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Review

Rhodium-catalyzed hydroformylation under green conditions: Aqueous/organic biphasic, “on water”, solventless and Rh nanoparticle based systems

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ABSTRACT

Hydrofomylation is an important industrial process for aldehyde production which follows the atom-economy principle. In this homogeneous process, the separation and subsequent recycling of the expensive catalyst are fundamental problems. In the Ruhrchemie/Rhone-Poulenc process, hydroformylation is carried out in water and the soluble rhodium catalyst is separated and reused. However, long chain olefins, less soluble in water, are not suitable for this process. Current research is focused on the development of methodologies applicable to longer olefins and compatible with green chemistry rules. Hydroformylation can be carried out using an aqueous/organic biphasic medium or in solventless conditions. Different modifications, including phase transfer agents, surfactants or cyclodextrins were introduced to improve the hydroformylation process in water. In terms of water application, the “on water” strategy applicable to fully hydrophobic systems has been illustrated for different substrates, such as alcohols, esters and dienes. The use of Rh NPs (Rh nanoparticles) as a rhodium source in hydroformylation, as an alternative to soluble coordination compounds, was also shown.

Contents

1. Introduction

Hydroformylation was discovered by Otto Roelen, in 1938, at the Ruhrchemie plant, when examining the cobalt-catalyzed Fischer–Tropsch reaction in a system containing ethylene and ammonia [1-6]. This discovery was based on the identification of propionaldimine, formed from propanal and ammonia at 170 °C. Hydroformylation is the reaction in which aldehydes are formed from three substrates; CO, H_2 and olefins. This synthesis is known only in the catalyzed version, with a transition metal catalyst. An important advantage of hydroformylation is the total use of all atoms in accordance with the principle of atom-economy (Fig. 1).

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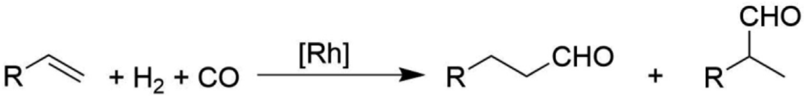


Fig. 1. Hydroformylation reaction.

Today, hydroformylation (also known as Oxo synthesis) is one of the largest industrial processes which is performed in a homogeneous system [7–12]. The annual production of aldehydes, mainly butanals, formed by hydroformylation of propene, is around 12 million tonnes. The large scale of the process and its importance to the chemical industry provides the motivation for further improvements of this technology.

In the homogeneous system each catalytic site is accessible for the substrates, which facilitates an efficient contact with the catalyst. However, due to the fact that all components are in the same phase, separation of the catalysts from the products is a challenging step. The high price of rhodium motivates a search for reusable catalysts that also enable achievement of high TOF values. Moreover, good separation of the catalyst from organic products is important for the further industrial applications in the production of pharmaceuticals or other biologically active components.

Aldehydes produced by the hydroformylation of olefins, diolefins, or any other unsaturated substrates, are usually processed into technologically important products, such as alcohols, carboxylic acid, aldols, diols, acetals, esters, ethers and amines [2–12]. These compounds, derived from aldehydes, are important raw materials for the production of fine chemicals, solvents, soaps, fragrance, detergents and surfactants, flavors, parfumes, pharmaceuticals, lubricants, and plasticizers [13].

In most cases, the catalytic system for hydroformylation contains a metal precursor and excess of a ligand which modulates the electronic and steric properties of the metal. The activity of transition metals as catalysts of hydroformylation decreases in the order Rh ≫ Co > Ir, Ru > Os > Pt > Pd > Fe > Ni, while the usefulness of monodentate modifying ligands [L] decreases in the series PPh_3, $P(OR)_3$ > $P(n\text{-}C_4H_9)_3$ ≫ NPh_3 > $AsPh_3$, $SbPh_3$ > $BiPh_3$ [2–8]. Rhodium-based catalysts used with P-ligands are more active and selective toward linear aldehydes (n) than non-modified catalysts which provide a lower n/iso ratio and require severe temperature and pressure conditions [3].

The first hydroformylation technology was implemented by BASF-Ruhrchemie for a $Co_2(CO)_8$ catalyst which formed catalytically active $CoH(CO)_4$ under catalytic conditions [2–12].

In this process, high pressure (200–300 bar) and high temperature (150–180 °C) were necessary to form C_4 aldehydes from propene with an n/iso ratio of ca. 2–4. An important improvement in the rate and selectivity of hydroformylation was achieved after the introduction of rhodium catalysts modified with phosphines. The BASF, Celanese, and Union Carbide technology of propene hydroformylation operates at 15–20 bar and 100 °C with PPh_3 excess 100–200 relative to Rh. The biphasic system, aqueous/organic, for propene hydroformylation was commercialized and made technically viable at Ruhrchemie-Rhône Poulenc in 1984 [14]. In this technology, the rhodium catalyst is soluble in water by the use of water-soluble sulfonated phosphine, TPPTS as ligand. One of the most important advantages of this biphasic system is efficient catalyst separation from the organic products by simple decantation. The catalyst recovered in the aqueous phase can be easily used for further processing [14]. It is worth noting that this system, containing water-soluble phosphine TPPTS, is not only environmentally friendly but also increases the selectivity to the normal aldehyde (n/iso ratio) [5–8].

The Ruhrchemie-Rhône Poulenc technology, originally designed for propene, can be also used for longer olefins, such as 1-butene and 1-pentene. The solubility of 1-hexene and longer chain substrates is not sufficient to perform the process efficiently. Interestingly, application of this methodology to a mixture of 1- and 2-butenes produced ca. 95% of n-pentanal whereas 2-butene did not react [11]. This indicated the advantageous selectivity of the catalytic system.

TPPTS was not the only water-soluble phosphine tested on a pilot plant scale. Sulfonated biphenyl (BISBIS) or binaphtyl (BINAS) derivatives (Fig. 2) presented even higher activity and selectivity than TPPTS [15–17]. However, TPPTS was chosen for industrial application based on the economical aspects and the stability of phosphine under hydroformylation conditions [11].

The effect of sulfonated phosphines on the catalytic activity of rhodium systems depends on their structure and the catalytic activity decreases in the order:

BINAS > NORBOS > BISBIS > TPPTS

In addition, an n/iso ratio as high as 98/2 or 82/18 was achieved by applying sulfonated diphosphines, BINAS and NORBOS, respectively. These selectivities are significantly higher than for not-sulfonated phosphines [18].

The hydroformylation reaction can be performed in various media such as organic solvents [2–12], water (aqueous biphasic systems) [2–12,19], supercritical CO_2 [20–24], fluorinated solvents [24–28], or ionic liquids [29–35], as well as under solventless conditions [36,37].

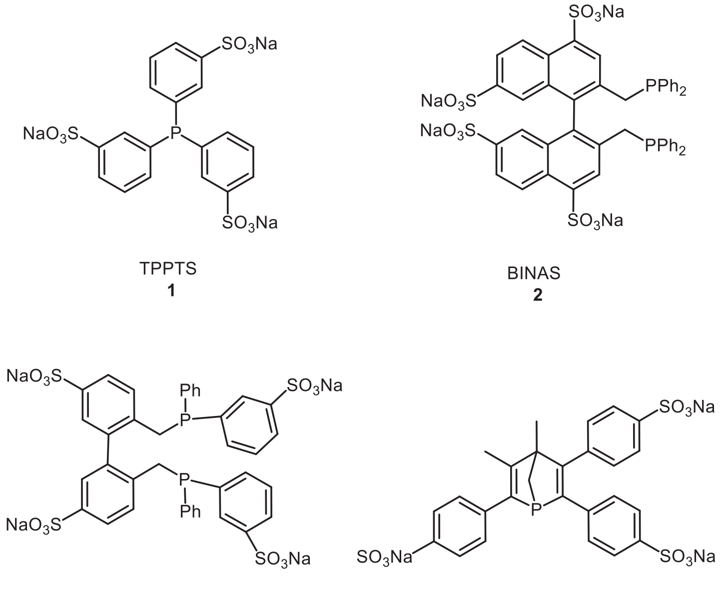
This review presents recent achievements in studies on biphasic aqueous/organic systems, including the application of different water-soluble phosphines and technical improvements leading to an increase in the catalytic efficiency. Aqueous biphasic reaction medium is beneficial from both, economic and environmental point of view. Water is undoubtedly a green solvent, as inflammable, non-toxic and naturally occurring. However, the rate of hydroformylation of hydrophobic substrates, such as longer chain olefins, in aqueous biphasic system is limited by mass transfer. Therefore, different additives were used to overcome these limitations. In particular, micellar catalysis plays an important role in this area.

Environmentally friendly, solvent-free hydroformylation, and the application of Rh NPs as precursors of hydroformylation catalysts are also discussed. The green aspect of these methodologies is to limit the use of organic solvents and to improve separation of the catalyst from organic products. The recovered catalyst can be used in the next catalytic runs which lowers the process cost. Efficient separation of the catalyst is also important for the fabrication of pure, metal-free, organic hydroformylation products, mainly aldehydes. Rh NPs, supported on different organic or inorganic carriers, present a promising class of hydroformylation catalysts which can be separated and reused with good results in several subsequent reactions.

2. Hydroformylation in aqueous/organic biphasic systems

2.1. Characteristics of biphasic aqueous/organic hydroformylation

Efficient separation of the hydroformylation products (aldehydes or alcohols) from the catalyst is the main objective for improving aqueous/organic biphasic catalytic systems. While C_4 aldehydes (butanals), obtained from propene, can be separated easily by distillation due to the relatively low boiling temperature,



TPPTS
1

BINAS
2

BISBIS
3

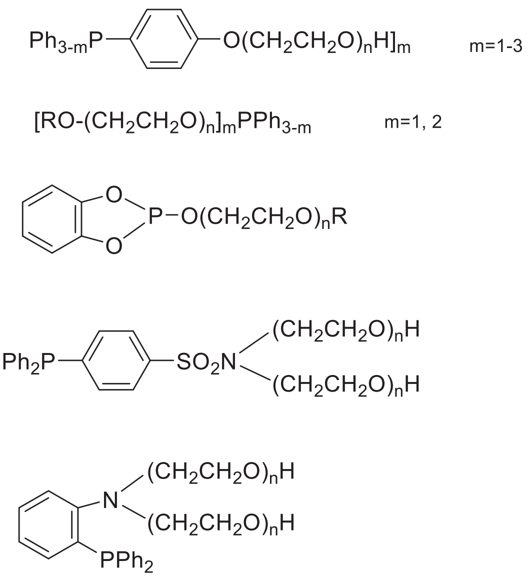
NORBOS
4

Fig. 2. Water-soluble phosphines.

the problem becomes more difficult for longer chain aldehydes. Biphasic systems, containing two immiscible phases, present a good option for the efficient separation of the catalyst soluble in one phase (e.g. in water) from organic reactants insoluble in this phase. Water is the preferred component of biphasic catalytic systems because it is considered a "green solvent", being nontoxic, inflammable, environmentally friendly, cheap and abundantly available.

However, the main problem related to the application of water as a reaction medium for hydroformylation is the low solubility of longer chain olefinic substrates [38]. In the aqueous/organic system, the efficient mass transport has a fundamental impact on the reaction course and its final productivity. The mass transport determines the access of substrates to the catalytically active centers allowing their efficient transformation to products [39,40]. Therefore, processes that occur at the interface can be decisive for the whole process. Several strategies have been developed to increase the efficiency of biphasic systems, such as the introduction of co-solvent, promoter or phase transfer agents, for example, surfactants or cyclodextrins [41–45]. These additives improve the contact of reactants with the catalyst by increasing the interfacial area of solubility. In the presence of surfactants, hydrophobic olefins undergo solubilization in micelles. Moreover, the interaction (attraction or repulsion) of surfactants with the negatively charged water-soluble phosphine ligand coordinated to the catalyst, e.i. TPPTS, can result in an increase of the hydroformylation efficiency [46–49].

Bergbreiter et al. introduced a concept of thermoregulated phase separation by using the "smart ligand" that control the catalytic process depending on temperature. In principle, the solubil-



PETPP 5

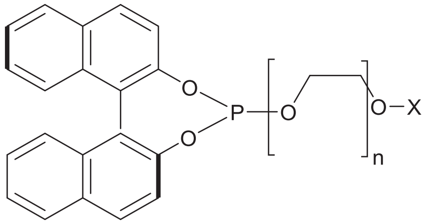
AEOPP 6

OPGPP 7

PEO-DPPSA 8

PEO-DPPPA 9

Fig. 3. Water-soluble phosphines with a poly(ethylene glycol) chain.



X=Me, n=16-17 **10**

X=PO_2R, n=4-5 (RO_2H_2 = (S)-Binol) **11**

Fig. 4. Chiral polyether-phosphite ligands.

ity of such ligand changed with temperature enabling its transfer between phases [50,51]. At a lower temperature, the catalyst bearing the "smart ligand" is soluble in the aqueous phase and organic substrates form the second phase. When the temperature increases, the catalyst is transferred to the organic phase due to its enhanced solubility. After cooling down at the end of the catalytic reaction, the catalyst returns to the aqueous phase to be separated from the products.

The progress in thermoregulated biphasic catalysis was recently reviewed by Jin et al. [52]. They studied the two-phase hydroformylation of higher olefins with water-soluble phosphines containing a poly(ethylene glycol) chain [53-62] (Fig. 3). By employment of these ligands, not only efficient phase separation but also high TOF values were obtained, up to 250 h^{-1} for 1-dodecene and 470 h^{-1} for styrene [51].

Jin et al. studied the influence of change hydrophilic and lipophilic groups on the cloud point and water solubility in a series of surface-active **5** and **6** phosphines [55]. The Rh/6 catalyst converted 96–98% of 1-dodecene to aldehydes, significantly more than Rh/TPPTS (15.3%) [57].

Two chiral polyether-phosphite ligands were obtained and used with $[Rh(cod)_2]BF_4$ to enantioselective thermoregulated phase-transfer hydroformylation of styrene [63] (Fig. 4). The Rh/**10** system was stable in the aqueous phase, but during recycling, its selectivity decreased. The second catalyst, containing ligand **11**, was leached to the organic phase. Nevertheless, reuse of the aqueous phase gave the same enantioselectivity (25% ee) as in the first reaction but at a lower yield.

A thermomorphic approach, based on the application of thermomorphic multicomponent solvent systems, was tested in the laboratory scale and a continuously operated miniplant [64-68].

The application of cyclodextrins (CD) as a supramolecular tool in hydroformylation was recently reviewed by Hapiot and Monflier [69-71] and by Matsinha et al. [72]. Cyclodextrins belong to the cyclic oligosaccharides formed by α-D-glucopyranose units. Depending on the number of connected units, different CDs are distinguished, namely α-CD (six), β-CD (seven), γ-CD (eight) (Fig. 5).

In aqueous/organic biphasic hydroformylation, CDs can act as mass transfer agents which increase the efficiency of the hydroformylation of hydrophobic olefins (Fig. 6). In principle, a phosphorus ligand interacting with the CD cavity coordinates the metal and forms an active catalyst which can then be easily transported from the aqueous phase to the interfacial layer and react with the hydrophobic substrates. The outer surface of CDs is hydrophilic and it can be further modified by the introduction of functional groups.

Interestingly, the presence of CDs in the hydroformylation of 1-decene with a rhodium catalyst containing alkyl sulfonated diphosphines [73] (Fig. 7) caused an increase in the activity but a decrease in the yield of normal aldehyde. The higher reaction rates were observed in the presence of methylated CDs due to the complexation of olefin inside the hydrophobic cavity. However, when such a complex approached the rhodium center, the bidentate ligand dissociated, forming the low coordinated catalyst, which was less selective.

