



Cite this: *Catal. Sci. Technol.*, 2017, 7, 3097

## ***N*-Pyrrolylphosphines as ligands for highly regioselective rhodium-catalyzed 1-butene hydroformylation: effect of water on the reaction selectivity†**

W. Alsalahi,<sup>a</sup> R. Grzybek<sup>b</sup> and A. M. Trzeciak  <sup>✉</sup><sup>a</sup>

The hydroformylation of 1-butene catalyzed by  $\text{Rh}(\text{acac})(\text{CO})_2$  with an excess of *N*-pyrrolylphosphine ligands,  $\text{L} = \text{P}(\text{NC}_4\text{H}_4)_3$ ,  $\text{PPh}_2(\text{NC}_4\text{H}_4)$  or  $\text{PPh}(\text{NC}_4\text{H}_4)_2$ , was investigated under constant pressure of synthesis gas (4–10 bar,  $\text{H}_2/\text{CO} = 1$ ) and 2 bar of 1-butene at temperatures ranging from 50 to 80 °C. *N*-Pyrrolylphosphine ligands facilitated excellent selectivity towards aldehydes and regioselectivity towards linear aldehydes. The application of a higher temperature, the presence of a small amount of water, and a  $[\text{L}]/[\text{Rh}]$  ratio of ca. 13 resulted in the achievement of the highest *n*/iso values in a short time. A further increase in selectivity was achieved after the addition of water to the reaction mixture. The catalytic performance of the studied systems showed an increase in selectivity (*n*/iso) with the increase of the number of pyrrolyl groups in phosphine:  $(\text{P}(\text{NC}_4\text{H}_4)_3 > \text{PPh}(\text{NC}_4\text{H}_4)_2 > \text{PPh}_2(\text{NC}_4\text{H}_4) > \text{PPh}_3)$ .

Received 1st February 2017,  
Accepted 5th June 2017

DOI: 10.1039/c7cy00200a

[rsc.li/catalysis](http://rsc.li/catalysis)

## 1. Introduction

The olefin hydroformylation reaction (also known as the oxo synthesis or Roelen's reaction) is the oldest, largest, and most important homogeneously catalyzed industrial process for the production of aldehydes. This reaction was accidentally discovered by Otto Roelen in 1938 at Ruhrchemie, Germany, while he was studying the cobalt-catalyzed Fischer–Tropsch reaction.

Today rhodium is a metal of choice in industrial installations which produce mainly C4 aldehydes by the conversion of propylene. To achieve a high yield and selectivity towards aldehydes, the rhodium precursor should be modified by applying a ligand (preferably phosphorus), in high excess with respect to the metal.<sup>1–9</sup> Several factors are used to characterize the activity of the catalytic system, such as the turnover number (TON), turnover frequency (TOF), yield, reaction rate, selectivity, and *n*/iso ratio.<sup>10</sup>

*N*-Valeraldehyde, manufactured by the hydroformylation of 1-butene, is used as a chemical building block in the production of amyl alcohol (*n*-pentanol) and valeric acid. It is also

employed as a flavoring, a fragrance additive, a rubber accelerator, and in resin chemistry.<sup>11,12</sup>

The catalytic system composed of  $\text{Rh}(\text{acac})(\text{CO})_2$  and an *N*-pyrrolylphosphine ligand exhibited high regioselectivity towards linear aldehydes in the hydroformylation of 1-hexene<sup>9</sup> and vinylsilanes.<sup>10</sup> The results were significantly better than when  $\text{Rh}(\text{acac})(\text{CO})_2$  was applied with an excess of  $\text{PPh}_3$ . During the reaction, rhodium hydrido complexes containing pyrrolylphosphine ligands of the type  $\text{HRh}[\text{PPh}_x(\text{NC}_4\text{H}_4)_{3-x}]_4$  ( $x = 0–2$ ) and  $\text{HRh}(\text{CO})[\text{PPh}_x(\text{NC}_4\text{H}_4)_{3-x}]_3$  were identified as catalytically active species. These complexes also exhibited good catalytic activity in the hydrogenation of olefins and arenes.<sup>13</sup>

Jackstell *et al.* applied the same catalytic system in the hydroformylation of 2-pentene at a high pressure (50 bar) and 120 °C with an  $[\text{L}]/[\text{Rh}]$  ratio of 100. A good *n*/iso ratio was also obtained at a low pressure of syngas (10 bar) with a  $\text{P}(\text{NC}_4\text{H}_4)$  ligand.<sup>14</sup> van Leeuwen *et al.* demonstrated the high activity (TOF) and excellent selectivity of ethene hydroformylation in the presence of  $\text{P}(\text{NC}_4\text{H}_4)_3$ .<sup>15</sup> Similarly, Luo *et al.* reported high selectivity towards dialdehydes in the hydroformylation of dicyclopentadiene in the presence of  $\text{P}(\text{NC}_4\text{H}_4)_3$ .<sup>16</sup> The same system was used by Zheng *et al.* and it exhibited a high activity in the hydroformylation of  $\alpha$ -methylstyrene and enhanced regioselectivity towards the linear aldehydes (99%) with a high TOF (5786  $\text{h}^{-1}$ ) under mild conditions (syngas pressure of 6 MPa, 110 °C).<sup>17</sup> In contrast, Breit used the  $\text{P}(\text{NC}_4\text{H}_4)_3$  phosphine for the hydroformylation of styrene with low conversion and poor regioselectivity.<sup>18</sup> A good

<sup>a</sup> University of Wrocław, Faculty of Chemistry, 14 F. Joliot-Curie St., 50-383 Wrocław, Poland. E-mail: anna.trzeciak@chem.uni.wroc.pl

<sup>b</sup> Grupa Azoty, Zakłady Azotowe Kędzierzyn-Koźle S.A., Mostowa 30A, Kędzierzyn-Koźle, Poland

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7cy00200a



regioselectivity and high activity has been achieved in rhodium catalyzed hydroformylation of 1-octene with bidentate *N*-pyrrolylphosphine.<sup>19</sup>

In this paper, we present the application of rhodium systems modified by *N*-pyrrolylphosphines in the hydroformylation of 1-butene in toluene and in a toluene–water mixture. These systems showed a high regioselectivity towards *n*-valeraldehyde, in most cases higher than with the use of  $\text{PPh}_3$ .

