Rhodium(I) N-Heterocyclic Carbene Complexes as Highly Selective Catalysts for 1-Hexene Hydroformylation

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Rhodium(I) carbene complexes of the type [Rh(NHC)(cod)X] (where NHC = N-heterocyclic carbene obtained from dialkylimidazolium cation; cod = 1,5-cyclooctadiene; X = Cl, Br, I, SCN) with $P(OPh)_3$ as a modifying ligand have been found to be very active catalysts for 1-hexene hydroformylation under mild conditions (80 °C, 10 atm of H_2/CO, 4 h). Even at a low rhodium concentration ([1-hexene]/[Rh] = 2000), aldehydes have been obtained in yields of up to 90% with a high n/iso ratio of ca. 7. During the catalytic process, rhodium(I) carbene complexes, $[Rh(NHC)(P(OPh)_3)_2X]$, reacted with H_2/CO, giving a catalytically active rhodium(I) hydrido complex containing an N-heterocyclic carbene ligand. The presence of $[HRh(CO)(P(OPh)_3)_3]$ and $[Rh(NHC)(P(OPh)_3)(CO)X]$ complexes in the catalytic system has been confirmed. When $P(OCH_2CF_3)_3$ was used as modifying ligand with [Rh(NHC)(cod)Br] as catalyst precursor, formation of $[HRh(CO)(NHC)(P(OCH_2CF_3)_3)_2]$ with a square-pyramidal structure was evidenced by ^1H and ^{31}P NMR.

Introduction

In the hydroformylation reaction, which is one of the most important industrial processes, soluble rhodium(I) complexes are typically used as catalyst precursors together with a high excess of phosphorus ligands.[1–3] Such modifying ligands usually make it possible to create sufficient electron density on the rhodium(I) center to facilitate maximum conversion of terminal olefins to linear aldehydes, the desired hydroformylation reaction products.[1–3] The appropriate selection of modifying ligand is based on a compromise between steric and electronic properties. Among monodentate phosphorus ligands, those having stronger π-acceptor properties often produce aldehydes with higher n/iso ratios. In the case of bidentate ligands, an essential role is played by both the P−Rh−P angle (bite angle) and the geometry of the active rhodium complex.[1–4]

N-heterocyclic carbenes are comparable to phosphorus ligands and therefore are of great interest as potential non-phosphorus modifying ligands for rhodium catalysts for olefin hydroformylation. The results of theoretical calculations have suggested that mixed-ligand systems, composed of NHC and phosphorus ligands, can also exhibit high catalytic activity in hydroformylation.[6]

In recent years only a few papers dealing with the application of Rh(I) carbene complexes as hydroformylation catalysts have been published. The first one presented the use of $[Rh(NHC)(PPh_3)_2Cl]$ and $[Rh(NHC)(CO)(PPh_3)Cl]$ complexes in the hydroformylation of styrene.[7] In this reaction, both conversion and selectivity to branched aldehydes were higher than those for $[RhCl(CO)(PPh_3)_2]$ used as a catalyst precursor. For rhodium carbene complexes with acetate instead of halogen ligands, even higher regioselectivity has been obtained in the hydroformylation of vinylarenes.[8] Different Rh(I) carbene complexes with imidazole, xanthin, and tetrazole derivatives as ligands have been used as catalysts in the hydroformylation of 1-octene at 50 bar of pressure.[9] Complexes with imidazol-2-ylidene ligands showed high activity, expressed by TOF values of 1150−1785 h^{-1}. In all cases the n/iso ratio dropped from 2.6 at the beginning of the reaction to 0.7 at ca. 50% conversion. The authors concluded that electron-poor carbene ligands led to a higher hydroformylation activity.[9] Rhodium complexes with carbenes obtained from substituted pyrimidines have been tested in 1-octene hydroformylation at 50 bar, and an influence of substituents on the reaction rate was found.[10]

A rhodium carbene complex immobilized on a water-soluble amphiphilic block copolymer was an active catalyst for 1-octene hydroformylation at 50 bar, giving TOF values of up to 2360 h^{-1}.[11] The n/iso ratio changed in successive cycles from 2.6 in the first cycle to 1.22 in the third and fourth cycles.[11] A dirhodium bisimidazolium−-carbene complex showed good selectivity for the branched aldehyde in styrene hydroformylation at 30−80 °C.[12] High-pressure NMR spectroscopy provides evidence that the dinuclear unit is maintained under catalytic conditions.[12] A rhodium complex with a noncyclic imino-NHC ligand was used in 1-octene hydroformylation at 8−55 bar, and aldehydes were obtained with yields of 10−99% and n/iso ratios

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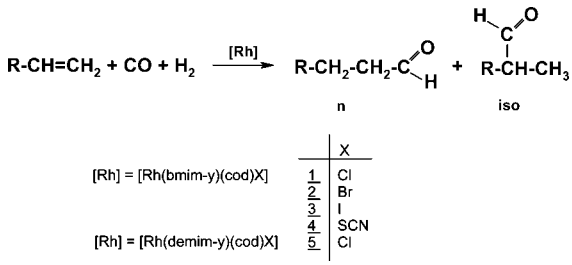
Scheme 1



of 0.82−1.9.[13] Thione complexes were found to be better catalysts for 1-hexene hydroformylation than carbene complexes, although rather low selectivity (n/iso = ca. 1) was noted for both types of precursors.[14]

The aim of the studies presented in this paper was to test Rh−NHC bond containing complexes as catalyst precursors for 1-hexene hydroformylation under mild conditions (10 atm, 80 °C). To achieve this goal, we selected a catalytic system in which Rh−NHC complexes of the general formula [Rh(NHC)(cod)X] were modified with an additional phosphorus ligand, in this case $P(OPh)_3$, and formed [Rh(NHC)$(P(OPh)_3)_2$X] precursors.

Results and Discussion

Five Rh(I) complexes with N-heterocyclic carbene ligands were synthesized and tested as catalyst precursors in 1-hexene hydroformylation: [Rh(bmim-y)(cod)Cl] (**1**), [Rh(bmim-y)(cod)Br] (**2**), [Rh(bmim-y)(cod)I] (**3**), [Rh(bmim-y)(cod)SCN] (**4**), and [Rh(demim-y)(cod)Cl] (**5**), where bmim-y = 1-butyl-3-methylimidazolin-2-ylidene and demim-y = 1,3-diethoxymethylimidazolin-2-ylidene (Scheme 1).

