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Water-soluble rhodium/phosphonate–phosphine catalysts for hydroformylation

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Abstract

We have developed new and efficient routes to modify phosphines with phosphonic acid groups. Phosphonate–phosphines showed high solubilities in water and were used to immobilise rhodium catalysts in the aqueous phase of biphasic systems. In the two-phase hydroformylation of propylene, some of the novel catalysts showed activities and regioselectivities similar to those of Rh/TPPTS. Amphiphilic Rh/phosphonate–phosphine catalysts were found widely superior to Rh/TPPTS in the hydroformylation of 1-octene. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium; Hydroformylation; Water-soluble catalyst; Aqueous catalyst; Biphasic; Phosphonate–phosphine

1. Introduction

Water-soluble tertiary phosphines are of continuing interest for many transition metal-catalysed reactions [1–12] and some of them have already been employed in industrial two-phase catalysis [13,14]. The main advantage of this technology is that the aqueous catalysts can be easily separated and recycled. Phosphines modified with phosphonic acid groups have been studied less intensively than other water-soluble ligands, probably because these compounds were difficult to access. Phosphonic acid–phosphines were isolated for the first time by Roundhill and coworkers [15] and mono-phosphorylated triarylphosphines were not reported until 1995 [16,17]. Phosphines modified with one or two phosphonate groups can be synthesised using Pd-catalysed C–P-coupling reactions with *p*-bromoiodobenzene and subsequent nucleophilic phosphinylation, as recently published by Stelzer and coworkers [18]. Using the cheaper fluoro-arenes as starting materials, we discovered novel and more effective methods to prepare mono-phosphorylated and bis-phosphorylated triarylphosphines [19]. Rh/dialkylphosphonate–phosphine catalysts have already been shown to be effective in homogeneous and heterogeneous carbonylations [20–24]. Therefore, the alkali salts of phosphonic acid–phosphines appeared promising for the immobilisation of rhodium catalysts in aqueous biphasic systems. In this paper, we will report on catalytic properties of water-soluble Rh/phosphonate–phosphine catalysts in the two-phase hydroformylations of propylene and 1-octene.

2. Experimental

All reactions were carried out using Schlenk techniques with argon as inert gas. Chemicals were purchased from Merck, Fluka and Aldrich and used as received. Water and the other solvents and styrene were distilled in an argon stream prior to their use. 1-Octene was deoxygenated by repeated evacuation

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and argon purging. The syngas (99.98%, $CO/H_2 = 1/1$) and the propylene were provided by Messer–Griesheim and used without further purification.

NMR spectra were recorded on a Varian UNITY-PLUS 300 and 500 (300 and 500 MHz). Quantitative Rh and P analyses were done with ICP-OES using an Optima 3000XL (Perkin Elmer).

2.1. Ligands and catalysts

Two grams of $Ph_2P–(CH_2)_2–P(O)(OEt)_2$ [15,23] were directly hydrolysed to $Ph_2P–(CH_2)_2–PO_3H_2$ (**1**) by adding the ester in small portions within 10 min to 50 ml of boiling concentrated and deoxygenated HCl_{aq}. After further refluxing in an argon stream over 5 h, the hydrochloric acid was evaporated in vacuum. The residue was washed with deoxygenated water and evaporated again to remove volatile components. The phosphonic acid–phosphine (**1**) was isolated as colourless viscous oil (more than 90% yield) but attempts to crystallise the compound failed. The bis-diethyl ester $Ph_2P–CH_2–CH(P(O)(OEt)_2)_2$ was prepared by stepwise addition of stoichiometric amounts of diphenylphosphine to $CH_2{=}C(P(O)(OEt)_2)_2$, whereas the temperature of the mixture increased from 25 to 80°C. The ester was formed quantitatively after 10 min and its hydrolysis with hydrochloric acid as described above afforded the bis-phosphorylated phosphine (**2**) (92% yield). ω-Bromoalkylphosphonates were prepared according to a known procedure [25]. The method described by Roundhill and coworkers [15] was applied to synthesise the diethyl esters of the ligands $Ph_2P–(CH_2)_6–PO_3H_2$ (**3**), $Ph_2P–(CH_2)_{10}–PO_3H_2$ (**4**), $Ph_2P–(CH_2)_{12}–PO_3H_2$ (**5**), and $PhP(–(CH_2)_{10}–PO_3H_2)_2$ (**6**). Direct ester hydrolysis with aqueous HCl afforded these phosphonic acid phosphines in yields over 90%. The phosphorylated triphenylphosphines $Ph_2P(4\text{-}C_6H_4–PO_3H_2)$ (**7**), $Ph_2P(4\text{-}C_6H_4–CH_2–PO_3H_2)$ (**8**), $PhP(3\text{-}C_6H_4–PO_3H_2)_2$ (**9**), and $PhP(4\text{-}C_6H_4–PO_3H_2)_2$ (**10**) were prepared by the reaction of fluorophenylphosphonamides with lithiumphosphides and subsequent amide hydrolysis as already reported elsewhere [19].

