New rhodium systems for biphasic hydrogenation and hydroformylation of 1-hexene

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Abstract

The catalytic activity of rhodium complexes formed in reactions of catalyst precursor, $[Rh(acac)(CO)_2]$ with water soluble phosphines: $Ph_2PCH_2CH_2CONHC(CH_3)_2CH_2SO_3Li$ **(PNS)**, $Ph_2PCH_2CH(COOLi)(CH_2COOLi)$ **(PC)**, $Ph_2PCH_2CH(CH_3)(COOH)$ **(PH)** or $Ph_2PCH_2CH(CH_3)(COONa)$ **(PNa)** in hydrogenation and hydroformylation of 1-hexene in mono- and biphasic systems have been studied. The yield of aldehydes obtained in hydroformylation of 1-hexene in the system $[Rh(acac)(CO)_2]$ + PNS strongly depends on the kind of solvent: 24% in toluene, 53–86% (n/iso 2.9–4.6) in the toluene–water–ethanol mixture and 77–94% (n/iso 2.5–3.8) in water–ethanol solution. The mixture of water–ethanol as a solvent was also found to be the best for hydrogenation of 1-hexene (96% of hexane) with $[Rh(acac)(CO)_2]$ + PNS system. Application of PH phosphine (in hydrogen form) produces ca. 2% of aldehydes in both solvents, toluene only and toluene–water mixture. However, conversion of PH phosphine into its sodium salt, PNa, increased the catalytic activity of rhodium catalyst up to 85% yield of aldehydes in toluene, 92% in toluene–water and 94% in toluene–water–ethanol mixture. Spectroscopic studies of the reaction mixture in situ (IR, ^{1}H-, ^{31}P-NMR) allowed to identify following rhodium complexes existing in hydroformylation reaction conditions in the system $[Rh(acac)(CO)_2]$ + PH/PNa: $[Rh(acac)(CO)(PH)]$, $[Rh(OH)(CO)(PH)_2]$, $[HRh(CO)(PNa)_3]$, $[Rh_4(CO)_{12-x}(PH)_x]$. $[HRh(CO)(PNa)_3]$ was found to be stable only when sodium hydroxide was introduced to the system. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The separation of catalyst from reaction products still appears to be one of the most important and difficult problems of homogeneous catalysis, especially when application to industry is considered. High temperature distillation, usually applied for separation, frequently leads to catalyst decomposition or at least significant deactivation.

Recently, much interest has been paid to biphasic hydroformylation in which the catalyst is usually dissolved in the water phase and both, substrates and products, in the organic phase [1–4]. This approach allows simple and effective catalyst separation of reaction products (i.e., decantation) causing no decrease of catalytic

activity and preventing formation of inactive species as the result of side reaction of catalyst with reaction products [5].

Synthesis of water soluble rhodium catalysts is done on the way of replacement of CO or PPh_3 ligands in starting rhodium complex by water soluble P-ligands which usually have hydrophilic polar groups like $-SO_3H$, $-COOH$, $-NR_3$, $-OH$ [1]. There are numbers of catalytic systems for hydrogenation, oxidation and hydroformylation of olefins in which water soluble phosphines are applied: $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ with $P(m\text{-}C_6H_4SO_3Na)_3$ (TPPTS) catalyzes hydroformylation of propylene with 96% yield of *n*-aldehyde [3]. Comparable high yield of *n*-aldehyde (93–97%) has been obtained in 1-hexene hydroformylation with $HRh(CO)[(TPPTS)_3]_3$ or $[Rh_2(\mu\text{-}SR_2)(CO)_2[(TPPTS)_3]_2$ [3]. Chelating diphosphine, BISBIS, as product of 2,2'-bis(diphenylphosphino-methyl)-1,1'-biphenyl (BISBI) sulphonation was successfully applied to hydroformylation both propylene as well as higher olefins (e.g., 1-hexene) [6]. Catalytic systems composed with $[Rh(acac)(CO)_2]$ precursor and different water soluble phosphines like: $P[(CH_2)_nC_6H_4SO_3Na]_3$, $P[C_6H_4(CH_2)_nC_6H_4SO_3Na]_3$, $Ph_2P(CH_2)_nSO_3Na$ and $P(C_6H_3FSO_3Na)_3$ [7–9] were also found to be active in hydroformylation. The same rhodium catalyst precursor was used with $Ph_2P(CH_2)_2CONHC(CH_3)_2CH_2SO_3Li$ (PNS) and $Ph_2PCH_2CH(COOLi)(CH_2COOLi)(PC)$ phosphines in hydroformylation of methyl acrylate with 83% yield of aldehydes and selectivity $\alpha/\beta \leq 25$ [10].

