



## Supported N-heterocyclic carbene rhodium complexes as highly selective hydroformylation catalysts

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### ABSTRACT

New supported rhodium(I) catalyst precursors were obtained in reaction of  $[\text{Rh}(\text{OMe})(\text{cod})]_2$  with polymeric monoliths containing methyl-imidazolium moieties and applied in 1-hexene hydroformylation at 10 atm of  $\text{CO}/\text{H}_2$ . Under solventless conditions with a small amount of  $\text{P}(\text{OPh})_3$  as a modifying ligand,  $[\text{P}(\text{OPh})_3]/[\text{Rh}] = 2$ , ca. 80% of aldehydes with a high n/iso ratio of ca. 6 was obtained in eight successive runs. When  $\text{P}(\text{OCH}_2\text{CF}_3)_3$  was used instead of  $\text{P}(\text{OPh})_3$ , n/iso ratios up to 49.8 were obtained, however, the systems were active only in two subsequent reactions. With  $\text{PPh}_3$  as a modifying ligand, the yield of aldehydes decreased to ca. 20% already in the third run and n/iso was ca. 3.

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### 1. Introduction

High catalytic activity of N-heterocyclic carbene (NHC–metal) complexes in homogeneous systems is well documented in the literature [1–10]. NHC–Ru complexes have found broad application in olefin metathesis and polymerization [11,12], whereas NHC–Pd complexes have been used in cross-coupling reactions, such as Suzuki–Miyaura, Heck, and Sonogashira [13–15]. There are also few examples of NHC–Rh complexes active in the hydroformylation of styrene and 1-octene [16–19].

Immobilization of NHC–metal catalysts on insoluble supports can facilitate their recycling and reuse. It is also expected that the use of supported catalysts may lead to minimization of metal content in organic reaction products, which is very important for their possible further application as pharmaceuticals [2,20]. In this context great interest has been recently focused on catalytic systems described as Supported Ionic Liquid Phase (SILP) catalysts [21–25]. In these systems the catalyst dissolved in ionic liquid is immobilized on the surface of a porous support material. The main advantages of SILP systems include good separation of the catalyst from reaction products and high efficiency of the use of both the metal catalyst and the ionic liquid. These features may lead to cost reduction; however, very often catalyst

leaching is a limiting factor for practical applications of such systems.

Another method of immobilization of NHC–metal complexes is through the application of specially synthesized polymers or other supports containing imidazolium terminal groups [26]. Such polymeric supports interact with corresponding metal complexes (usually those that have easily protonized ligands) to form relatively strong M–C (carbene) covalent bonding.

Till now there have been only a few reports describing the application of immobilized NHC–Rh complexes as catalyst precursors in hydroformylation [26–30]. For example, the concept of SILP was applied to the gas phase hydroformylation of 1-butene [25]. Immobilization of rhodium on a water-soluble amphiphilic block copolymer produced the catalyst of 1-octene hydroformylation active at 50 bar [26].

We have recently found that NHC–Rh complexes of the type  $[\text{Rh}(\text{NHC})(\text{cod})\text{X}]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$ ), in the presence of  $\text{P}(\text{OR})_3$  phosphorus modifying ligands, demonstrate very high selectivity in 1-hexene hydroformylation expressed by an n/iso ratio of ca. 7 [31]. It was therefore interesting to check whether similar selectivity can be also obtained with immobilized rhodium precursors. For this purpose we selected insoluble polymers functionalized with imidazolium cations as supports for rhodium, introduced in a form of  $[\text{Rh}(\text{OMe})(\text{cod})]_2$ . Such supports had previously been successfully used for immobilization of palladium catalysts designed for the Heck reaction [32,33] and for batch and continuous-flow Henry reactions [34].