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 before use. After stirring overnight, the yellow catalyst precursor solutions were filled up with deoxygenised water to volumes of 10 or 20 ml depending on the reaction.

2.2. Hydroformylation of propylene

Biphasic hydroformylations of propylene were usually conducted at 120°C and 30 bar in a 100 ml autoclave made of stainless steel (Parr). The autoclave was carefully purged with syngas before 10 ml of the aqueous catalyst containing 400 ppm Rh and 5 ml of nonane (unpolar phase), were introduced into the reactor. Nonane served also as internal standard for the determination of the products. Propylene was added until the organic phase was saturated with the olefin. Syngas $CO{:}H_2 = 1{:}1$ was used to further pressurise the reactor to 20 bar. After reaching the reaction temperature, the pressure was adjusted to 30 bar and stirring of the reaction mixture was started with a constant speed of 600 rpm. In separate experiments, the activities were found independent on the agitation speed beyond 400 rpm. The pressure was kept constant over the reaction time of 2 h by feeding syngas via a pressure controller. After the reaction, the autoclave was cooled down to room temperature and depressurised. The organic phases were analysed by gas chromatography (HP 5890, 25 m × 0.53 mm Poraplot Q, 60°C (start), 2 K/min (over 10 min), 4 K/min (over 27 min), inlet pressure 47 kPa) to determine the organic products and by ICP-OES to determine the leached-out rhodium and phosphorus.

2.3. Hydroformylation of 1-octene

The hydroformylation of 1-octene was carried out in the autoclave mentioned above. 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), were added using a steel burette. The autoclave was pressurised with 10 bar syngas and heated up to reaction temperature. In several experiments, the catalysts were pre-formed before 1-octene was added. The pre-formation of the catalysts was carried out by treatment of their aqueous solutions with syngas at 30 bar and 120°C for 2 h. Then the reactor was cooled down to 70°C and depressurised to a pressure of 20 bar. The autoclave was heated up again to reaction temperature and 5 ml 1-octene were transferred into the autoclave.

The pressure was adjusted to 30 bar and the reaction was started by stirring (600 rpm). Samples of 0.5 ml size were taken in several experiments. After 4 h, the reactor was cooled down to room temperature and depressurised. The organic phases were analysed by gas chromatography (HP 5890, 50 m × 0.25 mm HP5, He, 40°C (hold 5 min), 5 K/min (over 4 min), 20 K/min (over 7 min) and 200°C (hold 3 min), inlet pressure 120 kPa, constant flow). Rhodium and phosphorus leaching were determined by ICP-OES.

3. Results and discussion

3.1. Ligands

Table 1 shows the ligands used in our studies. To our best knowledge (**2**–**6**) and their salts have not been reported before by other authors. Mono-phosphorylated and bis-phosphorylated ligands as **7** and **10** have already been described in the literature [16–18] but we developed new methods to simplify the access to these interesting compounds. Ligands **8** and **9** have not been reported before and were also prepared by our novel syntheses. The sodium salts of the phosphonic acid–phosphines showed generally good solubilities in water. Excellent solubilities were achieved with the bis-phosphorylated triphenylphosphines, **9**-Na_4 and **10**-Na_4. In contrast, increasing the degree of phosphorylation did not enhance the water solubility of phosphorylated phosphines with alkylene phosphonate groups, as visible from the data for **2**-Na_4 and **6**-Na_4.

3.2. Hydroformylation of propylene

As expected, the ligand structure strongly influenced the performance of different water-soluble Rh catalysts in the hydroformylation of propylene (Table 2). The turnover numbers (TONs), obtained after 2 h reaction time, varied over a broad range. But none of the phosphorylated triphenylphosphine–Rh catalysts (ligands **7**–**10**) had the activity of the industrially applied TPPTS. Only ligand **4**-Na_2, which was designed as a tensidic phosphine for the hydroformylation of long-chained olefins, reached the activity of TPPTS and even higher regioselectivities. However, aldol condensation in the weakly basic catalyst solutions yielded 2-ethylhexenal and its hydrogenation product, 2-ethylhexanal. Additionally, *n*-butanol and isobutanol were found as hydrogenation products of the butyraldehydes and cumulated by-product selectivities of up to 25% were observed for aqueous Rh/**4**-Na_2 catalysts.

