KINETICS, CATALYSIS, AND REACTION ENGINEERING

Efficient Catalysts for the Two-Phase Hydroformylation of Long-Chain α-Olefins

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In this paper, we report on novel Rh/phosphonate−phosphine catalysts for the aqueous two-phase hydroformylation of long-chain olefins. The amphiphilic ligands $Ph_2P-(CH_2)_{10}-PO_3Na_2$ and $Ph_2P-(CH_2)_{12}-PO_3Na_2$ have been shown to form Rh catalysts that are superior to Rh/TPPTS systems. Aldehyde selectivities higher than 95% and high activities (e.g., TOF of 660 h^{-1} at 88% yield) were achieved. Counterions such as Na^+, K^+, NH_4^+, and NH_3Pr^+ influence the catalyst retention, whereas the lowest rhodium losses into the organic phase were found with a sodium phosphonate ligand. Phase separation by simple decantation was accelerated when methanol was added to the biphasic system.

1. Introduction

The hydroformylation of higher olefins still remains a challenge for aqueous two-phase catalysis. Although the advantages of this technology are obvious,[1−8] its industrial application in the field of hydroformylation has been limited to short-chain olefins.[9,10] As yet, the low solubilities of higher olefins (>C_7) in the aqueous catalyst phase represented a serious problem in extending the technology to a broader variety of substrates. Different approaches, such as addition of cosolvents, surfactants, or coligands to Rh/TPPTS catalysts, amphiphilic ligands, supramolecular auxiliaries or ligands, ionic liquids, supercritical CO_2, or fluorous biphasic catalysis, have been proposed to overcome the activity problems caused by the low water solubilities of the substrates.[11−25] However, none of the above concepts has been applied to industrial hydroformylations of higher olefins. There is still a need for aqueous catalysts that fulfill all of the strict requirements of a technical two-phase process, such as complete catalyst retention, high activity and stability, high aldehyde selectivity, simple phase separation, and low ligand costs.

Based on our previous work on phosphonate−phosphines,[26−28] we developed new syntheses for water-soluble ligands such as phosphonated triphenylphosphines or phosphonated tertiary phosphines with mixed alkyl and aryl groups[29,30] (Figure 1). Despite their simple structures, some of these compounds were previously unknown.

Especially phosphines with long-chain alkylene groups (C_{10}, C_{12}) between hydrophilic phosphonate groups and coordinating phosphine moieties can be synthesized with reasonable effort and have been found to form active and selective rhodium catalysts for the title reaction. In this paper, we report on the catalytic properties of these novel amphiphilic catalysts for aqueous two-phase hydroformylation of higher α-olefins.

2. Experimental Section

Chemicals were purchased from Merck, Fluka, and Aldrich and used as received. Water, methanol, and ethanol were distilled in an argon stream prior to use. The olefins were deoxygenated by repeated evacuation and argon purging. Syngas (99.98%, $CO/H_2 = 1/1$) and propylene were provided by Messer-Griesheim and used without further purification. NMR spectra were recorded on Varian UNITYPLUS 300 and 500 spectrometers (300 and 500 MHz, respectively).

Ligands were prepared as described elsewhere.[29,30] The catalyst precursors for the biphasic reactions were formed in situ by adding $Rh(CO)_2(acac)$ to the 0.2 M ligand solutions, which were checked by ^{31}P NMR spectroscopy prior to use. After the yellow catalyst precursor solutions were stirred overnight, deoxygenated water was added to them up to a volume of 20 mL.

Biphasic Hydroformylations. The catalytic runs were conducted in a 100-mL autoclave made of stainless steel (Parr) provided with a self-made sampling line. The sampling line also consisted of stainless steel and was assembled using the standard Swagelok fittings. A capillary served as the sampling tube. Two ball valves, connected to each other by a $^1/_8$-in. tube, were used as the sampling outlet. The line between them provided a sampling volume of about 0.2 mL. A capillary was used to transfer the samples into septum vials. Samples were taken by charging and emptying the volume between the ball valves. This was done twice for each sampling procedure, and the second sample was used for the GC analysis. *Caution*: When liquid samples are taken from a pressurized autoclave as described above, one must strictly avoid having both ball valves open at the same time! Failure to comply with this requirement causes uncontrolled deflation of the autoclave contents, which is dangerous.

