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Phosphorus-Free Nitrogen-Containing Catalytic Systems for Hydroformylation and Tandem Hydroformylation-Based Reactions

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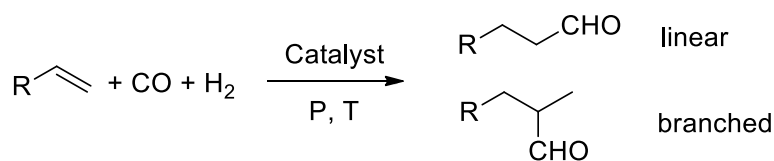
Abstract

Hydroformylation is an important industrial process applied for the production of many highly-demanded chemicals. For now, only the Co/phosphine, Rh/phosphine, or ligand-free systems are used in industry. Although most of the research dealing with hydroformylation also considers systems with phosphorus-containing ligands or heterogeneous materials, the interest in developing phosphorus-free nitrogen-containing systems tends to grow during the last decade. N-ligands can be easier to synthesize, more stable towards oxidation, and at the same time add some useful features, such as the higher activity in the tandem hydroformylation-based reactions. The review is focused on the progress made in the design of N-ligands for homogeneous and biphasic hydroformylation of unsaturated compounds, as well as N-containing heterogeneous catalysts for the process. In addition, the data on tandem reactions, such as reductive hydroformylation and hydroaminomethylation, are systematized and discussed.

1. Introduction

Hydroformylation reaction discovered by Otto Roelen in 1938 is of great importance for industrial organic synthesis nowadays [1]. The rapid growth of the polymer and detergent industries in the 1950s caused a demand for higher alcohols, and hydroformylation followed by

hydrogenation of available olefins has become the main route to obtain them. This transition-metal-catalyzed reaction is the interaction of syngas with double bonds of unsaturated hydrocarbons, which occurs with 100% atom efficiency and gives linear and branched aldehydes:



Scheme 1. Hydroformylation reaction.

Alcohols are typically produced by oxo-synthesis in which the hydroformylation stage is followed by aldehyde hydrogenation or aldol condensation–hydrogenation sequence, depending on the type of initial olefin. Most of the large-tonnage processes are aimed at the conversion of propylene and higher olefins to butanols, 2-ethyl-1-hexanol, and higher alcohols. These chemicals are of great demand as solvents and in the production of polymer plasticizers, synthetic detergents, and fuel and lubricating oil additives. Moreover, intermediate aldehydes are used as reactants to obtain other chemicals, such as carboxylic acids and esters. The annual global oxo-synthesis production capacity currently reaches 14 million tons in a product range of more than 50 items [1–3].

Hydroformylation is an example of the largest industrial application of homogeneous catalysis. It is also reasonably considered as a key reaction for developing novel processes, which will have such advantages as high chemo- and regioselectivity combined with easy catalyst separation and the possibility of involving new types of raw materials. One of the most promising trends in the field is the design of one-pot, in particular, tandem (or domino), hydroformylation-based reactions, in which desired products can be obtained using one loading of reactants in a single reactor [4]. Among such tandem reactions are hydroformylation–hydrogenation (also known as reductive hydroformylation, or hydrohydroxymethylation), hydroaminomethylation, hydroformylation–acetalization, and some others.

It is to be noted that, for successful application in hydroformylation and tandem reactions, the properties of catalytic systems should be fine-tuned. For this purpose, modifying ligands are widely used. The most commonly used type of ligands in hydroformylation is phosphorous-containing ones. Since they have strong σ -donor and π -acceptor properties, as well as steric effects, metal complexes with ligands of this type have high activity and ensure high regioselectivity of the reactions [1]. Along with homogeneous and biphasic [5] catalysts, attempts were also made to create polymeric phosphorus-containing materials [6,7] and heterogeneous [8,9] systems for catalysis of hydroformylation.

However, phosphorus-containing ligands have a number of disadvantages, such as their tendency to oxidation and hydrolysis, as well as the difficulty of their synthesis [1]. In addition, their rhodium complexes are insufficiently active in hydrogenation of aldehydes and, therefore, cannot ensure one-step conversion of olefins to alcohols. This is why, every now and then, there has been interest in studying catalytic systems with ligands containing other heteroatoms.

There is currently an emerging trend toward the creation and research of phosphine-free nitrogen-containing catalytic systems (Fig. 1).

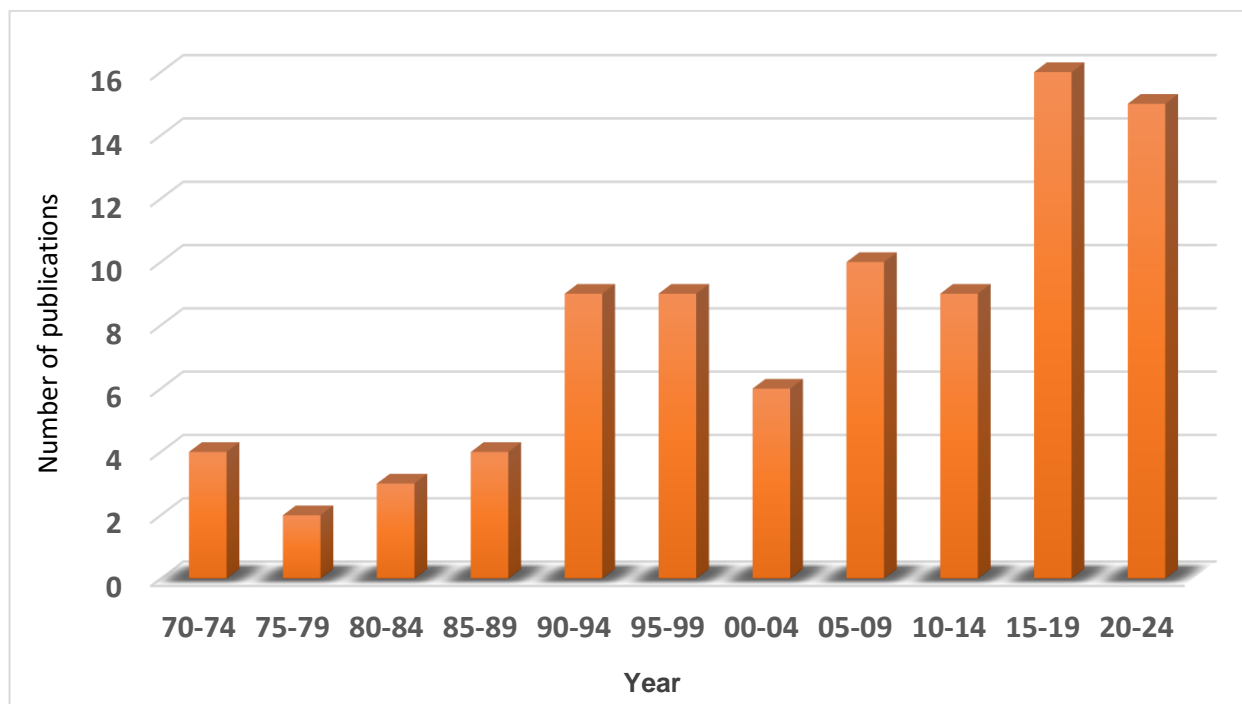


Fig 1. Number of new publications on hydroformylation in phosphorus-free N-containing systems in every 5 years since 1970.

Being rigid strong σ -donor ligands, they practically do not exhibit the π -back-donation effect [10]. These results in high lability of N-ligand metal complexes, and under catalytic conditions, such complexes tend to dissociate to form a range of particles of different types, including catalytically active ones. To the best of our knowledge, the information on the use of nitrogen-containing ligands in hydroformylation and tandem hydroformylation-based reactions has not been systematized so far. This review includes an analysis and description of works on these topics. Here, we considered various approaches to the creation of homogeneous, biphasic, immobilized, and heterogeneous nitrogen-containing catalytic systems based on Rh, Ru, and Co, as well as bimetallic systems, fields of their application, the effect of various factors on the activity and stability of catalytic systems, and discussed the advantages, disadvantages, and prospects in this area.

Although the review is focused on hydroformylation in the presence of catalysts with phosphorus-free nitrogen-containing ligands, it should be mentioned that many interesting results were also obtained using P–N systems, with P and N in one [11–17] or two different ligands [18,19]. In most cases, under reaction conditions, the active metal is bound only to the phosphorus atom [12], and the nitrogen atom does not directly affect the metal site. The functions of nitrogen-containing fragments in such systems can be different. They can enhance the activity of the system by electronic effects on the P atom [12–14,20,21] or serve for easier separation of the complex by extraction into a polar phase [22–24] or precipitation [18]. Diphosphorus ligands with a direct P–N bond on one of the P atoms were designed for asymmetric hydroformylation [15,25–27], in the best cases with *ee* >70% [15]. Another interesting approach to hydroformylation is the design of self-arranged systems, where two different P,N-containing molecules act as a bidentate phosphine ligand [16,17,28,29]. They can be bound to each other by hydrogen bonds between nitrogen-containing fragments [16,17] or by coordination between nitrogen and a metal atom [28,29]. Nitrogen fragments can also be useful for the molecular recognition of acidic unsaturated substrates for selective hydroformylation [30,31]. Finally, the P–N systems can catalyze tandem processes, such as hydroformylation–hydrogenation [32–35]. However, in all these cases, the main role is played by phosphorus, which is responsible for the stability and selectivity of a catalytic system in hydroformylation, so we did not consider such systems here. The other interesting sphere that was not discussed in this review is hydroformylation with N-heterocyclic carbene complexes. In most cases, they do not contain a Metal–N bond in their structure. The information about carbene complexes in hydroformylation was summarized elsewhere [36–38].

2. Hydroformylation of Olefins Using Catalytic Systems with N-Ligands

Starting this section, we should note that the mere fact of successful hydroformylation in the presence of complexes of cobalt, ruthenium, and especially rhodium with nitrogen-containing ligands does not suggest that the ligands in this system play a significant part. Such complexes are precursors of active forms of a catalyst and may decompose in the course of the reaction. Homogeneous systems containing complexes of rhodium in the oxidation state +1 with lability sufficient to form rhodium carbonyl hydrides under the syngas pressure are highly likely to be active in hydroformylation of olefins. Thus, for homogeneous systems, of particular interest is the effect of a ligand on the hydroformylation regioselectivity, which can be considered a sign of the direct participation of the complex with the nitrogen-containing ligand in the catalytic run, and also on the activity of the system because ligands can both increase and decrease it. There are additional issues concerning reactions occurring under biphasic or heterogeneous catalysis conditions, for which of special importance is how well a water-soluble ligand or a solid support

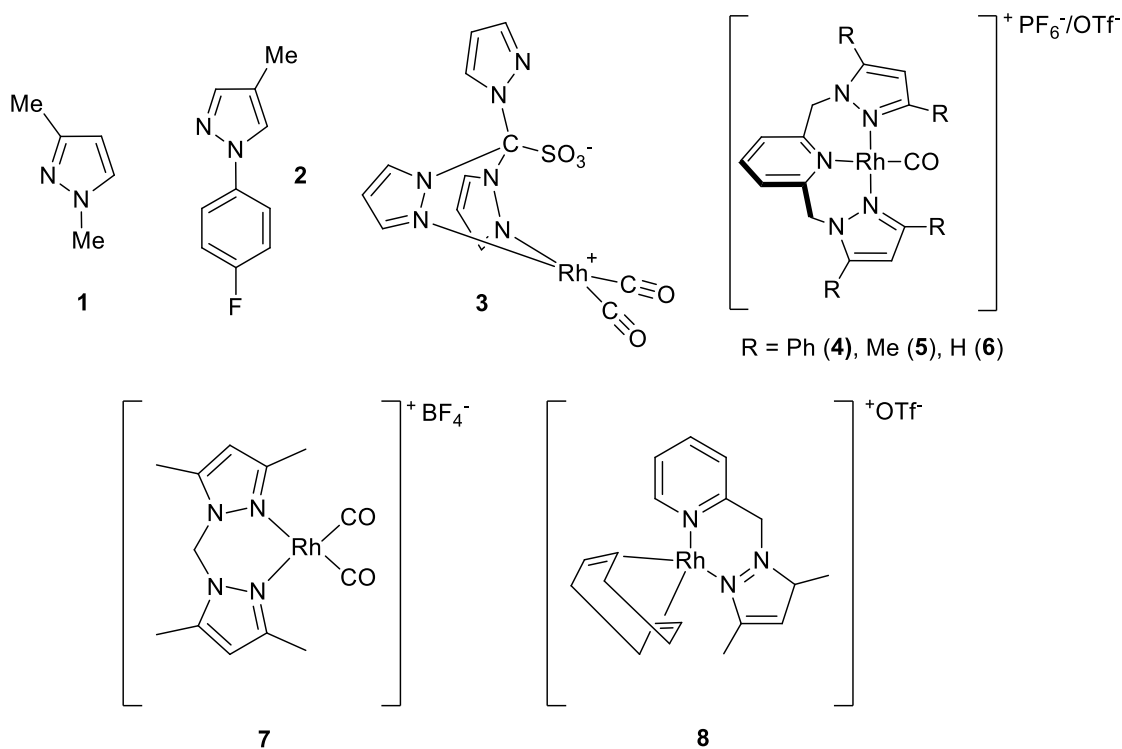
is bound to an active metal, and whether or not these compounds are stable enough to ensure a simple and efficient procedure of separation of a catalyst and a product. This section considers homogeneous, biphasic, and heterogeneous catalytic systems studied in hydroformylation to obtain aldehydes as end products. Tandem reactions, in which the role of a nitrogen-containing ligand is somewhat different, are described in Section 3.

2.1. Homogeneous Systems

The most widely used ligands for homogeneous rhodium catalytic systems are phosphorus-containing ones. Most of the phosphorus-containing ligands favor the preferential formation of products with the normal structure, and also increase the activity of the system within certain limits. At the same time, too much excess of a phosphine ligand decelerates the reaction [39]. This section considers the effect of nitrogen-containing ligands on these parameters in homogeneous hydroformylation.

Most of the works on this subject used rhodium complexes with ligands containing an imine group, a pyridine ring, or a pyrazole ring. These compounds contain a nitrogen atom in the sp^2 -hybridization with a lone electron pair, which can participate in complex formation. One ligand often contains two or more nitrogen atom for stronger binding of rhodium.

Table 1 presents the efficiency of rhodium pyrazole complexes **1–8** (Scheme 2) in hydroformylation.



Scheme 2. The structures of ligands and complexes **1–8**.

Table 1. Homogeneous hydroformylation with ligands and complexes **1-8**.

Complex	Substrate	Conditions	TOF ^a , h ⁻¹	Maximum yield of aldehydes	<i>n</i> - : <i>iso</i> - (max. yield)	Reference
2 /[1Rh(CO) ₂ Cl] 2 (1 : 2)	Styrene	2.5 MPa, 50°C, toluene	7 h ⁻¹	29% (4 h)	0.2	[40]
1 / [Rh(CO) ₂ Cl] ₂ (1 : 2)	Styrene	2.5 MPa, 60°C, supercritical CO ₂	25 h ⁻¹	100% (4 h)	0.1	[40]
3	1-Hexene	4.0 MPa, 60°C, acetone	67 h ⁻¹ , (20%)	72% (40 h)	2.4	[41]
4	1-Octene	4.0 MPa, 75°C, toluene	153 h ⁻¹ (84%)	92% (16 h)	0.9	[42]
5	1-Octene	2.0 MPa, 75°C, toluene	131 h ⁻¹ (71%)	96% (16 h)	0.9	[42]
6	1-Octene	3.0 MPa, 75°C, toluene	135 h ⁻¹ (12%)	72% (16 h)	1.8	[42]
8	1-Octene	2.0 MPa, 75°C, toluene	2 h ⁻¹	1% (16 h)	n/a	[42]
7^b	1-Octene	0.5 MPa, 85°C, THF	13 h ⁻¹	25% (3 h)	1.5	[43]

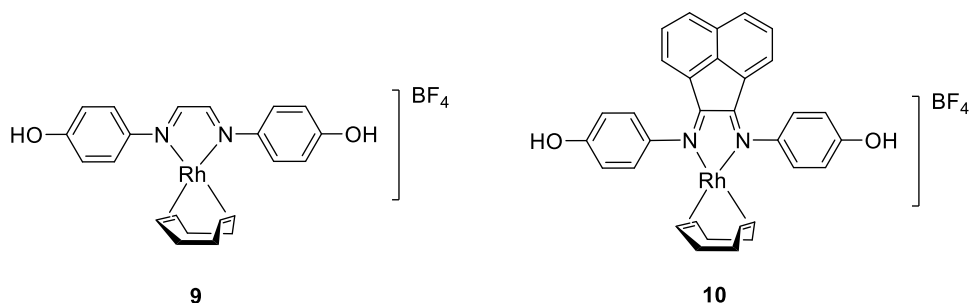
Here and further, the TOFs of aldehyde formation are given (unless otherwise stated). ^a In brackets, the aldehyde yields at which the TOFs were calculated are given (if not calculated at maximum yield). ^b It is not clear enough if the authors gave the yields or selectivities, so the real aldehyde production TOF could be a little lower (about 10 h⁻¹).

The most efficient complexes in this series were those synthesized by Gamede et al. [42], which contain not only pyrazole fragments, but also pyridine ones. Nonetheless, the regioselectivity of reactions using these catalysts at high conversions was approximately the same as that for rhodium catalysts without specific ligands (the *n*- : *iso*- ratio for C₉ aldehydes was about 1 : 1) [44]. Investigation of systems with ligands **5** and **6** showed that, unlike the rhodium complex with ligand **5**, the rhodium complex with ligand **6** was inactive in toluene; however, supercritical CO₂ as a reaction medium ensured 100% conversion of styrene. This system was successfully used for hydroformylation of other unsaturated substrates with both aromatic, and alifatic substituents. Systems with other pyrazole ligands in which the *sp*³-nitrogen of the pyrazole ring was nonalkylated were inactive in both studied reaction media. Complex **7** proved to be much less

active in hydroformylation of hexene than its phosphine-containing analogs synthesized in the same work [43], in which one CO ligand was replaced by phosphine or phosphite.

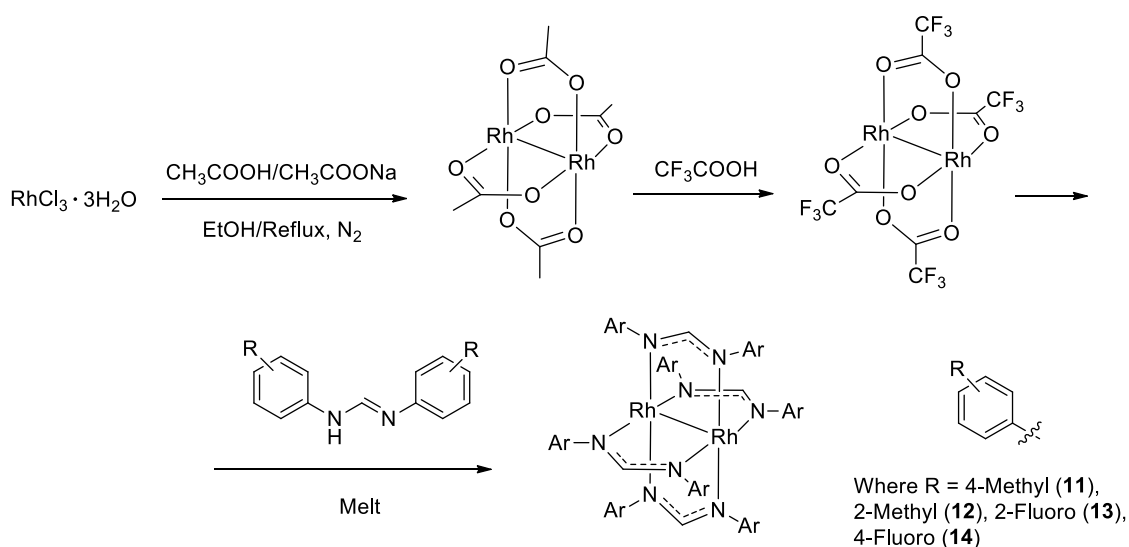
Kläui et al. [43] synthesized a water-soluble rhodium complex with Tpms (**3**), which, however, under the conditions of hydroformylation in an aqueous medium decomposed to form metallic rhodium. Nonetheless, the complex was successfully used in other solvents: hydroformylation of 1-hexene was particularly efficient in acetone, with the *n*- : *iso*- ratio being sufficiently high (2.4). Interestingly, the substitution of one CO for phosphine ligands significantly decreased the yields of aldehydes. Kläui et al. studied the catalytic system with complex **3** after 16-h reaction by NMR and IR spectroscopy, and detected that the solution contained a trivalent rhodium complex, $\text{TpmsRh}(\text{CO})(\text{COC}_6\text{H}_{13})_2$, which was also active in hydroformylation.