The activity of rhodium catalysts containing short-chained alkylenephosphonate–phosphine ligands **1**-Na_2 and **2**-Na_4 was strongly influenced by the ligand:Rh ratios. For instance, Rh/**1**-Na_2 showed only activities in the hydroformylation of propylene at ligand:rhodium ratios below 2.5 (Fig. 1). Higher ligand excesses caused significant deactivation. This was also observed in the hydroformylation of octene at 80°C. The low regioselectivities of Rh/**1**-Na_2 and Rh/**2**-Na_4 are remarkable and actually typical of supported Rh metal particles (e.g. Rh/activated carbon [26]). Although the optical consistence of the spent

Table 1
Water solubilities at 25°C and ^{31}P-NMR data of the ligands

Sodium phosphonate–phosphine		Solubility in water (g/l)	^{31}P-NMR, δ (ppm)	
			Phosphine	Phosphonate
$Ph_2P{-}(CH_2)_2{-}PO_3Na_2$	**1**-Na_2	340–370	−12.6	+21.0
$Ph_2P{-}CH_2{-}CH({-}PO_3Na_2)_2$	**2**-Na_4	260–290	−17.6	+19.3
$Ph_2P{-}(CH_2)_6{-}PO_3Na_2$	**3**-Na_2	400–420	−17.2	+23.5
$Ph_2P{-}(CH_2)_{10}{-}PO_3Na_2$	**4**-Na_2	310–330	−17.1	+23.4
$Ph_2P{-}(CH_2)_{12}{-}PO_3Na_2$	**5**-Na_2	230–250	−16.6	+23.7
$PhP({-}(CH_2)_{10}{-}PO_3Na_2)_2$	**6**-Na_4	95–100	−25.4	+25.6
$Ph_2P(4{-}C_6H_4{-}PO_3Na_2)$	**7**-Na_2	380–410	−6.7	+10.6
$Ph_2P(4{-}C_6H_4{-}CH_2{-}PO_3Na_2)$	**8**-Na_2	Not determined	−7.5	+17.4
$PhP(3{-}C_6H_4{-}PO_3Na_2)_2$	**9**-Na_4	>1000[a]	−5.8	+11.2
$PhP(4{-}C_6H_4{-}PO_3Na_2)_2$	**10**-Na_4	>1000[a]	−6.8	+10.1

[a] Solution becomes viscous beyond 500 g/l.

Table 2
Influence of the ligand structure on catalytic properties of aqueous Rh catalysts in the hydroformylation of propylene[a]

Ligand	Ligand:Rh ratio	TON ($n_{\text{aldehydes}}/n_{\text{Rh}}$)	*n*:*iso* ratio of butyraldehydes	Rh leaching (ppm)	P^{III}/Rh organic phase
TPPTS	5	630	82:18	0.7	6
1-Na$_2$	2.2	420	53:47	4.4	3
2-Na$_4$	5	140	50:50	4.3	1
4-Na$_2$	5	640	89:11	0.7	37
7-Na$_2$	10	340	91:9	2.4	60
8-Na$_2$	5	180	82:18	2.7	13
9-Na$_4$	5	260	79:21	0.8	3
10-Na$_4$	5	440	72:28	1	8

[a] Reaction conditions: 400 ppm Rh, 120°C, 30 bar, 2 h, 600 rpm.

catalyst solutions indicated Rh-colloid formation which would explain the low regioselectivity, Rh metal particles were not detected by transmission electron microscopy.

3.3. Hydroformylation of 1-octene

All of the rhodium/phosphonate–phosphine catalysts showed activity in the biphasic hydroformylation of 1-octene to nonanal and 2-methyloctanal. Internal octenes, formed by Rh-catalysed C–C-double-bond isomerisation, were found as undesired by-products. Table 3 compares the performance of several aqueous Rh catalysts in the hydroformylation of 1-octene.

