Diphosphinerhodium(I) and (Ether-diphosphine)rhodium(I) Complexes in Homogeneous and Biphasic Hydroformylation of 1-Hexene and in Homogeneous Hydrogenation of Carbon Dioxide

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(Diphosphan)rhodium(I)- und (Ether-diphosphan)rhodium(I)-Komplexe in der homogenen und Zweiphasen-Hydroformylierung von 1-Hexen und in der Hydrierung von Kohlendioxid

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Contents

COD	Cyclooctadiene
dppb	Diphenylphosphinobutane
EI	Electron ionization (mass spectroscopy)
FAB	Fast atom bombardment (mass spectroscopy)
FD	Field desorption (mass spectroscopy)
g	Grams
gc	Gaschromatography
h	Hours
Hz	Hertz
IR	Infrared spectroscopy
M	Molarity
min	Minute
ml	Mililiter
mmol	Milimole
MS	Mass spectroscopy
n	Non-branched alkyl chain
NMR	Nuclear magnetic resonance spectroscopy
P,O	P-coordinated ether-ligand
PPh_3	Triphenylphosphine
ppm	Parts per million
TPPTS	tris(*m*-sulfonylphenyl)phosphine

Greek Letters:

δ	Chemical shift
μ	Mikro
η	Hapticity
ν	Frequency

Introduction

Catalysis is of extraordinary importance to industry and society today. It is evident that the development of new catalytic processes is a key element for economically and ecologically improved chemical production in the future.

The hydroformylation of olefins is an extensively studied catalytic process [1,2] and from an industrial point of view, one of the most important homogeneously catalyzed reactions, since world-wide more than six million tons of aldehydes are generated each year [3]. Regarding the rapid developments and researches in hydroformylation processes their importance becomes evident. Starting 60 years ago heterogeneous catalysts were first applied in the hydroformylation [3], followed by homogeneous cobalt and rhodium systems. Nowadays ligand modified catalysts [4] and water-soluble complexes in two-phase catalysis were employed in the hydroformylation [5,6].

Since Wilkinson's discovery of the catalytic activity of the complex $HRh(PPh_3)_3(CO)$ in 1968 [7], rhodium based systems modified with different phosphine ligands occupied a predominant position in hydroformylation. The selectivity and activity are influenced by variation of steric and electronic properties of the ligands. Generally, chelating diphosphines show higher selectivities and activities in the hydroformylation of alkenes [1,8-12] than their monodentate counterparts. The application of such complexes in the presence of excess phosphine leads to selectivities for aldehyde formation of up to 99 % and to *n*-aldehyde portions in the range of 95 %.

Coordinatively unsaturated and hence very reactive metal complexes are usually generated in situ and are protected by the temporarily coordination of solvent molecules [13,14]. It is important that the solvent forms only a weak bond to the metal in order to enable a fast displacement of the metal-solvent contact by an incoming substrate. The introduction of

bifunctional ether-phosphines (O,P) has significantly affected the isolation of coordinatively unsaturated species [15-21]. These ligands are provided with oxygen atoms incorporated in open-chain ether moieties which form a weak metal-oxygen contact while the phosphorus atom is strongly coordinated to the metal. In these “hemilabile“ ligands the ether moiety is regarded as an intramolecular solvent molecule stabilizing the vacant coordination site by chelation. Moreover steric and electronic properties of this kind of phosphines can be varied in a wide range. Ether-phosphine ligands which were employed in the present investigations can be adapted for many special aims.

In catalytic processes the separation of products from the catalysts is still the main obstacle for commercial application. Further, the necessity for improved technologies due to environmental challenges and economic profitability are essential motives to investigate new processes for the hydroformylation of olefins. To overcome these problems, the use of water-soluble catalysts in biphasic systems received much attention, considering the ecologic aspects of replacing an organic solvent by water. A simple decantation after the reaction allows the separation of the catalyst from the organic products. Thus, in 1984 the biphasic Ruhrchemie/Rhône-Poulenc oxo process was industrially introduced for the hydroformylation of propene to butyraldehyde which is based on the water-soluble rhodium complex $HRh(CO)(TPPTS)_3$ (TPPTS = tris(*meta*-sulfonylphenyl)phosphine) [22]. However, the application of this system is limited by the solubility of the olefins in water. While propene can be successfully hydroformylated in this two-phase system, the activity for higher alkenes is lower, due to their lower solubility in water. Because of the ambition to transfer biphasic systems also for the hydroformylation of higher olefins novel water-soluble rhodium complexes are subject of many investigations in the last years [8,23,24].

To impart water-solubility often phosphine ligands were sulfonated and attached to the precursors [25,26]. Sometimes co-solvents were used to increase the solubility of the substrate in the aqueous phase [27]. Other possibilities are the addition of emulsifiers to the two-phase

reaction mixture or the employment of surface active phosphines [28]. Studies considering surface active phosphines show an increase in the reaction rate as the alkyl chain length and hence the surface activity increases [29].

CO_2 is a thermodynamically stable compound, and its utilization requires high energetic reaction conditions or electroreductive processes. Currently, toxic carbon monoxide, is used in many processes, because CO_2 is much less reactive. Hence its efficient catalytic conversion is rather limited, although carbon dioxide is cheap, non-toxic, abundant, and ubiquitous.

The transition metal catalyzed hydrogenation of CO_2 to formic acid in homogeneous phase has recently gained considerable interest as a promising approach to the exploitation of inexpensive carbon dioxide as a raw material in chemical syntheses [30,31]. The use of carbon dioxide as a C1 building block seems to be an attractive way of cutting down CO_2 emissions, considering CO_2 as the major atmosphere pollutant, responsible for the greenhouse effect. The amount of carbon dioxide to be fixed that way is, however, very small compared to the huge amount of CO_2 produced by burning fossil fuels. Recycling rather than storage of CO_2 would be more attractive if economic processes are available for its conversion to useful products [32].

Formic acid is one of the fundamental feedstocks in organic chemical industry. It has been used as a starting material for the production of formate esters, which is utilized in the production of a large variety of different organic derivatives. Formic acid is applied in the perfume, fragrance, and in dying industry, as well as a desinfectant, and a reducing agent [33,34].

The synthesis of formic acid by hydrogenation of CO_2 was first discovered by Farlow and Adkins in 1935 using Raney nickel as the catalyst [35]. The first homogeneous catalyzed example was reported by Inoue et al. in 1976 [36]. The homogeneous catalysts which have

been found to be effective for this reaction are complexes of 4d and 5d groups eight through ten metals, usually with halides or hydrides as anionic ligands and phosphines as neutral ligands. Catalytic systems described in the literature operate in organic solvents [33,36-40], aqueous solution [41,42], or in supercritical phase [43].

The addition of H_2 to CO_2 is an exothermic (-31 kJ/mol), but endergonic process under standard conditions (eq 1) [39]. The unfavourable thermodynamics are mainly due to entropic reasons, since two gaseous molecules are transformed to a liquid. If reasonable yields are aspired the equilibrium must be shifted to the right side by a suitable choice of the reaction conditions and the necessity to decrease the entropic difference between the gaseous substrate and the liquid formic acid. For example the addition of a base improves the enthalpy of the

$$CO_2\,(g) + H_2\,(g) \rightleftharpoons HCOOH\,(l)$$

$$\Delta G° = +32.9 \text{ kJ/mol}, \quad \Delta H° = -31.2 \text{ kJ/mol}$$

Equation 1.

reaction, while dissolution of the gases improves the entropy [39]. Dipolar aprotic solvents are best suited for CO_2 hydrogenation, dissolving high amounts of carbon dioxide and rising the entropy of formic acid via cleavage of the strong hydrogen bonds. Nevertheless, there remains still a large kinetic barrier for this reaction, which may, however, be overcome by a suitable catalyst.

The addition of amines is a necessary prerequisite for high yields of formic acid [37,42] and the presence of a phosphine ligand is necessary for a high activity and stability of the catalyst. In some cases an enhancement of the catalytic activity is observed if traces of water are present [33,36].

The rhodium catalyzed formation of formic acid from carbon dioxide and dihydrogen is a very clean process under all conditions tested up to now. Other reduction products like

CO, formaldehyde or methanol have rarely been observed by GC or NMR analysis of the gaseous or the liquid phase. In the presence of alcohols, alkyl formates are possible products from hydrogenation of CO_2 [32,44,45], but methyl formate was not detected by ^1H NMR spectroscopy when methanol was used as a solvent.

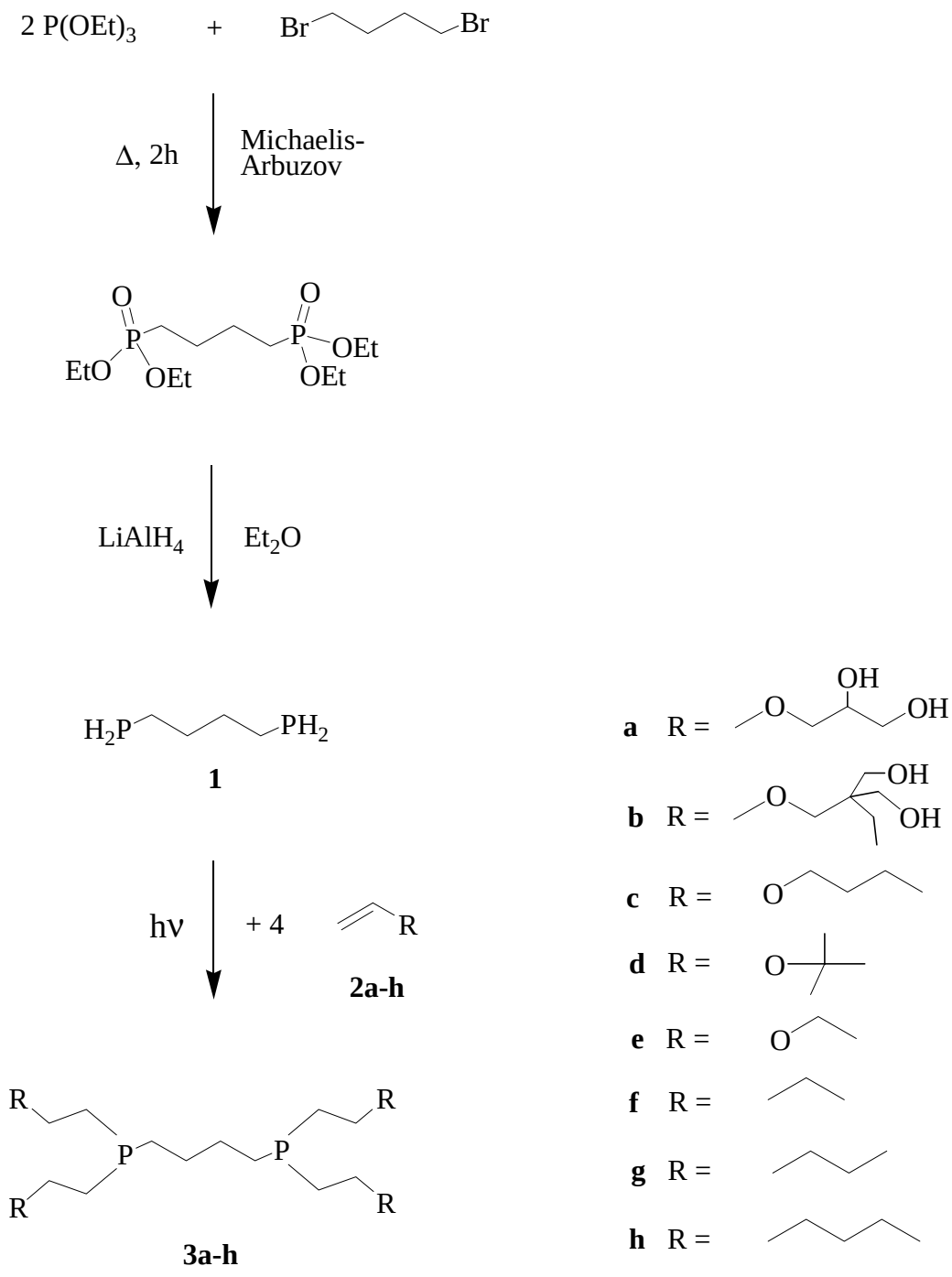
This thesis deals with the synthesis of a variety of diphosphines provided with a C_4 backbone and long or steric demanding alkyl substituents (Scheme 1) and their cationic rhodium(I) complexes (Scheme 2). The water-solubility of a part of the rhodium(I) complexes was achieved by an alternative concept in which hydroxyalkoxyalkyl chains were attached at the phosphorus atoms of the ligands. Some rhodium complexes in particular those which are water-soluble were employed in the homogeneous and biphasic hydroformylation of 1-hexene under different reaction conditions (e.g. solvent, pressure). Furthermore the water-insoluble rhodium catalysts were applied in the hydrogenation of carbon dioxide to formic acid in methanol and in presence of tertiary amines, too.

General Section

1. Synthesis and Characterization of the Diphosphine Ligands 3a-h and their Rhodium(I) Complexes 4a-h

1.1. Preparation of the Ligands 3a-h

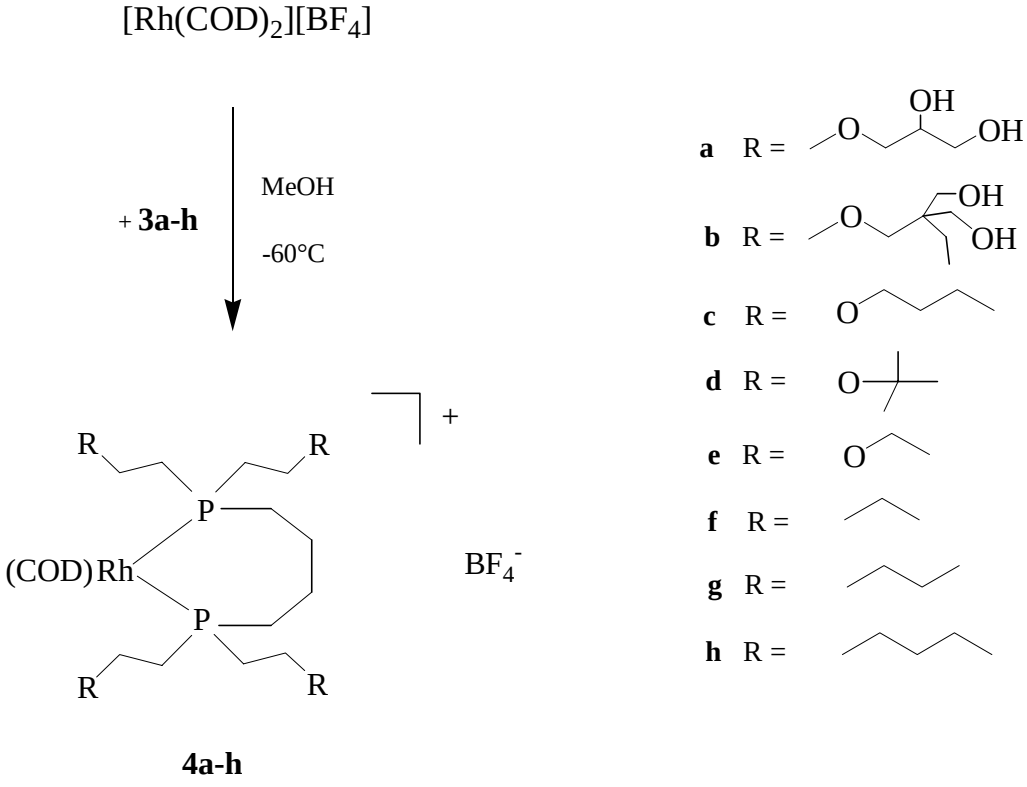
The diprimary phosphine $H_2P(CH_2)_4PH_2$ (**1**) was synthesized via a Michaelis-Arbuzov reaction (Scheme 1) by heating $P(OEt)_3$ with 1,4-dibromobutane, followed by reduction of the resulting diphosphonate with $LiAlH_4$ in diethyl ether [46]. The diphosphines **3a-h** were obtained by photochemically induced hydrophosphination of the corresponding alkenes **2a-h** with the diprimary phosphine $H_2P(CH_2)_4PH_2$ (**1**) over night. This convenient synthesis is nearly quantitative and simplifies the purification of the products [47,48]. Purification is achieved by removing excess alkene under reduced pressure. All phosphines **3a-h** are colourless and air-sensitive. In particular the diphosphines **3a,b** being provided with eight hydroxy groups are highly viscous liquids and as expected, the hydroxyalkyl functionalized species are soluble in alcohols and water. The liquid diphosphines **3c-h** are readily soluble in dichlormethane and acetone and insoluble in water. The $^{31}P\{^1H\}$ NMR spectra of the diphosphines **3a-h** reveal a singlet each between δ –25 and –31. Their composition was established by mass spectra displaying in each case the expected molecular peak. All ligands were characterized by means of MS, IR, and NMR.



