Chapter 1

Introduction
1. INTRODUCTION

1.1 Transition metal complex and Catalysis

The transition metal is "an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell". A transition metal complex is species consisting of a transition metal coordinated (bonded to) one or more ligands (neutral or anionic non-metal species). Transition metals and their complexes have an extensive application as catalysts in organic chemistry [1–4]. Transition metals and their compounds act as catalysts either because of their ability to adopt multiple oxidation states and to form complexes or in the case of the metals, to adsorb other substances on to their surface and activate them in the process. Generally, transition metal complexes act in different ways within the catalytic reaction; they bring the substrates together, activate the substrates by coordinating to the metal and lower the activation energy of the reaction between substrates. As a result, the use of a transition metal complexes catalyst in a reaction provides a new pathway, because the reactants interact with the metallic complex. These interactions make it possible for thermodynamically favored reactions, which need long times to reach equilibrium, to be accomplished within hours. Therefore, transition metal complexes as catalysts can be used to synthesize compounds which can hardly be obtained by conventional methods [2,3]. In addition, transition metal atoms have one s, three p, and five d orbitals that possess geometrical and energetic features suitable for bonding with the ligands. This kind of versatility is the basis for the catalytic activity of certain transition metal complexes to a great extent. Upon coordination to a metal ion, changes take place in the electronic distribution in a ligand, which result in the modification of the reactivity of the ligand molecule, at times dramatically. Thus, the various transition metals or complexes as catalysts are extensively used to catalyze industrial useful reactions for which there is no uncatalyzed equivalent [3,4]. For examples, vanadium (V) oxide (in Contact Process), finely divided Iron (in Haber process), and Nickel (in Catalytic Hydrogenation) are some of the examples of transition metals as catalysts.

Many transition metal have feature can coordinate with organic ligands, if any of the organic ligands form a direct M-C bond, then complex is usually considered to be organometallic, e.g., \([(C_6H_6)Ru(H_2O)_3]^{2+}\). Originally, organometallic complex may be defined as metal complexes with one or more metal–carbon bonds. Nowadays,
metal complexes with ligands such as phosphines, hydrides or amines are also accepted as Organometallics. The first organometallic complex of Pt, K[PtCl₃(CH₂=CH₂)] ‘Zeise salt’ that had a significant impact on the subject was prepared by a Danish pharmacist Zeise in 1827. The organometallic chemistry has grown enormously although most of its applications have only been developed in recent decades. The notable contributions of Victor Grignard and Paul Sabatier, K. Ziegler and G. Natta and E. O. Fischer and G. Wilkinson in this area of chemistry fetched them the Nobel prizes in 1912, 1963 and 1973 respectively. Their pioneering work is the stepping stone for the development of homogeneous catalysis by organometallic complexes. One of the key points in the fast expansion of organometallic chemistry is the selectivity (chemo, regio or enantio-) of organometallic complexes in organic synthesis [2–5]. A great number of soluble metal complexes are now being employed in industry as catalysts for the generation of a variety of useful compounds. More are being developed in order to find processes that would yield products in greater selectivity and in high yields. The success of organometallic catalysts lies in the easy modification of their environment by ligand exchange. A very large number of different types of ligands can coordinate to transition metal ions. Once the ligands are coordinated, the reactivity of the metals may change dramatically. In fact the rate and selectivity of a given process can be optimized to the desired level by controlling the ligand environment. Understanding the role played by the different ligands coordinated to a metal is one of the main themes in homogeneous catalysis [2–5]. Because organometallic complexes are highly soluble in organic solvents their behavior throughout the catalytic reaction can be studied using different techniques to do in-situ measurements. Fundamental knowledge about the catalytic systems and studies about the steps of the catalytic processes can help to improve the efficiency of the catalysts.

Homogeneous organo transition metal catalysts are increasingly being applied in many C-X (X= C, H, hetero-atom) bond transformations to obtain varieties of chemicals and polymers. For examples, polyethylene and polypropylene are produced via organometallic catalysts, usually via Ziegler-Natta catalyst (organo-aluminium-titanium catalyst) to give stereo regular polymers. Acetic acid is produced via metal carbonyl catalysts in the Monsanto process and Cativa process. Most synthetic aldehydes are produced via hydroformylation of olefins using cobalt or rhodium catalysts (oxo processes). The bulk of the synthetic alcohols, at least those larger than
ethanol, are produced by hydrogenation of hydroformylation derived aldehydes using nickel or ruthenium catalysts. The Wacker process is used in the oxidation of ethylene to acetaldehyde using Pd/cu catalyst and Hydrocyanation of alkenes using nickel phosphite complexes. In present thesis, special attention is given on hydroformylation and hydrogenation using transition metal complex catalysts.

1.2 Hydroformylation

Hydroformylation is one of the largest volume homogeneously transition-metal catalyzed reactions of alkenes and is established as an important industrial tool for the production of aldehydes. The hydroformylation reaction was discovered in 1938 by Otto Roelen while working for Ruhrchemie in Germany during an investigation of the origin of oxygenated products occurring in cobalt catalyzed Fischer-Tropsch reactions. [5–7]. Hydroformylation is the reaction between alkenes and synthesis gas (syngas), an equimolar mixture of carbon monoxide (CO) and hydrogen (H₂) to form aldehydes, linear (n) and branched aldehyde (iso) in the presence of a Cobalt or Rhodium based catalyst (Scheme 1.1).

\[
\text{Alkene} + \text{CO} + \text{H}_2 \xrightarrow{1) \text{Catalyst}} \text{Aldehydes} \]

**Scheme 1.1. Hydroformylation of 1-alkene**

A typical feature of hydroformylation is the fact that both sides of the double bond are in principle reactive, so ethene yields only propanal as a single product while hydroformylation of propene yields two regioisomer; linear butanal and 2-methylpropanal (branched product). With longer chain 1-alkenes, the isomerization of the double bond to the thermodynamically more favored internal positions is possible, yielding the respective branched aldehydes (Scheme 1.1). Depending on the substrate, it is interesting to obtain one regioisomer than other. With a terminal higher alkene as
substrate, normal-chain aldehyde, the more desirable products, usually are hydrogenated, affording straight-chain alcohols, or self-condensed, affording more complex aldehydes. While some products are desired in the branched i.e. hydroformylation of styrene into a branched aldehyde is especially important because it is a precursor for the synthesis of arylpropionic acid, which are important anti-inflammatory drugs such as ibuprofen [5]. Thus, not only stability, activity, and chemoselectivity of the catalysts are important, a key parameter is also the regioselectivity expressed by the n/i ratio. The normal/branched or branched/normal aldehyde ratio is an important parameter in the industrial hydroformylation process; the higher the ratio the better.

1.2.1 Application of hydroformylated products

Starting from mid 1950s hydroformylation gained an importance and over the recent years a steady and continuous growth in production capacity of aldehydes has taken place. Production of aldehydes by the hydroformylation process is now well beyond 10 million metric tons annually. Aldehydes are considered as industrially important raw materials and typical chemicals obtainable from aldehydes are shown in Scheme 1.2. For examples, aldehydes can be used to form other compounds like alcohols (via hydrogenation), carboxylic acids (via oxidation) and amines (via reductive amination). By Aldolization, branched alcohols, carboxylic acids, and amines with a double carbon number can also be synthesized.

![Scheme 1.2 Chemicals obtain from Aldehydes](image)

Main consuming industries of aldehydes are the plasticizer, polymer (n-butanal is converted to 2-ethylhexanol which is used in the production of dioctyl phthalate DOP, a plasticizer that is used in the poly vinyl chloride (PVC) applications) and detergent
industry followed by solvents, chemical intermediates, flavors and fragrances and lubricants.

1.2.2 Hydroformylation Catalysts

1.2.2.1 Active Metals and ligand

The compounds of platinum group metals are known to be active in hydroformylation, but the main interest lies in catalysis by cobalt and rhodium compounds [5]. Initially, hydroformylation was performed with cobalt based catalyst, but it was recognized that rhodium is by far the most active metal being used. On the other hand platinum and ruthenium catalysts are mainly subjects of academic interest, not thoroughly investigated by industrial researchers [5,8]. The general accepted order of catalytic activity for the group VIII metals in hydroformylation reaction [9] is as

\[ \text{Rh} \gg \text{Co} > \text{Ir}, \text{Ru} > \text{Os} > \text{Pt} > \text{Pd} > \text{Fe} > \text{Ni} \]

The hydroformylation catalysts consist of a transition metal ion (M) which interacts with CO and hydrogen to form metal carbonyl hydride species, which is an active hydroformylation catalyst. If complexes containing only carbonyl ligands are known as unmodified catalysts, on the other hand, introduction of tailor made ligand to the transition metals are known as modified catalysts. Typical complexes are \( \text{HCo(CO)}_4 \), \( \text{HCo(CO)}_3\text{PBu}_3 \) and \( \text{HRh(CO)(PR}_3)_3 \) [10].

The improvement of the catalyst’s performance has mainly been achieved by variation of modifying ligand [11]. Among the compounds, which are able to coordinate to a transition metal to form complexes, phosphines are most used and accepted ligands [11,12]. Nitrogen containing ligands showed lower reaction rates than phosphine and carbon monoxide due to their stronger coordination to the metal centers. A comparative study of \( \text{Ph}_3\text{R} \) (where \( \text{R} \) = elements of Main Group V) in the hydroformylation of 1-dodecane [13] showed following order

\[ \text{Ph}_3\text{P} > \text{Ph}_3\text{N} > \text{Ph}_3\text{As}, \text{Ph}_3\text{Sb} > \text{Ph}_3\text{Bi} \]

Catalysts that are used for industrial hydroformylation processes are cobalt and rhodium based metal complexes. Cobalt-catalyzed hydroformylation is used since the 50s. Cobalt processes are mostly used in the production of medium- to long chain olefins. While Rhodium catalyst processes are used since the 70s. Rhodium catalysts
are more expensive than cobalt catalysts and have higher activity, but have lower activity in case of branched olefins. Three developmental stages of hydroformylation catalysts can be visualized Fig. 1.1.