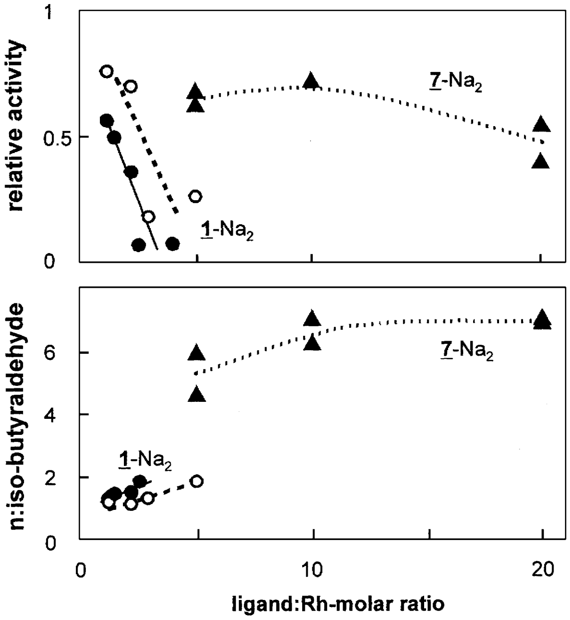

Fig. 1. Influence of the ligand:rhodium molar ratio on the activity related to Rh/TPPTS and on the regioselectivity of Rh/**1**-Na$_2$ at 80°C (filled circles), at 120°C (open circles) and of Rh/**7**-Na$_2$ at 80°C (filled triangles); other reaction conditions as in Table 2.

High activities were obtained with the short-chained alkylenephosphonate–phosphine **1**-Na$_2$ but the aldehyde selectivities and the yields were low. Additionally, significant amounts of Rh were found in the organic phases. As in the hydroformylation of propylene, a very low regioselectivity (*n*:*iso* ratio below 1) was obtained with ethylene-bridged ligand **1**-Na$_2$(Table 2, Fig. 1). Compared to this ligand, the phosphonate–phosphine **3**-Na$_2$, bridged by six methylene groups, showed a higher chemoselectivity and regioselectivity. The best results were achieved with the phosphonate–phosphines **4**-Na$_2$ and **5**-Na$_2$ having 10 or 12 carbon atoms, respectively, in the alkylene chains. Pre-treatment of the catalyst precursor solutions [27] with syngas at 120°C for 2 h improved the activities and chemoselectivities. Usually, aldehyde selectivities above 90% were obtained with the Rh/**4**-Na$_2$and Rh/**5**-Na$_2$ catalysts.

Aqueous Rh/**5**-Na$_2$ systems catalysed the hydroformylation with initial rates of about 1200 mol-nonanals/mol-rhodium/h. Such high initial rates were also reported by Van Vyve and Renken [28], but the modified Rh/TPPTS catalysts studied in that work afforded only the low aldehyde selectivity of 47% while our Rh/**5**-Na$_2$ catalysts produced aldehydes with much higher selectivities. At a yield of 88%, an average turn over frequency of 660 h^{-1} was determined for Rh/**5**-Na$_2$. This can compare with the activity of the sulphonated tensidic triphenylphosphine

Table 3
Influence of the ligand structure on catalytic properties of aqueous Rh catalysts in the biphasic hydroformylation of 1-octene[a]

Ligand	Ligand/Rh ratio	1-Octene conversion (%)	Aldehyde yield (%)	Selectivity (%)			Rh leaching (ppm)	P^{III}/Rh organic phase
				Aldehydes	Internal octenes	*n*:*iso* ratio		
1-Na_2[b]	5	89	25	28	72	42:58	4.2	4
3-Na_2	5	31	13	43	57	73:27	0	–
4-Na_2[b]	5	52	47	91	9	87:13	0.8	11
5-Na_2[b]	10	56	53	94	6	84:16	0.3	7
6-Na_4[b]	5	89	36	40	60	69:31	0	–
10-Na_4	10	32	14	43	57	73:27	1.7	6
TPPTS[c]	10	90	15	17	83	71:29	0	–

[a] Reaction conditions: 0.0194 mmol Rh, 120°C, 30 bar, reaction time 4 h, 600 rpm.

[b] Pre-treatment at 120°C, 30 bar syngas over 2 h.

[c] At 100°C.

$P(4\text{-}C_6H_4\text{–}(CH_2)_{10}\text{–}C_6H_4\text{–}4\text{-}SO_3Na)_3$, for which a turnover frequency of 435 h^{-1} at 89% yield was reported [29]. Hence, Rh/**5**-Na_2 catalysts belong to the most active and selective ones in aqueous biphasic hydroformylation of higher olefines. Moreover, phosphorylated phosphines like **4**-Na_2 and **5**-Na_2 are much less expensive on materials and labour than the above-mentioned amphiphilic sulphonated triphenylphosphine. This is considered a major advantage of our systems. Other cheap and effective water-soluble hydroformylation catalysts have recently been published by Li and coworkers [30] who added cationic surfactants to Rh/TPPTS systems. However, no data on the chemoselectivities of these active hydroformylation catalysts were reported.

