# Chapter 3
# Hydroformylation of Renewables

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## 3.1 Introduction

The formal addition of a hydrogen atom and a formyl group to a double bond in the presence of a transition metal catalyst is called hydroformylation or oxo-synthesis. This reaction, discovered by Otto Roelen in 1938 during his investigations about the Fischer–Tropsch reaction, is one of the most important industrial applications of homogeneous catalysis [1]. In the year 2012, more than 12 million tons of hydroformylation products were synthesised [2]. A schematic hydroformylation of a terminal olefin is shown in Fig. 3.1.

The formyl group can be added to each of the double bond carbon atoms, yielding either in a linear (*n*-) or in a branched (*iso*-) aldehyde. Due to the rule of Keulemans, the formyl group is preferably added to the lower substituted carbon atom; thus, formation of the *n*-aldehyde is favoured [3].

While phosphine-modified complexes of cobalt and rhodium are, due to their high activity, the only catalysts applied in industrial processes yet, there are several transition metals as hydroformylation catalysts described in literature, e.g. ruthenium, palladium, iridium, platinum-tin [4]. In particular, ruthenium- and iridium-based catalysts become increasingly attractive due to the development of new ligands, which improve the activity of these catalysts [5, 6].

A detailed overview about the hydroformylation was recently published by Franke and Börner [7].

### 3.1.1 Mechanisms

A mechanism for cobalt-catalysed hydroformylation of olefins was developed by Heck and Breslow in the 1960s (Fig. 3.2) [8].

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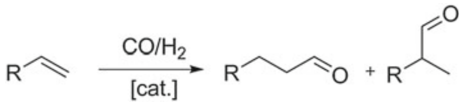


**Fig. 3.1** Hydroformylation of a terminal olefin

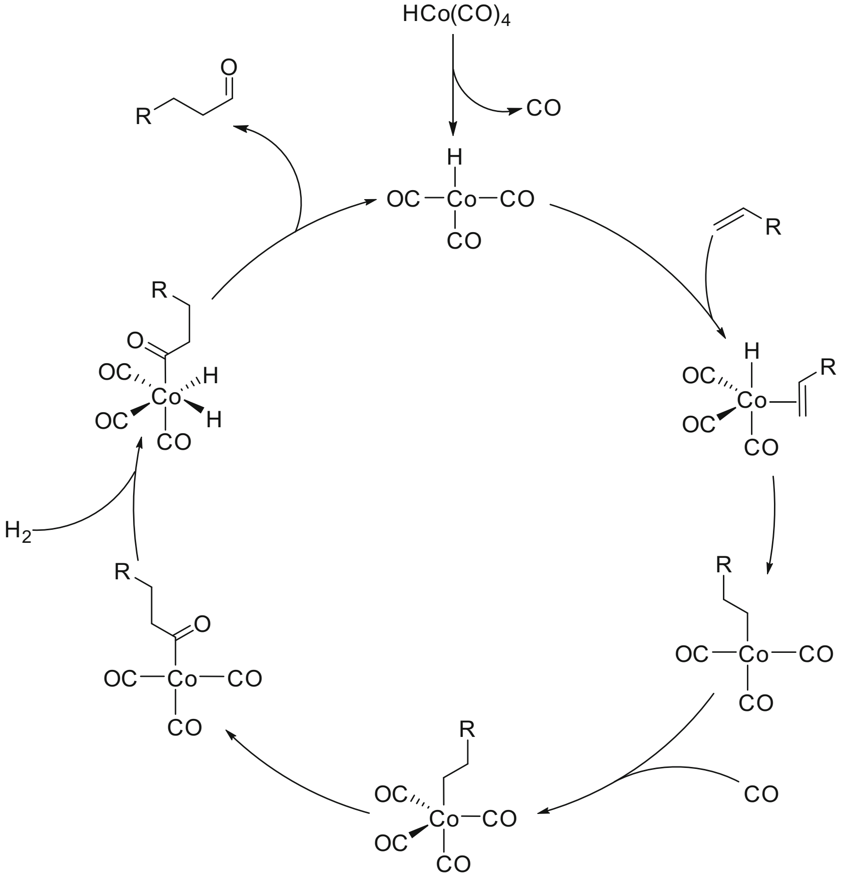


**Fig. 3.2** Mechanism of the cobalt-catalysed hydroformylation

Starting from the cobalt (I) precursor tetracarbonylhydridocobalt, the active catalyst is formed by loss of one molecule carbon monoxide. The resulting tricarbonylhydridocobalt is able to associate an olefin, which undergoes insertion into the Co–H bond. This step determines whether the *n*-aldehyde or the *iso*-aldehyde is formed. After insertion in the Co–H bond, the complex associates a carbon monoxide molecule and insertion of carbon monoxide into the Co–alkyl bond

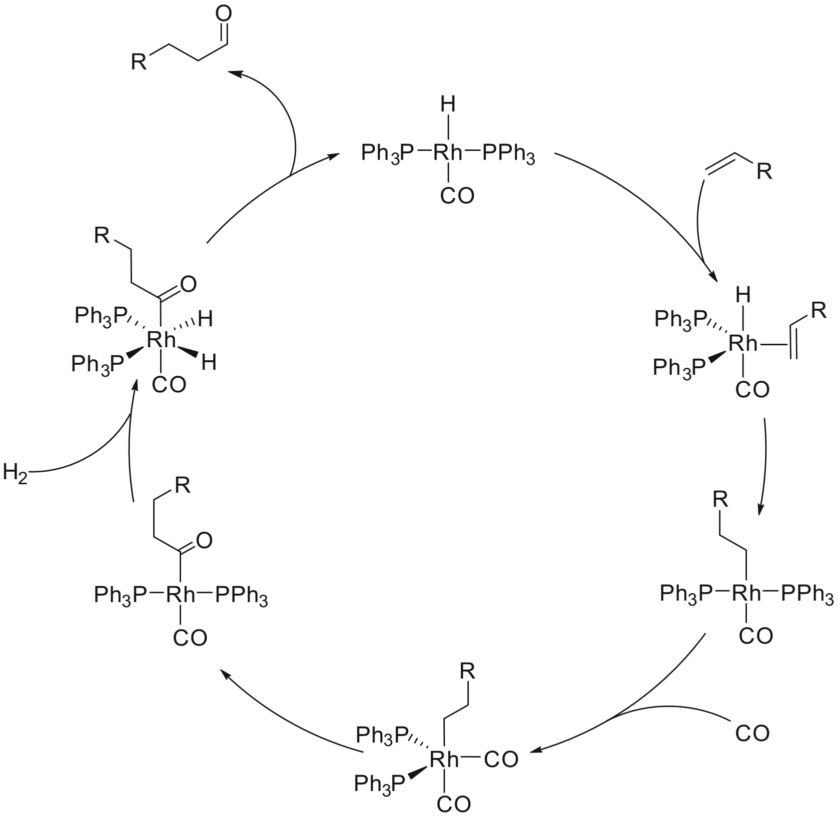


**Fig. 3.3** Mechanism of the rhodium-catalysed hydroformylation

occurs. Finally, the oxidative addition of dihydrogen followed by reductive elimination of the free aldehyde under recovery of the active catalyst takes place.

G. Wilkinson made a suggestion for a mechanism of the alkene hydroformylation by use of rhodium–phosphine complex catalysts (Fig. 3.3) [9].

The reaction steps proceed in the same sequence compared to the mechanism of the cobalt-catalysed hydroformylation, but by use of an additional phosphine ligand, there are many possible intermediates involving different number of phosphine ligands bonding to the rhodium or geometric arrangements [10].