Complexes **1**−**3** have been previously tested by us in the polymerization of phenylacetylene.[15] Complexes **4** and **5** were obtained for the first time, and the molecular structure of **4** was determined by X-ray diffraction (Figure 1). The most characteristic Rh−C11 distance in **4**, amounting to 2.046(2) Å, is similar to that in other carbene rhodium complexes.[8,16,17]

[Rh(NHC)(cod)X] complexes **1**−**5**, used without any phosphorus modifying ligand added, did not produce aldehydes or 2-hexene under the applied reaction conditions (80 °C, 10 atm). However, after $P(OPh)_3$ addition, a catalytic system was formed in situ and aldehydes were obtained with a yield of ca. 80% together with ca. 20% of 2-hexene. The n/iso ratio is clearly dependent on the amount of $P(OPh)_3$ and increased from 3.6 at $[P(OPh)_3]/[Rh] = 1$ to 7.8 at $[P(OPh)_3]/[Rh] = 3$. It is interesting to note that the amount of phosphite impacted on the value of the n/iso ratio but not on the total yield of aldehydes, as illustrated by the data in Table 1.

All of the tested rhodium(I) complexes with NHC ligands used with the addition of $P(OPh)_3$ produced aldehydes with a high n/iso ratio, ca. 7−8, remarkably higher than that obtained with other precursors under similar conditions.[18,19] The yield of aldehydes, 80−85%, only slightly depended on the catalysts concentration. When the molar ratio [1-hexene]/[Rh] increased from 500 to 2000, both the yield of aldehydes and the n/iso ratio decreased only slightly. Only in the case of **3** did the yield of aldehydes drop to 32% at the [1-hexene]/[Rh] ratio of 2000 (Table 2). Two parameters were used for characterization of the catalytic activity of the systems under studies (Table 2). The first one was a rate of pressure drop in time and the second, catalyst turnover frequency, TOF, that is usually used for description of the catalytic systems. Both parameters indicated the similar and reasonably high catalytic activity of the systems containing complexes **1**−**5** and $P(OPh)_3$.

Under the same reaction conditions, the complex [HRh(CO)$(P(OPh)_3)_3$], known as a catalytically active form of rhodium in all systems with $P(OPh)_3$ as a modifying ligand,[20] was tested for comparison. Its very high activity not only in hydroformylation but also in isomerization of 1-hexene to 2-hexene may explain the low n/iso ratio (1.3) obtained in hydroformylation with that complex alone (Table 3). Another reaction was conducted in the presence of imidazolium ionic liquid, using a [HRh(CO)$(P(OPh)_3)_3$] + [bmim]Br mixture as a catalyst. First, the mixture was heated in 1-hexene for 20 min; next, H_2/CO was added and the reaction was carried out for 4 h. In this

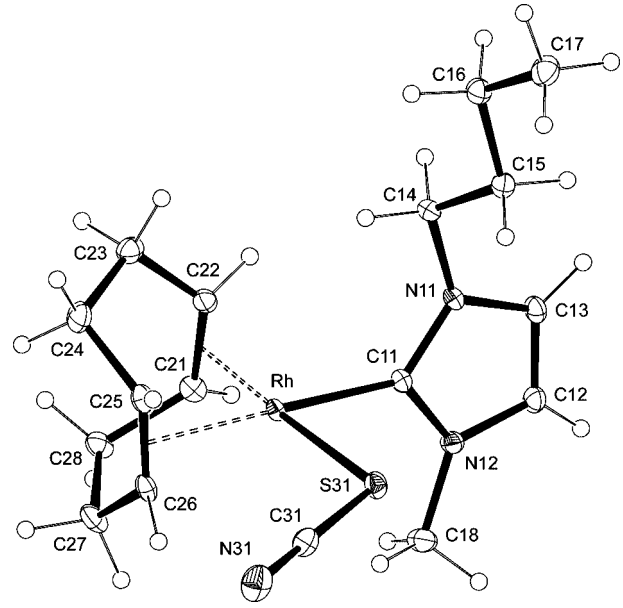


Figure 1. Crystal structure of [Rh(bmim-y)(η^4-1,5-cod)SCN], (4). Selected bond distances (Å) and angles (deg): Rh−C11, 2.046(2); Rh−Cg1, 2.020(2); Rh−Cg2, 2.086(2); Rh−S31, 2.3638(8); C11−Rh−Cg1, 91.28(6); C11−Rh−S31, 84.48(4); Cg1−Rh−Cg2, 86.63(6); Cg2−Rh−S31, 97.57(6). Cg1 and Cg2 denote the midpoints of the C21−C22 and C25−C26 double bonds, respectively.

Table 1. Influence of $P(OPh)_3$ Concentration on the Yield of Aldehydes Obtained in the Hydroformylation of 1-Hexene Catalyzed by 1[a]

$[P(OPh)_3]/[1]$	aldehyde (%)	*n*-heptanal (%)	2-hexene	n/iso
1	79.9	62.5	2.9	3.6
2	81.7	71.1	5.2	6.7
3	79.7	70.3	19.6	7.5
4	76.0	67.4	17.9	7.9

[a] Reaction conditions: [Rh] = 1.38×10^{-5} mol, [1-hexene]/[Rh] = 1000, 80 °C, 10 atm of H_2/CO, 4 h.

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Table 2. Influence of [1-Hexene]/[Rh] Ratio on the Yield of Aldehydes and n/iso Ratio[a]

		amt (%)					
cat.	[1-hexene]/[Rh]	aldehydes	*n*-heptanal	2-hexene	n/iso	activity[b] (atm/min)	TOF[c] (h^{-1})
1	500	81.5	72.2	16.4	7.8		
1	1000	81.7	71.1	5.2	6.7	0.088	350
1	2000	79.9	68.7	4.2	6.2		
2	500	80.4	71.3	5.5	7.8		
2	1000	80.8	71.1	5.6	7.3	0.098	404
2	2000	76.1	66.4	17.2	6.9		
3	500	79.1	70.1	17.4	7.8		
3	1000	76.9	67.5	18.2	7.2	0.054	231
3	2000	32.0	27.7	4.9	6.4		
4	1000	81.4	70.7	5.0	6.6	0.108	407
4	2000	73.7	64.7	15.2	7.2		
5	1000	80.8	70.3	5.3	6.7	0.087	485
5	2000	78.5	67.2	19.6	5.9		

[a] Reaction conditions: $[P(OPh)_3]/[Rh] = 2$, 80 °C, 10 atm of H_2/CO, 4 h. [b] The activity (rate of pressure drop in time) was determined as tan α taken from the linear part of the plot pressure vs time (after an induction period). [c] TOF in units of (mol of aldehyde) (mol of Rh)$^{-1}$ h^{-1}.