The amphiphilic bis-phosphonate phosphine, **6**-Na_4, formed Rh catalysts with lower aldehyde selectivities and with rather high isomerisation activity. This is explained by the higher basicity of this ligand compared **4**-Na_2 and **5**-Na_2. Under hydroformylation conditions, CO and the phosphines compete for the co-ordination sites of the Rh catalyst. Strongly co-ordinating basic phosphines, such as **6**-Na_4 could hinder the necessary CO-insertion into Rh-alkyl species and the double-bond isomerisation, which does not require this step, would be the remaining reaction path. Undesired C–C-double-bond isomerisation was also predominant with the bis-phosphorylated triphenylphosphine catalyst, Rh/**10**-Na_4. Rh/TPPTS showed a similar behaviour in our experiments and the obtained regioselectivities are typical of Rh/triphenylphosphine systems.

Further improvements in activities and selectivities of our amphiphilic catalysts were observed when methanol or ethanol were added to the aqueous catalyst phases. Upon addition of these co-solvents, nonanals were formed with selectivities of up to 98% (Table 4).

3.4. Leaching

Like TPPTS, the bis-phosphorylated triarylphosphine ligands, **9**-Na_2 and **10**-Na_2, held back the rhodium in the aqueous phase and only small amounts of the metal transferred into the organic phase. Also mono-phosphorylated tensidic ligands **4**-Na_2 and **5**-Na_2 immobilised the Rh in the aqueous phase very effectively (Tables 2 and 3). In contrast, higher Rh leaching values into the organic phase were observed for the mono-phosphorylated triphenylphosphines **7**-Na_2 and **8**-Na_2 and also for the sodium phosphonate phosphines **1**-Na_2 and **2**-Na_4 with the short alkylene chains. Not only rhodium but also small amounts of the water-soluble ligands leached out to the organic phase, as concluded from the P^{III}/Rh ratios in the organic phases after the reaction. Lower leaching values were found for the more hydrophilic bis-phosphorylated triphenylphosphines than for their mono-phosphorylated counterparts. Therefore, the rhodium leaching of our catalysts is assumed to be caused by partial dissolution of phosphonate–phosphines and their rhodium complexes in the unpolar organic phase. No Rh leaching into the organic phase was observed when

Table 4
Influences of co-solvents on the hydroformylation of 1-octene in aqueous two-phase systems; ligand: $\underline{\mathbf{4}}$-Na$_2$ (Ph$_2$P–(CH$_2$)$_{10}$–PO$_3$Na$_2$)[a]

Co-solvent	$V_{\text{co-solvent}}$/$V_{\text{cat.-solution}}$ (%)	TON[b]	Aldehyde yield (%)[c]	Aldehyde selectivity (%)[c]	*n*:*iso* aldehyde ratio[c]
None	0	210	44	97	5.6
MeOH	10	160	30	96	4.5
	25	170	30	95	3.3
	38	370	61	97	3.2
	50	800	96	98	2.6
EtOH	10	170	29	96	5.1
	25	390	43	94	2.9
	38	830	83	93	2.9
	50	1050	84	97	2.6

[a] Reaction conditions: 100 ppm Rh, ligand:Rh = 10 : 1; $v_{\text{cat}} = 20$ ml; $v^0_{\text{1-octene}} = 5$ ml; CO/H$_2$ = 1/1; 100°C; 30 bar.
[b] TON after 1 h.
[c] TON after 4 h.

the co-solvents, methanol and ethanol, were used in volume fractions below 25%. Further addition of the alcohols caused Rh-losses into the organic phase of up to 17 ppm and also the ligand $\underline{\mathbf{4}}$-Na$_2$ was partly transferred into the unpolar phase ($\underline{\mathbf{4}}$-Na$_2$:Rh ratios between 6 and 15). Hence, the activity enhancements at the high alcohol contents (Table 4) cannot be ascribed exclusively to the catalyst in the aqueous phase.

4. Conclusions

Phosphorylated phosphines are accessible in uncomplicated syntheses and can be used for the immobilisation of transition metal catalysts in aqueous biphasic systems. Amphiphilic alkylenephosphonate phosphines can form highly active and selective rhodium catalysts for the biphasic hydroformylation of 1-octene. The phosphorylated ligands have also a potential for other olefinic substrates with low water solubility and for other biphasic reactions, such as selective hydrogenation of unsaturated aldehydes.

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