The use of water as a medium for the organic reaction also offers additional advantages, such as increasing the reaction rate and improving its selectivity to normal aldehydes. According to Breslow, these features are related to the hydrophobic effect, namely the aggregation of nonpolar species in water causing a decrease in the olefin/water interface space [74]. The importance of the hydrophobic effect is clearly seen in biological systems in which the structures of proteins and nucleic acids as well as the binding of substrates to enzymes are determined by these interactions [74]. Reek et al. performed the detailed studies to demonstrate an influence of supramolecular interactions on the hydroformylation selectivity. In this research bidentate phosphines with an anion binding site were used to preorganize a substrate molecule for highly selective formation of a linear product [75].

Supramolecular hydrogels formed from α-CD and the high-molecular weight PEG improved catalytic performance in hydroformylation due to the stabilization of olefin/water emulsions [76].

Breit evidenced that the formation of hydrogen bonds leading to a self-assembling system is another important factor that affects the catalyst's activity and selectivity [77].

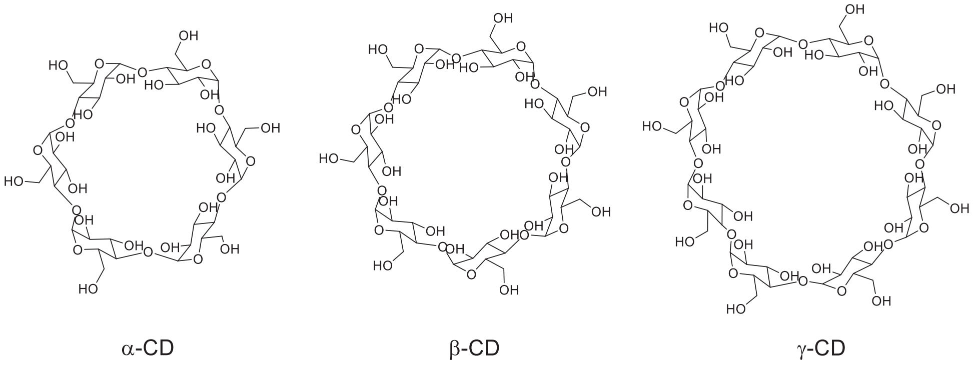


Fig. 5. Structures of cyclodextrins.

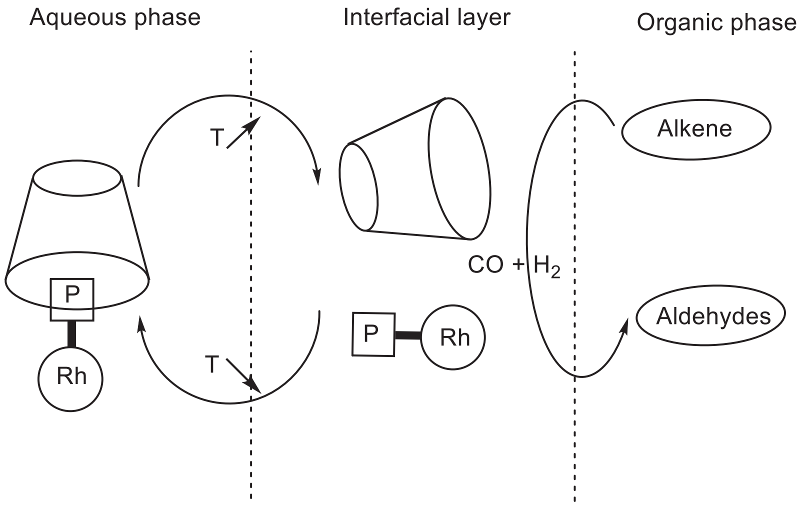
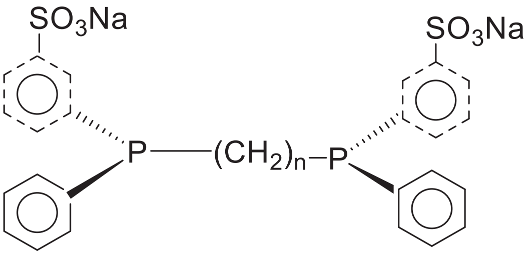


Fig. 6. Thermocontrolled phase-transfer using cyclodextrine [63].



n=2, DPPETS **12**

n=3, DPPPTS **13**

n=4, DPPBTS **14**

Fig. 7. Alkyl sulfonated diarylphosphines.

In 2005, Sharpless reported the efficient reaction of water insoluble substrates stirred intensively in a water suspension [78]. This phenomenon, first described for organic syntheses such as Diels-Alder cycloaddition or Claisen rearrangement, was denoted as “on water” conditions. The “on water” approach can be also used for the metal-catalyzed transformations of organic substrates [79-81].

2.2. Studies on the Rh/TPPTS system

Many research studies have been devoted to the Rh/TPPTS system, despite its successful technological application [82]. The selected examples illustrate possible modifications and improvements, mainly for the hydroformylation of longer chain olefins by this system. Moreover, mechanistic studies allow understanding of the catalyst transformations during hydroformylation [83]. The presented results illustrate applicability of the various approaches improving hydroformylation efficiency in reactions performed with the same phosphine, TPPTS. This selection enables comparison and evaluation of effectiveness of these methodologies.

In 1995, Chaudhari et al. reported a new methodology for the promotion of interphase catalysis in an aqueous/organic system by using a hydrophobic PPh_3 ligand [84]. They found that hydroformylation of 1-octene catalyzed by the water-soluble catalyst formed from [R h(COD)Cl]$_2$ and TPPTS (Fig. 2) in a biphasic toluene-water system was less active, whereas the addition of a hydrophobic ligand (PPh_3) increased its activity significantly. It was found that the promoter ligand, PPh_3, coordinated to the Rh-TPPTS catalyst and increased the concentration of the catalytic form at the interfase. As a result, the reaction rate and the turnover frequency (TOF) increased by a factor of 10–50 and only a very small amount of rhodium was leached into the organic phase (<5 ppm). Experimental data indicated that the increase of the reaction rate in an aqueous/organic system resulted from the interface phenomenon. Accordingly, Chaudhari et al. concluded that catalysis took place at the water-organic interface, and the catalyst was kept in the water phase [84]. Interestingly, the water-soluble TPPTS ligand acted as a promoter in the hydroformylation of allyl alcohol with a hydrophobic $[RhH(CO)(PPh_3)_3]$ catalyst and a five-fold increase in the reaction rate was noted. Thus, the “reverse” effect of the promoter ligand was operating in this case [84].

The kinetics of hydroformylation in the two-phase system was first studied by Delmas and Purwanto [85]. They used 1-octene as a substrate, Rh/TPPTS as a catalyst and ethanol as a co-solvent. The reaction was first order with respect to the substrate and the catalyst, while an inhibiting effect of CO was found at the higher pressure. A rate-determining step was assumed coordinating 1-octene to the active catalyst, $[RhH(CO)_2(TPPTS)_2]$ [86].

The pH of the aqueous phase strongly influenced the reaction rate in the Rh/TPPTS system. For example, the rate of hydroformylation increased when the pH changed from 7 to 10. The inhibiting effect of CO partial pressure was noted at pH 10 but not at pH 7 [87].

Delmas et al. analyzed the kinetic data obtained for 1-octene hydroformylation in a mechanically agitated batch reactor using a pseudo-homogeneous gas–liquid–liquid model, which considered the dispersed organic phase. In these conditions the mass transfer of 1-octene to the aqueous phase was rapid and it did not limit the reaction rate [88].

A new kinetic approach was proposed by Mao et al. for the evaluation of interfacial 1-dodecene hydroformylation in the presence of a CTAB surfactant. By a combination of numerical and experimental results in a laminar-flow reactor, the mass transfer resistance between phases was eliminated [89,90]. An effect of emulsification on the reaction course was also shown [91].

Kalck et al. investigated the hydroformylation of 1-octene by using $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ or $[RhH(CO)(TPPTS)_3]$ as the catalyst with the addition of a small amount of PPh_3 to retain the water-soluble catalyst at the interface. With the addition of one equivalent of PPh_3 to the $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ the n/iso ratio was 3, close to that obtained in the previous studies of hydroformylation carried out in an organic solution [92,93]. A higher n/iso ratio would be expected for the reaction occurring in the aqueous phase [94]. It was concluded that the reaction occurred in the organic phase with rhodium active forms leached from the water phase. In fact, ^{31}P NMR analyses showed that active species, $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2]$ and $[RhH(CO)(PPh_3)_3]$, were leached into the organic phase and they were considered responsible for the increase in the reaction rate [94].

High-pressure NMR studies showed that $[RhH(CO)(TPPTS)_3]$ was the only form of the catalyst identified in solution in the presence of excess TPPTS and at a pressure of H_2/CO up to 200 bar [83]. It is an important finding because this complex is responsible for the formation of a linear aldehyde (n), while dissociation of the phosphine ligand and formation of $[RhH(CO)_2(TPPTS)_2]$ or $[RhH(CO)_2(TPPTS)]$ promotes creation of the branched product (iso). The presence of $[RhH(CO)(TPPTS)_3]$ can explain the high selectivity to n-aldehyde (high n/iso ratio) in a catalytic system with TPPTS [11,94]. In contrast, $[RhH(CO)(PPh_3)_3]$ reacted differently and undergoes quantitative transformation to $[RhH(CO)_2(PPh_3)_2]$ under hydroformylation conditions [3].

Under microemulsion conditions, in the presence of a nonionic surfactant, the formation of unmodified rhodium carbonyl was suppressed, enabling working at lower TPPTS/Rh ratios than under biphasic conditions [95]. However, in the hydroformylation of 7-tetradecene, the amount of unmodified $[RhH(CO)_3]$ increased in a microemulsion stabilized by an alkyl-polyglycolether type surfactant [96]. Acceleration of aqueous-biphasic hydroformylation of higher olefin ($>C_5$) was achieved after addition of 1-octyl-3-methyl imidazolium salt, due to the formation of micelles in which the olefin substrate was solubilized [97].

An important issue in biphasic aqueous/organic systems is determining where the reaction takes place, which may be the interface area or in the bulk water phase, in which the catalyst is soluble. These aspects were intensively studied by theoretical and experimental methods [98,99]. Hydroformylation of propene with Rh/TPPTS system was investigated by molecular dynamics [98]. The studies revealed the interfacial activity of the catalytically active $[Rh\ H(CO)(TPPTS)_2]^{6-}$ and $[RhH(CO)(TPPTS)_2(propene)]^{6-}$ intermediate which migrated across the interface. Interestingly, the attractions of the intermediate complex with organic phase increased in the presence of butyraldehyde (a hydroformylation product). Moreover, it was found that the reaction with rhodium catalysts occured at the interface, because the concentration of propene was higher at the water surface than in the bulk propene [98].

Analogous catalytically active rhodium intermediates with the coordinated 1-hexene substrate can adsorb at the interface of the binary mixture of 1-hexene and $[bmim]PF_6$. Thus, an interfacial reaction is favored over a reaction which occurs in the bulk water phase [100].

Molecular dynamic simulations applied to the biphasic system promoted by β-CDs revealed the surface activity of the less charged intermediates and their increased concentration at the interface. The importance of adsorption at the interface in the efficient hydroformylation of higher olefins was underlined [101,102].

Studies on the hydroformylation of a series of olefins, 1-hexene, 1-octene, 1-decene and 1-dodecene using the $[RhCl(cod)]_2/TPPTS$ system, showed that the reaction occurred in the interlayer between the phases, not in the water bulk. Consequently, the majority of the aqueous catalyst phase was not used in the catalytic process. The observed acceleration of the hydroformylation can be explained by an increase in catalyst concentration at the interface [99]. Enlargement of the interfacial area can be achieved in the special Jet-Loop Reactor (JLR) in which a liquid reaction stream is introduced to the top of the reactor via an external loop. Due to this, classical stirrers or other rotating parts can be eliminated [103].

Barcelli et al. studied the catalytic activity of $[RhH(CO)(TPPTS)_3]$ in the reaction of real naphtha cut and the selected olefins present in a real naphtha in toluene/water and naphtha/water medium [104]. Naphtha contains a mixture of C4–C7 olefins, with a volume of up to 50% of C5–C7. The hydroformylation of some olefins present in naphtha into aldehydes or alcohols can improve the combustion properties of the fuel and eliminate the need to add oxygenated additives to increase its octane rating. Kinetic studies performed for 1-hexene hydroformylation confirmed that the rate determining step is hydrogeneolysis of the rhodium acyl intermediate. In general, the reaction mechanism was found to be similar to that established for $[RhH(CO)(PPh_3)_3]$ in the homogeneous phase [105,106], however, the inhibiting effect of the higher CO pressure was not observed [104].

The Rh/TPPTS system was applied to the hydroformylation of long chain (from 1-hexene to 1-dodecene) and cyclic (cyclohexene, dicyclopentadiene) alkenes in methanol. During the reaction, one phase was formed and when the methanol was removed at the end, the system became two phases, facilitating efficient separation. The products were separated from the precipitated rhodium catalyst. The leaching of Rh in the organic phase was below ppm and stable catalytic efficiency was noted for five recycling experiments. The presence of $[RhH(CO)(TPPTS)_3]$ in the reaction mixture was confirmed by ^{31}P NMR [107].

Seidensticker et al. modified hydroformylation of methyl oleate with a Rh/TPPTS catalyst by the introduction of an alcohol co-solvent to the aqueous phase (Fig. 8) [108]. Interestingly, the results obtained with EtOH, BuOH and ^iPrOH were different and ^iPrOH was the superior one. The advantages of the ^iPrOH/water mixture consisted of high selectivity to aldehydes and clean separation of the product by decantation. The desired branched aldehyde, methyl 9/10 formyl stearate, was formed with a yield of 98% after 12 h, while 77% was already obtained after 2 h. The aqueous phase was recycled ten times with good catalyst stability and catalyst leaching up to 2% [108].

Vorholt et al. studied the effect of different stirring techniques on the rate of biphasic hydroformylation of 1-octene in a miniplant scale. The Rh/TPPTS catalyst was dissolved in the water phase and rhodium leaching to the organic phase was below 2 ppm. High TOFs (3245 h^{-1}) and STYs (space time yields) up to 65.5×10^{-2} $mol\,L^{-1}h^{-1}$ were obtained in a 3.6 L miniplant reactor without the use of any additives [109].

Rhodium catalysts with PPh_3 and TPPTS ligands, $[Rh(CO)(OH_2)(PPh_3)]OTf$ and $[Rh(CO)(OH_2)(TPPTS)_2]OTf$, were anchored on mesoporous silica (MCM-41 and SBA-15) due to the non-covalent interactions and used for the hydroformylation of 1-octene. It was found that the presence of rhodium complexes did not influence the hexagonal ordered structure of the silica supports. Hydroformylation performed in toluene with an 8-fold excess of a phosphorus ligand produced 80–90% of nonanal. These results were similar to those obtained in a homogeneous system with PPh_3, however, the advantageously immobilized catalysts showed

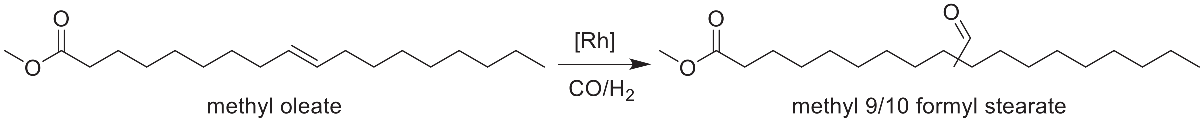


Fig. 8. Hydroformylation of methyl oleate.