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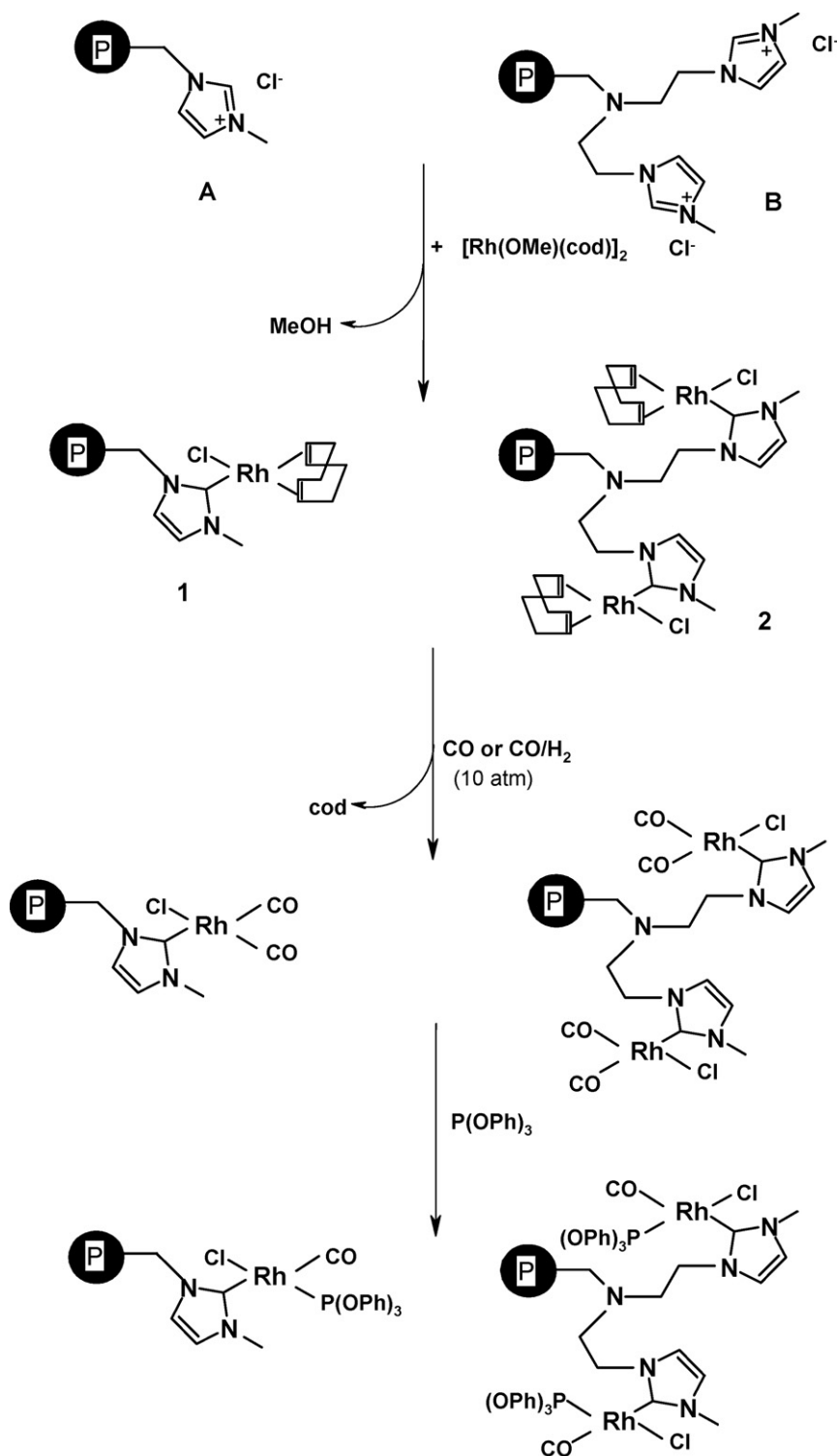


Fig. 1. Formation of catalysts **1** and **2** and their transformations under hydroformylation reaction conditions.

## 2. Results and discussion

### 2.1. Characterization of supported rhodium complexes

Two polymers functionalized with imidazolium cations, **A** and **B** (Fig. 1), have been obtained according to [33]. The reaction of a Merrifield resin (1% DVB – cross-linked) with neat methyl-imidazole led to **A**. The pincer ligand **B** was obtained in reaction of a Merrifield resin with diethanolamine,

followed by the reaction with thionyl chloride under reflux [33].