### 3.1.2 Side Reactions

In the presence of a transition metal catalyst and synthesis gas, several side and consecutive reactions can occur. The most prominent side reactions are the

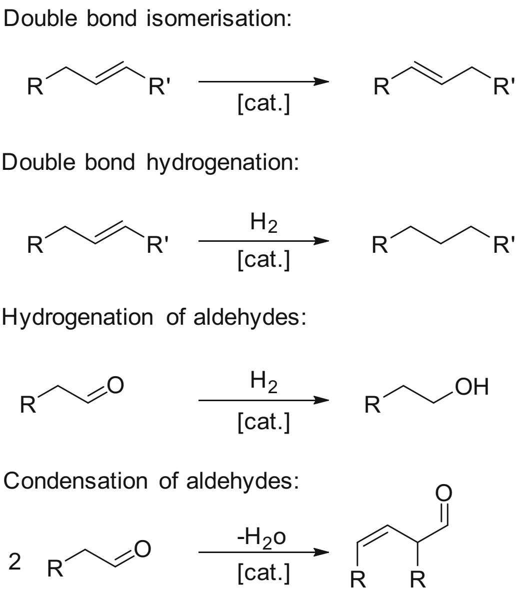


**Fig. 3.4** Side reactions

hydrogenation and the isomerisation of the C=C double bond. Consecutively, resulting aldehydes can be reduced to the corresponding alcohols or undergo a condensation reaction (Fig. 3.4) [4].

Double bond isomerisation constitutes an interesting side reaction in hydroformylations. In respect of formation of linear aldehydes, isomerisation is boon and bane depending on the starting material. Starting from substrates with internal double bonds, linear aldehydes are available through double bond isomerisation to the end of the carbon chain and subsequent hydroformylation. If the starting material already contains a terminal double bond, isomerisation is disadvantageous and leads to formation of internal aldehydes or decelerates the reaction [11].

The hydrogenation of double bonds is an undesired side reaction, leading to loss of substrate to low-value chemicals and lower selectivity in hydroformylation (see Chap. 7).

Hydrogenation of nascent aldehydes can be used to synthesise corresponding alcohols in a tandem reaction [12]. This reaction can be either desired or not. On the one hand, alcohols are an important class of chemical intermediates and a tandem reaction consisting of hydroformylation and consecutive aldehyde reduction offers an easy access for them. Consequently, this reaction is implemented on industrial scale via the Shell process in which a phosphine-modified cobalt catalyst is used. On the other hand, aldehydes are straightforward convertible into further classes of chemical intermediates (e.g. carboxylic acids and amines). In this case, formation of aldehydes is undesired.

Condensation of two aldehydes is also described in literature. Again, this can be an interesting consecutive reaction for the synthesis of chemical intermediates. For

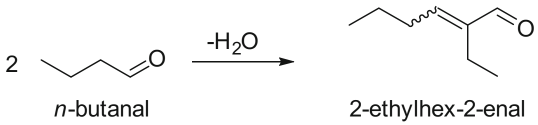


**Fig. 3.5** Condensation of *n*-butanal

example, condensation of two molecules of *n*-butanal to 2-ethylhex-2-enal (Fig. 3.5) is a crucial reaction step for the synthesis of 2-ethylhexanol, which is an important intermediate in the syntheses of PVC plasticisers [13].

### *3.1.3 Catalyst Development in Industrial Hydroformylation Processes*

In hydroformylation, several transition metals are suitable catalysts, e.g. rhodium, cobalt, ruthenium, iridium, and platinum-tin [6]. However, only cobalt and rhodium catalysts have gained industrial importance until today. The first hydroformylation, discovered by Otto Roelen, was realised with a cobalt catalyst as side product of Fischer–Tropsch experiments [2]. Cobalt catalysts require relative high pressures and temperatures for satisfying yields in hydroformylation. Rhodium as the most active catalyst metal enables hydroformylation under milder conditions compared to cobalt [4].

The industrial implementation of hydroformylation ensues in four steps. The first catalyst generation consists of unmodified cobalt carbonyl hydride complexes. Corresponding processes were developed by BASF and Exxon in the 1950s. In these processes, high pressures (200–300 bar) and temperatures between 110 and 180 °C are required. The cobalt catalyst was recycled via chemical precipitation.

In the second hydroformylation catalyst generation, catalyst relies on phosphine-modified cobalt catalysts and is applied in the Shell process. Corresponding alcohols are obtained as main products and a reduced synthesis gas pressure compared to the first catalyst generation (50–100 bar) is applicable. Separation of the catalyst is realised via product distillation after reaction.

In the 1970s, Union Carbide Corporation designed the low-pressure oxo (LPO)-process applying a rhodium–phosphine catalyst, which is referred to as the third catalyst generation, for hydroformylation under mild conditions (15–20 bar, 85–115 °C). The rhodium catalyst in the LPO process can be recycled either via gas or via liquid recycle. In the gas recycle process, the products are evaporated under process conditions. In the liquid recycle process, both the catalyst and the products leave the reactor as a liquid and the hydroformylation products are separated from the products via distillation.

The Ruhrchemie/Rhône-Poulenc process uses water-soluble phosphine-modified rhodium catalysts (fourth catalyst generation) in the hydroformylation of short chain olefins, enabling a straightforward catalyst recycling via phase separation after reaction. Hydroformylation with this technique is limited to short chain olefins due to poor solubility of higher olefins in water [4, 14].

## 3.2 Oleocompounds in Hydroformylation

The development of hydroformylation catalysts and catalyst recycling strategies was mainly focussed on the conversion of non-functionalised olefins based on petrochemicals. Indeed, the hydroformylation is also applicable to renewable feedstocks that contain naturally C=C double bonds. In comparison with substrates based on petro chemicals, oleocompounds usually contain one or more internal double bonds and an additional functional group (e.g. carboxylic acid and ester). The implementation of renewables in industrial chemistry is of great interest due to the shortage of fossil resources and their volatile prices. The hydroformylation of oleocompounds offers access to interesting intermediates for the polymer, lubricant, or surfactant industry [15].

### *3.2.1 Catalyst Development*

First investigations of hydroformylation with unsaturated oleocompounds were carried out by Natta et al. using a cobalt/iron catalyst on a bentonite support to transform methyl oleate, olive oil, and grape-stone oil into the corresponding aldehydes. Under 110 °C and 10–20 bar synthesis gas, they mainly obtained branched aldehydes as products. Heating the reaction mixture up to 140 °C results in the formation of the corresponding alcohols [16].

16 years later, Ucciani et al. investigated the homogeneously catalysed hydroformylation of unsaturated fatty acid esters. They used cobalt laurate and $Co_2(CO)_8$ as catalyst precursors in the conversion of methyl oleate under high syngas pressures (240–310 bar) and temperatures between 175 and 190 °C (Fig. 3.6). Resulting, branched aldehydes are immediately reduced to the corresponding alcohols under these conditions [17].

The hydroformylation of methyl oleate, methyl linolate, methyl linoleate, soybean oil, safflower oil methyl esters, and linseed oil methyl esters by use of cobalt catalysts was also investigated by Frankel et al. While at 100 °C the formation of aldehydes in yields up to 84% is observed, higher temperatures lead to subsequent hydrogenation of resulting aldehydes to corresponding alcohols. The use of tributylphosphine as additional ligand leads to formation of linear oxo-products due to the higher activity in double bond isomerisation of the modified cobalt catalyst [18].