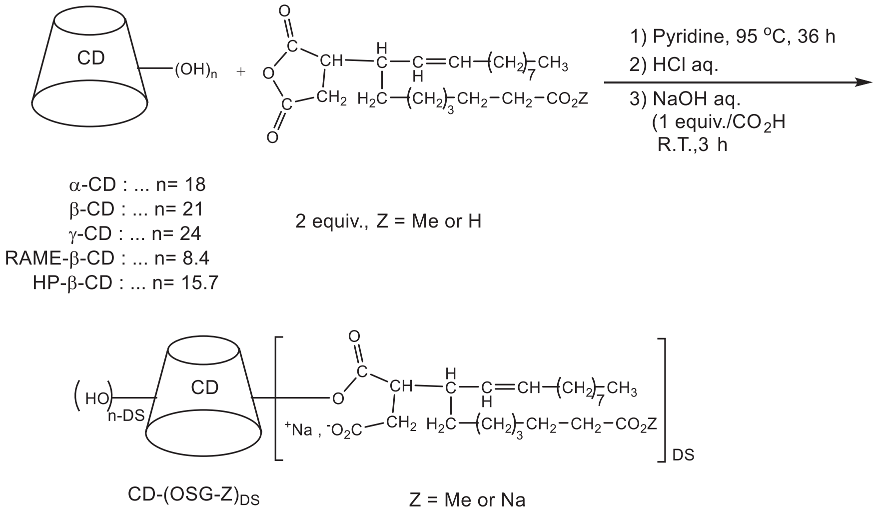


Fig. 9. Functionalization of cyclodextrines [111].

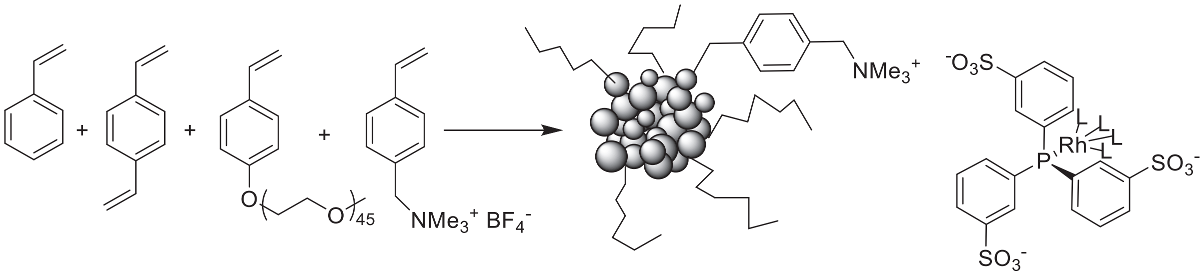


Fig. 10. Synthesis of the polymer particles and interaction with the anionic catalyst [112].

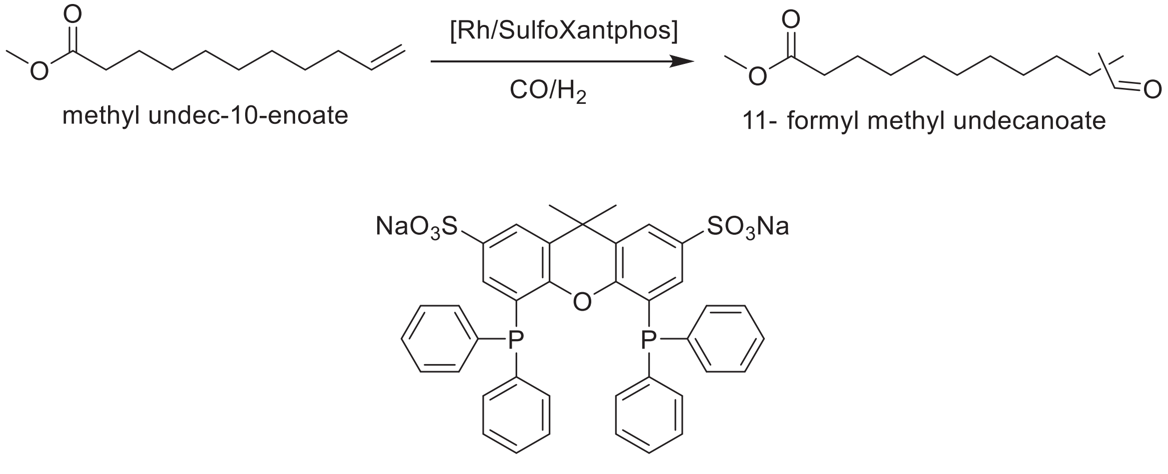
good conversion and selectivity in five subsequent runs. However, a significant decrease of catalytic activity was noted in the 6th and 7th runs for all catalysts [110].

Monflier et al. reported synthesis of amphiphilic oleic-succinyl cyclodextrines (OS-CDs) from oleic acid derivatives and maleic anhydride (Fig. 9) [111].

These OS-CDs were used in the hydroformylation of 1-decene and 1-hexadecene with the catalyst formed from [Rh(acac)(CO)$_2$] and TPPTS in water. In the reaction carried out without CDs, conversion of 1-decene and 1-hexadecene was 3% and 1% only. RAME-β-CD (randomly methylated β-CD) provided low conversion, up to 18%, with high selectivity to aldehydes (90%). The OS-CDs strongly influenced the productivity of the catalysts and revealed conversion of 1-hexadecene up to 94% and 1-decene of even 100%, however, at lower selectivity to aldehydes [111]. The promoting effect of OS-CDs can be explained by improvement of the mass transfer in the catalytic system.

Vogt et al. elaborated an original strategy of using functionalized colloidal polymers for two purposes, namely immobilization of the water-soluble hydroformylation catalyst and phase transfer action in a multiphasic system. A series of polymer particles was obtained by a radical emulsion polymerization in water (Fig. 10). The rhodium catalyst, formed from [Rh(acac)(CO)$_2$] and TPPTS, was effectively attached to the polymer, which was confirmed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) measurement. An electrostatic interaction between the rhodium complex and the polymer was proposed. Hydroformylation of 1-octene performed at 100 bar of H_2/CO in water with a Rh/TPPTS catalyst and a colloidal polymer as a phase transfer agent produced aldehydes with a high conversion (74.6–85.1% depending on the polymer sample) and an n/iso ratio equal to 2.5–2.6. The catalytic system showed good stability in recycling experiments, and rhodium leaching into the product phase was below 0.5 ppm [112].

Hydroformylation of methyl oleate to 9/10 formyl stearate was studied using a Rh/TPPTS system. Two experimental techniques, based on the application of a Jet-Loop Reactor (JLR) and a stirred bath autoclave (SBR), were tested for an improvement in the catalyst efficiency. The JLR gave better results due to the more efficient mixing of the gas–liquid–liquid mixture. In this case, a large liquid–liquid interface was created, facilitating coordination of the substrates to the active rhodium center. As a result, aldehydes were formed even at a low substrate loading of 30%. Under the same conditions, no reaction occurred in the SBR. Good results



SulfoXantphos

15

Fig. 11. Hydroformylation of methyl undec-10-enoate with Rh/SulfoXantphos catalyst [113].

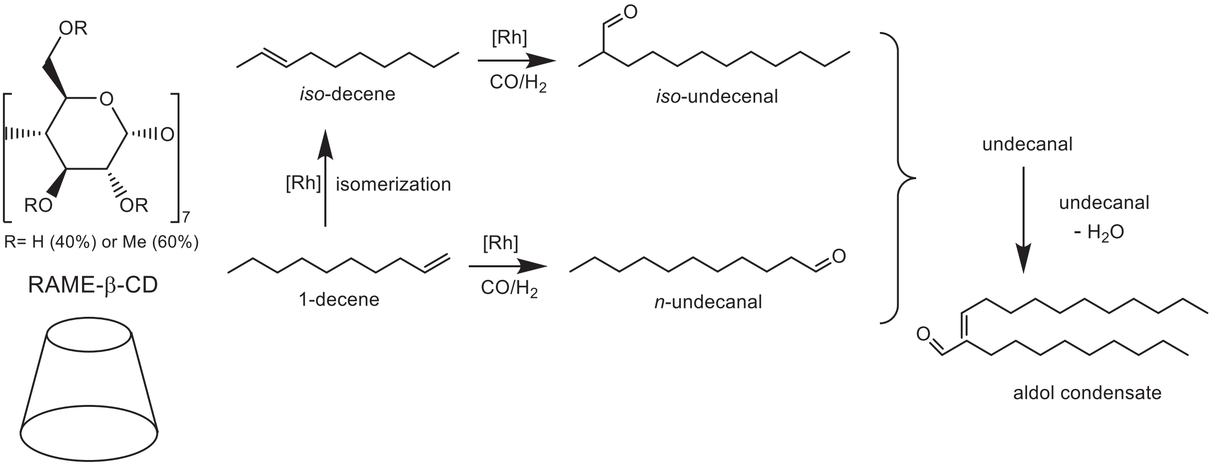


Fig. 12. Hydroformylation of 1-decene using randomly methylated β-CD (RAME- β-CD) [114].

were also obtained by applying JLR for the hydroformylation of methyl-10-undecanoate with a Rh/Sulfoxantphos catalyst (Fig. 11) [113].

Vogt et al. reported the first time application of randomly methylated β-CD (RAME-β-CD) as the mass transfer agent in the continuous hydroformylation of 1-decene in water with Rh/TPPTS and Rh/Sulfoxantphos catalysts (Fig. 12) [114]. First, both systems were scaled up to 1000 mL in a high-pressure autoclave. The influence of the stirrer speed and stirrer type on the reaction productivity was noted. In a continuous miniplant process, the rhodium leaching was very low (rhodium loss was 0.0027% h^{-1}).

The studied system demonstrated the highest chemo- and regioselectivities and the lowest rhodium leaching when compared with other commercialized processes, however the TOF values were lower. The authors concluded that an aqueous/organic biphasic hydroformylation with β-CDs is a very promising option for higher olefins [114].

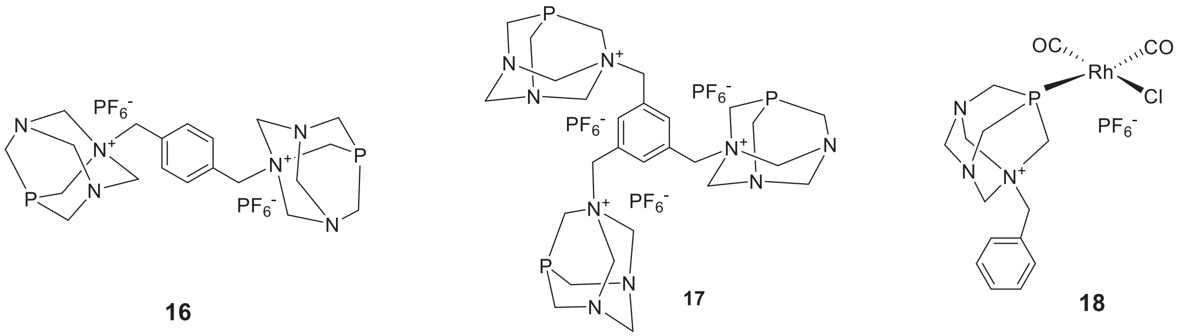
Yuan et al. found a beneficial influence of amphiphilic phosphine $n\text{-}C_{16}H_{33}P(m\text{-}C_6H_4SO_3Na)_2$ (CDPPDS) on the rate and selectivity of hydroformylation catalyzed by a rhodium catalyst with TPPTS or TPPDS ligands [115]. The phosphine CDPPDS played the double role of ligand and surfactant, and facilitated mass transfer in the aqueous hydroformylation of higher olefins, such as 1-hexene and 1-dodecene.

The hydroformylation of acyclic terpenes catalyzed by Rh/TPPTS was studied in an aqueous/toluene biphasic system in the presence of cationic surfactant, cetyltrimethylammonium chloride, [CTACB]Cl. The catalyst was immobilized in the water phase and fully separated from the products after the reaction. Several fragrance compounds were formed in high yields from bio-substrates according to this procedure [116].

A thermoregulated ionic liquid biphasic system for 1-dodecene hydroformylation with an Rh/TPPTS catalyst was elaborated. It contained quaternary ammonium alkanesulfonate salt with a polyether chain bonded to the alkyl group. Efficient separation of the ionic liquid phase containing the catalyst was performed at room temperature. High activity of this system was achieved in several reuses [117].

2.3. Water-soluble ligands for biphasic systems

In this chapter there are presented water-soluble ligands, different from TPPTS, used in biphasic systems. It is well accepted in the literature that ligands play a fundamental role in the hydroformy-



16 **17** **18**

Fig. 13. The water-soluble PTA-derivatives [118].

lation reaction. By the steric and electronic influence ligands create an environment around the rhodium center suitable for activation and transformation of different olefins [3]. There are also phosphorus ligands which play an additional role as phase-transfer agents.

Smith et al. reported synthesis of alkylated PTA (1,3,5-triaza-7-phosphaadamantane) water-soluble ligands enabling an increase in the number of metal centers in the hydroformylation catalyst (Fig. 13) [118]. Using these ligands, mononuclear, dinuclear and trinuclear rhodium complexes were obtained as the hydroformylation catalysts of 1-octene. It was found that catalytic results depended on the kind of additional ligand present in the coordination sphere of the rhodium, and better results were obtained for 1,5-cyclooctadiene (cod) than for the CO analog. For example, complex **18** showed lower conversion than its analog with cod coordinated instead of two CO ligands. Moreover, the trinuclear rhodium complex displayed a higher reaction rate than the mononuclear one. The regioselectivity of hydroformylation was moderate, with n/iso in the range of 0.7–3.8 and the highest value was obtained for complex **18** [118,119].

The PTA based ligands provided very high chemoselectivity in 1-decene hydroformylation in the presence of RAME-β-CD. It was evidenced that these phosphines do not interact with RAME-β-CD [120].

The water-soluble pirydyl-triazolyl N,N-bidentate ligand was used with the $[RhCl(cod)]_2$ precursor in the hydroformylation of styrene and 1-hexene in aqueous/toluene solution (Fig. 14). Styrene was hydroformylated mainly to the branched aldehyde (2-phenylpropanal), favoured by electronic reasons [3,10]. A decrease in catalytic activity was observed in subsequent reuses of the aqueous phase and it was explained by the formation of Rh NPs, confirmed by TEM. In agreement with this observation, a mercury poisoning test was positive and the reaction was strongly inhibited in the presence of Hg. It should be underlined that in longer reactions (18 h) these Rh NPs undergo dissolution when forming the active catalyst. Therefore, recycling was quite efficient when each reaction was prolonged for 18 h [121].

A new cage-like triazaphosphane ligand CAP (1,4,7-triaaza-9-phosphatricyclo[5.3.2.14,9]tridecane), soluble in water and stable in air, was obtained and used with $[Rh(acac)(CO)_2]$ in the hydroformylation of styrene, 1-hexene and longer olefins in toluene/water or water solutions (Fig. 15). It is worth noting that CAP is a strong electron-donor, comparable to PCy_3 (tricyclohexyl phosphine). The authors claimed that these donor properties are responsible for the higher activity and selectivity of the Rh/CAP system when compared to the Rh/PTA under the same conditions. Moreover, the Rh/CAP presented high chemoselectivity to aldehydes and good stability during reuse [122].

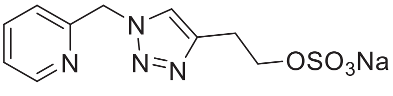


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Fig. 14. The water-soluble pirydyl-triazolyl ligand [121].

PTA

20

CAP

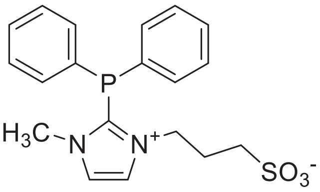
21

Fig. 15. The water-soluble PTA and CAP ligands [122].