The rhodium catalyst precursors **1** and **2** (Fig. 1) were obtained in corresponding reactions of the carrier with a rhodium complex,  $[\text{Rh}(\text{OMe})(\text{cod})]_2$ , in  $\text{CH}_2\text{Cl}_2$  in 1 h. On the basis of elemental analysis of the polymer before and after the reaction with the rhodium complex, it was established that one Rh(I) ion was bonded to each imidazolium group (Fig. 1). The analysis of IR spectra of the catalyst precursors **1** and **2** allowed to propose formation of

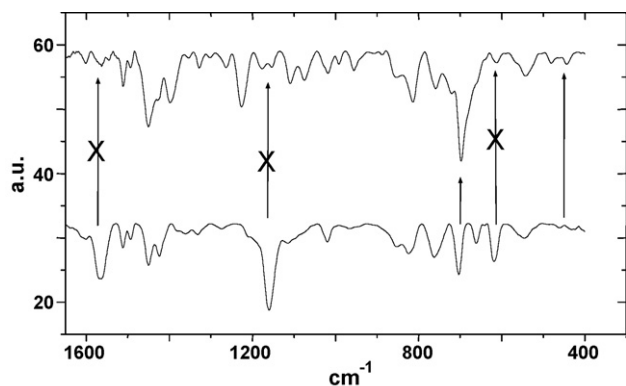


Fig. 2. IR spectra of polymer A (bottom) and **1** (upper).

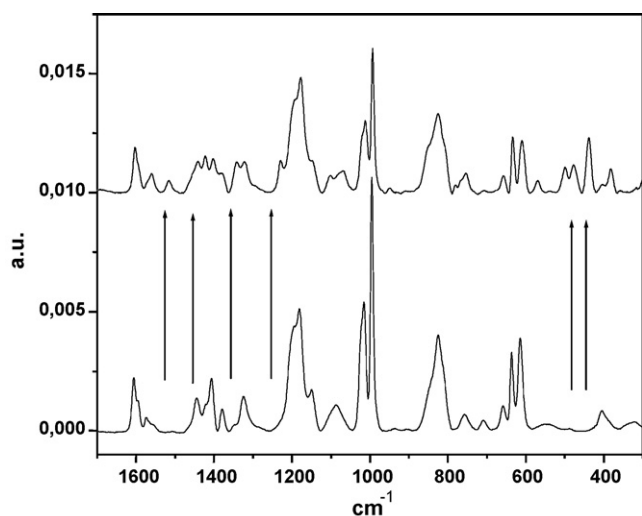


Fig. 3. Raman spectra of polymer A (bottom) and **1** (upper).

NHC–Rh complexes in both cases. The disappearance of  $\nu(\text{CO})$  at  $1074\text{ cm}^{-1}$  corresponding to the OMe ligand in  $[\text{Rh}(\text{OMe})(\text{cod})_2]$  after immobilization suggested elimination of MeOH, as a result of protonation of OMe with C(2)–H proton originated from imidazolium group. The similar process was observed during formation of  $[\text{Rh}(\text{NHC})(\text{cod})\text{X}]$  type complexes in reaction of  $[\text{Rh}(\text{OMe})(\text{cod})_2]$  with imidazolium halides [31]. In the IR spectra of **1** and **2** the intensities of the bands corresponding to the imidazolium units ( $1160$  and  $620\text{ cm}^{-1}$ ) were sharply reduced after reaction with the rhodium complex, suggesting the formation of NHC–Rh complex (Fig. 2). Such conclusion was supported by the observation that the intense band at  $1168\text{ cm}^{-1}$  in the IR spectrum of  $[\text{bmim}]\text{Cl}$

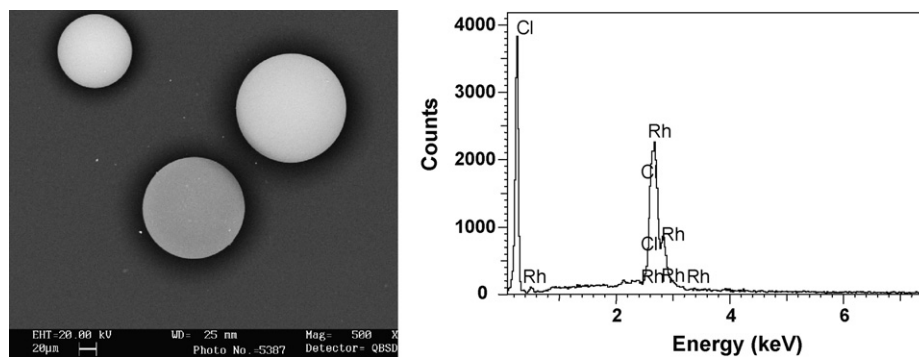


Fig. 4. SEM and EDX of **1**.