Scheme 1. Preparation of the diphosphines **3a-h** by hydrophosphination

1.2 Preparation of the Complexes 4a-h

Treatment of the starting complex $[Rh(COD)_2][BF_4]$ (COD = cyclooctadiene) with stoichiometric amounts of the diphosphines **3a-h** in methanol at –60°C results in the formation of the monomeric, cationic rhodium complexes **4a-h** (Scheme 2). Under these reaction conditions only one COD molecule is replaced by one diphos ligand and the phosphorus atoms are *cis* oriented. The cationic diphosphine rhodium(I) complexes **4a-h** represent bright orange-red, moderate air-sensitive oils and are soluble in polar organic solvents like methanol or acetone. As expected, complexes **4a,b** are soluble in water. Nevertheless, there is a difference in solubility between both compounds. Whereas complex **4a** is good soluble in water and poor soluble in CH_2Cl_2, complex **4b** shows a different behaviour, less soluble in water and readily soluble in CH_2Cl_2 .

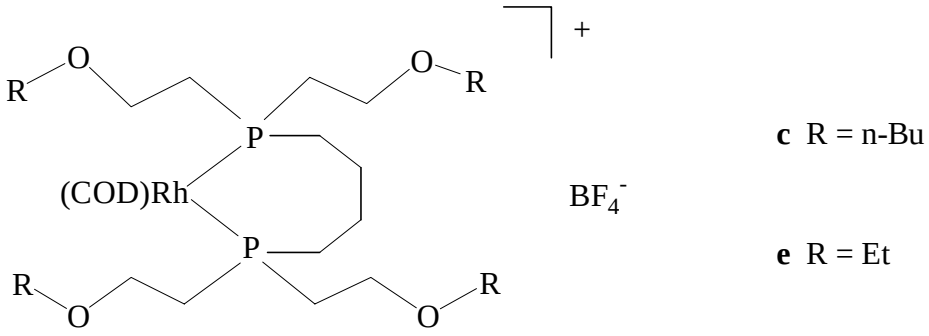


4a-h

Scheme 2. Preparation of the cationic rhodium(I) complexes **4a-h**

Their composition was verified by the respective molecular peaks in the FD or FAB mass spectra. The $^{31}P\{^{1}H\}$ NMR spectra of complexes **4a-h** display a doublet each between δ 10 and 14 with a rhodium phosphorus coupling constant of approximately 140 Hz. Additional analytic data for compounds **1-4** are summarized in the Experimental Section.

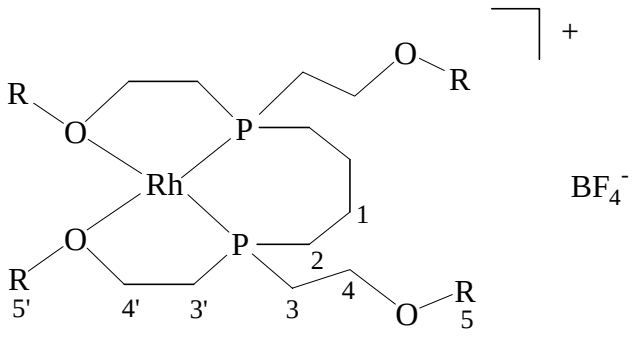
An outstanding feature of hemilabile, multidentate O,P ligands is their capability of coordinating to a metal center in either an η^1-mode through phosphorus, or in an η^2-mode through phosphorus and oxygen [15]. The vacant coordination site generated by the loss of the COD ligand in solution (CH_2Cl_2) in complexes **4c,e** is occupied by an intramolecular



c R = n-Bu

e R = Et

4c,e



5c,e

Scheme 3. Formation of the bis chelated (ether-diphosphine)rhodium(I) complexes **5c,e**

coordination of two ether moieties to the metal center to give the cationic (ether-diphosphine)-rhodium(I) complexes **5c** and **5e** (Scheme 3). The shift of the ^{31}P resonance in the ^{31}P {^{1}H} NMR spectra to lower field is about δ 55 compared to complexes **4c,e** showing the bidentate nature of the (ether-diphosphine) complexes **5c** (δ = 65.68) and **5e** (δ = 65.72). This shift to lower field is attributed to ring formation and indicates the existence of a five-membered M-P-C-C-O metallacycle [15]. Along with this observation, further evidence is proved by ^{13}C NMR data showing the disappearance of the coordinated CH moiety of the COD ligand at δ 96 and the occurrence of signals of the free COD at δ 129 and 28.

Fluxional behaviour is a property of complexes with hemilabile ligands [49-53] in which the oxygen atoms belonging to different O,P ligands or to several ether moieties, respectively, compete for one common coordination site. Since no major structural changes are necessary to interconvert the corresponding species, the activation enthalpy of such processes is comparatively low [15]. At suitable temperatures, the rate of these dynamic exchanges should be slow enough to be monitored by variable-temperature $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectroscopy [52]. The η^4-(O,P;O‘,P‘) coordination mode in **5c,e** is responsible for a center of chirality at both phosphorus atoms resulting in three diastereomers [(R,R), (S,S), meso]. However, at room temperature a typical A_2X pattern in the $^{31}P\{^{1}H\}$ spectra is observed, indicating a rapid exchange process between the coordinated and the non-coordinated ether oxygen atoms. Compared to **4c,e** the signals of both carbon atoms adjacent to the ether function in the $^{13}C\{^{1}H\}$ NMR spectra of **5c,e** are shifted to lower field, a further hint for the η^4-(O,P;O‘,P‘) coordination. Instead of two signals for each coordinated (C4‘, C5‘) and non-coordinated (C4, C5) ether moiety only two averaged resonances for the four carbon atoms are observed. $^{13}C\{^{1}H\}$ temperature-dependent spectra of compound **5c** have been recorded between 25 and -80°C by cooling the sample in order to decelerate the exchange process. Below the coalescence temperature the resonances of the mentioned carbon nuclei should split in pairs, revealing coordinated and non-coordinated oxygen atoms.

Nevertheless, using the (diphosphine)rhodium complex **5e** no splitting of the ^{13}C signals could be observed at –80 °C because of the low coalescence temperature. The carbon signals start to coalesce, the exchange of the four ether moieties at this temperature becomes slower.

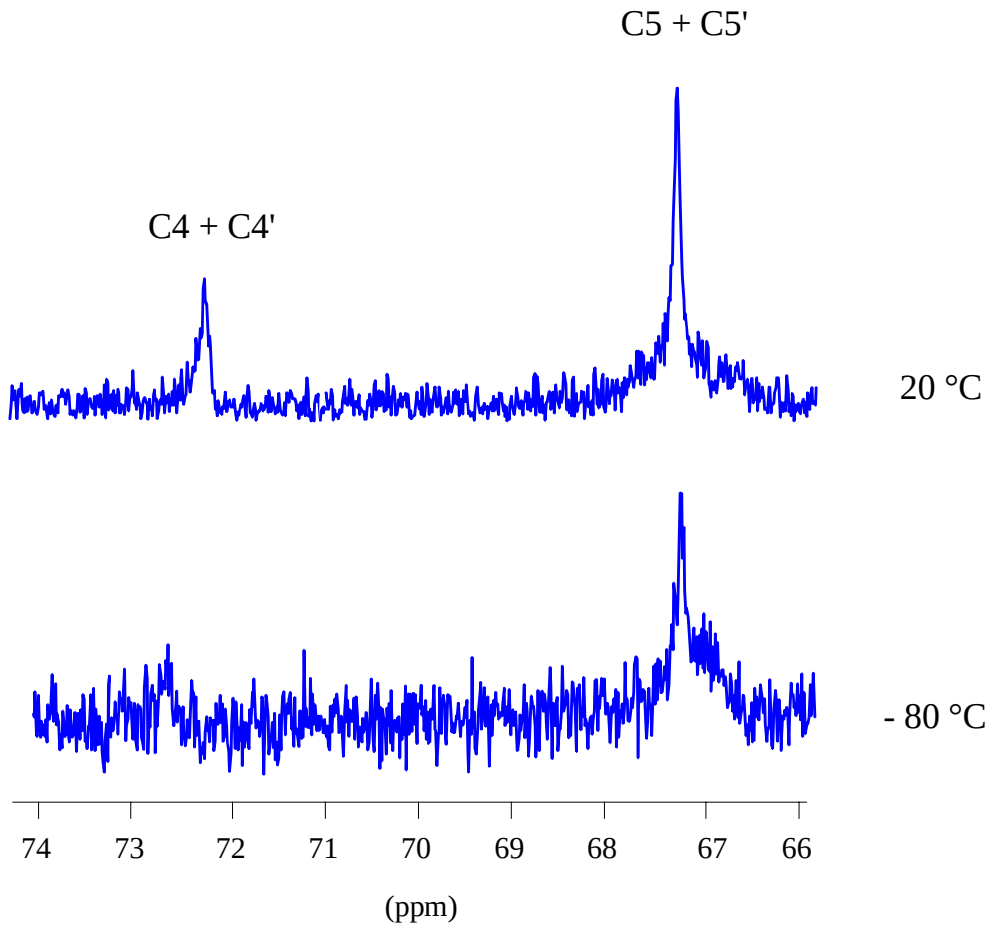
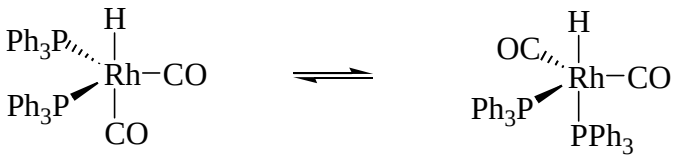


Figure 1. Temperature-dependent $^{13}C\{^{1}H\}$ NMR spectrum of **5e**

2. Homogeneous Hydroformylation of 1-Hexene

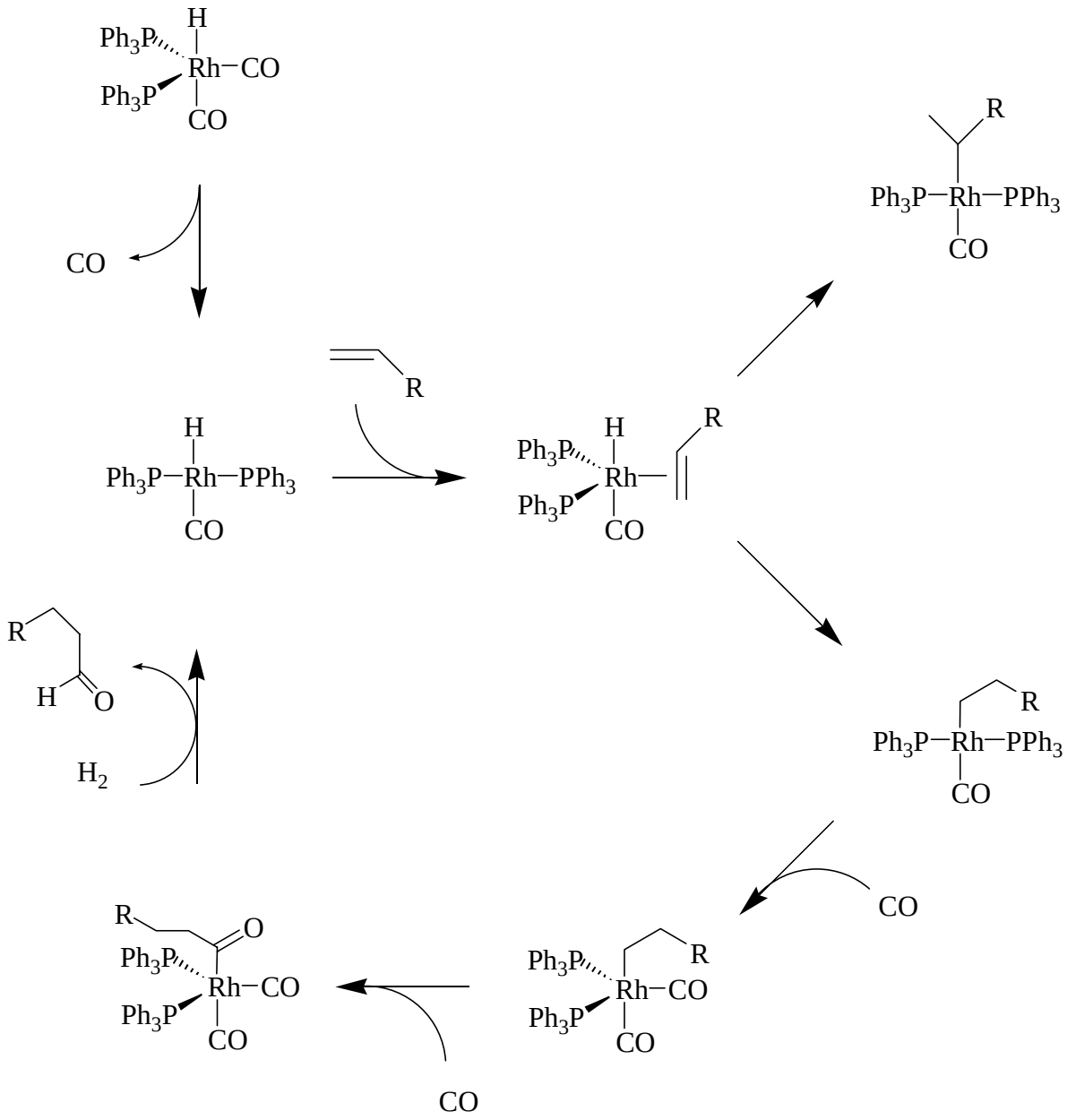
2.1. General Considerations

The generally accepted dissociative mechanism for the rhodium catalyzed hydroformylation is proposed by Wilkinson and shown in Scheme 4 [7,54,55]. Wilkinson's dissociative hydroformylation mechanism suggests that aldehyde regioselectivity is determined in the hydride addition step, that converts a five-coordinated H(alkene)Rh(CO)L_2 into either a primary or secondary four-coordinated (alkyl)Rh(CO)L_2. However, contrary to the $L_2Rh(CO)_2H$ precursor complex, the H(alkene)Rh(CO)L_2 intermediate has not been observed directly so far. To understand regioselectivity, it is important to know the detailed structure of the key five-coordinated H(alkene)Rh(CO)L_2 intermediate. Two monodentate phosphine ligands might occupy two equatorial or one equatorial and one apical site in a trigonal bipyramidal intermediate. Brown's NMR studies for the PPh_3 precursor complex $(PPh_3)_2Rh(CO)_2H$ (Figure 2) showed the existence of a mixture of two rapidly equilibrating trigonal bipyramidal isomers in a diequatorial (ee) to apical-equatorial (ae) isomer ratio of 85:15 [56]. Therefore the stereoelectronic properties of phosphine ligands of the alkene complex play a crucial role in controlling the regioselectivity [57,58].



ee **ae**

Figure 2. 85:15 diequatorial : apical-equatorial mixture of isomers of $(PPh_3)_2Rh(CO)_2H$



Scheme 4. Wilkinson's dissociative mechanism for the rhodium-catalyzed hydroformylation

Tolman introduced the concept of the cone angle θ and the electronic parameters χ which are dependent on the steric bulk and the electronic properties of the phosphine ligands, respectively [59,60]. Casey and co-workers developed the concept of natural bite angle as an

additional feature of diphosphine ligands based on molecular calculations [61]. They set out the hypothesis that different regioselectivities might be obtained from diequatorial diphosphine rhodium complexes and from apical equatorial diphosphine rhodium complexes (Figure 3).

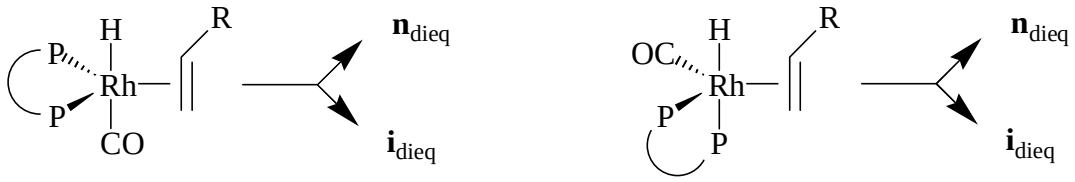


Figure 3. Diequatorial and apical equatorial diphosphine rhodium complexes

2.2. Influence of Solvent and Temperature on Conversion and Selectivity of 1-Hexene Hydroformylation with 4c

Since Alper et al. observed high selectivities in the homogeneous hydroformylation of allyl acetates with the cationic complex [(COD)Rh(dppb)][BPh_4] (dppb = 1,4-bis(diphenyl-phosphino)butane) [62] the above-mentioned diphos ligands were furnished with a C_4 backbone.