![Fig. 1.1](image)

**Fig. 1.1** Three stages of the catalyst development for the hydroformylation reaction

The first stage of hydroformylation was exclusively based on cobalt-based catalyst having the pressure and temperature range between 240-300 bars and 150-200 °C because of instability of cobalt carbonyl (Process 1) [12]. Subsequently, the ligand modification introduced by Shell (1964) was significant progress in hydroformylation [14]. The replacement of CO with phosphines enhances the selectivity towards linear aldehyde (n/b) and the stability of cobalt carbonyl, leading to reduced CO pressure (Process 2). The second stage of hydroformylation was the combined development in ligand modification and appearance of rhodium as a replacement for cobalt metal. It took almost a decade of research before first rhodium catalyst based commercial process was launched in 1974 in Celanese [15], followed by Union Carbide Corporation (1976) [16] and the Mitsubishi chemical corporation (1978) [17] using phosphine as a ligand (Process 4). Because the reaction conditions were much milder, the process was called Low Pressure Oxo (LPO) process. The unmodified rhodium carbonyl complex is only used for the reaction of special olefins (Process 3). Compared to cobalt-based processes, many advances were made in the second developmental stage of hydroformylation. However, the industrial problems of first stage like separation of products from reaction mixture, catalyst recovery, loss of costly metals, use of corrosive solvents etc. remained same in second stage too.

In the third stage, the research was largely focused to design such a process wherein the separation of products from reaction mixture is facile and easy. Hydroformylation can be carried out in biphasic aqueous systems using a rhodium
catalyst associated with the water-soluble ligand, sodium salt of tri sulfonated triphenyl phosphine (TPPTS). This system was first used in 1984 by Ruhrchemie/Rhone-Poulenc in the industrial hydroformylation of Propene (Process 5) [18]. This procedure is much simpler and more cost effective than those of the other oxo processes, mainly due to the new principle of catalyst separation and recycling. Some of the most important industrially implemented oxo process based on Co and Rh catalysts are shown in Table 1.1.

Table 1.1 Industrially implemented hydroformylation process based on Co and Rh catalyst

<table>
<thead>
<tr>
<th>Catalyst metal</th>
<th>Ligand</th>
<th>Process</th>
<th>Cobalt</th>
<th>Cobalt</th>
<th>Rhodium</th>
<th>Rhodium</th>
<th>Rhodium</th>
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<tr>
<td></td>
<td>none</td>
<td>1</td>
<td>none</td>
<td>phosphines</td>
<td>none</td>
<td>phosphines</td>
<td>phosphines</td>
</tr>
<tr>
<td>Active catalyst species</td>
<td>HCo(CO)₄</td>
<td>HCo(CO)₃PPh₃</td>
<td>HRh(CO)₄</td>
<td>HRh(CO)(PPh₃)₃</td>
<td>HRh(CO)(TPPTS)₃</td>
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<tr>
<td>T (°C)</td>
<td>150–180</td>
<td>160–200</td>
<td>100–140</td>
<td>60–120</td>
<td>110–130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P (bar)</td>
<td>200–300</td>
<td>50–150</td>
<td>200–300</td>
<td>10–50</td>
<td>40–60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst/olefin</td>
<td>0.1–1</td>
<td>0.6</td>
<td>10⁻⁴–0.01</td>
<td>0.01–0.1</td>
<td>0.001–1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Products</td>
<td>aldehydes</td>
<td>alcohols</td>
<td>aldehydes</td>
<td>aldehydes</td>
<td>aldehydes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>By-products</td>
<td>high</td>
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<td>low</td>
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<td>low</td>
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<td>88:12</td>
<td>50:50</td>
<td>92:8</td>
<td>&gt;95:5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 = BASF, Ruhrchemie process; 2 = Shell process; 3 = Ruhrchemie process; 4 = Union Carbide process (LPO); 5 = Ruhrchemie/Rhone-Poulenc process.

1.2.3 Hydroformylation reaction Mechanism

Mechanism of hydroformylation reaction has been proposed for both modified and un-modified cobalt and rhodium complexes as a catalyst [19]. However, most accepted and generalized mechanism for hydroformylation using Rh/PPh₃ system is discussed (Fig 1.2). This is so-called dissociative mechanism. The dissociative mechanism (Scheme 2) is initiated by dissociation of PPh₃ ligand from the complex HRhCOPPh₃ (1) (18e) to form complex 2 (16e) to create vacant site on the metal center. The vacant site created can now be occupied by incoming alkene molecule to form complex 3. The next step, which consists of insertion of alkene and hydride...
transfer, is the elementary steps to determine the regioselectivity of in the hydroformylation.

![Fig. 1.2 General accepted mechanism for hydroformylation of 1-alkene](image)

In this step, the complex 3 forms a metal alkyl complex by insertion of alkene and the hydride transfer to give complexes 4a and 4b. A β-elimination of hydride in species 4 leads to isomerization when higher alkenes are used, or it can react with CO to form complex 5. A migratory insertion of CO into complex 5 leads to the formation of acyl complex 6. Next step is oxidative addition of H₂ to the complex 6 gives the complex 7.
Chapter 1

The oxidative addition of \( \text{H}_2 \) molecule is generally believed to be rate-determining step in hydroformylation reaction. Finally the cycle completes by reductive elimination of aldehyde (product) and regenerates the unsaturated species. Reductive elimination can be enhanced by electron withdrawing ligand on the metal centre. The attack of formyl group to alkene follows Markonikov and anti-Markonikov addition depending on the conditions and catalyst used. It has been observed that anti-Markonikov addition gives linear products. Reaction path for the side reactions that lead to isomerization is also included.

1.2.4 Critical factors and current problems in industrial applied hydroformylation processes

There is a big market for aldehydes and there are several limitations in the current industrial applied processes. The most important are mentioned here.

1. It is also complicated to get high conversions with high chemo as well regioselectivity of the desired product. A key issue in the hydroformylation process is the control of regioselectivity, i.e. the ratio between linear and branched aldehyde produced. Furthermore, other side reactions like hydrogenation or isomerization leading to internal should also be suppressed.

2. The conversion of higher olefins in aqueous biphasic systems is difficult because of the low solubility in the aqueous phase. In the current processes it hard to get high conversions and control selectivity’s of the products.

3. In case of the homogeneously processes, separation of the product mixture and the catalyst complex is difficult because the mixture is in the same phase. Separation of long chain olefins is even more difficult because distillation at high temperatures causes degradation of the catalyst. Recovery of the catalyst is very important because it is an expensive metal complex base on rhodium.

4. Another problem is that organic solvents, used in hydroformylation, are environmental unfriendly. Other solvent are therefore preferred. The use of organic solvents to dissolve the catalyst, organic solvents cause environmental pollution and are toxic.

5. There is also very little knowledge of the kinetics of the reaction.

In order to improve the industrial processes and overcome the biggest problems mentioned above, there is a lot of research and development on hydroformylation reactions.
1.2.5 Ligand development

The discovery of PPh$_3$ as ligand by Wilkinson 1965 [20] and the subsequent development of an industrial process in the 1970s represented a break-through for hydroformylation catalysis. The mechanism for hydroformylation reveals that the selectivity to linear aldehyde is controlled by the way of metal hydride migration to $\pi$-bound olefin. Two factors, the acidity of the hydride and the steric constraints of the ligands, control the selectivity of the addition. Sterically demanding ligands such as PPh$_3$ favor linear aldehyde formation by anti-Markownikov addition. It has been also shown that excess ligand can minimize the formation of the unwanted byproduct preventing both isomerization and hydrogenation and the regioselectivity to aldehyde generally increase. However excess phosphine also reduces the reaction rate. Therefore, extensive studies have been emerged in the area of hydroformylation regarding the ligand modification and their influences on conversion, selectivity, regioselectivity and product distributions. The ligands modify the coordination sphere of the metal electronically and sterically can alter activity and selectivity. Over the past few years, a myriad of Phosphorus based ligands have been developed by tuning their steric and electronic properties [21].

1.2.5.1 Ligand parameters

Ligand effects can have a dramatic influence on the reaction rate, selectivity and on the amount of side-products. Therefore, extensive studies have been carried out on their steric and electronic properties.

1.2.5.1.1 Steric considerations

Many attempts have been undertaken to define a reliable steric parameter complementary to the electronic parameter. One of the most widely applied concepts for quantifying the steric bulk of monodentate P ligands; the cone angle (θ) was introduced by Tolman [22]. Tolman proposed to measure the steric bulk of a phosphine ligand from CPK models in the following way. The metal centre, located at a distance of 2.28 Å from the phosphorus atom in the appropriate direction, a cone is constructed with the sides’ tangent to the Van der Waals radii of the outermost atoms on the substituents on the phosphorus atom (Fig. 1.3a). A similar approach which alleviates some of the limitations of Tolman’s cone angle was described by White et al. They introduced the concept of solid angle (Fig. 1.3b) by using crystallographic
data or calculated structures the ligand atoms radii are projected onto the metal surface providing a measure of steric bulk around the metal [23].

![Fig. 1.3](image)

**Fig. 1.3** (a) Tolman’s cone angle, (b) White’s solid angle, (c) Casey and Whiteker’s bite angle.

For bidentate ligands like diphosphines Casey and Whiteker developed the concept of the natural bite angle ($\beta_n$) as an additional characteristic (Fig. 1.3c). They were first to describe the natural bite angle ($\beta_n$); the chelate angle (P-M-P) preferred by the organic backbone in the metal/ligand complex [24]. Based on simple molecular mechanics the bite angle is calculated in a manner similar to Tolman’s cone angle; a dummy atom is introduced, coordinating the phosphine donor atoms at a constant distance, 2.315 Å, ensuring only allowed bidentate geometries are included in the calculation.