Table 3. Results of 1-Hexene Hydroformylation Catalyzed by $[HRh(CO)(P(OPh)_3)_3]$ and $[Rh_4(CO)_8(P(OPh)_3)_4]$[a]

		amt (%)			
entry	cat.	aldehyde	*n*-heptanal	2-hexene	n/iso
1	$HRh(CO)P_3$	88.8	50.9	11.0	1.3
2	$HRh(CO)P_3$ + [bmim]Br	88.0	50.6	11.9	1.4
3	$HRh(CO)P_3$ + **2**	82.1	49.4	17.8	1.5
4	$HRh(CO)P_3$ + **2** + 2 P	86.3	53.7	11.0	1.6
5[b]	$Rh_4(CO)_8P_4$	80.0	47.1	19.7	1.4
6[b]	$Rh_4(CO)_8P_4$ + 4 [bmim]Br	82.0	54.1	17.8	1.9
7	$Rh(acac)P_2$	85.9	48.8	14.1	1.3
8	$Rh(acac)P_2$ + [bmim]Br	85.7	50.6	14.3	1.4

[a] Reaction conditions (unless otherwise noted) and abbreviation: $[Rh] = 7.0 \times 10^{-6}$ mol, [1-hexene]/[Rh] = 2000, 80 °C, 10 atm of H_2/CO, 4 h; $P = P(OPh)_3$ [b] $[Rh] = 1.38 \times 10^{-5}$ mol, [1-hexene]/[Rh] = 1000.

experiment the yield (88%) and the n/iso ratio (1.4) obtained were similar to those with $[HRh(CO)(P(OPh)_3)_3]$ alone (Table 3). Additional experiments were performed with the equimolar mixture of **2** and $[HRh(CO)(P(OPh)_3)_3]$ to see whether or not this composition of catalyst precursor changes the selectivity and whether or not the induction period remains. In both reactions (Table 3) the induction period was not observed and the reaction was complete in ca. 2 h. The final n/iso ratio was equal to 1.5 or 1.6, almost the same as with $[HRh(CO)(P(OPh)_3)_3]$ only. The presence of **2** had practically no influence on the reaction course catalyzed by carbene-free hydride. This may suggest that the less selective $[HRh(CO)(P(OPh)_3)_3]$ is more active than the rhodium hydrido carbene complex, but in a real catalytic system it exists in a very low concentration. Probably the carbene-free hydride is formed after the induction period necessary to produce the rhodium hydrido carbene, a less active but more selective species. This conclusion is to some extent supported by the analysis of the n/iso ratio over time in the reaction catalyzed by **2** + 2 $P(OPh)_3$. The n/iso ratio changed only slightly and was equal to 5.1, 6.6, and 6.3 after 30, 60, and 120 min, respectively.

When$[Rh_4(CO)_8(P(OPh)_3)_4]$ was used as a hydroformylation catalyst precursor, aldehydes were formed with a yield of ca. 80% and the n/iso ratio was 1.4. In the same reaction carried out with the addition of [bmim]Br, 82% of aldehydes with an n/iso ratio of 1.9 was obtained (Table 3). Similarly, the presence of [bmim]Br had practically no effect on the composition of products formed in hydroformylation catalyzed by $[Rh(acac)(P(OPh)_3)_2]$ (Table 3).

It was found that the presence of [bmim]Br caused inhibition of the isomerization of 1-hexene to 2-hexene. When the complex

Table 4. Effect of [bmim]Br in the Isomerization Reaction of 1-Hexene Catalyzed by $HRh(CO)(P(OPh)_3)_3$[a]

		amt (%)	
entry	cat.	1-hexene	2-hexene
1	$HRh(CO)P_3$	81.5	18.5
2	$HRh(CO)P_3$ + [bmim]Br	100	0

[a] Reaction conditions: $[Rh] = 7.0 \times 10^{-6}$ mol, [hexene]/[Rh] = 2000, 80 °C, 20 min.

Table 5. Effect of [bmim]Br in the Hydroformylation Reaction Catalyzed by $[Rh(acac)(CO)_2]$[a]

		amt (%)			
entry	cat.	2-hexene	*n*-heptanal	iso aldehyde	n/iso
1	$Rh(acac)(CO)_2$	90.4	3.7	2.5	1.4
2	$Rh(acac)(CO)_2$ + [bmim]Br	51.5	0.4		

[a] Reaction conditions: $[Rh] = 7.0 \times 10^{-6}$ mol, [hexene]/[Rh] = 2000, 80 °C, 10 atm of H_2/CO, 4 h.

$[HRh(CO)(P(OPh)_3)_3]$ alone was warmed with 1-hexene for 20 min under an N_2 atmosphere, 18.5% of 2-hexene was produced. Isomerization was completely restrained in the presence of [bmim]Br (Table 4). Similar inhibition of isomerization was also observed for $[Rh(acac)(CO)_2]$ used as a catalyst precursor, which was very active in the isomerization of 1-hexene under an H_2/CO atmosphere and produced 90.4% of 2-hexene. The addition of an equimolar amount of [bmim]Br caused a decrease in the yield of 2-hexene to 51.5% (Table 5).

Unexpectedly, catalytic systems composed with [Rh(NHC)-(cod)X] complexes and stoichiometric amounts of $P(OPh)_3$ do not lose their catalytic activity after the first cycle and the recycled catalyst can be successfully used again. The organic products and unreacted substrates can be removed easily by the vacuum transfer technique, and a new portion of 1-hexene can be added to the solid residue containing the rhodium species. In most such experiments an increase in aldehyde yield and a small decrease in the n/iso ratio were observed (Table 6, Figure 2).

The measure of the pressure drop during the hydroformylation reaction made it possible to note the induction period for all catalyst precursors. During the induction time, lasting ca. 50 min, the pressure in the autoclave was constant at ca. 12 atm, after increasing from 10 atm as a result of the temperature increase to 80 °C. Only in the case of catalyst **5** did the reaction start more quickly. It is also characteristic that recycled reactions started practically without any induction time, which may

Table 6. Results of 1-Hexene Hydroformylation in Recycling Experiments with Catalysts 1−5[a]

		amt (%)					
[1-hexene]/[Rh]	recycled cat.[a]	aldehydes	*n*-heptanal	2-hexene	n/iso	activity[c] (atm/min)	TOF[c] (h^{-1})
1000	**1**	92.4	73.1	6.1	3.8	0.165	792
2000[b]	**1**	88.6	65.0	1.3	2.8		
1000	**2**	86.9	70.9	1.7	4.4	0.148	852
2000[b]	**2**	75.9	62.8	6.3	4.8		
1000	**3**	83.2	68.7	2.8	4.7	0.168	713
2000[b]	**3**	65.7	55.4	13.0	5.4		
1000	**4**	83.2	71.4	2.9	6.0	0.108	624
2000[b]	**4**	77.8	65.7	19.1	5.4		
1000	**5**	84.8	69.5	2.3	4.5	0.112	509
2000[b]	**5**	70.8	57.4	26.3	4.3		

[a] The catalysts **1−5** have been obtained from experiments collected in Table3. Reaction conditions (unless otherwise noted): [Rh] = 1.38×10^{-5} mol, [P]/[Rh] = 2, 80 °C, 10 atm of H_2/CO, 4 h. [b] [Rh] = 7.0×10^{-6} mol. [c] See Table2.