Table 1 lists the results of the hydroformylation with the rhodium complex [(COD)Rh{(*n*-BuO$(CH_2)_2)_2$P$(CH_2)_4$P$((CH_2)_2$O*n*-Bu$)_2$}] (**4c**) in solvents of different polarity and in a temperature range from 50 to 90 °C. The pressure was kept constant during the catalytic run (2.5 h) at 40 bar (1:1) and the diphosphine : rhodium ratio was always 1:1. Hydroformylation of 1-hexene at 50°C in CH_2Cl_2 (entry 1) gave poor conversion but was improved from 16 to 86 % when the reaction time was increased to 800 min (entry 2), while the product distribution remained similar. When the temperature was raised to 90°C the

conversions increase up to 96 % independent on the solvent (entry 4, 6, 7). At lower temperatures the hydrogenation of 1-hexene to *n*-hexane in CH_2Cl_2 achieved higher values, whereas at elevated temperatures the isomerization becomes more important. If the catalytic run was carried out in ethanol, the formation of by-products show a reverse course. The hydroformylation of 1-hexene in acetone at 90°C results in the formation of *n*-hexane (37%).

Applying solvents like alcohols under these hydroformylation conditions, some of the already formed aldehydes are converted to the corresponding acetals (entry 5[f]-7[f]). As reported in the literature rhodium phosphine catalysts generally require an additional acid catalyst if acetals are the desired products instead of aldehydes [63]. Pyridinium *p*-toluenesulfonate has been reported to efficiently catalyse the acetalization of aldehydes [64]. The addition of an acid catalyst is not necessary with the (ether-phosphine)rhodium complexes [(COD)Rh(P_2)] **4c** and **4d**. In the gas chromatogram the acetals appear at higher retention time and were characterized after fractional distillation by means of ^{13}C NMR and mass spectra. In these cases no formation of alcohols is observed.

Table 1.
Influence of solvent and temperature on conversion and selectivities with complex **4c** [a]

Entry	Solvent	Temp [°C]	Conv[b] [%]	Hydrog[c] [%]	Isom [%]	Aldehydes [%]	*n/n+iso* [%]	TOF[d]
1	CH_2Cl_2	50	16.29	12.40	6.50	81.18	61.49	65.2
2[e]	CH_2Cl_2	50	86.12[e]	12.32	4.59	83.11	66.07	64.8
3	CH_2Cl_2	70	73.16	2.73	35.43	61.84	70.44	293
4	CH_2Cl_2	90	96.90	2.84	8.04	86.02	52.91	388
5[f]	Ethanol	70	56.52	1.96	13.63	35.31 49.09[f]	55.05	226
6[f]	Ethanol	90	96.07	6.23	1.54	28.45 63.72[f]	55.08	384
7[f]	Acetone	90	95.88	8.46	37.44	41.68 12.42[f]	57.39	383

[a] Reaction conditions: solvent: 20 ml; time: 2.5 h; pressure: 40 bar (CO/H_2 = 1); [Rh] = 25 µmol; catalyst : hexene ratio = 1:1000. [b] Converted olefin as percentage of the initial amount; detected by gas chromatography. [c] Percentage of products relative to the olefin converted. [d] TOF: turnover frequency (mol_{sub} mol_{cat}^{-1} h^{-1}). [e] Time: 800 min. [f] Aldehydes transformed to acetals.

2.3. Influence of H_2/CO Partial Pressure on Conversion and Selectivity of 1-Hexene Hydroformylation with 4d

The (ether-phosphine)rhodium complex **4d** provided with *t*-butyl groups at the ether oxygen atoms was employed to investigate the influence of the partial pressure of hydrogen and carbon monoxide on the hydroformylation in a range from 20 to 40 bar. The catalytic run was carried out in methanol at 90°C. Under these conditions the conversions are not severely affected by the pressure, yielding conversions between 92.3 and 95.5 %. Using methanol as solvent already formed aldehydes are partially transformed to the corresponding dimethyl acetals. Higher H_2 than CO partial pressures lead to 30 % dimethyl acetals (entries 3 and 5). The summarized amounts of aldehydes and acetals are in the same range (87 %) for all partial pressures except for entry 3. The formation of by-products increases markedly to one third of the product distribution at a total pressure of 30 bar (20 H_2 / 10 CO) (entry 3). The *n/n+iso* ratios are approximately 68% and independent from the pressure. The hydrogenation of 1-hexene to *n*-hexane is the predominant part of the by-products.

Table 2.
Partial pressure of hydroformylation of 1-hexene with complex **4d** [a]

Entry.	H_2/CO [bar]	Conv[b] [%]	Hydrog[c] [%]	Isom [%]	Aldehydes [%]	*n/n+iso* [%]	TOF[d]
1	10/10	92.60	9.85	2.97	66.78 20.40[e]	70.55	370
2	10/20	92.31	8.58	3.03	69.39 18.99[e]	69.88	369
3	20/10	93.26	25.38	12.84	31.74 30.04[e]	67.97	373
4	10/30	93.27	8.62	2.96	69.05 19.36[e]	68.56	373
5	30/10	95.52	8.52	3.25	55.89 32.33[e]	69.61	382

[a] Reaction conditions: 20 ml methanol; temperature = 90°C; time = 2.5 h; [Rh] = 25 μmol; catalyst : substrate ratio = 1:1000. [b] Converted olefin as percentage of the initial amount; detected by gas chromatography. [c] Percentage of products relative to the olefin converted. [d] TOF: turnover frequency ($mol_{sub}\ mol_{cat}^{-1}\ h^{-1}$). [e] Aldehydes transformed to acetals.

2.4. Comparison Between TPPTS, PPh_3, and dppb Ligands

For the purpose of comparison the three known complexes $[(COD)Rh(PPh_3)_2][BF_4]$ (**PPh_3**) [65], $[(COD)Rh(TPPTS)_2][BF_4]$ (TPPTS = tris(*m*-sulfonylphenyl)phosphine) (**TPPTS**) [66] and $[(COD)Rh(dppb)][BF_4]$ (dppb = 1,4-bis(diphenylphosphino)butane) (**dppb**) [67] were synthesized according to the literature and investigated in the hydroformylation of 1-hexene under identical conditions. Each of these complexes was applied in the hydroformylation using methanol at 90 and 110°C for 2.5 h. No influence of the temperature on the conversion was determined. If monodentate phosphines are employed, the main part of the aldehydes is transformed to the corresponding linear and branched dimethyl acetals. The *n/n+iso* ratios are similar for **PPh_3** and **dppb**, while the ratio decreases for **TPPTS** (entries 3-4). It is noteworthy that no isomerization occurs with the **TPPTS** complex and at elevated temperature even less *n*-hexane is produced compared to **PPh_3** and **dppb** (entries 1-2, 5-6).

Table 3.
Hydroformylation of 1-hexene in methanol [a]

Entry	Complex	Temp [°C]	Conv[b] [%]	Hydrog[c] [%]	Isom [%]	Aldehydes [%]	*n/n+iso* [%]	TOF[d]
1	**PPh_3**	90	95.24	4.62	1.98	7.60 85.79[e]	70.73	381
2	**PPh_3**	110	94.92	6.51	1.22	6.35 85.91[e]	68.83	380
3	**TPPTS**	90	96.27	5.19	-	3.97 90.83[e]	54.84	385
4	**TPPTS**	110	95.89	1.55	-	3.75 94.70[e]	61.34	383
5	**dppb**	90	95.86	6.71	2.16	24.07 67.06[e]	70.90	383
6	**dppb**	110	95.65	8.24	2.74	23.76 65.25[e]	69.96	383

[a] Reaction conditions: solvent: 20 ml methanol; pressure: 40 bar (1:1); time: 2.5 h; [Rh] = 25 μmol; catalyst : hexene ratio = 1.1000. [b] Converted olefin as percentage of the initial amount; detected by gas chromatography. [c] Percentage of products relative to the olefin converted. [d] TOF: turnover frequency ($mol_{sub}\ mol_{cat}^{-1}\ h^{-1}$). [e] Aldehydes transformed to acetals.

2.5. Homogeneous Hydroformylation with the Water-Soluble Complexes 4a,b in Polar Organic Solvents

To compare the hydroformylation results of the water-soluble rhodium complexes **4a,b** (section 1.3) with those of the catalysts **4c,d**, **PPh_3**, **dppb**, and **TPPTS**, the two hydrophilic complexes **4a,b** were employed in the homogeneous hydroformylation of 1-hexene in polar organic solvents. The catalytic runs were carried out at 90°C and a total pressure of 40 bar (1:1). The conversions are not affected by the different polar organic solvents like alcohols, acetone or CH_2Cl_2. Using a mixture of methanol and water as

Table 4.
Homogeneous hydroformylation with complexes **4a** and **4b** [a]

Entry/ Complex	Solvent	Conv[b] [%]	Hydrog[c] [%]	Isom [%]	Aldehydes [%]	*n/n+iso* [%]	TOF[d]
1 / **4a**	Methanol	96.09	10.70	2.68	11.75 74.83[e]	71.76	384
2 / **4b**	Methanol	96.05	9.29	2.91	7.97 79.82[e]	71.57	384
3 / **4a**	Ethanol	94.98	4.39	1.51	53.82 40.19[e]	71.83	379
4 / **4b**	Ethanol	95.97	4.91	1.64	29.77 63.67[e]	70.58	384
5 / **4a**	Acetone	95.42	23.49	7.56	62.57 6.38[e]	55.70	382
6 / **4b**	Acetone	95.14	22.99	6.84	55.48 14.65[e]	52.70	381
7 / **4a**	CH_2Cl_2	96.50	3.18	1.50	95.31 -	42.08	386
8 / **4b**	CH_2Cl_2	95.27	11.22	4.08	84.70 -	41.68	381
9 / **4a**	20 H_2O/ 6 MeOH	88.00	30.95	10.41	45.71 12.87[e]	62.98	352
10 / **4b**	20 H_2O/ 6 MeOH	89.73	29.31	7.25	56.33 7.06[e]	66.34	359

[a] Reaction conditions: 20 ml solvent (entries 1-8); time = 2.5 h; temperature = 90°C; pressure = 40 bar (1:1); [Rh] = 25 μmol; catalyst : substrate = 1:1000; [b] Converted olefin as percentage of the initial amount; detected by gas chromatography. [c] Percentage of products relative to the olefin converted. [d] TOF: turnover frequencies (mol_{sub} mol_{cat}^{-1} h^{-1}). [e] Aldehydes transformed to acetals.

solvent (entries 9-10) the conversions decrease due to limited mass-transfer in water [2,68] and the formation of by-products increases strongly. In acetone the hydrogenation and isomerization of 1-hexene comprises a third of the product distribution (entries 5-6), while the transformation of already formed aldehydes to acetals is low. The largest acetal generation occurs in methanol (entries 1-2). As already mentioned in section 1.2.2. (Table 1) no acetal formation is observed in CH_2Cl_2 (entries 7-8). In these cases the selectivities to aldehydes are higher, but the *n/n+iso* ratios remain low. The highest *n/n+iso* values are obtained in alcohols (entries 1-4). The hydrogenation to *n*-hexane is dominating the by-products in all cases. There is no crucial difference between the two hydrophilic complexes **4a,b** in polar organic solvents. In each solvent both complexes behave similar, except in CH_2Cl_2 where complex **4b** generates more by-products, in particular more *n*-hexane (entry 8).

2.6. Conclusion

The described diphosphinerhodium(I) complexes **4a-e** (Scheme 2) were applied in the catalytic homogeneous hydroformylation of 1-hexene in different solvents and at different temperatures and pressures.

Interestingly, these cationic phosphine rhodium(I) complexes **4a-e** transform some of the generated linear and branched aldehydes to the corresponding acetals even in the absence of an acid catalyst. In methanol this effect is predominant, while in CH_2Cl_2 no acetals occur. Homogeneous hydroformylation with complex **4c** shows a temperature dependence in a range of 50 to 90°C (Table 1). At 90°C the catalytic runs gave considerably higher conversions (96%) compared to lower temperature. To some extent the solvent exerts an impact on the conversions but leads to different product distributions. If the temperature is increased no further improvement was observed employing the complexes **PPh_3**, **dppb**, and **TPPTS** (Table

3). Using complex [(COD)Rh(TPPTS)$_2$][BF_4] as a catalyst no isomerization of 1-hexene appears. Different partial pressures do not lead to significant changes in the conversions (Table 2), but influences the product distributions. Higher H_2 partial pressures result in an enhanced transformation of aldehydes to the corresponding acetals. The conversions which were achieved with the hydrophilic complexes **4a** and **4b** are alike in different organic solvents. In acetone the hydrogenation and isomerization by-products attain one third of the products but the amount of by-products is modest in ethanol. If the catalytic run was carried out in a mixture of water and methanol the conversions decrease due to limited mass-transfer in water and hydrogenations and isomerizations increase. There is no crucial difference between both complexes **4a** and **4b** in polar organic solvents. Employing the rhodium complexes **4a-e** in organic solvents no formation of alcohols is observed.

3.1. Biphasic Hydroformylation in Water with Complexes 4a,b

To impart water-solubility often phosphine ligands were sulfonated and attached to the active metal centers [25,26]. Another possibility is the addition of emulsifiers to the two-phase reaction mixture or the employment of surface active phosphines [28]. Studies considering surface active phosphines show an increase in reaction rate as the alkyl chain length, and hence the surface activity, increases [29]. For that purpose four seven-membered hydrocarbon chains were introduced into the diphosphines. To increase the polarity and hence the water-solubility one methylene group per hydrocarbon chain was replaced by an isoelectronic oxygen atom and the ligands were provided with eight hydroxy functions.

The water-soluble complexes **4a,b** were investigated in their performance for the hydrocarbonylation of 1-hexene in water without any co-solvent. Throughout all experiments the substrate to complex ratio was 1000:1 and total pressures of H_2 and CO of 40 bar (1:1) were applied (Table 5). The catalytic results comprised in Table 5 are average values of three reproducible runs. After a reaction time of 2.5 hours at 90°C the conversions achieved values of 83 and 63 % for complexes **4a** and **4b**, respectively (entries 1 and 7). No alcohol formation was observed under these conditions. An increase of the temperature to 110°C also affects the conversions which are raised to 91 and 89 % in the case of **4a,b**. Whereas with catalyst **4a** more isomerization and hydrogenation products are formed, the amounts of these undesirable by-products are divided into halves by employing catalyst **4b** (entries 1, 2 and 7, 8). Concomitant with these observations the *n/n+iso* ratio is becoming smaller, however, turnover frequencies rise with increasing temperature. Extending the reaction time from 2.5 to 13.3 hours (800 min) results in an increase of the conversion and makes the differences between **4a** and **4b** smaller. Side reactions with respect to isomerization and hydrogenation drop dramatically in the case of complex **4a** under these conditions (entries 2, 3 and 8, 9). At longer reaction times (13.3 h) catalyst **4b** hydrogenates some of the formed aldehyde to heptanol compared to **4a** (entries 3 and 9).

Table 5.
Two-phase hydroformylation of 1-hexene with complexes **4a,b**[a]

Entry	Complex	[L]/[Rh]	Time [h]	Conversion[b] [%][b]	Isomerization[c] [%]	Hydrogenation [%]	Heptanol [%]	Aldehydes[b] [%]	*n/n+iso* [%]	TOF[d]
1	**4a**[e]	1	2.5[e]	83.05	9.51	29.02	-	61.48	54.30	332
2	**4a**	1	2.5	91.09	11.09	32.57	-	56.33	44.21	372
3	**4a**	1	13.3	94.72	0.61	1.44	0.63	96.44	37.44	71.3
4	**4a**	2	2.5	94.69	45.17	54.52	0.17	0.14	50.41	388
5	**4a**	4	2.5	95.03	44.93	54.74	0.23	0.10		380
6	**4a**	5	2.5	95.89	45.06	54.71	0.23	-	-	384
7	**4b**	1	2.5[e]	63.05	3.34	8.84	-	87.82	70.34	252
8	**4b**	1	2.5	89.56	1.82	5.41	0.21	92.56	50.98	358
9	**4b**	1	13.3	90.76	0.09	0.55	4.69	94.67	28.68	68.2
10	**4b**	2	2.5	87.60	22.32	31.48	-	46.19	18.36	350
11	**4b**	4	2.5	91.32	38.86	47.23	0.15	13.76	45.32	365
12	**4b**	5	2.5	84.52	45.09	54.51	0.16	0.24	55.34	338
13	**TPPTS**	1	2.5	93.06	17.82	47.30	-	34.87	51.95	372
14	**TPPTS**	1	13.3	95.53	5.18	15.35	-	79.48	36.35	71.8
15	**4a**[f]	1	2.5	93.10	3.98	12.00	19.53	64.49	41.17	372

[a] Reaction conditions: water (20 ml); pressure: H_2 / CO = 1 (40 bar); temperature: 110 °C; [Rh] = 25 µmol; catalyst : hexene ratio = 1:1000.
[b] Converted olefin as percentage of the initial amount; detected by gas chromatography. [c] Percentage of products relative to the olefin converted.
[d] TOF = turnover frequency = (mol_{sub} mol_{cat}^{-1} h^{-1}). [e] Temperature = 90°C. [f] Addition of 0.5 ml heptanol.

