alkene stage,
- But if the catalyst is suitably deactivated, addition to the triple bond can be achieved without further addition occurring to the resulting double bond.

Advantages of Catalytic Poisons

- The preferred catalyst for selective hydrogenation of alkynes is palladium partially ƒpoisonedò with a lead salt (Lindlar catalyst).
- This catalyst shows little affinity for adsorbing alkenes and hence is ineffective in bringing about hydrogenation to the alkane stage

Lindlar catalyst

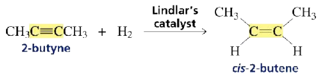
- A Lindlar catalyst is a heterogeneous catalyst that consists of palladium deposited on calcium carbonate which is then poisoned with various forms of lead or sulphur.
- It is used for the hydrogenation of alkynes to alkenes
  - ☐ Without further reduction into alkanes
- Named after its inventor **Herbert Lindlar**

Advantages of Catalytic Poisons

Reduction by Catalytic Hydrogenation

$$\underset{\text{1-butene}}{CH_3CH_2CH{=}CH_2} + H_2 \xrightarrow{\text{Pt, Pd, or Ni}} \underset{\text{butane}}{CH_3CH_2CH_2CH_3}$$

$$\underset{\text{1-pentyne}}{CH_3CH_2CH_2C{\equiv}CH} + 2\,H_2 \xrightarrow{\text{Pt, Pd, or Ni}} \underset{\text{pentane}}{CH_3CH_2CH_2CH_2CH_3}$$



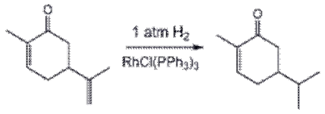
Homogeneous Catalysis

Homogeneous Catalysis

- Homogeneous catalysis is catalysis in a solution by a soluble catalyst.
- Homogeneous catalysis are catalytic reactions where the catalyst is in the same phase as the reactants,
  - ☐ This applies to reactions in the gas phase and even in a solid.

Homogeneous catalysts

- Illustrative homogeneous catalysts include the rhodium-based compound known as Wilkinson's catalyst and the iridium-based Crabtree's catalyst.
  - ☐ An example is the hydrogenation of carvone



Wilkinson's Catalyst

- Wilkinson's catalyst is the common name for a coordination compound with the formula

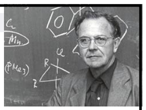
$RhCl(PPh_3)_3$

(Ph = phenyl)

chlorotris(triphenylphosphine)rhodium(I)

- It is named after the chemist and Nobel Laureate, Sir Geoffrey Wilkinson who popularized its use.

Wilkinson's Catalyst

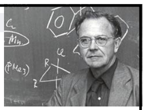


- $RhCl(PPh_3)_3$ was the first highly active homogeneous hydrogenation catalyst and was discovered by Geoffrey Wilkinson (Nobel prize winner for Ferrocene) in 1964.

$RhCl_3{\cdot}H_2O$ + xs PPh_3 ⟶ $RhCl(PPh_3)_3$ + $Ph_3P{=}O$ + oxidzed solvent

- Wilkinsonõs Catalyst is a Rh(I) complex, $Rh(PPh_3)_3Cl$ containing three phosphine ligands and one chlorine.

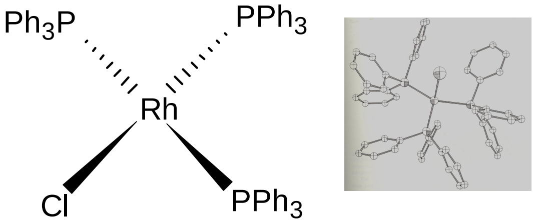
Wilkinson's Catalyst



- As a result of the olefin insertion (hydrogen migration) we obtain a Rh (III), 16e-, five coordinate species.
- A solvent occupies the sixth coordination site to take it to a 18e- species
- Reductive elimination occurs to give the hydrogenated product and the catalytically active species.

Wilkinson's Catalyst

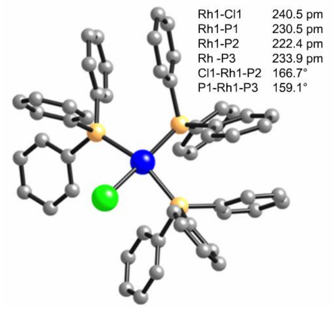
- The compound is a square planar, 16-electron complex.



Chlorotris(triphenylphosphine)rhodium(I)

square planar **d^8 configuration**

Wilkinson's Catalyst



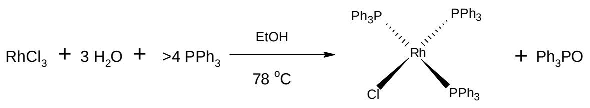
Rh1-Cl1	240.5 pm
Rh1-P1	230.5 pm
Rh1-P2	222.4 pm
Rh -P3	233.9 pm
Cl1-Rh1-P2	166.7°
P1-Rh1-P3	159.1°

Wilkinson's Catalyst

- The compound is a square planar, 16-electron complex.
- It is usually obtained in the form of a red-violet crystalline solid from the reaction of **rhodium(III) chloride** with excess **triphenylphosphine**.
    - ☐ The synthesis is conducted in refluxing ethanol which helps with the reduction.
    - ☐ Triphenylphosphine serves as the reducing agent yielding triphenylphosphine oxide.