Water soluble phosphines are already used in industry, i.e., TPPTS in propylene hydroformylation (Ruhrchemie/Rhône–Poulenc process) [13,14].

Sometimes, additional components named cosolvents or phase-transfer (PT) agents are used in biphasic systems. Usually, they are alcohols: methanol, ethanol, *iso*-propanol, but also ketones like acetone or acetamides like dimethylacetamide. Usually they cause increase of substrate solubility what facilitates catalytic re-

action course in water phase and next, increases reaction rate and yield [3,11,12].

It is quite important to select a proper cosolvent for a given system. For example in hydrogenation of cyclohexene or 1-octene (totally insoluble in water) ca. 90% of conversion has been achieved when methanol was introduced as cosolvent [11]. Results for other solvents were much worse and reaction rate decreased in order: methanol > ethanol > dimethoxyetane > dimethylacetamide [11]. Hydroformylation of 1-octene was the fastest in presence of ethanol as cosolvent [12] but decreased when other cosolvents have been used in order: acetone > acetonitrile > methanol.

As a phase transfer agents also ammonium salts, ethylene glycol, polyethylene glycols (PEG) as well as crown ethers or polyethers of general formula $R(OCH_2CH_2)_nOH$ have been used [3,15–23]. These compounds, interacting with ligands in catalytic complexes, facilitate selective transfer of catalyst from water to organic phase. Therefore, catalytic reaction proceeds rather in the organic than in the water phase in opposition to the case when cosolvent is applied [3,14].

Usefulness of PT-agent application may be demonstrated in benzylchloride carbonylation reaction catalyzed with $[Co_2(CO)_8]$. In typical biphasic system, reactive anionic form of catalyst, $[Co(CO)_4]^-$ was distributed between water (70%) and organic phase (30%) and reaction yield was ca. 67%. When PEG was introduced to the system 100% of $[Co(CO)_4]^-$ form was transferred to the organic phase and the reaction yield increased to ca. 98% [22].

Glycols and polyglycols are successfully used as PT agents in oxidation of inner and terminal olefins [17,19], halogenobenzene alkoxylation [18] and acethylene hydrogenation [21]. Possible application to hydroformylation of higher olefins increased interest on biphasic systems.

In this paper we present rhodium catalytic systems with application of a new water soluble phosphines: PC, PH (PNa) and PNS (see below) to 1-hexene hydrogenation and hydroformyla-

tion in toluene and in biphasic system (water–organic phase). Two of phosphines, PC and PNS, have been earlier used with good result in hydroformylation of methyl acrylate [10].

PH   (PNa)

PC

PNS
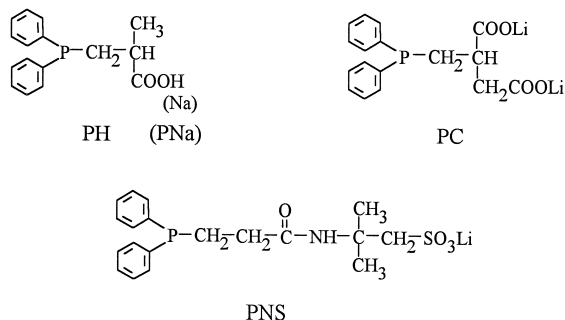
2. Results and discussion

2.1. Hydrogenation of unsaturated and aromatic hydrocarbons catalyzed by [Rh(acac)(CO)$_2$] + P system (P = PNS, PH)

The following hydrocarbons: 1-hexene, toluene, o-xylene, cyclohexene in mono- and biphasic systems have been tested in hydrogena-tion (with [Rh(acac)(CO)$_2$] + PNS), however only 1-hexene was hydrogenated with 88% yield, after 4 h. Other hydrocarbons, except toluene (ca. 5% of methylcyclohexane) were not reactive (Table 1).