In complexes **9** and **10** [45], rhodium is coordinated to the imine nitrogen atoms (Scheme 3). Both complexes were active in hydroformylation of 1-octene at 75°C and 4.0 MPa (TOF = 327 and 317 h⁻¹). The yields of aldehydes were about 70% with an *n*- : *iso*- ratio of 2.3.



Scheme 3. The structures of complexes **9** and **10**.

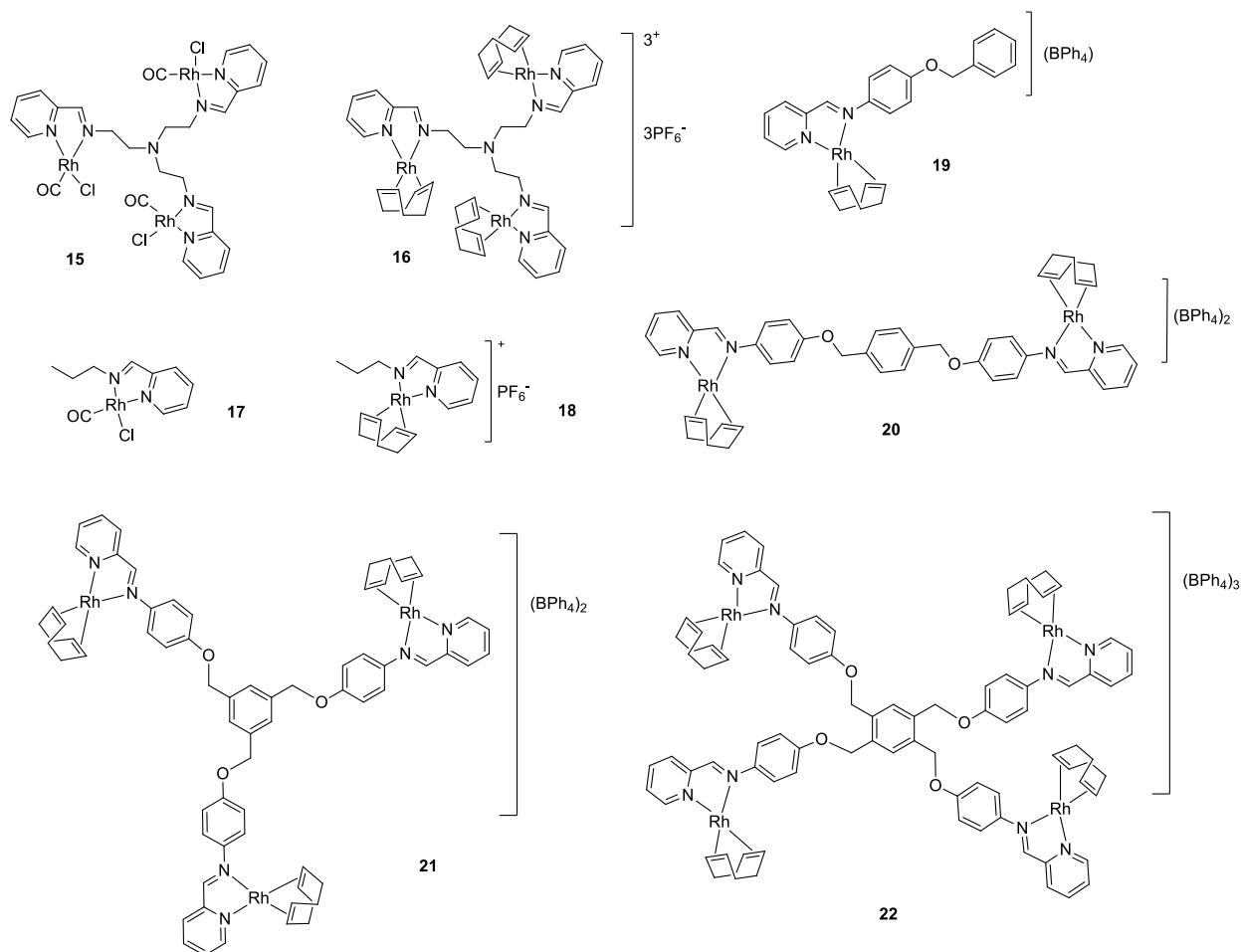
Dirhodium complexes with diphenylformamidine ligands were synthesized, in which rhodium was in the oxidation state +2 (Scheme 4) [46].



Scheme 4. The synthesis of complexes **11-14**.

All the systems containing complexes **11–14** were active in hydroformylation of 1-octene. In 4 h of the reaction (5.0 MPa, 95°C), the yields of C₉ aldehydes proved to be as high as 87% (TOF = 545 h⁻¹) using complex **11** and about 60% (TOF = 360–375 h⁻¹) using complexes **12–14**. The regioselectivity was highest for the reaction in the presence of complex **13** with the *ortho*-fluorosubstituted ligand (*n*- : *iso*- = 2.5), whereas the *para*-fluorosubstituted ligand ensured a much lower *n*- : *iso*- ratio of 1.9 at a similar total yield of aldehydes. Complex **12**, which has a methyl substituent in the same position as the fluorine in complex **13**, also caused lower regioselectivity (*n*- : *iso*- = 1.8). Thus, one can assume that the selectivity of the reaction toward *n*-products is affected by both steric, and electronic properties of diphenylformamidine ligands.

A number of rhodium complexes with iminopyridyl ligands were obtained by Makhubela et al. [47] and October and Mapolie [48] (Scheme 5). The main purpose of both of those works was to produce dendrimeric complexes containing several rhodium sites, but their low-molecular-weight analogs were also tested for hydroformylation.



Scheme 5. The structures of complexes **15–22**.

Table 2 presents the results of experiments on hydroformylation of 1-octene using these complexes.

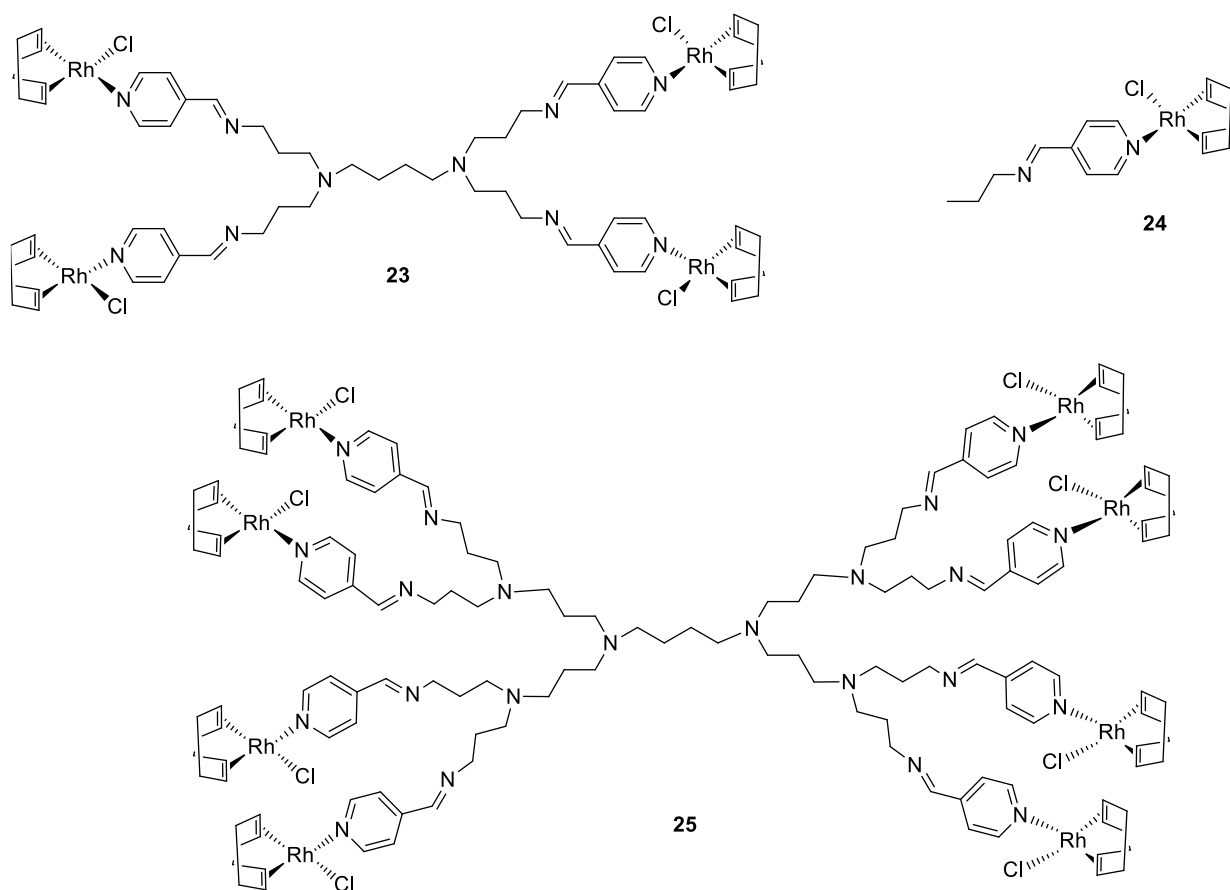
Table 2. Homogeneous hydroformylation of 1-octene with complexes **15-22**.

Complex	TOF, h ⁻¹	Yield, %	<i>n</i> - : <i>iso</i> -	Reference
15	320	88	15.7	[47]
16	200	85	2.1	[47]
17	273	89	0.9	[47]
18	261	84	0.7	[47]
19	92	37	2.2	[48]
20	143	58	2.2	[48]
21	71	28	2.2	[48]
22	127	51	2.2	[48]

Conditions: 75°C, 3.0 MPa, 8 h; TOF was calculated for rhodium atoms.

The environments of rhodium in these complexes are similar; however, complexes of the first group, which have no benzyl substituents at the imine nitrogen atom, turned out to be much more active in hydroformylation of 1-octene. The reaction with the participation of complex **15** also had high regioselectivity: under similar conditions for the classical precursor Rh(acac)(CO)₂ with a yield of C₉ aldehydes of 92%, the *n*- : *iso*- ratio was only 0.9 [49]. Dendrimeric complex **16** also favors the formation of the *n*-product to a greater extent than low-molecular-weight complexes **17** and **18**. Ruthenium complexes with the structure similar to that of complexes **19–22** were tested for hydroformylation under harsher conditions (120°C, 4.5 MPa), but their productivity was much lower than that of their rhodium analogs (TOF = 1.7–5.3 h⁻¹).

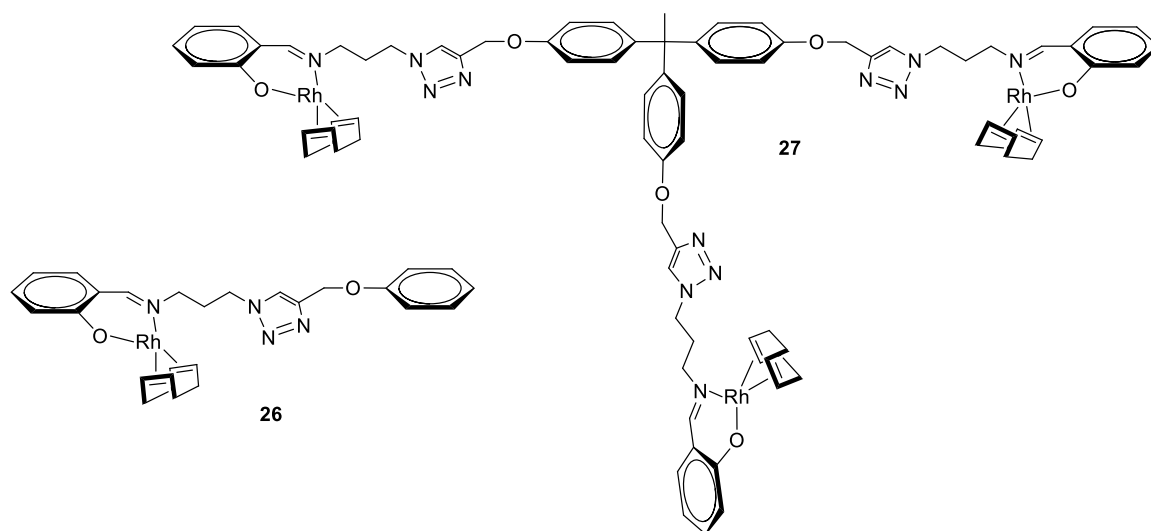
The ligands used to form complexes by Antonels et al. [49] also contain an imine group and a pyridine group, but the difference in their relative position leads to the fact that rhodium is coordinated only to the pyridine nitrogen (Scheme 6) as shown by NMR spectroscopy data.



Scheme 6. The structures of complexes **23–25**.

Under similar conditions (75°C, 3.0 MPa, 8 h), hydroformylation of 1-octene in the presence of complexes **23–25** occurred with a yield of aldehydes of 57–69% with an *n* : *iso*- ratio of 2.5–2.7 (TOF = 162–195 h⁻¹), and no significant increase in the regioselectivity was observed in going from low-molecular-weight complex **25** to dendrimers **23** and **24**.

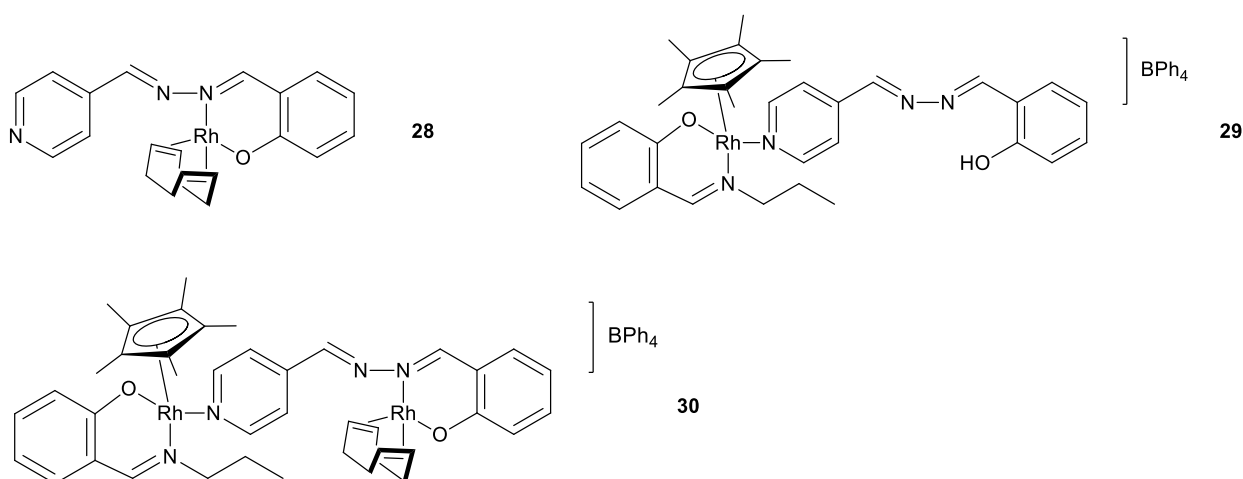
Salicylaldimine complexes of rhodium, in which the rhodium site is chelated by the nitrogen and oxygen atoms, were investigated in a number of studies of biphasic hydroformylation (Section 2.2); however, Siangwata et al. [50] used complexes of such a type in a homogeneous system using another promising catalyst separation method—membrane nanofiltration. For these purposes, complexes **26** and **27** were obtained (Scheme 7).



Scheme 7. The structures of complexes **26** and **27**.

Hydroformylation of 1-octene in the presence of complex **26** with a substrate : rhodium ratio of 2700 : 1, a temperature of 75°C, and a syngas pressure of 4.0 MPa, the selectivity toward aldehydes was 77% (n - : iso - = 1.22). Both complexes were successfully used in five consecutive reactions without a significant decrease in the yield of aldehydes. The regioselectivity of the reaction under most of the tested conditions at relatively high yields was characterized by an n - : iso - ratio of about 1 : 1 and less. Addition of mercury to the catalytic system with precursor **26** (“mercury poisoning test”) decreased the yield of aldehydes by approximately 40%, based on which it was concluded [50] that the activity of the catalytic system is at least partially caused by the presence of rhodium nanoparticles.

In another study of salicylaldimine complexes of rhodium [51], complexes **28–30** were synthesized and used in hydroformylation (Scheme 8).

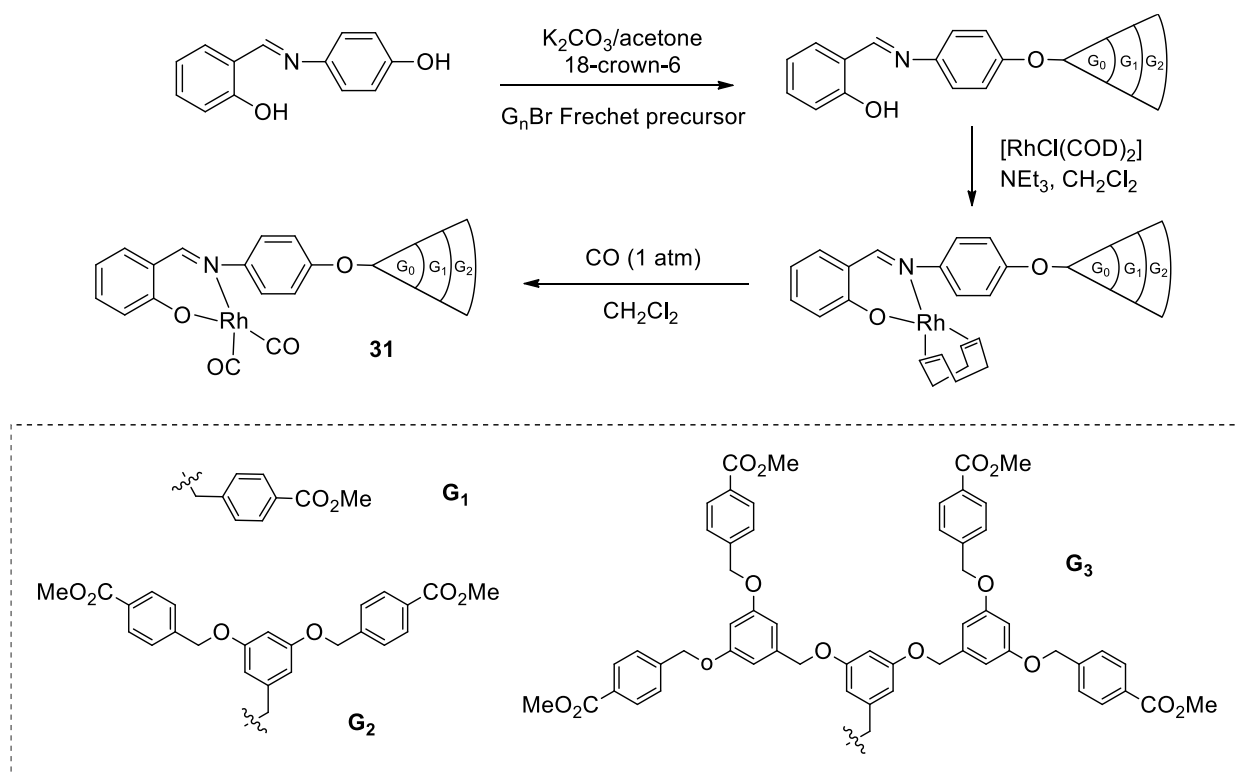


Scheme 8. The structures of the complexes **28–30**.