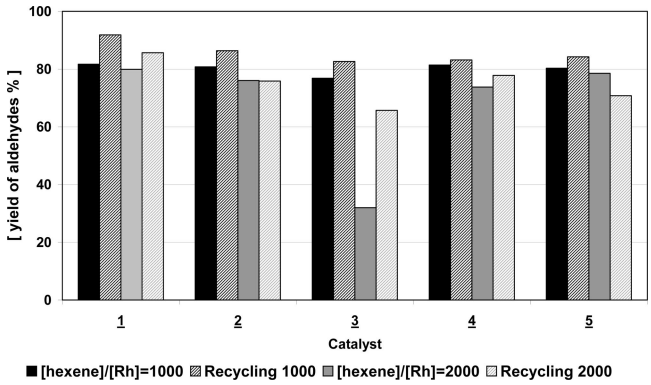


Figure 2. Yield of aldehydes obtained in two cycles of 1-hexene hydroformylation at different [1-hexene] to [Rh] ratios.

confirm the presence of catalytically active forms in a postreaction mixture. In all recycling experiments TOF values were remarkably higher than in the first entries; only for the catalyst **5** were similar results observed in both cases (Table 6).

It was expected that not only $P(OPh)_3$ but also other phosphorus ligands can form attractive catalytic systems with Rh(I) N-heterocyclic carbene precursors. Thus, hydroformylation experiments were performed under standard conditions, and surprisingly, only for $P(NC_4H_4)_3$ and $P(OCH_2CF_3)_3$ did the yield of *n*-heptanal exceed 55% with n/iso ratios of 7.1 and 7.8, respectively. Very low yields of aldehydes were obtained in the presence of all other phosphines tested. The application of triethyl phosphite led to 83% of aldehydes; however, the n/iso ratio was only 3.2 (Table 7).

Mechanistic Studies. The results obtained for the hydroformylation reaction suggested a very positive *cooperative* effect of carbene and $P(OPh)_3$ ligands in the system. Using NMR, we were able to identify some complexes participating in the catalytic process. In the first stage of the reaction, the cod ligand in the precursor [Rh(NHC)(cod)X] is replaced by $P(OPh)_3$, leading to the formation of *cis*-[Rh(NHC)$(P(OPh)_3)_2$X] (Scheme 2).[15]

[Rh(NHC)$(P(OPh)_3)_2$X] reacts with the H_2/CO mixture at 80 °C, giving two compounds, [Rh(NHC)$(P(OPh)_3)$(CO)X] and [HRh(CO)$(P(OPh)_3)_3$],[20] both identified by ^{31}P NMR (Scheme 3, Figure 3). To confirm the identification of [Rh(NHC)-$(P(OPh)_3)$(CO)Cl], this complex was independently obtained in the reaction of [Rh(NHC)$(CO)_2$Cl] with 1 equiv of $P(OPh)_3$.

It is interesting to note that it is possible to obtain a mixture of [Rh(NHC)$(P(OPh)_3)$(CO)X] and [Rh(NHC)$(P(OPh)_3)_2$X] compounds in reactions between [HRh(CO)$(P(OPh)_3)_3$] and [bmim]X, but only in the absence of H_2/CO. Under 10 atm of H_2/CO the only product observed was [HRh$(CO)_2(P(OPh)_3)_2$].

Table 7. Results of 1-Hexene Hydroformylation Catalyzed by 2 in the Presence of Different Phosphines or Phosphites as Modifying Ligands[a]

		amt (%)			
entry	phosphine/phosphite	aldehydes	*n*-heptanal	2-hexene	n/iso
1[b]	PPh_3	1.5	1.1	0.6	2.4
2[b]	$P(p\text{-}CH_3\text{-}C_6H_4)_3$	3.3	2.4	0.7	2.5
3[b]	$P(p\text{-}CH_3O\text{-}C_6H_4)_3$	3.7	2.6	0.7	2.4
4	$P(C_6F_5)_3$	1.5	1.0	30. 5	2.2
5	$P(NC_4H_4)_3$	66.5	54.7	33.0	4.7
6[c]	$P(NC_4H_4)_3$	67.8	59.5	31.5	7.1
7[c]	$P(2\text{-}CH_3O\text{-}C_6H_4)(Ph)_2$	2.5	1.8	0.6	2.7
8	$P(O\text{-}C_6H_3\text{-}2,4\text{-}t\text{Bu}_2)_3$	57.9	38.2	38.2	1.9
9	$P(OC_6H_4\text{-}m\text{-}CH_3)_3$	25.1	20.1	5.5	4.0
10	$P(OCH_2CF_3)_3$	18.7	17.6	5.2	16.6
11[d]	$P(OCH_2CF_3)_3$	69.1	61.3	30.4	7.8
12[c]	$P(OCH_2CF_3)_3$	26.2	25.2	5.1	27.7
13	$P(OCH_2CH_3)_3$	83.0	63.4	15.7	3.2

[a] Reaction conditions (unless otherwise noted): [Rh] = 7.0×10^{-6} mol, [hexene]/[Rh] = 2000, [P]/[Rh] = 2, 80 °C, 10 atm of H_2/CO, 4 h. [b] Phosphines dissolved in 0.5 cm^3 of toluene. [c] [P]/[Rh] = 3. [d] Time 8 h.

Analysis of the ^{31}P NMR spectrum also revealed that [Rh(NHC)$(P(OPh)_3)$(CO)X] did not react with H_2/CO.

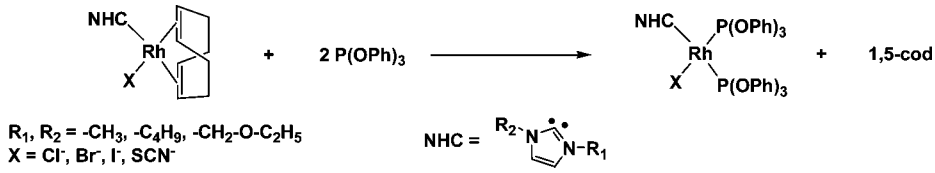
In contrast to [HRh$(CO)(P(OPh)_3)_3$], the Rh(0) complex [$Rh_4(CO)_8(P(OPh)_3)_4$] reacted with [bmim]Br at 80 °C under 10 atm of H_2/CO, giving a mixture of [HRh$(CO)(P(OPh)_3)_3$] and [Rh(NHC)$(P(OPh)_3)$(CO)Br] after 1 h.

On the basis of the performed experiments, we propose that the main hydroformylation cycle is based on the activity of the carbene hydrido complex [HRh(CO)(NHC)$(P(OPh)_3)_2$], which is responsible for an increase in reaction selectivity in comparison with a carbene-free system. In Scheme 3 we propose heterolytic splitting of H_2 coordinated to rhodium with elimination of HX bonded next to $P(OPh)_3$. As a result, phosphonium halide, $[HP(OPh)_3]X$, is formed, as evidenced by the presence of resonances at ca. 0−5 ppm. The other active form, [HRh(CO)-$(P(OPh)_3)_3$], appeared in the reaction course as a result of Rh−C(carbene) bond splitting and the formation of imidazolium halide, $[HNHC]^+X^-$ (Scheme 3).