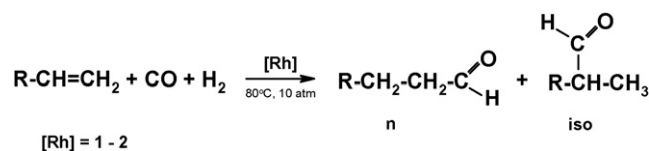


Fig. 5. Hydroformylation reaction.

(bmim = 1-butyl-3-methyl-imidazolium cation) disappeared completely when  $[\text{bmim}]\text{Cl}$  reacted with  $[\text{Rh}(\text{OMe})(\text{cod})_2]$  forming  $[\text{Rh}(\text{bmim-}y)(\text{cod})\text{Cl}]$  [30]. The appearance of new bands below  $500\text{ cm}^{-1}$  in the Raman spectrum also evidenced the formation of new Rh–C bond (Fig. 3). SEM and EDX showed the homogeneity of the complexes **1** and **2** and the presence of rhodium in the synthesized polymers of uniform shape (Fig. 4).

Small samples of complexes **1** and **2** were treated with CO and CO/H<sub>2</sub> at 10 atm in the absence of any solvent and reaction products were characterized by means of IR spectroscopy. In IR spectra of species **1** and **2** after reaction with CO, two intense  $\nu(\text{CO})$  bands appeared, confirming the coordination of two CO groups in *cis* positions as a result of cod replacement. The new bands were observed for **1**+CO at  $2079$  and  $1994\text{ cm}^{-1}$  and for **2**+CO at  $2076$  and  $1994\text{ cm}^{-1}$ . Almost the same results were obtained for products of reaction of complexes **1**–**2** with an equimolar mixture of CO and H<sub>2</sub>. Thus, we were unable to detect hydride ligands in complexes obtained under these conditions.

## 2.2. Hydroformylation of 1-hexene with supported rhodium complexes

The supported Rh–NHC complexes **1** and **2** were tested as catalyst precursors for the hydroformylation of 1-hexene at  $80^\circ\text{C}$  and 10 atm under solventless conditions (Fig. 5), but without phosphorus modifying ligand they did not yield any products. However, after the addition of  $\text{P}(\text{OPh})_3$  in the ratio  $[\text{P}(\text{OPh})_3]/[\mathbf{1}] = 2$ , a catalytic system formed *in situ* became active and produced ca. 70% of aldehydes and ca. 15% of the isomerization product, 2-hexene, after 4 h (Table 1). The yield of aldehydes and the n/iso ratio were dependent on the amount of  $\text{P}(\text{OPh})_3$  used. At the ratio  $[\text{P}(\text{OPh})_3]/[\mathbf{1}] = 0.3$ , only 51.3% of aldehydes was obtained. The best results, ca. 70% of aldehydes with n/iso 6.4–6.7 were obtained at a ratio  $[\text{P}(\text{OPh})_3]/[\mathbf{1}] = 2$ . Further increase of  $\text{P}(\text{OPh})_3$  excess to  $[\text{P}(\text{OPh})_3]/[\mathbf{1}] = 3.9$  led to decrease of the yield to 57.6%, but a higher selectivity towards linear aldehyde was achieved (n/iso 7.1).

Similar dependence was also observed for **2** (Table 2) and at  $[\text{P}(\text{OPh})_3]/[\mathbf{2}] = 2$  ca. 82% of aldehydes with n/iso 6.0–6.7 and 17% of 2-hexene were obtained.

To check whether the system  $\mathbf{1}/\text{P}(\text{OPh})_3$  is active with other substrates, 1-octene was used instead of 1-hexene. After 4 h 26% of aldehydes was obtained with n/iso 5.3. Prolongation of