The first rhodium-catalysed hydroformylation of oleocompounds (methyl oleate in this case) was also reported by Frankel et al. In contrast to cobalt-catalysed hydroformylations, double bond isomerisation can be suppressed by use of rhodium

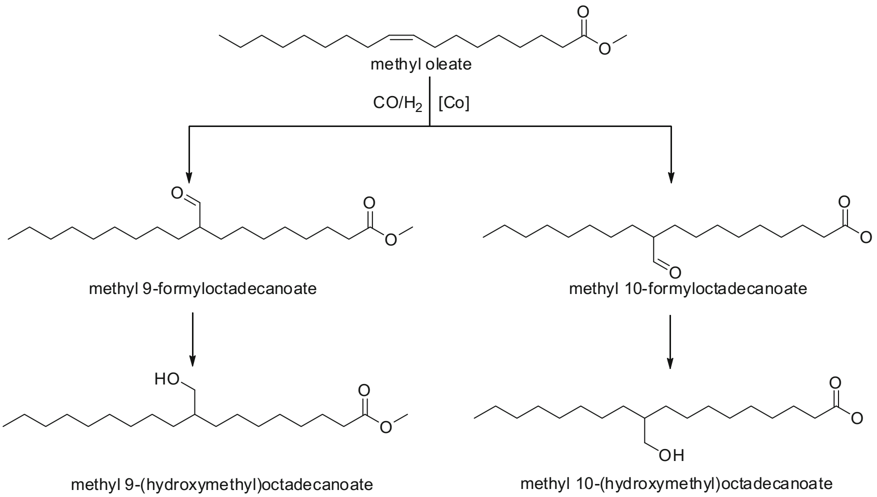


**Fig. 3.6** Cobalt-catalysed hydroformylation of methyl oleate

with triphenylphosphine as additional ligand. This leads to a hydroformylation mainly in position 9 and 10 of the carbon chain (yield up to 99%, selectivity towards hydroformylation in position 9 and 10 >80%) [19].

A comparison of rhodium and cobalt catalysts shows that rhodium has a higher activity in hydroformylation under lower pressures and temperatures. Furthermore, rhodium catalysts are less active in double bond isomerisation under operating conditions.

Technical-grade fatty acid esters and triglycerides (methyl oleate and soybean oil in this case) are also suitable starting material in hydroformylation reactions. If [$RhH(CO)(PPh_3)_3$] with additional triphenylphosphine is used as catalyst, yields for the aldehyde of up to 91% are observed under mild conditions (100 °C and 40 bar) [20].

Kinetic studies of the hydroformylation of oleocompounds with rhodium catalysts were carried out by Kandanarachchi et al. [21]. If triglycerides (soybean oil, high oleic safflower oil, safflower oil, and linseed oil) are used as substrate, the reactivity seems to be independent of the type of used triglyceride and if the triglyceride contains multiple unsaturated fatty acids. In contrast, free fatty acid methyl esters or fatty acids containing two or three double bonds are less reactive than monoolefins due to the formation of a $\pi$–allyl complex leading to an inactive rhodium complex. In the hydroformylation of soybean oil influences of temperature, syngas pressure and substrate concentration were investigated. The reaction rate increases with higher temperatures until 100 °C. Further temperature increase leads to formation of phosphido-bridged dimeric rhodium clusters which are catalytic inactive. An increasing total syngas pressure ($CO/H_2 = 1/1$) leads to higher reaction rates. For the substrate concentration, a first-order dependence was estimated. Also the effect of the ligands triphenylphosphine and triphenylphosphite was examined. The activation

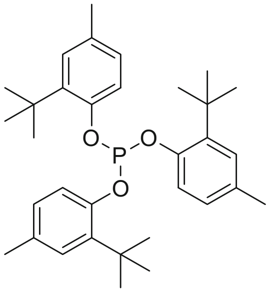


**Fig. 3.7** *Tris*-(2-*tert*-butyl-4-methylphenyl) phosphite

energy for the hydroformylation of soybean oil in the presence of triphenylphosphine is lower (66.1 kJ/mol) compared to triphenylphosphite (77.4 kJ/mol) resulting in a higher activity of the rhodium/triphenylphosphine catalyst system.

Several investigations regarding different ligands in rhodium-catalysed hydroformylation of oleocompounds were conducted. Van Leeuwen and co-workers [22] used bulky phosphite-modified rhodium catalysts in the hydroformylation of methyl oleate. These catalysts allow higher turnover frequencies (400–500 $h^{-1}$) under moderate conditions (100 °C and 20 bar syngas) compared to phosphines like triphenylphosphine. If technical methyl oleate, containing 14% 9, 12-diene methyl linoleate, is used as substrate, the reaction rate is lower due to the formation of the already mentioned $\pi$–allyl intermediates. Figure 3.7 shows *tris*-(2-*tert*-butyl-4-methylphenyl)phosphite which was applied as ligand.

Börner et al. [23] applied several lactam-based phosphoramidite ligands in the rhodium-catalysed hydroformylation of methyl oleate. Under mild conditions (80 °C and 30 bar syngas pressure), hydroformylation occurs with high chemoselectivities up to 99%. The best performance is achieved with a ligand based on a four-membered lactam ring (Fig. 3.8). This ligand is also the most stable towards water compared to the other tested ligands [23].

The application of alternative catalyst metals is also an interesting field of research in the hydroformylation of oleocompounds. Carpentier et al. [24–26] published detailed studies regarding the application of Rh, Ir, Pd, and Ru as catalyst metal in combination with the biphephos ligand in the hydroformylation of terminal unsaturated 10-undecenitril (Fig. 3.9).

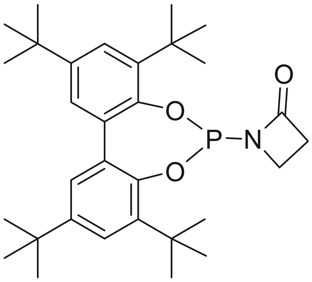
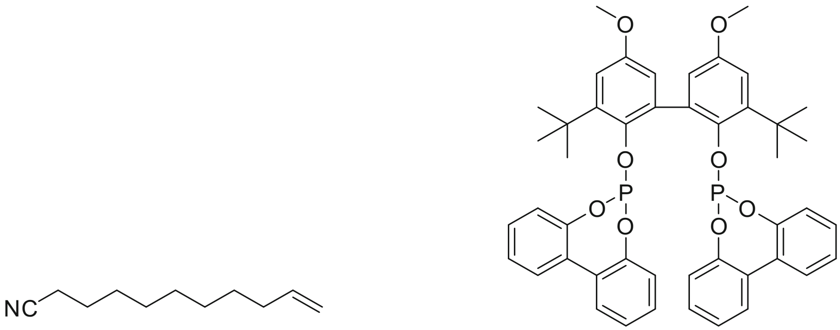


**Fig. 3.8** Phosphoramidite ligand [23]



10-undecenitril biphephos

**Fig. 3.9** 10-undecenitril and biphephos ligand

**Table 3.1** Comparison of different metals in the hydroformylation of oleocompounds [24–26]

| Catalyst metal | Price ($/oz) [27] | TOF ($h^{-1}$) | $S_{\text{aldehyde}}$ (%) | *l/b* | TTON |
|---|---|---|---|---|---|
| Rh | 765 | 3320 | 88 | 99/1 | 250.000 |
| Pd | 735 | 210 | 76 | 99/1 | Not recycled |
| Ir | 675 | 770 | 75 | 99/1 | 58.000 |
| Ru | 40 | 310 | 76 | 99/1 | 55.000 |

While a rhodium catalyst provides highest catalyst activity (TOF 3320 $h^{-1}$), chemo selectivity ($S_{\text{aldehyde}}$ 88%), and productivity (total turnover number (TTON) 250.000), excellent regio selectivities (*l/b* 99/1) can be achieved with all applied catalyst metals (Table 3.1). With the exception of the palladium complex, all catalysts can be recycled by high vacuum distillation. In particular the Ru/biphephos catalyst seems to be a very attractive alternative since nowadays, the price for Ru is about 20 times lower compared to Rh [27].