In complexes **28** and **29**, the rhodium atoms are in the oxidation states +1 and +3, respectively, whereas complex **30** contains two rhodium atoms in different oxidation states. All

the three complexes were active in hydroformylation of 1-octene. In the reaction at 3.0 MPa and 75°C, precursor **28** ensured a yield of nonanals of 88% (n - : iso - = 1.3), which corresponds to TOF = 245 h⁻¹. The activity of the system with complex **29** under the same conditions was by a factor of approximately 1.5 lower. In the system containing two rhodium atoms in different oxidation states (complex **30**), the yield of aldehydes reached 76% in 4 h (n - : iso - = 1.5). Calculation of the TOF per equivalent of rhodium gave 475 h⁻¹, which is much higher than that in the monorhodium systems.

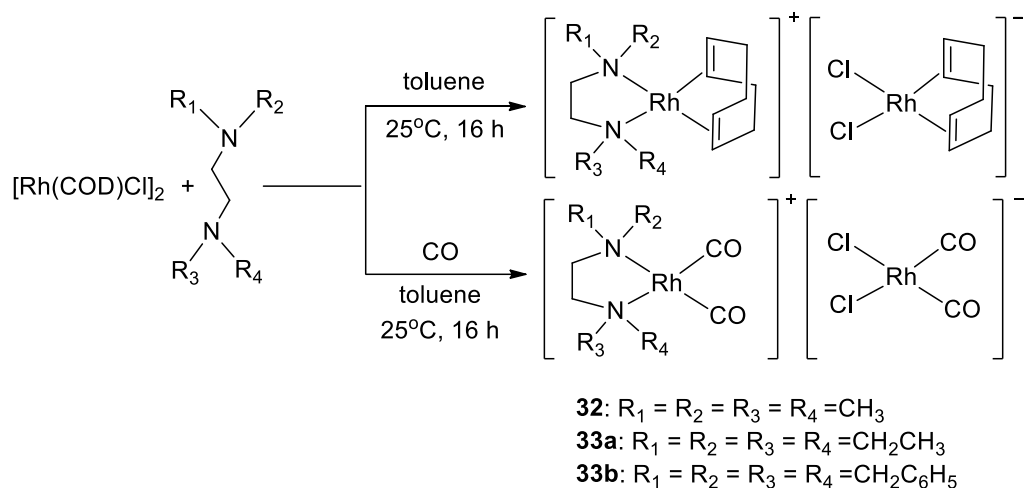
A series of organometallic dendrons with N,O-salicylaldimine entities at the focal point (Scheme 9) was developed. [52] Rhodium carbonyl complexes based on dendrons (G0, G1, G2) demonstrated high activity and chemoselectivity in hydroformylation of 1-octene (4 h, 75°C, 4.0MPa, yield of aldehydes >99%, TOF = 591 h⁻¹). The n : iso - ratio at high conversions to aldehydes was in the range 0.8–1.4. Besides, the catalyst precursor Rh(CO)₂G₀ (**31**) was active in hydroformylation of a number of substrates: styrene, 7-tetradecene, methyl oleate, triolein, D-limonene, and *R*-citronellal. The chemoselectivity toward aldehydes in the case of tetradecene, methyl oleate, triolein, and D-limonene was quite high (86–100%). Mercury poisoning test showed that the catalysis performed by this system is a combination of homogeneous and heterogeneous catalysis (the addition of mercury drops to the system decreased the activity of the catalyst); i.e., the system contains not only rhodium complexes, but also metal nanoparticles.



Scheme 9. Synthesis of the organometallic dendrons with Rh(I) N,O-salicylaldimine complexes.

Borole and Chaudhari [53] carried out hydroformylation of vinyl acetate using precursors containing various hydroformylation-active metals and ligands. In particular, this reaction was performed in the presence of $\text{Rh}(\text{acac})(\text{CO})_2$ with pyridine and bipyridine. The addition of these ligands increased the initial reaction rate, which with $\text{Rh}(\text{acac})(\text{CO})_2$ was reported to be $0.1 \text{ mol}/(\text{L} \times \text{s})$ at 100°C , whereas in the systems $\text{Rh}(\text{acac})(\text{CO})_2$ -pyridine and $\text{Rh}(\text{acac})(\text{CO})_2$ -bipyridine at a lower temperature (80°C), it was 0.3 and $0.14 \text{ mol}/(\text{L} \times \text{s})$, respectively (data under completely identical conditions are not presented). As with the system without ligands, the main product is aldehyde with the branched structure (about 99% in both cases). Phosphorus-containing ligands ensured higher chemoselectivity and, in most cases, higher reaction rate. Borole and Chaudhari [53] also presented data on the effect of pyridine ligands on the rate of hydroformylation of vinyl acetate in the presence of dicobalt octacarbonyl $\text{Co}_2(\text{CO})_8$. In this case, addition of a ninefold excess of pyridine increased the initial rate of hydroformylation of vinyl acetate by a factor of four; however, this was accompanied by the active formation of acrolein and acetic acid (>40%) from the produced aldehyde. A good result was obtained by using 3-phenylpyridine: at a pressure of 3.1 MPa and a temperature of 120°C , the initial rate of hydroformylation of vinyl acetate reached $2.47 \text{ mmol}/(\text{L} \times \text{s})$ with the preferential formation of the branched product (the metal concentration was 12 times higher than that in the experiments with rhodium).

An unusual study in this field was conducted by Kim and Alper, [54] who investigated a catalytic system of a fundamentally different type (Scheme 10). They synthesized complexes, each containing two rhodium atoms in the oxidation state +1. One of them—in the cation—was coordinated to a bidentate amine ligand, and the other formed the anionic site. These catalytic complexes were used in hydroformylation of styrene and vinyl acetate. At a substrate : catalyst ratio of 500 : 1, room temperature, and a syngas pressure of 7.0 MPa, rhodium complexes **32**, **33a**, and **33b** have higher catalytic activity in hydroformylation of styrene (conversion 42–60%, TOF = $26\text{--}37 \text{ h}^{-1}$, and *n*- : *iso*- = 1 : 30) in comparison with complex **32** [$\text{Rh}(\text{COD})\text{Cl}]_2$, from which they were synthesized (conversion <5%). With increasing temperature to 45°C , TOF reached 159 h^{-1} . Addition of bases, including tertiary amines, is known to promote the formation of hydride complexes of rhodium, because of which the activity of the complexes in hydroformylation can increase. However, the activity of the catalytic system containing [$\text{Rh}(\text{COD})\text{Cl}]_2$ and Et_3N also turned out to be lower than that of the ionic complexes of rhodium under the same conditions; this suggests that the promotion of the reaction by the ionic complexes does not reduce to the action of the tertiary amine on the rhodium site as a base, which was observed in the case of their separate addition.



Scheme 10. The structures of complexes **32**, **33a**, and **33b**.

Interestingly, Kim and Alper [54] did not report the presence of alcohols in the mixture of products, whereas Rh–tertiary amine systems are actively used for tandem hydroformylation–hydrogenation of unsaturated compounds (see Section 3.1). Probably, the ionic nature of the complexes studied by Kim and Alper [54] prevents the activity of rhodium in hydrogenation of aldehydes.

Süss-Fink [55] described hydroformylation of propylene in the presence of a ruthenium-based cluster complex, $\text{N}(\text{C}_2\text{H}_5)_4[\text{HRu}_3(\text{CO})_{11}]$. The yields of *n*-butyraldehyde and isobutyraldehyde were 60 and 3%, respectively, in 60 h at 100°C in DMFA using a gas mixture of CO (2.5 MPa) and H_2 (1.5 MPa).

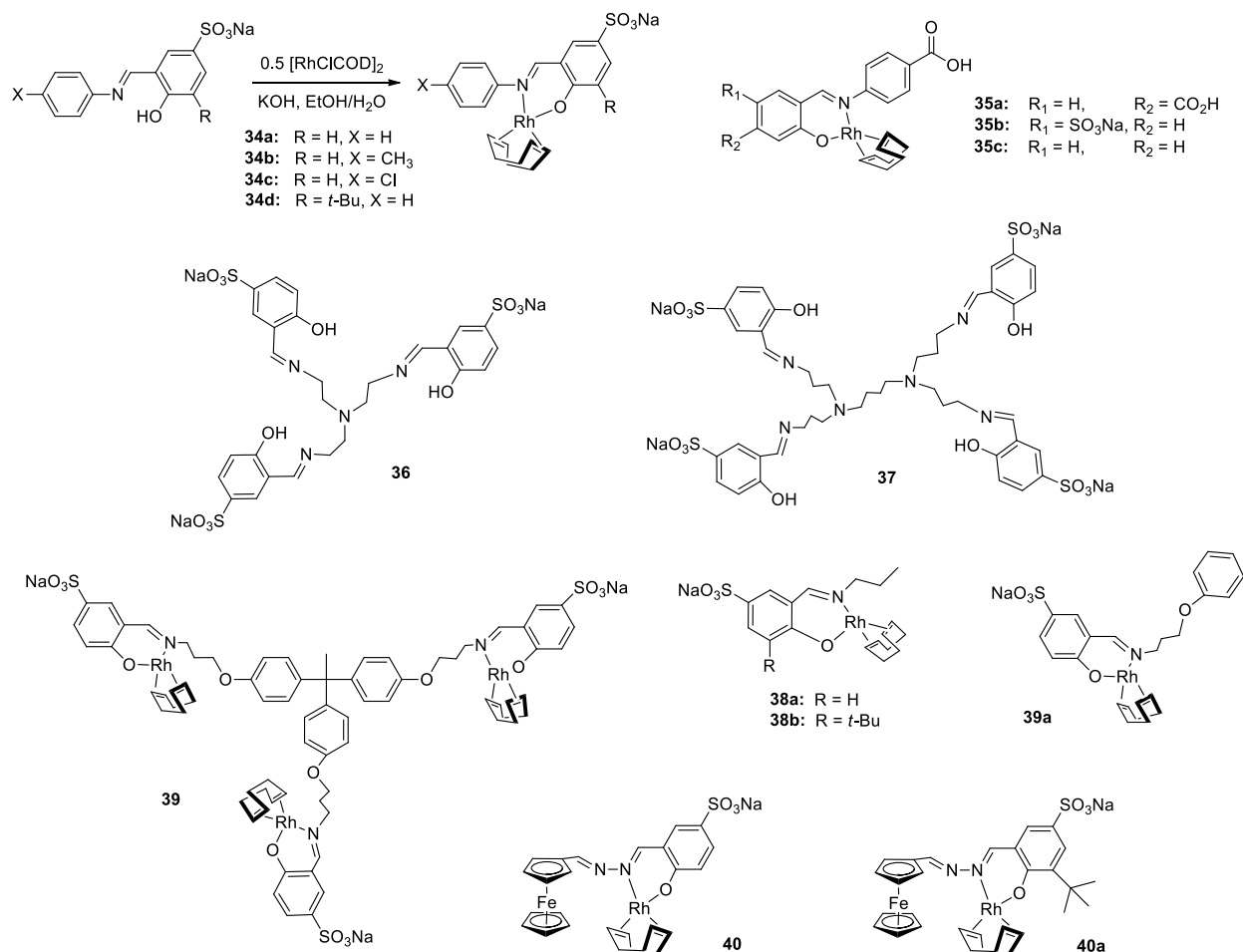
Carbonyl acetate complexes of ruthenium with bipyridine ligands were tested as catalysts of hydroformylation of 1-hexene under homogeneous conditions. In a 6 : 1 mixture of tetrahydrofuran and water at 150°C and 10.0 MPa in 24 h using the complex $[\text{Ru}_2(\text{CO})_4(\text{MeCO}_2)(\text{bip})_2](\text{MeCO}_2)$, the yield of aldehydes reached 26% with a fourfold excess of the linear product. Despite quite harsh conditions, the isomerization of the substrate was fairly moderate, and the yield of the hydrogenation product did not exceed 2%. No formation of alcohols was also observed [56].

Hydroformylation of α -olefins, styrene, and acrylates using the $\text{Ru}_3(\text{CO})_{12}$ –1,10-phenanthroline catalytic system in various amide solvents was studied. [57,58] In hydroformylation of propylene at 120–130°C and 8.0 MPa in 20 h, the yield of aldehydes was 65–93% with a selectivity toward *n*-butyraldehyde of 95%. Hydroformylation of styrene in this system at 10.0 MPa and 120°C in DMFA gave the corresponding branched and linear aldehydes at yields of 58 and 22%, respectively. However, using quinuclidine instead of 1,10-phenanthroline in *N,N*-dimethylacetamide, the corresponding branched (53%) and linear (28%) oxo alcohols were obtained, with the yield of aldehydes being only 4%.

2.2. Biphasic Systems

Functionalization of nitrogen-containing ligands with highly polar groups makes it possible to develop biphasic catalytic systems on their basis. As a rule, the water solubility of ligands is ensured by introducing a sulfate group, as in the classical biphasic system with TPPTS [5]. In systems of such a type, it is particularly important that a rhodium atom is sufficiently strongly bound to a water-soluble ligand; otherwise, the main purpose of the creation of biphasic systems—simple and efficient catalyst separation—cannot be reached because of the leaching of rhodium into the organic phase as organosoluble carbonyl complexes.

Most of the currently described systems for biphasic hydroformylation with nitrogen-containing ligands contain salicylaldimine complexes of rhodium (Scheme 11). Such systems were investigated in a series of works by Smith and colleagues. The water solubility of the complexes characterized in their works is due to the presence of polar groups (most frequently, sulfate one) in the nitrogen-containing ligand.



Scheme 11. The structures of the water-soluble ligands and complexes **34-40**.

All the data in Table 3 show that the studied systems can be used in consecutive reactions.

Table 3. Biphasic hydroformylation of 1-octene with ligands and complexes **34-40**.

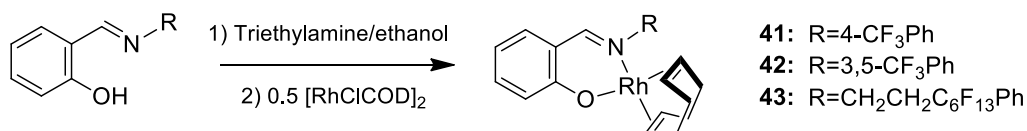
Complex	<i>P, T</i>	Run 1			Yield of aldehydes (last run tried)	Reference
		Yield of aldehydes	<i>n- : iso-</i>	TOF, h ⁻¹		
34a	5 MPa, 95°C	98%	0.8	276	99% (5)	[59]
34b	5 MPa, 95°C	99%	0.6	276	97% (5)	[59]
30c	5 MPa, 95°C	99%	0.2	277	90% (5)	[59]
30d	5 MPa, 75°C	99%	2.4	276	99% (5)	[59]
35a	4 MPa, 85°C	99%	0.8	276	90% (3)	[60]
35b	4 MPa, 85°C	99%	1.2	290	90% (3)	[60]
35c	4 MPa, 85°C	99%	0.7	272	80% (3)	[60]
36 /[RhCl(COD)] ₂	4 MPa, 75°C	76%	1.5 ^b	294	79% (5)	[61]
37 /[RhCl(COD)] ₂	4 MPa, 75°C	77%	1.6 ^b	312	80% (5)	[61]
38a	4 MPa, 75°C	94%	1.3 ^b	349	81% (5)	[61]
38b	4 MPa, 75°C	88%	1.6 ^b	334	71% (5)	[61]
39a	5 MPa, 85°C	89%	1.2	557	24% (5)	[62]
39	5 MPa, 85°C	87%	1.2	555	19% (5)	[62]
40	4 MPa, 95°C	98%	0.6	313	70% (5) ^c	[63]
40a	4 MPa, 95°C	72%	1.2	229	55% (4) ^{c,d}	[63]

Conditions: the substrate is 1-octene; the 1-octene : Rh molar ratio is 2200–2500; biphasic water–toluene systems; 8 h; ^a4 h; ^bthe regioselectivity is indicated in 2 h, ^cthe conversions of 1-octene are indicated because the cited work presented no data on the chemoselectivity in catalyst reuse runs, and ^din the fifth run, the activity was completely lost.

Note, however, that, in experiments on reuse of the aqueous phase with a yield of aldehydes of about 98–99%, the decrease in the activity may remain unnoticed. The rhodium leaching estimated by elemental analysis proved to be quite significant (90% after the 4-5th runs [63], 65% after the 1st run [60], and the lowest value 9–22% after the 1st run [61]). In the system with complex **34c**, mercury poisoning test showed a significant role of rhodium nanoparticles in hydroformylation in both the first, and the subsequent experiments: the addition of mercury considerably decreased the yield of aldehydes, and already in the fourth run, no conversion of 1-octene was observed. Meanwhile, the fundamental reusability of the mercury-free system implies that rhodium nonetheless largely remains in the aqueous phase. Probably, the presence of a nitrogen-containing ligand favors the stabilization of nanoparticles in the aqueous layer. The adverse effect of mercury on the activity of the system was also demonstrated for compounds **9** and **39**. Intriguingly, for complexes **35a–35c** with a similar structure, no effect of mercury on the yield of aldehydes was detected. Noteworthy, complexes **9** and **39** obtained by Siangwata et al. [62] turned out to be more active in a biphasic system without nonpolar solvent, in which the organic phase was the substrate—in both the first, and the subsequent runs.

Most of the reactions had rather low regioselectivity. An exception is the reaction in the presence of chlorine-containing complex **34c**, which catalyzes the formation of aldehydes with the branched structure; however, such a significant excess of the branched aldehydes was observed only in the first run. Further, the yields of the branched aldehydes and nonanal became equal, which supports the assumption of the formation of nanoparticles in the course of the reaction in systems of this type.

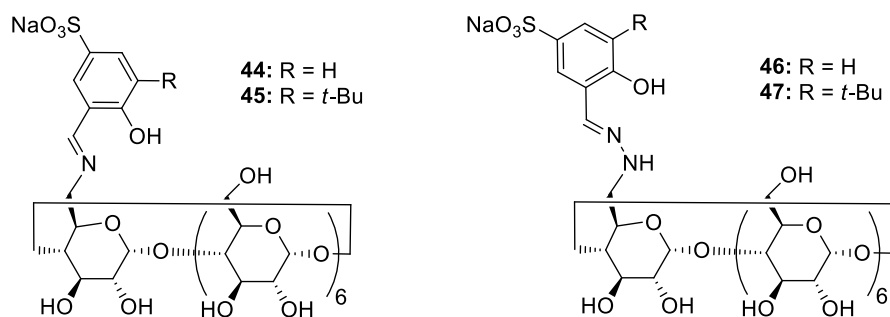
Fluorine-containing salicylaldimine ligands were obtained and used in hydroformylation of 1-octene (Scheme 12) [64]. The polar phase was not water, but perfluoromethylcyclohexane. The quantitative yields of C₉ aldehydes were reached in all the three systems in 4 h (4.0 MPa, 75°C), and the presence of fluorine in the structure of the ligand also favored the formation of the branched products (98, 73, and 97% of *iso*-aldehydes for complexes **41**, **42**, and **43**, respectively).



Scheme 12. The synthesis of complexes **41-43**.

However, reuse of the fluoroorganic layer (complex **43**) led to a decrease in the conversion of 1-octene to 20%. The nonpolar phase after the reactions was colored, which is indicative of a significant leaching of rhodium.

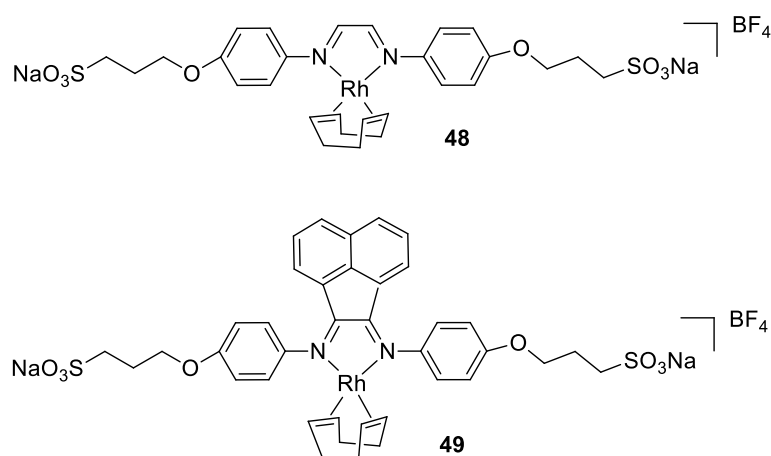
In a series of studies intended to improve the catalytic activity of biphasic systems in hydroformylation of long-chain substrates after the addition of amphiphilic cyclodextrin fragments [65] water-soluble ligands **44–47** containing salicylaldehyde and salicylhydrazone groups (Scheme 13) were obtained [66].