The observation of a higher alcohol production in the case of complex **4b** which is accompanied by the formation of less by-products gave rise to change the reaction conditions according to entry 15 (Table 5). Additional heptanol in the catalytic run with **4a** at short reaction time leads to a decrease of the by-products to nearly one third, compared to the results given in entry 2. To monitor the formation of by-products in dependence on the time in the case of complex **4a** eleven runs between three and thirteen hours were carried out (Figure 3). Within the first six hours the hydrogenation and isomerization products decreased below 5 %, while the alcohol formation is slightly increased after that time.

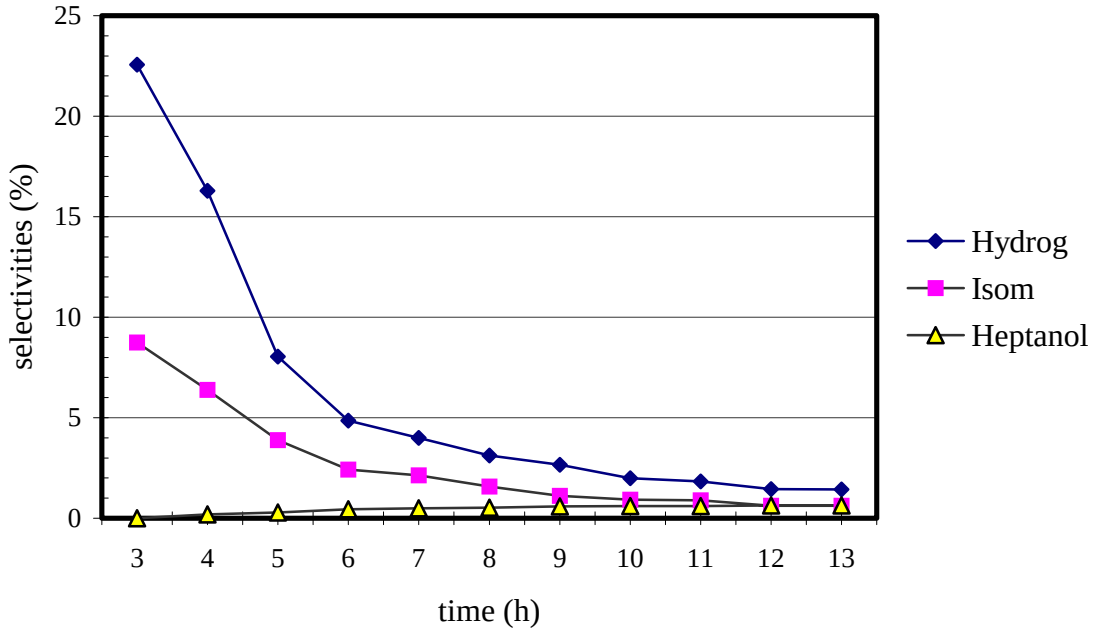


Figure 4. The formation of by-products in dependence of time with catalyst **4a**.
Reaction conditions: water (20 ml); pressure: H_2/CO = 1 (40 bar); temperature = 110 °C; [Rh] = 25 µmol; catalyst : hexene ratio = 1:1000.

It is obvious to compare the catalytic properties of the structurally related water-soluble complex $[(COD)Rh(TPPTS)_2][BF_4]$ with the described results herein. Its tendency to

form aldehydes is less distinct than for **4a,b** (entry 13). Conspicuous is the high amount of hydrogenation which decreases to about one third at longer reaction times (entry 14).

3.2. Application of Catalysts with Excess Phosphine

It is reported that the catalytic activity of phosphine rhodium(I) complexes in hydroformylation is improved if excess phosphine is employed [9,69,70]. However, such an observation was not made in the case of complexes **4a** and **4b.** Rapidly cyclooctadiene is replaced under these conditions by another diphos ligand **3a,b**, respectively, to give the largely catalytic inactive bis(diphos)rhodium complexes $[(\mathbf{3a})_2Rh][BF_4]$ and $[(\mathbf{3b})_2Rh][BF_4]$ for hydroformylation [71-74]. When the hydroformylation of 1-hexene was carried out with **4a,b** using L/Rh ratios of 2:1, 4:1 and 5:1 as expected only the formation of by-products was increased to the disadvantage of the aldehydes (Table 5, entries 4-6 and 10-12).

3.3. Emulsifiers

To meliorate the solubility of 1-hexene in water each an anionic (potassium dodecyl sulfate), cationic (benzalkonium tetrafluoroborate), and neutral emulsifier (polyethylene glycol 400) was introduced (Table 6). Yet, compared to the results summarized in Table 5 no better conversions and selectivities were ascertained. Using the anionic emulsifier the results are approximately unchanged, whereas the neutral solubilizing agent polyethylene glycol exerts a negative influence on the conversion, while with the cationic emulsifier the conversion drop significantly and high amounts of isomerization and hydrogenation are observed. The employed emulsifiers form stable emulsions with the organic/aqueous mixture and a phase separation was not possible within a reasonable time. In such a case it is known that the catalytic activity is decreased [28,75,76].

Table 6.
Application of emulsifiers in the two-phase hydroformylation of 1-hexene with complex **4a** and **4b**[a,b]

Entry	Catalyst	Emulsifier	Time [h]	Conversion[c] [%][c]	Isomerization[d] [%]	Hydrogenation [%]	Alcohols [%]	Aldehydes [%]	*n/n+iso* [%]	TOF[e]
1	**4a**	A	2.5	91.94	8.40	25.29	-	66.31	41.74	368
2	**4a**	A	13.3	93.36	0.41	1.25	1.78	96.56	37.17	70.2
3	**4a**	N	2.5	89.28	8.11	24.36	-	67.53	44.16	357
4	**4a**	N	13.3	95.63	0.30	1.19	2.58	95.94	40.51	71.9
5	**4a**	C	2.5	64.20	16.21	44.98	-	38.80	59.09	257
6	**4a**	C	13.3	85.85	2.72	7.35	0.55	89.39	40.48	64.6
7	**4b**	A	2.5	89.88	1.36	4.27	0.30	94.33	43.47	360
8	**4b**	A	13.3	95.45	0.80	0.69	4.96	94.26	36.80	71.7
9	**4b**	N	2.5	78.94	3.47	10.79	0.18	85.56	42.67	316
10	**4b**	N	13.3	85.99	0.16	0.80	6.13	92.93	41.07	64.4
11	**4b**	C	2.5	72.76	1.29	2.59	0.57	95.55	60.86	291
12	**4b**	C	13.3	88.63	0.06	0.33	7.92	91.67	48.67	66.6

[a] Emulsifier: A = potassium dodecylsulfat; N = polyethylene glycol 400 (M = 380-420 g/mol); C = benzalkonium tetrafluoroborate.
[b] Reaction conditions: water (20 ml); pressure: H_2 / CO = 1 (40 bar); temperature = 110 °C; [Rh] = 25 µmol; catalyst : hexene ratio =1:1000.
[c] Converted olefin as percentage of the initial amount; detected by gas chromatography. [d] Percentage of products relative to the olefin converted.
[e] TOF = turnover frequency ($mol_{sub}\ mol_{cat}^{-1}\ h^{-1}$).

3.4. Reuse Experiments

An important point in biphasic catalysis is the easy and effective separation of the catalyst from the products. After the catalytic runs this separation process could be achieved by a simple decantation of the organic phase which is accompanied by a recycling of the catalyst. Unlike **4b**, during five reuse experiments the conversions with complex **4a** were slightly increased. Interestingly the *n/n+iso* ratios experience a remarkable improvement in the course of the reuse investigations (Figure 5). A nearly constant distribution of the products was observed during the first three experiments. After three runs the formation of by-products is favoured at the expense of the aldehydes (Figure 6). In the case of complex **4a** in particular the occurrence of hexane is observed.

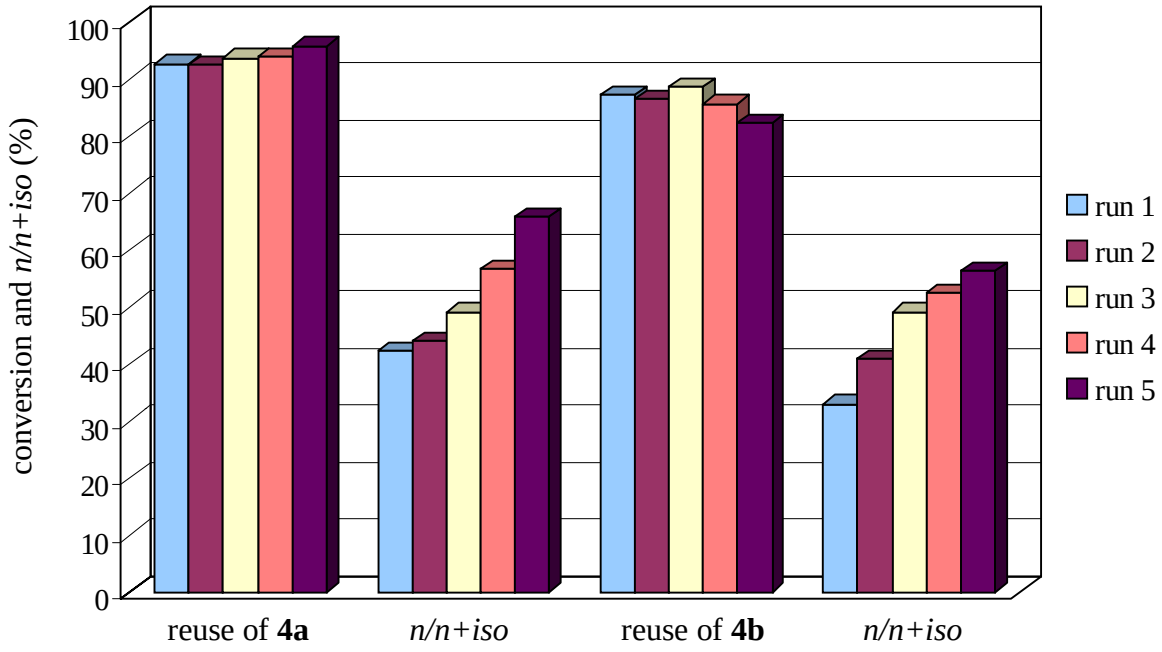


Figure 5. Conversion and *n/n+iso* ratio of complex **4a** and **4b** in five reuse runs.
Reaction conditions: 20 ml water; pressure: H_2/CO = 1 (40 bar); time = 2.5 h; temperature = 110°C; [Rh] = 25 µmol; catalyst : hexene ratio = 1:1000 (3.1 ml). Reuse = decantation of the organic layer, addition of substrate to the water phase.

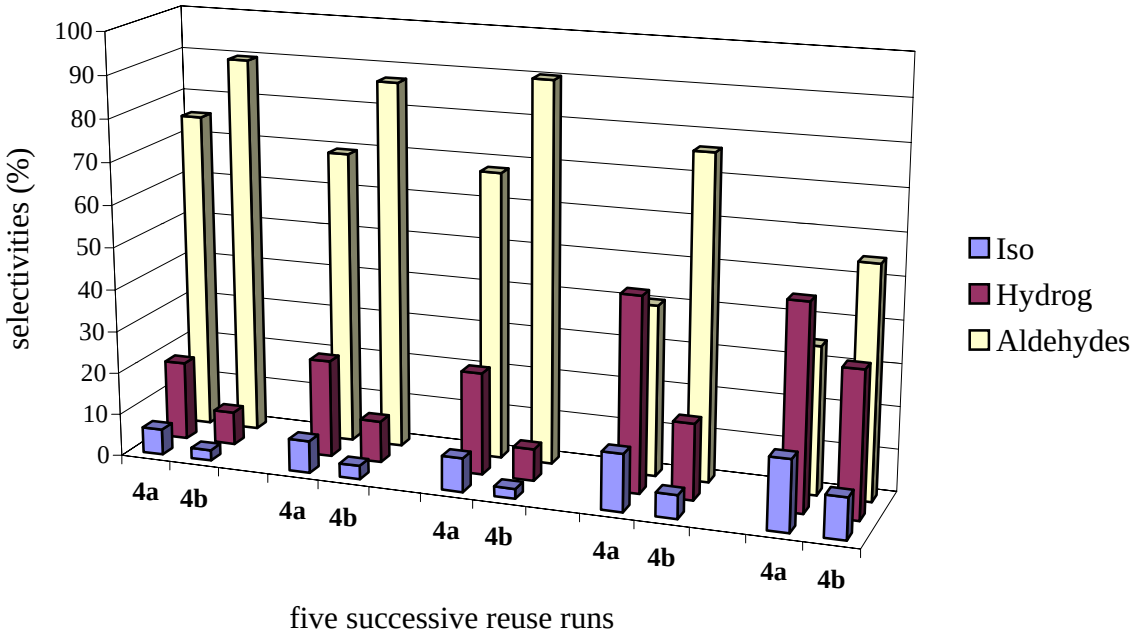


Figure 6. Distribution of products in the reuse experiments with complex **4a,b**.
Reaction conditions: 20 ml water; pressure: H_2/CO = 1 (40 bar); time = 2.5 h; temperature = 110°C; [Rh] = 25 μmol; catalyst : hexene ratio = 1:1000. Reuse: decantation of the organic layer, addition of substrate to the water phase.

Another feature of a biphasic reaction is the metal content extracted into the organic phase during the catalytic runs. According to atom absorption spectroscopy 25 % and 50 % of the rhodium complexes **4a** and **4b**, respectively, was found in the combined orange coloured organic phases after five reuse runs. Due to four long alkyl chains provided with hydroxy functions the phosphines **3a,b** ensure a good contact between the organic substrate and the water phase. Because of this reason, however, they contribute to a high rhodium leaching of the complexes **4a,b** to the organic layer. As a result the advantage of the enhanced surface activity of the complexes **4a,b** disappeared.

3.5. Conclusion

The water-soluble rhodium(I) complexes **4a** and **4b** with four hydroxypropoxypropyl functions are employed in two-phase hydroformylation of 1-hexene without a co-solvent. Compared to the structurally related TPPTS rhodium(I) complex, the water-soluble alternatives **4a** and **4b** seem to be more surface active than $[(COD)Rh(TPPTS)_2][BF_4]$. The ligands **3a** and **3b** do not serve only to complex the rhodium center but also facilitate the mixing of the immiscible phases. Thus they are able to bring the reactive center in a better contact with the substrate in aqueous phase. Moreover complexes **4a** and **4b** can be reused up to three times without loss of their catalytic activity. The observed high extraction of rhodium to the organic layer could be traced back to the long alkyl chains of the ligands. On the one hand these ligands facilitate the mixing of the phases but on the other hand they lead to a high extraction into the organic phase. Because of the formation of stable emulsions which may arise from an interaction between the surfactant and the hydroxypropoxypropyl functions of the diphosphines **3a** and **3b** no improvements were observed with the employed emulsifiers. In particular at shorter times complex **4b** reveals a higher selectivity towards aldehydes compared to catalyst **4a**. This observation may be traced back to the structure of ligand **3b** in complex **4b**. Both hydroxy groups of each alkyl chain are at the ends of a branched position, pointing to the outer sphere. These polar hydroxy functions are able to form micelles through which the binding of the substrate is facilitated [77]. The differences in selectivity to aldehydes between **4a** and **4b** disappears at longer reaction times.

If the results of complexes **4a,b** obtained in homogeneous and biphasic hydroformylation are compared with each other a difference is shown in lower conversions and lower turnover frequencies in water due to limited mass-transfer (compare Table 5, entry 1 and 7 with Table 4). In the two-phase catalysis no acetals occur but sometimes alcohols are observed. The formation of by-products is more favoured in water than in organic solvents.