Amphiphilic phosphines (**22** and **23**) of strong π-acceptor character, containing $-SO_3^-$ groups, were obtained and employed for styrene hydroformylation (Fig. 16). Both ligands contained an imidazolium core, however, their properties were different. In **23**, the aminogroup of piperidyl is incorporated, making this ligand potentially hemilabile. **22** is very soluble in water, while **23** is nearly insoluble. A strong promoting effect of water was observed for the $[R\ h(acac)(CO)_2]$/**23** system illustrated by the increase in TOF from 195 to 470 h^{-1} and conversion from 39% to 94% [123].

Bayon et al. synthesized the new strong π-acceptor, water-soluble ligands (Danphos) by direct sulfonation of trifluoromethylated phosphines (Fig. 17). They are more resistant toward oxidation than phosphines without CF_3 substituents, such as TPPTS, and are also weaker σ-donors. Moreover, the position of the CF_3 group in the phenyl ring influenced the σ-donor properties and the *ortho*-substituted isomer is less σ-donating than the *para*-substituted one. In the catalytic tests performed with vinyl acetate and allyl cyanide, the Rh/Danphos catalysts showed remarkably higher efficiency and provided a higher reaction rate than the Rh/TPPTS system. Thus, a positive effect of CF_3 substitution was evidenced [124].

Rhodium complexes with sulfonated α-diimine ligands bearing a 1,4-diazabutadiene skeleton were used by Smith et al. in the hydroformylation of 1-octene in water (Fig. 18). For comparison, non-sulfonated analogs were studied in toluene for the same reaction. The highest yield of product and the highest TOF values were obtained in the reaction performed in water. The water-soluble rhodium catalysts were reused up to four times, although some decrease in catalytic activity was noted after the third cycle. The



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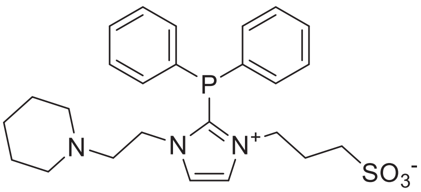

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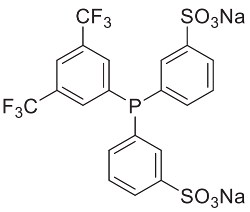
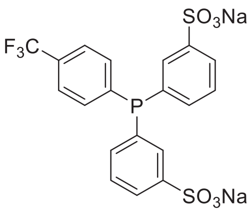
Fig. 16. The hydrophilic zwitterionic phosphines [123].



Danphos
24



p-Danphos
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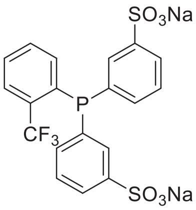
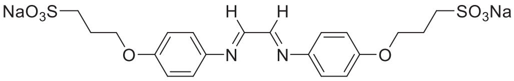


o-Danphos
26

Fig. 17. The sulfonated trifluoromethylated phosphines [124].



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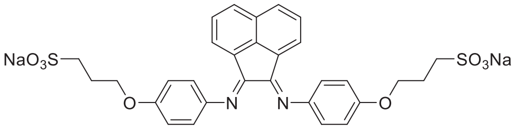

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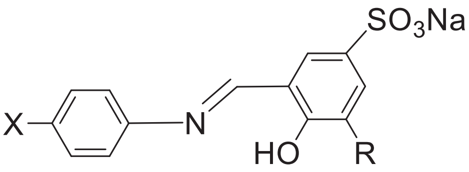
Fig. 18. The sulfonated α-diimine ligands [125].



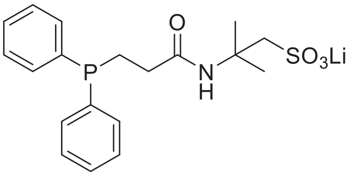
R = H, X = H **29**

R = H, X = CH_3 **30**

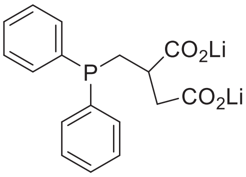
R = H, X = Cl **31**

R = H, X = ^{t}Bu **32**

Fig. 19. Sulfonated salicyldimine ligands [126].



PNS
33



PC
34

Fig. 20. Structures of PNS and PC phosphines [127–129].

reason for the loss of activity was not clear, however, eventual formation of Rh NPs was excluded on the basis of mercury test [125].

Smith et al. applied the water-soluble rhodium complexes with sulfonated salicylaldimines (Fig. 19) in the hydroformylation of 1-octene. Advantageously, aldehydes were formed in very high yields in the absence of any phase transfer agents, co-solvents or hydrophobic ligand [126].

Mieczynska et al. reported the hydroformylation of unsaturated alcohols, such as 1-buten-3-ol, 2-methyl-2-propen-1-ol and 2-buten-1-ol, in water catalyzed by [Rh(acac)(CO)$_2$] modified with water-soluble phosphine PNS (PNS = $Ph_2PCH_2CH_2CONHC(CH_3)_2$-$CH_2SO_3Li$) (Fig. 20). This catalytic system exhibited high catalytic activity and regioselectivity to the desired aldehyde. Due to hydroxyaldehyde cyclization, the main products were 2-hydroxytetrahydrofuran derivatives obtained with a high yield of up to 95, 92 and 77% respectively [127]. The same system used for the hydroformylation of 1-hexene provided 14% of aldehydes in toluene-water solution, whereas in ethanol–water the yield increased to 93% [128]. Hydroformylation of methylacrylate with a Rh/**33** catalyst in a toluene-water mixture produced up to 77% of aldehydes at an α/β ratio equal to 2.7. A decrease in temperature to 50°C enabled an increase of the α/ β ratio to **22**, however, it gave a lower yield of aldehydes (60%). In the hydroformylation of methylacrylate performed at 50°C better results were obtained with Rh/**34** catalyst. This system formed ca. 80% of aldehydes with α/β ratio ca. 20 [129].

The water-soluble diphosphine Sulfoxantphos, **15** (Fig. 11), possessing a large bite angle, was successfully employed with [Rh(acac)(CO)$_2$] in the hydroformylation of different olefins such as propene, 1-hexene and 4-styrenesulfonate in water. The high selectivity to n-aldehydes was related to the bis-equatorial coordination of diphosphine to rhodium [130].

An activity enhancement of the Rh/**15** system was achieved when randomly methylated α- or β-CDs were added. The steric effect of both, diphosphine and CD cavity, resulted in a significant increase of the selectivity towards linear aldehyde [39].

A non-ionic surfactant was also used by Schomäcker for the same reaction to improve the solubilization of 1-dodecene in the aqueous phase. In these conditions TOF values ca. 300 h^{-1} were reached [131].

Amphiphilic diphosphines based on a xanthene-type backbone (Fig. 21) were used in rhodium-catalyzed hydroformylation in water. The formation of stable aggregates by the ligands and their complexes increased solubility of 1-octene and led to a higher reaction rate [132].

The biphasic hydroformylation of 1-octene and 1-dodecene catalyzed by [Rh(acac)(CO)$_2$] and **15** was studied in the presence of polymer lattices and non-ionic surfactants as phase transfer agents [133]. By applying a polymer latex, normal micelles were created in the water phase. The system remained biphasic and 1-octene was transferred to the interface and reacted with the water-soluble catalyst. In the second system, non-ionic surfactants transferred the rhodium catalyst to the substrate under reaction conditions (Fig. 22). The TOF values calculated at a conversion of 20% ranged from 65 h^{-1} to 25 h^{-1} during recycling runs in the system containing the polymer and from 266 h^{-1} to 152 h^{-1} in recycling with the surfactant. It was also observed that surfactants are better phase transfer agents in biphasic hydroformylation at higher temperatures due to their better thermal stability [133].

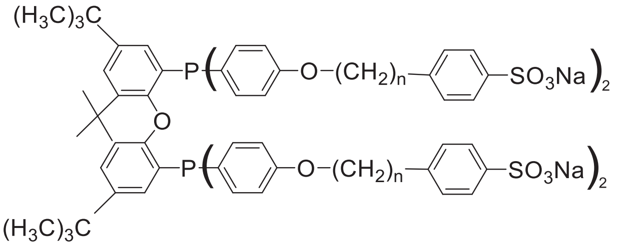


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Fig. 21. Diphosphines based on a xanthene-type backbone [132].

Shimizu et al. described the synthesis of water-soluble calix[4]arene ligands with phosphane groups (Fig. 23) and their application together with [Rh(acac)(CO)$_2$] in 1-octene and 1-decene hydroformylation. It was expected that these compounds would function not only as ligands coordinated to rhodium but also as phase-transfer agents. In fact, the obtained olefin conversions were higher than with TPPTS and a yield of aldehydes up to 86% was achieved in the recycling experiment [134].

The effect of methoxy substituents was studied by using TPPTS derivatives in the aqueous hydroformylation of 1-dodecene in the presence of CTAB. The catalytic activity and selectivity for aldehydes were found lower than with TPPTS because of the strong electron-donating properties of the methoxy group [135].

The application of water-soluble P(CH$_2$OH)$_3$ ligand in the hydroformylation of 1-pentene in the biphasic water/benzene system was reported by Fukuoka et al. [136].

Hydroformylation of an oleyl alcohol in an aqueous/organic two-phase system was performed by using water-soluble polyether substituted triaryl phosphine oxides. Under the applied conditions, at 120 °C and 5 MPa pressure, substituted phosphine oxides provided significantly better results than TPPTS. For example, by using $Ph_2P(O)[p\text{-}C_6H_4(OC_2H_4)_{25}OH]$, 76.4% of formyl stearyl alcohol was formed [137].

Poly(4-pentenoic acid), PPA, was used to form a water-soluble complex Rh/PPA(Na$^+$)/DPPEA where DPPEA is bis[2-diphenylphosphino)ethyl]amine. This polymeric catalyst was active in the regioselective hydroformylation of aliphatic olefins, vinyl ethers and vinylarenes [138].

Xi et al. reported the synthesis of four water-soluble dendritic phosphonated ligands with hydrophobic amine or sulfonic acid groups on the surface of the dendrimer. These ligands were next used to form rhodium catalysts for the two-phase hydroformylation of styrene and 1-octene [139].

A supported aqueous phase catalyst (SAPC) was used by Nikov et al. for linalool hydroformylation. The kinetic parameters for this reaction were determined and the activation energy was equal to 14.5 kcal mol^{-1} [140]. The same catalyst was also used for 1-octene hydroformylation and here the activation energy was determined as 71 kJ mol^{-1} [141].

The successful immobilization of the Rh/NHC catalyst on a water-soluble amphiphilic block copolymer was presented by Weberkich et al. They tested the obtained catalyst in 1-octene hydroformylation and received very good results in four subsequent runs (Fig. 24) [142].

The block copolymer-supported catalyst, used in 1-octene hydroformylation under micellar conditions, resulted in an increase in the selectivity of n/iso when compared with a monomeric analogue [$CH_3CON(Py)_2RhCl(COD)$] [143].

Aqueous biphasic hydroformylation of 1-octene was performed using phosphine-functionalized core-cross-linked micelles (CCM) containing a hydrophilic shell and amphiphilic block copolymer micelles (M) as rhodium nanoreactors. The CCM system was slightly less active than the M latex but the Rh leaching was lower [144].

The application of core–shell nanoreactors in biphasic hydroformylation was explored by Poli and coworkers [145-147]. In their approach, unimolecular nanostructures were constructed to form an environment for the catalyst active in water. Thus, triphenylphosphine (TPP) – functionalized cross-linked micelles

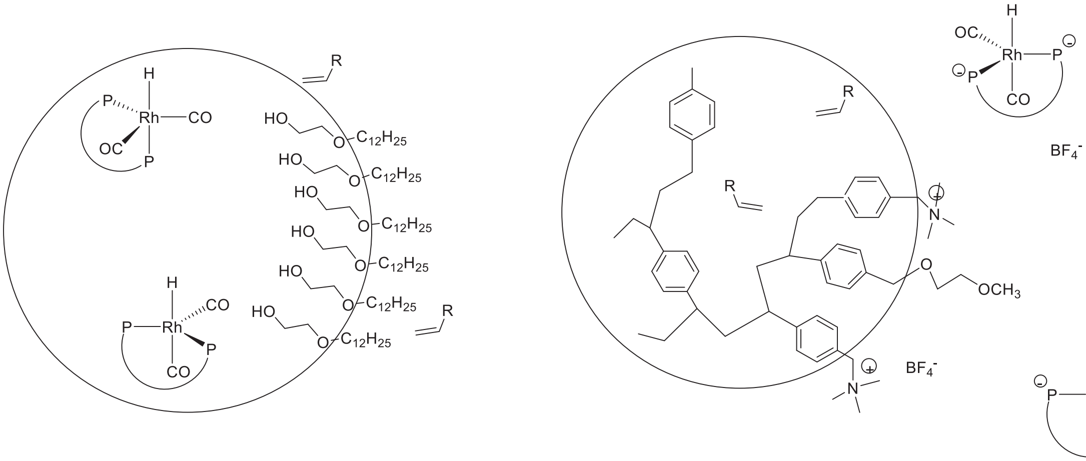

Fig. 22. Inverse micelle with the water-soluble Rh-catalyst and normal micelle with alkene [133].

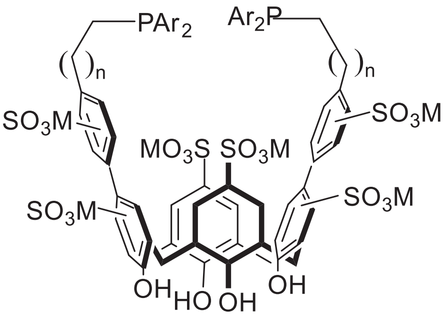

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Fig. 23. Water-soluble phosphacalix[4]arene [134].

(TPP@CCM) were obtained by one-pot emulsion polymerization (Fig. 25) [145]. The rhodium complex, [Rh(acac)(CO)$_2$] was bonded to the hydrophilic flexible arm of the polymer. The obtained results of 1-octene hydroformylation confirmed an efficient transport of substrates into the hydrophobic core. However, at a higher concentration of rhodium, mass transfer limitations were observed due to rhodium-polymer interactions [145].

In the modified version, the nanoreactor was functionalized with bis(4-methoxyphenyl)phenylphosphine (BMOPPP). This system exhibited similar activity to the TPP@CCM in the biphasic hydroformylation of 1-octene [146].

In order to reduce interactions of rhodium with two phosphine ligands from different particles, a nanogel nanoreactor was elaborated. In this procedure, a significant decrease of rhodium leaching was achieved. However, TOF values were in the range 350–650 h^{-1}, slightly lower than by using the TPP@CCM system in which TOF was up to 700 h^{-1} [147].

2.4. “On water” hydroformylation (with a phosphine ligand insoluble in water)

The “on water” approach, related to hydrophobic effect, was first defined for organic reactions. In organic chemistry, the term “on water” was assigned by Sharpless to the reaction in which insoluble reactants are stirred in aqueous emulsions or suspensions [78]. On the other hand, several terms such as “in water” “in the presence of water” or “on water” are used in the literature for similar systems. In this review the term “on water” is used in reference to the catalytic systems containing hydrophobic, water-insoluble, phosphine.