## *3.2.2 Catalyst Recycling*

In homogeneous catalysed hydroformylation, the catalyst recovery often is a great challenge in order to design an economic feasible process. In principle, a homogenous catalyst can be separated from the product by different approaches such as distillation, extraction, or catalyst immobilisation on solid or liquid carriers.

Catalyst recycling concepts on industrial-scale hydroformylation, which were already described in Sect. 4.1, are designed for the conversion of unfunctionalised, relatively short-chained olefins. Resulting oxo-products have relatively low polarity and low boiling points. In the hydroformylation of oleo compounds, these methods are often not applicable, since resulting products have high boiling points and contain an additional functional group compared to oxo-products gained from

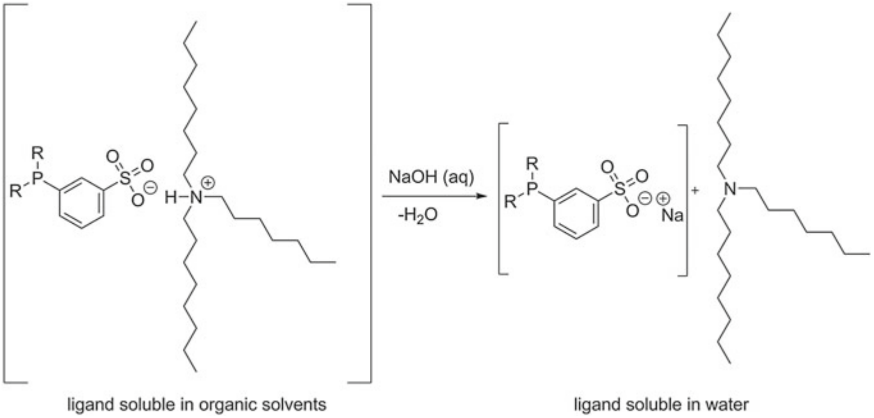


**Fig. 3.10** Switchable ligand for the catalyst extraction in hydroformylations

short-chained olefins. For this reason, there are many affords to find suitable catalyst recycling strategies in literature.

Bahrmann et al. [28] used sulfonated aromatic phosphine ligands in combination with rhodium precursors in the hydroformylation of oleyl alcohol. Coupling sulfonate groups on the ligand with long-chained ammonium groups offers access to rhodium-ligand complexes which are soluble in organic solvents like toluene. Reaction takes place under 100–170 °C and 100–450 bar syngas pressure. After reaction, the solution is treated with aqueous sodium hydroxide solution leading to loss of the ligands ammonium counter ions. In consequence, the catalyst complex gets soluble in water and can be separated from the product phase via extraction with water (Fig. 3.10). The catalyst can be regenerated by treatment with mineral acids and subsequent extraction with ammonium containing toluene.

Recently, Monflier et al. [29] reported about the application of naturally occurring cyclodextrins as supramolecular emulsifiers in the hydroformylation of triglycerides in water. The substrate and the cyclodextrins form a supramolecular complex, which allows the interaction between the substrate and the water-soluble Rh/TPPTS (TPPTS = trisulfonated triphenylphosphine) catalyst. With this system, yields of the desired aldehyde of 74% after 6 h are reached. Stopping stirring the reaction mixture after reaction induces the separation of the aqueous catalyst phase and the product phase. The catalyst phase was reused three times without significant loss of activity, which demonstrates the applicability of this elegant approach.

Another approach for hydroformylation of oleocompounds is the micellar two-phase catalysis. This technique uses surfactants to take the hydrophobic substrates into the aqueous catalyst containing phase. Fell et al. [30] determined the influence of several surfactants. In particular, cationic and amphoteric detergents provide promising results in the hydroformylation of methyl 10-undecenoate, which is available from pyrolytic cleavage of ricinoleic acid (Fig. 3.11). With this system, it is possible to generate more than 90% formyl products after three hours with 0.5 mol% rhodium and 30 mol% sulfonated triphenylphosphine in water. Without

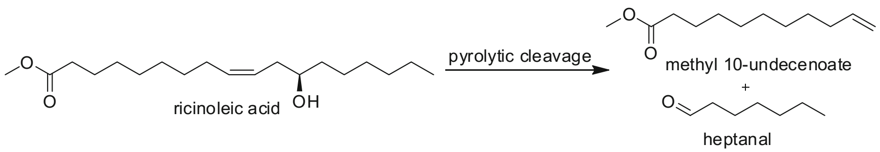


**Fig. 3.11** Pyrolytic cleavage of ricinoleic acid

surfactants, a quantitative conversion of methyl 10-undecenoate in aqueous media was only achieved after 20 h. Furthermore, the multiple hydroformylation of linolenic acid methyl ester and linseed oil is possible with micellar two-phase catalysis.

Also activated charcoal was tested as mass transfer additive for the hydroformylation of methyl oleate in water. Sulfonated triphenylphosphine in combination with a rhodium precursor was used as catalyst in these investigations. After 24 h, the yield of oxo-products is up to 93% under relatively mild conditions in water. Monflier et al. [31] were able to show that there is no loss of catalyst activity within two recycles. The concentration of rhodium and phosphorus in the product phase is less than 0.2 ppm. Further substrates such as technical-grade methyl oleate, methyl 10-undecenoate, or linolenic acid methyl ester are also convertible into oxo-products in high yields with this technique.

Catalyst immobilisation can also be received by use of ionic liquids instead of water as solvent for the catalyst. Suarez et al. [32] examined this approach for a rhodium recycle in hydroformylation of soybean oil. Their reaction system enables quantitative yields for oxo-products applying 100 °C and 40 bar syngas pressure after 8 h if triphenylphosphine is used as additional ligand. Compared to a reaction without ionic liquids, a higher selectivity can be reached in the presence of an ionic liquid due to a catalyst stabilising effect. In the absence of triphenylphosphine, the reaction is distinctly slower, and after 24 h, formation of rhodium nanoparticles is observed. Unfortunately, the loss of rhodium into the product phase is very high (about 20%).

Thinking of industrial applications catalyst stability is an important point. Tulchinsky et al. [33] designed a new class of sulfonated water-soluble phosphine ligands without aryl–phosphorus bonds. Ligands containing aryl–phosphorus bonds tend undergoing alkyl–aryl exchanges through reaction of the phosphine ligand with olefins. Due to the elimination of the possibility of aryl–alkyl exchange, these ligands are pretend to have an improved stability and catalyst life time. Use of the corresponding rhodium complexes leads to aldehyde yields up to 80% in the hydroformylation of soybean methyl esters. Figure 3.12 shows three examples of these ligands.