1.2.5.1.2 Electronic considerations

The electronic properties of phosphines arise from two contributions; $\sigma$-donation and $\pi$-acidity. The primary component is $\sigma$-donation of the phosphine lone pair to an empty orbital on the metal. The second component is back donation from a filled metal orbital to an empty orbital on the phosphine ligand (Fig. 1.4).

![Fig. 1.4](image)

**Fig. 1.4** Types of Metal-phosphine bonding
As electron-withdrawing (electronegative) groups are placed on the phosphorous atom, the $\sigma$-donating capacity of the phosphine ligand tends to decrease. At the same time, the energy of the $\pi$-acceptor (sigma*) on phosphorous is lowered in energy, providing an increase in back bonding ability. Therefore, phosphines can exhibit a range of $\sigma$-donor and $\pi$-acceptor capabilities (Fig. 1.4), and the electronic properties of a metal center can be tuned by the substitution of electronically different phosphines.

The $\sigma$-donation and $\pi$-acceptor character of phosphorus ligands have been studied by looking at the stretching frequencies of the coordinated CO ligands in complexes [25,26]. Strong $\sigma$-donor ligands give a high electron density on the metal and hence a substantial back-donation to the CO ligands and lowered IR frequencies. Strong $\pi$-acceptor ligands will compete with CO for the electron back-donation and the CO stretch frequencies will remain high (Fig. 1.5).

**Fig. 1.5** Electronic effects of phosphine ligands

Alkyl phosphines are strong bases and as expected they are good $\sigma$-donors ligand. Organophosphites are strong $\pi$-acceptors and they form stable complexes with electron rich transition metals. General empirical order of various P ligands is given below,

$$PMMe < PPh_3 < P(OMe)_3 < P(OPh)_3 < P(NMe)_3 < PCl_3 < CO < PF$$

Greater $\pi$-acidity  
Greater $\sigma$ donation

The effects of phosphorus ligands on hydroformylation reactions or properties of metal complexes were rationalized mainly in terms of $\sigma$-donation and $\pi$-acceptor character of phosphorus ligands. The numerous studies have appeared in literature indicates the how the electronic and steric effect of P ligands influence selectivity and
activity of hydroformylation reactions in various transition metal catalyzed reaction which is summarized below in briefly. Designing the new modified ligand is a common approach for improving the catalysis activity. Recently, one of the main activities in hydroformylation research is in the field of new ligand design and synthesis and modified catalysts.

1.2.6 Cobalt catalyzed hydroformylation

The first catalyst used in hydroformylation was cobalt. Initially, hydroformylation was performed with heterogeneous cobalt catalysts of the Fischer Tropsch type. But it was established that the catalytic active species in the cobalt-catalyzed hydroformylation is the complex hydridocobaltcarbonyl; HCo(CO)₄, a yellow liquid and strong acid (stable only under high CO/H₂ pressure) is formed from precursors Co₂(CO)₈. Heck and Breslow (1960) [19]. The Co₂(CO)₈ reacts with H₂ under catalysis reaction conditions to form two equivalents of HCo(CO)₄ (scheme 1.3). Both species are extremely toxic, similar to Ni(CO)₄.

![Scheme 1.3 Interaction of Co₂(CO)₈ with H₂ and ligand](image)

The stability of the HCo(CO)₄ complex is strongly dependent upon the partial pressure of syngas (200–300 bar) and temperature (110–180 °C) as it produces metallic cobalt if the CO partial pressure is not kept high enough [12]. The regioselectivity of HCo(CO)₄ or HCo(CO)₃ for producing the more valuable linear aldehydes varies with reaction conditions and alkene substrates used and can typically get linear to branched aldehyde ratios of 2–3 to 1. The ligand modification in HCo(CO)₄ was significant progress in hydroformylation. The replacement of carbon monoxide with trialkylphosphine such as PBu₃ (Shell, 1964) enhances the selectivity towards linear aldehyde (n/b) and the stability of cobalt carbonyl, leading to reduced carbon monoxide pressure [14]. Instead of 200–300 bars of H₂/CO pressure needed for HCo(CO)₄, the monophosphine substituted complex HCo(CO)₃(PR₃) needed only
50–100 bars of pressure, and could be run at higher temperatures without any decomposition of catalyst to cobalt metal. However, the higher stability of the HCo(CO)$_3$(PR$_3$) catalyst, due to stronger Co–CO bonding means that this catalyst is less active than HCo(CO)$_4$ (about 5–10 times slower). From a sterical viewpoint the bulkier trialkylphosphine ligand favors formation of linear products. While linear to branched ratios of only 2–3:1 are typically found for HCo(CO)$_4$, higher regioselectivity of 6–7:1 occur for HCo(CO)$_3$(PR$_3$). Another advantage is that the separation of the products by distillation is possible in contrast to unmodified cobalt catalysts. Consequently, the phosphine modified cobalt catalyst system is still used by SHELL for the production of surfactant alcohols from internal linear olefins. It suggested a renewed interest in modification of HCo(CO)$_4$ by phosphorous based ligands as result hydroformylation with cobalt catalyst was developed and are in significant progress [27].

The hydroformylation of cyclohexene catalyzed by Co$_2$(CO)$_6$(PBu$_3$)$_2$ has been tested in the presence of an increasing pressure of the additional gas such as N$_2$, He, Ar, and Xe in order to investigate the influence of inert gas as pressure media along with syngas. These results indicate that the formation of an additional gas containing complex reduces the concentration of the active cobalt intermediate available for the catalysis and as a consequence, the hydroformylation rate [28]. The various phosphine ligands containing functionalized alkyl groups, 1–4 (Fig 1.6.) and their cobalt complexes, Co$_2$(CO)$_6$(L)$_2$ were synthesized by L. Rosi et al [29].

![Fig. 1.6](image)

Fig. 1.6 Structure of various ligands used for Co catalyzed hydroformylation
The catalytic activity of cobalt complexes was evaluated in hydroformylation of 1-hexene and propene and results were compared with Co$_2$(CO)$_6$(PBu$_3$)$_2$. The presence of polar functional groups in the P ligands coordinated to the metal improves the hydrophilicity of these complexes compared to that of Co$_2$(CO)$_6$(PBu$_3$)$_2$ and are active both in polar solvents and in a water containing solvent. However, the activity and selectivity of the catalysts tested are analogous to Co$_2$(CO)$_6$(PBu$_3$)$_2$.

A range of tertiary phosphine ligands derived from (R)-(+) limonene (5) were studied by C. Crause et al in cobalt-catalyzed hydroformylation of 1-dodecene at 170 °C under 85 bar syngas pressure (H$_2$:CO = 2:1) with phosphine to cobalt ratio of 2:1. The activity and selectivity of the catalyst was observed to be governed by the equilibria between the modified and unmodified cobalt catalytic species in the reaction. It was found that the modified cobalt catalyst is less reactive than the unmodified catalyst, but exhibited significantly improved regioselectivity towards the desired linear products ranged from 2.6 to 4.9 and hydrogenation of the alkene varied within a narrow band from 5–6% [30].

The dimeric cobalt complex of P(p-CF$_3$C$_6$H$_4$)$_3$, Co$_2$(CO)$_6$[P(p-CF$_3$C$_6$H$_4$)$_3$]$_2$ catalyzed hydroformylation of olefins in supercritical carbon dioxide was investigated by M.J. Chen et al [31]. The composition of the cobalt complexes in supercritical carbon dioxide under hydroformylation conditions has been studied by in situ high-pressure NMR spectroscopy. It was also observed that the cobalt complex, Co$_2$(CO)$_6$[P(p-CF$_3$C$_6$H$_4$)$_3$]$_2$ reacts reversibly with hydrogen to produce HCo(CO)$_3$[P(p-CF$_3$C$_6$H$_4$)$_3$] and in contrast to the unsubstantiated Co$_2$(CO)$_8$, the phosphine modified catalyst system is stable under low CO pressures. Consequently, the hydroformylation reactions can be carried out at low pressures. However, the catalyst has a catalytic activity which is about 1/10 of that of Co$_2$(CO)$_8$ [31]. The P(OPh)$_3$ modified cobalt complex, Co$_2$(CO)$_6$[P(OPh)$_3$]$_2$ was synthesized and evaluated in the hydroformylation of 1-pentene at temperatures in the range 120–210 °C and pressures between 34 and 80 bar [32]. High pressure infrared studies revealed the formation of [HCo(CO)$_3$P(OPh)$_3$] at 110 °C, but at higher temperatures absorption bands corresponding to [HCo(CO)$_4$] were observed. The results from experiments account that the activity of HCo(CO)$_4$ is higher than the activity for HCo(CO)$_3$P(OPh)$_3$. Very low TOF and fair selectivities with the large amount internal alkenes were obtained due to the low steric nature of the P(OPh)$_3$ and form a stable monosubstituted hydride under the narrow range of temperature and ligand excess.
[32]. The cobalt catalyzed hydroformylation of olefins was also studied in presence of aromatic diphosphines as co-catalysts by W. Cornely and B. Fell. It was found that catalytic activity decrease drastically in contrast to monotertiary phosphine ligands, however, the concomitant isomerization is suppressed with the effect that in hydroformylation almost exclusively those aldehydes are formed, which correspond directly to the original position of the double bond in the employed olefin [33].