Scheme 13. The structures of ligands **44–47**.

Biphasic catalytic systems containing these ligands and $[\text{Rh}(\text{COD})_2]\text{BF}_4$ as a source of rhodium were active in hydroformylation of 1-decene (at a pressure of 2.0 MPa and a temperature of 60°C in 6 h, the conversion was 89–99% with a selectivity toward aldehydes of 40–50% and an *n*- : *iso*- ratio of about 2.3); however, as early as after the first run, the complexes decomposed, and most of the rhodium was in the organic phase.

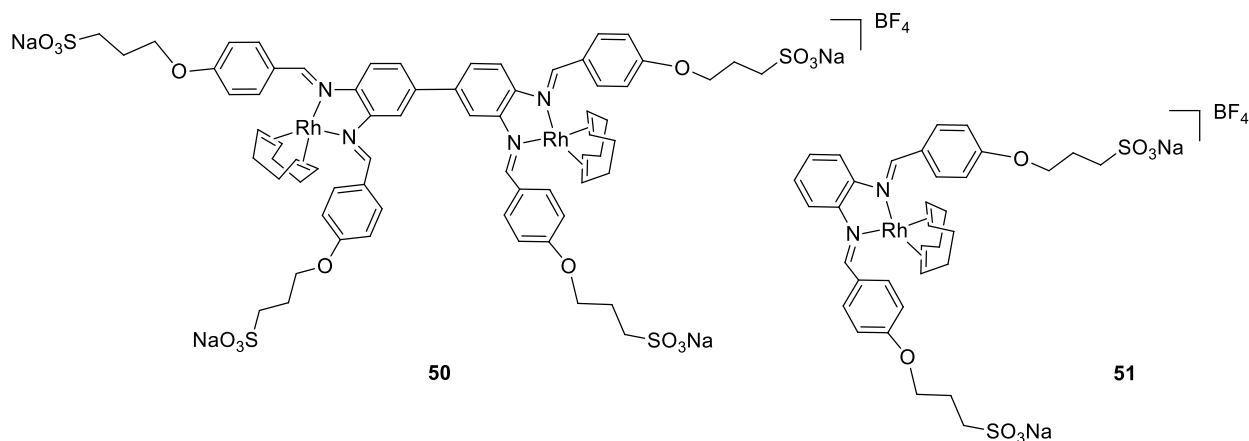
Along with organosoluble diimine complexes **9** and **10**, Omosun and Smith [45] synthesized water-soluble complexes **48** and **49** (Scheme 14), which were used in biphasic hydroformylation of 1-octene.



Scheme 14. The structures of complexes **48** and **49**.

The biphasic systems studied by Omosun and Smith [45] contained no nonpolar solvent: the second phase was the substrate and the products. The catalytic systems with complexes **48** and **49** at 75°C and 4.0 MPa in 8 h ensured the complete conversion of 1-octene at selectivities toward aldehydes of 86 and 88%, respectively, and *n*- : *iso*- ratios of 1.91 and 2.73, respectively (TOF =

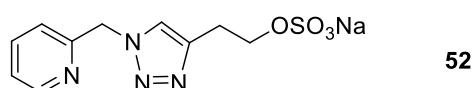
522 and 539 h⁻¹, respectively). Both systems were used in four consecutive reactions, in which their activity in hydroformylation gradually decreased: in the fourth use, the conversion of 1-octene in both cases was about 60%. Mercury poisoning test detected the absence of a contribution of nanoparticles to the activity in hydroformylation. The sterically hindered ligand in complex **49** favored quite high regioselectivity toward *n*-aldehyde for catalysts of this type, which somewhat decreased in the second use and remained in the subsequent runs with an *n* : *iso*- ratio of about 2. Complexes with a similar structure with one or two rhodium atoms (Scheme 15) were produced in the next work of the same research group [67]



Scheme 15. The structures of complexes **50** and **51**.

Under similar conditions, these precursors had close TOF values (581 and 528 h⁻¹ for complexes **50** and **51**, respectively). The aqueous phase was also used in four consecutive reactions and gradually lost its catalytic activity.

The synthesis of pyridyl–triazole ligand **52** (Scheme 16) was described [68].



Scheme 16. The structure of ligand **52**.

This ligand and the rhodium precursor [RhCl(COD)]₂ were used in the water–toluene system for hydroformylation of styrene and 1-hexene. At 80°C and 8 MPa in 18 h at a styrene : rhodium ratio of 500 : 1, the conversion of styrene to aldehydes was 99%; ethylbenzene (about 1%) also formed. In hydroformylation of 1-hexene, the yield of aldehydes was about 90% with an *n* : *iso*- ratio of 1.3. It was shown that the aqueous phase can be used without a decrease in the yield in at least four consecutive reactions. Transmission electron microscopy determined that, already after the first run, rhodium in the aqueous phase occurred as nanoparticles (Fig. 2). Addition of mercury in the reuse of the aqueous phase decreased the yield in hydroformylation to 2%, which is also indicative of a decisive role of rhodium nanoparticles in the catalysis.

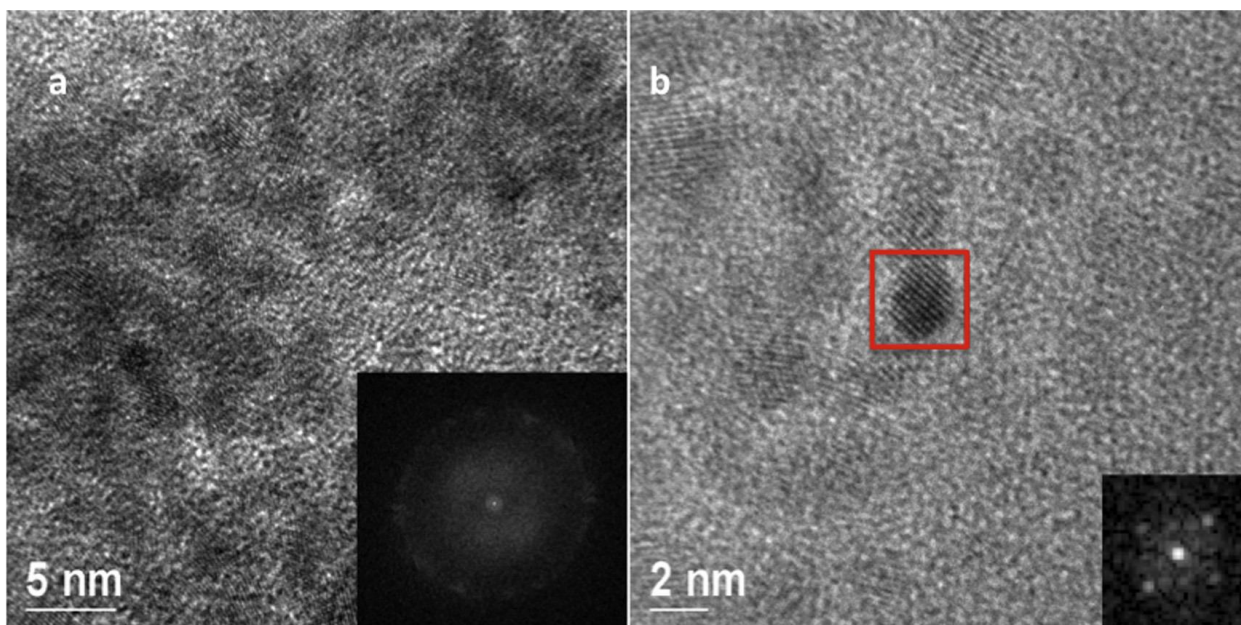
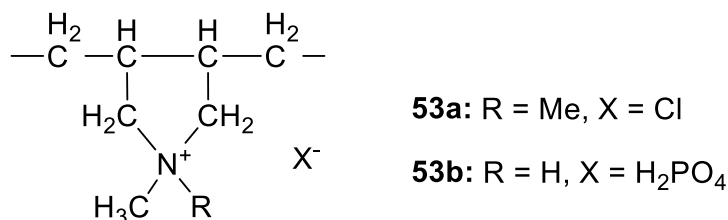


Fig. 2. HREM micrographs of the specimen at the end of the first catalytic run. The two insets report the FFT of the crystalline nanoparticles and the FFT of the outlined (red square) nanoparticle in (b) (Reproduced with permission from [68]).

Water-soluble polycations containing a quaternary nitrogen atom were used as components of catalytic systems in hydroformylation of 1-hexene under biphasic conditions using rhodium trichloride as a precursor (Scheme 17) [69].



Scheme 17. The structures of polymers **53a** and **53b**.

The activity of the system depended on the pH of the aqueous phase, and based on the results of comparison experiments with no modified rhodium carbonyl, Kolesnichenko et al. [69] assumed that rhodium is washed out into the organic phase as a complex with the polymeric ligand. Therefore, to increase the stability of the system, it was necessary to find conditions that favor the highest possible retention of the polymer in the aqueous medium. Addition of a salt with a triply charged anion — sodium phosphate — enabled one to perform three consecutive reactions with the aqueous phase containing the complex RhCl₃/**53b** without a decrease in the activity from run to run; however, this rate was six times lower than that without adding phosphate. It was assumed [69] that the increase in the stability is due to the formation of inter- and intramolecular salt bridges after introducing the polyvalent anions.

The ability of carbonyl compounds of cobalt to interact with Lewis bases, in particular, pyridine derivatives, was used [70–72] to develop an original approach to recycling a cobalt catalyst of hydroformylation under biphasic conditions using ionic liquids. Cobalt tetracarbonyl hydride $[\text{HCo}(\text{CO})_4]$ formed under hydroformylation conditions (10.0 MPa, 130°C) is well soluble in the organic phase, in which the reaction occurred. With decreasing temperature and pressure, tetracarbonyl is destabilized and reacts with pyridine to form $[\text{PyH}]^+[\text{Co}(\text{CO})_4]^-$ or $[\text{Co}(\text{Pyr})_6]^{2+}[\text{Co}(\text{CO})_4]^{2-}$. Both of these ionic compounds have high affinity for the ionic phase, are immobilized in it, and are easily separated from the organic phase containing the reaction products, thus enabling multiple use: the activity of the system did not decrease over four runs, remaining 90% per hour with a selectivity toward aldehydes of 87% and an *n*- : *iso*- ratio of 1.8. The reaction rate was noted [70–72] to depend on the Py : Co ratio (an excess of the ligand inhibited the reaction) and on the basicity of the pyridine base (replacement of pyridine (*pKa* 8.8) by 2-methoxypyridine (*pKa* 10.9) led to the quantitative conversion of the substrate under the same conditions).

2.3. Immobilized and Heterogeneous Systems

This section considers materials in which metal sites active in hydroformylation are stabilized by the interaction with nitrogen-containing functional groups that enter into the composition of a polymeric support or modify the surface of an inorganic matrix.

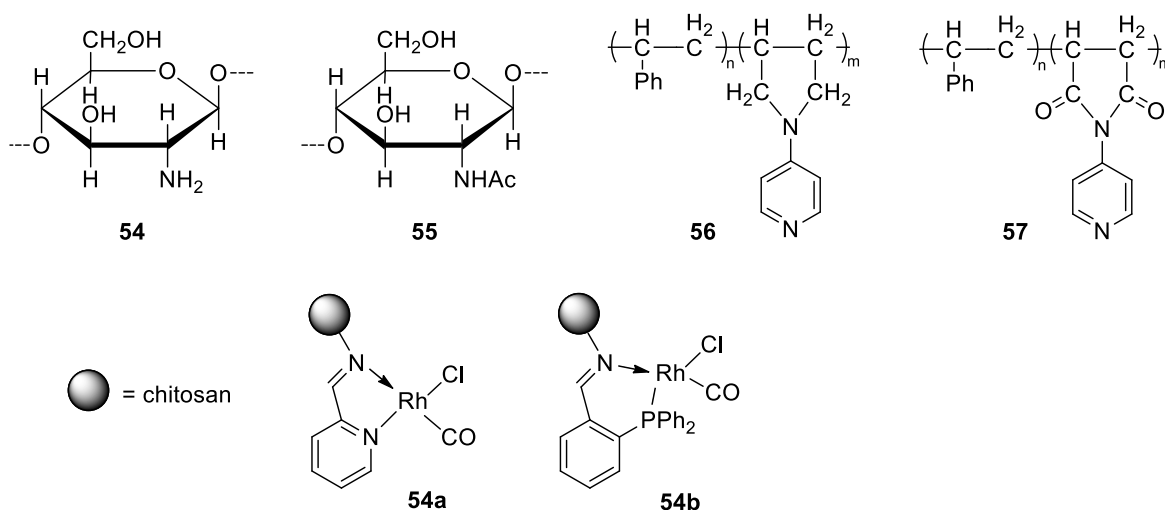
Heinrich et al. [73] described an example of using a heterogeneous rhodium catalyst based on a crosslinked copolymer of 2-vinylpyridine, methyl acrylate, and ethylene diacrylate in hydroformylation of propylene in a flow-through reactor. In reuse, the activity of the catalyst decreased by 50%, which was attributed [73] to the fact that rhodium is reduced during the reaction to the metallic state (the color of the catalyst was observed to change).

Another rhodium catalyst, based on a vinylpyridine–divinylbenzene copolymer, showed relatively high activity in hydroformylation of 1-octene (at an initial rate of 4800 mol/(mol Rh h) as against 7800 mol/(mol Rh h) for a homogeneous analog) at 130°C and 9.0 MPa. [74] No experiments on reuse of the catalyst were carried out, but investigation of the liquid phase after the reaction demonstrated that the leaching of rhodium was insufficient. In liquid-phase hydroformylation of propylene, the catalyst proved to be inefficient in the absence of phosphine ligand additives.

Kontkanen et al. [75] noted a dependence of the activity of catalysts based on a poly(4-vinylpyridine)–divinylbenzene copolymer on the degree of crosslinking (Rh–P4VP-2% and Rh–P4VP-25%). For example, the polymer complex Rh–P4VP-25% actively catalyzed hydroformylation of 1-hexene at 80°C and 2.0 MPa and remained active for three cycles, and the

yield of aldehydes in 17 h was 56% (at a total conversion of 1-hexane of 86%), whereas in the case of using Rh–P4VP-2%, the yield of aldehydes was only 19% and considerably decreased in reuse, which was believed [75] to be due to microencapsulation of the active metal.

Styrene copolymers containing pyridylmaleimide and 4-N-pyrrolidinopyridine groups (Scheme 18) [76,77] and natural nitrogen-containing polymers chitin and chitosan [78] were used to heterogenize rhodium trichloride. The obtained catalytic systems had high stability, and also were active in hydroformylation of olefins, in particular, low-reactive, internal, and *iso*-olefins. For example, hydroformylation of isobutylene to isovaleraldehyde occurred at high rate (360 mol/(L min)) under the conditions (90°C, 6.0 MPa) under which conventional homogeneous catalysts are low-active (80 mol/(L min)). The rhodium catalytic system based on STPP remained active in reuse.



Scheme 18. Structure of nitrogen-containing polymer ligands: chitosan, chitin, styrene copolymers containing 4-N-pyrrolidinopyridine (STPP), and styrene copolymers containing pyridylmaleimide (STPM)

The catalyst based on chitosan modified with pyridine fragments (54a) [79] was much inferior in activity in hydroformylation of 1-octene to its phosphorus-containing analog (54b) and also was inactive in reuse. Under optimal conditions in 8 h at 75°C and 3.0 MPa, the yield of aldehydes in the presence of the phosphorus-free catalyst was only 37% as against 71% in the presence of its phosphorus-containing analog.

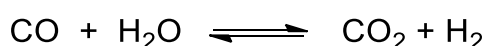
An epoxy resin with rhodium additives was produced by a one-step synthesis from N,N-diglycidyl-4-glycidyoxyaniline using a metal complex (in this case, $\text{Rh}(\text{C}_8\text{H}_{12})[(i\text{Pr})_2\text{PC}_6\text{H}_4\text{CH}(\text{OMe})_2]\text{Cl}$) as a polymerization initiator and, simultaneously, a catalytic precursor; i.e., no separate procedure was necessary for metal deposition to perform the catalytic reaction. [80] In hydroformylation of 1-octene, the yield of aldehydes reached 59% in 8

h at 110°C and 5.0 MPa; the reaction was carried out in the absence of a solvent in the pure alkene. After the first run, the activity of the catalyst decreased, but in the subsequent four runs, the conversion and the selectivity remained unchanged.

In the literature, there are also several examples of rhodium-free catalytic systems immobilized on polymeric supports hydroformylation of unsaturated compounds. For example, Marrakchi et al. [81] used a chloromethylated copolymer of styrene and divinylbenzene to create a material containing positively charged groups NR_3^+ with quaternized nitrogen atoms, by which the $[\text{HOs}_3(\text{CO})_{11}]^-$ and $[\text{HFe}_3(\text{CO})_{11}]^-$ anions are held on the surface of the material. These quite nonstandard catalysts showed low activity in hydroformylation of 1-hexene, which was described [81] by a considerable leaching of metals from the support.

Cobalt carbonyl immobilized on poly-2-vinylpyridine was tested as a catalyst of hydroformylation of olefins [82,83]. It was assumed that the catalysis is homogeneous, and that the role of the polymer is to bind cobalt after the reaction to facilitate its removal. Later, Hartley et al. [84] made a number of comparative experiments and concluded that the pyridine fragments of the support do enter into the coordination interaction with some of the cobalt metal sites, thus increasing both the hydroformylation rate, and the yield of the linear products.

The transportation, storage, and use of hydrogen both in laboratory, and industry are significantly restricted. Therefore, instead of syngas, the water gas shift reaction (WGSR) is often used, which is the reaction between carbon monoxide and steam to form carbon dioxide and hydrogen (Scheme 19) [85,86].



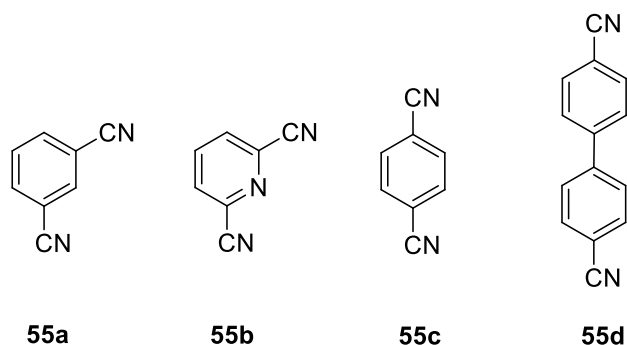
Scheme 19. Water-gas shift reaction.

This reaction, as well as hydroformylation, can be catalyzed by rhodium complexes in the presence of nitrogen-containing bases, [87] which allows one to perform two consecutive reactions within a single catalytic system. Rhodium trichloride heterogenized on a nitrogen-containing polymer, poly-4-vinylpyridine (P4VP), was tested in hydroformylation of 1-hexene under WGSR conditions [88]. Water and carbon monoxide in this process are sources of hydrogen to form metal-alkyl intermediates, which then react with CO to give aldehydes. This catalytic system was more active in hydrogenation ($\text{TOF} = 19.2 \text{ h}^{-1}$) and isomerization ($\text{TOF} = 32.4 \text{ h}^{-1}$) of 1-hexene than in the formation of aldehydes ($\text{TOF} = 4.5 \text{ h}^{-1}$).

In the case where the precursors were a series of ionic amine complexes $[\text{Rh}(\text{COD})(\text{amine})_2]\text{PF}_6$ (COD is 1,5-cyclooctadiene; and amine is 4-picoline, 2-picoline, or 2,6-lutidine), [89,90] the activity in the formation of aldehydes decreased in the order 2-picoline ($\text{TOF} = 2.9 \text{ h}^{-1}$) > 4-picoline ($\text{TOF} = 2.6 \text{ h}^{-1}$) > 2,6-lutidine ($\text{TOF} = 2.4 \text{ h}^{-1}$). It was believed [89,90] that

the electronic and steric effects induced by the amine ligands may influence the observed catalytic activity. The process was carried out in a medium of 80% aqueous 2-ethoxyethanol in a CO atmosphere (0.9 atm) at 100°C. The isomerization of the substrate was more active in this case, too (TOF = 14–16 h⁻¹), and no formation of alcohols was detected. The [Rh(COD)(2-picoline)₂][PF₆]-poly-4-vinylpyridine system also catalyzes hydroformylation and isomerization of 1-octene.