A process concept for a hydroformylation of oleocompounds with subsequent extraction of the catalyst was developed by Dow Technologies (Fig. 3.13) [34, 35]. The concept is based on water-soluble sulfonated phosphine-modified rhodium catalyst. The first step is a non-aqueous hydroformylation of the starting material. For this reaction, an organic solubilising agent for the catalyst is necessary. This can

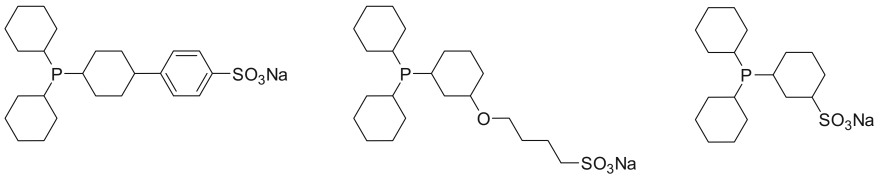


**Fig. 3.12** Water-soluble ligands without aryl–phosphorus bonds

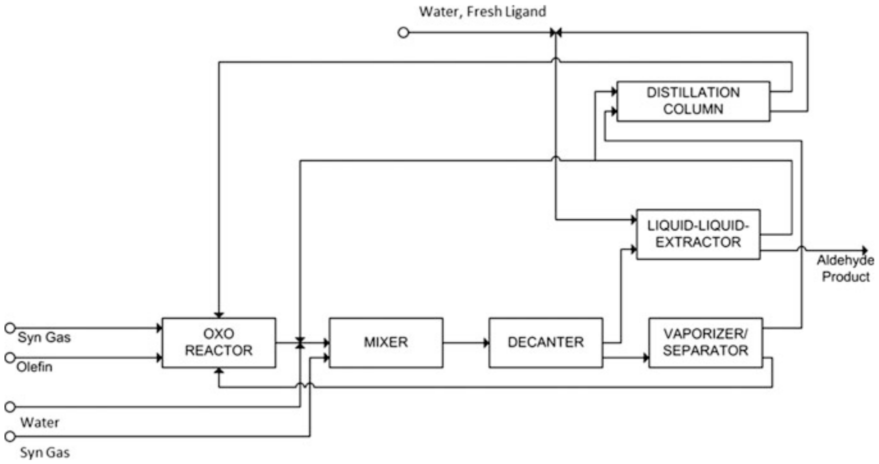


**Fig. 3.13** Process concept for the hydroformylation of oleocompounds [34, 35]

be polar, an organic solvent such as *N*-methyl-2-pyrrolidone or *N*,*N*-dimethylformamide. After reaction, an extraction with water is executed in order to separate the catalyst from the product. After phase separation, the water in the catalyst phase is removed via distillation and the catalyst can be recycled into the reactor. The rhodium concentration in the product phase is lower than 1 ppm.

Recently, our group reported about a new process concept for the conversion of fatty compounds in aqueous thermomorphic solvent systems (TMS-systems). TMS-systems take advantage of the temperature dependent miscibility of a polar, catalyst containing solvent and a non-polar, substrate/product containing solvent. Heating up theses mixtures lead to the formation of one single phase and the reaction takes place homogeneously without mass transport limitations. Cooling down after reaction induces phase separation and the catalyst can be separated from the product via simple decantation. The hydroformylation of methyl 10-undecenoate was chosen as model reaction. The use of a thermomorphic solvent system consisting of water and 1-butanol in combination with a water-soluble rhodium/SulfoXantphos (sulfonated bidentate xantphos-type ligand) catalyst enables very high turnover frequencies of 1500 $h^{-1}$ and a highly regio selective reaction towards the linear hydroformylation product (89%). The catalyst was reusable in three recycling runs. The reaction was also transferred into a continuously operated miniplant to show the applicability of this system for technical approaches (see Sect. 11.3) [36].

### 3.2.3 Applications

Usually, hydroformylation products are not used directly but are converted to more stable and useful bifunctional molecules. Figure 3.14 shows the most common consecutive reactions of hydroformylation products of oleocompounds (see also Chap. 7 for tandem reactions).

Table 3.2 gives an overview about application possibilities of hydroformylated oleocompounds.

Polyhydroformylated triglycerides are mostly hydrogenated to corresponding polyols (Fig. 3.15) [37].

Hydrogenation can be executed either in a one-step process by cobalt-catalysed tandem hydroformylation/hydrogenation sequence or in a two-step process through rhodium-catalysed hydroformylation followed by hydrogenation of resulting aldehydes with Raney nickel. Resulting polyols are used for polyurethane synthesis. Cobalt-catalysed hydroformylation/hydrogenation leads to lower yields of polyols compared to rhodium/nickel catalysis due to double bond isomerisation. Corresponding polyurethanes have different properties. If polyols are synthesised with rhodium/nickel, resulting polyurethanes are rigid. Hard polyurethane rubbers with lower mechanical strength are obtained if cobalt catalysts are applied for polyol synthesis. Often, fatty acid methyl esters are used as substrate for alcohol synthesis. Polymers based on alcohols from oleocompounds can be used for foams, adhesives, elastomers, coatings, and mastics.

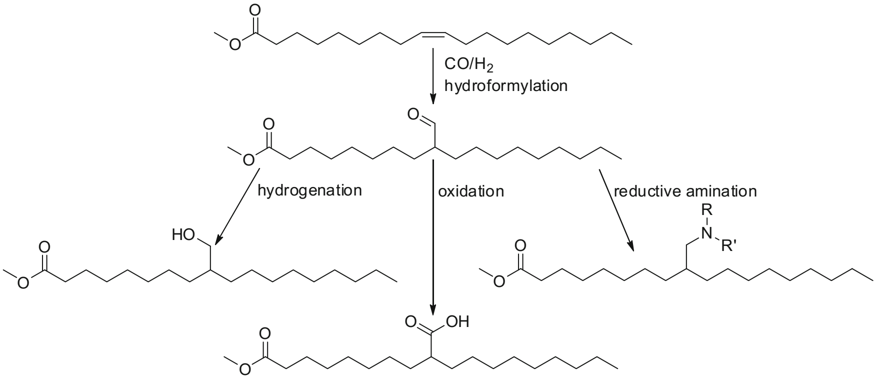


**Fig. 3.14** Consecutive reactions of hydroformylated oleocompounds

**Table 3.2** Possible applications for hydroformylated oleocompounds

| Substrate | Consecutive reaction | Application |
|---|---|---|
| Polyhydroformylated triglycerides | Reduction to the corresponding alcohols | Synthesis of polyurethanes |
| Polyhydroformylated triglycerides, polyhydroformylated fatty acids or methyl esters | Reductive amination | Building blocks for polyamide synthesis |
| Polyhydroformylated triglycerides, polyhydroformylated fatty acids or methyl esters | Oxidation to the carboxylic acid and subsequent esterification | Lubricants |
| polyhydroformylated fatty acids or methyl esters | Reduction to the corresponding alcohols and subsequent esterification with acetic anhydride | Plasticisers |

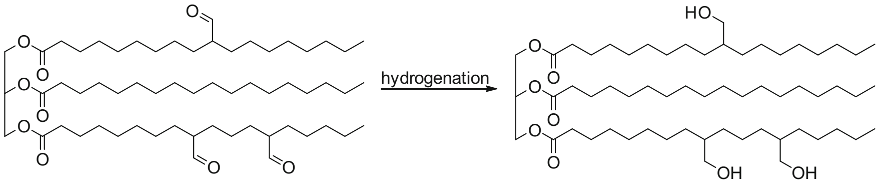
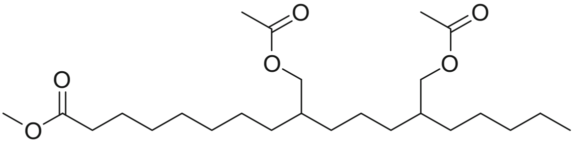


**Fig. 3.15** Example of the synthesis of polyols from hydroformylated triglyceride

**Fig. 3.16** Bio-based plasticiser



Besides polyols, polyamines are synthesised via consecutive reductive amination or hydroaminomethylation of fatty esters, which can be monomers for polyamides. Oxidation of aldehydes to carboxylic acids enables access to polyesters or polyamides.