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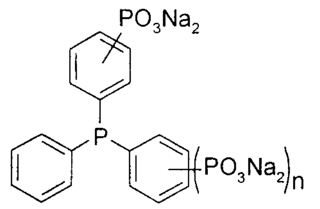
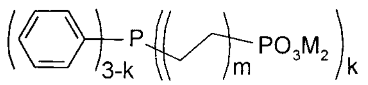


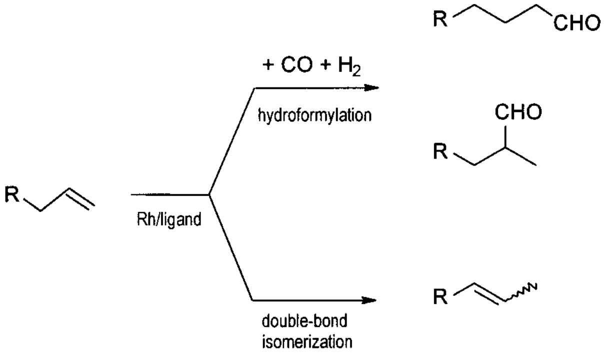
ligand	n	$-PO_3Na_2$ position
1	0	4
2	1	4
3	1	3



ligand	k	m	M^+
4	1	1	Na^+
5	1	3	Na^+
6a	1	5	Na^+
6b	1	5	K^+
6c	1	5	NH_4^+
6d	1	5	$NH_3{}^nPr^+$
7	1	6	Na^+
8	2	5	Na^+

Figure 1. Water-soluble phosphonate–phosphine ligands.

Before the catalytic runs, the reactor was flushed with argon, and 20 mL of an aqueous catalyst solution, formed from 0.0194 mmol $Rh(CO)_2(acac)$ and the water-soluble ligands (pH between 8 and 9), was added using a stainless steel buret. Syngas ($CO/H_2 = 1/1$) was used to pressurize the reactor to 20 bar. After the reaction temperature was reached, the pressure was adjusted to 30 bar, and stirring of the reaction mixture was started with a constant speed of 600 rpm. Separate experiments showed that the rates were independent of the stirring speed beyond 400 rpm. Optionally, the catalyst was pretreated before the addition of 1-octene as follows: After three purging cycles, the catalyst solution was treated with syngas at 30 bar and 120 °C for 2 h (preformation). Then, the reactor was cooled to 70 °C and depressurized to a pressure of 20 bar. The autoclave was heated again to the reaction temperature, and 5 mL of 1-octene was transferred into the autoclave. The pressure was adjusted to 30 bar, and the reactions were conducted at 120 °C. Samples were taken in several experiments. After 4 h, the reactor was cooled to room temperature and depressurized. The organic phases were decanted and analyzed by gas chromatography [HP 5890; 50 m × 0.25 mm HP5; He; 40 °C (hold for 5 min), heat at a rate of 5 K/min (over 4 min), heat at a rate of 20 K/min (over 7 min), and 200 °C (hold for 3 min); inlet pressure of 120 kPa, constant flow]. To determine rhodium and phosphorus leaching, the decanted organic phases were evaporated, and after removal of the volatile organic compounds, the residues were treated with 5 mL of concentrated HNO_3 for 24 h. This acidulation was analyzed by ICP-OES using a Perkin-Elmer Optima 3000 XL instrument.



$R = C_5H_{11}; C_9H_{19}$

Figure 2. Rh-catalyzed conversions of 1-octene and 1-dodecene with syngas.

3. Results and Discussion

3.1. Influences of the Ligand Backbone. High water solubilities of several hundred grams to about one kilogram per liter have been achieved by modifying tertiary phosphines with hydrophilic phosphonate groups.[30] In the case of triarylphosphines **1**–**3**, the water solubility was enhanced with increasing degree of phosphonation, while the bis-phosphonated phosphine **8** showed an even lower water solubility (~100 g/L) than the mono-phosphonated counterparts (**6a**, ~320 g/L; **7**, ~240 g/L).