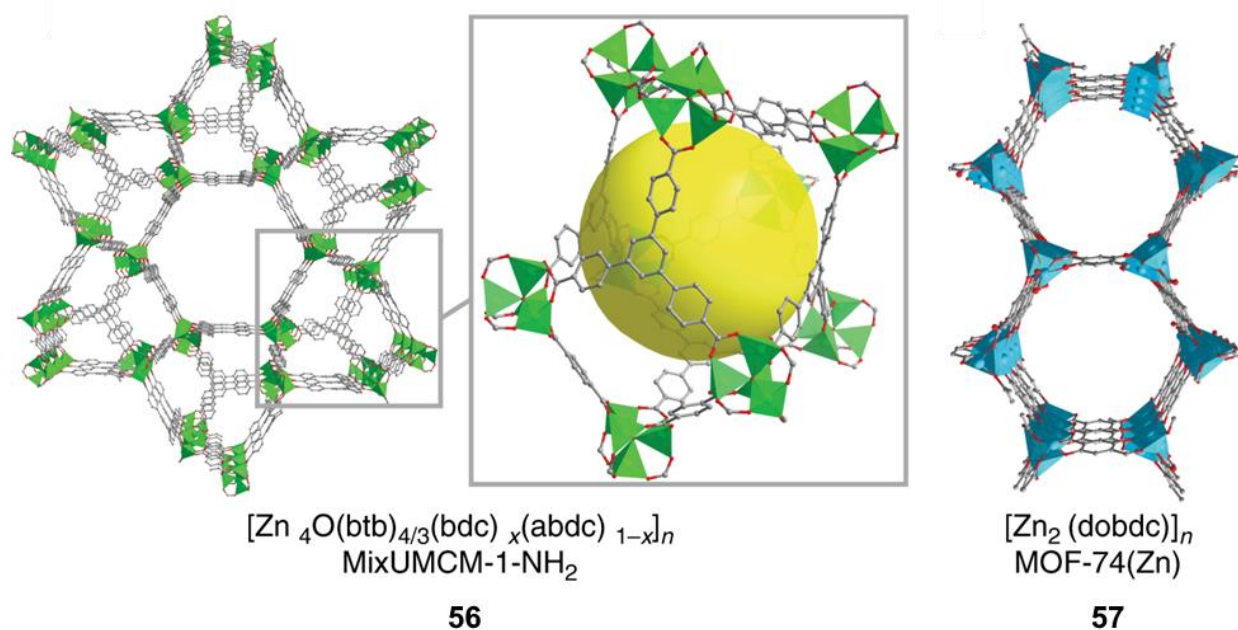
Highly porous covalent triazine frameworks produced from nitrogen-containing monomers (Scheme 20) were used as supports for immobilization of metal complexes and tested in hydroformylation of 1-octene [91].



Scheme 20. Chemical structure of monomers **55a-55d** used for porous covalent triazine frameworks synthesis.

The porosity of the materials depended on the structure of the monomer and the synthesis conditions. The obtained frameworks had high specific surface area (1690–1859 m²/g). It was shown that the porosity and polarity of the support substantially affected the catalytic activity: using mesoporous and less polar supports, such as **55a** and **55c**, the conversion of 1-octene in 20 h at 80°C and 8.0 MPa was 69 and 62%, respectively. The activity was lowest for material **55b** with the microporous structure and the highest surface polarity; the conversion in this case was 10%. The rhodium catalysts on the obtained frameworks retained the initial activity in at least four or five consecutive reactions and were superior in activity to the Rh/C catalyst.

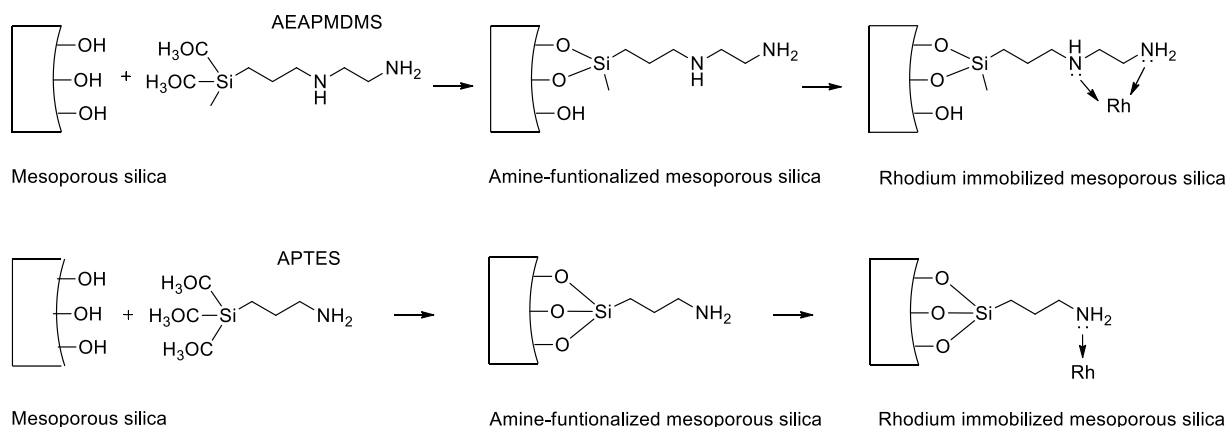
Bauer et al. [92] described the synthesis of metal–organic frameworks MOF-74(Zn) and MixUMCM-1-NH₂ (Scheme 21) and their use as kinetic modulators in hydroformylation of a number of olefins. Under optimal conditions (100°C, 3.0 MPa CO–H₂, 17 h) with cobalt carbonyl as a precursor, the conversion of 1-hexene reached 36% with an unexpectedly high *iso*- : *n*- ratio of 85 : 15.



Scheme 21. Structures and molecular formulas of metal–organic frameworks MixUMCM-1-NH₂ (**56**) and MOF-74(Zn) (**57**). (Reproduced with permission from [92])

In reuse, the conversion was only 5% with a selectivity toward the branched product of 64% for MixUMCM-1-NH₂ and 35% with a selectivity of 68% for MOF-74(Zn).

One of the most available supports for heterogenization of catalysts of many processes has been silica gel and its various modifications. Yim and colleagues [93,94] described the synthesis of rhodium catalysts immobilized on mesoporous silicas with different pore sizes (MCM-41 and SBA-15) and also amorphous silica that were functionalized with (3-aminopropyl)triethoxysilane (APTES) and N-(2-aminoethyl)-3-aminopropylmethyl-dimethoxysilane (AEAPMDMS) (Scheme 22). The highest catalytic activity in hydroformylation of 1-octene was observed for the material that was based on SBA-15 (which has larger pores than MCM-41) functionalized with AEAPMDMS (which has stronger electron-donor properties). However, the activity of the catalysts without adding a phosphine ligand turned out to be quite low and comparable to that of homogeneous $HRh(CO)_4$. Unfortunately, Yim and colleagues neither mentioned catalyst reusability, nor discussed rhodium leaching.



Scheme 22. Surface modification with (a) AEAPMDMS and (b) APTES by grafting and immobilization of rhodium on the mesoporous materials [93]

At the same time, Huang et al. [95] and He et al. [96] reported quite a high catalytic activity of rhodium carbonyl and rhodium trichloride, immobilized on MCM-41–APTES, in hydroformylation of cyclohexene and styrene under similar conditions: a pressure of 2.0 MPa and a temperature of 80 to 120°C. For example, in hydroformylation of styrene using the $\text{RhCl}_3/\text{MCM-41-APTES}$ catalyst at 80°C, the yield of aldehydes was 37%, and at 100°C, it was as high as 67% in 20 h. An increase in temperature promoted the hydrogenation of styrene. For comparison, the $\text{RhCl}_3/\text{MCM-41-PPh}_2$ system was taken, which had higher activity: even at 80°C, the yield of aldehydes reached 66%. However, an attempt of reuse showed that, for the $\text{RhCl}_3/\text{MCM-41-PPh}_2$ system, rhodium was almost completely washed out as early as after the first run, whereas the $\text{RhCl}_3/\text{MCM-41-APTES}$ system remained active in three consecutive experiments, with the rhodium loss being only 0.3%. Addition of triphenylphosphine significantly increased the yield of aldehydes using the $\text{RhCl}_3/\text{MCM-41-APTES}$ system.

Chen et al. [97] have fairly recently reported the use of a similar system, a rhodium complex supported on APTES-modified mesoporous SiO_2 , in hydroformylation of formaldehyde. Silica was modified by grafting of (3-aminopropyl)triethoxysilane, and then rhodium was deposited from an ethanol solution of dicarbonyl(acetylacetonato)rhodium(I). The synthesized material was characterized in detail, and from the obtained results, it was judged [97] that rhodium is immobilized on the support by the formation of a Rh–N bond. Under optimal conditions (12 MPa, 95°C), the hydroformylation of formaldehyde gave 50% glycolaldehyde in 3 h, and the chemoselectivity approached 90%. Note that, in the catalytic experiments, triphenylphosphine was added as a ligand to the reaction mixture; no experiments were made in the absence of PPh_3 ; and the activities were compared only for the catalyst obtained by impregnation of nonmodified silica gel, the activity of which was much lower (30–40% aldehyde). Neither reuse of the catalyst, nor leaching of rhodium was reported.

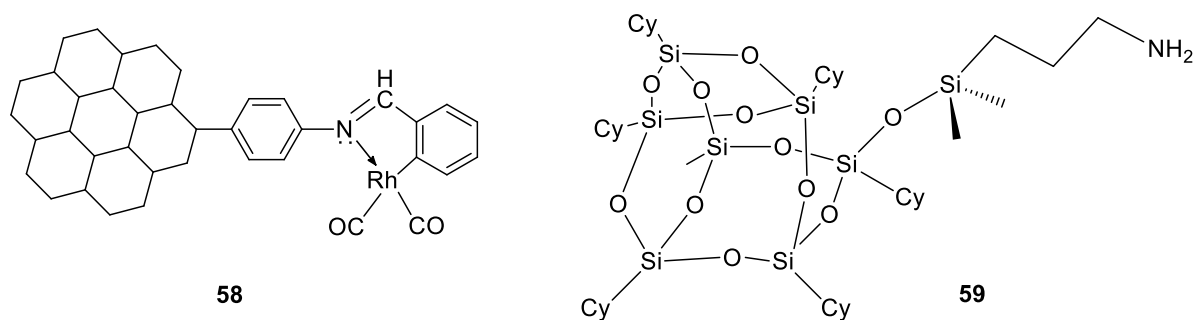
Nandi et al. [98] described the synthesis and catalytic use of mesoporous silica with covalently anchored rhodium(I) (**58**) (Scheme 23). The material was synthesized by nitration of the phenyl group grafted on the surface of silica with subsequent reduction to amine and condensation with a Schiff base. Treatment with a rhodium trichloride solution in a CO atmosphere gave a heterogeneous catalyst, which showed high activity in hydroformylation of 1-hexene at a syngas pressure of 5 MPa and a temperature of 70°C in N,N-dimethylformamide (DMF) as a solvent. The conversion of 1-hexene was 74% with a selectivity toward aldehydes of 84% and an *n*- : *iso*- ratio of 4.6. The catalyst remained active after five runs of use, and rhodium was hardly leached into the liquid phase. Having interpreted the FTIR spectra, Nandi et al. [98] concluded that rhodium is covalently anchored in the structure of the catalyst by ortho metalation of the aromatic fragment (Scheme 23).

Another approach to immobilizing homogeneous catalysts is based on using nanomaterials, which makes it possible to obtain “soluble” analogs of heterogeneous catalysts. Thus, nanoparticles are attractive semi-heterogeneous supports, which are easily dispersible in common solvents, high specific surface area, and high density of active sites [99].

Significant progress has been achieved to date in hydroformylation of alkenes on catalysts based on rhodium nanoparticles; however, Rh nanoparticles are typically highly prone to agglomeration, which leads to a rapid decrease in the activity of the catalyst and to its low stability. Shi et al. developed a method to produce monosized Rh nanoparticles using graphite-like carbon nitride g-C₃N₄ doped with sulfur [100] and boron [101]. These materials contain many “pyridine-like” nitrogen atoms and can therefore stabilize Rh nanoparticles to form potential active sites, whereas the doping heteroatom can modify the textural, electronic, and structural properties of g-C₃N₄; favor the electron transfer; and give rise to a more stable π -conjugated system, which enhances the adsorption and deposition of Rh nanoparticles and alkenes on g-C₃N₄. The obtained catalysts were used in hydroformylation of styrene at a temperature of 100°C and a syngas pressure of 6.0 MPa. A virtually complete conversion of the substrate was reached in 3 h with a regioselectivity toward the branched aldehyde of 60% for both types of the catalyst. Both of them were used several times without a decrease in the activity and selectivity. The undoped catalyst also had rather high activity: the conversion of styrene to aldehydes reached 65% at the same chemo- and regioselectivity.

Ruthenium oxide nanoparticles heterogenized on micro- and mesoporous silica and titania, which were produced by controlled calcination with aminosilsesquioxane ligand (**59**) (Scheme 23) and RuCl₃ [102] were tested as catalysts of hydroformylation of 1-octene. The maximum yield of aldehydes (37%) with a selectivity toward the linear product of 83% was reached at 130°C and a CO pressure of 2.0 MPa and an H₂ pressure of 2.5 MPa in 66 h using the titania-supported catalyst.

It was noted that the use of the silsesquioxane ligand in the production of the catalyst considerably increased the activity of Ru/TiO₂ and Ru/SiO₂ in hydroformylation of 1-octene. One of the possible causes can be the formation of very fine ruthenium oxide particles on the surface of the catalysts. It was assumed [102] that the silsesquioxane ligand is converted during calcination into silica, which acts as an inorganic separator for ruthenium nanoparticles by suppressing their sintering to form larger particles during calcination and hydroformylation. It was briefly mentioned [102] that the catalysts could be reused, and that no leaching of ruthenium into the reaction mixture was observed.



Scheme 23. Rh(I) complex anchored on mesoporous support **58** and ligand **59** [98]

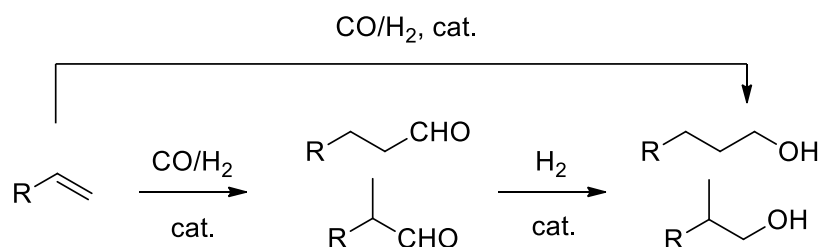
A series of heterogenized cobalt catalysts were synthesized by Beller and colleagues [103] by impregnation of commercially available supports (carbon, titania, silica, ceria, alumina) with cobalt(II) acetate in the presence of various nitrogen-containing organic ligands with subsequent pyrolysis at 800°C. The activity of the produced materials in hydroformylation was comparable to that of homogeneous cobalt carbonyl; however, in all the cases, Co was leached, and it was concluded [103] that the hydroformylation reactions occur mainly in the solution. Nonetheless, the active sites on the surface are also productive to a certain extent, and the materials deposited on TiO₂ and carbon proved to be stable, nonvolatile, and easy-to-handle alternatives to the toxic homogeneous catalyst based on cobalt carbonyl.

The multifunctional composite material FeOCN was synthesized in a single step by sintering of iron(III) nitrate and urea at 500°C at high heating rate [104]. This material was determined to be an active heterogeneous catalyst of hydroformylation of 1-octene in toluene at a syngas pressure of 5.0 MPa and a temperature of 95°C, ensuring a conversion to 88% in 6 h, a chemoselectivity toward aldehydes of 44%, and a regioselectivity toward the linear product of 75%. The composite also demonstrated significant activity in catalytic hydration of alkynes and nitriles. The possibility of reuse was tested only for hydration of alkynes: in this process, the catalyst remained active for five consecutive runs.

3. Catalytic Systems with Nitrogen-Containing Ligands for Tandem Hydroformylation-Based Reactions

3.1. Reductive Hydroformylation

Reductive hydroformylation, or hydroformylation–hydrogenation, attracts the attention of researchers by the fact that it enables one-stage conversion of olefins to primary alcohols, which are, in most cases, the end products of industrial processes using hydroformylation. Hydrogenation is most frequently performed as a separate step. To reduce capital costs, the Shell Oil Company in 1966 developed an industrially adopted tandem process of hydroformylation–hydrogenation (Scheme 24) using cobalt complexes with trivalent phosphorus compounds, which can convert alkenes to primary alcohols in a CO–H₂ atmosphere. [105] However, this process requires sufficiently harsh conditions (160–200°C, 5.0–10.0 MPa). More efficient reductive hydroformylation methods continue to be sought.



Scheme 24. The production of alcohols through hydroformylation.

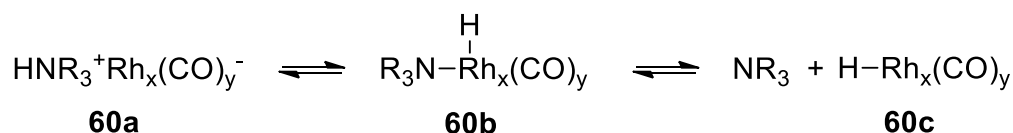
Rhodium-containing systems, which are the most active in oxo synthesis, are less prone to catalyze hydrogenation of aldehydes in comparison with systems based on cobalt under hydroformylation conditions. [106] Among phosphine ligands, alkylphosphines as stronger donors more efficiently promote the second step of the tandem process in comparison with arylphosphines. [107] Alkylphosphines are still less resistant to oxidation than arylphosphines; therefore, the successful use of other donor ligands—tertiary amines—in this process seems to be particularly interesting. In a number of works, both homogeneous, as heterogeneous catalytic systems containing tertiary amines as ligands for production of alcohols were developed and studied.

3.1.1. Homogeneous Systems

One of the first systematic studies of rhodium catalytic systems using nitrogen-containing ligands was made in 1972 by Fell and Geurts [108]. The catalytic precursor was rhodium(III) oxide. Among the ligands tested (N-alkylpyrrolidines, N-alkylpiperidines, N,N,N',N'-tetramethylethylenediamine, some other tertiary amines, pyridine), the highest activity in tandem hydroformylation–hydrogenation of the model substrate 1-octene was demonstrated by the system

containing N-methylpyrrolidine. At 125°C and 18 MPa, the yield of alcohols was 81% in 2 h. The dependence of the yield of alcohols on the amine concentration passes through a maximum at very high ligand : rhodium molar ratios of about 2500 : 1.

The next important investigation of Rh/N systems in hydroformylation–hydrogenation was performed in 1974 by Jurewicz et al. [109]. The precursor in most reactions was rhodium trichloride. Among the homogeneous catalytic systems studied in that work, the highest selectivity was shown by the systems with N,N-dimethylbenzylamine (DMBA), triethylamine, and N-methylpyrrolidine, the pK_b of which are in the range 3–7. For DMBA at a conversion of 1-hexene to oxygen-containing compounds of 80%, the selectivity toward alcohols was 29%. The reaction was carried out under relatively mild conditions (100°C, 7.0 MPa). IR spectroscopy in situ detected that the $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ –triethylamine and $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ –DMBA catalytic systems contained the anionic carbonyl complex $\text{Rh}_{12}(\text{CO})_{30}^{2-}$, whereas in the absence of a tertiary amine, no formation of such complexes was observed. Therefore, it was assumed [109] that the rhodium complexes are in equilibrium described by the Scheme 25.