1-Hexene hydrogenation at presence of PH produced at comparable conditions 99% of hex-ane. [Rh(acac)(CO)$_2$] itself hydrogenates 1-hexene with almost 98% yield but the reaction is accompanied with significant catalyst reduc-tion to Rh(0) species. Rhodium reduction was not observed when PH or PNS phosphines were introduced to the system.

Hydrogenation of 1-hexene in water gives after 4 h only 42% hexane when PH phosphine was used and 67% with PNS phosphine. At lower temperatures the yield of hexane was even lower and equal in the system with PNS 47% at 333 K and 28% at 303 K, respectively. To improve the yield of hydrogenation reaction with [Rh(acac)(CO)$_2$] + PNS system different cosolvents or PT agents as ethanol, diglym, tetraglym, ethylene glycol, polyethylene glycol, THF, decamethylene glycol and crown ether were added. The best result (83% of hexane after 3 h reaction at 353 K) was obtained after ethanol use as a solvent (Table 1).

Table 1
1-Hexene hydrogenation with the catalytic system [Rh(acac)(CO)$_2$] + PNS in water at presence of ethanol or different ethers

Solvent: water + cosolvent	Time (h)	1-Hexene (%)	2-Hexene (%)	Hexane (%)
Water[a]	4	10	23	67
Ethanol	3	–	13	83
Diglym[b]	3	1	18	80
Tetraglym[c]	3	3	24	73
Ethylene glycol[d]	3.5	1	24	75
Poliethyleneglycol[e]	4	14	42	44
Tetrahydrofurane	1.5	2	45	53
Tetrahydrofurane	3	1	42	57
Decamethylene glycol[f]	4	52	14	35
Crown ether[g]	4	40	22	38

[Rh] = 5 × 10^{-3} M, [P]/[Rh] = 11, [1-hexene]/[Rh] = 800, p(H$_2$) = 1 MPa, T = 353 K, 1 cm^3 H$_2$O + 0.5 cm^3 of ethanol or ether.
[a] 1.5 cm^3 H$_2$O.
[b] (CH$_3$OCH$_2$CH$_2$)$_2$O.
[c] CH$_3$(OCH$_2$CH$_2$)$_4$OCH$_3$.
[d] (CH$_2$OH)$_2$.
[e] 0.1 g; mol weight = 1000, 1.5 cm^3 H$_2$O.
[f] 0.05 g; HO(CH$_2$)$_{10}$OH, 1.5 cm^3 H$_2$O.
[g] C$_8$H$_{16}$O$_4$.

Independent experiment of hydrogenation without dihydrogen showed no hexane in reaction product, what proves that ethanol is not the source of hydrogen in this reaction. It seems that ethanol is only responsible for 1-hexene solubility increase in water phase which contains also catalyst. Comparing with ethanol, hydrogenation reaction yields in presence of ethers were lower: 80% of hexane with diglyme, and 73% with tetraglyme but higher yield of isomerization reaction product was observed (18–24% of 2-hexene).

2.2. 1-Hexene hydroformylation catalyzed by [Rh(acac)(CO)$_2$] + P (P = PNS, PC, PH) in mono- and biphasic systems. Hydroformylation of 1-hexene in toluene (monophasic system)

The highest yield of aldehydes (24%) was obtained for reaction in toluene with PNS phosphine as modifying ligand. A rather low yield of aldehydes may be explained as a result of relatively low solubility in toluene of both rhodium complex and phosphine what causes low concentration of catalytically active form of rhodium complex with coordinated PNS phosphine.

The use of crown ether for eventual coordination of lithium ion did not increase phosphine solubility in toluene. 1-hexene hydroformylation with PC phosphine is much less effective and corresponding yields of aldehydes and 2-hexene are 12% and 81%, respectively. Also application of PH phosphine was not effective and only 2% conversion of 1-hexene after 4 h was observed.