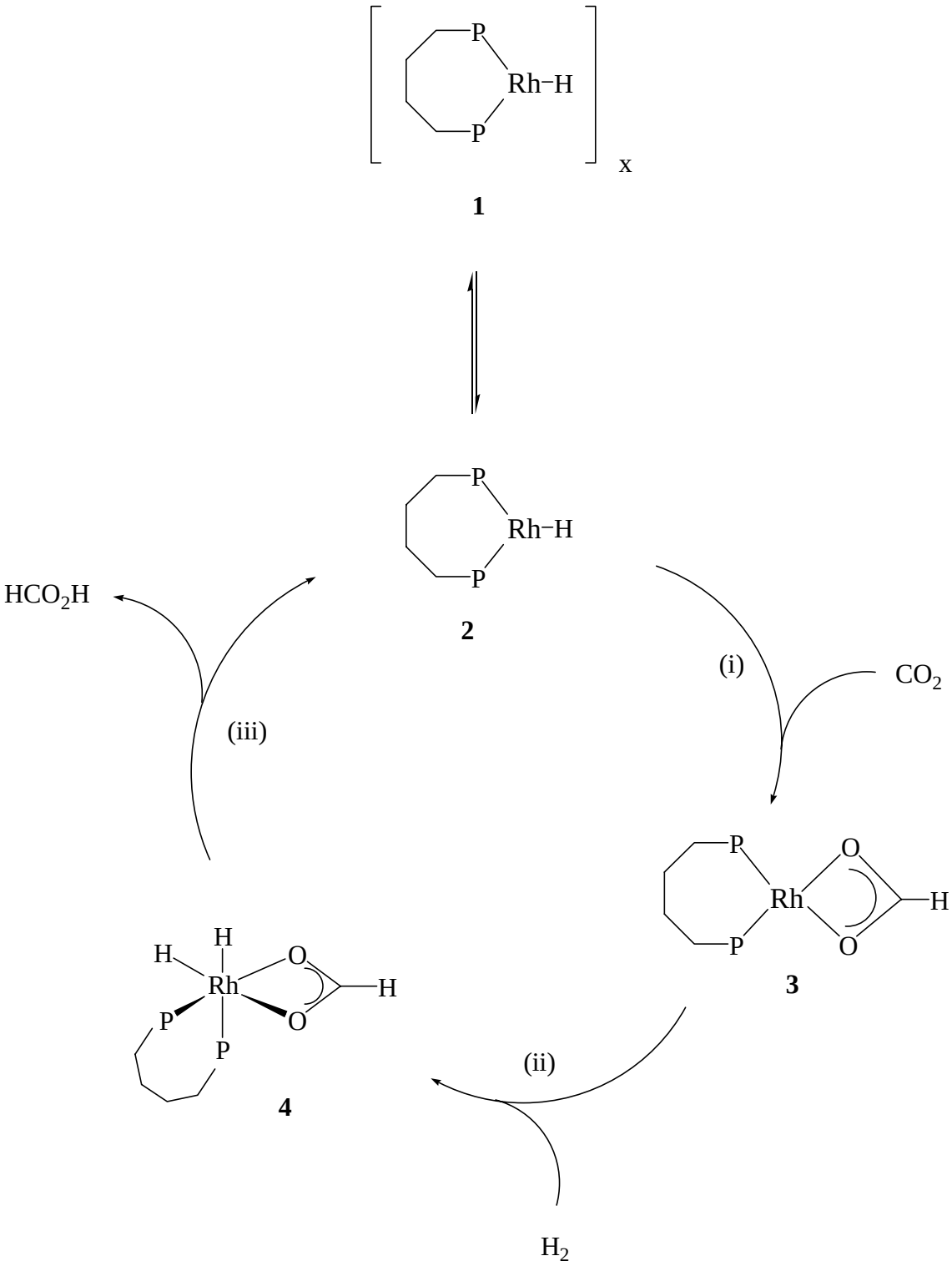
However, if acetone is employed in the homogeneous hydroformylation of 1-hexene high amounts of hydrogenation and isomerization products are observed. Unlike in the homogeneous phase the differences of complexes **4a** and **4b** in the two-phase catalysis is more pronounced, particular at short reaction times.

4. Hydrogenation of Carbon Dioxide

4.1. General Considerations

To understand the mechanism of the hydrogenation of carbon dioxide an insight into the coordination chemistry of CO_2 is necessary. Studies on stoichiometric reactions of CO_2 with active metal complexes provide useful informations and form the fundamentals for new catalytic procedures [78]. The binding of CO_2 to a metal center generally leads to the activation of a CO_2 molecule and various reactions of coordinated carbon dioxide are known. Many studies [79-83] of stoichiometric reactions of carbon dioxide with a metal hydride complex reveal the insertion of CO_2 into a M-H bond to yield a metal formate complex. Indeed such a species is postulated to be the active catalytic intermediate in the Noyori system [84]. Leitner supports the proposal [85] that a neutral rhodium hydride species $[P_2RhH]_x$ is the active species in the hydrogenation of CO_2 (Scheme 5). This intermediate may exist either as a mononuclear complex (x = 1) or as polynuclear hydride bridged cluster (x = 2-4) [86,87]. This catalytic cycle for the hydrogenation of CO_2 using rhodium complexes is most widely accepted, involving three steps, as shown in Scheme 5. (i) Insertion of the incoming CO_2 molecule into the Rh-H bond of the unsaturated T-shaped neutral 14-valence electron (VE) active species (complex **2** in Scheme 5) results in the formation of complex **3**. (ii) Oxidative addition of H_2 to the vacant site of complex **3**. (iii) Reductive elimination of HCOOH from complex **4** to recover the catalytic species **2**. Experimental [33] and theoretical studies [88-90] have shown that the reductive elimination of formic acid from the $[P_2RhH(HCO_2H)]$ complex is the rate determining step of the entire process.

The transition state for the first step in the catalytic cycle requires an interaction of the central metal atom with the Lewis-basic oxygen atom of CO_2. Therefore it should be stabilized by electron-withdrawing phosphine ligands. On the other hand, the activation of dihydrogen and the reductive elimination of formic acid should be enhanced by



Scheme 5. Catalytic cycle for the rhodium-catalyzed hydrogenation of carbon dioxide

electron-donating ligands. This consideration leads to the assumption that only ligands of medium basicity allow the stabilization of transition states for all parts of the reaction sequence without suppressing other steps [91].

It was found that the induction period shows a remarkable dependence on the rhodium concentration. Lower concentrations are responsible for longer induction periods [39]. Finally the absence of the induction period in the second formation period proves unambiguously that the catalytically active species is slowly formed from the *in situ* catalyst in the early stages of the first catalytic run, but remains active for a long period.

Although, the hydrogenation of CO_2 to CO, hydrocarbons, and alcohols is thermodynamically favourable, because of the concomitant production of water, the hydrogenation to formic acid, however, is thermodynamically unfavourable [32]. The addition of H_2 to CO_2 is an exothermic, but endergonic process ($\Delta G° = + 32.9$ kJ/mol, $\Delta H° =$ -31.2 kJ/mol) [39]. The unfavourable thermodynamics is mainly due to entropic reasons, as two gaseous molecules react to a liquid. To yield formic acid the equilibrium of eq. 1 (page 4) must be shifted to the right side by a suitable choice of reaction conditions such as elevated pressure and temperature. The necessity to decrease the entropic difference between the gaseous educts and the liquid product is achieved by lowering the entropy of the substrates via solvation and by rising the entropy of formic acid via cleavage of the strong hydrogen bonds. Dipolar aprotic solvents are best suited for CO_2 hydrogenation, such as DMSO. These solvents dissolve extremely large amounts of CO_2 under the applied reaction conditions. The solution of such a large amount of gas leads to an appreciable increase in volume of the liquid phase, visually observable [39]. The solubility of H_2 is small, but is certainly higher in nonpolar solvents than in very polar systems [39].

The fact that the reaction equilibrium is shifted to the right side in polar aprotic solvents can therefore mainly be attributed to interactions of the strongly polarized solvent molecules with HCOOH disfavouring hydrogen bonding between formic acid molecules [92].

Further possibilities to achieve high yields are the addition of a base which improves the enthalpy [32,33,36] or the trapping of formic acid as alkyl formates or formamides [44,45]. If traces of water are present the catalytic activity is enhanced [33,36] and some of the described catalysts tolerate a water content of up to 20 % in volume. But too high water concentrations may even exhibit a negative effect on the performance of the reaction system [39,42]. This detrimental influence of water must be attributed to a deactivation of the hydrophobic catalyst, since water has been shown to be an excellent solvent for CO_2 hydrogenation when water-soluble catalysts are used [42]. This emphasizes the fact that the solvent system does not only determine the equilibrium constant, but may strongly affect the activity of the catalyst. Nevertheless, thoroughly dried polar aprotic solvents should be employed for the hydrogenation of carbon dioxide using hydrophobic phosphine complexes of rhodium as catalysts.

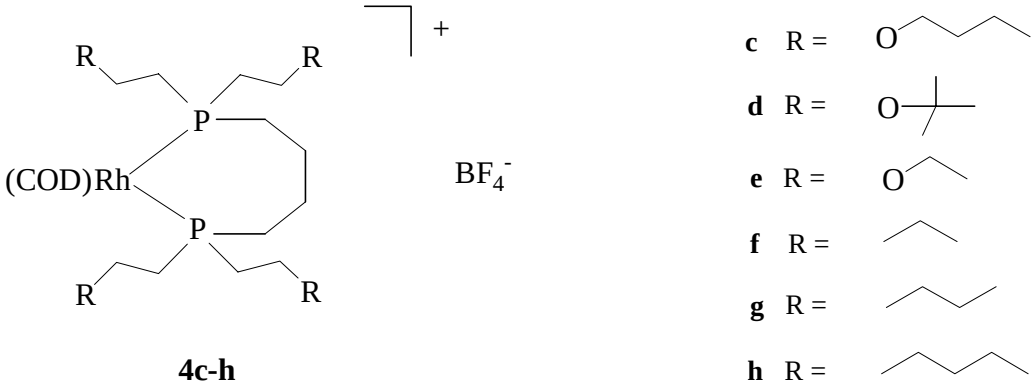
The addition of amines is a necessary prerequisite for the hydrogenation of carbon dioxide to formic acid [39]. Various amines can be used, but tertiary amines like triethyl amine are most effective. It is important to note, that the role of the amine in the stabilization of formic acid is not the formation of a simple 1 : 1 formate salt. Wagner [93] and Sekyia [94] demonstrated that mixtures from HCO_2H and NR_3 form azeotropes in the molar ratios between 3 : 2 and 6 : 2. The azeotrope composition of HCO_2H/NEt_3 at 20 bar is almost 5 : 2 [94]. If no amine is added, only very small amounts of formic acid are formed.

Monodentate and bidentate phosphines PR_3 and $R_2P(CH_2)_nPR_2$, respectively, were systematically investigated by Leitner et al. to study the influence of structural changes of the ligands on the efficiency of *in situ* catalysts [91]. Mono- and bidentate phosphines show a distinct behaviour upon variation of the P/Rh ratio (10:1 to 2:1) and upon structural changes when used as ligands for in situ catalysts for the CO_2 hydrogenation. Leitner observed that catalysts with chelating ligands prior to use must be activated with HCO_2H in order to avoid an induction period. No such activation is necessary if monodentate phosphines are used as

kinetic experiments revealed. Furthermore, the size of the chelate ring formed at the metal center exerts a strong influence: five- and eight-membered rings lead to extremely low activities [91]. Nevertheless, the catalytic activity increases with an increasing size of the backbone (from n = 1 to n = 4) and increasing basicity of the substituents at the phosphorus atoms.

4.2. Hydrogenation of Carbon Dioxide with Complexes 4c-h in Methanol

Considering the fact that Leitner [70,91] obtained considerable results with chelating diphosphines like dppb (dppb = bis(diphenylphosphino)butane) or dchpb (dchpb = bis(dicyclohexylphosphino)butane) in the hydrogenation of carbon dioxide and the assumption of coordinatively unsaturated species as reactive intermediates in this catalytic cycle prompted the investigation of the cationic (ether-diphosphine)rhodium(I) complexes **4c-e** in the hydrogenation of CO_2. The diphosphines **3c-h** were furnished with a C_4 backbone and different alkyl substituents at the phosphorus atom. The terminal alkyl substituents (e.g. ethyl,



4c-h

Figure 7. Complexes **4c-h** employed in the hydrogenation of carbon dioxide to formic acid

n-butyl, *t*-butyl) at the ether oxygen atoms in the ether-diphosphine ligands **3c-e** exert different steric demands. To investigate the influence of the ether moiety in the diphosphine ligands on the hydrogenation of CO_2 to formic acid, the oxygen atom in the alkyl chain was replaced by a methylene group. Hence diphosphines **3f-h** and their rhodium complexes **4f-h** were prepared.

4.3. Influence of Tertiary Amines on the Yield of Formic Acid using Complexes 4c-h

The yield of formic acid obtained by reacting CO_2 with H_2 in an 1 : 1 ratio in methanol for 21 hours using the complexes **4c-h** at a total pressure of 50 bar at room temperature are summarized in Figure 7. The pressure was maintained constant during the entire catalytic run. Complexes **4c-h** were dissolved in methanol and a mixture of the tertiary amine (2 ml of NEt_3

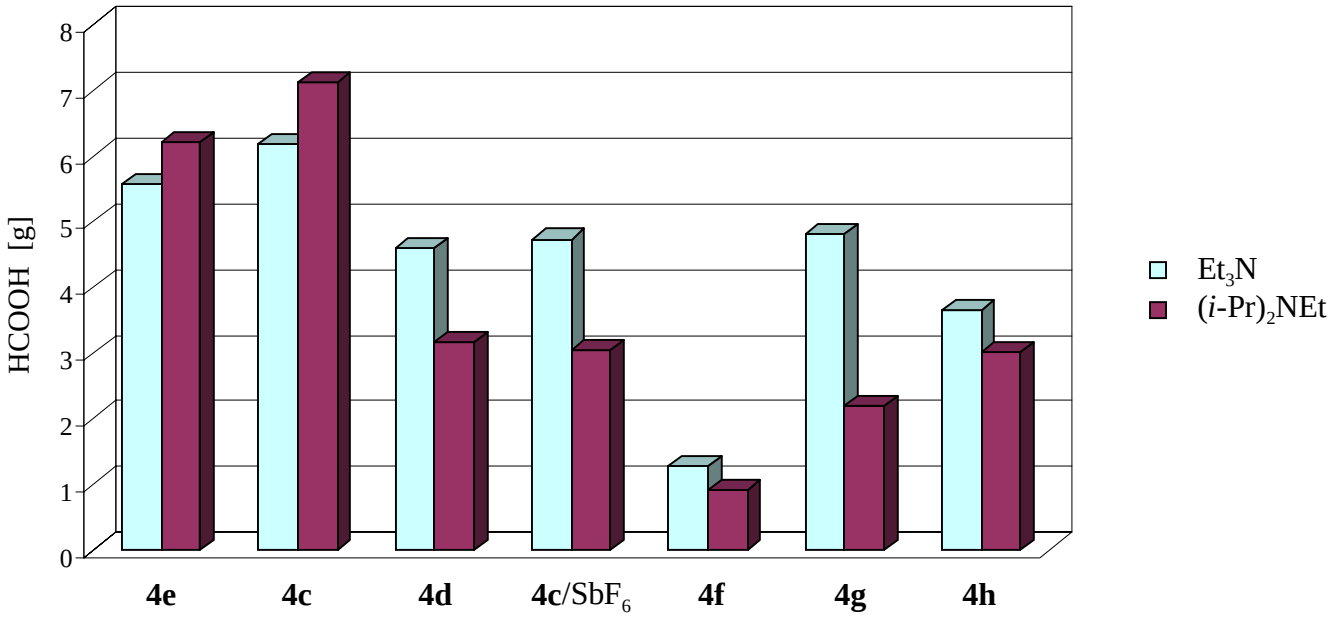


Figure 8. Influence of the tertiary amine on the yield of formic acid with complexes **4c-e**

or (*i*-Pr)$_2$NEt) and catalytic amounts of water (~ 0.1 ml) were added. 1 ml of cyclooctadiene was employed as a stabilizing agent for these complexes **4c-h**.

Upon addition of a tertiary amine no ethyl formate was detected by GC analysis. Obviously the produced formic acid has formed a salt or a stable adduct with the amine [39]. The best yields of formic acid were obtained with (*i*-Pr)$_2$NEt and **4c**. Compared to NEt_3 the tertiary amine (*i*-Pr)$_2$NEt is more effective in the formation of formic acid employing complexes **4e** and **4c**. In all other cases with NEt_3 as a base higher yields and turnover numbers were achieved. The change of the counterion in complex **4c** from BF_4^- to SbF_6^- resulted in a decreased yield of formic acid. The amount of formic acid decreased as the steric demand of the alkyl group at the ether oxygen atom was raised.