### 1.2.7 Rhodium catalyzed hydroformylation

The fundamental work by Wilkinson [20] showed that rhodium (Rh) complexes with PPh$_3$ allowed the reaction to proceed at much lower pressures and the subsequent development of an industrial process in the 1970s represented a breakthrough for Rh catalysis. Higher price of Rh was offset by mild reaction conditions, simpler and therefore cheaper equipment, high efficiency, and high yield of desire linear products. However, for detergent alcohol production though, even today, the cobalt systems are still in use, because there is no good alternative yet for the hydroformylation of internal and higher alkenes.

Recent progress in hydroformylation reactions has been caused mainly by the ligands development lead to the tremendous variety of P ligands modified Rh catalysts known today [21]. Designing new modifying P ligands has become an art, important for the creation of highly effective and selective new catalytic systems for hydroformylation. In this section, different examples of phosphorus mono- and bidentate ligands are collected in which the donor–acceptor or steric properties of ligands allow one to modify the activity and selectivity of Rh homogeneous catalysts are discussed.

#### 1.2.7.1 Monodentate phosphine

The Phosphine based ligands are extensively studied in Rh-catalyzed hydroformylation. The most famous Rh-catalyst precursor for hydroformylation is HRhCO(PPh$_3$)$_3$ [20,21]. The activity and selectivity of the catalysts based on PPh$_3$ has been extensively studied. The regioselectivity of the catalyst based on PPh$_3$ varies from 70 to 92 % for the linear aldehyde [21]. The highest selectivity is obtained at high concentrations of PPh$_3$ and low pressures of CO [34]. It was also observed that steric and electronic properties of a ligand influence the rate and selectivity of the hydroformylation reaction. In this section, the “ligand effect” for monodentate phosphines on activity and selectivity is exemplified by literature data.
H. K. Reinius et al synthesized a set of closely related non polar o-alkyl-substituted ligands, 6–10 (Fig. 1.7) differing in their steric properties and studied their effect on the activity and regioselectivity in Rh-catalyzed propene hydroformylation. The results suggest that o-alkyl-substituted triphenylphosphine ligands enhance the selectivity to branched aldehyde, isobutanal; however, the activity was decreased. It was concluded that the regioselectivity and activity is controlled through the steric properties of the active complex in which one side of the complex is blocked by the alkyl substituents [35].

![Fig 1.7 Various o-alkyl or aryl substituted arylphosphines](image_url)

In order to determine the relationship between the catalytic behavior and stereoelectronic properties of the ligands, a wider group of o-substituted arylphosphine or arylalkylphosphine ligands, 11–15 (Fig. 1.7) were synthesized by H. Riihimäki et al [36,37] and tested in rhodium-catalyzed hydroformylation of propene and 1-hexene. Geometrical arrangement and steric size (cone angle) of the free and coordinated ligands were studied theoretically by ab initio Hartree–Fock and DFT methods. The steric stress of o-alkyl-substituents has significant influence both on the formation of active rhodium species and catalytic reaction. These ligands having steric bulk due to the o-modification increased the selectivity to the branched aldehyde formation compared to PPh$_3$. However, initial activity was decreased as the cone angle increased. Most probably sterically hindered o-modified phosphines favor the formation of HRh(CO)$_3$(PR$_3$) species in turn are i/n ratio increased.

Neibecker, Reau and others introduced phospholes and phosphanorbornadiene 16–18 (Fig. 1.8) to oxo synthesis [38]. In the case of phospholes, activity and
selectivity are independent of the phosphine/Rh ratio. The phosphanorbornadienes are sterically demanding ligands comparable to triphenylphosphine (TPP) (Tolman’s cone angle $\Theta$: 147” vs. 145” for TPP). Therefore, the regioselectivities in the hydroformylation of I-hexene and styrene are similar to those obtained with TPP, but activities are five times higher [38].

**Fig. 1.8** Structure of phospholes, phosphanorbornadiene and bulky phosphabenzene ligands

Bulky Phosphabenzene 19, 20 (monodentate $\pi$–acceptor ligand) modified rhodium complexes were found to be highly efficient hydroformylation catalysts for internal and terminal olefins. The rhodium catalyst modified with o,o’–diphenyl substituted mono phosphabenzene 20 showed 74 time higher activity than the Rh/PPh$_3$ catalyzed hydroformylation of cyclohexene at 90 °C in toluene at 20 bar initial total pressure of CO:H$_2$ = 1:1. The same catalyst for the hydroformylation of styrene at 25 °C showed four times higher activity than the Rh/PPh$_3$ catalyst leading to a branched/linear aldehyde ratio of 20/1 with 100% selectivity [39].

**1.2.7.2 Diphosphines as ligands**

Bidentate ligands have played an important role in the development of the chemistry of metal organic complexes. The significance of the bidentate phosphines has been increasing especially in the areas of homogeneous catalysis, because the special properties of phosphines can be accentuated by chelating. Synthesis of the bidentate phosphines began with dppe (diphenylphosphinoethan) Ph$_2$PCH$_2$CH$_2$PPh$_2$ 21 (Fig. 1.9). The synthesis of dppe was reported as early as 1959 [40]. Since then a bidentate phosphines have been the subject of research and considerable number of new and “tailor–made” phosphine ligands have been prepared.

In 1981, Hughes and Unruh (Celanese) used DIOP (23) together with the more common common dppe and dppp (22) in the rhodium catalyzed hydroformylation [41]. High n/b (5–8) ratios were obtained in systems consisting of HRhCO(PPh$_3$)$_3$ and
added DIOP. Unruh also developed (diphenylphosphino)ferrocene (24) and various derivatives of dppf by others found to be selective catalyst with Rh(acac)(CO)$_2$, giving n/b ratios of up to 11 [41,42]. Devon and co-workers from Texas Eastman (1987) published work with a new diphosphine ligand, BISBI (25) which was found to have a natural bite angle of 124°. The catalytic system containing this wide bite angle ($\beta_n$) ligand gave very high regioselectivity for linear aldehyde with n/b ratios of 24 compared to 0.8 with dppp or 4.0 with DIOP at moderate syngas pressures [43].

Casey and co-workers observed that the bite angle in the intermediate [HRh(CO)$_2$(P-P)] has considerable influence on the selectivity of the reaction. The equatorial–equatorial (ee) coordinated diphosphines complex (Fig. 1.9) lead to higher n/b values than complexes having structure axial-equatorial (ae), coordinated diphosphines. Thus, when BISBI (has a bite angle of 113° and coordinates in a bis-equatorial fashion) was used as a ligand in rhodium hydroformylation of 1-hexene, the linear to branched aldehyde ratio (n/b) obtained was high, whereas using dppe (bite angle = 90 °), which coordinates in a axial-equatorial fashion, gave low n/b ratio [24,44].

Van Leeuwen et al. developed a series of diphosphine ligands based on a xanthene–type backbone having bite angles outside the common range of 75 to 99° [45,46]. The bite angle effect on the rhodium diphosphine catalyzed hydroformylation was evaluated using an extensive series of Xantphos ligands, 26-29 (Fig. 1.10). Variation of the substituent at position-9 of the generic backbone structure enabled the
construction of a series of diphosphine ligands having a wide range of natural bite angles (from 102 to 121°). Hydroformylation of 1-octene with this series of ligands showed a correlation between the bite angle and regioselectivity. The regioselectivity increased regularly with increasing natural bite angle but at higher bite angles the correlation breaks down.

![Xantphos and Xantphos type bidentate phosphine ligands](image)

**Fig. 1.10** Xantphos and Xantphos type bidentate phosphine ligands

1.2.7.3 Phosphite-based catalysts

In metal ligand carbonyl complexes, π-back bonding contribute significantly to the strength of the metal-to-ligand bond. When electron-withdrawing substituents on ligands are used, the reaction rate increases as a result of the more facile CO dissociation and stronger alkene association [34]. Phosphites are better π-acceptors than phosphines and therefore have significant potential as ligands in rhodium-catalyzed hydroformylation [21,34]. An additional advantage of phosphites is their relative ease of synthesis and the fact that they are less prone to oxidation and reactions with sulphur compounds.

1.2.7.3.1 Monodentate phosphites

Pruett and Smith of Union Carbide Corporation (UCC) were among the first to report the beneficial effects of phosphites as ligands for rhodium-catalyzed hydroformylation of 1-alkenes [47]. However, the reports of bulky monophosphites giving high rates for internal and terminal alkenes were reported by van Leeuwen et al [48-51]. A rhodium complex containing tris(o-tert-butyl-4-methylphenyl) phosphite (31b) as bulky ligand gave extremely high rates up to 1,61,000 mol mol Rh⁻¹ h⁻¹ in the hydroformylation of 1-octene with moderate selectivity for the linear aldehyde [49]. As one would expect that increasing steric hindrance in the catalytically active rhodium complex will result in lower reaction rates, the results of Van Leeuwen and Roobeek seemed contradictory at first. They also used the bulky tris(o-tert-
butylphenyl)phosphite **31a** (Fig. 1.11) as a ligand and found high reaction rates in the rhodium catalyzed hydroformylation of otherwise unreactive alkenes like 1,2-and 2,2-dialkyalkenes (see table 1) [51].

![Fig. 1.11 Structure various monodentate phosphite ligands](image)

The high reactivity was explained by the exclusive formation of monoligated rhodium phosphite complexes, which was confirmed by in-situ IR and NMR studies [52]. Van Leeuwen and Roobeek also found remarkable reaction rates using strongly electron withdrawing ligands, even for the hydroformylation of less reactive internal alkenes [53]. It was found that the selectivity for the linear product increased using electron withdrawing ligands. By applying tris(2,2,2-trifluoroethyl)phosphite (32) they obtained 96% linear aldehyde starting from 1-alkenes and 66% linearity with internal alkenes as substrate. The explanation for the high rates and selectivity is mainly based on electronic factors. The strongly electron withdrawing phosphite ligand induces fast replacement of a carbonyl ligand by the alkene substrate, resulting in high reaction rates.