### 2.2.1. 1-Hexene hydroformylation in biphasic system (toluene–water)

Generally, the results of hydroformylation were similar to those obtained in toluene only. In reaction with application of PC the decrease of 1-hexene isomerization (from 81 to 31%) was noted. Similarly as in pure toluene conver-

sion of olefin in the system with PH phosphine was very low, c.a. 2.5%. Such low catalytic activity of that system may be explained by the presence of labile proton of carboxylic group in PH (PH ↔ P$^-$ + H$^+$) which may prevent formation of rhodium hydride reactive form of catalyst. Similar effect was observed for the systems with carboxylic acids [24]. IR and NMR studies of [HRh(CO)(PPh$_3$)$_3$] reaction with PH confirmed fast decomposition of complex and disappearance of Rh–H bond.

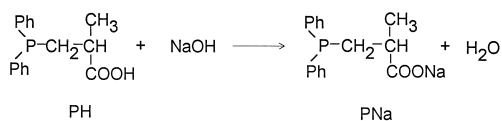### 2.2.2. Interaction of [Rh(acac)(CO)$_2$] with PH in hydroformylation reaction condition

New rhodium complex of formula [Rh(acac)(CO)(PH)] is formed in reaction of [Rh(acac)(CO)$_2$] with PH at [PH]:[Rh] = 2–5 in THF. Additionally, in THF–H$_2$O mixture, besides [Rh(acac)(CO)(PH)] also the hydroxyl complex [Rh(OH)(CO)(PH)$_2$] was found as a product of acac$^-$ replacement by OH$^-$ ligand.

In CO or CO/H$_2$ atmosphere at [PH]:[Rh] = 2, formation of [Rh$_4$(CO)$_{12-x}$(PH)$_x$] type complexes (with preference of [Rh$_4$(CO)$_{10}$(PH)$_2$]) was recorded (Scheme 1). It was found that reaction of [Rh(acac)(CO)$_2$] with PH proceeds according to earlier described reactions with PNS [10] and TPPTS [25].
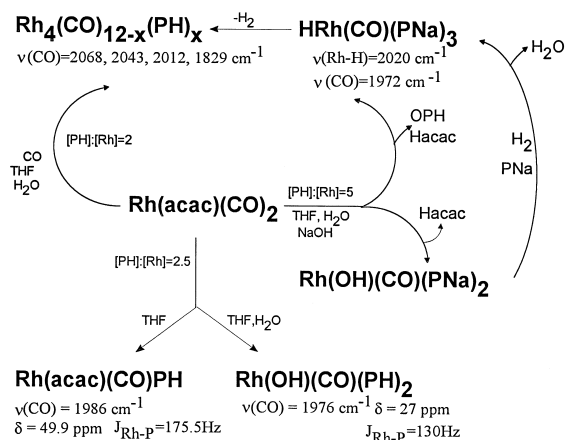
Scheme 1. Possible reactions of catalyst precursor, [Rh(acac)(CO)$_2$].

Formation of rhodium-hydride species was not evidenced in any reaction with PH phosphine, however, conversion of PH phosphine into PNa salt (by the stoichiometric treatment with NaOH) allowed to stabilize rhodium-hydride complex and identify it with IR (ν(Rh–H) = 2020 cm^{-1}, ν(CO) = 1972 cm^{-1}).

All reactions of [Rh(acac)(CO)$_2$] with PH and PNa are shown on Scheme 1.

2.2.3. 1-Hexene hydroformylation with [Rh(acac)(CO)$_2$] + PNa system

Application of PNa phosphine in mono- and biphasic system significantly increased the yield of aldehydes which reached after 3–4 h the values of 26% (in toluene) and 92% (in toluene–water), respectively (Table 2). The worse result (42% of aldehydes after 6 h) was obtained at application of PH with equimolar amount of NaOH instead of earlier prepared PNa. However, addition of ethanol to the same (PH/NaOH) system allowed to produce c.a. 94% of aldehydes in 2.5 h.

2.2.4. 1-Hexene hydroformylation by the catalytic system [Rh(acac)(CO)$_2$] + PNS

Hydroformylation of 1-hexene in toluene–water solution, catalyzed by [Rh(acac)(CO)$_2$] + PNS system is not very effective and after 4 h only 14% of aldehydes is obtained. The very low conversion of 1-hexene may be explained by rather poor solubility of olefin in water phase. Addition of different ethers to the system, like diglyme, tetraglyme, tetrahydrofurane did not increase 1-hexene conversion and yield of aldehydes. Significant improvement both, in yield of aldehydes and selectivity of hydroformylation has been observed when ethanol was introduced to the reacting system.