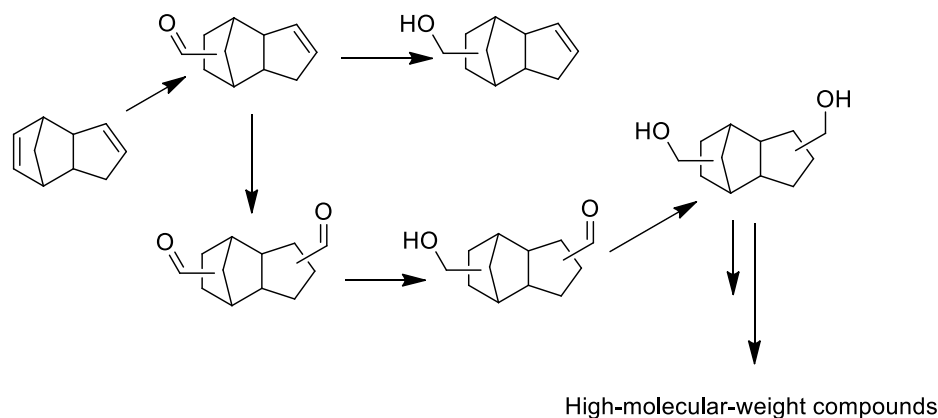
Scheme 25. The equilibrium in Rh/NR₃ system for reduction hydroformylation.

where complex **60c**, according to classical concepts, catalyzes the hydroformylation step, and complex **60b** favors the hydrogenation of the formed aldehydes. Based on the results of an experiment with the complex $(\text{Et}_4\text{N})_2[\text{Rh}_{12}(\text{CO})_{30}]$, in which no hydrogenation of aldehydes was observed, it was concluded [109] that anionic rhodium complex **60a** does not catalyze the formation of alcohols. In that work, a study was also made of tandem hydroformylation–hydrogenation on the heterogeneous catalyst PolyDMBA, which demonstrated high activity and selectivity toward alcohols. Judging from the low leaching of rhodium into the solution, which corresponds to the formation of complex **60c**, Jurewicz et al. [109] came to the conclusion that complex **60b**, which in the case of heterogeneous catalysis proved to be immobilized on the surface of the support, also participates in the hydroformylation step.

In recent decade, interest in homogeneous catalytic systems of this type has rekindled. In 2012, Cheung et al. [110] made a more detailed study of catalytic systems with tertiary diamine ligands in tandem hydroformylation–hydrogenation of styrene. The rhodium precursor was the dimer $[\text{RhCl}(\text{COD})]_2$. After optimization of conditions, it was found that, at 60°C and 2.76 MPa in THF, the yield of alcohols using the system of the dimeric rhodium complex $[\text{RhCl}(\text{COD})]_2$ and the diamine ligand $\text{Me}_2\text{N}(\text{CH}_2)_4\text{NMe}_2$ (at a Rh : amine molar ratio of 1 : 4) reached 82%, and the

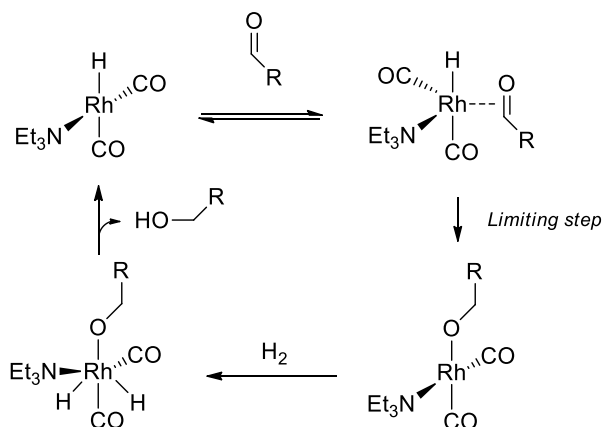
n- : *iso*- ratio was 1 : 9.6 in 21 h. The corresponding mixtures of alcohols were obtained at high yields from a number of other aromatic substrates.

Fuchs et al. [111,112] used the rhodium–tertiary amine catalytic system to synthesize tricyclodecanediol by tandem hydroformylation–hydrogenation of dicyclopentadiene. This diol can be a substrate to produce the corresponding acrylate, a promising monomer to obtain polymeric compounds (Scheme 26).



Scheme 26. Reductive hydroformylation of dicyclopentadiene.

In the reaction, catalytic systems containing various rhodium precursors ($[\text{Rh}(\text{octanoat})_2]_2$, $\text{Rh}(\text{acac})(\text{cod})$, $\text{Rh}(\text{acac})(\text{CO})_2$, $[\text{Rh}(\text{cod})_2]\text{BF}_4$) in combination with triethylamine and *n*-butyldimethylamine were tested [111]. The best selectivity toward alcohols was reached using the precursor $[\text{Rh}(\text{octanoat})_2]_2$ and the ligand triethylamine: in 4 h at 120°C and 6.0 MPa ($\text{CO} : \text{H}_2 = 3 : 1$), the yield of diol was 51%. In the absence of a solvent at 7.0 MPa, the yield of diol increased to 79%. The catalytic system can be reused after extraction of water-soluble reaction products with water *ex situ* and loses activity only after the third run, which was explained by a significant leaching of rhodium into the aqueous phase. The following mechanism of hydrogenation of aldehydes was proposed (Scheme 27) [111]:



Scheme 27. The mechanism of aldehyde reduction in Rh/NR_3 systems.

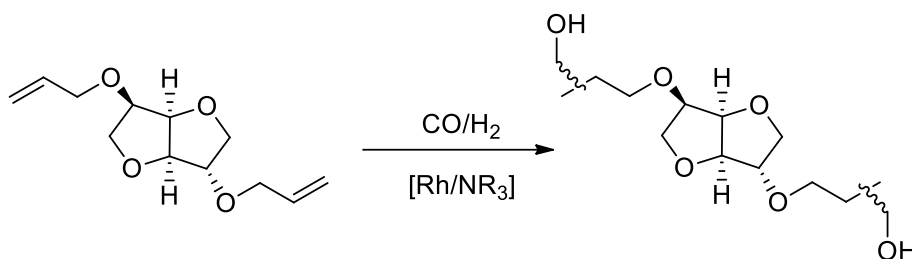
Triethylamine and rhodium form an active hydrogenating complex, which favors the introduction of aldehyde to the Rh–H bond. The electronic density is shifted from the nitrogen atom along the σ -bond to the active site. Unlike CO or PPh₃, triethylamine as a ligand is not characterized by π -back-donation; thereby, higher electronic density at the metal site of the Rh–amine complex is reached. This also leads to higher hydroformylation rate because the insertion of olefin to the rhodium–hydride bond turns out to be more preferable, and the reaction rate increases.

Interesting results were obtained by comparing the effect of triethylamine on the activity of group 8 and 9 transition metal chlorides and carbonyls in hydroformylation of 1-hexene [113]. It was determined that the presence of an amine ligand for rhodium-based catalysts in the reaction medium initiates virtually quantitative hydrogenation of aldehydes to alcohols, whereas for ruthenium compounds, such an effect is much weaker, and for cobalt compounds, it is virtually absent. The mixed carbonyl Co₂Rh₂(CO)₁₂ behaves as rhodium carbonyl: in the presence of triethylamine, aldehydes are quantitatively converted to alcohols. The regioselectivity for all the metals proved to be at a level that is characteristic of the corresponding binary carbonyl complexes.

The effect of the structure of tertiary amines on the activity of their complexes in hydroformylation–hydrogenation of the model substrate 1-octene has recently been investigated in detail by Rösler et al. [114] The highest yields of alcohols were reached using the complexes of tertiary amines with pK_a from 8.5 to 11.5 and a cone angle of 135–155°. IR and NMR spectroscopy detected that the system contains the anionic complexes [Rh₇(CO)₁₆]³⁻, [Rh₄(CO)₁₁]²⁻, [Rh₆(CO)₁₅]²⁻, and [Rh(CO)₄]⁻. Presumably, the counterion in these complexes is the R₃NH⁺ cation formed from a tertiary amine; however, because the selectivity of the reaction is affected by not only the basicity, but also the ligand cone angle, Rösler et al. [114] held to the view that the role of the nitrogen-containing base does not reduce to the formation of these cations and the stabilization of rhodium-containing anions. The active particle was assumed [114] to be the hydride complex HRh(CO)₃(NR₃). Note also that the ruthenium complexes and rhodium(III) salt RhCl₃ turned out to be much less efficient precursors (with a yield of alcohols to 3% in 8 h of reaction) than the rhodium(I) complexes (to 81% under similar conditions). Optimization of the conditions made it possible to reach a TOF of 93 h⁻¹, which is sufficiently high for tandem hydroformylation–hydrogenation of higher olefins.

Monflier and coll. have also studied the effect of the structure of tertiary amines in hydroformylation–hydrogenation of isosorbide diallyl ether (Scheme 28) [115]. The production of alcohols was only observed with tertiary amines with pK_a values comprised between 7 and 11. The highest yield in bis-primary alcohols (79%) was obtained in the presence of Rh(acac)(CO)₂ associated with the bidentate amine (*N,N,N',N'*-tetramethyl-1,4-butanediamine: TMBDA) at 8

MPa (CO : H₂ = 1 : 1) and 80°C for 6 h of reaction. Unexpectedly, the linear and branched products distribution was not impacted by the nature of the ligand (monodentate or bidentate), the amount of ligand or the CO/H₂ ratio. All these observations raise questions about the role of amines as ligands since their effectiveness seems to be essentially linked to their pK_a value and therefore to their basic nature.

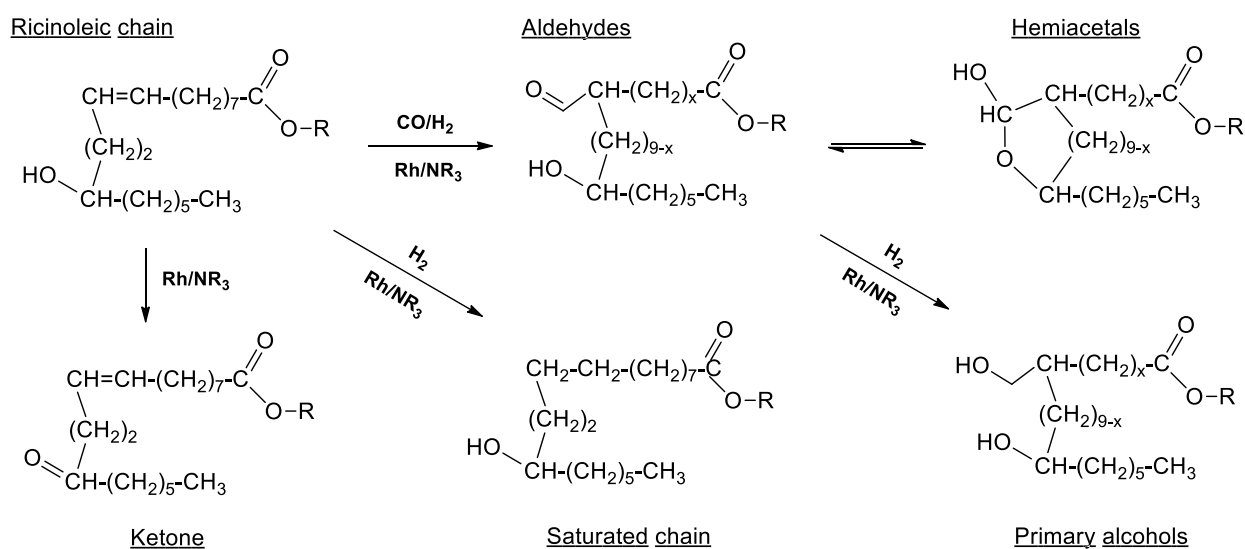


Scheme 28. Reductive hydroformylation of diallylisorbide into bis-primary alcohols.

The application range of Rh–tertiary amine catalytic systems was extended by Vanbésien et al. [116], who studied hydroformylation–hydrogenation of triolein. The best results in reductive hydroformylation of triglyceride were reached by using Rh(CO)₂(acac) and tributylamine as a ligand at 8.0 MPa (CO : H₂ = 1 : 1) and 140°C: under these conditions in 6 h, the yield of the corresponding alcohols was as high as 93%, and no unreacted aldehyde groups in the end product remained. The ruthenium-containing precursor [Ru(COD)Cl]₂ was low-active in hydrogenation of aldehyde groups (88% aldehydes and 8% alcohols). The Rh(CO)₂(acac)–Et₃N catalytic system was also successfully used for tandem hydroformylation–hydrogenation of commercial vegetable oils with monounsaturated hydrocarbon chains (olive and sunflower oils). In a further work [117], from sunflower oil functionalized by hydroxymethyl groups in such a process polyurethane was successfully obtained. In that work, an interesting specific feature of the Rh–NEt₃ catalytic system was found: as the reactor is cooled to room temperature at an incomplete conversion of double bonds (initial conditions: Rh(CO)₂(acac) : NEt₃ = 1 : 600, 80°C, 8 MPa, 3 h) while continuing stirring, the hydroformylation and hydrogenation of double bond stop, whereas the hydrogenation of the formed carbonyl groups continues until their complete conversion (20 h since the time of change of the temperature conditions). Thus, this demonstrated that the composition of the reaction products can be controlled, which, in the case of production of fat-based polymers, enables one to control the properties of the end materials. Vanbésien et al. managed to obtain polyurethane that retained about 20% double bonds of the initial fatty acids, which opens up the possibilities for further modification of the polymer.

In the field of valorization of biosourced substrates for application as monomers in bio-based polyesters and polyurethanes, the same group has studied the hydroformylation–hydrogenation of ethyl ricinoleate and castor oil in order to introduce an additional alcohol

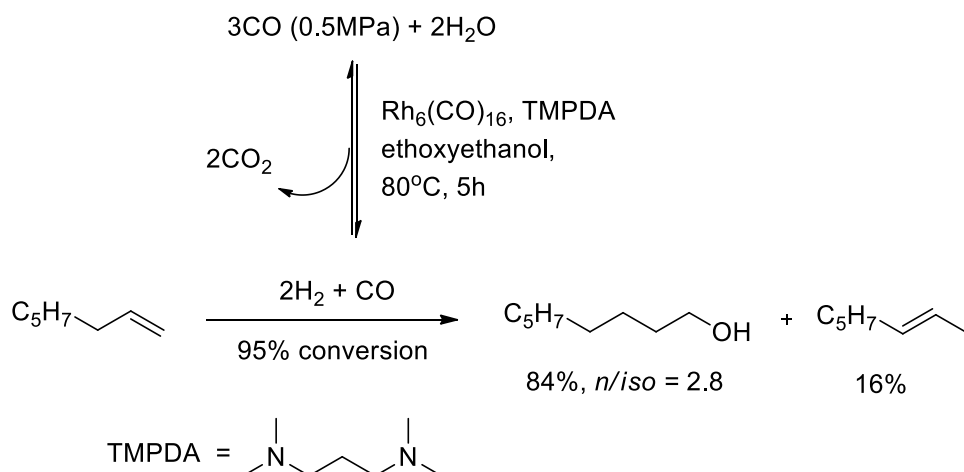
function (primary) on the chain[118]. Indeed, the ricinoleic acid is a C₁₈-fatty acid possessing a double carbon–carbon bond in the C-9 position and a hydroxyl group in the C-12 position. The hydrohydroxymethylation of ethyl ricinoleate (or castor oil) is a complex reaction leading to many products. Indeed, in addition to primary alcohols, two other kinds of co-products can be formed (Scheme 29). The first are cyclic hemiacetals coming from a lactolization reaction involving formyl, intermediately formed by hydroformylation reaction, and the hydroxyl group already present. The second is a ketone formed by isomerization of the double C=C bond leading to an enol giving by tautomerization a ketone. The challenge was to avoid the formation of hemiacetals and ketone. The typical reaction was carried out by using Rh(acac)(CO)₂ as a rhodium precursor, triethylamine (TEA) as ligand, and toluene as solvent under at 8.0 MPa (CO : H₂ = 1 : 1) at 80°C during 24 h. The conversion was completed and the yields in hemiacetals, ketone and primary alcohols were equal to 21%, 17% and 49%, respectively. In order to reduce the amount of ketone and to displace the formation of hemiacetals, the experimental conditions were modified. The best yield of 80% in primary alcohols was obtained by a two-step heating (80 °C during 48 h and then 100 °C during 32 h). No more hemiacetal was present and the by-products are ketone and saturated products (hydrogenation of the C=C). The hydroformylation–hydrogenation of castor oil was also performed in such conditions and a primary alcohols yield of 74% was reached.



Scheme 29. Transformations of a ricinoleic chain under CO/H₂ in the presence of the Rh/NR₃ catalytic system (R = Et or Glyceryl; x = 0-9).

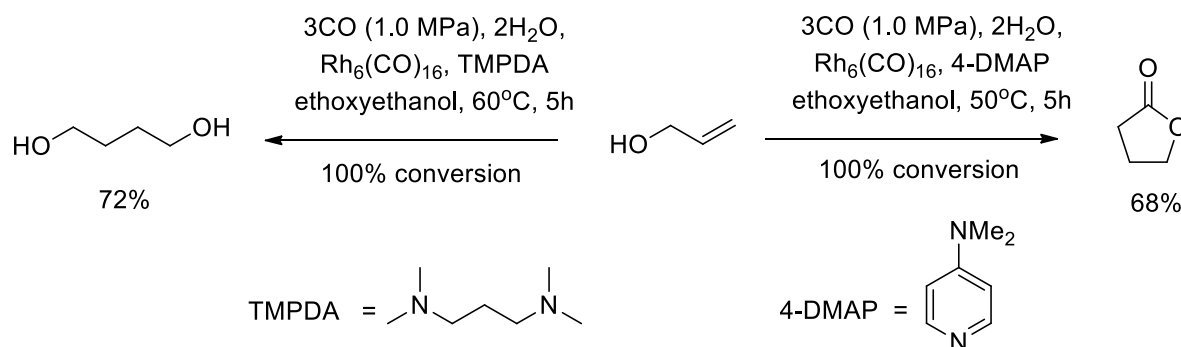
In 1981, [119] the water gas shift reaction was used as an alternative source of syngas for reductive hydroformylation in a Rh/amine system. Particularly high activity in conversion of 1-octene in a medium of ethoxyethanol (Scheme 30) was shown by a rhodium complex with N,N,N',N'-tetramethyl-1,3-propanediamine (TMPDA). The total conversion of 1-octene was 95%; *n*-nonanol was primarily produced (84% C₉ alcohols, *n* : *iso* = 2.8). 4-Dimethylaminopyridine

(4-DMAP) as a ligand was also efficient enough, whereas the systems with pyridine, N-methylpiperidine, and triethylamine only initiated migration of the double bond in 1-octene. The catalyst produced from the $\text{Rh}_6(\text{CO})_{16}$ cluster showed the highest activity in the tandem reaction, and the activity of the other catalysts changed in the order $\text{Rh}_4(\text{CO})_{12} > \text{Rh}_2(\text{CO})_4\text{Cl}_2 > \text{RhCl}(\text{PPh}_3)_3 > \text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. Unlike simple α -olefins, α,β -unsaturated carbonyl compounds, such as cinnamaldehyde and mesityl oxide, under the above conditions were only hydrogenated at the double bond and did not enter into hydroformylation.



Scheme 30. Reductive hydroformylation under WGSR conditions.

In 1983 [120], a similar catalytic system (Rh–N,N,N',N'-tetramethyl-1,3-propanediamine) was used for tandem hydroformylation–hydrogenation of allyl alcohol under WGSR conditions (Scheme 31), which gave 1,4-butanediol with a yield of 72%. Using the aromatic ligand 4-dimethylaminopyridine, the main product was γ -butyrolactone, the yield of which was 68%.