Ziólkowski and Trzeciak have extensively studied the use of triphenyl phosphite ligand (30) and its derivatives in the rhodium catalyzed hydroformylation of alkenes [54]. Phosphites with moderate cone angles and higher electron withdrawing characteristic give rise to acceptable n/b ratios. Good results were obtained by tri(4-chlorophenyl)phosphite, contrary to tri(2,6-dimethylphenyl) phosphite, having a cone angle of 190°.

One of the commercial applications of bulky phosphites is the production of 3-methylpentane-11,5-diol by hydroformylation of 3-methylbut-3-en-1-01 by Kuraray [55]. Furthermore, they reported the use of bulky phosphite in the hydroformylation of vinyl acetate and 7-octenal, the latter providing an intermediate for the preparation of nonanediol. The high reactivity induced by bulky phosphite ligands has also led to
the application of hydroformylation in the functionalization of natural product derivatives that are otherwise hardly reactive. Syntheses of important intermediates to fine chemicals have been reported by hydroformylation of dihydrofuran, glucal derivatives and methyl oleate [56]. Bryant from UCC reported an elegant application of bulky phosphite ligands. He utilized the high activity but moderate selectivity of bulky phosphites as an indicator for ligand depletion [57]. When the diphosphite ligand concentration becomes too low, as a consequence of ligand decomposition, the bulky phosphite ligand (33) coordinates to rhodium preventing rhodium plating or cluster formation.

1.2.7.3.2 Diphosphites as ligands

The diphosphites represent an important trade-off between the low selectivity and the poor reaction rates generally observed when using phosphines as ligands. The reaction rates were in general much lower than that of the bulky monophosphite system, but still relatively high compared to the triphenylphosphine based catalyst. The selectivity was found to be very dependent on the exact ligand structure [58]. Bryant and co-workers from Union Carbide reported diphosphites based on 2,2-dihydroxy-1,1'-biphenyl backbones and similar substituents on the phosphorus atoms 34 (Fig. 1.12). These (‘bulky’) diphosphites were shown to give highly active and selective Rh catalysts for the hydroformylation of 1-octene (and styrene) with n/b ratios up to 48 [58].

![Fig. 1.12 Structure of various Bulky diphosphites ligands](image)

**Fig. 1.12** Structure of various Bulky diphosphites ligands
Also with the internal alkene, impressive results were obtained, with low activities. Börner et al focused on internal octenes, with bulky bidentate phosphites with new oxaphosphepin moieties (35) [59]. Starting with a mixture of \( n \)-octenes, the selectivity for 1-nonanal reached up to 69%. Van Leeuwen et al also prepared ligands (36) based on the 9H-xanthene skeleton as a backbone. These ligands resulted in very active and selective hydroformylation catalysts for both terminal and internal alkenes [60].

1.2.7.4 P-N bonded ligands

Generally, the ligands that possess strong \( \pi \)-acceptor and weak \( \sigma \)-donor properties greatly influence the activity and selectivity led to investigations of a new class of \( \pi \)-acceptor ligands, i.e. N-pyrrolylphosphines. In recent years, a few examples of \( \pi \)-acidic phosphorus amides as ligands in the hydroformylation reaction have been published [61-64] which are briefly described. The results obtained with these ligands showed improved activity compared to phosphine systems.

Ziolkowski and co-workers demonstrated ability of N-pyrrolylphosphines, \( \text{P(NC}_4\text{H}_4)_3 \) (37 (Fig. 1.13) as modifying ligands in Rh-catalyzed hydroformylation 1-hexene. It was observed that the rhodium complexes of N-pyrrolylphosphines found to be very active and selective hydroformylation catalysts produce 80–90% of aldehydes with n/b 3–31/1 at 60 °C and 10 atm syngas pressure [61].

![Fig. 1.13 Structure of various pyrrol based phosphines](image)

R. Jackstell et al described the synthesis of a number of pyrrolyl-, indolyl-, and carbazolylphophines ligands as well as their application in the hydroformylation of an internal olefin. They observed that the ligand \( \pi \)-acidity influences regioselectivity and activity in the hydroformylation of 2-pentene. The best n/b ratios of about 60/40 was
obtained at low synthesis gas pressure (10 bar) in the presence of the P(pyrrolyl)₃ (37) ligand [62]. Van der Slot et al reported monodentate and bidentate phosphorus amidite ligands that contain two pyrrolyl substituents 38 (Fig. 13) and the performance of the catalyst based on these ligands compared with similar diphenyl-substituted phosphinite ligands (39). The catalyst formed with the bidentate phosphorus amidite ligand 38 (having high π-acidity) revealed high regioselectivity for the linear aldehyde (l/b ~ 100) with high rate [63]. Higher regioselectivity was also achieved in the Rh-catalyzed isomerization hydroformylation of internal olefins using pyrrol-based tetraphosphorus ligand 40 compared with its biphosphorus analogue (38). Normal/iso values up to 80.6 from 2-hexene and up to 51.7 from 2-octene were achieved with this catalytic system at 100 °C and 10 bar CO/H₂ = 1/1 [64].

1.2.8 Different approaches to the catalyst recovery and recycling and hydroformylation of higher olefins

The catalyst being soluble in the reaction medium makes its separation from the products often a challenging task. Beside economical considerations, the loss of catalyst in the product is not acceptable for environmental reasons. The immobilization of precious homogeneous catalysts has become a field of intense research in order to recover and recycling the catalyst and several approaches have been pursued for this [65] during the last two decades (Fig. 1.14).

Fig. 1.14 Various approaches to Immobilization of homogeneous catalyst
However, two strategies are commonly used in literature; (i) the immobilization of the homogeneous catalyst in a second phase for example, in aqueous [66], fluorous [67], ionic liquid and supercritical CO₂ [68] phase or (ii) the heterogenization of the homogeneous complex on a solid support [69]. This section introduces and discusses the various concepts of catalyst recovery and recycling. The hydroformylation of higher olefins is covered in aqueous biphasic catalysis subsection.

1.2.8.1 Aqueous biphasic catalysis

The aqueous biphasic catalysis constitutes a very elegant approach which allows an easy separation of products and the catalyst. This approach was first introduced in the 1980s by Ruhrchemie (now Celanese) on the basis of an older patent of Kuntz from Rhône Poulenc. The first plant came on stream in 1984 in oberhausen (Germany) and had a capacity of 100,000 tons/year. Its capacity was then expanded. Ruhrchemie-Rhône-Poulenc process produces around 8,00,000 tons/year of C₄ and C₅ aldehydes based on this methodology using a catalyst having rhodium as a metal and the sodium salt of trisulfonated triphenyl phosphine (TPPTS) as ligand [65,66].

In aqueous biphasic catalysis, the reactants and products stay in the organic phase while metal-complex, the hydroformylation catalyst resides in the aqueous phase (Fig. 1.15). The metal-complex catalyst is solubilized in water by incorporating hydrophilic ligand. The most common ways of developing a water-soluble ligand is by sulphonating the ligand. By careful sulfonation of the original ligand triphenylphosphine at low temperature complete water solubility is achieved, and with the ligand, rhodium is also transferred to the water phase by complexation. The ligand forms complexes with rhodium that are most likely similar to the ordinary triphenylphosphine complexes (i.e. RhH(CO)(PPh₃)₃) [66].

Fig. 1.15 Aqueous biphasic hydroformylation

The products being sparingly soluble in the aqueous catalyst phase, separation from the products is achieved by simple settlers (Fig. 1.16). The separation step is
simplified enormously in comparison to distillation techniques. Furthermore, the use of water as a solvent has numerous advantages, such as water is non-toxic, odorless, and available in sufficient quantity at a low cost. The non-flammability of water also makes it an environmentally safe solvent for industrial application.

Sulphonated arylphosphines have been applied extensively in variety of biphasic hydroformylation reactions due to their inherent qualities like, high solubility in water (1.1 kg/L), insoluble in common non-polar solvents and sufficiently stable under most catalysis conditions. The high solubility of the ligand enables stabilization of the catalyst in aqueous phase. For these reasons the most of ligands used in aqueous biphasic catalysis in both academia and industry are the sulfonated phosphines.

![Fig. 1.16 Two-phase process of Ruhrchemie/Rhône Poulenc](image)

However, the hydrophilicity in the complexes is also achieved by introducing polar functional groups like ammonium, phosphonium and carboxyl group on the ligand [70]. Besides the TPPTS ligand a number of other sulfonated phosphine ligand systems were investigated to develop more active water-soluble sulfonated ligand. Among the various ligands synthesized, the ligands which are derived from sulfonation of BISBI {BISBIS = sulfonated bis(diphenylphosphinomethyl)biphenyl} and NAPHOS (Fig. 1.17) binaphthyl structures (BINAS = sulfonated NAPHOS) receive special mention. It turned out that rhodium-BINAS is the most active and selective water-soluble catalyst for the hydroformylation of short chain alkene likes...
propene [65]. Its reactivity is up to 10 times higher than TPPTS, even low Rh/P ratios (P/Rh = 7/1) give n/b ratios of 98/2 (TPPTS: 94/6 with P/Rh = 80/1). Compared to TPPTS, these more complicated systems carry higher manufacturing costs as a consequence were never used industrially.