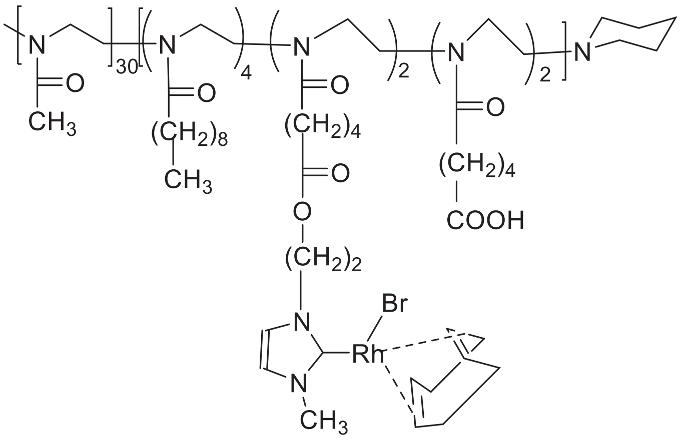

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Fig. 24. Rhodium complex with water-soluble macroligand [142].

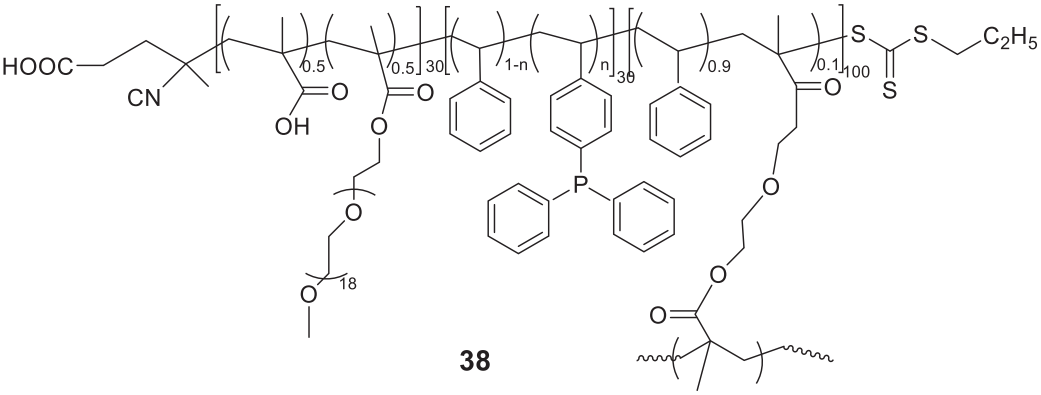

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Fig. 25. Cross-linked TPP@CCM micelle [145–147].

A rhodium catalyst, Rh/PAA, obtained by the immobilization of $[Rh(acac)(CO)_2]$ on water-soluble polyacrylic acid (PPA), was used for the hydroformylation of 1-hexene in water [148]. However, only 8% conversion was achieved and 2-hexene was formed as the main product. The conversion increased to 62% after the addition of a 5-fold excess of hydrophobic PPh_3 and to 90% when a 13-fold excess of PPh_3 was applied. The yield of aldehydes in these reactions was 57% and 86%, respectively. A strong effect of the solvent was also noted for the Rh/PAA/PPh_3 system. In toluene, the conversion of 1-hexene was only 3% and it increased to 96% when water was added. Similar good results were also obtained in pure water, where only the Rh/PAA catalyst was soluble. In these conditions, efficient recycling of Rh/PAA was performed for three runs. However, due to the decrease in activity, a longer reaction time was required to get a high conversion, namely 70, 120, and 180 min in the three subsequent runs. Interestingly, in the toluene-methanol mixture the conversion was lower (77%), although 1-hexene, Rh/PAA and PPh_3 are soluble in methanol [148]. Leaching of rhodium to the organic phase during hydroformylation of 1-hexene with Rh/PAA/PPh_3 was evidenced by the ^{31}P NMR spectrum of the reaction solution which exhibited the presence of a doublet at 32.2 ppm characteristic for $[RhH(CO)_2(PPh_3)_2]$ species [148].

Hydroformylation of 1,7-octadiene and 1,5-hexadiene (Fig. 26) performed in “on water” conditions using the same catalytic system, Rh/PAA/PPh_3, occurred with 100% conversion and high selectivity toward dialdehydes. the effect of water was observed in the increase of the 1/(2 + 3) ratio to 3.28 for 1,7-octadiene and to 4.1 for 1,5-hexadiene while the maximum value of this parameter obtained with $[Rh(acac)(CO)_2]/PPh_3$ was 2.7 [148]. It can be assumed that aggregation of hydrophobic phosphines (PPh_3) around the catalytically active rhodium species limits formation of the branched alkyl intermediate, directing the reaction toward the linear product. Interestingly, this effect was stronger for the water-soluble Rh/PPA than for the insoluble $[Rh(acac)(CO)_2]$ precursor.

The Rh/PAA/PPh_3 also presented very good activity in the “on water” hydroformylation of phenylacetylene, styrene and 1-hexyne, providing results similar to those with fully hydrophobic $[Rh(acac)(CO)_2]/PPh_3$ [148].

The catalytic system composed of $[Rh(acac)(CO)_2]$ and PPh_3, used in the Union Carbide technology for propene hydroformylation, was also found to be very efficient in a water medium. In such conditions, the reaction meets the criteria of the “on water” system, in particular when the solubility of the substrate in water is very low. Interestingly, the addition of water to the catalytic system for propene hydroformylation resulted in a significant increase of TOF when compared to the reaction in toluene.

High TOF values, up to 1658 h^{-1}, were achieved using this system in 1-hexene hydroformylation at 10 bar H_2/CO. At a lower pressure, 4–6 bar, the reaction was slower, however, very high selectivity was noted with n/iso 21–25.2. An even higher TOF value, 1903 h^{-1}, was obtained when applying $[RhH(CO)(PPh_3)_3]$ in water. Notably, the $[RhH(CO)(PPh_3)_3]$ complex, considered a precursor of the catalytically active form ($[RhH(CO)_2(PPh_3)_2]$) in catalytic systems with PPh_3 [3], can be easily obtained in water in the reaction of $[Rh(acac)(CO)_2]$ with PPh_3 under 1 bar H_2. The stability of the Rh-H species in water can be important for very good catalytic results obtained with the $[Rh(acac)(CO)_2]/PPh_3$ catalyst in this medium [149].

Water had an improving influence on the hydroformylation of phenylacetylene with the $[Rh(acac)(CO)_2]/PPh_3$ system. In solvent-free conditions, the conversion was 28% with 11% selectivity to saturated aldehydes (3-phenylpropanal and 2-phenylpropanal) and an n/iso ratio of 0.6. In contrast, in the “on water” reaction, 34% of saturated aldehydes were formed, with an n/iso ratio of 1.6 (Fig. 27) [149]. An increase in the temperature and pressure resulted in a further conversion increase.

Good regioselectivity toward the linear aldehyde was obtained in the hydroformylation of 1-hexyne using $[Rh(acac)(CO)_2]$ and PPh_3. In the “on water reaction”, the n/iso ratio was equal to 3.6, while in the solventless reaction it was 2.4 [149].

The hydroformylation of unsaturated alcohols was investigated by applying the $[Rh(acac)(CO)_2]/PPh_3$ catalytic system in a water medium [149]. In the case of shorter alcohols (1-propen-3-ol, 3-buten-1-ol, and 1-buten-3-ol), cyclic products were formed, similarly as in organic solutions [150,151]. For example, tetrahydrofuran-2-ol was obtained from the cyclization of 4-hydroxybutanal in the hydroformylation of 1-propen-3-ol (Fig. 28).

In contrast, the hydroformylation of 5-hexen-1-ol and undecen-1-ol with longer carbon chain, led to hydroxyaldehydes as the final products, without cyclization [149]. In most cases, hydroformylation of alcohols performed in water provided a mixture of linear and branched aldehydes at a satisfactory conversion of substrates. These reactions were efficient, independently of the solubility of the alcohols in water. However, the effect of water on the selectivity enhancement was stronger for hydrophobic 2-allylphenol than for water-soluble 1-propen-3-ol [149].

Catalytic systems formed by $[Rh(acac)(CO)_2]$ and π-acceptor *N*-pyrrolylphosphines ($P(NC_4H_4)_3$, $PPh(NC_4H_4)_2$, $PPh_2(NC_4H_4)$) were successfully applied to the hydroformylation of propene and 1-butene in the presence of water [152]. These systems were biphasic, with an organic phase containing toluene and aldehydes and a water phase. In the hydroformylation of propene, the addition of water to the reaction mixture caused an increase in the yield and selectivity to n-butanal. An increase of the n/iso ratio correlated

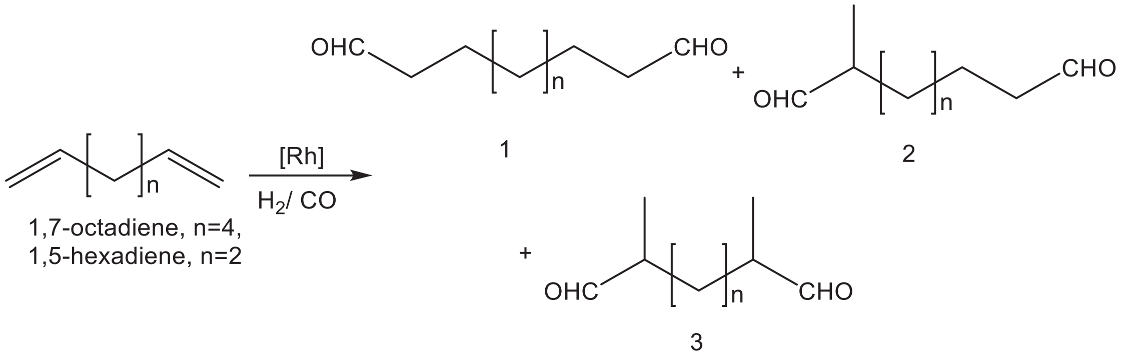

Fig. 26. Hydroformylation of 1,5-hexadiene and 1,7 octadiene.

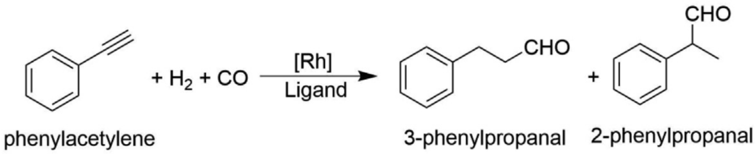

Fig. 27. Hydroformylation of phenylacetylene.

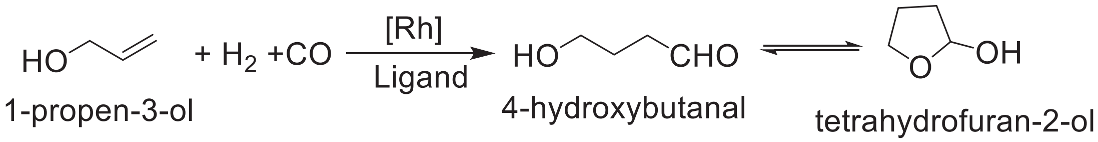

Fig. 28. Hydroformylation of 1-propen-3-ol.

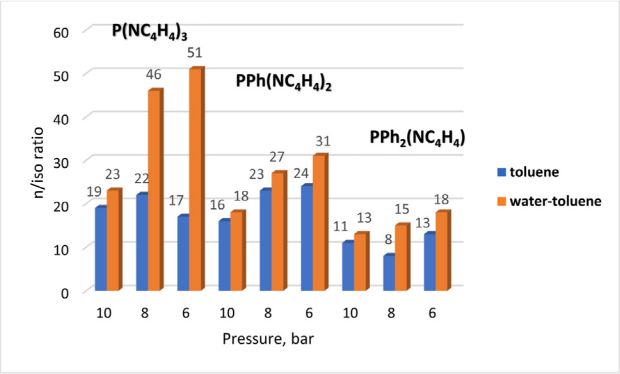

Fig 29. The effect of pressure and water on 1-butene hydroformylation catalyzed by $[Rh(acac)(CO)_2]$ with different pyrrolylphosphines [153].

well with the π-acceptor properties of the P-ligand and the highest n/iso, 27.1, was noted for the most π-acceptor phosphine, $P(NC_4H_4)_3$ in a 1/1 toluene/water mixture. It was proposed that water stabilized the Rh-H intermediate, facilitating formation of the linear aldehyde. A similar, positive effect of water on the formation of the linear aldehyde was observed in the hydroformylation of butene in the same catalytic systems with *N*-pyrrolylphosphines [153]. In all cases, the n/iso ratio was higher in the toluene-water mixture than in toluene only (Fig. 29). A further increase in the regioselectivity toward the linear aldehyde was achieved in this system by decreasing the total pressure of the H_2/CO to 6 or 8 bar. An increase in the selectivity in the presence of water was observed for three *N*-pyrrolylphosphine ligands, but for $P(NC_4H_4)_3$ it was the most spectacular, up to an n/iso ratio of 50.9, achieved at 6 bar [153].

The improving effect of water in catalytic systems with *N*-pyrrolylphosphines is quite promising, considering both parameters of reaction rate and selectivity. It should be noted, however, that van Leeuwen applied a $P(NC_4H_4)_3$ ligand with very good results in the hydroformylation of ethene, but he also mentioned its low stability in the reaction conditions [154].

Panda et al. presented the hydroformylation of allylic alcohols in water catalyzed by $[RhH(CO)(PPh_3)_3]$ with additional PPh_3 dissolved in a film of ionic liquid $[(Bmim)PF_6]$ supported on silica (Rh/PPh_3/SILPC) (SILP = Supported Ionic Liquid-Phase Catalyst). This system showed high catalytic activity and regioselectivity to linear aldehydes [155].

The effect of water on the hydroformylation of 1- hexene catalyzed by rhodium(I) complexes with a hydrophilic bidentate

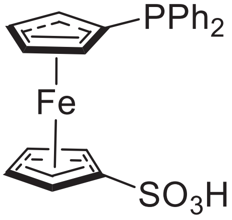

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Fig. 30. Structure of phosphinoferrocene sulfonate ligand (1′-(diphenylphosphino)-ferrocene-1-sulfonic acid) [156].

phosphinoferrocene sulfonate ligand, $[Rh(CO)(PR_3)(Ph_2PfcSO_3\text{-}\kappa^2O,P)]$ (1a – d; R = Ph (a), cyclohexyl (b), 2-furyl (c), and OMe (d); fc = ferrocene-1,1′-diyl), $[Rh(nbd)(Ph_2PfcSO_3\text{-}\kappa^2O,P)]$ ((2); nbd = $\eta^2{:}\eta^2$-norbornadiene), trans-$(Et_3NH)_2[RhCl(CO)(Ph_2PfcSO_3\text{-}\kappa P)_2]$ (3) and (Et_3NH)- $[Rh(CO)(Ph_2PfcSO_3\text{-}\kappa^2O,P)(Ph_2PfcSO_3\text{-}\kappa P)]$ (4), (Fig. 30) has been investigated [156].

It is worth noting that catalyst **1a** formed mainly 2-hexene (71%) in toluene, while in water 81% of aldehydes were formed. Good results were also obtained by using **1c** (56% of aldehydes) whereas the other catalysts produced worse results probably due to their low solubility in water [156].

A superhydrophobic porous framework, phosphite-POP, was prepared using vinyl-functionalized tris(2-tertbutylphenyl)phosphite and azobisbutylonitryle (AiBN) and then metallated with $[Rh(acac)(CO)_2]$ to form a catalyst for 1-octene hydroformylation [157]. When water was used as a solvent, the yield of aldehydes and selectivity to nonanal significantly increased. Thus, the n/iso ratio increased from 0.32 to 0.61. A similar effect was also observed for a homogeneous system with tris(2-tertbutylphenyl)phosphite, however, this ligand decomposed in water. In contrast, the phosphite moiety was protected against hydrolysis in the superhydrophobic framework. The authors assumed that the positive effect of water on the reaction course can be rationalized by the facilitated formation of rhodium hydride and enhancement of the hydride transfer step. Moreover, water increased stabilization of the trasnsition state leading to the linear Rh-alkyl intermediate and, as a result, the amount of linear aldehyde increased. The Rh/phosphite-POP system also produced very good results for the hydroformylation of cyclic olefins in water [157].