## 2. Experimental

### 2.1. Materials

The rhodium complex  $\text{Rh}(\text{acac})(\text{CO})_2$  was synthesized according to the literature.<sup>20</sup> The *N*-pyrrolylphosphine ligands  $\text{P}(\text{NC}_4\text{H}_4)_3$ ,  $\text{PPh}(\text{NC}_4\text{H}_4)_2$ , and  $\text{PPh}_2(\text{NC}_4\text{H}_4)$  were synthesized as described in the literature.<sup>21</sup> Triphenylphosphine ( $\text{PPh}_3$ ) was purchased from Avocado; 1-butene was purchased from Air Liquide; hydrogen ( $\text{H}_2$ , 99.999%) and carbon monoxide ( $\text{CO}$ , 99.97%) were procured from Air Products.

### 2.2. Synthesis of $\text{HRh}(\text{CO})\{\text{P}(\text{NC}_4\text{H}_4)_3\}_3$ and $\text{HRh}\{\text{P}(\text{NC}_4\text{H}_4)_3\}_4$

The synthesis of  $\text{HRh}(\text{CO})\{\text{P}(\text{NC}_4\text{H}_4)_3\}_3$  and  $\text{HRh}\{\text{P}(\text{NC}_4\text{H}_4)_3\}_4$  was performed in a stainless autoclave (50 ml) under pressure of syngas ( $\text{H}_2/\text{CO} = 1$ ) and hydrogen, respectively. In a typical synthesis,  $\text{Rh}(\text{acac})(\text{CO})_2$ ,  $\text{P}(\text{NC}_4\text{H}_4)_3$  and toluene were introduced into the autoclave under a nitrogen atmosphere (Table 1), the autoclave was closed and flushed with  $\text{H}_2$  (5 bar) three times, and thereafter pressurized with syngas ( $\text{H}_2/\text{CO} = 1$ ) or hydrogen, heated to 80 °C and stirred for 1 h. After that time, the solvent was removed under vacuum and ethanol was added to precipitate the white complex<sup>9</sup> which was filtered and dried. In the case of  $\text{HRh}\{\text{P}(\text{NC}_4\text{H}_4)_3\}_4$ ,<sup>13</sup> the product was filtered and dried.

### 2.3. Hydroformylation of 1-butene

Hydroformylation reactions were carried out in 50 and 100 ml stainless steel autoclaves, each provided with a manometer, a thermostat, a magnetic stirrer, and a gas inlet/outlet system. The catalyst,  $\text{Rh}(\text{acac})(\text{CO})_2$  ( $1.5 \times 10^{-5}$  mol), with a 13-fold excess of  $\text{PPh}_3$ ,  $\text{P}(\text{NC}_4\text{H}_4)_3$ ,  $\text{PPh}_2(\text{NC}_4\text{H}_4)$ , or  $\text{PPh}(\text{NC}_4\text{H}_4)_2$ , was introduced into the autoclave. Next, 0.5 mL of toluene (solvent) and 0.25 mL of cyclohexane (internal standard) were added under a dinitrogen atmosphere. In the case of reactions carried out with water, 0.5–2 mL of distilled water was added. The autoclave was closed, flushed with 1-butene (2 bar) two or three times, and thereafter pressurized

with 1-butene (2 bar) and then with the synthesis gas ( $\text{H}_2:\text{CO} = 1:1$ ) to 10 bar and heated to 50–80 °C. After the reaction was finished, the autoclave was cooled to room temperature and the residual gases were depressurized. The catalyst was separated by vacuum transfer, and the obtained products were analyzed by means of GC and GC-MS (Hewlett Packard).

## 3. Results and discussion

The hydroformylation of 1-butene catalyzed by four catalytic systems containing the catalyst precursor  $\text{Rh}(\text{acac})(\text{CO})_2$  with a 13-fold excess of *N*-pyrrolylphosphine,  $\text{P}(\text{NC}_4\text{H}_4)_3$ ,  $\text{PPh}(\text{NC}_4\text{H}_4)_2$ ,  $\text{PPh}_2(\text{NC}_4\text{H}_4)$ , or triphenylphosphine  $\text{PPh}_3$ , was first investigated in toluene. Aldehydes were formed as the main reaction products, namely 1-pentanal (a linear aldehyde) and 2-methyl-butanal (a branched aldehyde) together with small amounts of 2-butene (isomerization product) (Scheme 1).