Fig. 1.17 Structure of bidentate Sulfonated phosphines

1.2.8.2 Hydroformylation of higher olefins

The major limitation to further application of aqueous biphasic hydroformylation catalysis is the solubility of higher olefin in water. Alkenes higher than butene are not soluble enough in water. The low solubility of the alkenes in water dramatically reduces the reaction rate [65,66] as a result the hydroformylation of higher alkenes in aqueous systems is not economically viable. For this reason, numerous attempts have been undertaken to hydroformylate higher alkenes with a two-phase system. In principle the difference in polarity between the organic and the catalyst phase has to be decreased compared to the aqueous phase system as entire biphasic catalysis relies on the transfer of organic substrates into the aqueous phase containing the catalyst or at the interphase. Therefore, the researchers have paid attention on improving the affinities between these two phases. The various principal approaches have been investigated for examples, (i) the addition of co-solvent [71], co-ligand [72], surfactant [73] (ii) modified cyclodextrines [74], (iii) Surface-active phosphines [75] in order to enhance the mutual solubility of the components across the phase periphery led to enhance the reaction rate are discussed below.
1.2.8.2.1 Addition of co-solvent and co-ligand

The first approach was addition of organic water miscible co-solvents to an aqueous solution which increase the mass transfer of the substrate in the aqueous phase. It has been shown that co-solvents such as ethanol, acetonitrile, methanol, ethylene glycol and acetone can enhance the rate of the hydroformylation. Monteil et al. [71] studied the effect of adding various co-solvents when dinuclear rhodium complex with TPPTS ligand in the hydroformylation of 1-octene were used. Ethanol was found to be the best in terms of activity although the selectivity towards linear aldehyde decreased. The addition of lower alcohols was also studied [65] and found that methanol led to the highest rate increase. However, the disadvantages of these co-solvents are leaching of catalyst into the organic phase, formation of side product such as acetals and drop in n/b selectivity with increasing amount of co-solvent. This implies that the solvent inter with the catalyst.

According to a proposal of Chaudhari and Delmas et al, even triphenylphosphine (TPP) dissolved in the organic phase, acts as a co-solvent and as a co-ligand (‘promotor ligand’) and as reaction rate-increasing additive. The role of mixed complexes like HRh(CO)(TPPTS)(TPP), is uncertain [72].

1.2.8.2.2 Addition of surfactant

The addition of surfactants (micellar systems) is another way to increase the solubility of the organic substrate in the aqueous phase and have been extensively studied as additives in aqueous biphasic catalysis. The term surfactant is a compression of “Surface active agent”. Surfactants are usually organic compounds that contain both hydrophobic and hydrophilic groups when added to a liquid at low concentration, changes the properties of that liquid at a surface or interface and lower the surface tension of a liquid, congregate together and form micelles [73]. The hydrophilic end is water-soluble and is usually a polar or ionic group. The hydrophobic end is water-insoluble and is usually a long fatty or hydrocarbon chain. Surfactants are generally characterized by the hydrophilic group into the following categories: anionic, cationic, nonionic and amphoteric.

The combination of hydrophobic and hydrophilic properties within one molecule presents unique properties to surfactants upon dissolution in water. Depending on the concentration of the surfactants the molecules are organized in different ways. At low concentrations, surfactants behave as normal electrolytes and
favor a surface arrangement but if their concentration is increased above the so-called critical micelle concentration (C.M.C), then have ability to aggregate forming micelles or vesicle (Fig. 1.18). In polar solvent such as water, the hydrophilic groups are in the external part of the micelle and the hydrophobic groups are oriented inside the micelle called regular micelles. In non-polar solvents, the distribution is just the opposite and these kinds of micelles are called reverse micelles.

![Organization of surfactants](image)

**Fig. 1.18** Organization of surfactants

Surfactants can dissolve molecules, which are normally not soluble in common solvents as results various studied have been made of different surfactants results were best when concentration of surfactant was above C.M.C. It has been shown that the addition of a surfactant, cetyltrimethylammonium bromide (CTAB) to Rh/TPPTS two phase hydroformylation catalyst increases the reaction activity of aqueous biphasic hydroformylation of 1-hexene [73]. Effect of different surfactants for the hydroformylation of 1-dodecene is well documented by Li et al. [73]. They observed that addition of cationic surfactants enhanced dramatically the reaction rate. Addition of nonionic surfactants did not enhance the rate of 1-dodecene hydroformylation and the anionic surfactants inhibited the reaction. The rate of hydroformylation of 1-dodecene increased with increasing stirring rate, but the normal/iso ratio of aldehydes decreased as the vigorous stirring conditions disturb the meta stable micelle structure and decrease in selectivity of n-aldehydes. Although, overuse of surfactants should be avoided since the formation of highly stable emulsions is in conflict with the goal of two phase systems, namely easy product-catalyst separation.

1.2.8.2.3 Addition of cyclodextrins

Cyclodextrins have also been used as mass transfer agents in aqueous biphasic hydroformylation of higher olefins using water-soluble complexes [74]. Among the
different approaches proposed to increase the solubility of higher olefins, the use of chemically modified β-cyclodextrins preserves some economical viability. The cyclodextrin is a cheap, non-toxic and bulk commercially available compound allowed one to achieve the hydroformylation of 1-decene with an initial turnover frequency and aldehyde selectivity of 300 h\(^{-1}\) and 95%, respectively, while avoiding the formation of an emulsion and the partition of the rhodium catalyst between the organic and aqueous phases [74].

Cyclodextrins are cyclic oligosaccharides composed of 6, 7 or 8 glucose units linked by α-(1-4) glucosidic bond. Their molecular geometries are characterized by the shape of a truncated cone with the 3-OH and 6-OH hydroxyl groups of the respective glucose units occupy the wider and the narrower rim of the cone, respectively. The cyclodextrin cavity is essentially hydrophobic and can host a wide range of organic molecules (Fig. 1.19). Substitution of the alcohol functions of by other groups leads to the chemically modified Cyclodextrins. The role played by modified cyclodextrins in biphasic catalysis is ascribed to their complexing properties and operate as inverse phase transfer catalysts according to the mechanism depicted in Fig 1.19. Cyclodextrins form an inclusion complex with the substrate in the organic phase and/or at the liquid–liquid interface. Owing to its significant solubility in water and organic phase the inclusion complex can migrate into the aqueous phase, allowing the substrate to react with the catalyst. After reaction, the reaction product is released in the organic phase and the transfer cycle can go on.

![Diagram of cyclodextrin cavity and hydroformylation](image)

**Fig. 1.19** (a) Structure of cyclodextrins schematically represented by a truncated cone (b) hydroformylation of higher olefins in the presence of cyclodextrin.
One approach is to design a phosphine which has some characteristic features of a surfactant, but is not expected to stabilize emulsions. A surface-active phosphine is defined as a phosphine which bears a hydrophobic end and several hydrophilic ends. The molecule then serves not only as a phosphine ligand to satisfy the coordination chemistry of the central metal atom, but as a surfactant as well. The surface activity of such a phosphine is shown by its ability to aggregate in aqueous solution. Aggregation of phosphines may improve the solubility of organic substrates in water. Since the surface activity of such phosphine does not arise from external additives, the activity and selectivity of such catalyst can be studied and understood mechanistically by simplifying two separate issues, namely the electronic and steric aspect of a phosphine and the surface active feature of an external additive, into a single issue of surface active phosphine. Many of the sulfonated phosphines reported in the literature are expected to be surface active. Even phosphine as simple as mono sulfonated triphenylphosphine (TPPMS) shows surface-active character when used as a water-soluble ligand in 1-hexene hydroformylation [65]. Hanson et al synthesized a series of trisulfonated tris(ω-phenylalkyl)phosphines \( P[(CH_2)_n(p-C_6H_4SO_3Na)_3] \) \( n = 1, 2, 3, 6 \) [75]. These sulfonated phosphines have a well-separated hydrophobic part and three hydrophilic ends. The two phase hydroformylation of 1-octene with these phosphines, especially with trisulfonated tris(6-phenylhexyl)phosphine, showed better activity and moderately enhanced selectivity at low ligand/rhodium ratios.

**1.2.8.3 Other biphasic catalysis**

Apart from aqueous phase, non-aqueous liquid/liquid systems of homogeneous catalysis have also been developed and demonstrate the same advantages in principle as aqueous phase system [67,76–78]. These phases can consist of:

- **Fluorous organic phase - organic liquid**
- **Ionic liquid - organic liquid**
- **Organic polar phase/Non polar organic phase**

**1.2.8.3.1 Fluorous biphasic system (FBS)**

Hydroformylation has been investigated in fluorinated solvents by Horvath et al which is based on the based on the miscibility gap of partially or fully fluorinated compounds with non-fluorinated compounds [67]. The hydroformylation reaction
takes place at appropriate temperatures in one phase due to the solubilities between both liquid phases is dependent upon temperature. At higher the temperature, miscibility of the solvents increases. Upon completion of the hydroformylation reaction, the reaction mixture is cool down to room temperature and separates into two phases. Thus the application is similar to the aqueous biphasic method as phases can be separated by simple decantation. This easy operation and the unlimited solubility of the starting olefin in the FBS at higher temperatures were highly acknowledged by the R&D community [67]. Because of the special nature of FBS (mostly mixtures of perfluorinated hydrocarbons, ethers and tertiary amines) the catalytically active organometallic complexes ought to be specially ‘catalyst tailored’. The Rh complex with ‘ponytailed ligands’ such as \[ \text{P(CH}_2\text{CH}_2\text{(CF}_2\text{)}_3\text{CF}_3\text{)}_3 \] is an example of these special hydroformylation catalysts [67].