"On water" tandem hydroformylation-hydrogenation of 1-octene was optimized for $[Rh(acac)(CO)_2]$/Xantphos catalyst at 36 bar of CO/H_2 = 1/2. Under these conditions, in a 2-propanol/water or MeOH/water solution, 1-octene was converted to 1-nonanal in an excellent conversion and selectivity. The synthetic procedure may be also adapted with very good results for longer chain and internal olefins [158].

Poli et al. applied cross-linked star polymer containing Nixantphos ligand for creation of nanoreactors for selective hydroformylation of 1-octene to n-nonanal in aqueous solution. The obtained selectivity, n/iso 69, was similar to that in toluene. Unfortunately, the yield of aldehydes was realatively low and it decreased significantly during recycling [159].

3. Hydroformylation under solventless conditions

Solvent-free catalysis is strongly recommended by green chemistry principles as a procedure leading to the elimination of organic solvents which are often dangerous and harmful to the environment. The other benefits of solvent-free processes are cost savings, decreased energy consumption and easier separation and purification of products. Examples of solvent-free hydroformylation have also been reported in the review article of Walsh et al. in 2007 [160].

Koeken et al. reported hydroformylation in neat 1-octene catalyzed by $[Rh(acac)(CO)_2]$ with the excess of different fluorinated phosphines, (tris[3,5-bis(trifluoromethyl)phenyl]phosphine (**40**), bis[3,5-bis(trifluoromethyl)phenyl]phenylphosphine (**41**), tris(3-trifluoromethylphenyl) phosphine (**42**) (Fig. 31), or triphenylphosphine) at 4.9 MPa of H_2/CO at 70 °C [161].

All ligands exhibited almost the same conversion and selectivity toward aldehydes; however, the n/iso ratio was higher for fluorinated ligands (4.48–5.37) than for PPh_3 (3.38). Moreover, the hydroformylation reaction in neat 1-octene was faster than in a one-phase supercritical CO_2-rich system [161].

Clarke et al. studied the solvent-free hydroformylation of methyl acrylate catalyzed by $[Rh(acac)(CO)_2]$ with the addition of different ligands, such as 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane (^{Me}CgPPh) (**43**), tris(2-benzofuryl)phosphine (**44**), tris[3,5-bis(trifluoromethyl)phenyl]phosphine or a caged ligand [162] (Fig. 32).

The reaction was very slow, and selectivity toward aldehydes was low with a high yield of hydrogenation, polymerization, and aldol condensation products when using the ^{Me}CgPPh ligand. However, the linearity of aldehydes increased with the increase in the concentration of the rhodium catalyst. In contrast, the increased pressure and temperature and reduced concentration of the Rh catalyst ([substrate]/[Rh] = 10,000) resulted in an increase in the yield of aldehydes and regioselectivity toward the isoaldehyde. The same catalysts produced better results in organic solvents [162].

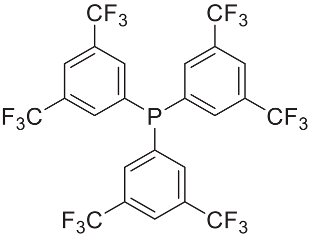
Fujita et al. investigated the hydroformylation of 1-hexene catalyzed by $[Rh(acac)(CO)_2]$ with PPh_3 (I) and different fluorinated phosphine ligands ((**45**)-(**50**)) (Fig. 33) at 40 bar of H_2/CO under solventless conditions [163].

It was found that the rhodium catalysts with ligands **45**, **46** and **49** were active under these conditions, and the conversion of 1-hexene was higher than with PPh_3. However, the n/iso ratio was almost the same for all the phosphine ligands [163].

Monnereau et al. reported that the [Rh(acac) (**51**)] complex used with an excess of free hemispherical 1,3-calix-diphosphite (Fig. 34) for the hydroformylation of olefins under solventless conditions exhibited a higher reaction rate compared with reactions performed in toluene [164].

Additionally, this catalytic system showed high regioselectivity toward the linear aldehyde in the hydroformylation of 1-octene, styrene, 1-hexene, and 2-vinylnaphthalene. For example, a high TOF of 17290 h^{-1} with 34.6% conversion of 1-octene and an n/iso ratio of 46.6 was obtained. Only allylbenzene was hydroformylated with lower selectivity (n/iso ca. 5) [164].

Gil et al. investigated neat 1-hexene hydroformylation catalyzed by rhodium(I) complexes of the type [Rh(NHC)(cod)X] (where NHC = N-heterocyclic carbene; cod = 1,5-cyclooctadiene; X = Cl, Br, I, SCN) with up to three-fold excess of $P(OPh)_3$ at



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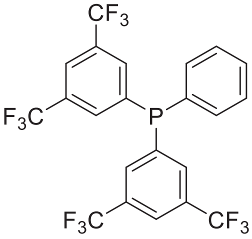

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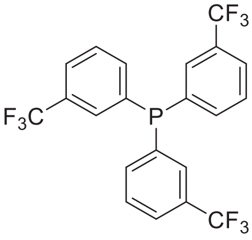

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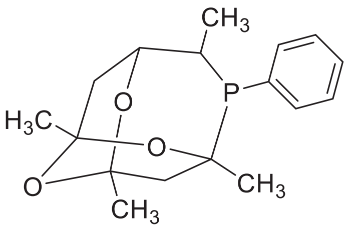
Fig. 31. Structures of trifluoromethyl substituted phosphines.



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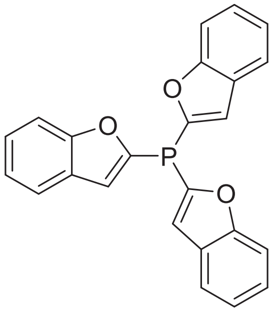

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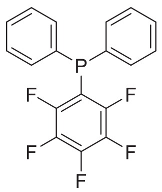
Fig. 32. Structures of phosphorus ligands used in hydroformylation of methyl acrylate [162].



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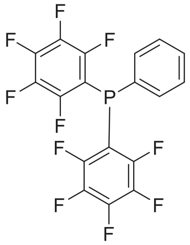

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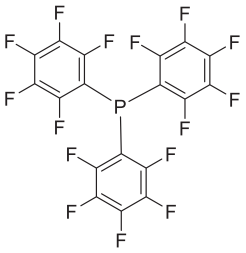

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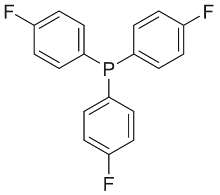

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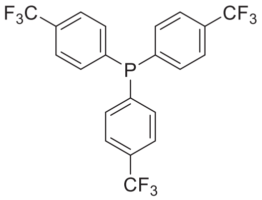

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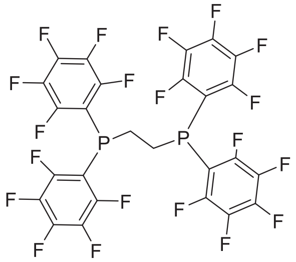

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Fig. 33. Structures of fluorinated phosphine ligands used in [163].

10 bar of $H_2/CO = 1$. High activity and selectivity toward aldehydes were obtained even at low concentrations of the rhodium catalyst ([1-hexene]/[Rh] = 2000), and 90% of the aldehydes were obtained with a high n/iso ratio of ca. 7 [165].

Gil et al. also reported immobilization of the rhodium (I) catalyst $[Rh(OMe)(cod)]_2$ on the polymer functionalized with methylimidazolium moieties. This catalyst was successfully applied for the hydroformylation of 1-hexene with additional $P(OPh)_3$ ($[P(OPh)_3]/[Rh] = 2$) under solventless conditions. It exhibited high activity and selectivity for eight runs with an n/iso ratio of 6. The n/iso ratio increased to 49.8 when the $P(OCH_2CF_3)_3$ ligand was used instead of $P(OPh)_3$ [166].

Cobley et al. investigated the asymmetric hydroformylation of allyl cyanide at a low concentration of the $[Rh(acac)(CO)_2]$ catalyst with two different chiral ligands ((R,S)-BINAPHOS **52** and (*S,S*)-Kelliphite) **53** (Fig. 35) without solvent [167].

The reaction was faster than in toluene and the rhodium complex with **53** was seven times more active than with (*R,S*)-BINAPHOS [167].

The catalytic system $[Rh(acac)(CO)_2]/PPh_3$, examined in the solventless hydroformylation of 1-hexene, 1-octene and 1-pentene, provided a complete conversion of substrates. Moreover, a high reaction rate and high selectivity to aldehydes were noted. The linear aldehyde was preferably formed at a lower pressure [168]. The catalyst was successfully recycled in the hydroformylation of 1-octene and 1-pentene under solventless conditions for five and four times. Good catalytic activity with a notable increase in the n/iso ratio from 4 to 7.3 over the five runs was found for

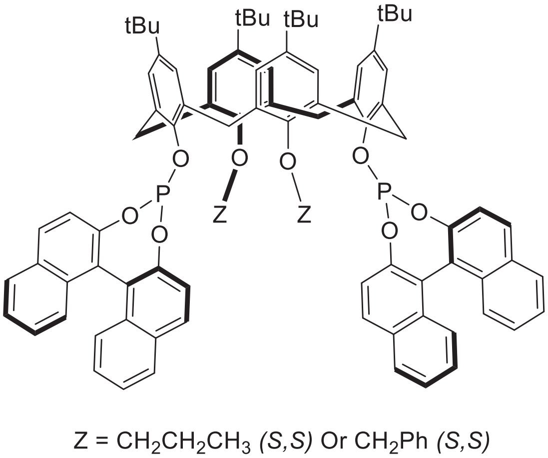

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Fig. 34. Structure of 1,3-calix-diphosphite ligands.

1-octene hydroformylation. Moreover, the catalytic results obtained using this catalyst under solventless conditions were better than these in toluene, owing to the high concentration of the reactants [168].

The hydroformylation of vinyl acetate under solventless conditions catalyzed with rhodium (I) complexes with the chelating ligand Ph_2PfcSO_3-κ^2O,P exhibited a high regioselectivity to isoaldehyde and the highest conversion was obtained by applying **1a** and **4** catalysts containing PPh_3 and Ph_2PfcSO_3-κP as monodentate ligands [156].

Hydroformylation of less reactive unsaturated substrates, namely allyl acetate, butyl acrylate, methyl acrylate, 2,3-dihydrofuran and vinyl acetate, was tested under solventless conditions with hydrido-carbonyl rhodium complexes of the type $[RhH(CO)L_3]$, containing different *N*-pyrrolylphosphines, such as $P(NC_4H_4)_3$, $PPh(NC_4H_4)_2$, or $PPh_2(NC_4H_4)$ (L) [169]. Even at room temperature, complete substrate conversion and high chemoselectivity toward the corresponding aldehydes were achieved in all cases. The strongest π–acceptor phosphine, $P(NC_4H_4)_3$, provided the best results, which were significantly better than those obtained for those substrates using other catalytic systems. The highest TOF values, 2376 h^{-1} and 2000 h^{-1}, were obtained for allyl acetate and vinyl acetate at 20 bar H_2/CO and 80°C [169].

The highly active $[RhH(CO)[P(NC_4H_4)_3]_3]$ complex was also employed for the asymmetric hydroformylation of vinyl acetate under solventless conditions. To this aim, chiral phosphines, BINAP **54** or Ph-BPE **55**, were added. Good results were obtained and the branched aldehyde was formed with enantioselectivity, *ee*, up to 44% and 81% and the Ph-BPE phosphine was found to be significantly more efficient in asymmetric hydroformylation than BINAP. High activity and high enantioselectivity were correlated with the formation of the mixed rhodium hydrides, $[HRh(CO)[P(NC_4H_4)_3]$ (**54**)] and $[HRh(CO)[P(NC_4H_4)_3]$(**55**)], identified by the NMR method (Fig. 36) [169].

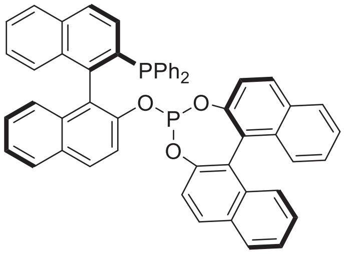
4. Rhodium-nanoparticle-catalyzed hydroformylation

Metal nanoparticles found already different application in technology and their potential as catalysts attracted researchers attention. The high specific surface area of nanoparticles facilitates an efficient contact of the active centers with substrate molecules. It can be therefore expected that the rhodium nanoparticles (Rh NPs) would promote the formation of the desired hydroformylation product with high efficiency in different solvent, including water. Catalytic properties of nanoparticles are strongly dependent on their shape and size, which can be modulated relatively easily by synthetic conditions and appropriate ligands. From the green chemistry point of view, an additional advantage of heterogeneously acting nanoparticles is effective separation from the reaction products. For this purpose, Rh NPs can be also immobilized on different carriers, for example on silica. In all these cases, separation can be carried out by decantation or filtration.

Smith patented the use of Rh NPs as the catalyst in hydroformylation in organic media in 1980. Rh NPs, 8–12 nm in diameter, were synthesized utilizing a styrene/butadiene copolymer as the stabilizing agent. The hydroformylation of 1-hexene, performed in xylene, at 100 °C and 42 bar of CO/H_2, resulted in 95% conversion to aldehydes and an n/iso ratio equal to 2 [170].

Tuchbreiter and Mecking prepared Rh NPs by the hydrogen reduction of $[Rh(acac)(C_2H_4)_2]$ employing poly(ethylene imine) amides with a hyperbranched polyamine core and a lipophilic periphery as the stabilizing agent in a toluene solution. The hydroformylation of 1-hexene with these Rh NPs carried out at 80 °C and 90 bar led to the complete conversion of 1-hexene with 96% aldehyde selectivity and an n/iso ratio of 1.4. Similar results were obtained using non-reduced Rh(I) complex or $Rh_6(CO)_{16}$ and the same polymer added separately. The authors supposed that soluble $[HRh(CO)_nL_m]$ complexes, formed from Rh NPs during the reaction, were catalytically active and the reaction occurred in solution, but not on the surface of the Rh NPs [171].

Bruss et al. reduced $RhCl_3{\cdot}3H_2O$ dissolved in a $[BMIM]BF_4$ ionic liquid using hydrogen. The obtained Rh NPs were employed in the solventless hydroformylation of olefins, with a modifying ligand or in an unmodified system. It was found that the conversion of



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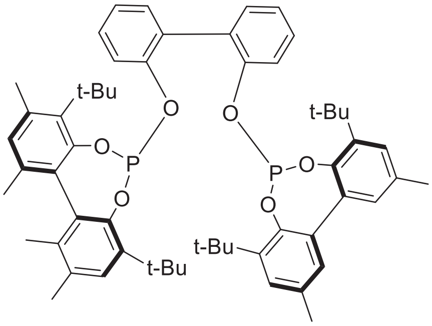

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Fig. 35. Chiral ligands, BINAPHOS and Kelliphite [167].