It was found, that the hydroformylation reaction yield and selectivity not only depend on the kind of solvent used but also on the concentration of particular components in the mixed solvent. This conclusion is spectacularly proved by experimental data, showing the effect of the [ethanol]:[water] concentration on the total yield of aldehydes (see Table 3). Nonlinear dependence of aldehydes yield on ethanol concentration was found. The amount of aldehydes increases with increase of ethanol concentration in the water–ethanol mixture. However, the hydroformylation reaction carried out in only ethanol solution did not produce the highest yield of aldehydes. This may be caused by lower solubility of catalyst in ethanol, compared with that in water–ethanol mixed solvent.

Table 2
1-Hexene hydroformylation reaction product composition obtained with catalytic system: [Rh(acac)(CO)$_2$] + PNa in solvent S

Solvent S (cm^3)	PNa:Rh	Aldehydes (%)	1-Hexene (%)	2-Hexene (%)	n/iso
Toluene	4	20	16	65	2.4
Toluene	11	26	70	3	2.0
Toluene (1), water (0.5)	11	88	–	12	1.6
Toluene (0.5), water (1)	11	92	–	8	2.3
Toluene (1), water (0.5)[a]	11	42	56	2	3.2
Toluene (0.3), water (0.7) ethanol (0.5)[a,b]	11	94	–	6	2.4

[Rh] = 5×10^{-3} M, [1-hexene]/[Rh] = 800, pH$_2$/pCO = 1, p(H$_2$ + CO) = 1 MPa, T = 353 K, t = 4 h.
[a] – PH + NaOH, 6 h.
[b] – PH + NaOH, 2.5 h.

Table 3

1-Hexene hydroformylation reaction product composition. Catalytic system: $[Rh(acac)(CO)_2]$ + PNS in the mixed solvents: toluene–water–ethanol and water–alcohol (alcohol = ethanol, methanol, isopropanol)

Mixed solvent (cm^3)	1-Hexene (%)	2-Hexene (%)	n-Heptanal (%)	iso-heptanal (%)	n/iso	S_p^*
Toluene (0.5):water (1)	86	–	9	5	1.7	
Toluene (0.5):water (0.5):ethanol (0.5)	40	7	43	10	4.3	0.65
Toluene (0.2):water (0.5):ethanol (0.8)	36	5	46	10	4.6	0.42
Toluene (0.2):water (0.5):ethanol (0.8)[a]	45	1	39	11	3.5	0.42
Toluene (0.2):water (0.2):ethanol (1.1)	11	2	64	22	2.9	0.27
Water (1):ethanol (0.5)	87	0.5	8	2	4.0	0.65
Water (0.5):ethanol (1)	7	1	69	18	3.8	0.31
Water (0.4):ethanol (1.1)	4	2	70	23	3.0	0.27
Water (0.4):ethanol (1.1)[a,c]	0.5	3.4	69	25	2.8	0.27
Water (0.4):methanol (1.1)[a,d]	1	2	69	25	2.8	0.43
Water (0.4):isopropanol (1.1)[a,d]	4	2	67	24	2.8	
Ethanol (1.5)	21	2	55	22	2.5	0.14

$[Rh] = 5 \times 10^{-3}$ M, $[P]/[Rh] = 11$, $pH_2/pCO = 1$, $p(H_2 + CO) = 1$ MPa, $T = 353$ K, $t = 5.5$ h.

[a]$[P]:[Rh] = 5$.

[b]4 h.

[c]1 h.

[d]2 h.

[*]S_p parameter was calculated according [26] with assumption of volume percentage of ethanol in solvents mixture.

The best yield of aldehydes for the three component, toluene–water–ethanol mixed solvent, was c.a. 86% whereas for two component water–ethanol system this was higher (94%). Similar high yield of aldehydes was obtained when ethanol was replaced by methanol or *iso*-propanol. However, the reactions were much slower (rate constant for ethanol containing solvent $k = 10.6 \times 10^{-4}$ mol ald. min^{-1}, but for methanol and *iso*-propanol are 5.1 and 2.8×10^{-4} mol ald. min^{-1}, respectively).