The results presented in Table 2 and in Fig. S1† illustrate the effect of temperature increase from 50 °C to 80 °C on the hydroformylation of 1-butene catalyzed by the catalytic system  $\text{Rh}(\text{acac})(\text{CO})_2 + \text{PPh}_2(\text{NC}_4\text{H}_4)$  with 2 bar of 1-butene and 10 bar of the synthesis gas ( $\text{H}_2/\text{CO} = 1$ ). An increase in the yield of aldehydes was observed with an increase in the temperature. Thus, when the temperature was raised from 50 to 80 °C, the *n*/*iso* ratio increased from 8.2 to 11.2. The TOF values also increased.

Much better results, in particular a higher rate and higher selectivity, were obtained in reactions performed with the addition of water to the reaction mixture. Thus, an increase in the water amount from 0.5 to 2 mL caused a remarkable increase in the *n*/*iso* ratio with a maximum value of 16.2. However, the TOF decreased during the same time from 800 to 667 h<sup>-1</sup> (Table 3, Fig. S2†). This is in agreement with our previous observation that regioselectivity was higher in the presence of water in a reaction mixture.<sup>22,23</sup> However, in contrast to other olefins,<sup>22</sup> the hydroformylation of 1-butene only in water was not successful because aldehydes were not formed.

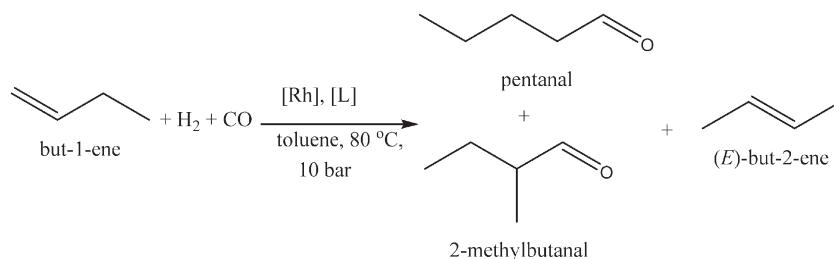
The effect of time was also studied in the catalytic system  $\text{Rh}(\text{acac})(\text{CO})_2 + \text{PPh}_2(\text{NC}_4\text{H}_4)$  at 80 °C (Table 4). The results showed an increase in the yield of aldehydes with the prolongation of the reaction time. However, simultaneously, *n*/*iso* also increased from 14.5 after a short time (4 min) (Table 3, entry 1) to 19.1 and 19.7 after 6 and 8 min of reaction time, respectively (Table 3, entries 2 and 3). Then, the *n*/*iso* ratio decreased to *ca.* 14 again. Fig. S3† displays the effect of time

Table 1 Synthesis of  $\text{HRh}(\text{CO})\{\text{P}(\text{NC}_4\text{H}_4)_3\}_3$  and  $\text{HRh}\{\text{P}(\text{NC}_4\text{H}_4)_3\}_4$  complexes<sup>a</sup>

Complex	$\text{Rh}(\text{acac})(\text{CO})_2$	$\text{P}(\text{NC}_4\text{H}_4)_3$	$P$ , bar	Yield
$\text{HRh}(\text{CO})\{\text{P}(\text{NC}_4\text{H}_4)_3\}_3$	0.078 g	0.24 g	10 bar of syngas ( $\text{H}_2/\text{CO} = 1$ )	0.18 g <sup>b</sup>
$\text{HRh}\{\text{P}(\text{NC}_4\text{H}_4)_3\}_4$	0.054 g	0.25 g	5 bar of $\text{H}_2$	0.085 g <sup>b</sup>

<sup>a</sup> Reaction conditions: toluene as the solvent (3 ml), 80 °C, 1 h. <sup>b</sup> 0.05 g of  $\text{HRh}(\text{CO})\{\text{P}(\text{NC}_4\text{H}_4)_3\}_3$  was also formed.





Scheme 1 Hydroformylation of 1-butene.

Table 2 Effect of temperature on 1-butene hydroformylation in toluene

Entry	T, °C	Conv. <sup>a</sup> %	Aldehydes, mol	n/iso	TOF, <sup>b</sup> mol mol <sup>-1</sup> h <sup>-1</sup>
1	80	95.0	0.010	11.2	667
2	70	94.6	0.011	10.2	733
3	60	92.7	0.010	8.3	667
4	50	45.5	0.003	8.2	200

Reaction conditions: [Rh] =  $1.5 \times 10^{-5}$  mol, [L]/[Rh] = 13, L = PPh<sub>2</sub>(NC<sub>4</sub>H<sub>4</sub>), P<sub>1</sub>-Butene = 2 bar, P<sub>(H<sub>2</sub>:CO=1:1)</sub> = 10 bar, toluene (0.5 mL), cyclohexane (0.25 mL), t = 1 h. <sup>a</sup> Conversion of 1-butene was calculated according to GC-FID analyses of the post-reaction mixture. <sup>b</sup> The TOF values were calculated as moles of the aldehyde/([moles of the catalyst]  $\times$  reaction time).

Table 3 Results of 1-butene hydroformylation in a toluene/water solution

Entry	Water, mL	Conv. <sup>a</sup> %	Aldehydes, mol	n/iso	TOF, <sup>b</sup> mol mol <sup>-1</sup> h <sup>-1</sup>
1	0.5	92.7	0.012	12.9	800
2	1	94.0	0.010	16.2	667
3	1.5	93.0	0.012	15.9	800
4	2	94.7	0.010	15.4	667

Reaction conditions: [Rh] =  $1.5 \times 10^{-5}$  mol, [L]/[Rh] = 13, L = PPh<sub>2</sub>(NC<sub>4</sub>H<sub>4</sub>), P<sub>1</sub>-Butene = 2 bar, P<sub>(H<sub>2</sub>:CO=1:1)</sub> = 10 bar, toluene (0.5 mL), cyclohexane (0.25 mL), t = 1 h, T = 80 °C. <sup>a</sup> Conversion of 1-butene was calculated according to GC-FID analyses of the post-reaction mixture. <sup>b</sup> The TOF values were calculated as moles of the aldehyde/([moles of the catalyst]  $\times$  reaction time).

Table 4 Results of 1-butene hydroformylation in toluene

Entry	t, min	Conv. <sup>a</sup> %	Aldehydes, mol	n/iso	TOF, <sup>b</sup> mol mol <sup>-1</sup> h <sup>-1</sup>
1	4	38.0	0.003	14.5	3000
2	6	53.9	0.005	19.1	3333
3	8	57.9	0.006	19.7	3000
4	10	75.3	0.008	15.5	3200
5	15	82.9	0.0105	14.4	2800
6	17	87.2	0.0109	14.2	2565

Reaction conditions: [Rh] =  $1.5 \times 10^{-5}$  mol, [L]/[Rh] = 13, L = PPh<sub>2</sub>(NC<sub>4</sub>H<sub>4</sub>), P<sub>1</sub>-Butene = 2 bar, P<sub>(H<sub>2</sub>:CO=1:1)</sub> = 10 bar, toluene (0.5 mL), cyclohexane (0.25 mL), T = 80 °C. <sup>a</sup> Conversion of 1-butene was calculated according to GC-FID analyses of the post-reaction mixture. <sup>b</sup> The TOF values were calculated as moles of the aldehyde/([moles of the catalyst]  $\times$  reaction time).

on the n/iso ratio, pressure drop, and the yield of *n* and iso aldehydes.

The effect of the [PPh<sub>2</sub>(NC<sub>4</sub>H<sub>4</sub>)]/[Rh] ratio on the reaction course was studied in the range from 2 to 13 at 80 °C and 10 bar. The results listed in Table 5 and in Fig. S4† show that, as the [PPh<sub>2</sub>(NC<sub>4</sub>H<sub>4</sub>)]/[Rh] ratio increased from 2 to 13, the *n*/iso ratio increased from 2.1 to 11.2. While selectivity increased in parallel with the amount of the phosphorus ligand; the highest TOF value was achieved at [L]/[Rh] = 6. A

further increase in the PPh<sub>2</sub>(NC<sub>4</sub>H<sub>4</sub>) amount caused a decrease in the TOF.

Applying the optimized reaction conditions, we tested three other catalytic systems composed of Rh(acac)(CO)<sub>2</sub> and P(NC<sub>4</sub>H<sub>4</sub>)<sub>3</sub>, PPh(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub> or PPh<sub>3</sub> (Table 6). It should be underlined that regioselectivity to *n*-pentanal was very high in both systems containing P(NC<sub>4</sub>H<sub>4</sub>)<sub>3</sub> or PPh(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub> ligands. An excellent conversion and lower regioselectivity were obtained by utilizing PPh<sub>3</sub>. On the other hand, a remarkable



Table 5 Effect of the [L]/[Rh] ratio on 1-butene hydroformylation

Entry	[L]/[Rh]	Conv. <sup>a</sup> %	Aldehydes, mol	n/iso	TOF, <sup>b</sup> mol mol <sup>-1</sup> h <sup>-1</sup>
1	2	83.2	0.008	2.1	533
2	4	91.7	0.010	2.4	667
3	6	96.7	0.011	4.3	733
4	8	95.2	0.010	7.2	667
5	10	96.6	0.010	8.9	667
6	13	95.0	0.010	11.2	667

Reaction conditions:  $[Rh] = 1.5 \times 10^{-5}$  mol,  $PPh_2(NC_4H_4)$  as the ligand,  $P_{1\text{-Butene}} = 2$  bar,  $P_{(H_2:CO=1:1)} = 10$  bar, toluene (0.5 mL), cyclohexane (0.25 mL),  $t = 1$  h,  $T = 80$  °C. <sup>a</sup> Conversion of 1-butene was calculated according to GC-FID analyses of the post-reaction mixture. <sup>b</sup> The TOF values were calculated as moles of the aldehyde/([moles of the catalyst]  $\times$  reaction time).

Table 6 Results of 1-butene hydroformylation using  $P(NC_4H_4)_3$ ,  $PPh(NC_4H_4)_2$  and  $PPh_3$  as modifying ligands

Entry	L	Conv. <sup>b</sup> %	Aldehydes, mol	n/iso	TOF, <sup>c</sup> mol mol <sup>-1</sup> h <sup>-1</sup>
1	$P(NC_4H_4)_3$	80.2	0.007	18.6	467
2 <sup>a</sup>		85.8	0.0082	23.1	547
3	$PPh(NC_4H_4)_2$	88.0	0.009	15.4	600
4 <sup>a</sup>		88.5	0.009	18.2	600
5	$PPh_3$	96.8	0.0132	5.8	880
6 <sup>a</sup>		94.5	0.0129	7.9	860

Reaction conditions:  $[Rh] = 1.5 \times 10^{-5}$  mol,  $[L]/[Rh] = 13$ ,  $P_{1\text{-Butene}} = 2$  bar,  $P_{(H_2:CO=1:1)} = 10$  bar, toluene (0.5 mL), cyclohexane (0.25 mL),  $t = 1$  h,  $T = 80$  °C. <sup>a</sup> Water (0.5 mL). <sup>b</sup> Conversion of 1-butene was calculated according to GC-FID analyses of the post-reaction mixture. <sup>c</sup> The TOF values were calculated as moles of the aldehyde/([moles of the catalyst]  $\times$  reaction time).

increase in the *n*/*iso* ratio was achieved after addition of water to the reaction media. It is also worth noting that the *n*/*iso* ratio increased with the increase in the number of pyrrolyl groups present in phosphine. It means that the *n*/*iso* ratio decreased in the following order:  $P(NC_4H_4)_3 > PPh(NC_4H_4)_2 > PPh_2(NC_4H_4) > PPh_3$  (Scheme 2).