The Rh-catalyzed biphasic hydroformylation of 1-octene and 1-dodecene produced linear and branched nonanals and tridecanals, respectively (see Figure 2). Hydrogenation of the alkenes has not been observed, but internal olefins and traces of nonanoic and tridecanoic acids, respectively, were found as byproducts. Table 1 shows that the ligand structure strongly influenced the activity, selectivity, and catalyst retention in the hydroformylation of 1-octene. The best results were achieved with the phosphonated alkyldiarylphosphines **6** and **7**. An initial rate of about 200 [(mol of aldehyde)/(mol of Rh)]/h was estimated for a Rh/**6a** catalyst at 100 °C and 30 bar (see Table 3), while the corresponding Rh/**7** system showed an initial activity of more than 500 [(mol of aldehyde)/(mol of Rh)]/h under identical conditions. As is visible in Table 1, pretreatment of both catalysts with syngas improved their performance significantly. Particularly, the undesired C–C double-bond isomerization to internal olefins was suppressed by this procedure. The water-soluble rhodium catalysts obviously need an induction period for their formation, and also rhodium precursor complexes that catalyze the olefin isomerization seem to be transformed into selective hydroformylation catalysts during the syngas pretreatment.

At 80 °C, the internal octene selectivity increased at the cost of aldehyde formation when the **6a**:Rh ratios

Table 1. Influence of the Ligand Structure on Catalytic Properties of Aqueous Rh Catalysts in the Biphasic Hydroformylation of Higher Olefins[a]

ligand	ligand/Rh ratio	substrate	conversion [%]	aldehyde yield [%]	selectivity [%] aldehydes	selectivity [%] internal olefins	selectivity [%] *n*/iso ratio	Rh leaching [ppm]	P^{III}/Rh organic phase
TPPTS[b]	10	1-octene	90	15	17	83	71:29	0	–
2	10	1-octene	32	14	43	57	73:27	1.7	6
4	5	1-octene	79	35	44	56	52:48	36.4	4
4[c]	5	1-octene	89	25	28	72	42:58	4.2	4
5	5	1-octene	31	13	43	57	73:27	0	–
6a	5	1-octene	38	32	84	16	72:28	1.7	4
6a[c]	5	1-octene	52	47	91	9	87:13	0.8	11
6a	10	1-dodecene	46	16	33	67	>99:1	0	–
6a[c]	10	1-dodecene	25	24	97	3	87:13	0	–
7	10	1-octene	59	39	66	34	87:13	0.3	23
7[c]	10	1-octene	56	53	94	6	84:16	0.3	7
7[c]	10	1-dodecene	47	45	95	5	86:14	n.d.[d]	n.d.[d]
8	5	1-octene	95	55	58	42	71:29	0	–
8[c]	5	1-octene	89	36	40	60	69:31	0	–

[a] Reaction conditions: 0.0194 mmol of Rh, $n^0_{1-\text{octene}}/n_{\text{Rh}} = 1640$, $n^0_{1-\text{dodecene}}/n_{\text{Rh}} = 1160$, 120 °C, 30 bar, reaction time of 4h, 600 rpm. [b] 100 °C. [c] Pretreatment at 120 °C with syngas (30 bar) over 2h [d] n.d. = not determined.

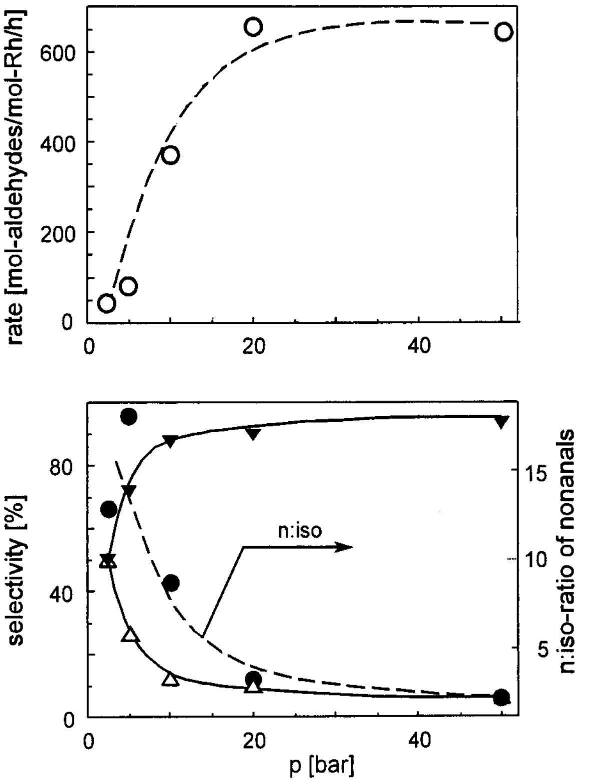


Figure 3. Influences of the syngas total pressure on the aldehyde formation rate (open circles) and on the selectivities (aldehydes, filled triangles; internal olefins, open triangles; regioselectivity, filled circles) in the hydroformylation of 1-octene. Reaction conditions: 100 ppm Rh, **6a**/Rh = 10/1, 120 °C, 600 rpm, 4h, CO/H_2=1/1, rates determined at conversions below 30%.

exceeded a value of about 5.[30] This effect was not observed at 120 °C. Strong influences on the chemoselectivity were exerted by the handling of the catalysts. Exposure of catalyst solutions containing **6** or **7** to air resulted in high isomerization rates and, consequently, low aldehyde selectivities below 50%.