$RhCl_3(H_2O)_3 + 4\ PPh_3$ Ÿ $RhCl(PPh_3)_3 + OPPh_3 + 2\ HCl + 2\ H_2O$

Synthesis of Wilkinson's Catalyst



Commercially available

Catalytic Steps

- **Oxidative Addition**
  - ☐ Occurs when a complex behaves simultaneously as a Lewis base and a Lewis acid
  - ☐ Metal must possess a non-bonding electron pair
  - ☐ Coordinatively unsaturated
  - ☐ Oxidation of metal by two units ï M to M^{+2}

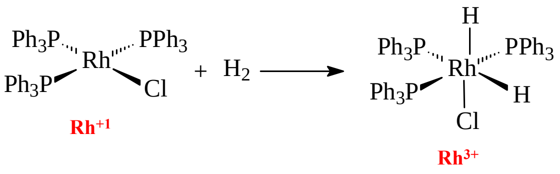
Catalytic Steps

- **Ligand coordination and dissociation**
  - ☐ Facile coordination of the reactant and facile loss of products.
  - ☐ Coordinatively unsaturated
    - 16-electron complexes

Catalytic Steps 1

WC in alkene Hydrogenation

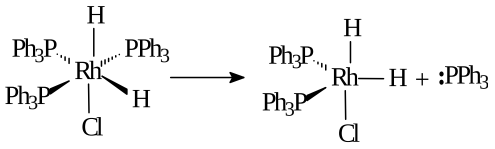
- **Oxidative addition**



Catalytic Step 2

WC in alkene Hydrogenation

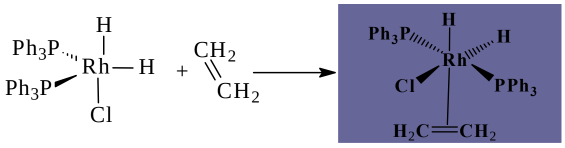
- **Ligand Dissociation**



Catalytic Step 3

WC in alkene Hydrogenation

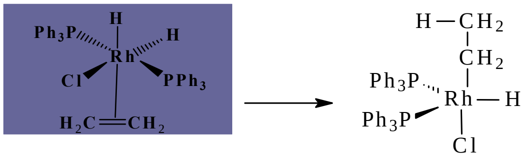
- **Ligand Association**



Catalytic Step 4

WC in alkene Hydrogenation

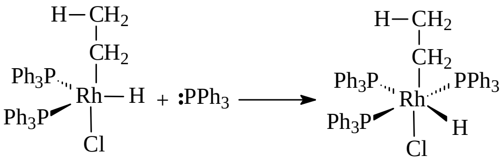
- **Migration/Insertion**



Catalytic Step 5

WC in alkene Hydrogenation

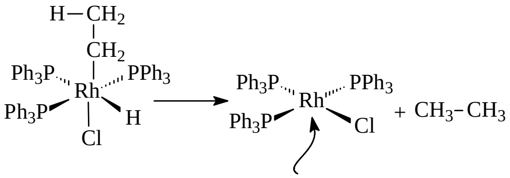
- **Ligand Association**



Catalytic Step 6

WC in alkene Hydrogenation

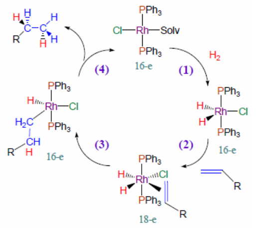
- **Reductive Elimination**



(note: regeneration of the catalyst)

Mechanism

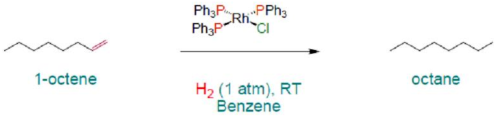
- Steps:
  1. H_2 addition,
  2. Alkene addition,
  3. Migratory insertion,
  4. Reductive elimination of the alkane, regeneration of the catalyst



$RhCl(PPh_3)_3$ + Solv ⇆ $RhCl(Solv)(PPh_3)_2$ + PPh_3

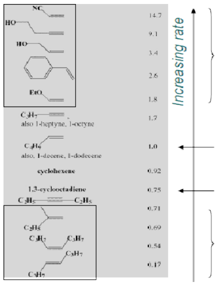
Other Reactions

- The complex $RhCl(PPh_3)_3$ became the first highly active homogeneous hydrogenation catalyst that compared in rates with heterogeneous counterparts.



Wilkinsonôs catalyst selectivity

The rate of hydrogenation depends on :
(a) presence of a functional group in the vicinity of the C=C bond
(b) degree of substitution of the C=C fragment



A polar functional group may accelerate catalysis by assisting olefin coordination to Ru

Terminal C_6-C_{12} alkenes are hydrogenated at the same rate

Conjugated dienes react slower

Hydrogenation of internal and branched alkenes is the slowest (note: *cis* is faster than *trans*!)

Wilkinsonôs catalyst selectivity

- *Cis*-disubstituted C=C react faster than *trans*-disubstituted C=C: