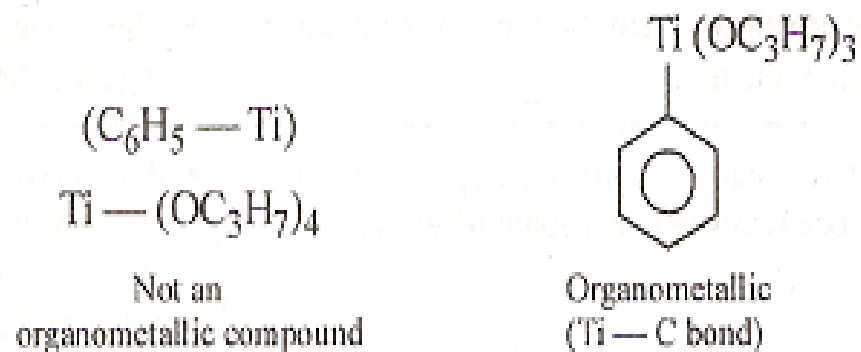


14.12 ORGANOMETALLICS

An organometallic compound is generally a compound which possesses a metal-carbon bond. Organometallic chemistry can be viewed as a bridge between organic and inorganic chemistry. The importance of organometallic compounds lies in the fact that these are excellent catalysts which play a major

role in the production of pharmaceuticals, agrichemicals, flavours and semiconductors etc. Organometallic chemistry is rapidly growing field of chemistry. The discovery of Grignard reagents in 1900 not gave versatile intermediates for a variety of organic preparations.

It may be noted that not all the compounds containing carbon and a metal atom are organometallic. The term 'organometallic' is reserved to the compounds which contain atleast one Metal-Carbon bond. An alkoxide such as $(C_3H_7O)_4 Ti$ is not considered as organometallic compound because here the organic group is bonded to Ti through oxygen and not through carbon. Whereas the compound $C_6H_5Ti(OC_3H_7)_3$ is an organometallic compound because in this compound Ti is bonded to carbon of the organic group



The common examples of organometallic compounds are those $\text{Pb}(\text{C}_2\text{H}_5)_4$ (tetraethyl lead), $(\text{C}_5\text{H}_5)_2\text{Fe}$ (ferrocene), $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ (Zeise salt) etc.

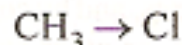
Despite the rigorous definition, the borderline that distinguishes organometallic chemistry from other branches is unclear. For example metal cyanides ($\text{M}-\text{CN}$) and metal carbides (CaC_2 , Al_4C_3 etc.) contain Metal-Carbon bond but are *not* considered organometallics because their properties are closely related to those of many other compounds of inorganic chemistry. On the other hand, $\text{Ni}(\text{CO})_4$ (nickel tetracarbonyl) and other complexes having the ligand CD are considered organometallic because of the resemblance of their properties to organometallics.

Organometallics are also known as organo-inorganics, metallo-organics and metalorganics. Organometallic compounds are named by prefixing the metal with organo-, e.g. organopalladium compounds, organophosphorus compounds, organomagnesium compounds.

Reactivity

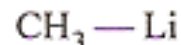
Organometallics are very reactive compounds and hence are kept in solutions in organic solvents (especially with H_2O , O_2 etc)

The organometallic compounds form electron rich or anionic carbon atoms i.e. carbanions during their reactions. This means, they will function as bases or nucleophiles. Thus it is reasonable to write the general formula of these compounds as R^-M^+ .



alkyl halide

Methyl group has lower electron density and hence is an electrophile



Organometallic alkyl lithium

The methyl group has higher electron density and hence is a nucleophile

The alkyl group in alkyl halides acts as electrophile whereas the alkyl group in organometallics acts as nucleophile. In other words organolithium and organomagnesium compounds are strong bases since the negative charge is on carbon.

It is the carbonionic nature of organometallics that is responsible for their usefulness as synthetic reagents.

CLASSIFICATION

The organometallic compounds can be classified on the basis of the nature of metal-carbon bond.

(1) Ionic compounds of electropositive metals:

The organosodium and organopotassium compounds are essentially ionic organometallic compounds. In these type of compounds the bonding between the metal and the carbon is ionic. The carbon of the organic group (hydrocarbon) carry a negative charge which is strongly attracted by the positively charged metal ion by electrostatic forces of attraction.

These organometallic compounds are formed by the most electropositive metals of group IA and IIA. The formation of these compounds is favoured if the negative charge on the carbon atom is stabilized i.e it is delocalized over several carbon atoms.

Example: $K^+C_5H_5^-$ (potassium cyclopentadienyl). The negative charge is stabilized due to delocalization over the five carbon atoms of cyclopentadienyl ring.



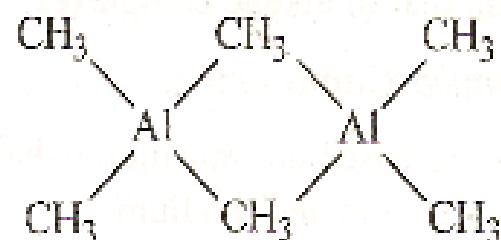
Other examples include $Na^+C_6H_5^-$, $Na^+C_4H_9^-$ etc. These compounds contain a very reactive C_5H_5 group. These compounds are referred to as metal cyclopentadienides. These organometallic compounds show behaviour typical of ionic compounds and are insoluble in organic or non-polar solvents. The reactivity of these compounds depend upon the stability of the anion. However, there are certain metal cyclopentadienides which have substantial amount of covalent character present.

(2) Covalent organometallic compounds:

These compounds have organic part bonded to the metal atom by a normal sigma covalent bond. These compounds are very common and are generally formed by Zn, Cd, Hg and representative elements of group III, IV and V. The covalent organometallic compounds are generally metal-alkyl compounds. Examples are $\text{Pb}(\text{C}_2\text{H}_5)_2$, $(\text{C}_6\text{H}_5)_2\text{Zn}$, $(\text{CH}_3)_2\text{Cd}$, $\text{C}_4\text{H}_9\text{Li}$ etc. The polarity of the covalent bond between metal and alkyl groups depends upon the difference in electronegativity between metal atom and carbon atom.

(3) Electron deficient organometallic compounds:

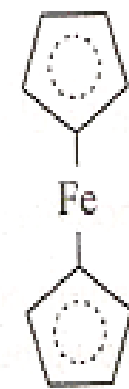
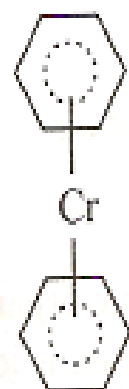
These type of compounds include the compounds having bridging alkyl groups. For example, dimeric trialkyl aluminium which have bridging alkyl groups.



Dimeric dialkyl aluminium

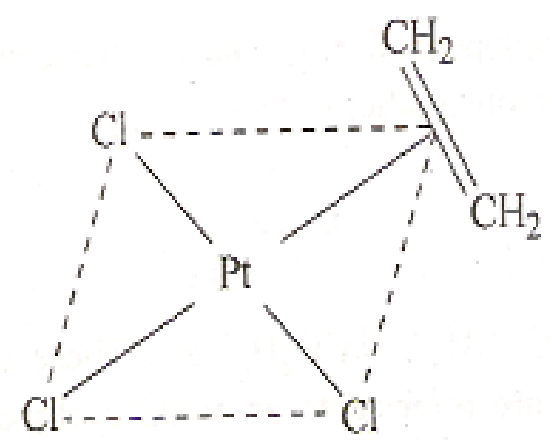
(4) Organometallics involving π bonds:

These constitute an important class of organometallics having metal-ligand bond between a metal and the π orbitals of organic ligands such as alkenes, benzene ring etc. Ferrocene was the first of many π complexes which came to be known as metallocenes. In these complexes the metal ion is sandwiched between two parallel carbocyclic rings became known as "sandwich" compounds. Example,



common example of ligands forming such type of organometallic compounds are :

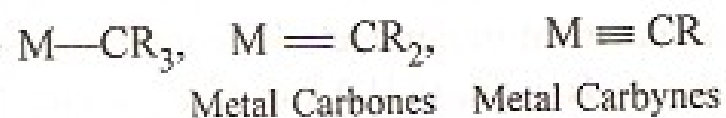
Complexes of alkenes are well known for transition metals like Pt(II), Pd(II), Cu(II), Ag(I), Hg(II) etc. The first compound of alkene with the metal ion was reported by Zeise (a Danish Chemist) and is known as Zeise salt. $K[PtCl_3.(C_2H_4)]$



Zeise salt
(π complex)

(5) *Carbene/Carbyne complexes:*

The chemistry of metal-carbon single bond dates back to 19th century (e.g. Grignard's reagent) Transition metal compounds containing metal carbon double bond or triple bond have come to be understood more recently.



If there occurs multiple bonding between metal and carbon, the bond strength would be increased. It has been observed that in carbene compounds, the metal-carbon bond is shorter than metal-alkyl sigma bond but larger than metal-carbon double bond. Thus metal carbenes are generally stable organometallics. The first carbene complex $(\text{CO})_5 \text{W}[:\text{CRX}]$ was synthesized by Noble Laureate in 1964 by E.O. Fisher.

Metal Carbynes have triple bonds. For example $(\text{CO})_4\text{M}(\equiv\text{CR})\text{X}$. The chemistry of alkyne complexes is more complicated than that of alkene complexes.

(6) *Transition-metal Organometallic Compounds:*

A large number of organometallics are based on transition metals. Examples include organometallics containing iron, nickel, chromium, platinum and rhodium.

A transition-metal complex consists of a transition-metal to which are attached groups called *ligands*. Essentially, anything attached to a metal is a ligand. A ligand can be an element (O_2 , N_2), a compound (NO), or an ion (CN^-); it can be inorganic as in the examples just cited or it can be an organic ligand. Ligands differ in the number of electrons that they share with the transition metal to which they are attached. Carbon monoxide is a frequently encountered ligand in transition-metal complexes and contributes two electrons; it is best thought of in terms of the Lewis structure $:\bar{\text{C}}\equiv\overset{+}{\text{O}}:$ in which carbon is the reactive site. An example of a carbonyl complex of a transition metal is nickel

(ii) Hexacarbonyl chromium (0), $\text{Cr}(\text{CO})_6$

Atomic number of Cr = 24

Cr(0)

Six CO groups (6×2)

= 24

= 12

EAN = 36

Thus, EAN rule is obeyed.

(iii) Pentacarbonyl iron (0), $\text{Fe}(\text{CO})_5$

Atomic number of Fe = 26

Fe(0)

Five CO groups (5×2)

= 26

= 10

EAN = 36

Thus, EAN rule is obeyed.

(iv) Pentacarbonyl manganate (-1) ion, $[\text{Mn}(\text{CO})_5]^-$

Atomic number of Mn = 25

Mn(-1)

Five CO groups (5×2)

= 26

= 10

EAN = 36

Thus, $[\text{Mn}(\text{CO})_5]^-$ obeys EAN rule.

General Methods of Synthesis of Organometallics

(1) By reductive substitution of alkyl halides: (Preparation of metal alkyls)

The first reported organometallic compounds were prepared by the reductive substitution of alkyl halides. The following equations illustrate these reactions for the commonly used metals lithium and magnesium (R may be hydrogen or alkyl groups in any combination).



The alkyl magnesium halides described in the second reaction are called *Grignard Reagents* after the French chemist, Victor Grignard, who discovered them. The solvent used in this reaction is anhydrous diethyl ether. Typical solvents are normally anhydrous diethyl ether but pentane or hexane can also be used.

The other metals react in a similar manner, but the two shown here are the most widely used.



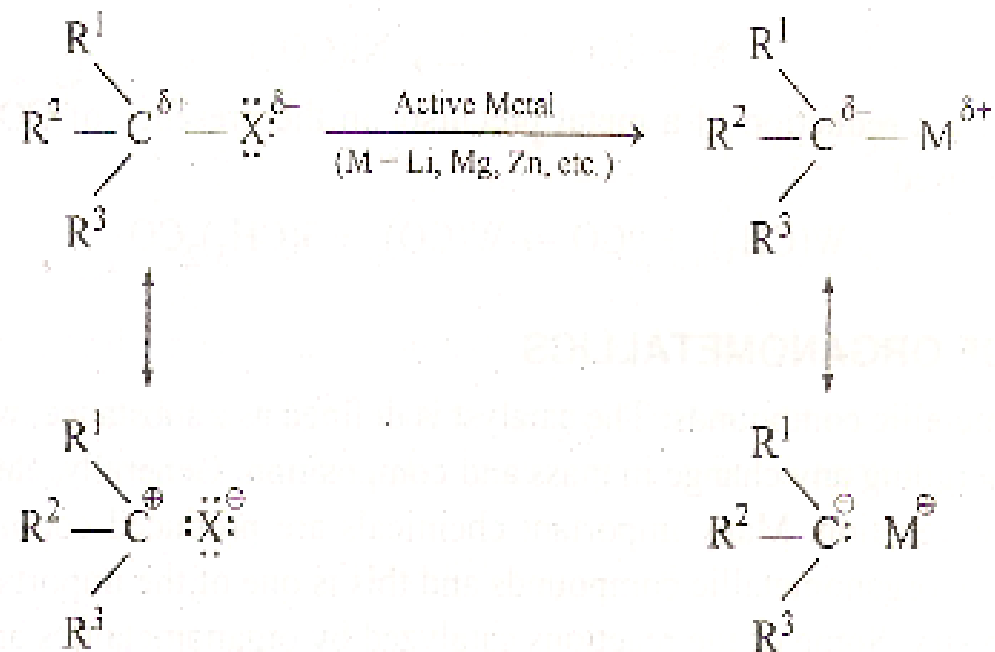
Reactions of organolithium and Grignard reagents reflect the nucleophilic (and basic) character of the functional carbon in these compounds

% Ionic Character of $H_3C - \text{Metal}$



These reactions are obviously substitution reactions, *but they cannot be classified as nucleophilic substitutions*, as were the earlier reactions of alkyl halides. Because the functional carbon atom has

been reduced, the polarity of the resulting functional group is inverted (an originally electrophilic carbon becomes nucleophilic). This change, shown below, makes alkyl lithium and Grignard reagents unique and useful reactants in synthesis.



(2) Metal Exchange Reactions:

Alternative methods of preparing a wide variety of organometallic compounds generally involve an exchange reaction in which a given metal is either moved to a new location or replaced by a new metal, which may include B, Al, Ti, V, Fe, Ni, Cu, Mo, Ru, Pd, Sn, Pt, Hg & Pb. Some of these reactions are:



Examples:



Type 2:

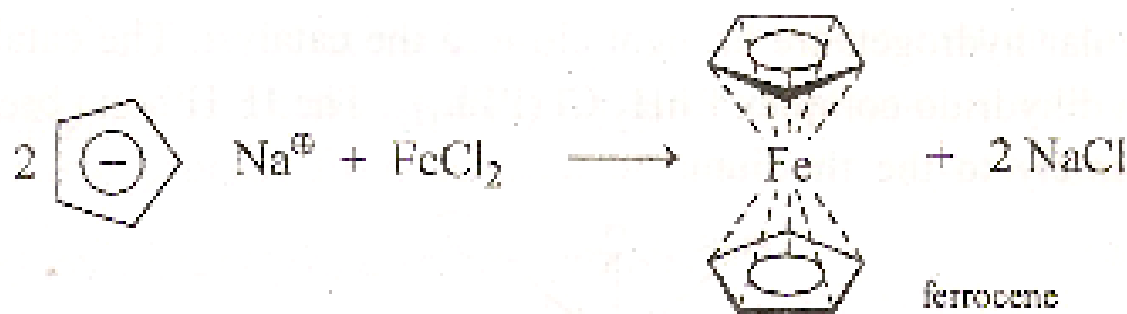


R-M is often a dialkylmercury compound.

Examples:



Type 3:



(3) Syntheses of metal carbonyls:

Metal carbonyls can be prepared in a variety of ways:

- For Ni and Fe, binary metal carbonyls can be made by the direct interaction with the metal



- In other cases, a reduction of a metal precursor in the presence of CO (or using CO as the reductant) is used



APPLICATIONS OF ORGANOMETALLICS

Catalysis by organometallic compounds: The catalyst is defined as a substance, which alters the rate of reaction without undergoing any change in mass and composition. Generally, catalyst is used to speed up an otherwise slow reaction. Many important chemicals are produced commercially by reactions which are catalyzed by organometallic compounds and this is one of the important factors for studying organometallic chemistry. Some of the reactions catalyzed by organometallics are given below:

(1) **Alkene Hydrogenation (Wilkinson's Catalysis)** Although the reaction of hydrogen gas with ethylene is thermodynamically favourable, it does *not* take place at room temperature and pressure.



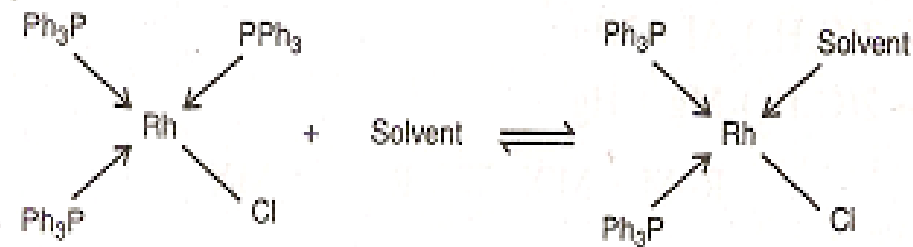
However, in the presence of the organometallic complex chlorotris (tri-phenylphosphine) rhodium(I), $(\text{Ph}_3\text{P})_3\text{RhCl}$, which is known as Wilkinson's Catalyst, the reaction is very fast.

Wilkinson's catalyst is most widely used for homogeneous hydrogenation. This catalyst was discovered by Sir Geoffrey Wilkinson. It is a complex of a transition metal rhodium called tris (triphenylphosphine) chloro rhodium (I) having the formula $\text{RhCl}(\text{PPh}_3)_3$ where Ph stands for phenyl group.

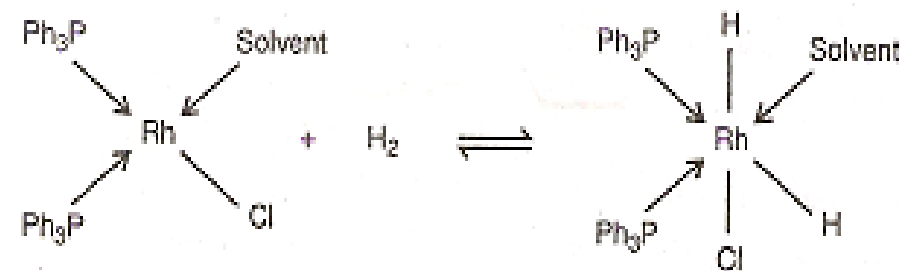
The phosphorus atom of phosphines has an unshared electron pair. It is through this electron pair, that triphenylphosphine is bonded to rhodium.

Rhodium can exhibit variable oxidation state of I and III and hence forms unstable intermediate with the reactant molecules. The mechanism can be explained as follows–

- It is believed that in solution the complex $\text{RhCl}(\text{PPh}_3)_3$ exchanges one of its PPh_3 for a solvent molecule, reversibly.

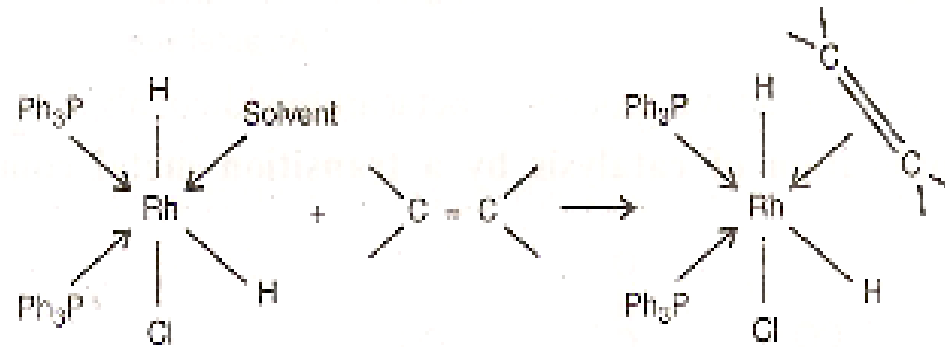


- The reactants, alkene and molecular hydrogen are brought close to the catalyst. The catalyst reacts with the hydrogen to form dihydrido complex $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$. The H–H bond breaks and each hydrogen attach separately to the rhodium.



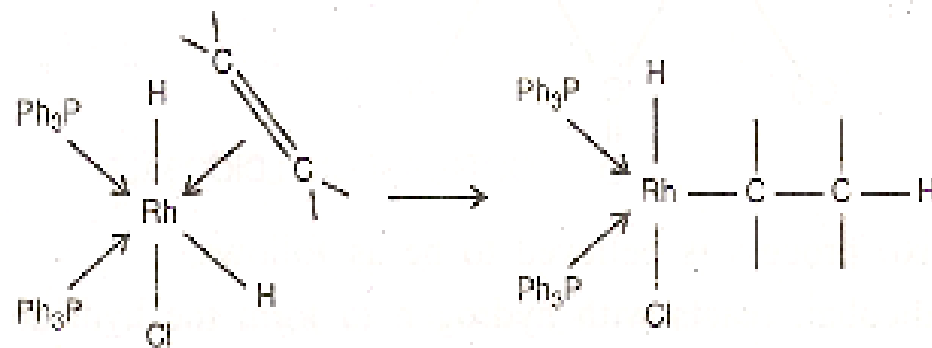
Thus in this step rhodium changes its oxidation state from (I) to (III).

- In the next step, alkene reacts with the catalyst by replacing a solvent molecule. The bond between the alkene and the metal atom rhodium is formed by the overlap of an empty orbital of the metal with the π cloud of alkene resulting in π complex.



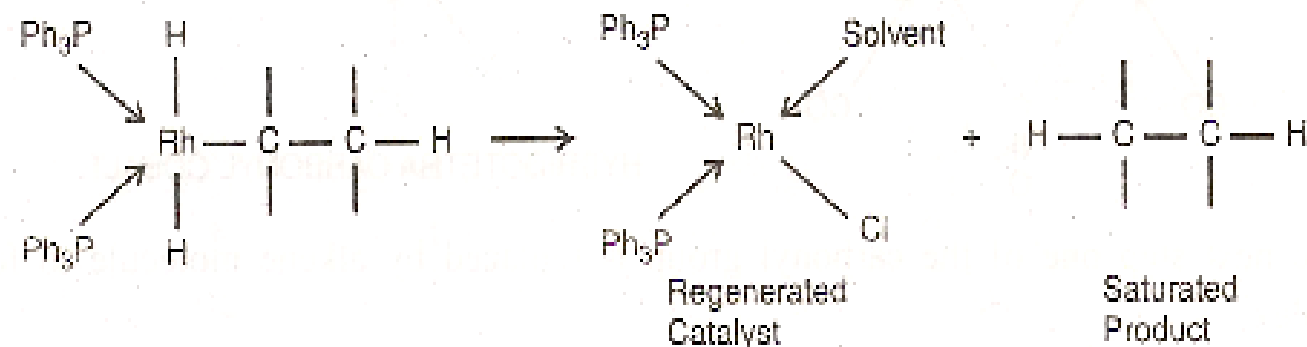
At this point both the reactants are bounded to rhodium and are in close proximity to react.

- A hydrogen atom migrates from the metal atom to one of the carbon atom of alkene whereas the other carbon attaches itself to the metal by a σ bond forming metal alkyl.



- The migration of alkene in between the metal hydrogen bond as in the above case is often referred to as insertion. Insertion can be defined as a process in which any atom or group is inserted between two other atoms initially bound together.

- Now, the second hydrogen migrates from the metal to carbon, which is still bonded to the metal atom, forming the hydrogenated product. The product detaches itself from the metal atom regenerating the catalyst. The rhodium atom regains its oxidation state of (I).



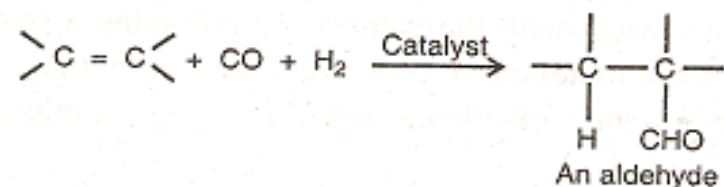
Evidence in Favour of the Above Mechanism

The most significant evidence comes from the fact that the above mentioned intermediates have been detected in solution and in some cases, isolated. Their structures have been well established by using spectroscopic techniques and have found to be in close agreement with the postulated structures.

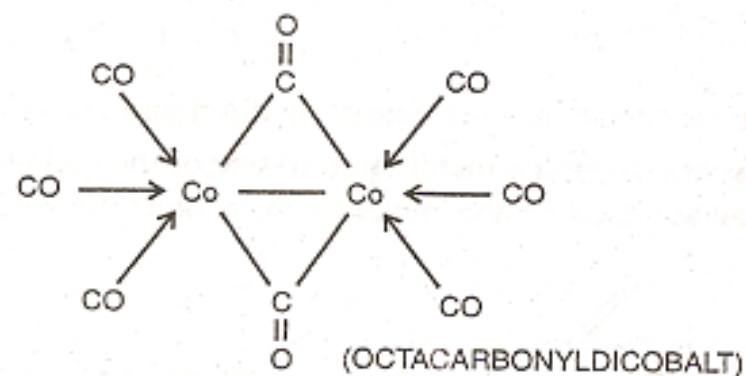
Metal catalyst makes a significant contribution in industrial applications of catalysts. For example, the alcohols which form the backbone of aliphatic organic synthesis, can be obtained by the oxo process from alkenes, by using metal carbonyl, as catalyst.

(2) Hydroformylation Oxo Process:

In presence of a metal catalyst, alkenes react with carbon monoxide and hydrogen to yield aldehydes. The aldehydes are again catalytically reduced to form alcohols.

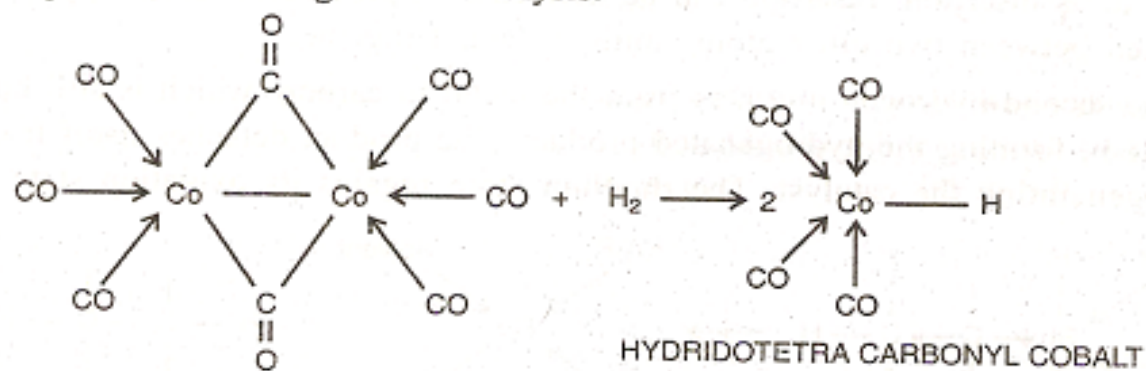


The catalyst employed in the above process is octacarbonyldicobalt, $Co_2(CO)_8$. This process is the first industrial application of catalysis by a transition metal complex.

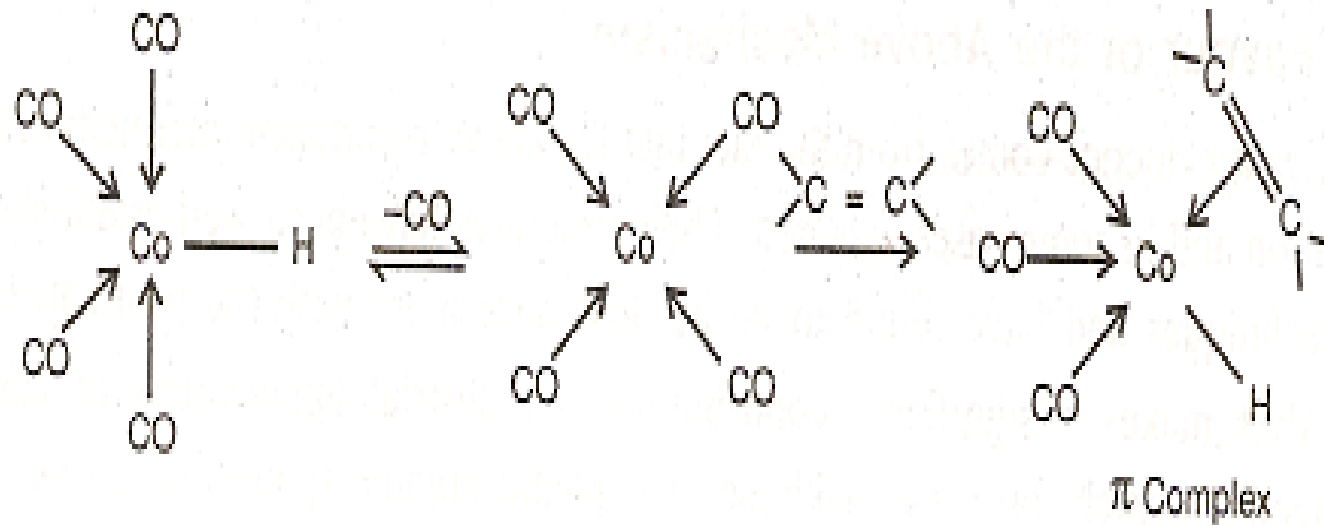


The mechanism of oxo process is believed to be as follows:

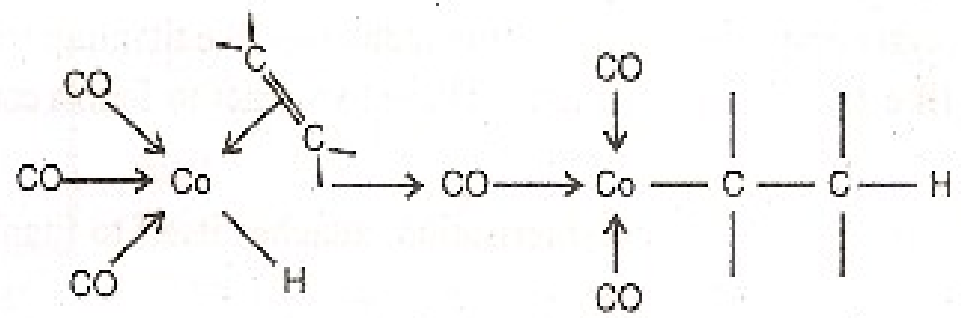
- The octacarbonyldicobalt reacts with hydrogen to form the hydrido complex $CoH(CO)_4$ which is the active catalyst. This catalyst is soluble in hydrocarbons, so oxo process can be grouped under homogeneous catalysis.



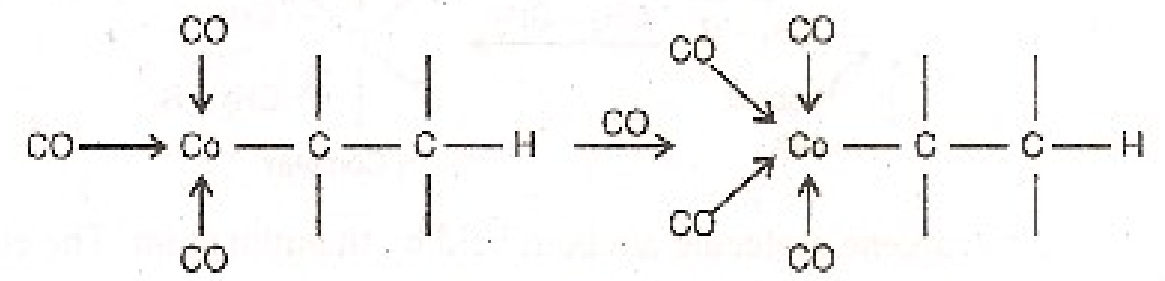
- In the next step one of the carbonyl group is replaced by alkene molecule to form a π -complex.



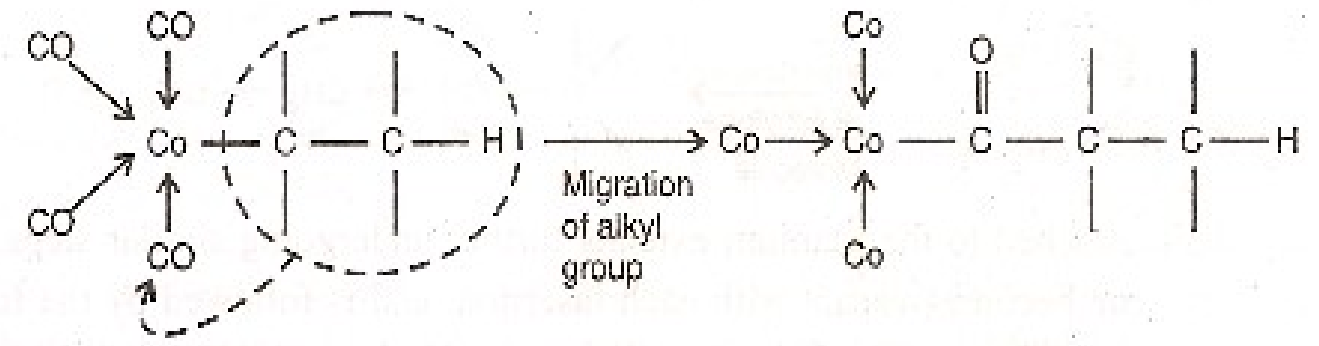
- Thus all the three reactants, viz CO , H_2 and alkene are in close proximity.
- The hydrogen migrates from Co to one of the carbon atom of alkene and the other carbon atom of alkene attaches itself to cobalt forming metal alkyl. In other words the alkene is inserted inbetween cobalt and hydrogen atom.



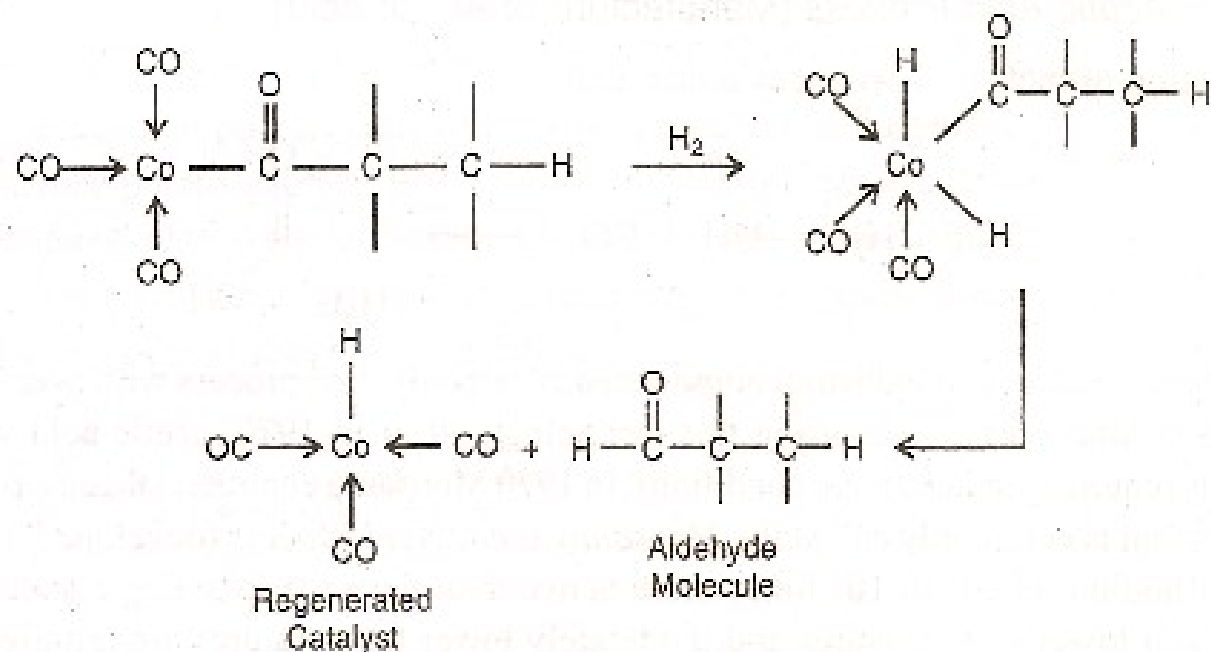
One molecule of CO is further added to the metal alkyl,



- The newly formed alkyl group then migrates to the carbonyl group, forming carbon-carbon bond.



- At this stage hydrogen is absorbed to form dihydrido complex. One of these hydrogens migrates to carbon of the C = O group and aldehyde molecule is formed which detaches itself from the metal complex, which becomes ready for fresh action.

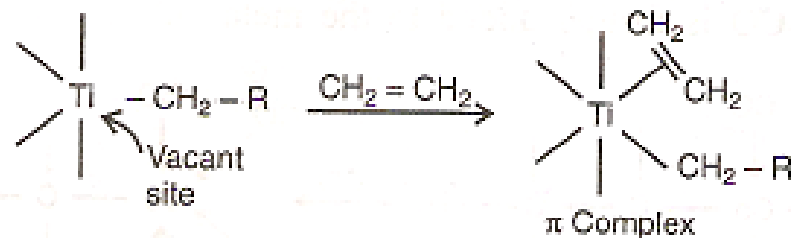


(3) Polymerization

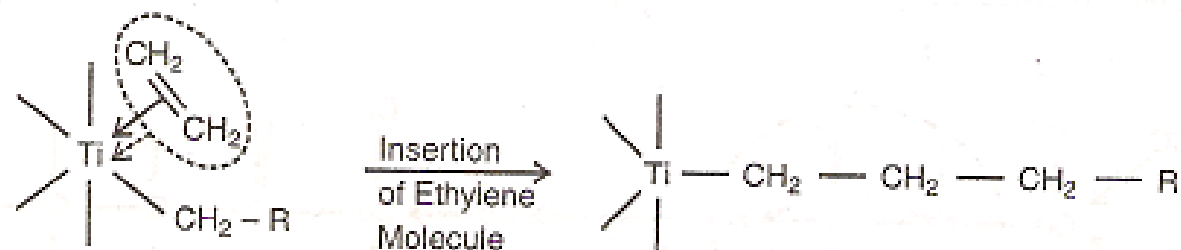
The catalyst which has revolutionised the field of polymer chemistry also belongs to metal salts i.e. the **Ziegler Natta catalyst**. This catalyst was discovered by Karl Ziegler and Giulio Natta who jointly received Nobel prize in 1963 for developing this catalyst. This catalyst exhibits remarkable power to control organic reactions.

Ziegler Natta catalyst comprises of a transition metal salt like titanium trichloride in combination with a metal alkyl like triethyl aluminium. These two react to form a complex having an ethyl group in situ.

The alkene which has to undergo polymerisation, attaches itself to titanium by π bond forming π complex.



Now the alkyl and the alkene molecule are both held by titanium atom. The ethylene unit inserts itself between the titanium and the alkyl group.

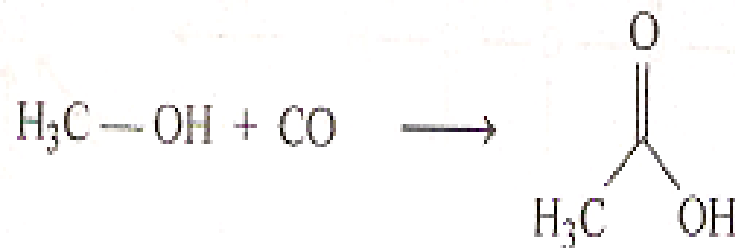


Thus, the chain attached to the titanium extends further undergoing similar steps. The bonding site which held ethylene becomes vacant with each insertion, and is followed by the formation of π complex with the next monomer unit. Thus the alkyl group keeps on growing with each cycle. The chain terminates finally by the insertion of hydrogen atom between titanium atom and the alkyl chain.

Ziegler Natta catalyst thus gives linear polymer molecules a great degree of stereochemical control.

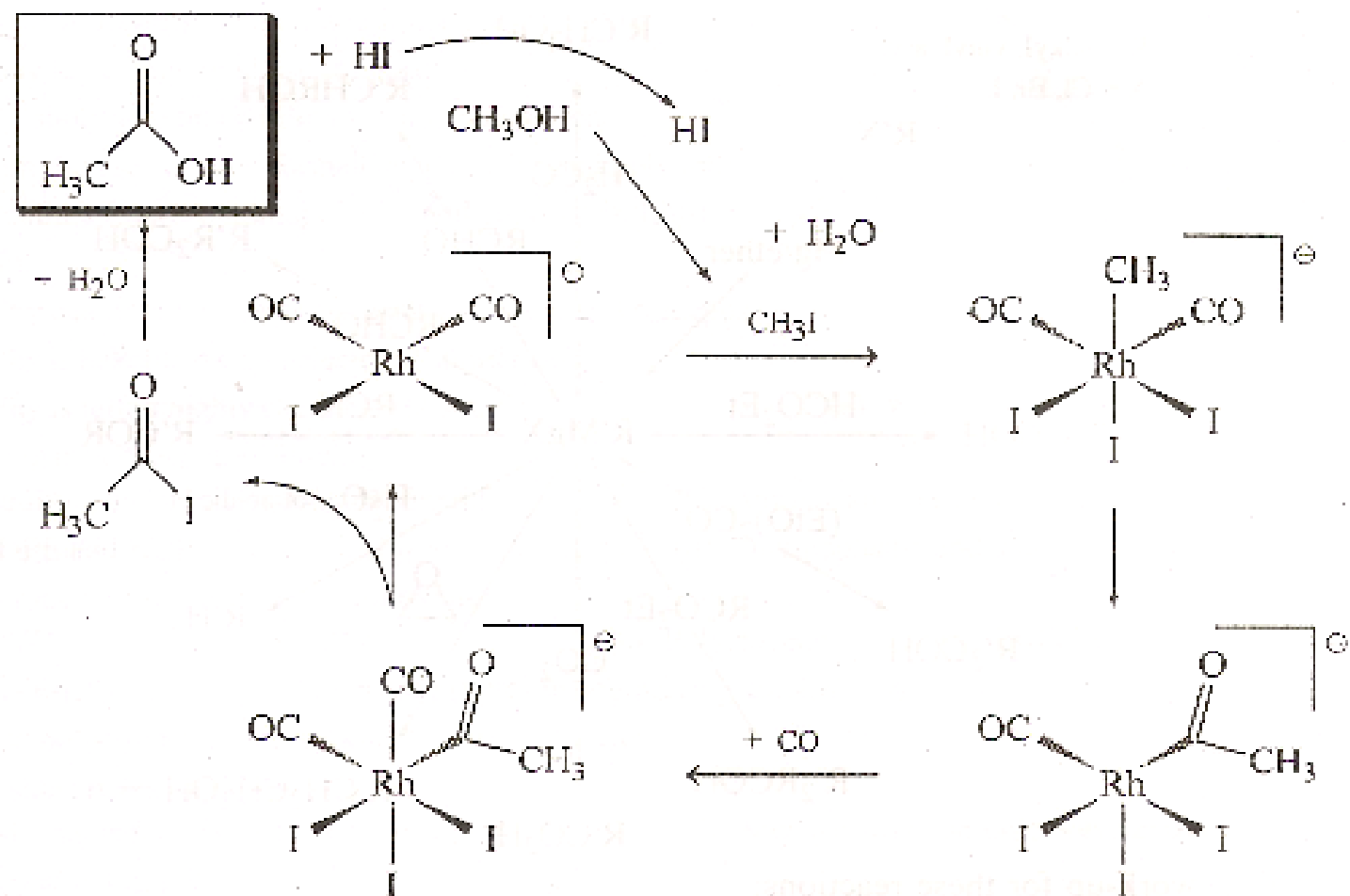
(4) Monsanto Acetic Acid Process (Manufacture of Acetic Acid):

The carbonylation of methanol produces acetic acid:



This is the second largest industrial homogeneous carbonylation process with over 7 billion pounds of acetic acid produced each year using this technology. Prior to 1970, acetic acid was made using cobalt catalysts requiring rather severe conditions. In 1970 Monsanto commercialized a rhodium carbonyl iodide catalyst that is commonly called the *Monsanto Acetic Acid Process* (developed in the late 60's by James Roth. Rhodium is 10^3 to 10^4 times more active than the corresponding cobalt catalyst, which means that much lower CO pressures and moderately lower temperatures are required. Most importantly, the rhodium catalyst gives extremely high selectivities to acetic acid:

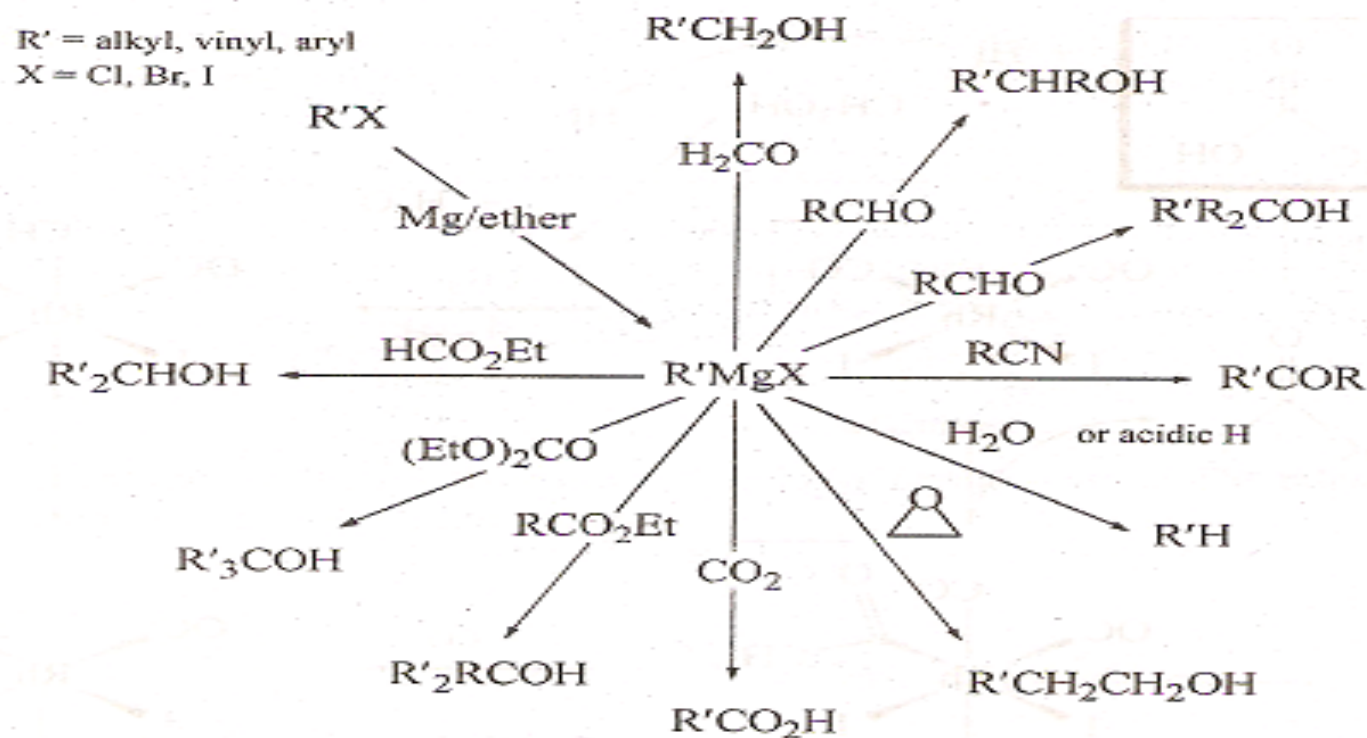
The mechanism has been extensively studied by Forster and coworkers at Monsanto and is shown below



This catalytic reaction is an unusual dual cycle system involving HI as one catalyst and $[\text{RhI}_2(\text{CO})_2]^-$ as the transition metal component. HI catalyzes the conversion of MeOH to MeI and H_2O at the beginning of the Rh-catalyzed carbonylation reaction, followed by regeneration of HI at the end of the Rh-cycle by hydrolysis of the acyl-iodide. The Rh catalyst carbonylates the MeI to produce the acyl-iodide.

(5) Synthesis of organic compounds using Grignad Reactions:

Insert Organometallic compounds are very useful as catalysts or reagents in the synthesis of organic compounds, such as pharmaceutical products. One of the major advantages of organometallic compounds, as compared with organic or inorganic compounds, is their high reactivity. Reactions that cannot be carried out with the usual types of organic reagent can sometimes be easily carried out using one of a wide variety of available organometallics



Typical work-up for these reactions:

1. Dilute aqueous acid or
2. Aqueous ammonium chloride