Also, in the hydroformylation of 1-dodecene, both ligands **6a** and **7** showed remarkable activities and selectivities. Rh catalysts made of ligand **8** showed excellent catalyst retention but only moderate aldehyde selectivities between 40 and 60%. In contrast to ligands **6a** and **7**, the high isomerization activity of Rh/**8** catalysts could not be suppressed by the syngas pretreatment. The higher phosphine basicity of **8**, as compared to those of **6** and **7**, is assumed to cause the observed low aldehyde selectivity. As with homogeneous single-phase Rh catalysts, increasing the phosphine basicity should hinder the coordination of the CO and, consequently, the aldehyde formation. Instead of CO insertion, the terminal olefin can then be isomerized partly to the thermodynamically more stable internal olefins, leading to higher isomerization selectivities.

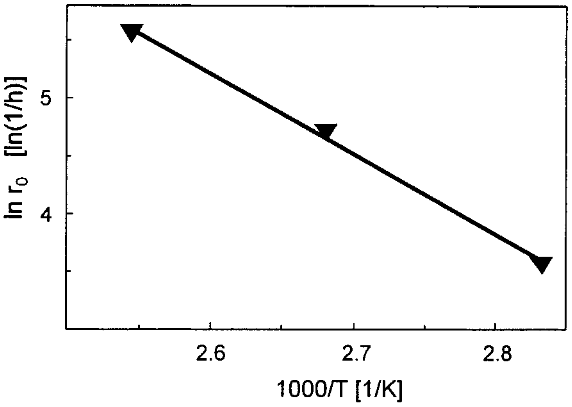


Figure 4. Arrhenius plot for aldehyde formation with an amphiphilic catalyst (Rh/**6a**) catalyst. r_0 = initial rate ([(mol of aldehyde)/(mol of Rh)]/h). Reaction conditions as in Table 2.

3.2. Pressure and Temperature Effects. Further studies were focused on rhodium catalysts based on **6** because of the special catalytic properties of the phosphonated monoalkyldiphenyl phosphines. As is visible in Figure 3, the aldehyde formation was strongly influenced by the syngas pressure. Below 20 bar, the initial rates increased with growing total pressure and then remained nearly constant at higher pressures. It is assumed that the excess of the strongly coordinating ligand (**6a**:Rh = 10) might cause a partial blocking of coordination sites for CO insertion and subsequent aldehyde formation. Thus, higher syngas pressures should enhance the essential coordination of both gaseous reactants, CO and H_2. This is confirmed by the high aldehyde selectivity at pressures higher than 20 bar, by the strong internal octene formation at lower pressures, and by the growing hydroformylation activity with increasing syngas pressure. The constant hydroformylation activity above a certain syngas pressure level can be interpreted by the diametrical effects of the

Table 2. Influences of the Counterions on the Properties of $Ph_2P-(CH_2)_{10}-PO_3M_2$/Rh Catalysts[a]

	T [°C]	Na^+	K^+	NH_4^+	$^+NH_3Pr$
aldehyde yield [%][b]	80	9	7	18	17
	100	25	30	35	
	120	65	76	77	
aldehyde selectivity [%][b]	80	96	97	99	98
	100	96	97	97	
	120	92	91	94	
n/iso aldehyde ratio[b]	80	81:19	81:19	77:23	79:21
	100	85:15	82:18	82:18	
	120	83:17	80:20	79:21	
Rh leaching [ppm][c]	80	0.8	5.6	5.6	27.9
	100	n.d.	5.6	5.3	
	120	0.8	19.6	0.6	

[a] Reaction conditions: 0.039 mmol Rh, $n^0_{1-\text{octene}}/n_{\text{Rh}} = 820$, **6**/Rh = 5/1, 30 bar, 600 rpm, preformation at reaction temperature over 2 h, 30 bar syngas. [b] Yields and selectivities after 2h. [c] Determined after cooling and depressurizing.