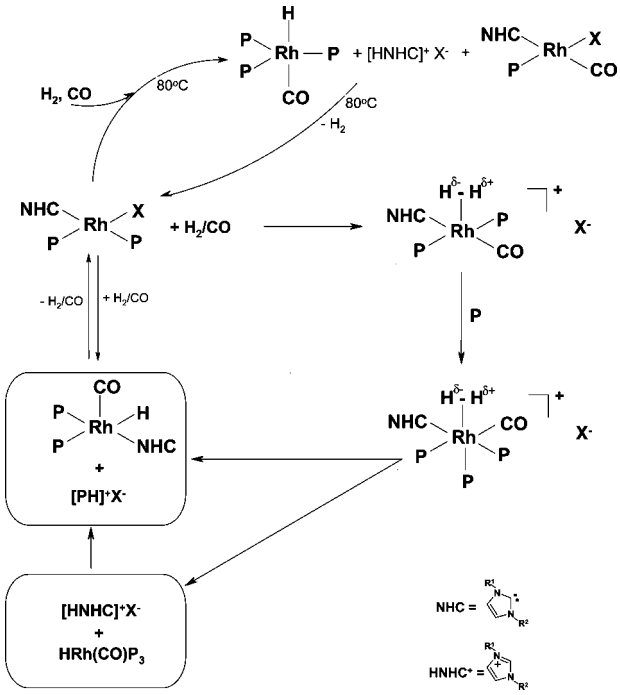
To confirm the presence of a rhodium hydrido carbene intermediate, a series of NMR experiments were performed for a system containing **2** + 3 $P(OPh)_3$ + H_2/CO. In addition to the previously identified complexes [HRh$(CO)(P(OPh)_3)_3$] and [Rh(bmim-y)$(P(OPh)_3)$(CO)Br], two new signals appeared, as a broad singlet at 123.3 ppm and a doublet at 119.7 ppm (J_{Rh-P} = 240.6 Hz). The doublet was observed only at −60 °C, pointing to the phosphito ligand exchange (Figure 3).

When instead of H_2/CO only H_2 was used, in ^{31}P NMR spectra another new compound was found, characterized by a doublet of doublets at 106.1 ppm (J_{Rh-P} = 240.2 Hz) observed

Scheme 2. Reaction of [Rh(NHC)(cod)X] Complexes with $P(OPh)_3$



Scheme 3. Reactions of $[Rh(NHC)(P(OPh)_3)_2X]$ Complexes with H_2/CO Mixtures



only at −30 °C (Figure 4). It is interesting to note that in contrast to all the familiar systems containing rhodium complexes with $P(OPh)_3$ ligands, the system under consideration presents dynamic behavior in ^{31}P NMR. This is the reason that under this conditions the precise detection of hydrido species was not successful.

Good evidence for the presence of a rhodium hydrido carbene intermediate was found for a system containing **2** + 3 $P(OCH_2CF_3)_3$ + H_2/CO. In the hydrido region of the ^1H NMR spectrum three different hydrido species were identified. A multiplet (doublet of quartets) at −11.52 ppm originating from $[HRh(CO)(P(OCH_2CF_3)_3)_3]$, a quintet of doublets at −11.76 ppm assigned to $[HRh(P(OCH_2CF_3)_3)_4]$, and four partially screened doublets at −11.83 ppm from the rhodium carbene hydride $[HRh(bmim\text{-}y)(CO)(P(OCH_2CF_3)_3)_2]$ (Figure 5) were detected and assigned. The shape of the last spectrum indicates that two nonequivalent phosphorus ligands are occupying cis positions in the plane of rhodium. The difference of 37.8 Hz between two J_{P-H} values clearly confirms that the hydrido ligand is located trans to phosphorus. The rather unexpected geometry of the rhodium hydrido carbene complex was additionally corroborated by the presence of two double doublets at 157.3 and 142.4 ppm (Figure 6). It was interesting to find that the system with $P(OCH_2CF_3)_3$ as modifying ligand also presents dynamic behavior in ^{31}P NMR, similarly to that observed for $P(OPh)_3$. Immediately after transfer of the solution from the autoclave to an NMR tube, two broadened lines were observed in the ^{31}P NMR spectrum; however, after 240 min these lines changed into narrow multiplets. This dynamic process can be explained by the exchange of CO and phosphorus ligands. In addition, the intensity of signals originating from the complex $[HRh(CO)(P(OCH_2CF_3)_3)_3]$ in ^1H and ^{31}P NMR spectra decreased ove time, in contrast to the signals of $[Rh(bmim\text{-}y)(P(OCH_2CF_3)_3)_2Br]$ in ^{31}P NMR. This observation in our opinion is important for explanation of the stability of the catalytic system in which less selective $[HRh(CO)(P(OCH_2CF_3)_3)_3]$ (or $[HRh(CO)(P(OPh)_3)_3]$) catalyst is converted into the carbene complex $[Rh(bmim\text{-}y)(P(OCH_2CF_3)_3)_2Br]$ (or $[Rh(bmim\text{-}y)(P(OPh)_3)_2Br]$ as the precursor of the most selective rhodium hydrido carbene species (Scheme 3).