With complex **4h** which is provided with an additional methylene function instead of an oxygen atom in the seven-membered alkyl chains, lower yields of formic acid were obtained compared to **4c**. This could be explained by a better stabilization of coordinatively unsaturated rhodium-containing intermediates in the catalytic cycle. It is known that ether-diphosphines behave as intramolecular solvents [15]. Within **4f-h** complex **4g** gave rise to an optimum in the formation of formic acid. However, they are all less active than the corresponding (ether-diphosphine)rhodium complexes **4c-d**. In this series with complex **4f** the worst results were obtained.

4.4. Influence of the Temperature on the Yield of Formic Acid with Complex 4c

The yield of formic acid obtained by the hydrogenation of CO_2 in methanol with (*i*-Pr)$_2$NEt catalyzed by complex **4c** follows the trend expected for an exothermic, but endergonic reaction of two gaseous molecules [39]. As also observed by Leitner there was no increase of formic acid with increasing temperature in the range of 20-35°C (Table 7, entries

1-3) [39]. Up to 1473 moles of formic acid per mole rhodium were generated (entry 1) at room temperature. If entries 1 and 4 are compared with each other the turnover number of the reaction with 5 ml of $(i\text{-Pr})_2$NEt is significantly higher than with 2 ml of that amine. The larger amount of the tertiary amine, results in an increased dissolution of carbon dioxide which may be responsible for a higher yield.

Table 7.
Hydrogenation of carbon dioxide to formic acid[a]

Entry	Complex	Tertiary Amine	Temperature [°C]	Formic acid[b] [g]	TON[c]	TOF[d]
1	**4c**	$(i\text{-Pr})_2$NEt	20	7.12	1473	70.1
2	**4c**	$(i\text{-Pr})_2$NEt	30	7.06	1461	69.6
3	**4c**	$(i\text{-Pr})_2$NEt	35	6.98	1443	68.7
4	**4c**	$(i\text{-Pr})_2$NEt 5 ml	20	11.5	2381	113.4
5	**4c** 0.06 mmol	$(i\text{-Pr})_2$NEt	20	7.13	2455	116.9

[a] Reaction conditions: solvent: 15 ml methanol; pressure 50 bar (CO_2 : H_2 = 1:1); reaction time : 21 h; [Rh] = 0.1 mmol; additives: 2 ml tertiary amine, 1 ml cyclooctadiene, catalytic amount of water (~ 0.1 ml); [b] The amount of formic acid was detected by gas chromatography, internal standard method; [c] TON: turnover numbers (mol_{sub} mol_{cat}^{-1}); [d] TOF: turnover frequencies (mol_{sub} mol_{cat}^{-1} h^{-1}).

Decreasing the amount of **4c** in the hydrogenation of CO_2 resulted in an substantial increase of the turnover numbers (entry 5). A similar dependence of the turnover numbers on the catalyst concentration was also been observed with other catalytic systems [37,38].

The dependence of the formation of formic acid on the pressure has not been studied yet. But it was observed that lower pressures led to a decrease of the turnover numbers [38,42] as expected for an exothermic but endergonic reaction.

4.5. Conclusion

The (diphosphine)rhodium(I) complexes **4c-h** were employed in the catalytic hydrogenation of carbon dioxide to formic acid in methanol at a total pressure of 50 bar (CO_2 : H_2 = 1 : 1). The highest yields of HCOOH were achieved with the (ether-phosphine)rhodium complex **4c** and (i-Pr)$_2$NEt as the tertiary amine. A different behaviour of the two employed tertiary amines was found. (i-Pr)$_2$NEt afforded better results with the (ether-phosphine)rhodium complexes **4c** and **4e**, whereas with all other complexes NEt_3 led to an enhanced formation of formic acid. The markedly steric demand of the (ether-diphosphine)rhodium complex **4d** with *t*-butyl groups explains the lower yields of HCOOH compared to complex **4c** (*n*-butyl groups). The better stabilization of unsaturated active species with the ether-moieties of complexes **4c-d** in the catalytic hydrogenation of carbon dioxide was pointed out. As expected for an exothermic but endergonic reaction, there was no increase in the formation of formic acid with increasing temperature. Up to 1473 moles of formic acid per mole rhodium were generated at room temperature. The hydrogenation of carbon dioxide is dependent on the concentration of the employed catalyst. Lower catalyst concentrations led to higher turnover numbers.

It should be emphasized that tertiary amines shift the equilibrium of the catalytic hydrogenation of carbon dioxide to the right side by forming a salt or a stable adduct with the formic acid [93,94]. Another role that the amine could play might be the further acceleration of the heterolytic cleavage of H_2 in an dihydrogen complex involved in σ–bond metathesis reaction [95].

5. ^{103}Rh-NMR-Spectroscopy

5.1. General Considerations

Like in organic chemistry NMR spectroscopy gained importance as a tool for the structural elucidation of organometallic compounds. The group of the standard nuclei ^{1}H and ^{13}C is extended by the incorporation of the ^{31}P nuclei which occurs often in coordination chemistry, whereas the NMR spectroscopic investigation of a transition metal center is still a non-routine technique. Reasons are the low sensitivity (^{57}Fe, ^{103}Rh, ^{107}Ag) or the quadrupolar moments which give raise to a strong line broadening (^{55}Mn, ^{59}Co, ^{61}Ni).

According to *Ramsay's* equation the shielding of a nucleus can be expressed by two terms, the diamagnetic and the paramagnetic part [96]. The diamagnetic term is defined basically by the electron density around the nucleus and is relevant for the light nuclei of the first period. Therefore chemical shifts can be best explained by electron density arguments for ^{1}H. The paramagnetic term in *Ramsay's* equation gains importance for heavier nuclei:

$$|\sigma_p| = \text{-const.}\ (\Delta E)^{-1} \langle r_d^{-3} \rangle \Sigma Q_N$$

ΔE = average electronic excitation energy

r_d = average radius of the d orbitals

Q_N = summation over electron densities

Because of the importance of this term for heavy nuclei a correlation of structural parameters with the magnetic shielding becomes difficult. Several attempts to find a relation between ^{103}Rh chemical shift and other data like catalytic activities, IR parameters, coupling

constants, steric effects, and kinetic data were made since this nucleus is available for NMR spectroscopy [97-102].

5.2. Techniques for the ^{103}Rh NMR Spectroscopy

Rhodium is one of the few elements that occur solely as one isotope with a nuclear-spin quantum number of I = ½. Nevertheless, the low magnetogyric ratio leads to an extremely poor sensitivity of 3.11 *10^{-5} compared to ^{1}H and thus to a difficult detection [96]. Direct observation of signals is rare in solution and only possible for concentrated samples at high fields using long experimental times. For this reason the method of choice is indirect detection via another, more sensitive nucleus like ^{1}H or ^{31}P [103]. Of course this technique can only be applied when the ^{103}Rh nucleus shows a significant coupling constant to the sensitive one. As all rhodium compounds investigated herein are provided with phosphine ligands ^{31}P has been taken as the sensitive nucleus. The resulting spectra are two-dimensional with the ^{31}P chemical shift in the detection dimension F2 and ^{103}Rh in F1.

In order to obtain a good resolution and signal to noise ratio three parameters must be taken into account: (i) the coupling of rhodium to the sensitive nucleus is needed for the first delay: it is easily extracted from an 1D spectrum of the sensitive nucleus. (ii) The approximate resonance frequency of ^{103}Rh in order to reduce the sweep width and to increase the resolution in the F1 dimension: this value is obtained by the use of the so called DECP90 technique in which the effect of ^{103}Rh is monitored in a spectrum of ^{1}H/^{31}P while the offset frequency of the rhodium channel is changed stepwise. (iii) The pulse length for rhodium: once the resonance is known the same DECP90 pulse sequence is used but this time the pulse length is adjusted.

As no compound could be defined in the literature to be used as a ^{103}Rh reference the chemical shift is related to an imaginary substance with an absolute resonance at 3.16 MHz on a spectrometer on which the frequency of 100 MHz is measured for TMS [104]. In this case 3.16 MHz is called the Ξ–value and is related to the chemical shift according to:

$$\delta = 10^6 \cdot \left(\frac{100}{3.16} \cdot \frac{\nu_R}{\nu_{TMS}} - 1 \right)$$

ν_r represents the absolute resonance frequency of ^{103}Rh and ν_{TMS} the resonance of TMS at the given spectrometer. Figure 9 shows a (^{31}P,^{103}Rh){^{1}H} correlation spectrum of [(COD)Rh(TPPTS)$_2$][BF$_4$].

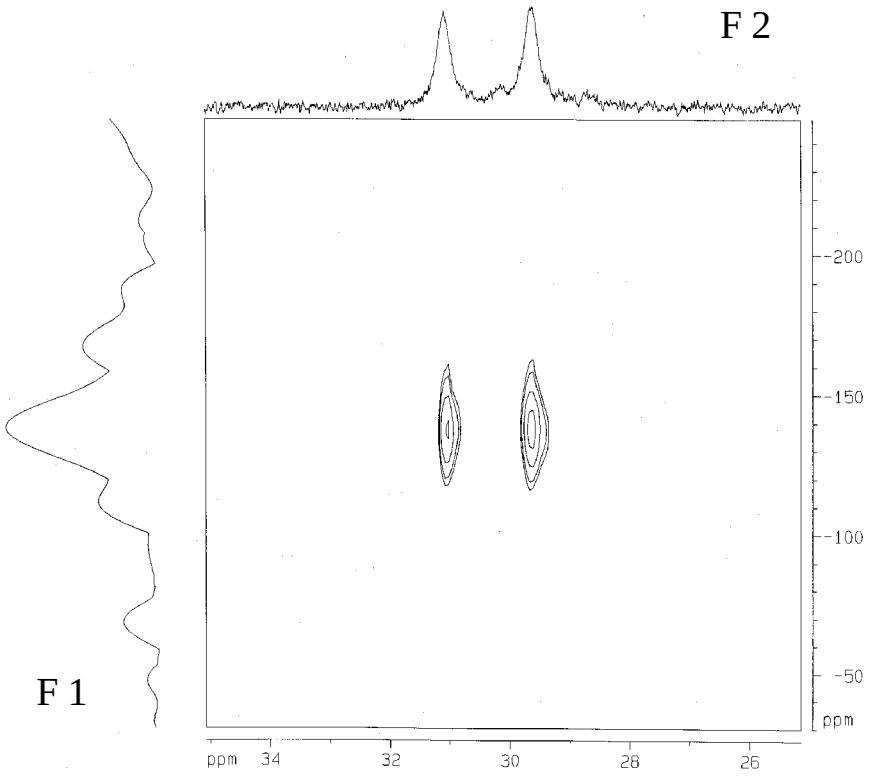


Figure 9. (^{31}P,^{103}Rh){^{1}H} correlation spectrum of complex [(COD)Rh(TPPTS)$_2$][BF$_4$] (**TPPTS**). The ^{103}Rh spectrum is projected in the F1 dimension while the F2 dimension represents the 1D^{31}P{^{1}H} spectrum.

5.3. Results of ^{103}Rh NMR Measurements

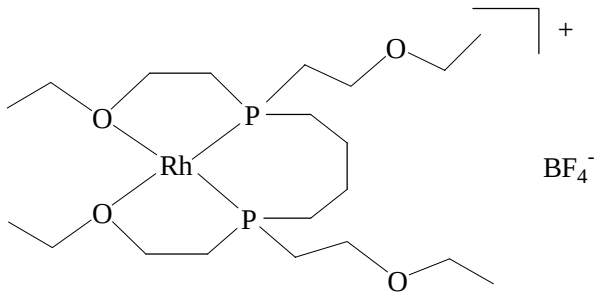
From a series of cationic (phosphine)rhodium(I) complexes ^{103}Rh NMR spectra have been recorded. The investigated compounds are described in this thesis or elsewhere [67] and the results are listed in Table 8. The phosphine rhodium(I) complexes have the same type of coordination mode: they are all square-planar and occupy the high field region in which rhodium complexes with the coordination number four are found generally [105,106].

Table 8.
δ(^{103}Rh) of (phosphine)rhodium(I) complexes

Entry	Complex [(COD)Rh(P_2)][BF_4]	δ (^{103}Rh) [ppm]
1	**4a** / P4P{$(CH_2)_3OCH_2CH(OH)CH_2OH$}$_2$	- 202
2	**4b** / P4P{$(CH_2)_3OCH_2C(CH_2OH)_2(C_2H_5)$}$_2$	- 195
3	**4c** / P4P{$(CH_2)_2O$*n*-Butyl}$_2$	- 196
4	P3P{$(CH_2)_2O$*n*-Butyl}$_2$	- 285
5	**4d** / P4P{$(CH_2)_2O$*t*-Butyl}$_2$	- 202
6	**4e** / P4P{$(CH_2)_2OC_2H_5$}$_2$	- 205
7	**4h** / P4P{heptyl}$_2$	- 191
8	**dppb** / P4P{phenyl}$_2$	- 258
9	**TPPTS** / P($C_6H_4SO_3Na$)$_3$	- 139
10	P3P{hexanol}$_2$	- 272
11	P4P{(CH_2)OCyclohexyl}$_2$	- 202
12	P4P{neohexyl}$_2$	- 148
13	**5e** / bis(chelate)	+ 2353

The chemical shifts of square-planar (cyclooctadiene)(diphosphine)rhodium(I) complexes are in the range of -145 to -285 ppm. Rhodium complexes with alkyl diphosphines reveal chemical shifts in a very narrow range of -190 to -205 ppm. The rhodium complex **dppb** with an aryl diphosphine gives rise to a signal at δ -258. Diphosphinerhodium(I) complexes provided with a C_3 backbone are characterized by a signal at higher fields (-270 to -285 ppm). However, as shown in entry 12, high steric demand of an alkyl diphosphine complex with four neohexyl groups results in a ^{103}Rh chemical shift of -145 ppm.

Only the bis(chelated) (ether-diphosphine)rhodium(I) complex **5c** without the ancillary ligand COD has a totally different chemical shift of + 2353 ppm. This particular ^{103}Rh



5c

Figure 10. The bis chelated (ether-diphosphine)rhodium(I)complex **5c**

resonance in the (^{31}P,^{103}Rh){^{1}H} NMR spectrum is traced back to the bidentate nature of the (ether-diphosphine)rhodium(I) complex **5c**.

Experimental Section

1. General Considerations

1.1. Working Procedures

All manipulations were performed under an atmosphere of argon by employing the usual Schlenk tube techniques. Methanol was dried with magnesium and distilled. Diethyl ether, THF, and 1-hexene were distilled from sodium benzophenone ketyl. Acetone was distilled twice from P_4O_{10}. Dichloromethane was dried with CaH_2 prior to distillation. Water was degassed prior to use. All solvents were stored under argon. For photochemical reactions a Heraeus Hg high-pressure lamp of the type TQ 150 Original Hanau was employed.

1.2. Materials

$RhCl_3 \cdot 3\ H_2O$ was a gift from Degussa AG. 3-Allyloxy-1,2-propanediol and 3-allyloxy-2-ethyl-2-hydroxymethyl-1-propanol were received from Aldrich. 1-Hexene and the emulsifiers potassium dodecyl sulfate, polyethylene glycol-400 and benzalkonium chloride were purchased from Fluka. Benzalkonium tetrafluoroborate was obtained from benzalkonium chloride with $NaBF_4$ in acetone. *n*-Butylvinyl ether, *t*-butylvinyl ether, ethylvinyl ether, 1-pentene, and 1-heptene were obtained from Merck-Schuchardt.

1.3. Characterization

Elemental analyses were carried out on an Elementar Analyzer, model vario EL. IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. The NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies and standards are as follows: $^{13}C\{^1H\}$ NMR: 62.90 MHz; $^{31}P\{^1H\}$ NMR: 101.25 MHz; Rh NMR: 7.90 MHz. ^1H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks which are

reported relative to TMS. ^{31}P chemical shifts were measured relative to 85 % H_3PO_4 ($\delta = 0$). The ^{103}Rh NMR resonances were measured using a 2D (^{31}P, ^{103}Rh){^{1}H} experiment [107]. Chemical shift values are referred to Ξ(Rh) = 3.16 MHz [104]. FAB mass spectra were recorded on a Finnigan MAT TSQ 70 (10kV, 50°C) instrument and FD mass spectra were acquired on a Finnigan MAT 711A (8kV, 333K) modified by AMD and reported as mass/charge *(m/z)*. The rhodium content was measured by atomic absorption spectrometry on a Varian SpectrAA 20 Plus spectrometer.