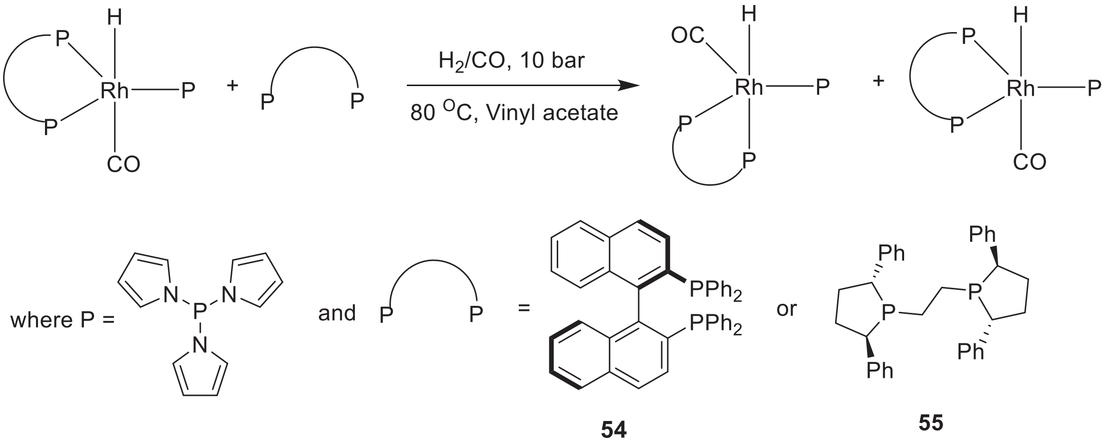


Fig. 36. Reaction of [$HRh(CO)[P(NC_4H_4)]_3$] with (*R*)-BINAP or Ph-BPE under solventless hydroformylation conditions [169].

olefins increased inversely to the size of the NPs. The highest n/iso ratio, 25, was achieved for small Rh NPs (5 nm) with the addition of Xantphos, while without added phosphine the n/iso ratio was 1.1–1.8. The interaction of Rh NPs with Xantphos was evidenced by ^{31}P NMR while the IR spectrum showed two v(CO) bands of the Rh $(CO)_2$ species formed during the reaction from small nanoparticles. These rhodium species contributed to the catalytic process [172].

Shi et al. synthesized Rh NPs stabilized in a TiO_2 nanotube (TNTS) by the chemical reduction of an aqueous solution of [$Rh_2(OAc)_4$] using different reduction methods, such as chemical reduction with potassium borohydride or ethanol, as well as photoreduction with a 300 W high-pressure mercury lamp. The size of the Rh NPs depended on the method used; however, they exhibited similar good catalytic activity and high regioselectivity toward 2-acetoxypropanal in the hydroformylation of vinyl acetate. The catalyst prepared by photoreduction showed the highest activity. It was found that Rh NPs formed $RhH_y(CO)_x$/TNTS species in the H_2/CO atmosphere [173].

The same group reported studies on Rh NPs, supported on boron modified TiO_2 nanotubes (B-TNTs) and on TiO_2 nanotubes (TNTs), obtained by an impregnation-photoreduction procedure with [$Rh_2(OAc)_4$] as the Rh source [174]. The catalytic studies in the hydroformylation of styrene showed higher catalytic activity of Rh/B-TNTs than Rh/TNTs. The difference in activity was explained by the more efficient styrene adsorption on the B Lewis acid sites of the boron modified TNTs. Addition of PPh_3 resulted in an increase of the regioselectivity to the branched aldehyde, however, with a significant conversion decrease. At an 8-fold excess of PPh_3, styrene conversion was only 13.3%, while it was 71% without PPh_3 [174].

Rh NPs supported on boron doped g-C_3N_4 (g-C_3N_4 graphitic carbon nitride) were prepared by means of an impregnation-chemical reduction procedure utilizing $RhCl_3 \cdot 3H_2O$ as the rhodium precursor [175]. It was evidenced by TEM that the boron modified the delocalized π-structure of g-C_3N_4 and increased dispersion of the Rh NPs. According to XPS analysis, two forms of rhodium were present in the Rh/B-g-C_3N_4 nanocatalyst, namely Rh^0 and Rh^{3+}. Excellent catalytic activity in the hydroformylation of styrene with high selectivity to aldehydes and a 55–58% yield of the *iso*-isomer was obtained with this catalyst. It could also be easily separated from the reaction mixture and recycled seven times without any loss of activity [175].

Garcia et al. prepared Rh NPs stabilized by tetraoctylammonium bromide (TOAB). The prepared Rh/TOAB nanoparticles were immobilized on a magnetic support containing diphenylphosphine groups ($Fe_3O_4@SiO_2$-$N(CH_2PPh_2)_2Rh$) and applied in the hydroformylation of 1-octene and styrene, with good results (Fig. 37). In subsequent catalytic runs, the yield of nonanals formed from 1-octene was ca. 82–86% and the n/iso ratio was ca. 2.2–2.4. Raman spectra indicated that during the reaction rhodium active soluble species were formed *in situ*. However, they were maintained on the magnetic support enabling efficient catalyst recycling [176].

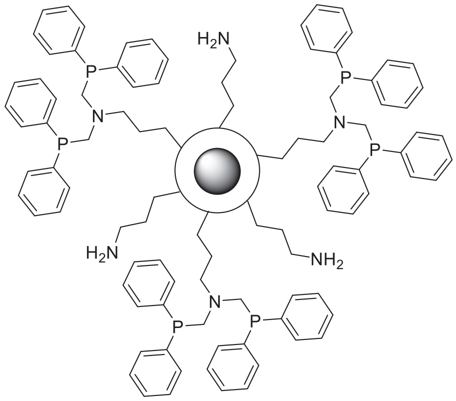


Fig. 37. The Rh/TOAB nanoparticles immobilized on a magnetic support [176].

Preparation of the hyper branched polymer with terminal phosphine groups and its application for the functionalization of silica-coated magnetite and then for the immobilization of Rh NPs was reported (Fig. 38) [177]. The enhanced number of terminal phosphine groups improved the catalytic activity of $Fe_3O_4@SiO_2$-HYP-$N(CH_2PPh_2)$ in the hydroformylation of monoterpenes (estragole, limonene, β-pinene). The Raman spectra indicated the interaction of Rh with the functional groups of the support in the reused catalyst, confirming its stability [177].

Rh NP-catalyzed hydroformylation in biphasic media has been rarely investigated. Han et al. synthesized Rh NPs stabilized with poly(vinylpyrrolidone) (PVP) by chemical reduction using alcohol as a reducing agent. The Rh/PVP catalyzed the hydroformylation of propene in aqueous biphasic systems with the addition of TPPTS at 90 °C and 40 bar of syngas. The Rh NPs were successfully recycled as many as seven times and exhibited high catalytic activity with TOF 110.1 h^{-1}–203.5 h^{-1}. XPS studies confirmed only the presence of Rh^0 in the catalyst recovered after the catalytic reaction and, consequently, the heterogeneous mechanism was proposed [178].

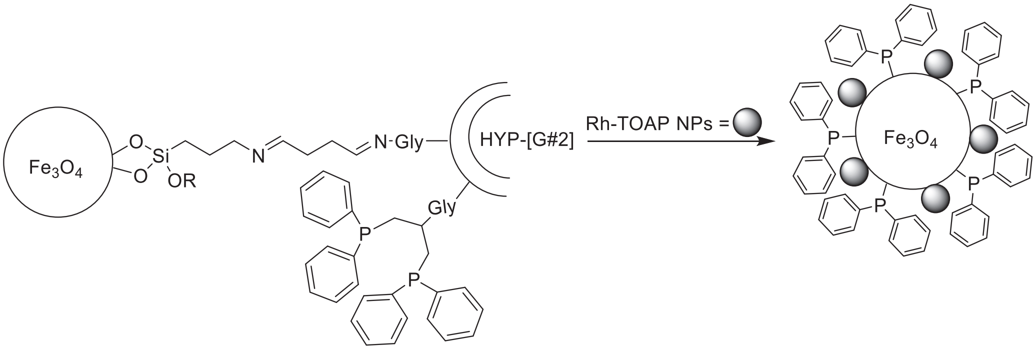


Fig. 38. The Rh NPs immobilized on functionalized silica-coated magnetite [177].

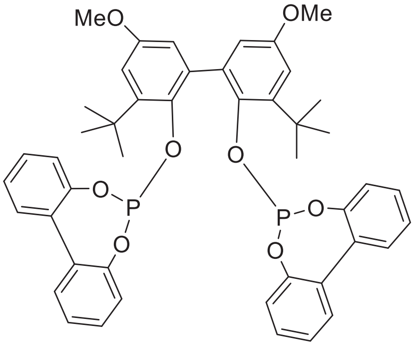
Wen et al. studied 1-octene hydroformylation using a thermoregulated aqueous phase transfer $CH_3(OCH_2CH_2)_mPPh_2$ phosphine (TRPT) and $[Rh(acac)(CO)_2]$ [179]. The results indicated high activity and regioselectivity toward aldehydes (up to 97.5%); however, the aldehyde yield decreased after three recycles. This is because the Rh NPs formed *in situ* after the first run under aqueous conditions undergo Ostwald ripening in the next recycle. Similar behavior was demonstrated by an Rh/TRPT colloid synthesized by the chemical reduction of anhydrous $RhCl_3$ with tetraalkyl ammonium triorganohydroborate in THF. The introduction of Hg (0) had virtually no effect on the catalytic activity, confirming that the black precipitate formed during the reaction was not catalytically active. Thus, the observed decrease in aldehyde yield during recycling can be explained by the decrease in the amount of catalytically active Rh caused by its partial precipitation [179].

Kaoxue et al. prepared Rh NPs by the simple hydrogen (4 MPa) reduction of $RhCl_3{\cdot}3H_2O$ in the presence of the thermoregulated ligand $Ph_2P(CH_2CH_2O)_{16}CH_3$ in a 1-butanol-water mixture at 70 °C [180]. The Rh NPs displayed high activity and selectivity toward aldehydes in the hydroformylation of higher alkenes (1-octene, 1-decene, 1-dodecene, styrene) in an water/1-butanol biphasic system. The aqueous phase containing the catalyst was efficiently separated from the organic products and recycled three times without loss of activity [180]. Wang et al. studied the hydroformylation of olefins using ionic liquid/organic biphasic systems. Rh NPs were stabilized with the thermoregulated ionic liquid $[CH_3(OCH_2CH_2)_{16}N^+Et_3][CH_3SO_3]$ (IL_{PEG750}). Under optimized reaction conditions (5 MPa, 90 °C), in a toluene/n-heptane mixture, the conversion of 1-octene, chemoselectivity toward aldehyde, and the n/iso ratio were 99%, 91%, and 1.4, respectively. The catalyst was easily separated and reused eight times. During recycling, rhodium leaching in the organic phase decreased from 4.3% to 0.3% and the yield remained stable, ca. 90% [181]. Xu et al. in the same group synthesized Rh NPs by the H_2 reduction of $RhCl_3{\cdot}3H_2O$ using another thermoregulated ionic liquid of the ammonium methanesulfonate type. The Rh NPs were successfully applied in the biphasic (ionic liquid/cyclohexane) hydroformylation of higher olefins. At room temperature, the ionic liquid phase containing Rh NPs was immiscible with the cyclohexane phase, while at 118°C this biphasic system formed a single phase. During cooling, two phases were again formed, facilitating catalyst separation. The catalyst was recovered and reused five times showing constant activity and low rhodium leaching of ca. 0.3 wt%. The presence of ν(CO) bands was found by IR suggesting the formation of Rh-carbonyl species; however, the nature of this catalyst remained open [182].

Rh NPs stabilized by a quaternary ammonium based ionic liquid with thermoregulated properties were synthesized. The thermoregulated phase-separable Rh nanocatalyst exhibited complete conversion of alkenes and excellent selectivity to aldehydes. Moreover, it was reused five times for the hydroformylation of 1-octene and twenty times for the hydroformylation of styrene without any remarkable loss of activity and selectivity [183]. This system presents the advantages of both homogeneous (high catalytic activity) and heterogeneous (easy separation and good recyclability) systems.

Behr et al. prepared Rh NPs stabilized in thermomorphic multicomponent solvents (TMS) (TMS system: DMF/n-decane wt.-50%/wt.-50%), by the chemical reduction of $[Rh(acac)(CO)_2]$ using 20 bar of hydrogen in a polar solvent such as DMF or propylene carbonate (PC) [184]. The TMS system combines the advantages of homogeneous catalysis with highly efficient phase separation facilitating catalyst recycling. Rh/TMS catalyzed the hydroformylation of 1-dodecene and complete conversion in both solvents was obtained within 20 h. The aldehyde selectivity depended on the solvent. A 97% yield of aldehydes was achieved in DMF with an n/iso ratio of 2.6, while in PC, the yield of aldehydes was 25% (n/iso ratio of 1.1). The addition of a PPh_3 ligand decreased the yield of aldehydes in DMF to 36% with an n/iso ratio of 0.96, however, 85% of aldehydes with a 24 n/iso ratio were obtained using a biphephos ligand **56** (Fig. 39). The best results, 97% aldehydes with an n/iso ratio of 70:30, were obtained by applying nanoparticles derived from $[Rh(acac)(CO)_2]$ in DMF without any addition of a ligand [184].

Another thermoregulated system, containing poly (ethylene glycol) (PEG 4000), was reported by Sun et al. Rh NPs of 1.7 ± 0.4 nm in diameter were obtained by hydrogen reduction of $RhCl_3{\cdot}3H_2O$ and used for the hydroformylation of 1-hexene, 1-octene, 1-decene and cyclohexene. Complete conversion and selectivity toward aldehydes were obtained and the catalyst was easily separated and recycled over 20 times [185]. Hou et al. reported Rh NPs immobilized in the ZIF-8 framework for the



56

Fig. 39. Biphephos ligand [184].

$$2Rh(acac)(CO)_2 + H_2O \longrightarrow 2Rh^0 + Hacac + CO_2 + CO$$

$$H_2O + CO \rightleftharpoons CO_2 + H_2$$

$$H_2 \longrightarrow 2H^+ + 2e^-$$

$$2Rh^I + 2e^- \longrightarrow 2Rh^0$$

Fig. 40. Reduction of Rh^I to Rh^0 with CO and H_2O [187].

hydroformylation of alkenes with different chain lengths. The yield of aldehydes ranged from 76% for 1-dodecene to 94% for 1-hexene and the n/iso ratio changed from 0.4 to 0.9, respectively. The catalyst could be easily separated and reused five times without any remarkable loss in activity [186].

Green and simple methodology was used by Alsalahi for the synthesis of Rh NPs by the reduction of [$Rh(acac)(CO)_2$], in water at 80°C, without any addition of a reducing agent or an organic solvent (Fig. 40) [187]. Different polymers, such as polyvinylpyrrolidone (PVP-K30 and PVP-K15) and polyvinyl alcohol (PVA), were used to stabilize the Rh NPs. The stabilized Rh NPs were tested in 1-hexene hydroformylation with an excess of hydrophobic phosphine, PPh_3, in a water medium. The procedure, following the "on water" conditions, enabled high catalytic activity and chemoselectivity to aldehydes with an n/iso ratio up to 5.4. Interestingly, the non-stabilized Rh NPs were also quite active under the same conditions. According to the XPS analysis, the Rh/PVP-K30 catalyst isolated after the hydroformylation reaction contained 92.5% of Rh^0 and 7.5% of Rh^{3+}. In this system, Rh NPs formed soluble, catalytically active species and a homogenous reaction pathway could be proposed [187].

Lyubimov et al. prepared Rh NPs bonded to a hypercross-linked polystyrene matrix (Purolite Macronet® MN100 resin) by the impregnation of an ethanolic solution of $RhCl_3{\cdot}4H_2O$ followed by reduction with $NaBH_4$. These nanoparticles exhibited high catalytic activity in the hydroformylation of different olefins, e.g. styrene or (*R*)-limonene in supercritical carbon dioxide ($scCO_2$). The catalyst was recycled six times without any loss in the yield and selectivity to aldehydes [188].