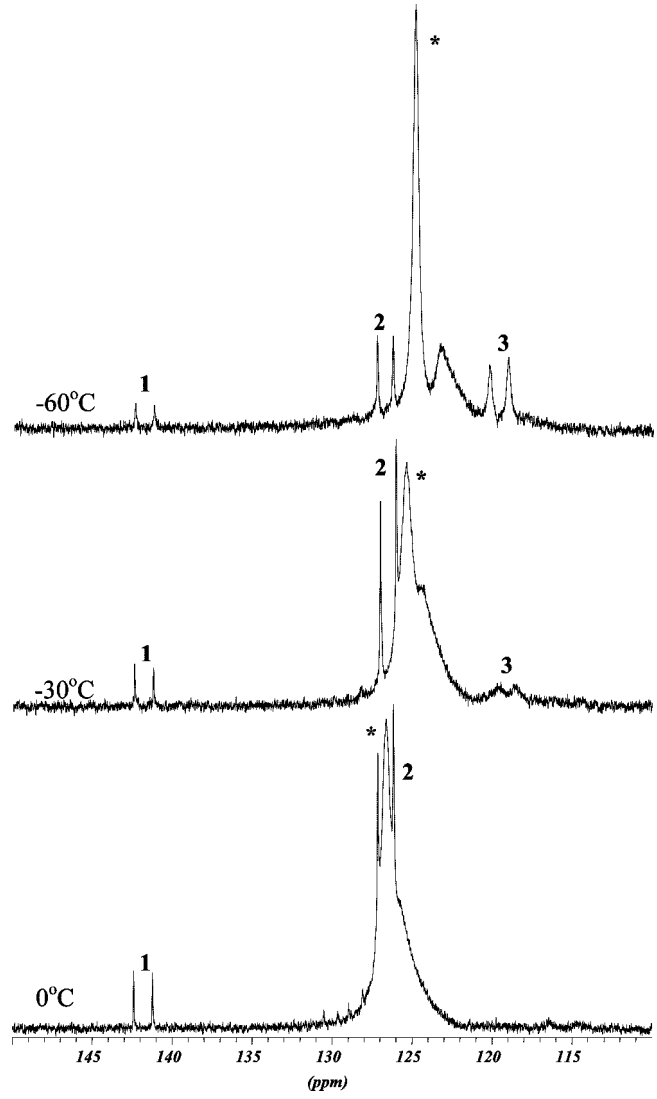


Figure 3. ^{31}P NMR (202.5 MHz, in toluene-d_8) of a [Rh(bmim-y)(cod)Br] + 3 $P(OPh)_3$ mixture after reaction with H_2/CO (1 h, 80 °C, 10 atm): (1) $[HRh(CO)(P(OPh)_3)_3]$ (141.8 ppm, J_{Rh-P} = 239.0 Hz); (2) $[Rh(bmim\text{-}y)(CO)(P(OPh)_3)Br]$ (126.8 ppm, J_{Rh-P} = 196.9 Hz); (3) $[HRh(bmim\text{-}y)(CO)(P(OPh)_3)_2]$ (119.7 ppm, J_{Rh-P} = 240.6 Hz); (*) $P(OPh)_3$.

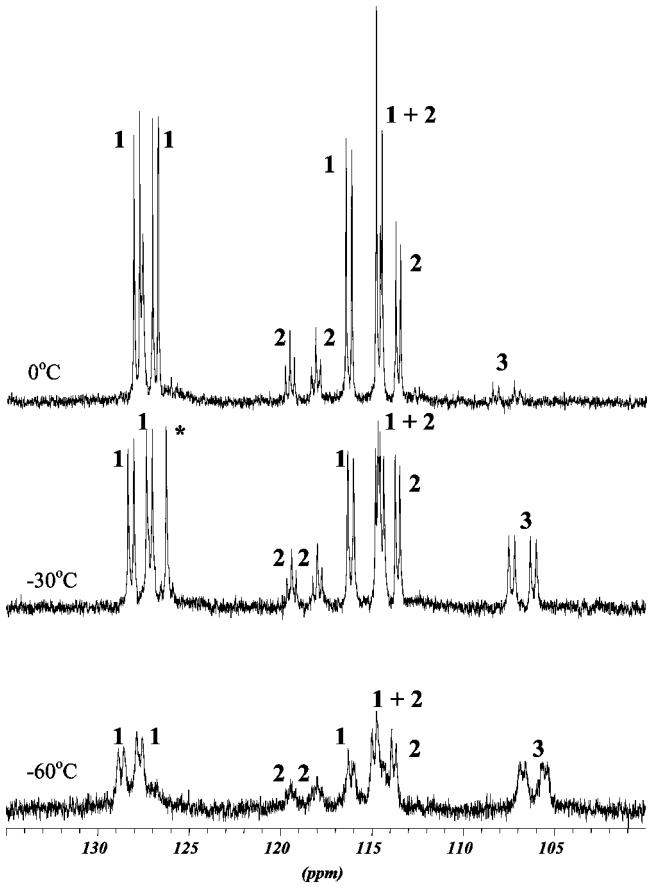


Figure 4. ^{31}P NMR (202.5 MHz, in toluene-d_8) of a [Rh(bmim-y)(cod)Br] + 3 $P(OPh)_3$ mixture after reaction with H_2 (1 h, 80 °C, 10 atm): (1) [Rh(bmim-y)$(P(OPh)_3)_2$Br] (127.6 ppm, J_{Rh-P} = 204.3 Hz, J_{P-P} = 63.2 Hz; 115.3 ppm, J_{Rh-P} = 336.2 Hz); (2) [RhBr$(P(OPh)_3)_3$] (118.6 ppm, J_{Rh-P} = 289.0 Hz, J_{P-P} = 50.3 Hz; 114.1 ppm, J_{Rh-P} = 219.2 Hz); (3) unidentified complex; (*) $P(OPh)_3$.

Conclusion

We have shown that a catalytic system based on Rh(I) carbene complexes of the general formula [Rh(NHC)(cod)X], modified by a small amount of $P(OPh)_3$, presents attractive activity and selectivity in the hydroformylation of 1-hexene under mild conditions. The results of hydroformylation are better than in analogous carbene-free systems with [HRh(CO)$(P(OPh)_3)_3$] and [Rh(acac)$(P(OPh)_3)_2$] as catalyst precursors. In addition, the new system can be easily reused, which is often complicated with homogeneous catalysts. We expect that even better results could be obtained after optimization of the recycling procedure.

Spectroscopic (^{1}H and ^{31}P NMR) studies allowed us to identify the rhodium hydrido carbene intermediate in the model system containing **2** + 3 $P(OCH_2CF_3)_3$ + H_2/CO. In contrast to the case for many known rhodium hydrido complexes, this new complex exists in a square-pyramidal structure, not in a trigonal-bipyramidal one (like [HRh(CO)$(P(OPh)_3)_3$] or [HRh(CO)$(P(OCH_2CF_3)_3)$]). This is undoubtedly the influence of the carbene ligand, which is probably also important in the high selectivity of the hydroformylation reaction.

Experimental Section

General Considerations. All manipulations were performed under an atmosphere of nitrogen by use of standard Schlenk techniques. Solvents were dried and purified by standard methods. 1-Hexene was distilled prior to use.

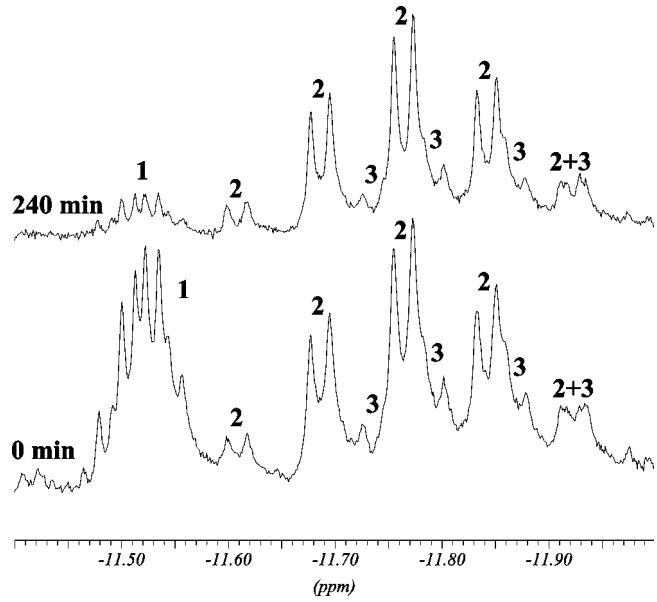


Figure 5. ^{1}H NMR (500 MHz, in toluene-d_8) of a [Rh(bmim-y)(cod)Br] + 3 $P(OCH_2CF_3)_3$ mixture after reaction with H_2/CO (1 h, 80 °C, 10 atm): (1) [HRh(CO)$(P(OCH_2CF_3)_3)_3$] (−11.52 ppm, J_{P-H} = 10.2 Hz, J_{Rh-H} = 6.3 Hz); (2) [HRh$(P(OCH_2CF_3)_3)_4$] (−11.76 ppm, J_{P-H} = 39.0 Hz, J_{Rh-H} = 9.2 Hz); (3) [HRh(bmim-y)(CO)$(P(OCH_2CF_3)_3)_2$] (−11.83 ppm, J_{P1-H} = 66.1 Hz, J_{P2-H} = 28.3 Hz, J_{Rh-H} = 9.4 Hz).