Hydroformylation of fatty acids or fatty esters allows introduction of side groups in order to gain attractive lubricants. Besides their low toxicity, these bio-based lubricants have several benefits compared to oil-based lubricants such as higher viscosity index, lower volatility, or higher fire resistance.

The product in Fig. 3.16 obtained by esterification of hydroformylated/hydrogenated linolic acid methyl ester with acetic acid is a well-suited plasticiser with higher heat stability and higher tensile strength compared to phthalate diesters. A more detailed overview can be found in the review of Monflier et al. [37].

## 3.3 Terpenes and Naturally Occurring Allylbenzenes

Terpenes and naturally occurring allyl benzenes are a promising renewable olefin source. Their good availability and reasonable price make them attractive as raw material for further functionalisation (see Sect. 1.2). Hydroformylated terpenes can be applied in perfume, flavour, surfactant, or pharmaceutical chemistry. Also use as chiral building blocks is thinkable [38].

### *3.3.1 Catalyst Development*

Clement et al. [39] compared the reactivity of several terpenes with different substituted double bonds and conjugated double bonds (Fig. 3.17) in cobalt-catalysed hydroformylation. They also investigated the influence of the solvents hexane, methanol and 6% aqueous acetone at 150 °C and 250 bar syngas pressure.

Table 3.3 shows the relative reaction rates of the terpenes in different solvents, while the reaction rate of α-pinene in hexane is assigned a value of one.

Limonene shows high hydroformylation activity in all tested solvents. The activity of α-pinene in methanol and 6% aqueous acetone is comparable to limonene. Myrcene and α-terpinene are less active due to their conjugated double bonds which can form less active π–allyl complexes with cobalt. In all cases, complex product mixtures containing alkanes, alcohols, and high boilers are obtained. Multiple hydroformylation was not observed at all.

Himmele and Siegel [40] studied the hydroformylation of α- and β-pinene with rhodium and cobalt catalysts. By use of a cobalt catalysts, (-)-α-pinene is converted to (-)-2-formylbornane (Fig. 3.18) under relative harsh conditions (120 °C, 300 bar). Use of (+)-α-pinene leads to formation of (+)-2-formylbornane.

Rearrangement of the ring structure from the α-pinene to the bornane structure is ascribed to the presence of acidic hydridocarbonyl cobalt species under hydroformylation conditions. If rhodium is used as catalyst, no rearrangement to bornane structure is observed, but an isomerisation of the double bond can occur leading to addition of the formyl group to the outstanding methylene substituent (Fig. 3.19).

The ratio of the products depends on applied pressure ratio of CO and $H_2$ and temperature. While higher temperatures (110 °C), high pressures (650 bar), and high CO/$H_2$ ratios (70/30) shift the product spectrum towards A (Fig. 3.19), lower

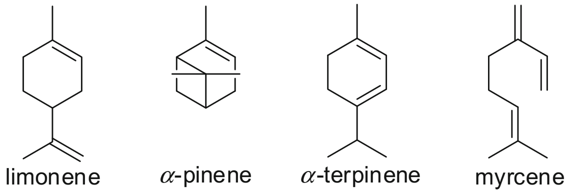


**Fig. 3.17** Terpenes (investigated by Clement [39])

**Table 3.3** Comparison of the reaction rates of several terpenes in hydroformylation [39]

| | Hexane | Methanol | 6% aqueous acetone |
|---|---|---|---|
| α-pinene | 1.0 | 5.0 | 4.8 |
| Limonene | 5.6 | 4.8 | 4.2 |
| α-terpinene | 0.3 | 0.5 | 0.3 |
| Myrcene | 1.1 | 2.3 | 0.3 |

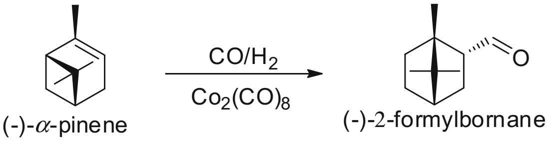


**Fig. 3.18** Cobalt-catalysed hydroformylation of (-)-α-pinene

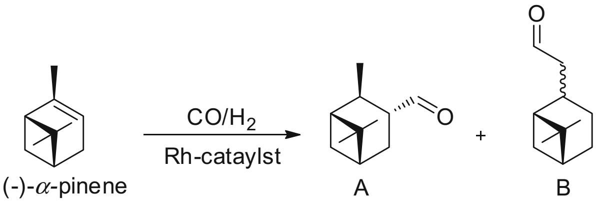


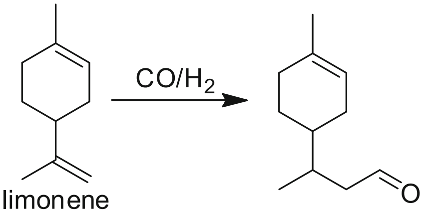
**Fig. 3.19** Rhodium-catalysed hydroformylation of (-)-α-pinene

temperatures (70 °C), lower pressures (350 bar), and lower $CO/H_2$-ratios (50/50) lead to higher amounts of B.

Hydroformylation of limonene (Fig. 3.20) with phosphine- and phosphite-modified rhodium catalysts under mild conditions (90 °C, 14 bar) was reported by van Leeuwen and Robeek [41]. Comparison of different ligands shows strong enhanced catalyst activity in the presence of tris(*o*-*tert*-butylphenyl)phosphite (3.500 $h^{-1}$) compared to triphenylphosphine (100 $h^{-1}$).

Chalchat et al. tested several monoterpenes and sesquiterpenes in rhodium-catalysed hydroformylation under relatively mild conditions. Yields of the hydroformylation products are in the range of 25 and 82% depending in the nature of the terpene (e.g. see Fig. 3.21) [42].

**Fig. 3.20** Limonene hydroformylation



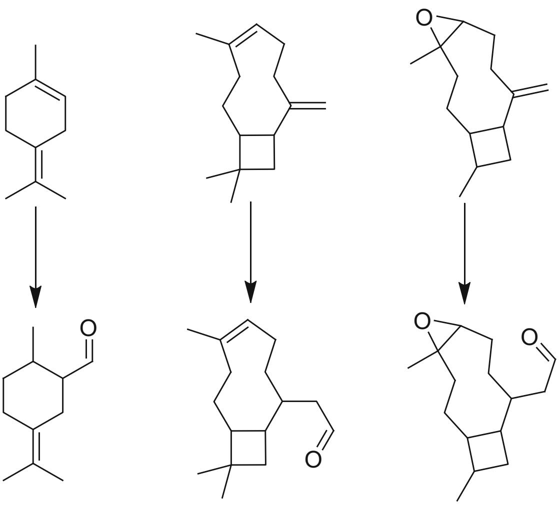


**Fig. 3.21** Terpene hydroformylation from Chalchat et al.

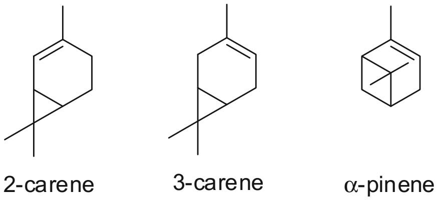


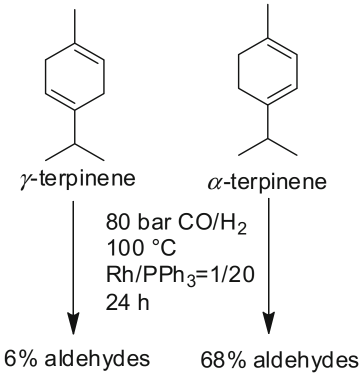
**Fig. 3.22** Examples for sterically encumbered double bonds in terpenes

Hydroformylation of sterically encumbered trisubstituted endocyclic double bonds of terpenes (Fig. 3.22) is a particular challenge.