Tan et al. prepared Rh NPs supported on a reduced graphene oxide (Rh/RGO) by the one-pot liquid-phase chemical reduction of $Rh(NO_3)_3$ with a glycol–water mixture (Fig. 41) [189]. XPS data revealed the presence of non-stoichiometric oxidation state Rh^{n+}, between Rh^0 and Rh^{3+}. Thus, Rh^{3+} was reduced in part to Rh^0 because of the high electronegativity of GO. This catalyst was successfully applied in the hydroformylation of 1-hexene under various conditions. Selectivity to the linear aldehyde was the highest at low temperatures, in a short reaction time. With increased temperature, the selectivity to side reaction products, such as 2-hexene (isomerization product) and hexane, formed by hydrogenation, increased. For comparison, Rh NPs supported on activated carbon (Rh/AC) and carbon nanotubes (Rh/CNTs) were tested, however, the results were worse those with Rh/RGO. The high activity and selectivity correlate well with the 2D nanosheet structure of Rh/RGO, small nanoparticle size, high nanoparticle dispersion and the large exposed Rh surface area compared with the 3D porous and 1D nanotube structures of Rh/AC and Rh/CNTs, respectively [189].

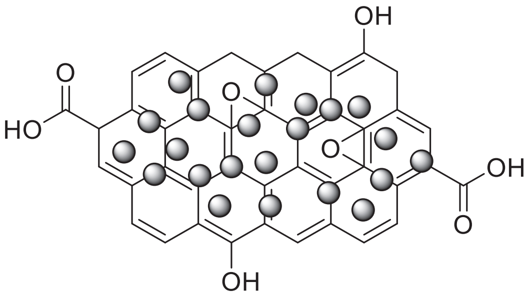


Fig. 41. Rh immobilized of a reduced graphene oxide (Rh/RGO) [189].

Methylated graphene oxide supported Rh NPs, Rh/GO_{mod}, (Fig. 42) prepared by the chemical reduction of $RhCl_3{\cdot}4H_2O$ in methanol with an excess of dry $NaBH_4$, showed high catalytic activity and selectivity to the desired aldehydes in the hydroformylation of different olefins (styrene, 4-methyl styrene, 4-bromo styrene, 3,3-dimethyl but-1-ene) in supercritical carbon dioxide ($scCO_2$). The regioselectivity of hydroformylation was higher in $scCO_2$ than in toluene or benzene [190].

Different Rh NPs and Ru NPs supported on TiO_2 nanotubes, namely Rh/TNTs, Ru/TNTs, Rh-Ru/TNTs (Ru/TNTs was used as a carrier to support Rh NPs), Ru-Rh/TNTs (Rh/TNTs was used as a carrier to support Ru NPs), were prepared via an impregnation-photoreduction procedure. These catalysts were tested in the hydroformylation of vinyl acetate and cyclohexene. Interestingly, the presence of Ru increased the catalytic activity of Rh in the hydroformylation of vinyl acetate. In contrast, Rh-Ru/TNTs and Ru-Rh/TNTs were less active than Rh/TNTs in the hydroformylation of cyclohexene, indicating the inhibiting effect of ruthenium in this case [191].

Rh/Cu_2O, synthesized via a microwave route in an aqueous medium, used in the hydroformylation of 1-hexene, showed high regioselectivity to isoaldehyde. The presence of Rh/Cu_2O nanoparticles was evidenced by TEM and XRD/EDS methods with mapping analysis. In particular, the XPS analysis confirmed the presence of Rh^0. Optimization of the reaction parameters also allowed the formation of, mainly, branched aldehydes from other olefins [192]. The reaction performed with only $RhCl_3$ in the absence of Cu_2O occurred with lower conversion, confirming the beneficial effect of the Rh/Cu_2O catalyst which can be explained by its high surface area. In this conditions Cu_2O without Rh was not active. During recycling, the rhodium leaching was low, ca. 1.1% [192].

4.1. Asymmetric hydroformylation catalyzed by Rh NPs and chiral phosphines

Rh NPS supported on a DNA biopolymer, Rh/DNA, were applied as a catalyst for the asymmetric hydroformylation of styrene in water. As expected, the hydroformylation of styrene principally led to a branched aldehyde and the DNA had a significant impact on the reaction's regioselectivity (Fig. 43). A high iso/n ratio, up to 6.1, was obtained when Rh/DNA was used with a 13-fold excess of PPh_3, while a much lower iso/n value, of 1.9, was obtained under

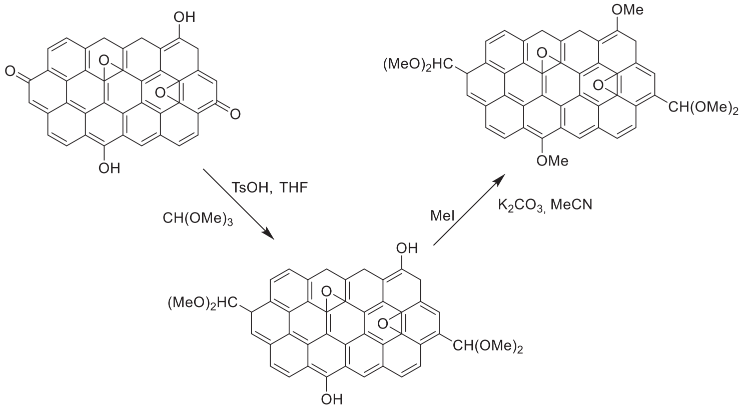


Fig. 42. Synthesis of the methylated graphene oxide [190].

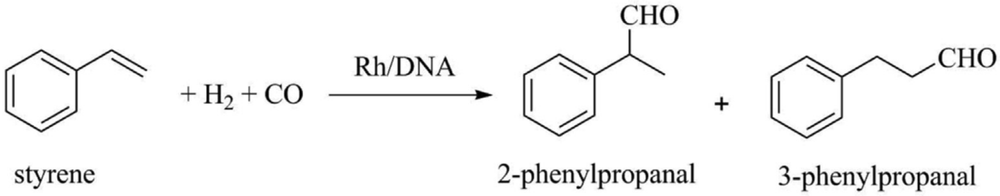
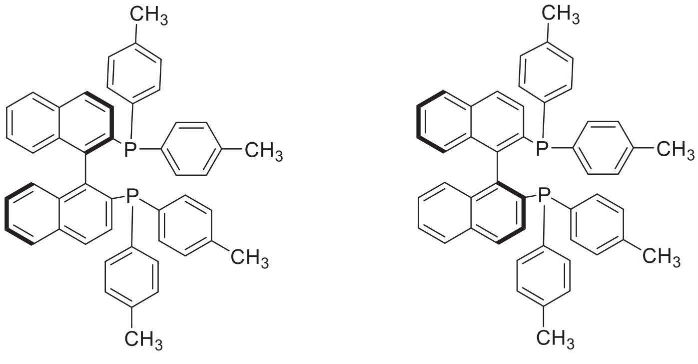


Fig. 43. Hydroformylation of styrene.



57 **58**

Fig. 44. Chiral phosphines, (*R*)- and (*S*)-T-BINAP.

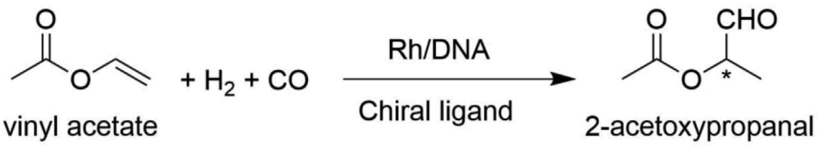


Fig. 45. Hydroformylation of vinyl acetate.

the same conditions for [Rh(acac)(CO)$_2$] and a 13-fold excess of PPh$_3$ [193].

The introduction of a three-fold excess of chiral ligands (*R*)-BINAP **57** or (*S*)-BINAP **58** (Fig. 44) significantly increased the iso/n ratio, up to 16.7 and 16.2. Moreover, high enantioselectivity, expressed by specific rotation [α] values, was obtained. In contrast, the efficiency of the substituted BINAP derivatives ((*R*)-T-BINAP and (*S*)-T-BINAP) in this reaction was much worse considering the reaction selectivity [193].

Vinyl acetate was hydroformylated under ‘‘on water” conditions using Rh/DNA and with chiral ligands ([L]/[Rh] = 3) ((*R*)-BINAP, (*S*)-BINAP, (R)-T-BINAP and (S)-T-BINAP). For comparison, [Rh(acac)(CO)$_2$] was tested in the same conditions. The main reaction product was 2-acetoxypropanal in both systems and almost the same conversion of vinyl acetate was obtained (Fig. 45).

However, enantioselectivity differed significantly, and an *ee* value up to 50 was obtained with Rh/DNA, while with [Rh(acac)(CO)$_2$], the *ee* value was only up to 10 (Fig. 46) [193].

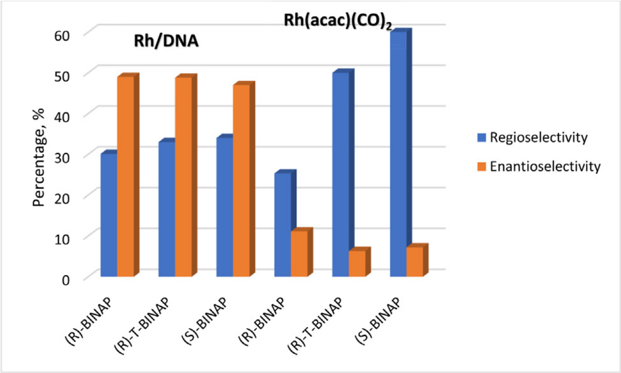
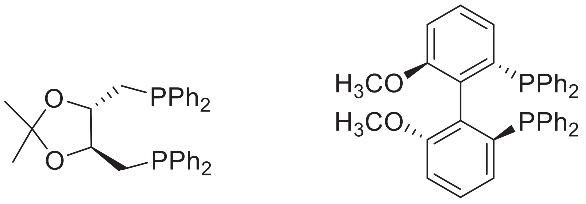


Fig 46. Hydroformylation of vinyl acetate in a water medium catalyzed by a) Rh/DNA and b) [Rh(acac)$(CO)_2$], modified with different phosphorus ligands [193].



(+)-(*S*,*S*)-DIOP
59

(*S*)-MeO-BIPHEP
60

Fig. 47. Chiral diphosphines.

Thus, Rh/DNA nanoparticles modified with a chiral ligand produced significantly higher enantioselectivity than the system without DNA. The synergistic effect of DNA and chiral phosphine is most probably responsible for these results. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra and IR analyses evidenced the formation of the catalytically active rhodium species with the composition [RhH$(CO)_2$(BINAP)] from Rh NPs under hydroformylation conditions [193].

Han et al. studied the asymmetric hydroformylation of styrene and vinyl acetate, catalyzed by Rh/SiO_2 modified by a chiral ligand ((*R*)-BINAP **54** (Fig. 36), (+)-(*S, S*)-DIOP **59**, (*S*)-MeO-BIPHEP **60** (Fig. 47) [194].

These catalysts provided very promising results, such as up to 72% *ee* and 100% regioselectivity to isoaldehydes for vinyl acetate hydroformylation in the presence of **54** (54/Rh = 1) in toluene under 50 bar of CO/H_2. However, the conversion was very low, only 5%. Under the same conditions, in the presence of **54**, regioselectivity to the branched aldehyde increased from 67/33 to 92/8 with 30% *ee* in the hydroformylation of styrene. Simultaneously, the conversion of styrene decreased significantly, from 99 to 6%. ^{31}P MAS NMR and IR spectra of the reaction mixture indicated the formation of the chiral active sites on the surface of Rh/SiO_2 [194]. Axet et al. examined the asymmetric hydroformylation of styrene catalyzed by Rh NPs modified with chiral carbohydrate-derived diphosphite ligands in toluene [195]. The Rh NPs were synthesized from two different rhodium precursors [Rh(η^3-C_3H_5)$_3$] and [Rh(μ-OMe)(cod)]$_2$ under hydrogen atmosphere (3 bar) in tetrahydrofuran. Their characteristics from TEM, WAXS, and elemental analysis allowed the conclusion that the metal precursor strongly influenced the size, shape, and dispersion of the nanoparticles. The Rh NPs exhibited high catalytic activity under 20 bar of CO/H_2, enabling high conversion and regioselectivity toward the branched aldehyde. However, only moderate enantioselectivity was noted in the presence of the chiral phosphite ligand. According to ^{1}H and ^{31}P{^{1}H} NMR spectra, during hydroformylation, Rh NPs undergo transformation to catalytically active hydrido-carbonyl complexes. Thus, Rh NPs acted here as a reservoir for the molecular catalysts. It should be noted, however, that colloidal catalysts achieved higher enantioselectivities than those obtained with the corresponding molecular catalysts [195].

In 2008, Li et al. synthesized small Rh NPs (1.5–2.0 nm) stabilized by amphiphilic tetraoctylammonium bromide (TOAB). The asymmetric hydroformylation of styrene and vinyl acetate was performed in the presence of **54**, also after immobilization of the nanoparticles on silica. IR and NMR analyses clearly showed a coordinative interaction between the **54** ligand and rhodium. **54**-modified Rh NPs catalyzed the asymmetric hydroformylation of styrene and vinyl acetate at 50 bar of syngas, and high regioselectivity and enantioselectivity were achieved, up to 92:8 iso/n, 26% *ee* for styrene and 99:1 iso/n, 59% *ee* for vinyl acetate. On the other hand, only a very low conversion of both substrates was achieved, 5% for styrene and 1% for vinyl acetate [196].

The development of a heterogeneous catalysts for hydroformylation is highly desirable and Rh NPs are an attractive option. However, under reaction conditions, Rh NPs often undergo leaching to the reaction solution, forming soluble species of different catalytic activity. In several catalytic systems formation of soluble Rh carbonyl species was evidenced. In such a case, Rh NPs can be considered as a reservoir of the catalytically active molecular forms. When they are coordinatively unsaturated, what is highly probable, they can be more active than the pre-made precursors. On the other hand, in this case, separation of the catalyst from hydroformylation products may not be complete.

5. Conclusions

Water, the most friendly solvent, is a promising medium for hydroformylation, not only for short olefins but also for long-chain hydrophobic ones. However, due to the mass transfer limitations, appropriate additives should be used to increase the hydroformylation effciciency. Very promising results were obtained by using surfactants or cyclodextrins as well as surface-active phosphorus ligands.

It should be also underlined that the separation of products from the catalyst is strongly influenced by the ligands present in the catalytic system. In particular, in an aqueous/organic system, ligands bonded to rhodium can facilitate leaching of the catalyst to organic phase and limit the effectiveness of separation. Moreover, ligand useful in the hydroformylation of one olefin is not necessarily good in the hydroformylation of other substrate, i.e. unsaturated alcohol due to the solubility difference. These issues should be considered in design of new ligands for the hydroformylation. Furthermore, the thermoregulated systems enabling easier separation of organic products from the catalyst are very promising.

Interestingly, the presence of water in the systems with hydrophobic catalysts, increased the reaction rate and, in some cases, the hydroformylation selectivity as well. These positive effects can be partly explained by the interphase interactions. The results presented in the article indicate the possibility of improving hydroformylation by the addition of water to the hydrophobic reaction mixture. Although theoretical explanation of these effects is not completed yet, the use of hydrophobic systems in the presence of water seems to be promising and worth to study.

Supported Rh NPs can be considered as a rhodium source, an alternative to soluble rhodium complexes. In the majority of cases reported, Rh NPs acted as a supplier of soluble species, and the real catalytic systems were not fully heterogeneous. However, despite some solubilization, better catalytic results were obtained using supported Rh NPs than soluble rhodium complexes under the same conditions. Further mechanistic studies are needed to better assess the suitability of Rh NPs as hydroformylation catalysts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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