Table 3. Influences of Added Methanol on the Hydroformylation of 1-Octene in Aqueous Two-Phase Systems[a]

$V_{\text{methanol}}/V_{\text{cat. solution}}$ [vol %]	TON[b]	aldehyde yield [%][c]	aldehyde selectivity [%][c]	*n*/iso aldehyde ratio[c]
0	210	44	97	5.6
10	160	30	96	4.5
25	170	30	95	3.3
38	370	61	97	3.2
50	800	96	98	2.6

[a] Reaction conditions: 100 ppm Rh, **6a**/Rh = 10/1, 100 °C, 30 bar, $V_{\text{cat. solution}} = 20$ mL. [b] After 1h. [c] After 4h.

CO and H_2 partial pressures, as known for both, homogeneous and aqueous biphasic rhodium catalysts.[13,31]

Figure 4 shows the temperature dependence of the initial aldehyde formation rates in two-phase systems. In good agreement with literature data,[31] an apparent activation energy of 60 kJ/mol has been determined for the hydroformylation of 1-octene with an aqueous Rh/**6a** catalyst. Rhodium catalysts made of **6a** and **7** produced aldehydes selectively in the temperature range between 80 and 120 °C. Although aldehyde selectivities higher than 95% could also be obtained at 120 °C, the highest aldehyde selectivities and the lowest internal olefin selectivities were generally observed at the lower temperatures. Low aldehyde selectivities of 70% and higher internal olefin selectivities were obtained at the higher temperature of 140 °C. After reaction at 150 °C, the initially yellow aqueous catalyst solution (Rh/**6a**) became colorless, and a gray precipitate of Rh was found in the organic phase. Furthermore, this phase contained 10 times more dissolved Rh (80 ppm) than the aqueous phase, indicating strong Rh losses. Obviously, a critical temperature should not be exceeded with the amphiphilic catalysts based on phosphorylated alkyldiarylphosphines.

3.3. Effects of Counterions. Consisting of hydrophilic phosphonate groups and of long-chain lipophilic groups, ligands **6** and **7** have surfactant character and should form micelles. Critical micelle concentrations (cmc's) of about 7 mmol/L, as are typical for anionic surfactants, were determined in water for the ligands **6a** and **6b**. To determine whether the cations of amphiphilic ligands exert influences on the catalytic properties, sodium, potassium, and ammonium salts of ligand **6** were employed in the two-phase hydroformylation of 1-octene (Table 2).

Because of the long alkylene chain between the functional groups in ligands **6**−**8**, the variation of the cations in the phosphonate groups should not affect the electronic properties of the phosphine groups. Accordingly, only small differences in the chemo- and regioselectivities were found for the different counterions. Rhodium catalysts made of the potassium salt **6b** and the ammonium salt **6c** showed slightly higher activities than those made of the sodium salt **6a**. Even higher activities were found for the *n*-propylammonium salt **6d**. The observed increases in the activity correlated with the rhodium losses into the organic phase. Unacceptably high leachig levels above 1 ppm were found for the salts **6b**, **6c**, and **6d** but not for the sodium salt **6a**. The leached-out rhodium was accompanied by phosphorus (see also Table 1). Therefore, it is concluded that rhodium species leach out as phosphine complexes. Because the ligands and complexes cannot transfer into the organic phase without their counterions, the catalyst losses from the aqueous phase should be influenced by the radius of hydration of the cation and, thus, by the degree of ion separation. The best catalyst retention in the aqueous phase was achieved with the sodium salt, while the counterions with the smaller radii of hydration, K^+, NH_4^+, and NH_3Pr^+, afforded only weaker catalyst retentions. Leached-out catalysts in the organic phase, where mass transfer does not restrict the rates,[32] can explain the activity enhancements with ligands **6b**−**6d**.

Generally, the rhodium losses were determined after the reactions were stopped and the autoclave was cooled. In several runs (beyond 70 °C with **6d** and beyond 100 °C with **6c**), the leaching seemed also to be influenced by the amount of aldehyde formed. In these experiments, the organic phases of samples taken after 1 or 2 h were colorless, but yellow organic phases of the subsequent samples indicated significant rhodium leaching. The nonanals formed also can act as surface-active additives and could enhance the extraction of the water-soluble catalysts into the organic product phase.