**Table 1**  
Results of 1-hexene hydroformylation catalyzed by **1** with P(OPh)<sub>3</sub> as modifying ligand.

Entry	[P]/[Rh]	atm (%)		n/iso	activity (atm/min)	TOF (h <sup>-1</sup> )
		Aldehydes (n + iso)	2-Hexene			
1	0.3	51.3	19.1	3.5		
2	2	70.7	15.3	6.7		
2a (rec. 1)	–	77.3	22.5	3.6		
2b (rec. 2)	–	69.2	29.5	3.6		
3	3.9	57.6	10.2	7.1		
4	2	64.6	16.4	6.4	0.10	219
4a (rec. 1)	2	87.1	11.8	6.1	0.31	1152
4b (rec. 2)	2	91.4	7.7	5.7	0.31	1417
4c (rec. 3)	2	86.7	12.4	5.6	0.30	1262
4d (rec. 4)	2	82.0	17.2	5.7	0.14	608
4e (rec. 5)	2	80.0	19.4	6.2	0.10	432
4f (rec. 6)	2	78.7	15.8	6.3	0.06	253
4g (rec. 7)	2	66.9	10.8	5.8	0.03	152

Reaction conditions: 80 °C, 10 atm CO/H<sub>2</sub> = 1, 4 h, [1-hexene] = 1.75 cm<sup>3</sup>, [Rh] = 1.4 × 10<sup>-5</sup> mol, and [1-hexene]:[Rh] = 1000.

the reaction time to 8 h increased the yield to 73% with n/iso 6.1.

Improvement of the hydroformylation reaction in the presence of P(OPh)<sub>3</sub> can be explained by its modifying influence of the rhodium, facilitating activation of substrates. It was checked that P(OPh)<sub>3</sub> substituted CO in supported Rh(P-NHC)X(CO)<sub>2</sub> complex forming Rh(P-NHC)X(CO)(P(OPh)<sub>3</sub>) characterized in the IR spectrum by ν(CO) at 1983 and 1984 cm<sup>-1</sup> for derivatives of **1** and **2**, respectively (Fig. 1).

In the recycling experiments, when the catalyst was separated from the reaction mixture by decantation and reused, the yield of aldehydes was still good, 77.3–69.2% for **1** and 81.3–66.3 for **2**, but the n/iso ratio decreased to 3.6 for **1** and to 3.4 for **2**. However, when a new portion of P(OPh)<sub>3</sub> was added to the catalyst **1** separated by decantation, the yield of aldehydes and selectivity remained almost unchanged in eight subsequent runs with the n/iso ratio amounting to 5.6–6.4 (Table 1, Fig. 6).

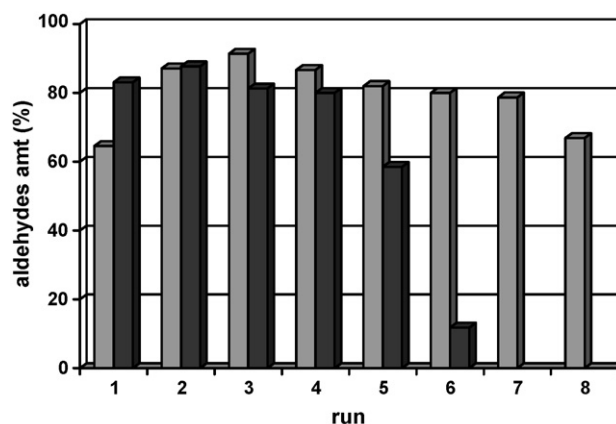
Very good results were also obtained in reactions catalyzed by **2**, when in each successive experiment a new portion of P(OPh)<sub>3</sub> was added to the catalyst. In four subsequent reactions 80.0–87.7% of aldehydes and n/iso 5.5–7.3 were formed (Table 2, Fig. 6). In the fifth run the yield decreased to 58.5% and in the sixth one only 11.8% of aldehydes were produced.

The yield and n/iso ratios were similar to those obtained with catalyst **1**, although the system was less stable, and already in the sixth run the yield of aldehydes dropped down (run 9e, Table 2, Fig. 6). To characterize the catalytic activity of the systems under study, the rate of pressure drop over time was determined from the linear part of the plot of pressure vs. time after the induction period (Tables 1 and 2). The catalyst turnover frequency, TOF, was