1.2.8.3.2 Ionic liquids as solvents

Ionic liquids have become an attractive option for the possible replacement of conventional molecular solvents [76]. Features that make ionic liquids attractive include their lack of vapour pressure and the great versatility of their chemical and physical properties. A further advantage is the possibility of biphasic catalysis. This can be achieved where the catalyst and reactants are miscible in the ionic liquid and the products are insoluble. Ionic liquids are the salts consisting of ions, which exist in the liquid, state at ambient temperature. They are typically consisting of organic nitrogen-containing heterocyclic cations and inorganic anions. Hydroformylation of various alkenes have successfully done by using ionic liquids as a solvent system [76]. In all these cases the conversions and selectivities are comparable with the established processes. Chauvin et al [76] have reported, rhodium complex catalyzed 1-pentene hydroformylation in presence of 1,3-dialkylimidazolium salts as an ionic solvent. The results were quite interesting, the high TOF as well as yield for 1-pentene can be obtained using 1-\text{-}n\text{-}butyl-3-methylimidazolium hexafluorophosphate (BMI\text{PF}_6) as a solvent with Rh/PPh\text{3} system. However, under the similar conditions, the TOF for 1-pentene got an unpredictably decrease for the Rh/TPPMS or TPPTS systems.

1.2.8.4 Thermoregulated phase transfer catalysis (TPTC)

The concept of “thermoregulated phase transfer catalysis” based on cloud point of nonionic phosphine ligand has been effectively introduced to the biphasic hydroformylation of long chain alkenes [77]. Principally, “thermoregulated phase
transfer catalysis (TPTC)” is insoluble in common organic solvents at room temperature. On heating the catalysts becomes soluble in organic solvents indicated by the color change of the solution. Hence, at the reaction temperature of hydroformylation reaction, which is normally more than room temperature, the reaction proceeds homogeneously. After the completion of reaction i.e. on cooling to room temperature, the catalyst precipitates from organic phase, which restrains the products and can be separated from the catalyst by decantation only and can recycle without loss of activity. So the advantage of TPTC is the combination of homogeneous and heterogeneous catalysis.

1.2.8.5 Supercritical carbon dioxide as a solvent

Supercritical fluids (SCFs) are attractive alternatives to organic solvents as reaction media for a number of reasons. The reasons include their pressure tunable properties, physical properties and solvent powers as well as the high miscibility of the reactant gases, efficient mass transfer, local clustering, and possible weakening of the solvation of the reactants [68]. The most recent idea in homogeneous catalysis including hydroformylation topic is the use of supercritical carbon dioxide (scCO₂) and ionic liquids as a solvent. scCO₂ has received attention as a versatile, environmentally benign solvent for a variety of reaction. Hydroformylation of alkenes in presence of scCO₂ is getting a great response from engineering point of view. As a solvent in homogeneous hydroformylation catalysis, scCO₂ offers many advantages over conventional organic solvents. However, one of the main problems with using scCO₂ as a solvent for homogeneously catalyzed reactions is that conventional organometallic catalysts have low solubility, which is a major obstacle for the development of this area. Nevertheless, several approaches have shown that hydroformylation catalysts can be solubilized into scCO₂ via addition of perfluorinated chains to organic portion of the catalysts.

1.2.8.6 Heterogenization of the hydroformylation catalyst

Numerous attempts have been made to immobilize rhodium or its complexes on polymeric or on inorganic supports. Immobilization without ligands leads to systems that mainly hydrogenate the alkene. The problems of homogeneous medium have been avoided to some extent by taking the heterogenized homogeneous system for hydroformylation. The interaction between the support and the metal complex is either coordination by an immobilized coordinating ligand or the immobilization in a
liquid phase which is adsorbed on the carrier [69]. Examples are polymer-bound metal complexes and SLPC (supported liquid phase catalysts). In SLPC, the catalyst is immobilized in a thin adsorbed film of a solvent on a solid support. If the solvent is water and a water-soluble complex is used, these catalysts are referred to as SAPC (supported aqueous phase catalysts). Supported aqueous phase technique is one of the branches of Supported liquid phase technique. Supported aqueous phase catalysts (SAPC) have been developed in 1989 by Davis and Hanson and used for hydroformylation [78]. Supported aqueous-phase catalysis shows high capacity in the conversion, selectivity and also the easy recovery of the catalyst from the organic phase. An important problem however is the hydration of the catalyst. The activity of SAPC is strongly dependent on the water content of the solid particle.

1.3 Hydrogenation

Hydrogenation is a powerful tool in a wide range of organic synthesis, is the most attractive way to carry out the reduction with respect to economical and industrial process considerations. The process is commonly employed to reduce or saturate organic compounds [79]. The term hydrogenation refers to the addition reaction of molecular hydrogen (H₂) with a multiple bond (C=C, C≡C, C=O, C≡N, C≡N, N=O, N≡N, etc) to reduce it to a lower bond order usually in the presence of a catalyst [80, 81].

![Scheme 1.4. Hydrogenation of various unsaturated substrates](image)

The most common and simple type of hydrogenation is the reduction of a C=C double bond to a saturated alkane (Scheme 1.4). Hydrogenation of organic unsaturated substrates is usually performed with gaseous hydrogen (H₂). Gaseous hydrogen is produced industrially from hydrocarbons by the process known as steam
reforming [80,81]. It is also possible to derive hydrogen from other molecules acting as hydrogen donors, such as hydrazine, isopropanol, and formic acid [82,83], these processes are called transfer hydrogenations. A reaction where bonds are broken while hydrogen is added is called hydrogenolysis, a reaction that may occur to carbon-carbon and carbon-heteroatom (oxygen, nitrogen or halogen) bonds.

Numerous important applications of hydrogenation are found in the petrochemical, pharmaceutical fine chemicals and food industries [84]. (i) For the petrochemical industry, many of the compounds found in crude oil are of little use since they contain multiple double bonds; they must be first converted to saturated compounds before use as commodities such as gasoline. In addition, countless other molecules are produced from petroleum; hydrogenation is most often the first step in their production. (ii) In the fine chemical and active pharmaceutical ingredient industries, the hydrogenation reaction is often an important step in producing the end product. (iii) The food industry uses hydrogenation to completely or partially saturate the unsaturated fatty acids in vegetable oils to convert them into solid or semi-solid fats (e.g. margarine). (iv) Hydrogenation is a critical step in the upgrading of biocrude to usable, renewable biofuels. Biocrude has been hydrogenated to minimize its negative aspects. The instability of oil is reduced by reaction of the most unstable functional groups. Concurrently, the oxygenated component of the oil was also reduced, resulting in an improved energy density. Hydrotreated biocrude is also more miscible with refined petroleum products.

1.3.1 Catalysts used in the hydrogenation

Hydrogenation has three components, the unsaturated substrate, the hydrogen (or hydrogen source) and a catalyst. The reaction is carried out at different temperatures and pressures depending upon the substrate and the activity of the catalyst. The common catalysts used in the hydrogenation reactions are based on the metals such as palladium, platinum, rhodium, ruthenium, iridium and nickel. Particularly, platinum, palladium, rhodium, ruthenium and iridium form highly active catalysts, which operate at lower temperatures and lower pressures of H₂. Non-precious metal catalysts, especially those based on nickel (such as Raney nickel) have also been developed as economical alternatives, but they are often slower or require higher temperature and high pressure [84,85]. Basically two types of catalysts are known (I) homogeneous catalysts and (II) heterogeneous catalysts [84].
Homogeneous catalysts dissolve in the solvent that contains the unsaturated substrate. Heterogeneous catalysts are solids that are suspended in the same solvent with the substrate.

1.3.1.1 Homogeneous catalysts

Homogeneous hydrogenation constitutes an important synthetic procedure and is one of the most extensively studied reactions of homogeneous catalysis [86]. RhCl(PPh₃)₃ known as Wilkinson’s catalyst was the first highly active homogeneous hydrogenation catalyst and was discovered independently in 1965 by Geoffrey Wilkinson (a recipient of the Nobel Prize in 1973) and other groups [87]. This burgundy-red compound can be easily prepared by reacting RhCl₃·3H₂O with triphenylphosphine in refluxing ethanol (Scheme 1.5). This compound catalyzes the chemo specific hydrogenation of alkenes in the presence of other easily reduced groups such as NO₂ or CHO, and terminal alkenes in the presence of internal alkenes [88]. The most accepted mechanism for alkene hydrogenation supported by careful kinetic and spectroscopic studies of cyclohexene hydrogenation [89] is shown in Scheme 1.5.

\[
\begin{align*}
\text{RhCl}_3 \cdot 3\text{(H}_2\text{O)} + 4 \text{PPh}_3 & \rightarrow \text{RhCl(PPh}_3\text{)}_3 + \text{O=PPh}_3 + 2 \text{HCl} + 2 \text{H}_2\text{O}
\end{align*}
\]

\[\text{Scheme 1.5 Mechanism for alkene hydrogenation with Wilkinson catalyst, RhCl(PPh}_3\text{)}_3.\]
It has been clearly shown that PPh$_3$ is readily lost due to steric crowding and that the inner catalyst cycle with a weakly coordinated solvent molecule is more active than has three PPh$_3$ ligands coordinated to the metal.

After the Wilkinson’s discovery of [RhCl(PPh$_3$)$_3$] as an homogeneous hydrogenation catalyst, various homogeneous catalysts have been further developed by changing the metals and ligands and have extended the scope of catalytic hydrogenation in particular, for highly selective transformations. The complex of ruthenium RuCl$_2$(PPh$_3$)$_3$, analogues to RhCl(PPh$_3$)$_3$ was also prepared by Wilkinson et al and shown to be active precursor for homogeneous hydrogenation [90]. It was observed that active catalytic species is HRuCl(PPh$_3$)$_3$ 43 and is an exceedingly effective for the hydrogenation of terminal alkenes. The catalytic potential of cationic [Rh(diene)(PR$_3$)$_3$]+ complexes 44 (Fig. 1.20) as hydrogenation catalysts was discovered by Osborn and coworkers during the period 1969 to 1976 [91]. Coordinatively unsaturated cationic catalysts those were considerably more active for hydrogenation. The reason for this is that the cationic metal center is more electrophilic and this favors alkene coordination, which is often the rate determining reaction step. In contrast to Wilkinson’s catalyst, a large number of donor ligands can be used and several easy preparative routes are available. NBD was the preferred diene for the [Rh(diene)L$_n$]+ catalyst precursors, but other dienes such as 1,5-cyclooctadiene (COD) have also been used [91].