3.4. Cosolvents. Addition of alcohols such as methanol or ethanol to aqueous biphasic systems is a common operation for improving their activities.[11,13,20−22] Rather high methanol contents of over 25% were necessary to accelerate the hydroformylation with Rh/**6a** catalysts significantly (Table 3). Acetals of 2-methyloctanal and nonanal were not found even for the high methanol contents. The added methanol can boost the undesired catalyst leaching, and 17 ppm rhodium were found in the organic phase when the catalyst solution contained 50 vol % methanol. No leaching was detected below 25 vol % methanol. However, in these experiments, the activities were even lower than in the activities found in the absence of the alcohol. This inhibition could be explained by the disruption of catalyst aggregates[33] such as micelles or vesicles that may have higher activity than the corresponding nonaggregated catalysts. Further studies are necessary to clarify this phenomenon. Methanol addition hardly affected the aldehyde selectivity but, as is evident in the *n*- to iso-aldehyde ratios, also brought about decreases in the regioselectivity.

Usually, the surface activity of ligands **6** and **7** lead to the formation of foam over stirred solutions. Also, when the hot or cold autoclave contents were transferred into a separation funnel, emulsions containing droplets that were 1−2 mm in size were obtained. These emulsions broke up spontaneously into two phases within 30 min. The lower phases contained the catalyst and still consisted of yellow emulsions of a smaller droplet size that cleared up within several hours. The organic phases were found to be clear and colorless from the beginning of the phase separation. When more than 5 vol % methanol was added to the catalyst solutions, the breakup of the emulsions occurred within several minutes, and the thickness of the emulsion layer in the separation funnel was much smaller immediately after the autoclave was emptied. Thus, the positive effect of the added methanol lies in the efficient breakup of the formed emulsions, which greatly accelerates the separation of the two liquid phases.

3.5. Comparison with Other Water-Soluble Catalysts. In our experiments, Rh/TPPTS catalysts showed low activities and unsatisfactory chemoselectivities. The activity of Rh/TPPTS can be greatly enhanced by using reverse micelles. With this concept, turnover frequencies (TOF) of 1500/h have been reached, but the selectivity problem still remains ($S_{\text{aldehydes}} = 47\%$).[14] Recently, Li et al. reported on efficient Rh/TPPTS catalysts modified with cationic surfactants.[15] Turnover numbers (TON) of about 1100 after 2h were achieved in the hydroformylation of 1-dodecene using these micellar systems. However no data on the chemoselectivities were reported by the authors. Our ligands **6a** and **7** formed tridecanals with high selectivities and TONs of 280 and 520, respectively, after 4 h (Table 1). High activities and aldehyde selectivities were already achieved with the amphiphilic sulfonated triphenylphosphine, $P(4\text{-}C_6H_4{-}(CH_2)_{10}{-}C_6H_4{-}4\text{-}SO_3Na)_3$, developed by Hanson et al.,[21,22] and an average TOF of 435 h^{-1} at 89% yield was reported for the hydroformylation of 1-octene at 120 °C and 15 bar. Our Rh/**7** catalysts formed nonanals selectively ($S_{\text{aldehydes}} > 90\%$) with an average TOF of 660 h^{-1} at a yield of 88% (120 °C, 30 bar) and, hence, can compare with this catalyst. In addition to the high activity and selectivity of the Rh/phosphonate−phosphine catalysts, ligands such as **6** or **7** are much less expensive in terms of materials and labor than the amphiphilic sulfonated triphenylphosphine. Whereas the preparation of $P(4\text{-}C_6H_4{-}(CH_2)_{10}{-}4\text{-}C_6H_4{-}SO_3Na)_3$ requires a multistep synthesis with an overall yield of less than 6%, the phosphonated ligands **6** and **7** are accessible by shorter and simpler syntheses in overall yields of about 55%, which is considered a major advantage.

4. Conclusions

Phosphonated alkyldiphenyl phosphines can form excellent rhodium catalysts for the two-phase hydroformylation of long-chain olefins. Especially catalysts made of **6a** and **7** compare favorably to the cheaper Rh/TPPTS systems and show the high activities and selectivities of the more expensive amphiphilic sulfonated catalysts. Although there are some indications with regard to the way in which our amphiphilic phosphonated catalysts work, the role of the ligands is not fully understood. The ligands can form micellar structures in water, but it is still unclear whether this is important for the catalytic process at the typical reaction temperature of 120 °C. More detailed investigations should shed some light on the question of whether the rhodium complexes work in the aqueous/organic interfacial layer[34] or in the aqueous bulk phase,[35] and resolution of this issue appears to be a precondition for further improvements of the catalysts presented in this paper.

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