**Table 2**  
Results of 1-hexene hydroformylation with catalyst **2** with P(OPh)<sub>3</sub> as modifying ligand.

Entry	[P]/[Rh]	atm (%)		n/iso	activity (atm/min)	TOF (h <sup>-1</sup> )
		Aldehydes (n + iso)	2-Hexene			
7	2	81.3	18.3	6.7		
7a (rec. 1)	–	79.9	20.0	3.4		
7b (rec. 2)	–	66.3	31.8	3.5		
8	3.7	73.2	20.4	7.8		
9	2	83.1	15.4	6.0	0.19	619
9a (rec. 1)	2	87.7	11.3	5.5	0.25	1071
9b (rec. 2)	2	81.3	18.1	6.9	0.24	944
9c (rec. 3)	2	80.0	18.7	7.3	0.11	464
9d (rec. 4)	2	58.5	10.9	6.5	0.03	152
9e (rec. 5)	2	11.8	4.1	6.1	0.01	29

Reaction conditions: 80 °C, 10 atm CO/H<sub>2</sub> = 1, 4 h, [1-hexene] = 1.75 cm<sup>3</sup>, [Rh] = 1.4 × 10<sup>-5</sup> mol, and [1-hexene]:[Rh] = 1000.



**Fig. 6.** The yield of aldehydes obtained in hydroformylation of 1-hexene with catalyst **1** (left) and catalyst **2** (right) and P(OPh)<sub>3</sub> as modifying ligand in consecutive runs.

also calculated (Tables 1 and 2). The first reaction (run 4, Table 1) was characterized by an induction period of ca. 2 h. In the following three experiments (run 4a–4c) a remarkable increase in the reaction rate was observed. It is interesting to note that the pressure drop was even faster than in a homogeneous system [30]. In subsequent experiments the reaction rate slowed down and at the same time the n/iso ratio increased from 5.6 (run 4c) to 5.7 (run 4d).

An induction period observed in first reaction can be related to the formation of hydrido-carbonyl supported complex of the type

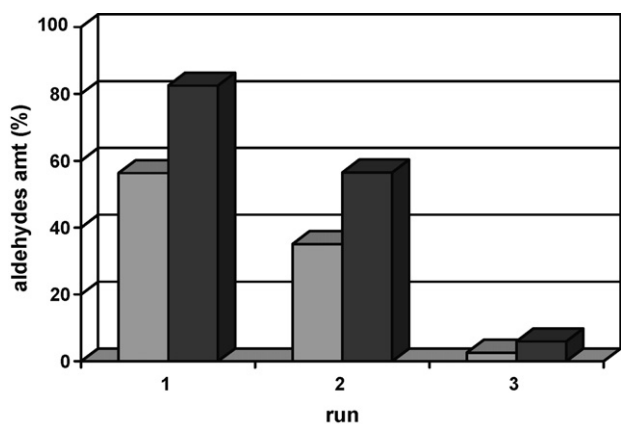


Fig. 7. The yield of aldehydes obtained in hydroformylation of 1-hexene with catalyst **1** (left) and catalyst **2** (right) and  $\text{P}(\text{OCH}_2\text{CF}_3)_3$  as modifying ligand in three consecutive runs.

$\text{Rh}(\text{P-NHC})\text{H}(\text{CO})(\text{P}(\text{OPh})_3)_2$ , analogue of the homogeneous catalyst [31].

The average concentration of rhodium leached, determined by ICP analysis of the reaction solution, was *ca.* 57 ppm in recycling experiments with **1** and *ca.* 71 ppm in reactions with **2**.

Relatively high *n*/*iso* noted in the recycling experiments (runs 4–4g, Table 1, runs 9–9c, Table 2) may suggest that catalytically active species is bonded to the support as NHC–Rh species. Such a suggestion is based on the observation made for homogeneous systems that the high *n*/*iso* selectivity could be reached only when NHC ligand was present in coordination sphere of rhodium [30].

To determine the catalytic activity of the leached rhodium after one reaction performed with catalyst **1**, only solution was used for the next experiment. The new portions of 1-hexene and  $\text{P}(\text{OPh})_3$  were added and pressured with 10 atm of  $\text{CO}/\text{H}_2$ . After 4 h aldehydes were obtained with the yield 85%, however *n*/*iso* was equal to 1.5 only. These results differ remarkably from those obtained in the first cycle – 85% of aldehydes, *n*/*iso* 8.2.  $^{31}\text{P}$  and  $^1\text{H}$  NMR analysis of the solution confirmed the presence of  $\text{HRh}(\text{CO})(\text{P}(\text{OPh})_3)_3$  only. Thus, it can be suggested that catalysts **1** and **2** are responsible for high *n*/*iso* values in the studies reactions.