Dos Santos et al. [43] investigated the influence of different phosphine and phosphite ligands in rhodium-catalysed hydroformylation of these terpenes. If unmodified rhodium precursors are used as catalysts, a high double bond isomerisation rate is observed which leads to complex mixture of alcohols and aldehydes. In the presence of ligands such as triphenylphosphine or triphenylphosphite in high P/Rh ratio (20/1), isomerisation was suppressed but activity in hydroformylation decreases dramatically. This circumstance is traced back to formation of rhodium complexes containing two or three ligands. These complexes are not very active in hydroformylation of these substrates. In contrast, if the bulky phosphite ligand $P(O\text{-}o\text{-}^tBuPh)_3$ is used, double bond isomerisation is reduced and a relatively high activity in hydroformylation is observed even with high P/Rh ratio of 20/1. Due to ligands large cone angle rhodium complexes containing only one ligand are mainly formed.

If monoterpenic multiple unsaturated olefins are used as substrates, conjugation of double bonds leads to a different activity for hydroformylation. In case of myrcene, uncommon effects in terms of reaction conditions are observed. High concentrations of ligand, high basicity of ligand, and high pressures of CO and $H_2$

**Fig. 3.23** Monoterpenic endocyclic dienes



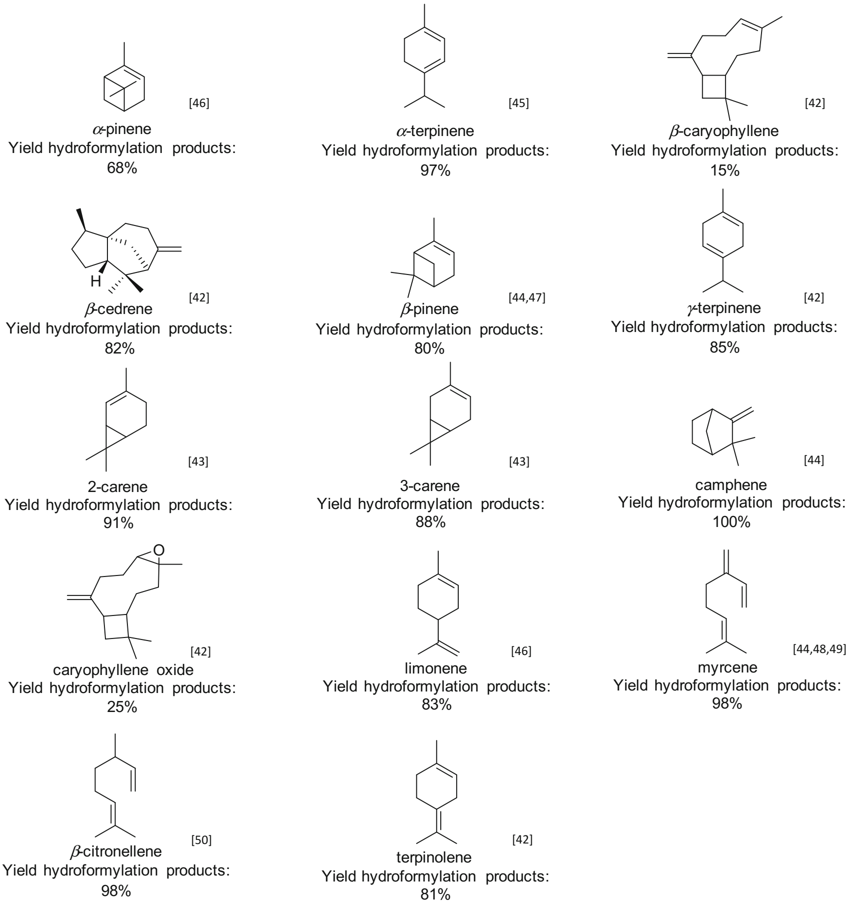


**Fig. 3.24** Hydroformylation of estragole

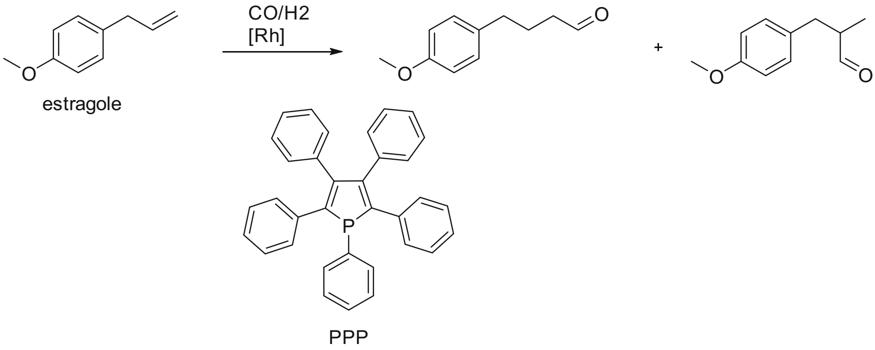


**Fig. 3.25** Overview of the hydroformylation of several terpenes

accelerate the hydroformylation reaction. These results lead to the assumption that conversion of less active $\eta^3$-allyrhodium intermediates into $\eta^1$-complexes is a critical step in myrcene hydroformylation. This effect is not observed if endocyclic conjugated dienes like α-terpinene are used as substrate. Non-conjugated monoterpenic endocyclic dienes are less reactive compared to conjugated ones (Fig. 3.23) [44, 45].

Figure 3.24 gives an overview about the hydroformylation of several terpenic substrates.

Also the hydroformylation of naturally occurring allylbenzenes leads to interesting products. Dos Santos et al. investigated the ligand influence in the rhodium-catalysed hydroformylation of estragole (Fig. 3.25). By application phosophole ligand PPP (Fig. 3.25), the regio selectivity for hydroformylation in the terminal position is 78% (aldehyde yield 96%). Similar results are obtained with triphenylphosphine (regio selectivity 75%; aldehyde yield 97%) (Fig 3.24).

Thinking of applications for functionalised terpenes in perfume or pharmaceutical industry, stereo- and diastereoselective hydroformylation is from great interest. In this context, Kóllar and co-workers [51] examined the hydroformylation of chiral terpenes (+)-*R*-limonene and (-)-*R*-carvone with platinum/tin catalysts and bidentate phosphine ligands (Fig. 3.26). Diastereoselectivity is controllable by choice of ligand. Highest selectivities towards one diastereomer are observed by using a catalyst system consisting of $PtCl_2$((+)-bdpp) and $SnCl_2$.