Table 8. Crystal Data and Structure Refinement Details for Compound 4

formula	$C_{17}H_{26}N_3SRh$
M_r	530.58
cryst syst	monoclinic
space group	$C2_1/n$
a/Å	11.936(3)
b/Å	8.874(2)
c/Å	16.722(5)
β/deg	97.10(3)
V/Å^3	1757.6(8)
Z	4
D_c/g cm^{-3}	1.540
μ/mm^{-1}	1.09
T/K	100(2)
color	yellow
cryst size/mm	0.54 × 0.48 × 0.16
abs cor	analytical
T_{min}/T_{max}	0.602/0.855
no. of measd rflns	23 526
no. of unique rflns	5092
no. of rflns with $I > 2\sigma(I)$	4210
R_{int}	0.033
θ range/deg	3.0−30.0
no. of data/restraints/params	5092/0/205
Goodness of fit on F^2	1.20
R1, wR2 (all data)	0.030, 0.071
R1, wR2 ($I > 2\sigma(I)$)	0.024, 0.066
max/min residual density/e Å^{-3}	1.04/−0.32

The ionic liquids [bmim]Cl and [bmim]Br were used as purchased from Fluka. The ionic liquid [bmim]I was obtained by the reaction of 2-methylimidazole with BuI. The ionic liquid [bmim]SCN was prepared by anion exchange between [bmim]Cl and [NH_4]SCN in 2-propanol, and [demim]Cl was prepared by Professor Juliusz Pernak of the Technical University of Poznań.

GC-FID measurements were performed on an HP 5890 II gas chromatograph. GC-MS measurements were performed on an HP 5890 II gas chromatograph with an HP 5971 mass detector and HP5 column.

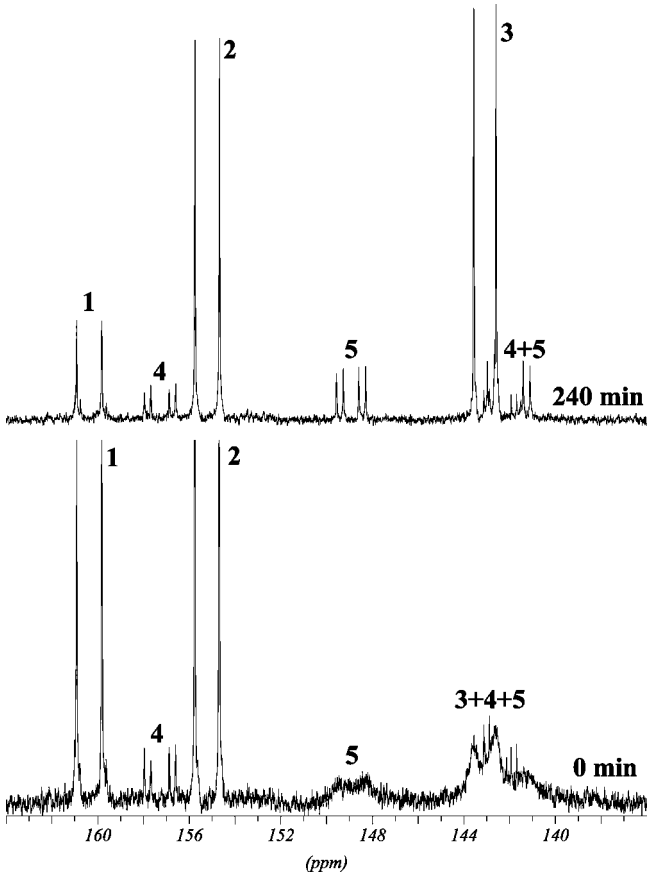


Figure 6. ^{31}P NMR (202.5 MHz, in toluene-d_8) of a [Rh(bmim-y)(cod)Br] + 3 $P(OCH_2CF_3)_3$ mixture after reaction with H_2/CO (1 h, 80 °C, 10 atm): (1) $[HRh(CO)(P(OCH_2CF_3)_3)_3]$ (160.4 ppm, J_{Rh-P} = 223.6 Hz); (2) $[HRh(P(OCH_2CF_3)_3)_4]$ (155.2 ppm, J_{Rh-P} = 216.4 Hz); (3) [Rh(bmim-y)(CO)$(P(OCH_2CF_3)_3)$Br] (143.0 ppm, J_{Rh-P} = 197.0 Hz); (4) [HRh(bmim-y)(CO)$(P(OCH_2CF_3)_3)_2$] (157.3 ppm, J_{Rh-P} = 220.8 Hz, J_{P-P} = 54.5 Hz; 142.4 ppm, J_{Rh-P} = 241 Hz); (5) [Rh(bmim-y)$(P(OCH_2CF_3)_3)_2$Br] (148.9 ppm, J_{Rh-P} = 197.8 Hz, J_{P-P} = 60.6 Hz; 142.0 ppm, J_{Rh-P} = 316.0 Hz).

^{1}H and ^{31}P NMR spectra were recorded on Bruker Avance III 300 and Bruker Avance 500 spectrometers with chemical shifts (δ) referenced to internal solvent resonances and reported relative to Me_4Si and H_3PO_4, respectively. IR spectra were recorded on a Nicolet Impact 400 spectrometer.

Preparation of Rhodium Complexes. Rh(bmim-y)(η^4-1,5-cod)Cl (**1**), Rh(bmim-y)(η^4-1,5-cod)Br (**2**), and Rh(bmim-y)(η^4-1,5-cod)I (**3**) (bmim-y = 1-butyl-3-methylimidazolin-2-ylidene) were prepared according to the literature.[15]

Rh(bmim-y)(η^4-1,5-cod)SCN (**4**) was prepared similarly to **1**, with [bmim]SCN used instead of [bmim]Cl. Anal. Calcd for $C_{17}H_{26}N_3SRh$: C, 50.12; H, 6.43; N, 10.31; S, 7.87. Found: C, 48.96; H, 6.59; N, 9.94; S, 7.96. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 1.02 (t, J_{H-H} = 7.35 Hz, CH_3, 3H), 1.46 (m, J_{H-H} = 7.35 Hz, CH_2, 2H), 2.02 (bm, CH_2, cod, 6H), 2.37 (m, cod, 4H), 3.49 (br, cod, 1H), 3.59 (br, cod, 1H), 3.99 (s, CH_3, 3H), 4.4 (double multiplet, CH_2, 2H), 4.73 (br, cod, 2H), 6.87 (s, 2 × CH, 2H).