Other phosphorus ligands, like  $\text{P}(\text{OCH}_2\text{CF}_3)_3$  and  $\text{PPh}_3$ , were also tested as modifying components of the catalytic system (Figs. 7 and 8). In reactions with  $\text{P}(\text{OCH}_2\text{CF}_3)_3$  the yield of aldehydes decreased already in the second run for both catalysts, **1** and **2** to 35.1 and 56.5%, respectively. At the same time very high *n*/*iso*

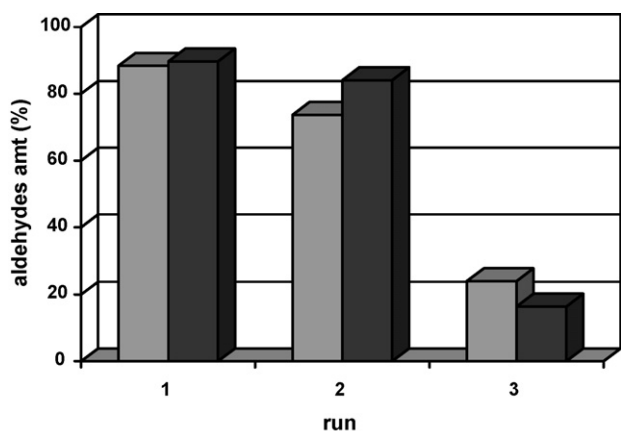


Fig. 8. The yield of aldehydes obtained in hydroformylation of 1-hexene with catalyst **1** (left) and catalyst **2** (right) and  $\text{PPh}_3$  as modifying ligand in three consecutive runs.

Table 3

Electronic and steric parameters of phosphorus ligands and *n*/*iso* ratio.

Ligand	Cone angle	$\chi$	<i>n</i> / <i>iso</i> <sup>a</sup>
$\text{P}(\text{OCH}_2\text{CF}_3)_3$	115 <sup>b</sup>	42.9 <sup>b</sup>	29.8
$\text{P}(\text{OPh})_3$	121	29.1	6.7
$\text{PPh}_3$	145	12.9	3.1

<sup>a</sup> For catalyst **1**, first cycle.

<sup>b</sup> Parameters for  $\text{P}(\text{OCH}_2\text{CCl}_3)_3$ .

values were achieved, up to 49.8 for **1** and 32.9 for **2**. Very good yields of aldehydes were obtained for catalysts **1** and **2** modified with  $\text{PPh}_3$ , not only in the first run but also in recycling experiments: 88.4 and 73.7% for **1** and 89.7 and 84.1% for **2**. The *n*/*iso* values were lower than in the presence of  $\text{P}(\text{OPh})_3$ , amounting to 3.1–2.6 for **1** and 3.2–2.7 for **2**. Surprisingly, in the third run only 24.0 and 16.4% of aldehydes was obtained with catalysts **1** and **2**, respectively. Such decrease of the yield of aldehydes cannot be explained by rhodium leaching, because rhodium concentration determined by ICP in solution was *ca.* 14 ppm only for both catalysts, **1** and **2**.

The observed effect of phosphorus ligands ( $\text{P}(\text{OPh})_3$ ,  $\text{P}(\text{OCH}_2\text{CF}_3)_3$  and  $\text{PPh}_3$ ) on the selectivity of hydroformylation can be discussed in terms of their electronic or steric properties [35]. In Table 3 there are collected parameters characteristic for ligands and *n*/*iso* ratio obtained in hydroformylation. Analysis of data made it possible to conclude that electronic influence is dominating and less basic ligands facilitate achievement of higher *n*/*iso* ratio.

### 3. Conclusions

Immobilized rhodium catalyst precursors for 1-hexene hydroformylation described for the first time in this paper present interesting alternative to the homogeneous systems with NHC–Rh soluble complexes [31]. The advantages of a heterogeneous system include not only the ease of catalyst separation but also the possibility of obtaining a high yield and high selectivity of hydroformylation in successive at least eight runs. The best catalytic system found in this work contains an NHC–Rh complex bonded to polymer **A** and a small amount of  $\text{P}(\text{OPh})_3$  ( $[\text{P}(\text{OPh})_3]/[\text{Rh}] = 2$ ). From the mechanistic point of view, it is worth noting that studies of immobilized systems presented in this paper confirm conclusions formulated for homogeneous NHC–rhodium catalysts. Thus, the highest selectivity in 1-hexene hydroformylation is observed when NHC–Rh precursor is applied together with suitable, less basic phosphorus modifying ligand.