Kóllar also compared rhodium and platinum/tin catalysts in asymmetric hydroformylation of several mono- and sesquiterpenes. In all cases, rhodium catalysts provide higher activities in hydroformylation while platinum/tin system is slightly more diastereoselective. The nature of the hydroformylated substrate has a high influence on stereoselectivity. Bicyclic terpenes provide distinctly higher diastereoselectivities. Best results are obtained if (+)-β-cedrene is converted with a $[Rh(NBD)Cl]_2/PPh_3$ catalyst system (Fig. 3.27) [52].

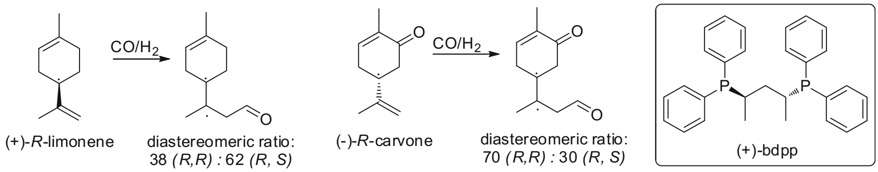


**Fig. 3.26** Diastereoselective hydroformylation with Pt/Sn catalysts

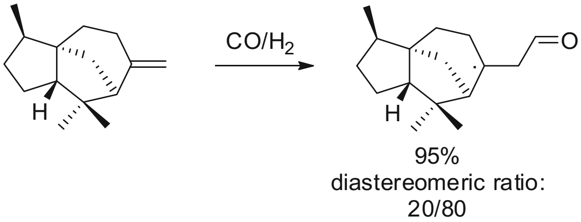


**Fig. 3.27** Rhodium-catalysed hydroformylation of (+)-$\beta$-cedrene

High diastereoselectivities in hydroformylation of (+)-$\beta$-pinene (up to 99%) and camphene (up to 82%) are reached if bimetallic cobalt/rhodium or platinum/tin catalysts are used at 100 °C and 60 bar [48, 53].

### 3.3.2 Catalyst Recycling

Catalyst recycling in terpene and allyl benzene hydroformylation is a challenging task. Due to the high boiling points of the hydroformylation products, separation via distillation in the presence of the catalyst can induce formation of by products or catalyst deactivation. Consequently, alternative catalyst recycling strategies like catalyst immobilisation in liquid phase or on a solid carrier have to be applied to regain the valuable catalyst.

Dos Santos and co-workers [54] pursued the approach of aqueous biphasic hydroformylation as a recycling concept in terpene hydroformylation. Resulting product phase can easily be separated by simple decantation after reaction. Toluene is used as non-polar solvent and additionally the cationic surfactant cetyltrimethylammonium chloride (CTAC, Fig. 3.28) is used as phase transfer

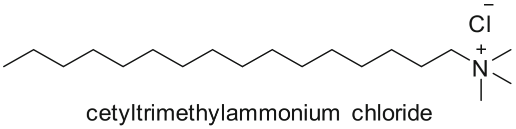


**Fig. 3.28** Cetyltrimethylammonium chloride (CTAC)

agent. A water-soluble sulfonated triphenylphosphine-modified rhodium complex is utilised as catalyst.

The authors determined coherence between nature of the terpene and required amount of surfactant. For conversion of myrcene with the additive CTAC, a strongly promoting effect in hydroformylation is described. In the presence of CTAC in a concentration of 25 mM, a conversion of 96% is observed. Without surfactant, no reaction is observed. For limonene, lower CTAC concentrations of 2.5 mM appear to be optimal under applied conditions resulting in a conversion of 86%. In case of camphene as substrate, CTAC even causes an inhibition in hydroformylation. Best results of 71% conversion are obtained in the absence of surfactant. In a later study, scope was extended to citronellene [55].

The biphasic hydroformylation of different naturally occurring allylbenzenes was done by Baricelli et al. [56]. A mixture of toluene and water was used as reaction medium in combination with CTAC as phase transfer agent. For the conversion of eugenol, estragole, safrole, and *trans*-anethole (Fig. 3.29), rhodium and ruthenium catalysts modified with TPPTS or TPPMS (monosulfonated triphenylphosphine) were applied. Reaction performances of both ligands in rhodium-catalysed hydroformylations are comparable, although TPPMS leads to slightly higher chemo selectivity for the hydroformylation. High aldehyde yields in the hydroformylation of eugenol (92%), estragole (72%), and safrole (70%) are obtained with rhodium catalysts. Aldehyde yield in the conversion of *trans*-anethole (31%) is lower due to its internal double bond. If ruthenium is used as catalyst metal, harsher conditions are necessary (100 °C and 62 bar instead of 80 °C and 20 bar). While results in the Ru-catalysed conversion of eugenol are comparable to the ones achieved with rhodium catalysts, conversion rates of safrole, estragole and anethole are lower. The rhodium catalyst can be recycled four times. In case of ruthenium, the catalyst activity in the first recycling experiment was even higher compared to that of the initial run, because the catalytically active species is already

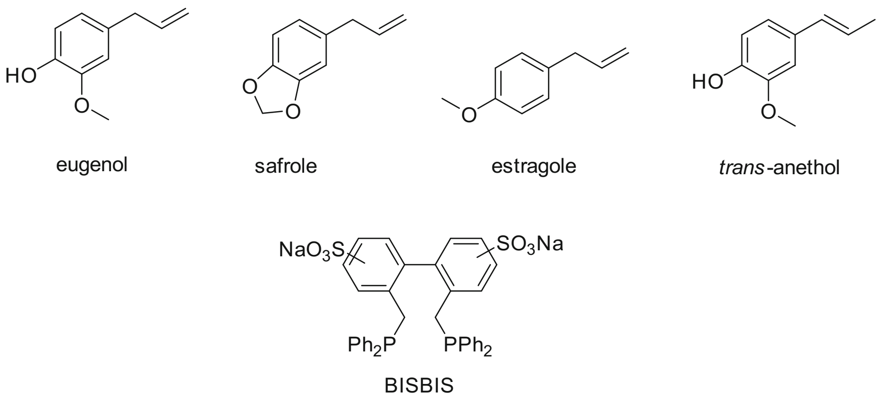


**Fig. 3.29** Different allylbenzenes in biphasic hydroformylation [56]

formed in the recycling experiment. Unfortunately, a second catalyst recycle was not possible.

Application of bidentate ligands in rhodium-catalysed hydroformylation of these substrates in biphasic mixtures strongly influences the regio selectivity in this reaction [57]. If BISBIS is applied, regio selectivity in the hydroformylation is up to 92%.

Dos Santos et al. [58] also investigated catalyst immobilisation on a solid support. They anchored a rhodium/TPPMS catalyst complex in a commercially available anion exchange resin. This catalyst shows reactivity comparable to conventional homogeneous rhodium systems in the hydroformylation of eugenol and estragole and can be reused several times.

## 3.4 Conclusions

Oleocompounds and terpenes are attractive renewbale starting materials in hydroformylation reactions, and resulting products have interesting properties and a wide application area. For industrial applications, robust processes have to be developed. In particular, recycling of the expensive noble metal catalysts and long catalyst life times have to be guaranteed for an economic hydroformylation process. Several good approaches are already been made, but all approaches lack an application in a continuous set-up.

Resulting aldehydes often are useful intermediates. If consecutive reactions can be realised in effective tandem reaction sequences including the hydroformylation step, application of hydroformylation of renewables can gain importance for industrial applications due to reduction of production costs (e.g. lower investment costs if only one reactor is needed, no costs for purification of intermediates). Hydroaminomethylation, for example, could be an elegant way to synthesise surfactant precursors if terpenes are used as substrates or polymer precursors if fatty acids are the starting material.

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