Fig. S5† shows an increase of hydroformylation selectivity achieved by addition of water to the reaction mixture. The effect was noted for all studied phosphines; however, it was most pronounced for the best  $\pi$ -acceptor one,  $P(NC_4H_4)_3$ .

It should be noted that the yield of aldehydes increased with an increase in the autoclave volume. It was demonstrated for the  $Rh(acac)(CO)_2 + PPh_3$  system (Table 7). The yields of aldehydes were 0.022 and 0.013 mol in reactions carried out using 100 and 50 mL autoclaves, respectively, and 2

mL of toluene (Table 7). The *n*/*iso* ratio was, however, almost the same.

Considering the fact that a higher yield of aldehydes could be obtained in a larger-volume autoclave, the effect of the total pressure of the syngas ( $H_2 : CO = 1 : 1$ ) on the catalytic activity and regioselectivity towards the linear aldehyde was studied using a 100 mL autoclave. The results obtained at 4–10 bar and 80 °C for 2 h employing the catalytic systems  $[Rh(acac)(CO)_2/P(NC_4H_4)_3$ ,  $PPh(NC_4H_4)_2$ , or  $PPh_2(NC_4H_4)$ ] are shown in Table 8. Thus, the effect of pressure on the catalytic activity of the three systems and the amount of aldehydes decreased when the pressure of the syngas decreased from 10 to 4 bar. The *n*/*iso* ratio was affected differently, greatly increasing with a pressure decrease from 10 to 6 bar and then starting to decrease at 4 bar. As a result, the highest

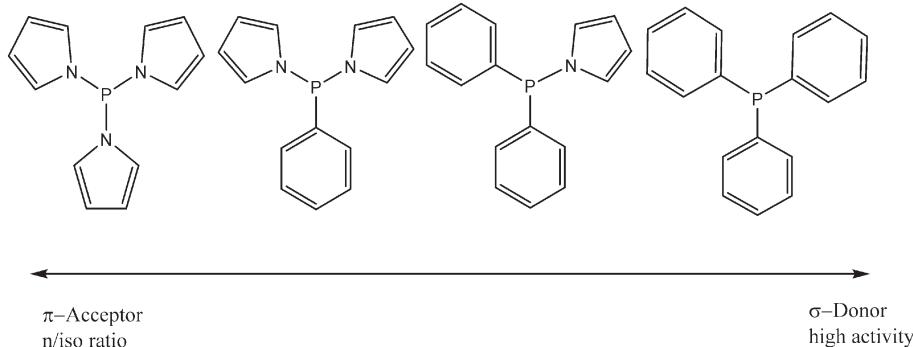
Scheme 2 The impact of the P ligand on the activity and the *n*/*iso* ratio.

Table 7 Hydroformylation of 1-butene using  $\text{PPh}_3$  as the ligand

Entry	Toluene, mL	Conv. <sup>b</sup> %	Aldehydes, mol	<i>n</i> /iso	TOF, <sup>c</sup> $\text{h}^{-1}$
1 <sup>a</sup>	2	97	0.022	3.6	733
2	2	95	0.013	3.8	867

Reaction conditions:  $[\text{Rh}] = 1.5 \times 10^{-5}$  mol,  $\text{PPh}_3$  as the ligand,  $[\text{L}]/[\text{Rh}] = 13$ ,  $P_{\text{1-Butene}} = 2$  bar,  $P_{(\text{H}_2:\text{CO}=1:1)} = 10$  bar, cyclohexane (0.25 mL),  $t = 1$  h,  $T = 80$  °C. <sup>a</sup> Autoclave 100 mL,  $t = 2$  h. <sup>b</sup> Conversion of 1-butene was calculated according to GC-FID analyses of the post-reaction mixture.

<sup>c</sup> The TOF values were calculated as moles of the aldehyde/([moles of the catalyst]  $\times$  reaction time).

Table 8 Effect of the  $\text{CO}/\text{H}_2$  pressure on hydroformylation of 1-butene catalyzed by  $\text{Rh}(\text{acac})(\text{CO})_2$  modified with different ligands

Entry	Ligand	<i>P</i> , bar	Conv. <sup>b</sup> %	Aldehydes, mol	<i>n</i> /iso	TOF, <sup>c</sup> $\text{mol mol}^{-1} \text{h}^{-1}$
1	$\text{P}(\text{NC}_4\text{H}_4)_3$	10	93.0	0.019	18.0	633
2		8	80.0	0.014	21.7	467
3 <sup>a</sup>			84.9	0.013	46.2	437
4		6	78.2	0.009	16.5	300
5 <sup>a</sup>			80.8	0.011	50.9	367
6		4	45.4	0.004	17.8	133
7	$\text{PPh}(\text{NC}_4\text{H}_4)_2$	10	96.0	0.021	11.2	700
8		8	94.0	0.018	22.5	600
9 <sup>a</sup>			90.7	0.017	26.8	567
10		6	93.2	0.017	24.2	563
11 <sup>a</sup>			81.5	0.011	31.2	367
12		4	68.8	0.007	20.0	233
13	$\text{PPh}_2(\text{NC}_4\text{H}_4)$	10	94.2	0.018	5.2	600
14		8	93.6	0.020	8.2	667
15 <sup>a</sup>			86.2	0.016	14.8	533.3
16		6	86.8	0.017	13.3	567
17 <sup>a</sup>			88.6	0.017	17.9	567
18		4	47.0	0.004	7.3	133