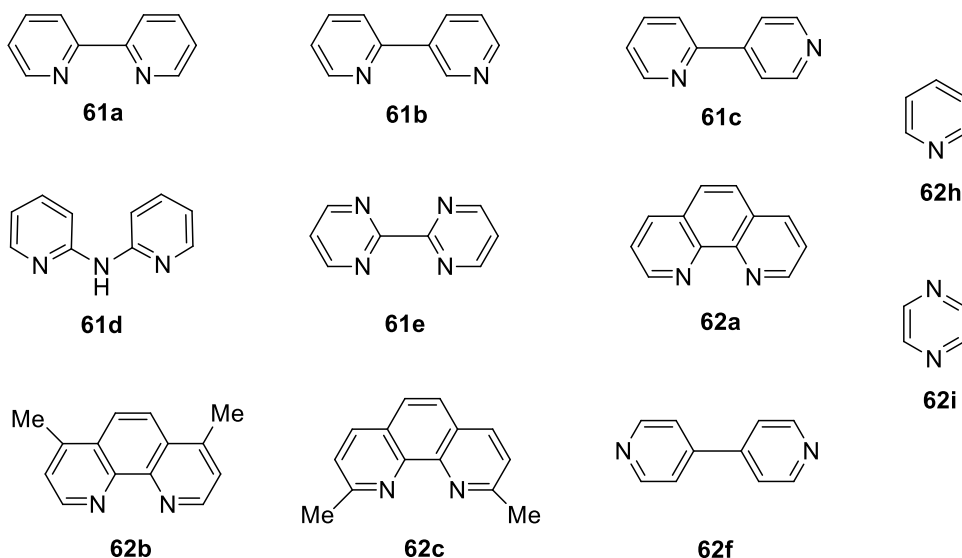
Scheme 31. The synthesis of 1,4-butanediol and γ -butyrolactone under WGSR conditions.

Polynuclear carbonyls of iron, ruthenium, osmium, iridium, and rhodium were tested as catalysts of hydroformylation of propylene under WGSR conditions at $100\text{--}180^\circ\text{C}$ in the presence of trimethylamine [121]. For all the studied systems, the formation of aldehydes (n : iso = 1.0–

11.5) and a certain amount of alcohols was observed. The formation of alcohols was found to depend on the pH of the system.

Addition of ruthenium complexes to rhodium–phosphine catalytic systems is one of the most successful approaches to ensuring the activity of the system in hydrogenation of aldehydes [106,122] because some of the ruthenium compounds are active in hydrogenation. Moreover, as noted above, ruthenium complexes can also catalyze hydroformylation. Monometallic ruthenium systems containing N-ligands were tested as catalysts of tandem hydroformylation–hydrogenation [123,124].

A number of bipyridine ligands (Scheme 32, **61a–61e**) in combination with a ruthenium precursor (RuO_2 or $\text{Ru}_3(\text{CO})_{12}$) were used in regioselective hydroformylation–hydrogenation of propylene and 1-octene in a medium of Bu_4PBr (180°C, 8.5 MPa, $\text{CO} : \text{H}_2 = 1 : 2$, 4 h) [123]. The best results were obtained by using the RuO_2 –2,2'-bipyridine system for 1-octene (the yield of alcohols was 79%, *n*- : *iso*- = 6.3) and $\text{Ru}_3(\text{CO})_{12}$ –2,2'-bipyrimidine for propylene (89% *n*-butanol at 100% regioselectivity). The catalytic activity of ruthenium carbonyl complexes with mono- and bidentate aromatic nitrogen-containing ligands was investigated in hydroformylation of 1-hexene in 1-methyl-2-pyrrolidone (2.0 MPa, 120°C, 17 h). [124] For the complexes with chelating and bridging ligands (Scheme 32, **62a–62e**), the yields of both aldehydes, and alcohols were much lower in comparison with pure ruthenium carbonyl chloride $[(\text{Ru}(\text{CO})_3\text{Cl}_2)_2]$, whereas for the complexes with monodentate ligands (Scheme 32, **62f, 62g**), the decrease in the activity was less pronounced. The most active was a mononuclear complex with pyridine, $[\text{Ru}(\text{py})(\text{CO})_3\text{Cl}_2]$: in 17 h at 120°C and 2.0 MPa, the yield of aldehydes was 51%, the yield of alcohols was 20%, and the total conversion was 86%, whereas using $[(\text{Ru}(\text{CO})_3\text{Cl}_2)_2]$, 41% aldehydes and 30% alcohols were produced, and the total conversion was 97%. This difference is explained by strong coordination interactions of the metal site with chelating and bridging ligands; these interactions complicate the dissociation of the initial metal complex, which is necessary for the formation of a catalytically active particle.



Scheme 32. The structures of ligands **61-62**.

3.1.2. Biphasic Systems

Recently, two independent works were published where the biphasic reductive hydroformylation was performed in non-phosphorous catalytic systems. Both used amino alcohols as water-soluble ligands for Rh complexes. The research made by Karakhanov's group [125] was focused on triethanolamine (TEOA) – a cheap and easily available liquid compound, which can be used as a water-soluble ligand and as a separate polar phase for biphasic reductive hydroformylation. $\text{Rh}(\text{acac})(\text{CO})_2$ was preliminary dissolved in TEOA at heating (Fig. 3). $\text{TOF} = 82 \text{ h}^{-1}$ was reached in the hydroformylation-hydrogenation of 1-octene (6.0 MPa, 100°C). Dodecane was more suitable as a non-polar phase than toluene because of the considerable amine leaching in the case of the aromatic solvent. The TEOA phase was used in six sequential reactions without loss in the alcohols' yields. IR and NMR studies showed that $[\text{Rh}(\text{CO})_4]^-$ is present in the freshly-recovered polar phase after the reaction.

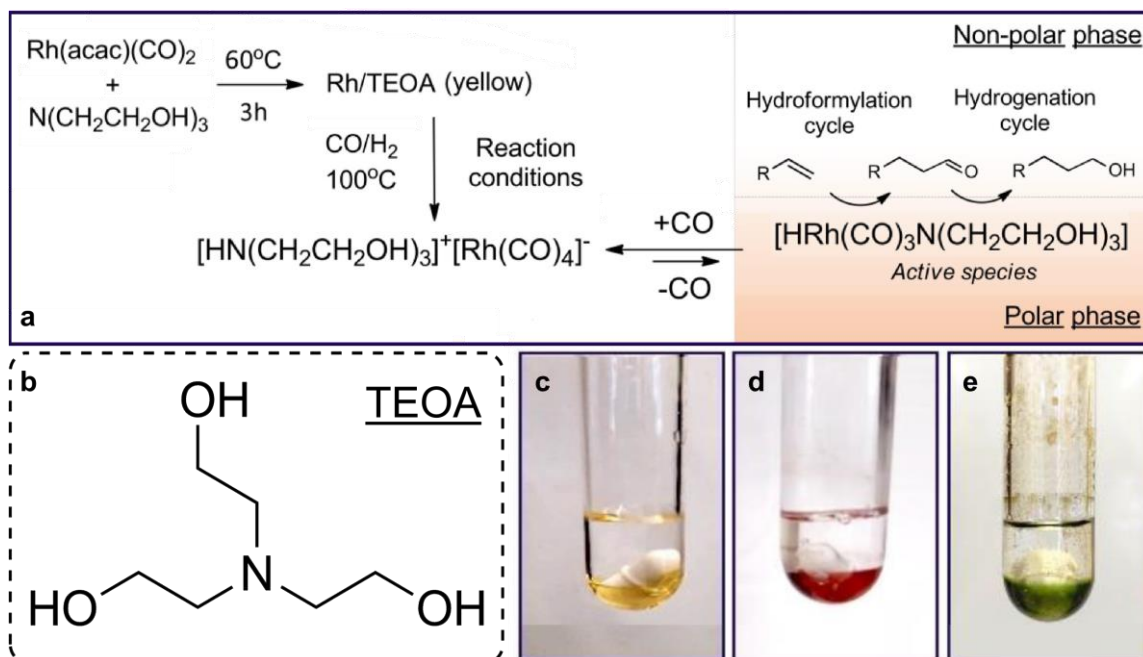


Fig. 3. Biphasic reductive hydroformylation in Rh/TEOA-dodecane system. (Adapted from paper [125])

In the work [126], published online only about a week later, several ligands of that type were tried. Dimethylaminoethanol turned out to be the most effective water-soluble ligand of the range under the conditions tested for the reductive hydroformylation (9.0 MPa, 100°C). Moreover, the system with it possessed one of the lowest Rh leaching values (0.5%). The continuous flow experiments (Fig. 4) showed stable hydroformylation yields for 50 hours with a gradual decrease in the alcohols' selectivity (total TON = 1236 for alcohols' production). The authors suggested that it is caused by the leaching of the amine into the product stream and hence the drop possibly can be diminished by controlling the amine concentration during the flow experiment.

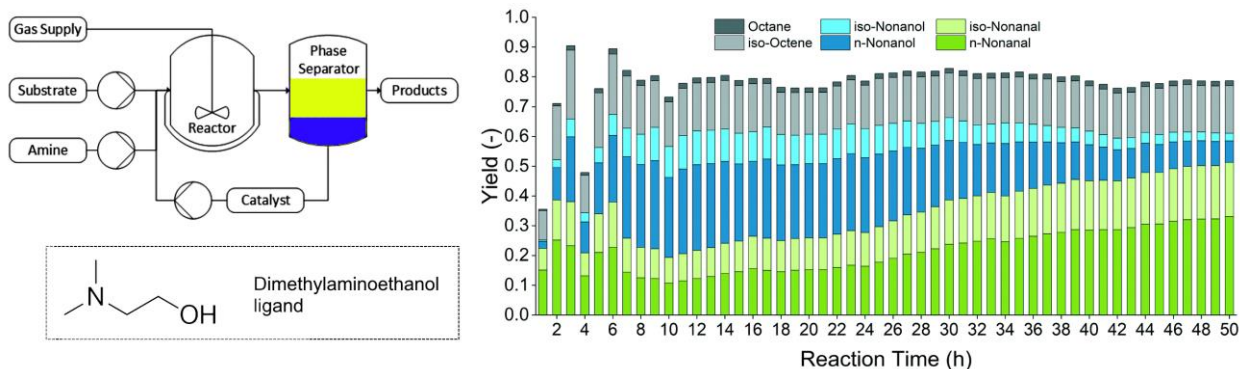


Fig. 4. Biphasic continuous flow reductive hydroformylation. (Adapted from paper [126])

3.1.3. Heterogeneous and Immobilized Systems

Particularly promising is the development of heterogeneous catalytic systems combining the activity in tandem reactions with the simplicity of their separation from reaction media. Along with homogeneous catalytic systems, Jurewicz et al. [109] studied systems based on functionalized crosslinked polymers, including polydimethylbenzylamine (PolyDMBA), which is a heterogeneous analog of dimethylbenzylamine. A catalyst based on this polymer demonstrated higher selectivity toward C₇ alcohols in tandem hydroformylation–hydrogenation of 1-hexene in comparison with homogeneous systems. Under the conditions of the reactions in the catalytic system, IR spectroscopy detected anionic complexes Rh₁₂(CO)₃₀²⁻, Rh₃(CO)₁₀⁻, and Rh₇(CO)₁₆³⁻ (rhodium was initially deposited as the complex Rh₂(CO)₄Cl₂).

Further, studies of tandem hydroformylation–hydrogenation on rhodium catalysts based on various polymers were continued [127–132]. The stability of such catalysts in hydroformylation–hydrogenation of dicyclopentadiene to dicyclopentadienedimethanol was investigated (Scheme 25) [127]. Scheme 33 presents the structures of Dowex, Amberlite, and Reilly polymers tested in that work. A rhodium precursor was deposited on the polymers in several states: as Rh₄(CO)₁₂ and RhCo₃(CO)₁₂ clusters and also as Rh₂O₃. The composition of the reaction products and the rate of their formation were independent of the type of the source of Rh, but the reaction rate depended on the Rh concentration.

Under the reaction conditions (130°C, CO : H₂ = 1 : 2, 28.0 MPa, 2 h), the most stable catalyst was Dowex/Rh₄(CO)₁₂: the yield of the diol did not decrease over 25 runs, remaining about 25%. The catalysts based on Reilly and Amberlite resins gradually lost efficiency in hydrogenation of aldehydes, and the selectivity toward alcohols decreased. It was assumed [127] that the deactivation of the catalyst is caused by the degradation of the structure of the polymer and its induced decrease in the accessibility of the tertiary nitrogen atom and, hence, in the number of accessible Rh–N sites necessary to catalyze the step of reduction of aldehyde to alcohol.

Bimetallic catalysts based on Dowex resin were also produced and investigated [129–132]. To synthesize them, the support was impregnated with a solution of the cluster Co₂Rh₂(CO)₁₂ and also with a solution of a mixture of Co₄(CO)₁₂ and Rh₄(CO)₁₂. Bound to the amine support, the mixed metal cluster Co₂Rh₂(CO)₁₂ and the Co₄(CO)₁₂–Rh₄(CO)₁₂ mixture demonstrated high efficiency in hydroformylation of 1-hexene [130]. The yields of alcohols in 17 h at 5.0 MPa and 130°C were 95% (*n-* : *iso-* = 0.7) and 99% (*n-* : *iso-* = 1.1) for Dowex/Co₂Rh₂(CO)₁₂ and Dowex/(Co₄(CO)₁₂–Rh₄(CO)₁₂) (Rh : Co = 2.6), respectively. The Rh : Co metal ratio in the

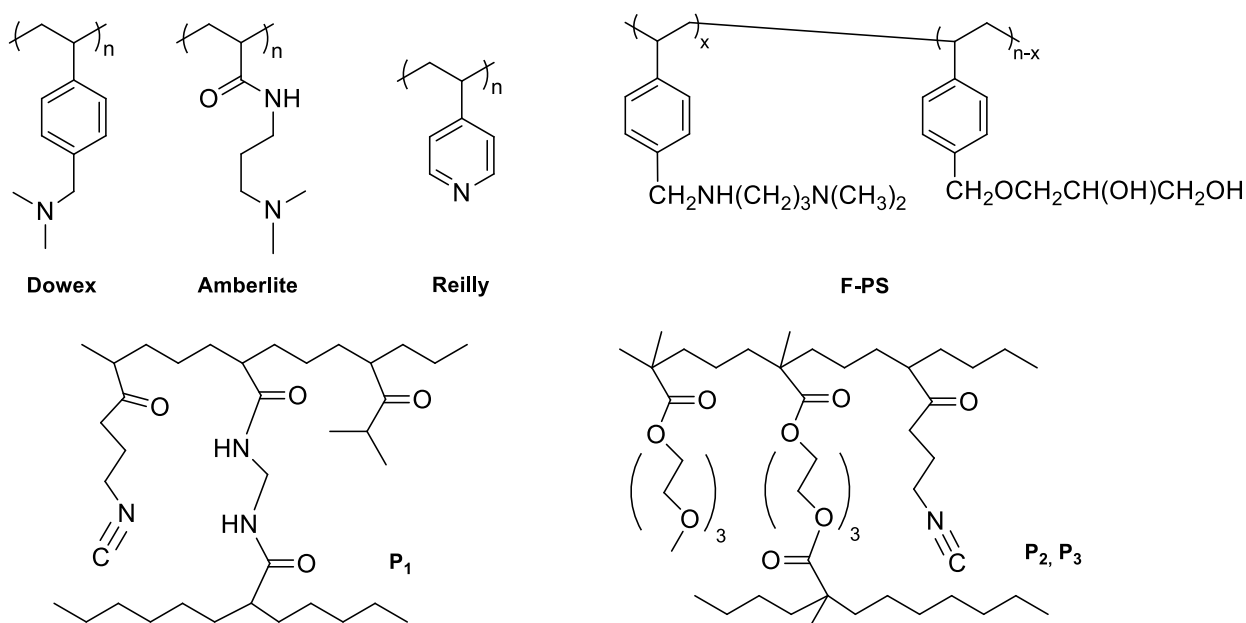
$\text{Co}_4(\text{CO})_{12}\text{-Rh}_4(\text{CO})_{12}$ mixture affects significantly the activity of the system and the selectivity of the reaction toward alcohols. Internal and cyclic olefins were also successfully subjected to hydroformylation–hydrogenation using these catalytic systems.

Kaneda et al. [133] studied hydroformylation–hydrogenation under WGSR conditions on a heterogeneous rhodium catalyst obtained from functionalized polystyrene containing ternary nitrogen atoms (Scheme 33).

Oxygen-containing groups were introduced to the structure of the polymer to increase the hydrophilicity in the environment of rhodium catalytic sites, which, in this variant of the process, should be active in not only hydroformylation and hydrogenation of aldehydes, but also water gas shift reaction. It was assumed [133] that the oxygen-containing functional groups also participate in the stabilization of anionic rhodium clusters. Interestingly, Kaneda et al. provided the only published example of hydroformylation–hydrogenation of an unsaturated substrate that is gaseous under normal conditions—1-butene – in a Rh/amine system. Using a catalyst based on polymer (F-PS), the yield of C_5 alcohols in tetrahydrofuran was 83% (n - : iso - = 1.68) after 24 h of the reaction (CO pressure 2.0 MPa, 80°C, Rh : 1-butene = 1 : 100). The catalyst remained active in at least one reuse.

Hydroformylation–hydrogenation on rhodium catalysts based on macromolecular isocyanides (Scheme 33) was investigated [134,135]. Polymers **P**₁ and **P**₂ were initially obtained as formamide precursors, which were then treated with sulfonyl chloride to produce isocyanide fragments, whereas **P**₃ was synthesized directly from an isocyanide monomer.

Rhodium was deposited on the polymers from a $\text{Rh}(\text{CO})_2(\text{acac})$ solution. IR spectroscopy data suggested that rhodium in the freshly prepared catalyst is bound to the isocyanide group of the polymer; however, in the course of the hydroformylation–hydrogenation, there occur hydrogenation of the isocyanide ligand and reduction of monovalent rhodium to metal clusters (2–7 nm), which were detected by scanning electron microscopy. The catalysts based on all the produced polymers were active in both steps of hydroformylation–hydrogenation of 1-hexene at 12°C, 12.0 MPa, and $\text{CO} : \text{H}_2 = 1 : 1$. The yields of C_7 alcohols in 5 h were 70–100% with an n - : iso - ratio of 0.8–1.1 for the first run. Each of the catalysts was used in three consecutive reactions. The rhodium loss due to leaching in each run was to 4%. The minimum rhodium loss was demonstrated by the catalyst based on polymer **P**₁ (the yield of alcohols in the third run was 100%).



Scheme 33. The structures of N-containing polymers used for reductive hydroformylation.

The creation of silica-gel-based heterogeneous catalysts of tandem hydroformylation–hydrogenation was reported [136,137]. In their synthesis, the material was functionalized by the interaction of alkoxy silane derivatives of primary amines with hydroxyl groups of the surface of silica gel; further, the material was treated with a mixture of formalin and formic acid (Eschweiler–Clarke reaction) to methylate amino groups. A patent [136] showed that the catalysts based on such materials have higher activity in tandem hydroformylation–hydrogenation of 1-hexene than the previously described catalysts based on the polymer containing dimethylbenzylamine fragments (at 100°C and 7.0 MPa). However, the results of experiments made to estimate the stability of catalysts of this type [137] suggested the strong leaching of rhodium into solution and the impossibility of multiple reuse of the catalysts without loss of activity.

In a recent work, [138] Karakhanov’s group has obtained rhodium catalysts based on hybrid materials, which were silica gel matrices with polyethyleneimine (WP-1) and polyallylamine (BP-1) grafted on the surface. The produced catalysts were active in both hydroformylation of olefins, and hydrogenation of the formed aldehydes: in 12 h at 6.0 MPa and 80°C, 92% of 1-octene was converted to C₉ alcohols (*n*- : *iso*- = 1.1). The catalyst K_N based on the modified material with polyallylamine (Fig. 5, a) was the most stable: the formation of C₉ alcohols from 1-octene occurred in at least five consecutive reactions; however, their yield gradually decreased from 33% in the first run to 9% in the fifth run in 5 h (Fig. 5, b). Transmission electron microscopy and X-ray photoelectron spectroscopy of the catalyst before and after the reaction showed that no nanoparticles form during the reaction, and that rhodium is on the surface as complexes in the oxidation state +1.