It was also found that the effect of phosphine concentration is also important. Decrease of $[P]:[Rh]$ ratio from 11 to 5 in the water (0.4):ethanol (1.1) system caused shortening of the reaction time necessary to reach 94% yield of aldehyde from 4 to 1 h (Table 3). In the system toluene (0.2):water (0.5):ethanol (0.8), decrease of $[P]:[Rh]$ ratio up to 5 did not increase the reaction rate but in opposition, decreased the yield of aldehydes (from 56 to 50%) and selectivity n/iso (from 4.6 to 3.5) (Table 3).

The role of alcohol in the systems under study may be explained on the ground of increasing solubility of olefin in water–alcohol

phase (water solubility in olefin may be neglected), i.e., on the solvophobic effect determined by the standard Gibbs energy of tranfer of a given solute from one to another solvent. Solvophobic strength of given solvent may be characterised by the S_p parameter which is equal 0 for water and 1 for the most hydrophobic solvent–*n*-hexadecane [26]. Solvents with S_p values close to 1 are hardly soluble in water. Some authors [12] have studied correlations between S_p parameter and hydroformylation reaction selectivity.

In the hydroformylation reaction reported in this paper it was found that 1-hexene, normally insoluble in water, is present in the water phase of water–alcohol–1-hexene mixture. Using the GC-MS method ca. 3% of 1-hexene was found in the water phase of water (0.4)–ethanol (1.1)–1-hexene (1.5) mixture, whereas at lower concentration of ethanol (water (1.0)–ethanol (0.5)–1-hexene (1.5), 1-hexene was not detected in the water phase. At assumption, that actually tri component (water–ethanol–olefin) system may be considered as two component (contribution of olefin can be neglected) the corresponding S_p parameter values for water–alcohol mix-

ture can be calculated following procedure described in [26]. The best yield of aldehydes was obtained for $S_p = 0.3$, what corresponds to the composition of water–ethanol–1-hexene mixture for which the highest 1-hexene concentration was found chromatografically in water phase.

2.3. Stability and reactivity of catalytic system: [Rh(acac)(CO)_2] + 5PNS at hydroformylation reaction condition

For testing stability of catalytic system containing $[Rh(acac)(CO)_2]$ precursor and PNS phosphine as modifying ligand was selected. This system was earlier found as very active in the hydroformylation of 1-hexene (94% yield of aldehydes in 1 h). The test reaction was carried out repeatedly with the products distilled out and the substrate introduction to the autoclave without catalyst removal out from the reactor.

The catalytic system had practically constant activity (almost the same yield and selectivity) in 9 consecutive catalytic cycles, what proves its relatively high stability as homogeneous catalyst (Table 4). However, some decrease of reaction rate, measured as the CO/H_2 pressure drop, was observed. The rate of aldehyde formation in cycle 1 determined as 10.6×10^{-4} mol ald. $\times min^{-1}$ was only 1.1×10^{-4} in cycle 9 what may be caused by increasing in time contribution of high molecular weight products

(e.g., products of aldehydes condensation) (Table 4).

2.4. Recapitulation

– 1-Hexene hydrogenation in water solution catalyzed by $[Rh(acac)(CO)_2]$ precursor modified with phosphines PNS or PH produced after 4 h 67% or 42% of hexane, respectively. Introduction of ethanol to the system with PNS increased the yield of hexane up to 83% in 3 h.

– In the hydroformylation reaction of 1-hexene carried out in toluene–water mixed solvent, catalyzed by $[Rh(acac)(CO)_2]$ precursor modified with PNa phosphine, the high yield of aldehyde (c.a. 92%) was obtained. In similar reaction with PNS only 12% of aldehydes has been produced. Introduction of ethanol to the system with PNS increased the yield of aldehydes up to 94% in 1 h. The highest yield and selectivity was found for mixed solvent (water–ethanol) with ca. 70% of ethanol.

– On the base of spectroscopic studies (IR, ^1H, ^{31}P NMR) the following rhodium complexes have been identified as a result of $[Rh(acac)(CO)_2]$ catalyst precursor reaction with PH or PNa phosphines at hydroformylation reaction condition: $[Rh(acac)(CO)(PH)]$, $[Rh(OH)(CO)(PH)_2]$, $[HRh(CO)(PNa)_3]$, $[Rh_4(CO)_{12-x}(PH)_x]$.