2. Preparation of the Compounds

2.1. Preparation of the Diphosphines 3a-h

2.1.1. 1,4-Bis{di[(1,2-dihydroxypropoxy)propyl]phosphino}butane (3a)

A mixture of 1,4-diphosphinobutane (1.84 g, 15.08 mmol) and 3-allyloxy-1,2-propanediol (7.97 g, 60.32 mmol) was UV irradiated in a quartz Schlenk tube over night to give pure **3a.** Yield 9.32 g (95 %). Anal. Calc. for $C_{28}H_{60}O_{12}P_2$: C, 51.69; H, 9.29. Found: C, 51.76; H, 9.42. FAB MS *m/z:* 651.2 (M^+). $^{31}P\{^{1}H\}$ NMR (*d*$_4$-MeOH): δ -31.93 (s). $^{13}C\{^{1}H\}$ NMR (*d*$_4$-MeOH): δ 35.85-23.81 (m, P*C*H$_2$*C*H$_2$CH$_2$CH$_2$P), 27.58 (d, $^{1}J_{PC}$ = 12.09 Hz, P*C*H$_2$CH$_2$CH$_2$O), 24.69 (d, $^{2}J_{PC}$ = 9.96 Hz, PCH$_2$*C*H$_2$CH$_2$O), 73.75 (d, $^{3}J_{PC}$ = 12.81 Hz, PCH$_2$CH$_2$*C*H$_2$O), 73.74 (s, O*C*H$_2$CH(OH)CH$_2$(OH)), 72.70 (s, OCH$_2$*C*H(OH)CH$_2$(OH)), 65.07 (s, OCH$_2$CH(OH)*C*H$_2$(OH)). IR (KBr, cm^{-1}): ν(OH) 3382, ν_{as} (C-O-C) 1115, ν (C-OH) 1044.

2.1.2. 1,4-Bis{di[(1-hydroxy-2-ethyl-2-hydroxymethylpropoxy)propyl]phosphino} butane (3b)

A mixture of 1,4-diphosphinobutane (2.43 g, 19.92 mmol) and 3-allyloxy-2-ethyl -2-hydroxymethyl-1-propanol (13.88 g, 79.67 mmol) was UV irradiated in a quartz Schlenk tube

over night to give pure **3b**. Yield 15.82 g (97 %). Anal. Calc. for $C_{40}H_{84}O_{12}P_2$: C, 58.66; H, 10.34. Found: C, 59.03; H, 10.75. FAB MS *m/z:* 818.9 (M^+). $^{31}P\{^1H\}$ NMR (*d*$_4$-MeOH): δ -30.61 (s). $^{13}C\{^1H\}$ NMR (*d*$_4$-MeOH): δ 35.8-23.78 (m, P*C*H_2*C*H_2CH_2CH_2P), 27.54 (d, $^1J_{PC}$ = 12.09 Hz, P*C*H_2CH_2CH_2O), 24.65 (d, $^2J_{PC}$ = 9.25 Hz, PCH_2*C*H_2CH_2O), 73.68 (d, $^3J_{PC}$ = 12.09 Hz, PCH_2CH_2*C*H_2O), 73.14 (s, O*C*H_2C), 45.12 (s, OCH_2*C*), 23.71 (s, C(*C*H_2CH_3)(CH_2OH)$_2$), 8.56 (s, C(CH_2*C*H_3)(CH_2OH)$_2$), 64.79 (s, C(CH_2CH_3)(*C*H_2OH)$_2$). IR (KBr, cm^{-1}): ν(OH) 3383, ν_{as} (C-O-C) 1111, ν (C-OH) 1061.

2.1.3. 1,4-Bis{di[(*n*-butoxy)ethyl]phosphino}butane (3c)

A mixture of 1,4-diphosphinobutane (2.78 g, 22.8 mmol) and *n*-butylvinyl ether (9.13 g, 91.2 mmol) was UV irradiated in a quartz Schlenk tube over night to give pure **3c**. Yield 11.56 g (97%). Anal. Calc. for $C_{28}H_{60}O_4P_2$: C, 64.34; H, 11.57. Found: C, 64.17; H, 11.29. FAB MS *m/z:* 522.7 (M^+). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -36.21 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 35.41-23.11 (m, P*C*H_2*C*H_2CH_2CH_2P), 29.03 (d, $^1J_{PC}$ = 14.94 Hz, P*C*H_2CH_2O), 68.56 (d, $^2J_{PC}$ = 20.63 Hz, PCH_2*C*H_2O), 70.49 (s, O*C*H_2CH_2CH_2CH_3), 32.78 (s, OCH_2*C*H_2CH_2CH_3), 20.26 (s, OCH_2CH_2*C*H_2CH_3), 14.73 (s, OCH_2CH_2CH_2*C*H_3). IR (KBr, cm^{-1}): ν_{as} (C-O-C) 1099.

2.1.4. 1,4-Bis{di[(*t*-butoxy)ethyl]phosphino}butane (3d)

A mixture of 1,4-diphosphinobutane (3.99 g, 32.71 mmol) and *t*-butylvinyl ether (13.1 g, 130.08 mmol) was UV irradiated in a quartz Schlenk tube over night to give pure **3d**. Yield 16.5 g (96.5 %). Anal. Calc. for $C_{28}H_{60}O_4P_2$: C, 64.34; H, 11.57. Found: C, 64.29; H, 11.70. FAB MS *m/z:* 522.7 (M^+). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -36.21 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 35.26-22.94 (m, P*C*H_2*C*H_2CH_2CH_2P), 29.84 (d, $^1J_{PC}$ = 12.80 Hz, P*C*H_2CH_2O), 60.42 (d, $^2J_{PC}$ = 22.05 Hz, PCH_2*C*H_2O), 73.60 (s, O*C*$(CH_3)_3$), 28.45 (s, OC$(CH_3)_3$). IR (KBr, cm^{-1}): ν_{as} (C-O-C) 1064.

2.1.5. 1,4-Bis{di[(ethoxy)ethyl]phosphino}butane (3e)

A mixture of 1,4-diphosphinobutane (2.13 g, 17.46 mmol) and ethylvinyl ether (5.08 g, 70.55 mmol) was UV irradiated in a quartz Schlenk tube over night to give pure **3e**. Yield 7.02 g (98 %). Anal. Calc. for $C_{20}H_{44}O_4P_2$: C, 58.52; H, 10.80. Found: C, 58.28; H, 10.50. FAB MS *m/z:* 410.5 (M^+). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -36.80 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.34-21.06 (m, P*C*H_2*C*H_2CH_2CH_2P), 27.04 (d, $^1J_{PC}$ = 14.23 Hz, P*C*H_2CH_2O), 67.30 (d, $^2J_{PC}$ = 20.63 Hz, PCH_2*C*H_2O), 65.03 (s, O*C*H_2CH_3), 14.21 (s, OCH_2*C*H_3). IR (KBr, cm^{-1}): ν_{as} (C-O-C) 1098.

2.1.6. 1,4-Bis[dipentylphosphino]butane (3f)

A mixture of 1,4-diphosphinobutane (2.12 g, 17.38 mmol) and 1-pentene (4.94 g, 70.5 mmol) was UV irradiated in a quartz Schlenk tube over night to give pure **3f**. Yield 6.79 g (97 %). Anal. Calc. for $C_{24}H_{52}P_2$: C, 71.60; H, 13.02. Found: C, 71.03; H, 12.97. FAB MS *m/z:* 402.6 (M^+). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -29.88 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 34.22-21.84 (m, P*C*H_2*C*H_2CH_2CH_2P), 33.35 (d, $^1J_{PC}$ = 12.09 Hz, P*C*H_2CH_2CH_2CH_2CH_3), 27.08 (d, $^2J_{PC}$ = 18.89 Hz, PCH_2*C*H_2CH_2CH_2CH_3), 26.56 (d, $^3J_{PC}$ = 12.58 Hz, PCH_2CH_2*C*H_2CH_2CH_3), 22.06 (s, PCH_2CH_2CH_2*C*H_2CH_3), 13.64 (s, PCH_2CH_2CH_2CH_2*C*H_3).

2.1.7. 1,4-Bis[dihexylphosphino]butane (3g)

A mixture of 1,4-diphosphinobutane (3.00 g, 24.6 mmol) and 1-hexene (8.27 g, 98.4 mmol) was UV irradiated in a quartz Schlenk tube over night to give pure **3g**. Yield 11.11 g (98.5 %). Anal. Calc. for $C_{28}H_{60}P_2$: C, 73.31; H, 13.18. Found: C, 72.93; H, 12.85. FAB MS *m/z:* 458.7 (M^+). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -30.20 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.80-21.71 (m, P*C*H_2*C*H_2CH_2CH_2P), 31.40 (d, $^1J_{PC}$ = 11.38 Hz, P*C*H_2(CH_2)$_4$CH_3), 27.52 (d, $^2J_{PC}$ = 12.81 Hz, PCH_2*C*H_2(CH_2)$_3$CH_3), 26.10 (d, $^3J_{PC}$ = 12.81 Hz, P(CH_2)$_2$*C*H_2(CH_2)$_2$CH_3), 31.84 (s, P(CH_2)$_2$*C*H_2CH_2CH_3), 22.79 (s, P(CH_2)$_4$*C*H_2CH_3), 14.27 (s, P(CH_2)$_5$*C*H_3).

2.1.8. 1,4-Bis[diheptylphosphino]butane (3h)

A mixture of 1,4-diphosphinobutane (2.05 g, 16.80 mmol) and 1-heptene (6.65 g, 67.90 mmol) was UV irradiated in a quartz Schlenk tube over night to give pure **3h**. Yield 8.43 g (97.5 %). Anal. Calc. for $C_{32}H_{68}P_2$: C, 74.66; H, 13.31. Found: C, 74.29; H, 13.08. FAB MS *m/z:* 514.8 (M^+). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -29.81 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 34.8-23.02 (m, P*C*H_2*C*H_2CH_2CH_2P), 31.71 (d, $^1J_{PC}$ = 13.52 Hz, P*C*H_2(CH_2)$_5$CH_3), 27.63 (d, $^2J_{PC}$ =13.52 Hz, PCH_2*C*H_2(CH_2)$_4$CH_3), 26.20 (d, $^3J_{PC}$ = 12.81 Hz, P(CH_2)$_2$*C*H_2(CH_2)$_3$CH_3), 29.34 (s, P(CH_2)$_3$*C*H_2(CH_2)$_2$CH_3), 32.34 (s, P(CH_2)$_4$*C*H_2CH_2CH_3), 22.90 (s, P(CH_2)$_5$*C*H_2CH_3), 14.29 (s, P(CH_2)$_6$*C*H_3).

2.2. Preparation of Complexes 4a-h

2.2.1. 1,5-Cyclooctadiene{1,4-bis[di[(1,2-dihydroxypropoxy)propyl]phosphino]-butane}rhodium (I) tetrafluoroborate (4a)

[Rh(COD)$_2$][BF_4] (249.5 mg, 0.614 mmol) was dissolved in 20 ml of MeOH and a solution of the diphosphine **3a** (397.8 mg, 0.610 mmol) in 20 ml of MeOH was added dropwise at – 60°C for 3 h. After stirring for 1 h diethyl ether (50 ml) was added, the solvent was removed and the oily product **4a** was dried in vacuum. Yield 506.73 mg (87 %). Anal. Calc. for $C_{36}H_{72}BF_4O_{12}P_2Rh$: C, 45.58; H, 7.65; Rh, 10.85. Found: C, 43.55 [108]; H, 7.42; ^{103}Rh, 10.59. FD MS *m/z:* 861.5 (M^+). $^{31}P\{^1H\}$ NMR (d_6-acetone): δ 12.8 (d, $^1J_{RhP}$ = 141.5 Hz). Rh NMR (d_6-acetone): δ -202. $^{13}C\{^1H\}$ NMR (d_4-MeOH): δ 98.15 (CH of COD), 32.18 (CH_2 of COD), 26.79 (P*C*H_2CH_2CH_2O), 25.97(PCH_2*C*H_2CH_2O), 73.48 (PCH_2CH_2*C*H_2O), 73.96 (O*C*H_2CH(OH)CH_2OH), 72.87 (OCH_2*C*H(OH)CH_2OH), 65.11 (OCH_2CH(OH)*C*H_2OH). IR (KBr, cm^{-1}): ν(OH) 3406, ν_{as} (C-O-C) 1114, ν (C-OH) 1044.

2.2.2. 1,5-Cyclooctadiene{1,4-bis[di[(1-hydroxy-2-ethyl-2-hydroxymethylpropoxy)-propyl]phosphino]butane}rhodium(I) tetrafluoroborate (4b)

$[Rh(COD)_2][BF_4]$ (259.9 mg, 0.64 mmol) was dissolved in 20 ml of MeOH and a solution of the diphosphine **3b** (520.0 mg, 0.635 mmol) in 20 ml of MeOH was added dropwise at – 60°C for 3 h. After stirring for 1 h diethyl ether (50 ml) was added, the solvent was removed and the oily product **4b** was dried in vacuum. Yield 636.2 mg (89 %). Anal. Calc. for $C_{48}H_{96}BF_4O_{12}P_2Rh$: C, 51.67; H, 8.66; Rh, 9.21. Found: C, 50.28 [108]; H, 8.61; Rh, 8.88. FD MS *m/z:* 1029.3 (M^+). $^{31}P\{^1H\}$ NMR (d_6-acetone): δ 13.5 (d, $^1J_{RhP}$ = 141.8 Hz). ^{103}Rh NMR (d_6-acetone): δ -195. $^{13}C\{^1H\}$ NMR (d_4-MeOH): δ 98.29 (CH of COD), 32.05 (CH_2 of COD), 26.97 ($PCH_2CH_2CH_2O$), 25.67 ($PCH_2CH_2CH_2O$), 72.79 ($PCH_2CH_2CH_2O$), 72.79 (OCH_2C), 45.21 (OCH_2C), 23.65 ($C(CH_2CH_3)(CH_2OH)_2$), 8.43 ($C(CH_2CH_3)(CH_2OH)_2$), 64.51 ($C(CH_2CH_3)(CH_2OH)_2$). IR (KBr, cm^{-1}): ν(OH) 3422, ν_{as} (C-O-C) 1112, ν (C-OH) 1059.

2.2.3. 1,5-Cyclooctadiene{1,4-bis[di[(*n*-butoxy)ethyl]phosphino]butane}rhodium(I) tetrafluoroborate (4c)

$[Rh(COD)_2][BF_4]$ (261.3 mg, 0.643 mmol) was dissolved in 20 ml of MeOH and a solution of the diphosphine **3c** (328.6 mg, 0.629 mmol) in 20 ml of MeOH was added dropwise at – 60°C for 3 h. After stirring for 1 h diethyl ether (50 ml) was added, the solvent was removed and the oily product **4c** was dried in vacuum. Yield 438.74 mg (85 %). Anal. Calc. for $C_{36}H_{72}BF_4O_4P_2Rh$: C, 52.69; H, 8.84; Rh, 12.54. Found: C, 51.57 [108]; H, 8.64; Rh, 12.19. FD MS *m/z:* 733.8 (M^+). $^{31}P\{^1H\}$ NMR (d_6-acetone): δ 10.58 (d, $^1J_{RhP}$ = 142.2 Hz). ^{103}Rh NMR (d_6-acetone): δ -196. $^{13}C\{^1H\}$ NMR (d_6-acetone): δ 96.04 (CH of COD), 30.95 (CH_2 of COD), 26.49 (PCH_2CH_2O), 67.29 (PCH_2CH_2O), 70.92 ($OCH_2(CH_2)_2CH_3$), 32.13

($OCH_2CH_2CH_2CH_3$), 19.60 ($O(CH_2)_2CH_2CH_3$), 13.68 ($O(CH_2)_3CH_3$). IR (KBr, cm^{-1}): ν_{as} (C-O-C) 1106.