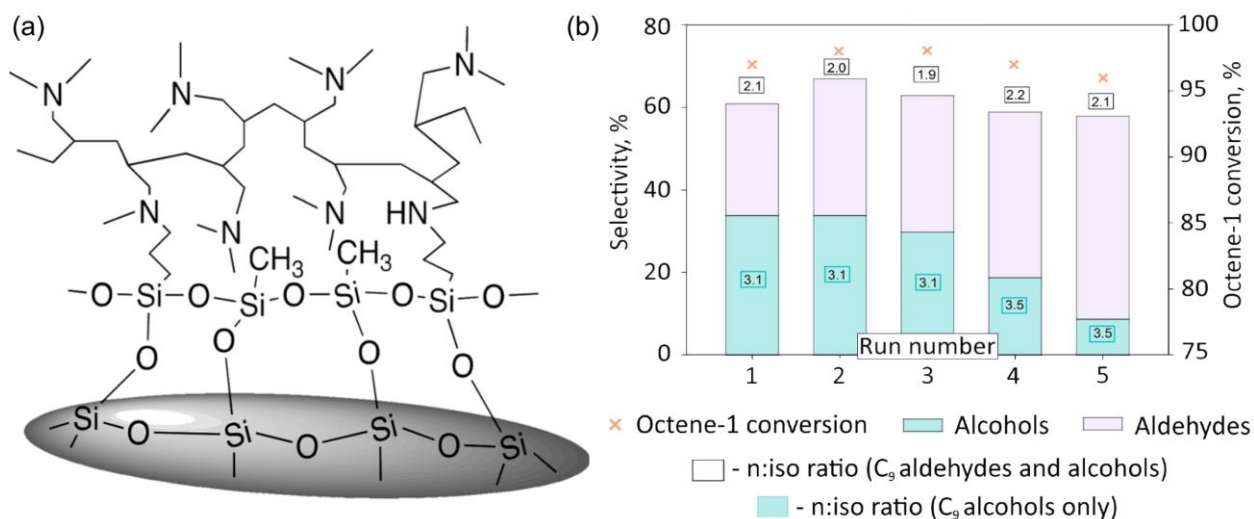


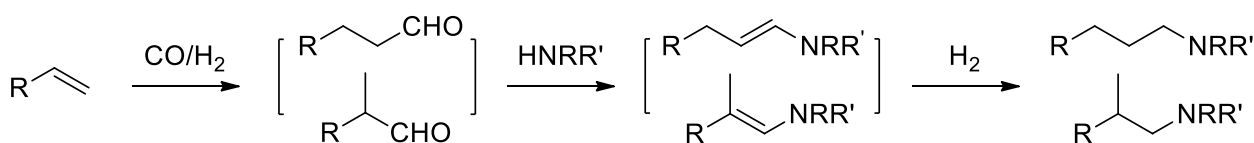
Fig 5. Structure of modified BP-1 support (a), results of K_N catalyst reuses. (Adapted from paper [138])

The activity of ruthenium complexes with 2,2'-bipyridine on various silicate supports was studied in tandem hydroformylation–hydrogenation of hexene and a number of other alkenes [139–142]. The best results were obtained with silica **f22** as a support (with a specific surface area of 400 m²/g): the yields of alcohols reached 40–97% (*n* : *iso* = 1.5–1.1) at 150°C and 5.0 MPa in 17 h. Leaching of ruthenium into the solution was detected visually, and no data were presented on the possibility of multiple reuse of the catalysts. Along with 2,2'-bipyridine, other nitrogen-containing heterocyclic bases were also tested (4,4'-dimethyl-2,2'-bipyridine, 2,2'-bipyrimidine, and 1,10'-phenanthroline), but the yield of alcohols using them was much lower (9–31%) [139]. Addition of a cocatalyst—rhodium—to the system led to a significant increase in the yield of alcohols to 86–96% (*n* : *iso* = 0.9) [141].

3.2. Other Tandem Reactions

3.2.1. Hydroaminomethylation

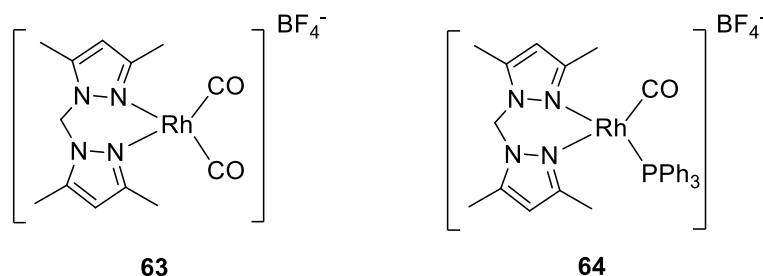
Another practically important tandem reaction is hydroaminomethylation (Scheme 34) [143]. It is a tandem process, which is a sequence of three steps: hydroformylation of olefin to *n*- and *iso*-aldehydes; condensation of the formed aldehydes with primary or secondary amines to form imines or enamines, respectively; and hydrogenation of imines and enamines to saturated secondary and tertiary amines.



Scheme 34. Hydroaminomethylation reaction.

In 2003, Kalck and colleagues [43] obtained complex **63** (Scheme 35) modified with a nitrogen-containing ligands, which was highly active in conversion of 1-octene in the presence of diethylamine: in 6 h at 80°C and 1.2 MPa (CO : H₂ = 1 : 1) at a conversion of 1-octene of 67%, the selectivity toward amines was 85% with an *n*- : *iso*- ratio of 1.6, with the only byproducts being isooctenes.

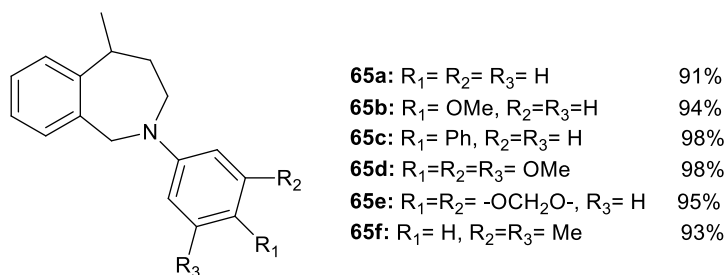
After substitution of triphenylphosphine for one of the carbonyl ligands (complex **64**), the regioselectivity of the reaction increased (*n*- : *iso*- = 2.57), but the fraction of amines in the mixture of the products was lower than that using complex **63**: 35% were aldehydes, and 24% were enamines.



Scheme 35. The structures of complexes **63** and **64**.

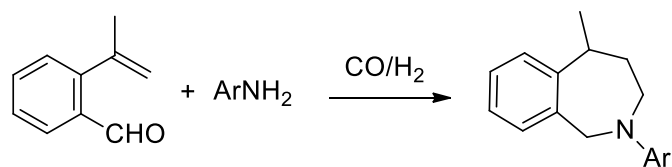
Alper and colleagues, who developed the above-described system for hydroformylation of olefins based on ionic rhodium complexes, [54] also investigated hydroaminomethylation using these compounds [144–146]. In those works, attempts were made to use intramolecular hydroaminomethylation to produce heterocyclic nitrogen-containing compounds. In 2007, they successfully performed intramolecular hydroaminomethylation of 2-isopropenylanilines to form 1,2,3,4-tetrahydroquinolines [144]. Tetrahydroquinolines play an important role in medicinal chemistry and are also used to synthesize agrochemicals. Under optimal conditions (120°C, 6.9 MPa, CO : H₂ = 7 : 3, 5–7.5 mol % catalytic complex, 48 h), a number of substituted 1,2,3,4-tetrahydroquinolines were obtained with yields of 70–98%.

In a next work published in the same year [145] by a similar reaction using the same catalytic system, Vieira and Alper obtained compounds containing a seven-membered heterocycle. Scheme 36 presents some of these compounds (**65a–65f**).



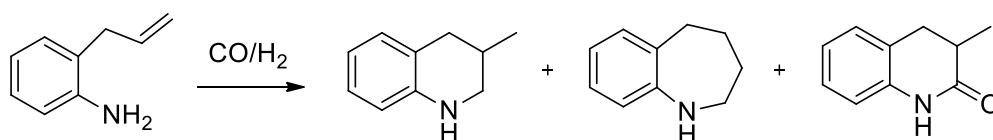
Scheme 36. The structures of compounds **65a–65f**.

The next step was also made by demonstrating the possibility to produce the initial secondary amine substrate *in situ* from the corresponding primary amine and aldehyde (Scheme 37).



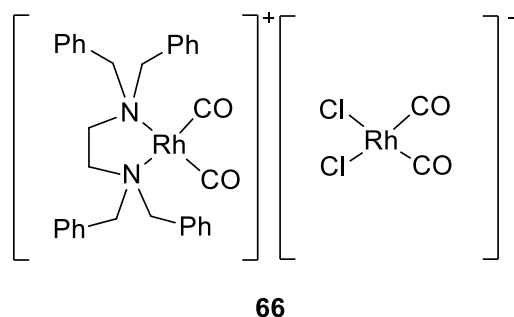
Scheme 37. One-pot synthesis of 2-benzazepines.

Tandem intramolecular hydroaminomethylation of 2-allylanilines was carried out to obtain compounds containing six- and seven-membered heterocycles (Scheme 38) [146].



Scheme 38. Intramolecular hydroaminomethylation.

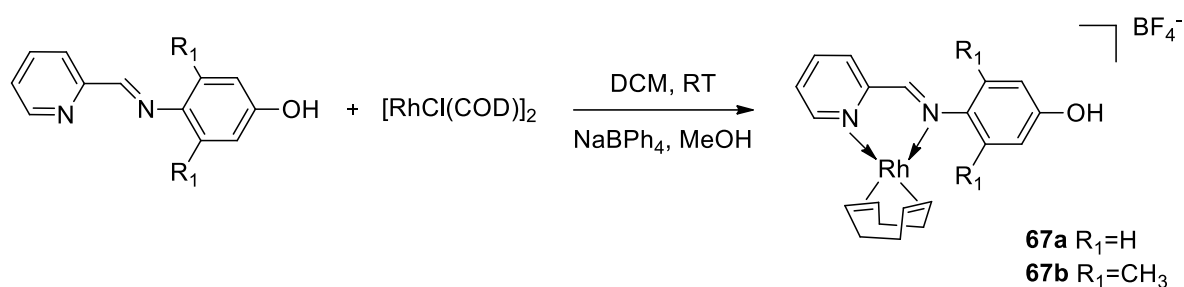
To increase the selectivity of the reaction, instead of the ethylenediamine ionic rhodium complex, sterically hindered complex **66** was used (Scheme 39).



Scheme 39. The structure of complex **66**.

For a number of substrates, this favored an increase in the selectivity toward six-membered heterocycles.

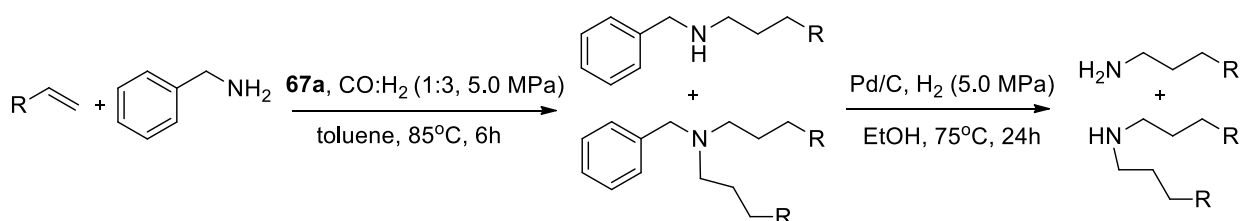
In continuation of the investigation of iminopyridine complexes of rhodium, October and Mapolie [147] studied hydroaminomethylation of aliphatic acyclic alkene using complexes of this type (complexes **67a** and **67b**, Scheme 40).



Scheme 40. The synthesis of complexes **67a** and **67b**.

Studying the reaction by the examples of 1-octene and piperidine, October and Mapolie [147] compared the catalytic activity of complexes **67a** and **67b** with that of the phosphine complex $HRhCO(PPh_3)_3$. As it was expected, the phosphine complex was more active in hydroformylation, but the selectivity toward the desired amines in the presence of the complex was only 11%, whereas that using complex **67a** was 52% (70°C, 3.0 MPa). Under optimal conditions (3.0 MPa, 85°C) in 2 h at a conversion of 99%, 89% desired amine and 10% isooctenes were obtained. Reactions with primary amines (aniline and benzylamine) as aminating agents were also investigated. Although the yields of the desired products can exceed 95% using both of the amine substrates, the high yields using benzylamine are reached under milder conditions than using aniline.

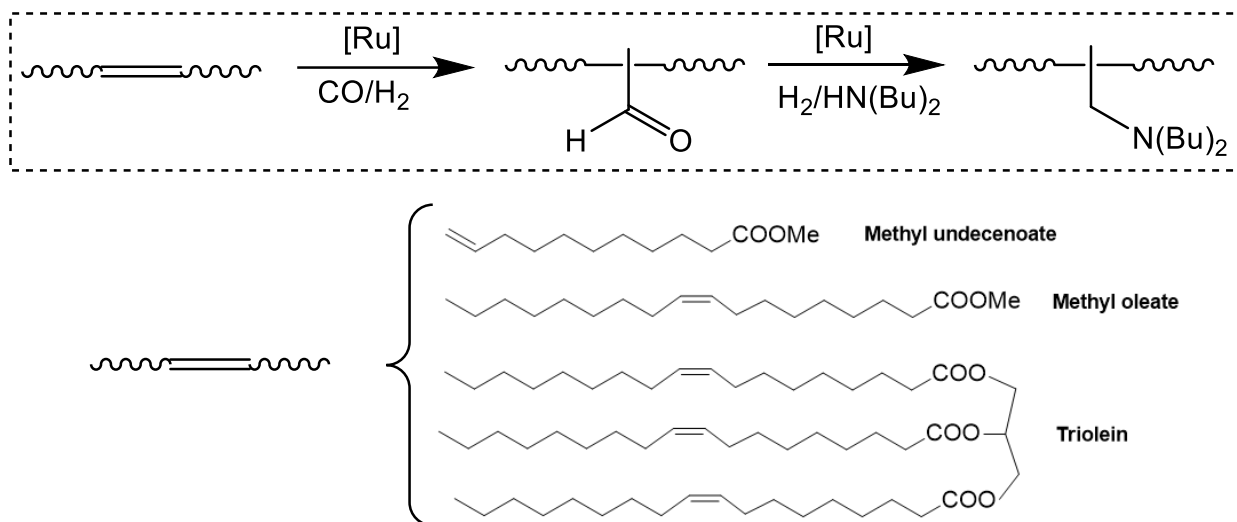
Further, the sequence of hydroaminomethylation in the presence of complex **67a** and hydrogenolysis on Pd/C [148] enabled one to convert benzylamine and various unsaturated substrates to a number of primary and secondary amines with high yields (Scheme 41).



Scheme 41. The production of primary and secondary amines through hydroaminomethylation step.

Monflier and coll. investigated Ru-catalyzed hydroaminomethylation of unsaturated oleochemicals (Scheme 42) [149]. Methyl undecenoate, methyl oleate and triolein were used as model substrates and Ru_3CO_{12} as a ruthenium precursor. Various secondary amines were tested as both reactants and ligands for ruthenium. For triolein, the best result was obtained by using dibutylamine and toluene as solvent under at 10.0 MPa ($CO : H_2 = 1 : 1$) at 110°C during 18 h. The conversion was equal to 45% and the selectivity in amino derivatives equal to 94%. For methyloleate and methyl undecenoate in the same conditions, the conversions were equal to 52% and 100%, and the selectivity in amino derivatives equal to 97% and 70%, respectively. Finally,

the best result (100% of conversion and 96% in amino derivatives; 10.0 MPa (CO : H₂ = 1 : 1) at 140°C during 66 h.) was obtained with methyl undecenoate in acetonitrile as solvent. To conclude, ruthenium complexes were less active than rhodium complexes but more selective in amino derivatives.

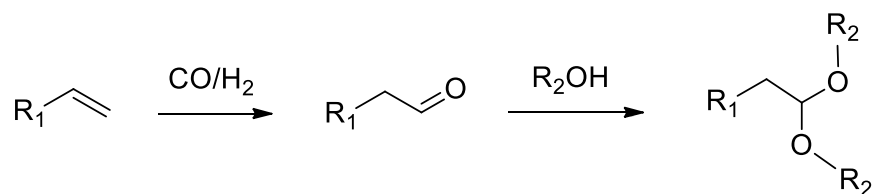


Scheme 42. Hydroaminomethylation of long-chained unsaturated esters.

In the recent work of Karakhanov's group [125], devoted mainly to tandem hydroformylation-hydrogenation in the biphasic system containing TEOA, the system was also tested in biphasic hydroaminomethylation. As far as we know, it was the first example of the phosphorus-free biphasic system with a water-soluble N-ligand for this reaction. The water phase contained a Rh/TEOA complex and dimethylamine, so both the catalyst and the amine were present in the same phase. The system was active in at least five sequential reactions of hydroaminomethylation of hexene-1 with no significant loss in the yields of the product amines.

3.2.2. Hydroformylation–Acetalization

In tandem hydroformylation–acetalization (Scheme 43), the formed aldehyde enters into the reaction of acetalization with the alcohol contained in the system. The end products of the reaction are acetals, which are highly promising as surfactants, oil additives, emulsifiers, and cosmetic ingredients [150–152].



Scheme 43. Hydroformylation-acetalization reaction.

A series of studies [153–155] were made to investigate the catalytic conversions of 1-hexene in the presence of the rhodium complexes $\text{Rh}(\text{CO})_2(\text{N-base})_2(\text{PF}_6)$ under the pressure of carbon monoxide in a medium of methanol. The nitrogen-containing ligands were various picolines and lutidines [153]. Under these conditions, several catalytic processes simultaneously occurred: methoxycarbonylation to form methyl heptanoate; hydroformylation to heptanal, which then interacted with methanol to give 1,1-dimethoxyhexane; and also WGSR to give hydrogen and CO_2 , which were detected by analyzing the gas mixture. An additional experiment determined that the acetalization of aldehyde in the system can also occur without addition of the catalyst. The dependences of the yields of ester and acetal on the CO pressure were different: the maximum yield of methoxycarbonylation in the range 1.5–5.5 MPa was at a pressure of 2.5 MPa, whereas the activity of the system in hydroformylation monotonically increased with increasing pressure in this range. At 100°C and 5.5 MPa (complex $[\text{Rh}(\text{CO})_2(4\text{-pic})_2](\text{PF}_6)$), the yield of acetal was 64% in 4 h, and almost no unacetalized aldehyde remained. In the series of methyl- and dimethylpyridines, the most efficient ligands for hydroformylation were 3-picoline and 3,5-lutidine. Intriguingly, if syngas is used instead of pure carbon monoxide, then no hydroformylation occurs in this system. It was assumed [153] that successful hydrogenolysis of the Rh–acyl complex requires specific intermediates formed by WGSR. A similar cyclooctadienyl complex was immobilized on poly(4-vinylpyridine) [154,155]. The leaching of rhodium in the first use was less than 0.1%. The total yield of oxygenates remained quite stable in five consecutive reactions; however, the selectivity changed toward higher fractions of acetal and lower fractions of ester in the final mixture of products, which probably suggests changes in the structure of the catalyst. Also of note are examples of successful tandem hydroformylation–acetalization on ruthenium carbonyl in ionic liquids, although, strictly speaking, in this case, nitrogen-containing compounds act as solvents, rather than ligands [156]. Addition of acetic acid allowed one to obtain isomeric cyclic acetals from 1-octene and ethylene glycol with a yield of 87% in 20 h of reaction (at a temperature of 140°C and a syngas pressure of 2.0 MPa). As side processes, alkoxycarbonylation and hydrogenation of aldehyde to alcohol were observed. Acetals were synthesized from a number of other diols, and also glycerol. The reaction products were separated from the ruthenium-

containing ionic liquid by extraction with a nonpolar solvent; thus, the system was used in three consecutive reactions without dramatic decrease in the activity.

4. Conclusions

Although the earliest works on hydroformylation on rhodium complexes with nitrogen-containing ligands were published about half a century ago, this subject is still insufficiently studied. In homogeneous systems, with few exceptions, ligands do not increase either the rate of hydroformylation, or its regioselectivity. The known water-soluble catalytic systems, with which the reaction can be performed under biphasic catalysis conditions, are mostly prone to relatively rapid deactivation, although certain significant success has been achieved in recent years in the development of water-soluble ligands. On the other hand, an obvious advantage of the systems with nitrogen-containing ligands is their high potential in tandem hydroformylation-based reactions which require additional hydrogenating activity: hydroformylation–hydrogenation and hydroaminomethylation.

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