Reaction conditions:  $[\text{Rh}] = 1.5 \times 10^{-5}$  mol,  $[\text{L}]/[\text{Rh}] = 13$ ,  $P_{\text{1-Butene}} = 2$  bar,  $P_{(\text{H}_2:\text{CO}=1:1)} = 4-10$  bar, toluene (0.5 mL), cyclohexane (0.25 mL),  $t = 2$  h,  $T = 80$  °C. <sup>a</sup> Water (0.5 mL). <sup>b</sup> Conversion of 1-butene was calculated according to GC-FID analyses of the post-reaction mixture. <sup>c</sup> The TOF values were calculated as moles of the aldehyde/([moles of the catalyst]  $\times$  reaction time).

selectivity (*n*/iso) was achieved at 6 bar, whereas for  $\text{P}(\text{NC}_4\text{H}_4)_3$  the maximum was reached at 8 bar. Addition of water caused a significant increase in regioselectivity, and the *n*/iso ratio reached 50.9 at 6 bar using  $\text{P}(\text{NC}_4\text{H}_4)_3$  (Table 8, en-

try 5). The positive effect of water was also evidenced for other phosphines (Fig. 1).

The  $^{31}\text{P}$  NMR spectra measured after the hydroformylation of 1-butene showed evidence of rhodium species formed during the catalytic reaction. Catalytically active hydrido-carbonyl rhodium species  $[\text{RhH}(\text{CO})\text{L}_3]$  were formed in the reactions of  $\text{Rh}(\text{acac})(\text{CO})_2$  with an excess of *N*-pyrrolylphosphine ligands during hydroformylation. As shown in Table 9, the  $^{31}\text{P}$ -NMR data of the reaction products are in agreement with those reported earlier.<sup>9,13</sup>

The effect of water on hydroformylation of 1-butene was also studied by utilizing  $\text{HRh}(\text{CO})\{\text{P}(\text{NC}_4\text{H}_4)_3\}_3$  and  $\text{HRh}\{\text{P}(\text{NC}_4\text{H}_4)_3\}_4$  complexes as catalysts. In the absence of an added ligand,  $\text{HRh}(\text{CO})\{\text{P}(\text{NC}_4\text{H}_4)_3\}_3$  exhibited high catalytic activity in both reaction media, namely toluene and the water–toluene mixture. Conversion and selectivity were almost the same in both system; however, the *n*/iso ratio was slightly higher in a water–toluene mixture (Table 10, entries 1 and 2). Addition of 3-fold excess of the  $\text{P}(\text{NC}_4\text{H}_4)_3$  ligand increased the *n*/iso ratio to 4 and 4.8, respectively (Table 10, entries 3 and 4). The reaction rate and conversion decreased at 13-fold excess of  $\text{P}(\text{NC}_4\text{H}_4)_3$  with a significant increase in regioselectivity towards the linear aldehyde. Thus, the *n*/iso ratio

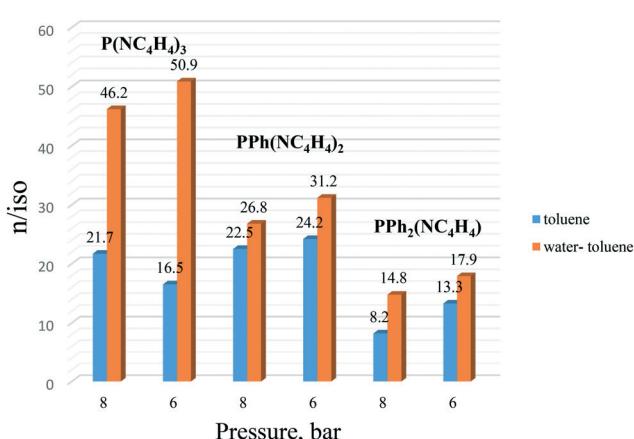


Fig. 1 Effect of water and pressure on 1-butene hydroformylation catalyzed by  $\text{Rh}(\text{acac})(\text{CO})_2$  modified with different ligands at 80 °C in a 100 mL autoclave.



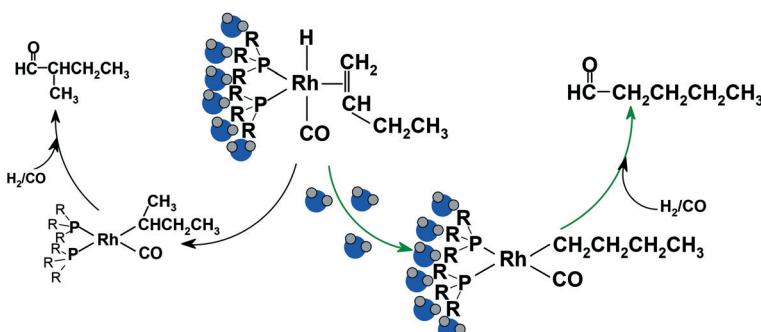
**Table 9**  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) data for  $[\text{RhH}(\text{CO})\text{L}_3]$  complexes obtained *in situ* during 1-butene hydroformylation catalyzed by  $\text{Rh}(\text{acac})(\text{CO})_2$ 