A crystal of **4** suitable for an X-ray structure determination has been crystallized from CH_2Cl_2. Cell parameters are given in Table 8, and selected structural parameters are given in Figure 1.

Rh(demim-y)(η^4-1,5-cod)Cl (**5**) (demim-y = 1,3-diethoxymethylimidazolin-2-ylidene) was prepared similarly to **1** with [demim]Cl used instead of [bmim]Cl. Anal. Calcd for $C_{17}H_{28}N_2O_2ClRh$: C, 47.4; H, 6.55; N, 6.50. Found: C, 46.26; H, 5.99; N, 6.04. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.24 (t, J_{H-H} = 6.95 Hz, 2 × CH_3, 6H), 1.94 (d, J_{H-H} = 1.99 Hz, cod, 4H), 2.34 (s, cod, 4H), 3.32 (s, cod, 2H), 3.67 (pseudo multiplet, J_{H-H} = 7.2 Hz, 2 × CH_2, 4H), 5.02 (s, cod, 2H), 5.82 (d, J_{H-H} = 9.6 Hz, CH_2, 2H), 5.97 (d, J_{H-H} = 9.6 Hz, CH_2, 2H), 7.06 (s, 2 × CH, 2H).

[Rh(bmim-y)$(P(OPh)_3)$(CO)Br] was prepared by stirring a solution of [Rh(bmim-y)(cod)Br] in benzene for 10 min under a CO atmosphere. Next the solvent was removed in vacuo and the residue was redissolved in benzene. One equivalent of $P(OPh)_3$ was subsequently added, and after the mixture was stirred for 10 min, the solvent was evaporated and the residue was dried in vacuo. ^{1}H NMR (300 MHz, C_6D_6, δ, ppm): 0.79 (t, J_{H-H} = 6.96 Hz, CH_3, 3H), 1.07 (m, J_{H-H} = 6.99 Hz, CH_2, 2H), 1.51 (t, 6.97 Hz, CH_2, 2H), 3.19 (s, CH_3, 3H), 3.83 (double multiplet, CH_2, 2H), 5.9 (s, CH, 1H), 6.03 (s, CH, 1H), 6.8−7.7 (multiplet, 3 × C_6H_5, 15H). ^{31}P NMR (121 MHz, C_6D_6, δ, ppm): 126.42 (d, J_{Rh-P} = 199.75 Hz). IR (KBr): 1984 cm^{-1} (ν_{CO}).

$[HRh(P(OCH_2CF_3)_3)_4]$ was prepared by dissolving 0.031 g of $Rh(acac)(CO)_2$ in benzene (1 cm^3); then 0.120 g of $P(OCH_2CF_3)_3$ was added and the resulting solution was stirred for 3 h under a CO/H_2 atmosphere. Next the solution was condenced in vacuo, and the white precipitate that formed was filtered off and analyzed by ^{1}H and ^{31}P NMR without purification. ^{1}H NMR (500 MHz, toluene-d_8, δ, ppm): −11.76 (q of d, J_{P-H} = 39.0, J_{Rh-H} = 9.2 Hz). ^{31}P NMR (121 MHz, toluene-d_8, δ, ppm): 155.5 (d, J_{Rh-P} = 216.4 Hz).

[Rh(bmim-y)$(P(OCH_2CF_3)_3)_2$Br] was prepared only in toluene-d_8 solution by addition of 0.0076 g of $P(OCH_2CF_3)_3$ to 0.005 g of [Rh(bmim-y)(cod)Br]. ^{1}H NMR (500 MHz, toluene-d_8, δ, ppm): 0.9 (t, 3H, J_{H-H} = 7.3 Hz), 1.4 (m, 2H, J_{H-H} = 7.3 Hz), 1.9 (m, 2H, J_{H-H} = 7.3 Hz), 3.8 (s, 3H), 4.4 (t, 2H, J_{H-H} = 7.3 Hz), 4.6 (m, 4H, J_{H-H} = 7.7 Hz), 6.84 (s, 1H), 6.85 (s, 1H). ^{31}P NMR (202.5 MHz, toluene-d_8, δ, ppm): 148.9 (dd, J_{Rh-P} = 197.8, J_{P-P} = 60.6, 142.0, J_{Rh-P} = 316.0 Hz).

Hydroformylation Reaction Procedure. Catalytic reactions were carried out in neat 1-hexene (1.75 cm^3) without extra solvent, in a 55 cm^3 steel autoclave, which was charged with 7.0 × 10^{-6} or 1.38 × 10^{-5} mol of the catalyst precursor (complexes **1**−**5**) and phosphite ($P(OPh)_3$; $[P(OPh)_3]/[Rh]$ = 1−3) under a dinitrogen atmosphere. Next, the autoclave was filled with an equimolar mixture of H_2 and CO to a pressure of 10 atm and heated to 80 °C. During the reaction the mixture was magnetically stirred. After the reaction was finished, the autoclave was cooled and then opened, and the organic products were separated from the catalyst by vacuum transfer and analyzed using a GC-FID HP 5890 II Hewlett-Packard instrument with toluene as an internal standard. In recycling experiments the residue left after vacuum transfer was again dissolved in 1.75 cm^3 of 1-hexene and used for the next reaction without phosphite addition.

Crystallographic Data collection and Refinement. A single crystal of **4** suitable for X-ray measurements was mounted on a glass fiber in silicone grease and cooled to −173 °C under a nitrogen gas stream, and the diffraction data were collected on a Kuma KM-4 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structure was subsequently solved using direct methods and developed by full least-squares refinement on F^2. Structural solution and refinement was carried out using the SHELX suite of programs.[21] Analytical absorption corrections (performed with CrysAlis RED[22]) were applied. C, N, S, and Rh atoms were refined anisotropically. The carbon-bonded H atoms were positioned geometrically and refined isotropically using a riding model.

Crystal data and structure refinement details of **4** are summarized in Table 8. The molecular structure plot (Figure 1) was prepared using the ORTEP-3[23] program.

(21) Sheldrick, G. M. SHELXS97 and SHELXL97; University of Göttingen, Göttingen, Germany, 1997.

(22) CrysAlis CCD and CrysAlis RED, Version 1.171; Oxford Diffraction Ltd, Wrocław, Poland, 2003.

Acknowledgment. The financial support from Grant No. PBZ-KBN-118/T09/2004 is gratefully acknowledged. We thank Professor Juliusz Pernak (Technical University of Poznań) for a generous gift of the ionic liquid [demim]Cl and Mr. Marek Hojniak (Faculty of Chemistry, University of Wrocław) for performing of GC-MS analyses.

Supporting Information Available: A CIF file giving X-ray crystal data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800143M

(23) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.