### 4. Experimental

#### 4.1. Preparation of catalysts

##### 4.1.1. Complex **1**

To a solution of 0.026 g of  $[\text{Rh}(\text{OMe})(\text{cod})_2]$  [36] in  $\text{CH}_2\text{Cl}_2$  ( $5 \text{ cm}^3$ ) was added 0.122 g of polymer **A**, and the mixture was stirred for 1 h at room temperature. After that time the catalyst was filtered off and washed four times with  $\text{CH}_2\text{Cl}_2$ . All the  $\text{CH}_2\text{Cl}_2$  solutions were collected and used for ICP analysis of the amount of non-reacted rhodium. Rhodium content in complex **1** was calculated from the difference before and after immobilization, and was found to be 7.4%.

The alternative method of rhodium content determination, based on the ICP analysis of the solution obtained after treatment of a known amount of complex **1** with  $\text{HCl}/\text{HNO}_3$ , did not give fully reproducible results.

Found: for polymer **A**: C 82.95; H 7.19; N 2.36%; complex **1**: C 76.01; H 6.60; N 2.01%.

Molecular ratio N:Rh = 2 (calc. 2).

IR  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$ : 2921, 1510, 1451, 1393, 1263, 1223, 1107, 1021, 761, 696, 539, 481. Raman  $\nu_{\max}$ / $\text{cm}^{-1}$ : 1602, 1421, 1322, 1011, 993, 825, 633, 610, 477, 438.

#### 4.1.2. Complex 2

Complex **2** was obtained in a similar method to that described for **1**, using 0.065 g of polymer **B** and 0.027 g of  $[\text{Rh}(\text{OMe})(\text{cod})]_2$  in  $\text{CH}_2\text{Cl}_2$  ( $5 \text{ cm}^3$ ). Rhodium content: 10.0%.

Found for polymer **B**: C 76.67; H 7.19; N 4.67%; complex **2**: C 69.42; H 6.24; N 3.48%.

Molecular ratio N:Rh = 2.56 (calc. 2.5).

IR  $\nu_{\max}$  (KBr)/ $\text{cm}^{-1}$ : 3023, 2920, 1559, 1492, 1452, 1028, 758, 698, 457, 436, 419.

Raman  $\nu_{\max}$   $\text{cm}^{-1}$ : 3053, 2907, 1602, 1583, 1540, 1328, 1182, 1021, 992, 767, 717, 634, 612, 470, 438.

#### 4.2. Hydroformylation reaction procedure

Catalytic reactions were carried out in neat 1-hexene ( $1.75 \text{ cm}^3$ ) without extra solvent, in a  $55 \text{ cm}^3$  steel autoclave, which was charged with the supported catalyst precursor containing  $1.5 \times 10^{-5}$  mol Rh and a modifying ligand (P), e.g.  $\text{P}(\text{OPh})_3$ , in an amount of  $[\text{P}]/[\text{Rh}] = 0.3\text{--}3$  under a dinitrogen atmosphere. Next, the autoclave was filled with an equimolar mixture of  $\text{H}_2$  and CO to a pressure of 10 atm and heated to  $80^\circ\text{C}$ . During the reaction the mixture was magnetically stirred. After the reaction was finished, the autoclave was cooled down, then opened, and the organic products were separated from the catalyst by decantation and analyzed using a GC-FID HP 5890 II Hewlett-Packard instrument with toluene as an internal standard. In recycling experiments a new portion of 1-hexene ( $1.75 \text{ cm}^3$ ) and phosphite were added to the solid residue left after decantation, and the next reaction was performed.

#### 4.3. Analysis of rhodium in the post-reaction solution

Organic components were separated from the post-reaction solution by vacuum transfer. Next,  $5 \text{ cm}^3$  of HCl and  $1 \text{ cm}^3$  of  $\text{HNO}_3$  were added to the dry residue. After 3 days the solution was diluted to  $25 \text{ cm}^3$  by addition of water, and the rhodium content was determined by the ICP method.

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