– It was proved that catalytic system of $[Rh(acac)(CO)_2]$ + PNS is stable at hydro-

Table 4

Products of repeated reaction of 1-hexene hydroformylation catalyzed by the system $[Rh(acac)(CO)_2]$ + 5PNS in water (1.6 cm^3-ethanol (4.4 cm^3) mixed solvent

No. of cycle	1-Hexene (%)	2-Hexene (%)	n-Heptanal (%)	Iso-heptanal (%)	n/iso	$k \times 10^4$ (mol ald. min^{-1})
1	38	1	44	15	2.9	10.6
2	33	4	45	17	2.7	8
4	34	5	44	17	2.7	8.8
5	33	6	44	17	2.6	6.2
6	32	6	45	17	2.6	4.4
7	33	9	42	16	2.6	5.2
8	30	10	43	17	2.5	1.5
9	37	8	40	16	2.5	1.1

$[Rh] = 5 \times 10^{-3}$ M, [PNS]:[Rh] = 5, [1-hexene]/[Rh] = 800, $pH_2/pCO = 1$, $p(H_2 + CO) = 1$ MPa, $T = 353$ K.

formylation reaction condition. During 9 following catalytic cycles, although reaction rate sligtly decreased, catalytic activity demonstrated by the yield of aldehydes was practically constant.

– A convenient method for separation of catalyst and reaction product, usefull for testing homogeneous catalyst have been elaborated.

2.5. Experimental

– [Rh(acac)(CO)$_2$] was prepared according to the literature method [27].

– Water soluble phosphines PNS, PC and PH were obtained as described in [28]. Some details of PH preparation are given below.

– Toluene, 1-hexene were distilled before use.

– Preparation of **PH** phosphine: Reaction of litium phosphide (Ph$_2$PLi) with methacrylic acid (CH$_2$=C(CH$_3$)COOH according to procedure described in [28] leads to obtaining of the mixture of products which composition have been established after molecular weight determination (osmometric) and analytical measurements as two different phosphines with one or two carboxylic groups respectively.

Optimal reaction condition for synthesis of PH with only one carboxylic group are corresponding to equimolar concentrations of the reagents (Ph$_2$PLi:CH$_2$=C(CH$_3$)COOH = 1:1), at the presence of PhLi (formed 'in situ') introducing metacrylic acid to the litium phosphide solution according to the reaction
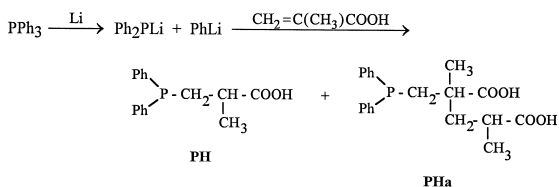
PH (C$_{16}$H$_{17}$O$_2$P): found (calc.): M = 275 (267); %C 71.6 (70.6), %H 6.4 (6.2), %P 10.8 (11.4); IR/KBr ν(COOH) 1709 cm^{-1}; ^{1}H-NMR/CDCl$_3$ δ(ppm) 1.28(d, CH$_3$), 2.55 (CH$_2$), 3.5(q, CH), 7.34 (Ph), 9.2 (OH); ^{31}P-NMR δ(ppm) − 19.9.

PHa (C$_{16}$H$_{17}$O$_2$P): found (calc.): M = 360 (354); %C 68.7 (67.0), %H 7.4 (6.4), %P 7.7 (8.6), ^{1}H-NMR/CDCl$_3$ δ(ppm) 1.34 (CH$_3$), 1.36(d, CH$_3$), 2.76 (CH$_2$), 2.71, 2.64(d, CH$_2$) 3.5(q, CH), 7.13 (Ph), 11.5 (OH); ^{31}P-NMR δ(ppm) − 19.7.

Catalyst precursor, [Rh(acac)(CO)$_2$] modified with phosphine containing two carboxylic groups (PHa) demonstrated rather low activity in 1-hexene hydroformylation (probably because of chelating effect), therefore for further studies phosphine PH with only one carboxylic group have been used.