Complex	$^1\text{H}$ [ $J(\text{P}-\text{H}), J(\text{Rh}-\text{H})/\text{Hz}$ ]	$^{31}\text{P}$ [ $J_{(\text{Rh}-\text{P})}$ , Hz]
$\text{RhH}(\text{CO})\{\text{PPh}_2(\text{NC}_4\text{H}_4)\}_3$ (ref. 9)	-8.9 [12.0, <1]	87.7 [168.8]
$\text{RhH}(\text{CO})\{\text{PPh}(\text{NC}_4\text{H}_4)\}_3$	-9.0 [9.3, 1.8]	108.5 [187]
$\text{RhH}(\text{CO})\{\text{P}(\text{NC}_4\text{H}_4)\}_3$ (ref. 9)	-9.1 [7.8, 2.7]	108.6 [211.5]

**Table 10** The effect of water on hydroformylation of 1-butene catalyzed by  $\text{HRh}(\text{CO})\{\text{P}(\text{NC}_4\text{H}_4)\}_3$  and  $\text{HRh}\{\text{P}(\text{NC}_4\text{H}_4)\}_4$ 

Entry	Catalyst	$[\text{L}]/[\text{Rh}]$	Conv. <sup>a</sup> %	Water, mL	Aldehydes, mol	$n/\text{iso}$	TOF, <sup>b</sup> mol mol <sup>-1</sup> h <sup>-1</sup>
1	$\text{HRh}(\text{CO})\{\text{P}(\text{NC}_4\text{H}_4)\}_3$	0	95.0	—	0.0129	1.7	860
2			96.5	0.5	0.012	1.9	800
3		3	95.5	—	0.0112	4.0	746.7
4			96.0	0.5	0.012	4.8	800
5		13	83.3	—	0.0097	19.7	646.7
6			84.5	0.5	0.0096	31.3	640
7	$\text{HRh}\{\text{P}(\text{NC}_4\text{H}_4)\}_4$	0	94.0	—	0.0115	2.5	766.7
8			90.0	0.5	0.0123	3.0	820

Reaction conditions:  $[\text{Rh}] = 1.5 \times 10^{-5}$  mol,  $\text{L} = \text{P}(\text{NC}_4\text{H}_4)_3$ ,  $P_{1\text{-Butene}} = 2$  bar,  $P_{(\text{H}_2:\text{CO}=1:1)} = 10$  bar, toluene (0.5 mL), cyclohexane (0.25 mL),  $t = 1$  h,  $T = 80$  °C. <sup>a</sup> Conversion of 1-butene was calculated according to GC-FID analyses of the post-reaction mixture. <sup>b</sup> The TOF values were calculated as moles of the aldehyde/([moles of the catalyst]  $\times$  reaction time).

**Scheme 3** The tentative illustration of the effect of water on hydroformylation selectivity.

increased from 19.7 to 31.3 (Table 10, entries 5 and 6). The unmodified  $\text{HRh}\{\text{P}(\text{NC}_4\text{H}_4)\}_4$  catalyst also displayed a higher  $n/\text{iso}$  ratio after the addition of water to the reaction (Table 10, entries 7 and 8).

## 4. Conclusions

The hydroformylation of 1-butene catalyzed by  $\text{Rh}(\text{acac})(\text{CO})_2$  with an excess of *N*-pyrrolylphosphine and  $\text{PPh}_3$  ligands at 50–80 °C and 4–10 bar of syngas ( $\text{H}_2:\text{CO} = 1:1$ ) in toluene and in a toluene/water mixture was investigated. Hydrido-carbonyl rhodium species were formed *in situ* during the hydroformylation. Regioselectivity towards the linear aldehyde increased with the increase in the number of the pyrrolyl groups in phosphine ligands. At the same time, the reaction rate decreased in the same order. Thus, better  $\pi$ -acceptor properties of the ligand promote the increase in the  $n/\text{iso}$  ratio.

Regioselectivity is highly dependent on the reaction conditions, such as temperature or the  $[\text{L}]/[\text{Rh}]$  molar ratio. In addition, remarkably high regioselectivity towards the linear aldehyde was noted in a shorter reaction time or at a lower syngas pressure.

Interestingly, a similar effect, namely a selectivity increase, was also observed after the introduction of water to the reaction mixture. Moreover, an increase in the  $n/\text{iso}$  ratio was in this case dependent on the kind of phosphine used. It can be, therefore, assumed that water interacted with the hydrido-olefin rhodium intermediate facilitating the formation of the linear alkyl complex in the migratory insertion step. The effect of water on the increase in the  $n/\text{iso}$  ratio was most clearly pronounced for the  $\text{P}(\text{NC}_4\text{H}_4)_3$  ligand, suggesting an important role of N atoms in the formation of hydrogen bonds. Such an interaction caused the decrease in the electron density on the rhodium center, which is then reflected in the migratory insertion step (Scheme 3) leading



to the anti-Markovnikov (linear) product. In summary, we suppose that selectivity of hydroformylation increased because  $\pi$ -acceptor properties of P-ligands were further enhanced by interactions with water molecules.