The complex of iridium with 1,5-cyclooctadiene, tricyclohexylphosphine PCy$_3$ and pyridine (Crabtree's catalyst) 45 was developed by Robert H. Crabtree and used as homogeneous catalyst for hydrogenation reactions [92]. One advantage of Crabtree’s catalyst is that it is about 100 times more active than Wilkinson’s and can hydrogenate even tri- and tetra-substituted alkenes. Crabtree’s catalyst has also been used as the basis for the development of newer catalysts; by modifying the ligands.

![Fig. 1.20 Structure of Ru, Rh and Ir based catalyst](image-url)
A variety of iridium complexes analogous to Crabtree’s catalyst have been prepared in which pyridine or the phosphine ligands have been replaced with N-heterocyclic carbene 46 [93]. In many reported cases, this change results in an improvement of the catalytic properties and stability of the compounds under the reaction conditions [93].

1.3.1.2 Heterogeneous catalysts

One of the major drawbacks of homogeneous catalytic processes is the difficulty to separate and reuse the catalyst. For this reason and for the consideration of the environmental aspects of chemical production, the heterogeneous catalysts are attracting great interest [6,7] and have many advantages such as the stability of catalyst, ease of separation of product from catalyst and a wide range of applicable reaction conditions. Heterogeneous transition metal catalysts for hydrogenation are usually employed in the states of metals or oxides that are either unsupported or supported. For fine chemicals manufacture activated carbon is the most common support material. Aluminas and silicas as well as CaCO$_3$ or BaSO$_4$ are preferred for special applications [84,85]. A broad range of heterogeneous catalysts are commercially available for catalytic applications in the fine and industrial chemicals synthesis and production. Due to the complexity and the individual requirements of synthetic processes in the fine chemicals industry catalyst design is of major importance for best process performance.

During the past years many approaches for the heterogenization of homogeneous catalysts have been described in the literature [84]. Motivation for all these efforts is based on the idea to complete the positive aspects of homogeneous catalysis by a facilitated catalyst separation and an improved catalyst overall performance (e.g. longer life-time). Like hydroformylation, among the various heterogenization strategies two basic concepts can be differentiated.

1. Heterogenization of homogeneous catalyst on solid support
   - The catalyst is bound (covalently or ionically) to inorganic and organic support such as silica, resins and polymers.
   - The catalyst is entrapped, encapsulated, adsorbed via chemi- or physisorption.

2. The catalyst and substrate are in immiscible phase (biphasic-system)
   - The catalyst is dissolved in aqueous phase or organic phase such as ionic liquids
Besides hydroformylation, various heterogenization strategies, such as heterogenization of homogeneous catalysts on solid supports, aqueous biphasic systems and nonaqueous biphasic systems (summarized in hydroformylation section) have also been extensively explored in hydrogenation. The selective examples are summarized below.

Quiroga et al immobilized Wilkinson catalysts on $\gamma$-Al$_2$O$_3$ and used for the hydrogenation of alkenes. Supporting Wilkinson’s complex rendered a high active catalyst; the activity was higher than that of the same complex unsupported, in the presence or absence of S-containing poison tetrahydrothiophene. [94]. Homogeneous catalyst, RhCl(PPh$_3$)$_3$ has also been successfully immobilized on mesoporous material (MCM-41) via bifunctional linkers like (OEt)$_3$Si(CH$_2$)$_3$PPh$_2$ by Shyu et al (Fig. 1.21) [95]. The immobilized catalyst resulted in a stable hydrogenation catalyst with enhancement in catalytic activity.

![Fig. 1.21 Immobilization of RhCl(PPh$_3$)$_3$ on mesoporous material (MCM-41)](image)

Due to the key role of rhodium and ruthenium complexes in the hydrogenation of unsaturated substrates, various water-soluble analogues of rhodium and ruthenium Wilkinson catalyst were also synthesized and the biphasic hydrogenation of unsaturated substrates with water-soluble Ru and Rh-catalysts has been reported [96,97]. Another rapidly growing area of non-aqueous biphasic catalysis is based on the application of ionic liquids as catalyst supporting phase. Hydrogenation reactions with Rh, Pd, Pt, Ru complexes dissolved in ionic liquids of biphasic systems are reported for a series of dienes [98], mono-olefines [99] arenes [100]. The hydrogenation of unsaturated substrates catalyzed by supported aqueous phase catalyst, SAPC (where a water soluble complex is supported as a thin film dispersed over the surface of a high-surface area solid) has also been investigated using water-
soluble Ru and Rh based catalysts [101,102]. An easy catalyst separation by simple filtration and a high contact area between the aqueous film and the reactant containing organic solvent is achieved.

1.3.1.3 Transition-metal nanoparticles catalysed hydrogenation

Recently, the application of transition-metal nanoparticles in catalysis has attracted much attention due to their distinct catalytic activities and selectivities in various transformations [103]. It is believed that nanoparticles have properties intermediate between those of bulk and single particles, and nano-sized catalysts dispersed in suitable media or support may combine the advantages of homogeneous and heterogeneous catalytic systems. Transition metal colloids and nanoparticles used in homogenization of heterogeneous catalysts are under active study due to their high surface specific area and their small size providing numerous potential active sites [104]. However, in their catalytic application one of the most important problems is the aggregation of nanoparticles into clumps and ultimately to the bulk metal which leads to a decrease in catalytic activity and lifetime. Metal nanoparticles designed for hydrogenation applications are usually synthesized from a metal salt, a reducing agent, and a stabilizer or are supported on various supports. The various methods have been developed for the preparation and stabilization of metal nanoparticles to avoid the formation of bulk metal and applied as catalysts for the hydrogenation of arenes or olefins [104,105]. The stabilizing agents usually utilized are polymers, surfactants and ionic liquids, although nanoparticles also stabilized by other molecules such as nitrogen and phosphorus donor molecules. Ru, Rh, Pt and Ir are currently the metals of choice for hydrogenation. For examples, (a) the rhodium nanoparticles (2 ± 2.5 nm) were synthesized by the reduction of RhCl$_3$·3H$_2$O with sodium borohydride and were stabilized by highly surfactant N-alkyl-N-(2-hydroxyethyl) ammonium salts (HEA-C$_n$). A colloidal system based on an aqueous suspension of rhodium (0) nanoparticles found to be an efficient catalyst for the hydrogenation of arene derivatives under biphasic conditions and can be reused without significant loss of activity [106]. (b) C. Hubert et al reported the preparation of ruthenium(0) nanoparticles (Fig. 1.22) stabilized by inclusion complexes formed between the N,N-dimethyl, N-hexadecyl, N-(2-hydroxyethyl)ammonium (HEA-16Cl) and randomly methylated cyclodextrins (RAME-β-CD) and the activity of these stabilized Ru(0) nanoparticles (NPs) to perform hydrogenation of various aromatic derivatives [107].
Researcher Aasif Dabbawala

Fig. 1.22 Proposed model for the stabilization of Ru NPs by HEA-16Cl (a) and (b) by RAME-β-CD/HEA-16Cl

(c) The ligand-stabilized Pd nanoparticles were synthesized, supported on TiO₂ and used as catalyst for hydrogenation [108]. (d) Immobilized nanoparticles on insoluble solid supports were also extensively studied for this process and present similar advantages to those of traditional heterogeneous catalysts. M. Zahmakırana et al prepared Ruthenium (0) nanoclusters stabilized by zeolite framework/hydroxyapatite and used as catalyst for the hydrogenation of benzene. Both catalysts gave unprecedented catalytic activity under mild conditions (22 °C, 40±1 psig H₂) [109].

1.4 Scope and objective of present thesis

The above discussion has outlined the present state of the hydroformylation and hydrogenation process with their industrial importance and a brief overview on problems linked with transition metal complexes and recent developments in the hydroformylation and hydrogenation catalysts for the synthesis of bulk and fine chemicals are discussed. The designing new modifying phosphorus ligands, effect of ligands in terms of steric and electronic properties on the activity and selectivity of transition metal complexes, conversion of higher olefins in aqueous biphasic systems and different approaches for recovery and recycling of catalyst with product separation are important topics of research in hydroformylation and hydrogenation and are in progress.

In spite of the development in commercial processes, there are still some possibilities to improve existing industrial processes, to make them simpler and more environmentally friendly. The further improvement of catalytic activity of systems based on homogeneous catalysts or water soluble phosphorus ligands is still interesting and subject of research as many catalyst precursors and ligands are very...
expensive, therefore a search for cheaper catalysts with the same performance is necessary. Transition metal organometallic complexes with new modifying ligands can allow one to design new active and selective catalysts to fulfilling requirements with respect to their application in hydroformylation and hydrogenation.

In view of above, the main objective of the present thesis is to develop an effective catalyst systems for hydroformylation as well hydrogenation reactions. The investigations have been focused on the major problems associated with transition metal catalyzed hydroformylation and hydrogenation reaction such as; (a) the recovery and recycling of the catalyst (b) conversion of higher olefins in aqueous biphasic systems (c) improvement in activity and selectivity (chemo/regioselectivity) of the reaction. The experimental investigations involved the synthesis, characterization of the ligands and their transition metal complexes catalysts and their detail investigations on the catalytic evaluations in hydroformylation or in hydrogenation. The investigations are performed in detail as the function of the various reaction parameters: temperature, pressure, amount of the catalyst, amount of substrate and rates of the reactions.
Chapter –1

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