2.5.1. Preparation of [Rh(acac)(CO)(PH)] and [Rh(OH)(CO)(PH)$_2$]

[Rh(acac)(CO)$_2$] (0.05 g, 1.9 × 10^{-4} mol) dissolved in 2 cm^3 THF was mixed with PH (0.1 g, 3.7 × 10^{-4} mol) in 2 cm^3 of water. After 12 h of stirring, yellow compound of [Rh(acac)(CO)(PH)] formula was precipitated and identified with spectroscopic methods: IR ν(CO) = 1986 cm^{-1}, ^{31}P-NMR δ = 49 ppm, $J_{\text{Rh−P}}$ = 175.7 Hz, ^{1}H-NMR 1.76 (3H, CH$_3$ acac), 2.0 (3H, CH$_3$ acac), 5.4 (1H, CH acac).

In the filtrate, after separation of [Rh(acac)(CO)(PH)], a complex [Rh(OH)(CO)(PH)$_2$] was identified (IR ν(CO) = 1978 cm^{-1}, ^{31}P-NMR δ = 27 ppm, $J_{\text{Rh−P}}$ = 130 Hz.

2.5.2. Preparation of [Rh$_4$(CO)$_{10}$(PH)$_2$]

[Rh(acac)(CO)$_2$] (0.05 g, 1.9 × 10^{-4} mol) dissolved in 1.5 cm^3 THF was mixed with PH (0.1 g, 3.7 × 10^{-4} mol) dissolved in 0.5 cm^3 of water and stirred under CO atmosphere during 12 h. The mixture of [Rh$_4$(CO)$_{12-x}$(PH)$_x$] type of Rh(0) substituted clusters was identified in solution with domination of [Rh$_4$(CO)$_{10}$(PH)$_2$]. (IR ν(CO) = 2068, 2043, 2012, 1829 cm^{-1}, ^{31}P-NMR δ = 24.7 ppm, $J_{\text{Rh−P}}$ = 122 Hz).

2.5.3. Hydrogenation and hydroformylation procedures

Hydrogenation and hydroformylation reactions have been performed in steel autoclave ($v = 50$ cm^3) at 353 K, under 1 MPa ($pCO/pH_2 = 1$) pressure. The autoclave was filled with [Rh(acac)(CO)$_2$] (3.9×10^{-3} g, 1.5×10^{-5} mol), 1-hexene (1.5 cm^3, 1.2×10^{-2} mol), one or more solvents (depending on experiment: toluene, water, alcohol) in total volume equal 1.5 cm^3.

The reagents were introduced to the autoclave in dinitrogen atmosphere. After reaction autoclave was cooled down, degassed and than liquid sample was taken for analysis.

2.5.4. Cyclic hydroformylation

9 catalytic cycles of hydroformylation reaction were performed with the same amount of catalyst. After each catalytic cycle, the products were distilled out and new portions of olefin and ethanol were introduced to the autoclave. Reactions were carried out at 353 K in steel autoclave (150 cm^3) with the valve to collect the gaseous samples durring the reaction connected with special glass receiver (ca. 25 cm^3) with a tap allowing connection to the vacuum. It was used both, for distillation out the products (mainly aldehydes) and for delivering in to the autoclave the substrates of hydroformylation reaction (1-hexene, solvents).

In dinitrogen atmosphere 0.015 g (6×10^{-5} mol) of catalyst precursor [Rh(acac)(CO)$_2$], 0.12 g of phosphine PNS (3×10^{-4} mol), 6 cm^3 (4.8×10^{-2} mol) of 1-hexene, 1.6 cm^3 of water and 4.4 cm^3 of ethanol were introduced into the autoclave. Than autoclave was filled up at room temperature with CO/H$_2$ equimolar mixture up to 1 MPa of total pressure. After reaction, the products were distilled out to the glass receiver, cooled in liquid nitrogen and analyzed (GC-MS). Using the same glass receiver a new portion of deoxygenated olefin and ethanol were introduced into autoclave and corresponding operations have been repeated.

3. Instruments

GC MS, Hewlett Packard 5890II + Hewlett Packard 5971A; NMR, Bruker 300; IR, Nicolet Impact 400.

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