However, interactions of water with the hydride ligand or with coordinated olefin could be also considered. Water can also facilitate the formation of rhodium hydride, which is catalytically active. It is possible that water enhances the hydride transfer step.<sup>24</sup>

According to the well accepted scheme of hydroformylation, based on theoretical calculations published till now, the insertion step is the rate-determining step for hydroformylation regioselectivity.<sup>25–28</sup> Thus, stabilization of the transition state leading to the linear Rh-alkyl intermediate results in an increase in the linear aldehyde amount and, consequently, in a higher *n*/iso ratio. This is observed in the presence of water in our system. It could be therefore proposed that nonbonding interactions of water molecules with phosphines, olefin and the hydride ligand present in the coordination sphere of rhodium decrease the activation energy of the transition state leading to the linear Rh-alkyl intermediate. In this way, the reaction pathway that leads to the linear aldehyde is favored. This hypothesis, based on experimental results, should be verified by theoretical calculations which are in progress.

## Acknowledgements

This work was done within the cooperation between Grupa Azoty Zaklady Azotowe Kedzierzyn S. A. and the Faculty of Chemistry, University of Wroclaw with the financial support from the Polish Ministry of Development under the grant POIR.02.01.00-00-0074/15-01.

## References

- 1 *Applied Homogenous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Two Volumes*, ed. B. Cornils and W. A. Herrmann, VCH Weinheim, 1996.
- 2 *Rhodium Catalysed Hydroformylation*, ed. P. W. N. M. van Leeuwen and C. Claver, Kluwer Academic Publisher, Dordrecht, 2000.
- 3 *Metal Catalysis in Industrial Organic Processes*, ed. G. P. Chiusoli and P. M. Maitlis, PSC Publishing, 2006.
- 4 *Transition Metals for Organic Synthesis. Building Blocks and Fine Chemicals*, ed. M. Beller and C. Bolm, Wiley-VCH Verlag GmbH & Co. KGaA, 2004.
- 5 M. Beller, B. Cornils, C. D. Frohning and C. W. Kohlpaintner, *J. Mol. Catal. A: Chem.*, 1995, **104**, 17.
- 6 A. M. Trzeciak and J. J. Ziolkowski, *Coord. Chem. Rev.*, 1999, **190**–192, 883.
- 7 A. M. Trzeciak, Hydroformylation, in *Comprehensive Inorganic Chemistry II: from elements to applications*, ed. J. Reedijk and K. Poeppelmeier, Elsevier, Amsterdam, 2013, vol. 6, p. 25.
- 8 W. Gil and A. M. Trzeciak, *Coord. Chem. Rev.*, 2011, **255**, 473.
- 9 A. M. Trzeciak, T. Glowiaik, R. Grzybek and J. J. Ziolkowski, *J. Chem. Soc., Dalton Trans.*, 1997, 1831.
- 10 A. M. Trzeciak, J. J. Ziolkowski and B. Marciniec, *C. R. Acad. Sci., Ser. IIc: Chim.*, 1999, **2**, 235.
- 11 *Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens*, ed. R. P. Pohanish, M. Sittig, 2008.
- 12 M. Yuan, H. Chen, R. Li, Y. Li and X. Li, *Appl. Catal., A*, 2003, **251**, 181.
- 13 A. M. Trzeciak, T. Glowiaik and J. J. Ziolkowski, *J. Organomet. Chem.*, 1998, **552**, 159.
- 14 R. Jackstell, H. Klein, M. Beller, K. D. Wiese and D. Rottger, *Eur. J. Org. Chem.*, 2001, 3871.
- 15 O. Diebolt, H. Tricas, Z. Freixa and P. W. N. M. van Leeuwen, *ACS Catal.*, 2013, **3**, 128.
- 16 R. Luo, H.-R. Liang, X.-L. Zheng, H.-Y. Fu, M.-L. Yuan, R.-X. Li and H. Chen, *Catal. Commun.*, 2014, **50**, 29.
- 17 X.-L. Zheng, C.-Y. Zheng, F.-D. Zhou, H.-Y. Fu, M.-L. Yuan, R.-X. Li, B. Xu and H. Chen, *Chin. Chem. Lett.*, 2016, **27**, 678.
- 18 (a) B. Breit, *Chem. Commun.*, 1996, 2071; (b) B. Breit, *J. Mol. Catal.*, 1999, **143**, 143.
- 19 L. Zhang, C. Li, X. L. Zheng, R. X. Li and H. Chen, *Asian J. Chem.*, 2015, **27**, 1371.
- 20 S. Yu. Varshavsky and T. G. Cherkasova, *Zh. Neorg. Khim.*, 1967, **12**, 1709.
- 21 K. G. Moloy and J. L. Petersen, *J. Am. Chem. Soc.*, 1995, **117**, 7696.
- 22 W. Alsalahi and A. M. Trzeciak, *RSC Adv.*, 2014, **4**, 30384.
- 23 W. Alsalahi and A. M. Trzeciak, *J. Mol. Catal. A: Chem.*, 2016, **423**, 41.
- 24 V. Polo, R. R. Schrock and L. A. Oro, *Chem. Comm.*, 2016, **52**, 13881.
- 25 M. Kumar, R. V. Chaudhari, B. Subramaniam and T. A. Jackson, *Organometallics*, 2014, **33**, 4183.
- 26 P. Dydio, R. J. Detz and J. N. H. Reek, *J. Am. Chem. Soc.*, 2013, **135**, 10817.
- 27 R. P. Dias, M. S. L. Prates, Jr., W. B. de Almeida and W. R. Rocha, *Int. J. Quantum Chem.*, 2011, **111**, 1280.
- 28 S. Aguado-Ullate, J. A. Baker, V. González-González, C. Müller, J. D. Hirst and J. J. Carbo, *Catal. Sci. Technol.*, 2014, **4**, 979.