2.2.4. 1,5-Cyclooctadiene{1,4-bis[di[(*t*-butoxy)ethyl]phosphino]butane}rhodium(I) tetrafluoroborate (4d)

$[Rh(COD)_2][BF_4]$ (146.0 mg, 0.359 mmol) was dissolved in 20 ml of MeOH and a solution of the diphosphine **3d** (187.8 mg, 0.359 mmol) in 20 ml of MeOH was added dropwise at – 60°C for 3 h. After stirring for 1 h diethyl ether (50 ml) was added, the solvent was removed and the oily product **4d** was dried in vacuum. Yield 254.8 mg (86.5 %). Anal. Calc. for $C_{36}H_{72}BF_4O_4P_2Rh$: C, 52.69; H, 8.84; Rh, 12.54. Found: C, 50.98 [108]; H, 8.51; Rh, 12.14. FD MS *m/z:* 733.8 (M^+). $^{31}P\{^1H\}$ NMR (d_6-acetone): δ 10.11 (d, $^1J_{RhP}$ = 141.4 Hz). ^{103}Rh NMR (d_6-acetone): δ -202. $^{13}C\{^1H\}$ NMR (d_6-acetone): δ 96.46 (CH of COD), 31.79 (CH_2 of COD), 28.84 (PCH_2CH_2O), 59.30 (PCH_2CH_2O), 74.35 ($OC(CH_3)_3$), 28.10 ($OC(CH_3)_3$). IR (KBr, cm^{-1}): ν_{as} (C-O-C) 1073.

2.2.5. 1,5-Cyclooctadiene{1,4-bis[di[(ethoxy)ethyl]phosphino]butane}rhodium(I) tetrafluoroborate (4e)

$[Rh(COD)_2][BF_4]$ (78.6 mg, 0.194 mmol) was dissolved in 20 ml of MeOH and a solution of the diphosphine **3e** (77.4 mg, 0.189 mmol) in 20 ml of MeOH was added dropwise at – 60°C for 3 h. After stirring for 1 h diethyl ether (50 ml) was added, the solvent was removed and the oily product **4e** was dried in vacuum. Yield 117.2 mg (87.5 %). Anal. Calc. for $C_{28}H_{56}BF_4O_4P_2Rh$: C, 47.47; H, 7.97; Rh, 10.73. Found: C, 46.69 [108]; H, 7.77; Rh, 10.52. FD MS *m/z:* 621.6 (M^+). $^{31}P\{^1H\}$ NMR (d_6-acetone): δ 10.17 (d, $^1J_{RhP}$ = 142.26 Hz). ^{103}Rh NMR (d_6-acetone): δ -205. $^{13}C\{^1H\}$ NMR (d_6-acetone): δ 95.95 (CH of COD), 30.91

(CH_2 of COD), 26.97 (PCH_2CH_2O), 67.31 (PCH_2CH_2O), 72.29 (OCH_2CH_3), 15.03 (OCH_2CH_3). IR (KBr, cm^{-1}): ν_{as} (C-O-C) 1103.

2.2.6. 1,5-Cyclooctadiene{1,4-bis[di(pentyl)phosphino]butane}rhodium(I)tetrafluoroborate (4f)

$[Rh(COD)_2][BF_4]$ (180.9 mg, 0.445 mmol) was dissolved in 20 ml of MeOH and a solution of the diphosphine **3f** (173.5 mg, 0.431 mmol) in 20 ml of MeOH was added dropwise at – 60°C for 3 h. After stirring for 1 h diethyl ether (50 ml) was added, the solvent was removed and the oily product **4f** was dried in vacuum. Yield 264.2 mg (87.5 %). Anal. Calc. for $C_{32}H_{64}BF_4P_2Rh$: C, 54.87; H, 9.21; Rh, 14.69. Found: C, 53.18 [108]; H, 8.89; Rh, 14.31. FD MS *m/z:* 613.7 (M^+). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.68 (d, $^1J_{RhP}$ = 140.71 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 95.73 (CH of COD), 28.34 (CH_2 of COD), 33.78 ($PCH_2(CH_2)_3CH_3$), 31.02 ($PCH_2CH_2(CH_2)_2CH_3$), 24.64 ($P(CH_2)_2CH_2CH_2CH_3$), 22.63 ($P(CH_2)_3CH_2CH_3$), 14.24 ($P(CH_2)_4CH_3$).

2.2.7. 1,5-Cyclooctadiene{1,4-bis[di(hexyl)phosphino]butane}rhodium(I)tetrafluoroborate (4g)

$[Rh(COD)_2][BF_4]$ (65.0 mg, 0.160 mmol) was dissolved in 20 ml of MeOH and a solution of the diphosphine **3g** (72.1 mg, 0.157 mmol) in 20 ml of MeOH was added dropwise at – 60°C for 3 h. After stirring for 1 h diethyl ether (50 ml) was added, the solvent was removed and the oily product **4g** was dried in vacuum. Yield 100.9 mg (85 %). Anal. Calc. for $C_{36}H_{72}BF_4P_2Rh$: C, 57.15; H, 9.59; Rh, 13.60. Found: C, 56.21 [108]; H, 9.35; Rh, 13.29 FD MS *m/z:* 669.8 (M^+). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.63 (d, $^1J_{RhP}$ = 140.67 Hz). ^{103}Rh NMR (*d_6*-acetone): δ -191. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 96.14 (CH of COD), 31.43 (CH_2 of COD), 31.80 ($PCH_2(CH_2)_4CH_3$), 25.97 ($PCH_2CH_2(CH_2)_3CH_3$), 25.21 ($PCH_2CH_2CH_2(CH_2)_2CH_3$), 31.43 (s, $P(CH_2)_3CH_2CH_2CH_3$), 22.86 (s, $P(CH_2)_4CH_2CH_3$), 14.37 (s, $P(CH_2)_5CH_3$).

2.2.8. 1,5-Cyclooctadiene{1,4-bis[di(heptyl)phosphino]butane}rhodium(I)tetrafluoroborate (4h)

$[Rh(COD)_2][BF_4]$ (220.1 mg, 0.542 mmol) was dissolved in 20 ml of MeOH and a solution of the diphosphine **3h** (277.9 mg, 0.540 mmol) in 20 ml of MeOH was added dropwise at – 60°C for 3 h. After stirring for 1 h diethyl ether (50 ml) was added, the solvent was removed and the oily product **4h** was dried in vacuum. Yield 390.6 mg (89 %). Anal. Calc. for $C_{40}H_{80}BF_4P_2Rh$: C, 59.12; H, 9.92; Rh, 12.66. Found: C, 57.83 [108]; H, 9.71; Rh, 12.39 FD MS *m/z:* 725.93 (M^+). $^{31}P\{^1H\}$ NMR (d_6-acetone): δ 11.66 (d, $^1J_{RhP}$ = 140.68 Hz). ^{103}Rh NMR (d_6-acetone): δ -191. $^{13}C\ \{^1H\}$ NMR (d_6-acetone): δ 95.69 (CH of COD), 31.02 (CH_2 of COD), 31.70 ($PCH_2(CH_2)_5CH_3$), 25.52 ($PCH_2CH_2(CH_2)_4CH_3$), 24.56 ($P(CH_2)_2CH_2(CH_2)_3CH_3$), 32.00 ($P(CH_2)_3CH_2CH_2CH_2CH_3$), 22.92 ($PCH_2(CH_2)_4CH_2CH_3$), 14.42 ($PCH_2(CH_2)_5CH_3$).

3. Catalytic experiments

3.1. Standard Hydroformylation Experiment

The catalytic hydroformylation runs were carried out in a 100 ml stainless steel autoclave under exclusion of oxygen equipped with a mechanical stirrer and a Flow Controller EL-Press (Bronkhorst hi-tec). Constant temperature was maintained by an electric heating mantle. The analyses for hydroformylation were performed on a GC 6000 Vega Series 2 (Carlo Erba Instruments) with a FID and a capillary column PS 255 [13.5 m; carrier gas He (40 kPa); integrator 3393 A (Hewlett Packard)]. Temperature program: 40°C (hold 3.30 min), 90°C (15°C/min), 115°C (5°C/min), 215°C (20°C/min, hold 12 min).

In a typical run, 25.0 μmol of the respective complex **4a-d** was dissolved in 20 ml of degassed water and 3.1 ml of 1-hexene ([Rh] : substrate = 1:1000) was added. The mixture was transferred into the evacuated autoclave, which was then pressurized to 40 bar (H_2/CO =

1/1) and heated to the desired temperature. At the end of the reaction, the vessel was cooled to room temperature and depressurized. Samples were analyzed by gas chromatography.

3.2. Standard Experiments for Hydrogenation of Carbon Dioxide

The catalytic runs of the hydrogenation of carbon dioxide were carried out in a 100 ml stainless steel autoclave under exclusion of oxygen equipped with a mechanical stirrer and a Flow Controller EL-Press (Bronkhorst hi-tec). Constant temperature was maintained by an electric heating mantle. The analysis for hydrogenation of carbon dioxide were carried out on a GC 6000 Vega Series 2 (Carlo Erba Instruments) with a WLD and a column Chromosorb [1.0 m; carrier gas He (300 kPa); integrator 3393 A (Hewlett Packard)]. The temperature was maintained constant at 180°C.

In a typical run, 0.1 mmol of the respective complex **4c-h** was dissolved in a mixture of 15 ml of methanol and 2 ml of a tertiary amine (NEt_3 or (**i**-Pr)$_2$NEt), and catalytic amounts (~ 0.1 ml) of water. The mixture was transferred to the evacuated autoclave and pressurized to 25 bar with CO_2. A total pressure of 50 bar was adjusted with H_2 and maintained constant during the catalytic run. At the end of the reaction, the vessel was depressurized and samples were analyzed by gas chromatography.

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Summary

Over the past decades, the ability of metal complexes in solution to catalyze reactions efficiently has served to make homogeneous catalysis a vigorously studied area. The efficiency of homogeneously catalyzed reactions lies in several factors including the mild conditions under which the reaction may proceed and the selectivity of the reaction. Several important successes have been achieved in translating homogeneously catalyzed reactions into viable commercial processes, and mechanistic studies of homogeneous catalysis have led to a detailed understanding of catalyst requirements and individual reaction steps.

The hydroformylation reaction is an elegant way to prepare a wide range of aldehydes starting from various alkenes. In particular, rhodium-catalyzed hydroformylation has received a great deal of attention in recent years both from academica and industry. Rhodium-phosphine catalysts operate at lower temperature and pressure than earlier cobalt-based catalysts. Furthermore, the control of reactivity and selectivity in transition metal catalyzed hydroformylation can be influenced by the steric and electronic properties of phosphine ligands. High selectivities in the hydroformylation of 1-alkenes have been obtained for catalysts modified with chelating diphosphines.

One of the major problems associated with homogeneous catalysts is the difficulty of recovering the catalysts from the products at the end of the reaction. To overcome this problem in homogeneous catalysis water-soluble complexes are applied in the biphasic hydroformylation. Herein the separation of the products from the catalyst is ensured by a simple decantation after the catalytic run. Furthermore, considering the ecologic aspects of replacing an organic solvent by water, the use of water-soluble catalysts in biphasic systems received much interest.

The attractiveness of carbon dioxide as a potential chemical feedstock and its perceived inertness have stimulated widespread interest in organometallic chemistry. In particular, the hydrogenation of carbon dioxide to formic acid in homogeneous phase has recently gained considerable attention as a promising approach to the use of abundant CO_2. This could be an attractive and alternative way to compounds which presently are derived from petroleum. Late transition metal complexes act as homogeneous catalysts for this process and efficient catalytic systems are known to operate in organic solvents, in aqueous solvent, and under supercritical conditions.

The topic of this work is the catalytic application of new water-soluble diphosphinerhodium(I) complexes and new (ether-diphosphine)rhodium(I) complexes incorporated in homogeneous and biphasic hydroformylation of 1-hexene and the application of (ether-diphosphine)rhodium(I) and their analogous alkyl diphosphinerhodium(I) complexes in which the oxygen atom of the ether-moiety is replaced by a methylene group in homogeneous hydrogenation of carbon dioxide.

The first part of this thesis deals with the synthesis of alkyl diphosphines provided with a C_4 backbone and their corresponding rhodium(I) complexes. The diphosphine ligands $\{RX\text{-}(CH_2)_n\}_2P(CH_2)_4P\{(CH_2)_n\text{-}XR\}_2$ {*n* = 2; X = O, CH_2; R = ethyl, *n*-propyl, *n*-butyl, *t*-butyl; *n* = 3; X = O; R = $CH_2CH(OH)CH_2OH$ or $CH_2C(CH_2OH)_2C_2H_5$} are accessible by photochemically induced hydrophosphination of the vinyl ethers CH_2=CH-OR, the alkenes CH_2=CH-R, or the allyl ethers CH_2=$CHCH_2$-OR, respectively, with the diprimary phosphine $H_2P(CH_2)_4PH_2$. Treatment of one equivalent of these ligands with $[Rh(COD)_2][BF_4]$ in methanol leads to the square-planar cationic diphosphinerhodium(I) complexes $[(COD)Rh[\{RX\text{-}(CH_2)_n\}_2P(CH_2)_4P\{(CH_2)_n\text{-}XR\}_2]][BF_4]$ (n = 2; X = O, CH_2; R = ethyl, propyl, *n*-butyl, *t*-butyl; *n* = 3; X = O; R = $CH_2CH(OH)CH_2OH$ or $CH_2C(CH_2OH)_2C_2H_5$). All

diphosphine ligands and their rhodium(I) complexes are characterized by means of MS, IR and NMR.

The following chapter is devoted to the homogeneous hydroformylation applying the diphosphinerhodium(I) complexes $[(COD)Rh[\{RX\text{-}(CH_2)_n\}_2P(CH_2)_4P\{(CH_2)_n\text{-}XR)_2\}]][BF_4]$ (n = 2; X = O; R = ethyl, *n*-butyl, *t*-butyl; n = 3; X = O; R = $CH_2CH(OH)CH_2OH$, $CH_2C(CH_2OH)_2C_2H_5$). These complexes proved to be active catalysts in the hydroformylation of 1-hexene in polar organic solvents. Unexpected, a high amount of the already generated aldehydes was transformed to the corresponding acetals even in the absence of an acid. This effect is predominant in alcohols, while in dichloromethane no acetals occur.

A further chapter presents the biphasic hydroformylation of 1-hexene with two new hydrophilic rhodium(I) complexes $[(COD)Rh[\{R(CH_2)_3\}_2P(CH_2)_4P\{(CH_2)_3R)_2\}]][BF_4]$ (R = $CH_2CH(OH)CH_2OH$ or $CH_2C(CH_2OH)_2C_2H_5$), which proved to be effective precursors. The substrate 1-hexene serves as a representative of higher alkenes. The water-soluble ligands of these complexes ensure the mixing of the immiscible phases. Both catalysts can be reused up to three times without loss of the catalytic activity. The employed water-soluble diphosphinerhodium(I) complexes remain superior to the well known complex $[(COD)Rh(TPPTS)_2][BF_4]$ with respect to catalytic activity and selectivity. However, the efficiency of the hydroformylation in aqueous phase could not be enhanced by addition of excess phosphine or emulsifiers. Due to limited mass-transfer lower conversions were found in the biphasic hydroformylation compared to hydroformylation in organic solvents. Unlike no cruical difference in polar organic solvents was found between both water-soluble complexes, they behave different in the biphasic system.

A further study in this thesis was dedicated to the hydrogenation of carbon dioxide by the (ether-diphosphine)rhodium(I) complexes $[(COD)Rh[\{RX\text{-}(CH_2)_2\}_2P(CH_2)_4P\{(CH_2)_2\text{-}$

$XR\}_2]][BF_4]$ (X = O; R = ethyl, *n*-butyl, *t*-butyl) and the analogous diphosphinerhodium(I) complexes $[(COD)Rh[\{RX\text{-}(CH_2)_2\}_2P(CH_2)_4P\{(CH_2)_2\text{-}XR\}_2]][BF_4]$ (X = CH_2; R = ethyl, *n*-propyl, *n*-butyl) in which the oxygen atom of the ether-moiety was replaced by a methylene group. Under a total pressure of 50 bar CO_2/H_2 (1 : 1) the cationic diphosphinerhodium(I) complexes were active catalysts in the hydrogenation of carbon dioxide to formic acid. A dependency of the catalyst amount on the yield of formic acid was found. It was shown that the yield is higher using the (ether-diphosphine)rhodium(I) complexes instead of their analogous diphosphinerhodium(I) complexes, in which the oxygen atom is substituted by a methylene group. This fact accounts for a better stabilization of unsaturated active species in the catalytic hydrogenation of carbon dioxide with the ether-moieties of the (ether-diphosphine)rhodium(I) complexes.

The last chapter is focused on the non-routine NMR spectroscopy of rhodium nuclei for structural elucidation. General problems of the measurement of nuclei with low sensitivity are presented. The methods used to determine the parameters that are necessary for recording ^{103}Rh NMR spectra are described as well as the measurement techniques. A series of squar-planar cationic diphosphinerhodium(I) complexes have been subjected to NMR investigations and their ^{103}Rh chemical shifts are discussed.

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